

Imperial College of Science, Technology and Medicine
Department of Materials

Unravelling the Atomic Mechanism of Mg Aqueous Corrosion through First-principles Calculation

Bingxin LI

Submitted in part fulfilment of the requirements
for the degree of Doctor of Philosophy in Materials at
Imperial College London, November 2023

I hereby declare that this thesis and the work reported herein was composed by and originated entirely from me. Information derived from the published and unpublished work of others has been acknowledged in the text and references are given in the list of sources.

Bingxin Li (2023)

The copyright of this thesis rests with the author. Unless otherwise indicated, its contents are licensed under a Creative Commons Attribution-Non Commercial 4.0 International Licence (CC BY-NC). Under this licence, you may copy and redistribute the material in any medium or format. You may also create and distribute modified versions of the work. This is on the condition that: you credit the author and do not use it, or any derivative works, for a commercial purpose. When reusing or sharing this work, ensure you make the licence terms clear to others by naming the licence and linking to the licence text. Where a work has been adapted, you should indicate that the work has been changed and describe those changes. Please seek permission from the copyright holder for uses of this work that are not included in this licence or permitted under UK Copyright Law.

Abstract

As a promising alkaline earth metal with significant potential across various industrial applications, magnesium (Mg) and its alloys are appealing due to their impressive lightweight nature among all engineering metals. Nevertheless, inadequate aqueous corrosion resistance has noticeably hindered the broader applications of Mg alloys. Despite several experimental observations and theoretical investigations providing a primary understanding of the underlying mechanism of Mg aqueous corrosion, some anomalous corrosion behaviour of Mg under voltage bias, *i.e.*, the negative difference effect (NDE) still eludes a comprehensive explanation. A detailed understanding of the electrified double-layer structure for Mg at the atomic scale, coupled with an in-depth knowledge of the thermodynamics and kinetics of corrosion reactions, is essential for unravelling the intrinsic mechanism of Mg aqueous corrosion.

Herein, first-principles simulations within the density functional theory (DFT) framework are employed to explore the electrochemistry and the atypical hydrogen evolution behaviour in Mg aqueous corrosion. To comprehend the basis of the Mg corrosion mechanism, the structure and the potential of zero charge (PZC) of the Mg/water interface are modelled using the *ab initio* molecular dynamics. The hydrogen adsorption process and the formation of hydride corrosion products that are assumed to contribute to the anodic hydrogen evolution reaction are investigated and found to be intricately regulated by electron localisation at the metal surface. To disclose the significance of sub-surface hydride in the NDE or other pivotal aspects of Mg aqueous corrosion electrochemistry, a thermodynamic study involving the construction of a surface Pourbaix diagram, with a kinetic investigation entailing the calculation of reaction energy barriers under various surface conditions, is presented in this thesis. This research contributes novel perspectives to the ongoing debate about the NDE during Mg aqueous corrosion and provides rational theoretical evidence derived from the *ab initio* simulations.

Acknowledgements

Four years flew by silently in a blink and I spent the most valuable period of time in my life as a PhD researcher on materials modelling at Imperial College London. First and foremost, I would like to express my deepest appreciation to my supervisors, Prof. Andrew Horsfield and Prof. Nicholas Harrison, for their unwavering support, guidance, and expertise throughout the entire journey of this doctoral study. Their insightful feedback and encouragement have been instrumental in shaping the direction and quality of this project. They have also brought me into the ivory tower of theoretical research, not only practical skills in coding and density functional theory, also a broad range of fundamental knowledge of electrochemistry of metals.

I am grateful to Imperial College London for providing a conducive academic environment and the necessary resources for the successful completion of this research. My special thanks also go to the China Scholarship Council for their financial support, without which I could not have the chance to finish my PhD project and study in one of the best research institutions in the world. I am also thankful to my colleagues and collaborators, Dr. Richard Fogarty, Dr. Chengcheng Xiao and Dr. Mira Todorova for their precious discussions, feedback, and support throughout the research projects.

My heartfelt thanks go to my family, friends and my soulmate for their unwavering support, understanding, and patience during this challenging and rewarding academic journey. Their love and encouragement have been a constant source of motivation for me to overcome difficulties and face challenges. Finally, I express my gratitude to all those who, whether directly or indirectly, contributed to the completion of my PhD study. Your support has been indispensable, and I am truly thankful for the collective effort that has gone into this academic achievement.

Publications

1. Fogarty, R. M., **Li, B. X.**, Harrison, N.M., & Horsfield, A. P. (2022). Structure and interactions at the Mg (0001)/water interface: An ab initio study. *The Journal of Chemical Physics*, 156(24), 244702.
2. **Li, B.**, Xiao, C., Harrison, N. M., Fogarty, R. M., & Horsfield, A. P. (2023). Role of electron localisation in H adsorption and hydride formation in the Mg basal plane under aqueous corrosion: a first-principles study. *Physical Chemistry Chemical Physics*, 25(8), 5989-6001.
3. **Li, B.**, Todorova, M., Harrison, N. M., & Horsfield, A. P. (2023). Quantifying the electrochemical stability and corrosion reaction pathway of Mg (0001) surface: insight from first-principles calculations. (*Working paper*)

"The more transparent something is, the more mysterious it becomes. The universe itself is transparent. You can see as far as your vision allows, but the farther you look, the more mysterious it becomes."

– *The Three-Body Problem*

Contents

Abstract	3
Acknowledgements	4
Publications	5
1 Introduction	17
1.1 Mg Aqueous Corrosion and Mg Corrosion Prevention	17
1.2 Computational Materials Science and Ab initio Simulation	19
1.3 Significance of Current Research	23
1.4 Overview of Chapters	24
2 Overview of Mg Corrosion Electrochemistry	25
2.1 General Overview of Mg and its Alloys	26
2.2 Corrosion Electrochemistry of Mg under Aqueous Conditions	36
2.2.1 Electrochemistry Stability of Mg in Aqueous Environments	36
2.2.2 Mg Corrosion Kinetics	44
2.2.3 Negative Difference Effect (NDE)	53
2.2.4 Surface Film Formed on Mg during Aqueous Corrosion	59
2.3 Theoretical Electrochemistry	62
2.3.1 Overview of Electric Double Layer (EDL)	62
2.3.2 Ab initio Study of Metal/Water Interface	66
2.4 Summary & Knowledge Gap	71
3 Method and Theory	74
3.1 Density Functional Theory (DFT)	75
3.1.1 From Many Body Schrödinger Equation to Density Functional Theory	75
3.1.2 Pseudopotentials and PAW Formalism	82
3.1.3 Reciprocal Lattice and Periodic DFT	84
3.2 Implicit (Continuum) Solvation Model	86
3.3 Nudged Elastic Band Theory	88
4 Atomic Structure and Potential of Zero Charge for Mg Surfaces	91
4.1 Introduction	92
4.2 Method	95
4.2.1 Ab initio Molecular Dynamics (AIMD)	95
4.2.2 Potential of Zero Charge (PZC) Calculations	96
4.3 Results	99
4.3.1 Mg (0001)/Water Interface Structure	99

4.3.2	Potential of Zero Charge for Mg (0001) Surface	101
4.3.3	Comparisons with Other Water/Metal Surfaces	105
4.4	Conclusion	109
5	H adsorption and Hydride Formation in Mg	111
5.1	Introduction	112
5.2	Theory and Methods	114
5.2.1	Theory of the Electron Localisation Function (ELF)	114
5.2.2	Computational Methods	115
5.3	Results and discussion	118
5.3.1	H Adsorption on or below the Mg (0001) Surface	118
5.3.2	H Adsorption below the hydroxylated or oxidised Mg (0001) Surface . . .	129
5.4	Conclusion	137
6	Electrochemical Stability of Mg Surfaces & Corrosion Reaction Pathways	139
6.1	Introduction	140
6.2	Methods	144
6.2.1	Grand-canonical approach extending method	144
6.2.2	Electronic structure modelling with DFT	146
6.3	Probing Mg Surfaces-states under Aqueous Conditions	148
6.3.1	Electrochemical stability of Mg (0001) on-surface adsorption configurations	149
6.3.2	Electrochemical stability of Mg (0001) sub-surface (H) adsorption configurations	154
6.4	Micro-kinetic Modelling for Surface-dependent Corrosion Reactions	160
6.4.1	Water dissociation reaction pathways on Mg (0001) surfaces	160
6.4.2	General HER pathways with on-surface hydrogen atoms on Mg (0001) surfaces	166
6.4.3	HER pathways with sub-surface hydrides in Mg (0001) surfaces	174
6.5	Conclusion	178
7	Conclusion and Future Work	181
7.1	Conclusion	181
7.2	Future Work	185
A	Appendix	187
A.1	Electron Localisation Function (ELF) and Charge Density (CD)	187
A.2	Defect-induced ELF Modification and H adsorption on the Mg (0001) Surface .	188
A.3	Influence of the Solvent Effect	190

List of Tables

2.1	Comparison of physical properties of Mg, Al and Fe (as reproduced from [1]). . .	26
2.2	Chemical potential, Gibbs formation enthalpy and magnesium oxidation states of pure Mg, Mg compounds and Mg ions at room temperature, 298.15 K (as reproduced from [2, 3]).	37
2.3	The reaction enthalpy and reaction energy barrier for some essential electrochemical surface reactions on the (0001) surface for Mg aqueous corrosion.	50
4.1	Results of the PZC calculations for Mg in water using different codes/basis set (VASP and CP2K). PW refers to the plane-wave basis and GPW refers to the mixed Gaussian and plane-wave approach used in CP2K. Note that for CP2K results the bracketed results are where ghost-atoms were used to calculate the pure metal work function value (Φ_M). The value of PZC is $\frac{\Phi_M + \Delta\phi_{total}}{e}$	103
4.2	Calculated potential difference between the PZC and the work function of 6 metal surfaces through DFT calculations based on a Water/Metal/Water model. The contribution of the water orientation and the electron redistribution to the total potential difference are also shown. All values are taken from the work of Li <i>et al</i> [4].	107
5.1	Distortion energy E_{dis} (meV/H) for the Mg (0001) surfaces with H at different adsorption sites when the total H coverage is no more than 1 ML. For comparison, the corresponding total H adsorption energy (meV/H) is marked within the parentheses.	120
5.2	Onsite ELF value at different adsorption sites (on-surface fcc, hcp and sub-surface OI, TI ₁ and TI ₂ sites) of a clean Mg (0001) surface. An ELF value approaching 0.5 means the local electron localisation is similar to a uniform electron gas. A higher ELF value indicates that electrons is highly localised onsite.	122
5.3	Onsite ELF value changes at different sub-surface interstitial sites as the on-surface fcc H coverage increases from 0 to 1 ML.	127
A.1	Onsite ELF value/Hydrogen adsorption energy (eV per H) at the on-surface adsorption sites of the pristine and the defective Mg (0001) surface. The H adsorption energy at the atomic vacancy site (position for the removed Mg atom) is also demonstrated in the table.	189

List of Figures

1.1	Different materials modelling methods for several systems with distinct sizes. Generally, the more atoms/molecules in the system, the required simulation timescale is larger. (as reproduced from [5])	20
2.1	Different applications of Mg alloys in several car components: (a) Hollow Mg alloy wheel produced by billet extrusion; (b) Cast Mg-based oil pan; (c) Cast Mg alloy front engine cover made by the U.S. Automotive Materials Partnership for the Mg Intensive V6 Engine; (d) Mg-based (die-cast) central control bracket of the Volvo new XC90 K426 Model; (e) Mg cylinder head over of Changan 465Q; (f) Mg alloy seat frame. (as reproduced from [6])	27
2.2	Current representative biomedical applications of Mg-based alloys: (a) Mg-based vascular stent implants, fabricated by BIOTRONIK; (b) Multiple biodegradable Mg alloy implants which are produced for orthopaedic applications; (c) Mg-based plate for mandibular implantation; (d) Mg-based intramedullary nail. (as reproduced from [7, 8])	30
2.3	Typical hcp crystal's basal, prismatic and pyramidal slip systems with Burgers vector $\langle \mathbf{a} \rangle$ and $\langle \mathbf{c} + \mathbf{a} \rangle$. (as reproduced from [9])	32
2.4	Mg Aqueous corrosion process and corrosion-induced surface morphology: (a) Mg specimen under aqueous corrosion in 0.01 M NaOH solution with additional 3.5 wt.% NaCl; (b) Magnified image of the Mg surface in (a) during corrosion; (c)-(e) Surface porous, spallation and multiple crevices of Mg alloys after exposure in a humid environment. (as reproduced from [10, 11])	35
2.5	Pourbaix diagram for aqueous Mg system at 298.15 K and 1 atm: (a) Fundamental Mg Pourbaix diagram (referenced to the SHE) in water with the concentration of soluble Mg ions of approximately 10^{-6} M; (b) Mg Pourbaix diagram including meta-stable Mg univalent ions and Mg hydride phase. (as reproduced from [12, 2])	39
2.6	DFT-calculated surface Pourbaix diagram of Mg (0001) surface in an aqueous environment: (a) the Mg (0001) surfaces are covered by hydroxyls at fcc site with varying coverage (θ); (b) the Mg (0001) surface with hydroxyls ($\theta = 0.06$) adsorbed at fcc and hcp site respectively. (as reproduced from [13, 14])	42
2.7	Schematic Evans diagram for (a) An arbitrary corrosion (redox) reaction with the potential as a function of the logarithm of the current density; (b) Mg aqueous corrosion reaction, with the cathodic reaction as the HER and anodic reaction as the Mg dissolution reaction. (as reproduced from [15])	46

2.8	Potentiodynamic polarisation method for Mg aqueous corrosion rate measurement: (a) Basic set-up of the potentiodynamic polarisation experiments for Mg corrosion using a rotating disk electrode; (b) the corresponding polarisation curves for Mg specimens with different (polished or pre-corroded) surface states, with the electrolyte as 5 <i>wt.</i> % NaCl and the polarisation scanning rate of 1 mV · s ⁻¹ . (as reproduced from [16])	47
2.9	Polarisation curves for the HER of Mg aqueous corrosion: (a) HER current densities as a function of the electrode potential for the high-purity (HP) and ultra high-purity (UHP) Mg samples in 0.1 M NaCl solution measured from experiments; (b), (c) DFT-calculated HER rate (proportional to the current density) for the hydrogen gas evolved through the Heyrovsky pathway, and through the Heyrovsky as well as a proposed anodic HER pathway. (as reproduced from [17, 18])	51
2.10	Polarisation curves for the anodic dissolution reaction on different Mg surfaces in Mg aqueous corrosion: (a) Experimental measurement of the Mg dissolution current densities under varying polarisation potential of the (0001) and (10 $\bar{1}$ 0) surface for AZ31 Mg alloys in a saturated Mg(OH) ₂ solution; (b) Theoretical calculated polarisation curves for the anodic dissolution of the (0001), two terminated-type (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0) Mg surfaces. (as reproduced from [19]) . . .	52
2.11	Negative difference effect of the HER in the aqueous corrosion of Mg: (a) Hydrogen evolution rate at different polarisation current densities in a 0.1 M NaCl solution; (b) Schematic Evans diagram for Mg aqueous corrosion highlighting the expected Tafel line for a general cathodic HER and that for the experimentally observed abnormal HER. (as reproduced from [20, 21])	53
2.12	(a) Schematic of theoretical models for the EDL structure of metal/aqueous solution interface; (b) Detailed models for (I) the Helmholtz model, (II) the Gouy–Chapman model and (III) the Gouy–Chapman–Stern model. (as reproduced from [22, 23])	63
4.1	Configuration of the Mg (0001)/water system at 9.5 ps. The orange atom refers to Mg atom, red one is the oxygen atom and H is represented by the white atom.	96
4.2	Probability distributions for a) solAds tilt angle, b) solPhys tilt angle, c) solNon-Ads tilt angle and d) the absolute values for roll angles.	100
4.3	Planar distribution of Mg atoms in the outer surface layer (<i>i.e.</i> , the 36 atoms closest to water). The value of zero is 5.27 Å from the average planar position of the third atomic layer (this value comes from the separation of first and third layers in vacuum). The “With Adsorbate” group refers to Mg atoms with $r_{\min}(\text{Mg} - \text{O}) < 3$ Å. Note the red vertical line marks the zero on the x-axis. . .	101
4.4	Potential energy for removing an electron from Mg through the metal/water interface minus the Mg work function ($\Delta\phi_{\text{total}}$) with respect to time calculated with a) VASP, and b) CP2K. Note that data in a) has a mean of -1.0 eV and standard deviation of 0.44 eV. Data in b) has a mean of -1.06 eV and standard deviation of 0.41 eV.	102

4.5	(a) Planar average electron density difference between the clean surface and distorted surface along the z-axis (CP2K results); (b) Planar average ionic charge density difference between the clean surface and distorted surface along the z-axis (CP2K results); (c) X-Y plane integrated electrostatic potential energy from the electron/ionic density difference between the clean surface and the distorted surface; (d) Planar average electrostatic potential of the clean surface and the distorted surface.	104
5.1	Schematic diagram of available on-surface and sub-surface adsorption sites at the Mg (0001) surface. Images (a) and (b) correspond to the top view of the Mg (0001) surface. The on-surface fcc and hcp sites are represented by the blue and black circles respectively. Top layer (TL) Mg atoms and second layer (SL) ones are indicated in the figure. Panels (c)-(e) demonstrate the octahedral (OI), tetrahedral-I (TI ₁) and tetrahedral-II (TI ₂) interstitial sites within the sub-surface region of the Mg basal plane from the side view.	117
5.2	Adsorption energy (per adsorbed atom) of H on Mg(0001) surfaces or in the sub-surface interstitial sites when the H coverage is less than 1 ML. A negative adsorption energy corresponds to an energetically favourable adsorption referring to the clean surface and H ₂ gas molecule. Insets are the stable on-surface fcc and hcp H adsorption structures.	119
5.3	Planar (XY-Plane) average ELF of Mg (0001) surface along Z-axis. Inset is the top-view ELF contour of the surface top-layer (a warmer colour region indicates electrons are more localised within this region). The side-view ELF contour is shown at the right of the figure. The vertical dashed lines (the purple line and the brown line) mark the average atomic position of the top layer (TL) and second layer (SL) respectively.	122
5.4	(a) Relative Coulomb interaction energy (calibrated by the Coulomb interaction energy of the octahedral adsorption) and ELF values at different sites for Mg (0001) surface with 0.25 ML H. A more positive relative Coulomb interaction energy suggests a weaker Coulomb interaction at the correspondent adsorption site. (b) Linear fit of the estimated ELF-related energy with respect to the onsite ELF value. The ELF-related energy is calculated as the energy remainder of the total adsorption energy subtracting the H ₂ dissociation energy, distortion energy and the Coulomb interaction energy, then calibrated by the highest value (the energy remainder of the octahedral adsorption is set as zero) to demonstrate the relationship between the ELF and the correlated energy. The Coulomb interaction energy and the ELF-related energy of the tetrahedral-I adsorption are excluded here because the 0.25 ML TI ₁ adsorption is energetically unfavourable.	123
5.5	Adsorption energy per adsorbed atom (* suggests that the reference is no longer the clean Mg surface) of H in the sub-surface interstitial sites of the Mg (0001) surface when the H coverage is larger than 1 ML: 1 ML H is pre-adsorbed on the on-surface fcc sites. A negative adsorption energy corresponds to an energetically favourable adsorption, and is evaluated relative to the 1 ML H (fcc) covered surface and an H ₂ gas molecule. The inset is the top view of the stable sub-surface tetrahedral-I (TI ₁) H adsorption structure for the 1 ML fcc-H covered Mg basal plane. The side view of the 4FCC-TI ₁ adsorption structure shows the position of two types of H within the surface.	126

5.6	Planar (XY-Plane) average ELF of the H (fcc) covered Mg (0001) surface along Z-axis as the increase of the H coverage from 0 to 1 ML. The side-view and the top-view of the ELF isosurface plot (isosurface level = 0.80) for the 1 ML H (fcc) covered Mg surface are shown at the right of the figure. A newly formed ELF maximum (small size yellow circles) could be found at the sub-surface tetrahedral-I (TI ₁) sites, which corresponds to the labelled peak in the planar average plot.	127
5.7	ELF contour map of the side view of the fcc H covered Mg (0001) surface with different H coverage in the sub-surface TI ₁ sites (from the left to the right, the sub-surface H coverage is 0, 0.50 and 1 ML). The leftmost schematic demonstrates the correspondent adsorption structures with the ELF maximum tagged as yellow oval. The H positions are also labeled in the contour figures.	129
5.8	(a) Adsorption energy per adsorbed radical of OH on the Mg (0001) surface. When the coverage is larger than 0.50 ML, the absorption of OH at hcp sites is more stable than at fcc sites. The inset shows the fcc adsorption pattern, with the Mg, O and H atoms represented by the orange, red and white spheres, respectively. (b) Adsorption energy per adsorbed O atom for O on the Mg (0001) surface. The hcp site is more energetically favourable for O adsorption at all surface coverages. The inset presents the stable hcp O adsorption structure. . .	130
5.9	(a) Distortion energy (meV per adsorbate) of the on-surface adsorption at fcc and hcp sites on the Mg (0001) surface for O atoms and OH radicals. (b) Variations of the spacing between the top and second layers of the Mg surface with O and OH adsorbed at the fcc and hcp sites at different coverages. Here the layer spacing is the percent change of the layer distance for the hydroxylated or oxidised Mg surface with respect to the distance for the clean Mg surface.	132
5.10	ELF contour map and the isosurface (level=0.76) plot for the side view of the Mg (0001) surface with 1 ML of OH and O on the fcc and hcp sites. In the ELF contour maps, the position of the top layer atoms is indicated by the space-filling sphere model.	134
5.11	(a) Adsorption energy per H atom of H in sub-surface interstitial sites within the Mg (0001) surface covered by 1 ML OH radicals at fcc sites. Negative adsorption energy suggests stable sub-surface H adsorption with respect to the hydroxylated Mg surface and H ₂ gas. The inset shows the structure of the most energetically favourable sub-surface H adsorption site (TI ₁), with the corresponding ELF contour map on the left. (b) Adsorption energy of H in the sub-surface region with the Mg (0001) surface covered by 1 ML of O at hcp sites. The inset shows the structure of the most stable H sub-surface adsorption in the oxidised surface (TI ₂). The related ELF contour map is also shown on the left.	136
6.1	Surface Pourbaix diagram of the Mg (0001) surface with on-surface adsorptions of H, OH and O under thermodynamic equilibrium: (a) surfaces without solvent; (b) surfaces in aqueous conditions modelled by the implicit solvent model. The dashed line labelled from ① to ③ indicates the phase boundary of bulk Mg/aqueous Mg ²⁺ , aqueous Mg ²⁺ /bulk Mg(OH) ₂ and bulk Mg/bulk Mg(OH) ₂ respectively. The grey hashed region indicates the water stability region, with the boundary ④ of water/O ₂ and ⑤ of water/H ₂	149

6.2	(a) Excess Gibbs free surface energy (without solvent) of the stable Mg (0001) on-surface adsorption configurations as a function of electrode potential at pH = 8; (b) excess Gibbs free surface energy (without solvent) of the stable Mg (0001) on-surface adsorption configurations as a function of pH when the electrode potential is -0.6 V _{SHE} ; (c)-(e) simulated STM images of the three lowest energy Mg (0001) surface states which are covered with 1 ML H at fcc sites, 1 ML OH at fcc sites and 1 ML O at hcp sites. The yellow circles (isosurface plot) refer to a partition charge accumulation onsite.	150
6.3	(a) Excess Gibbs free surface energy (with solvent effect) of the stable Mg (0001) on-surface adsorption configurations as a function of electrode potential at pH = 8; (b) excess Gibbs free surface energy (with solvent effect) of the stable Mg (0001) on-surface adsorption configurations as a function of pH when the electrode potential is -0.6 V _{SHE} ; (c) solvation energy of the stable Mg (0001) on-surface adsorption configurations; (d)-(f) isosurface plot of localised (excess) electrons above the Mg (0001) surface covered with 1 ML H (fcc), 1 ML OH (fcc) and 1 ML O (hcp), respectively.	151
6.4	(Sub)-Surface Pourbaix diagram of the Mg (0001) surface with on-surface adsorption of H, OH and O, along with sub-surface adsorption of H under thermodynamic equilibrium: (a) surfaces without solvent; (b) surfaces under aqueous conditions modelled by the implicit solvent model. The dashed line labelled of ① and ② suggests the phase boundary of bulk Mg hydride (MgH ₂) /aqueous Mg ²⁺ , and bulk MgH ₂ /bulk Mg(OH) ₂ respectively. The lower grey hashed region indicates the bulk hydride phase stability region [24].	154
6.5	(a)-(b) Excess Gibbs free surface energy (without and with solvent) of the stable Mg (0001) on-surface and sub-surface adsorption configurations as a function of electrode potential at pH = 8; (c)-(d) excess Gibbs free surface energy (without and with solvent) of the stable Mg (0001) on-surface and sub-surface adsorption configurations as a function of pH when the electrode potential is -0.6 V _{SHE} . . .	155
6.6	(a) Solvation energy of the electrochemically stable configurations of the Mg (0001) surface with sub-surface hydrogen adsorption; (b)-(d) side view of the surface geometries for the Mg (0001) surface with 1 ML O at hcp sites and different coverages of H (ranges from 1/4 ML to 3/4 ML) at sub-surface tetrahedral-2 site; (e)-(g) simulated STM images of three typical on-surface and sub-surface hybrid adsorption configurations: 1 ML H at fcc sites + 1 ML H at tetrahedral-1 sites, 1 ML OH at fcc sites + 1 ML H at tetrahedral-1 sites and 1 ML O at hcp sites + 1/2 ML H at tetrahedral-2 sites.	157
6.7	Water monomer dissociation reaction on the pristine Mg (0001) surface: (a) the minimum energy pathway of the water dissociation reaction on the clean Mg (0001) surface, as derived from the CI-NEB DFT calculations without/with the implicit solvent model; (b) Bader charge analysis of the dissociated water molecule on the surface; (c)-(e) initial state, transition state and final state of the system.	162
6.8	Water monomer dissociation reaction on the 1 ML H-covered Mg (0001) surface: (a) the minimum energy pathway of the water dissociation reaction on the hydride Mg (0001) surface, as derived from the CI-NEB DFT calculations without/with the implicit solvent model; (b)-(e) initial state, transition state 1, transition state 2 and final state of the system; (f)-(g) Bader charge analysis of the dissociated water molecule and Mg atoms within the surface.	163

6.9	Water monomer dissociation reaction on the 1 ML O-covered Mg (0001) surface: (a) the minimum energy pathway of the water dissociation reaction on the oxidised Mg (0001) surface, as derived from the CI-NEB DFT calculations without/with the implicit solvent model; (b)-(d) Bader charge analysis of the H atoms from the dissociated water molecule, the Mg atoms within the surface, and the O atoms from the water monomer or on the surface. OH _t labels the on-top adsorbed hydroxyl groups directly dissociated from the water molecule, and OH _h labels the hydroxyl in a hollow site converted from the surface oxygen; (e)-(g) surface geometries of the initial state, transition state and final state along the reaction pathway.	164
6.10	Sub-surface hydride formation reaction following the water dissociation reaction on the 1 ML O-covered Mg (0001) surface: (a) the minimum energy pathway of the sub-surface hydrogen formation reaction; (b)-(d) Bader charge analysis of the Mg atoms within the surface, the on-surface and sub-surface H atoms and the O atoms on the surface; (e)-(h) surface geometries of the initial state (which is the final state of the preceding water dissociation reaction), two transition states and final state along the reaction pathway.	165
6.11	Tafel-mechanism hydrogen evolution reaction on the 1 ML H-covered Mg (0001) surface: (a) the minimum energy pathway of the Tafel-mechanism hydrogen evolution from the hydride Mg (0001) surface; (b) Bader charge analysis of the Mg atoms within the surface and the on-surface H atoms; (c) The H-H (desorbed from the surface) distance evolution along the reaction pathway, with the dashed line corresponding to the referenced bond length of H ₂ [25]; (d)-(g) surface geometries of the initial state, transition states and top-view (TV) or side-view (SV) of the final state along the reaction pathway.	167
6.12	Heyrovsky-like hydrogen evolution reaction on the 1 ML H-covered Mg (0001) surface: (a) the minimum energy pathway of the Heyrovsky-like hydrogen evolution from the hydride Mg (0001) surface; (b)-(c) Bader charge analysis of the water molecule, the on-surface H atoms and the Mg atoms within the surface; (d) The H-H distance evolution along the reaction pathway; (e)-(h) surface geometries of the initial state, transition states and top-view (TV) or side-view (SV) of the final state along the reaction pathway.	169
6.13	Water-catalysis HER on the 1 ML OH-covered Mg (0001) surface: (a) the minimum energy pathway of the hydrogen evolution with water molecule as catalyst from the hydroxylated Mg (0001) surface; (b)-(d) Bader charge analysis of the H atoms of water molecule or on-surface OH radicals, the Mg atoms within the surface and the O from the OH groups; (e)-(h) surface geometries of the initial state, transition states and top-view (TV) or side-view (SV) of the final state along the reaction pathway.	170
6.14	HER on the 1 ML OH-covered Mg (0001) surface: (a) the minimum energy pathway of the hydrogen evolution directly from the hydroxylated Mg (0001) surface; (b)-(d) Bader charge analysis of the H atoms of the on-surface OH radicals, the Mg atoms within the surface and the O from the OH groups; (e)-(g) surface geometries of the initial state, transition states and the final state along the reaction pathway.	172
6.15	COHP analysis of the O-H bond for the hydroxyl groups on the Mg (0001) surface, or for those of the brucite (0001) surface. Higher value of the -ICOHP indicates a stronger bond strength.	173

6.16	HER on the 1 ML O + 0.25 ML H _{sub} -covered Mg (0001) surface: (a) the minimum energy pathway of the hydrogen evolution involving the sub-surface hydride within the oxidised Mg (0001) surface. This complex reaction pathway is composed of three essential steps: the water dissociation process (with sub-surface hydrogen interior diffusion), sub-surface outward diffusion with its combination with on-surface oxygen, and the hydrogen evolution reaction from the H of hydroxyls; (b)-(h) surface geometries of the initial state for step I (the blue diamond indicates the starting position underneath the top surface layer of the sub-surface hydrogen), final state for step I (initial step for step II), transition state for step II, final state for step II (initial step for step III), transition state for step III and the final state for step II along the reaction pathway; (i) Side-view (SV) of the transition state for the step II for the overall reaction.	174
6.17	Bader charge analysis of the HER on the 1 ML O + 0.25 ML H _{sub} -covered Mg (0001) surface: (a) Net charges on H atoms that form sub-surface interstitials and on H atoms from the water monomer; (b) Net charges on O atoms adsorbed at the surface hcp hollow sites and on those from water molecules; (c) Net charges on the Mg (0001) surface.	176
A.1	ELF and Charge density (CD) of Mg (0001) surface calculated from DFT calculations with different treatment of the valence electrons for Mg atoms (3s ² and 2p ⁶ 3s ² respectively). (a)-(c) ELF and CD isosurface plots of the Mg (0001) surface (Mg atoms with 3s ² as the valence electrons). (d)-(f) ELF and CD isosurface plots of the Mg (0001) surface (Mg atoms with 2p ⁶ 3s ² as the valence electrons). The unit of the ELF isosurface level is 1 and that of the charge density isosurface level is $e/Bohr^3$	187
A.2	Pristine Mg (0001) surface and defective Mg (0001) surface (with an atomic vacancy) with the corresponding top-view ELF contours. (a) The pristine Mg (0001) surface structure and the ELF contours. The on-surface hcp and fcc sites are also indicated by the circles and labelled as HCP and FCC. (b) The defective Mg (0001) surface structure with a point defect and the ELF contour. The atomic vacancy is demonstrated by the yellow hexagon. HCP* and FCC* indicate the general on-surface hcp and fcc adsorption sites of the defective Mg (0001) surface.	189
A.3	H/OH/O adsorption energy (eV per adsorbate) at different on-surface adsorption sites (hcp and fcc) of the Mg (0001) surface in the vacuum/implicit water. . . .	191

Chapter 1

Introduction

1.1 Mg Aqueous Corrosion and Mg Corrosion Prevention

Since being isolated initially by Davy in 1808, magnesium (Mg) has been investigated for approximately two centuries [11]. The burgeoning interest in Mg and its alloys has remained so far because they are lightweight and with outstanding mechanical properties. Although Mg-based alloys have been applied in numerous industries thanks to their outstanding performance, the overall property and further applications of Mg and its alloys are constrained by some important weaknesses, namely poor corrosion resistance, less ductility and inadequate creep resistance. Among all the undesirable properties, the inadequate aqueous corrosion resistance for Mg-based materials is investigated at the earliest but is found to be the most difficult to deal with. Traced back to 1831, Bussey put a piece of Mg in an outdoor environment and found the Mg sample was covered with hydroxide after being exposed to moist air [26]. Thirty years later, the aqueous corrosion behaviour of Mg was investigated and an abnormal hydrogen evolution reaction (HER) was detected when the metal electrode was under anodic polarisation, which is the first observation of the essential Mg corrosion phenomenon, the so-called negative difference effect (NDE) [27]. Later in 1953, Petty *et al.* suggested that the anodic hydrogen evolution on Mg could be attributed to the formation of the univalent Mg^+ dissolved from the corroding Mg electrode [28]. The surface film of Mg formed during aqueous corrosion, was firstly studied by Splinter *et al.* in 1993, with more detailed investigations on the composition

and morphology of the surface film by high resolution spectroscopy in the following decades [29, 30, 31]. The alloying of the Mg substrate with other elements was found to enhance some specific properties of the metal, and to modify its aqueous corrosion mechanism and behaviour significantly. Birbilis *et al.* have reviewed the role of different alloying elements plays in the Mg aqueous corrosion, and disclosed the underlying electrochemical kinetic mechanism for different Mg alloys corrosion [32]. The presence of anions in the electrolyte like halide, carbonate and sulphate anions are found to decrease the open circuit potential (OCP) and modify the surface topology of Mg, thus affecting the corrosion rate based on studies over the last decade [33, 34].

In addition to the classical experimental investigation on Mg aqueous corrosion, the rapid development of computational techniques and theoretical framework during the past decades has empowered the feasibility of modelling Mg aqueous corrosion at an atomic scale through supercomputer clusters. Since 2015, Williams *et al.* first studied the water dissociation and hydrogen evolution on the Mg (0001) surface using density functional theory (DFT) [13]. In the following five years, Taylor and Yuwono *et al.* have established a series of kinetic models within the DFT framework and have depicted several thermodynamic blueprints of aqueous Mg corrosion by theoretically studying the corrosion reaction happens at the Mg/water interface, which shed lights on the atomic-scale corrosion mechanism of Mg [14, 18, 35, 36].

Alongside studies of the fundamental mechanism of Mg aqueous corrosion, investigations of rational corrosion protection techniques and methods for Mg alloys have become a crucial topic. In the first place, it was found that reducing bad design, surface impurity and detrimental inclusion from the Mg matrix could improve the corrosion resistance moderately [37]. Modification of the chemical composition and phase distribution within the Mg substrate by adding different elements is reliable and feasible to prevent the metal from bad aqueous corrosion. For instance, Meng *et al.* found that doping Mg with some rare-earth (RE) elements could prompt the corrosion resistance of the Mg matrix by reacting with harmful impurities in the sample and forming some stable second phases [38]. Different types inhibitor molecular groups (adsorption-type, passivation-type and precipitation-type) introduced to the Mg surfaces could react with ions in the electrolyte and form insoluble films or deposition layers on top of the metal surface therefore preventing the further aqueous corrosion of the metal without altering

its intrinsic properties [39]. The most effective corrosion-prevention technique of Mg is to coat the Mg base with a uniform and porosity-free anti-corrosion coating. In the 1970s it was found that a Cu-Ni-Cr ternary coating is capable of preventing Mg from being badly eroded in a mild exterior environment [40]. With micro-arc oxidized coatings or plasma electrolytic oxidation (PEO) coatings which are produced from base silicate (or glycerol-added silicate) electrolyte, the aqueous corrosion resistance of AZ91D and AM50 Mg alloys is significantly enhanced [41, 42, 43]. In recent years, some novel types of coatings, like hydrophobic epoxy resin coating, graphene composite coating and metal-organic frameworks (MOF)-type sol/gel coating are coated with Mg-based alloys to suppress the deleterious aqueous corrosion [44, 45, 46]. Even though the anti-corrosion techniques of Mg alloys are developing rapidly and blossoming out in recent years, searching for a less expensive, more potent and more environmental-friendly corrosion prevention technique is still extremely urgent for several industries who need to expand and extend the application of the Mg-based alloys. Furthermore, uncovering the fundamental mechanism of Mg aqueous corrosion on the atomic scale is an essential link to the corrosion protection course.

1.2 Computational Materials Science and Ab initio Simulation

With the rapid rise in computing power during the last decades, computational materials science and atomic modelling techniques have expanded exponentially and led a new revolution in material science which bridges the gap between the macroscopic behaviour of materials and the microscopic (molecular and atomic) principles governed by nuclei and electrons [47]. Ranging from different dimensional sizes of the system being investigated, multi-scale modelling methods and theories are developed constantly in computational materials science as shown in Figure 1.1 [5]. For a complex engineering problem which involves a component at the macro-scale (the geometry generally on the order of millimetres and above), the finite element analysis (FEA) is preferable by subdividing the bulk system into several diminutive parts with the construction of mesh grid for an object. The interesting engineering materials properties or phenomena such as plastic/elastic deformation and heat transfer could be studied by solving relevant differential

or integration equations on the fine mesh grid. Concerning the system with a size similar to or marginally smaller than the macroscopic size (approximately in between micrometres and millimetres), the microstructure and properties of the material are possible to be investigated by the Monte Carlo (MC) method. The MC method is an efficient and simple method to be implemented because it is only based on statistical mechanics and requires some random atomic jump according to some specific rules to determine the lowest energy state of the system. For instance, the typical deposition process (physical vapour deposition and chemical vapour deposition) of coating materials or a thin film on substrate materials is widely simulated through the MC method [48].

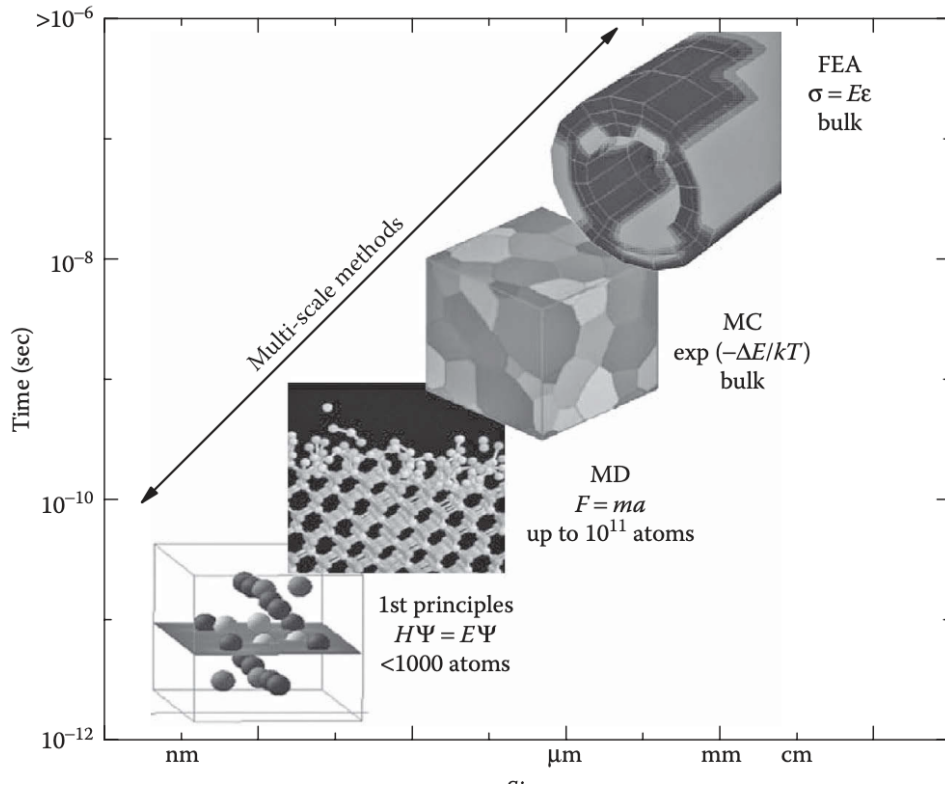


Figure 1.1: Different materials modelling methods for several systems with distinct sizes. Generally, the more atoms/molecules in the system, the required simulation timescale is larger. (as reproduced from [5])

In terms of studying the microstructure evolution of materials at a mesoscopic scale, such as the phase change in the metal solidification process, the phase-field approach is applicable and robust. The key idea of the phase-field method is to introduce an order parameter (with two distinct values in each phase, generally are 0 and 1) which varies smoothly near the interface of

two phases, thus transferring the mathematical description of the interface during the phase transition from a sharp model to a diffuse one [49]. The first groundbreaking work using the phase-field was done twenty years ago by Karma, who investigated the dendritic alloy solidification quantitatively [50]. Nowadays, after being deeply developed for decades, the phase-field method has been widely applied in several solidification dynamic problems, such as modelling the orientation selection in the dendrite growth for a binary alloy and investigating the microstructure evolution and creep deformation in some complex superalloys [51, 52].

For the classical many-body system with size at a mesoscopic scale or nanoscale (the number of atoms within the system up to 10^{11}), the traditional molecular dynamics (MD) approach, which describes the positions, velocities and forces on atoms as a function of time by solving the fundamental Newton's equations of motion ($\vec{F} = m\vec{a}$), is quite popular since originally developed in the early 1950s [53]. The force field between atoms or the potential energy surface within the framework of MD is generally calculated from some interatomic potentials or classical mechanical force fields, such as harmonic bond potential, finite-extensible nonlinear elastic potential and the empirical Lennard-Jones (LJ) potential. Furthermore, to extend the ensembles which could be described by the MD approach (the fundamental system is total-energy conserved, also nominated as NVE ensemble), the thermostats and the barostats are developed to describe a system with constant temperature or constant pressure (refers to the NVT and NPT ensemble) [54]. In the 1960s and the early 1970s, the classical MD method could only model some simple and small systems, like some monoatomic/molecular liquids, molten salts and small polymers [55]. However, thanks to the rapid development of algorithms and the quick improvement of computing power, it is possible to simulate a very large polymer or even a complex protein-DNA system within a solution using the MD approach implemented in a modern computer cluster in a rational timescale. Although remarkably robust and effective, the MD approach still has some inevitable limitations. First, the interatomic potentials are commonly parameterized from experimental or *ab initio* calculation data, thus making them less accurate and untransferable. Second, some quantum effects for low-temperature or light-atom motions are always ignored in the MD approach, which could lead to inaccuracy or errors in the results.

To investigate the properties of a system with a nanoscale size (containing up to several

thousands of atoms), a first-principles model based on quantum mechanics is more flexible and reliable. Compared with the traditional MD approach, the first-principles (or equivalently *ab initio*) method does not depend on any pre-acquired parameters or fitting data from experiments but only on some basic constants of atoms and electrons so that the fundamental many-body Schrödinger equation (SE) could be solved productively with different approximations. The common denominator of various first-principles materials simulation theories or techniques is nominated as density functional theory (DFT), which reduces the complexity of the many-body SE by substituting the troublesome electron-electron interaction term with an “average” Hartree potential term and the exchange-correlation potential term [56]. According to the famous Hohenberg-Kohn theorem, the total energy of a many-electron system in its ground state is a functional of the electron density ($n(\vec{r})$), which could be estimated through the summation of the probabilities of finding electrons in all occupied states [57]. Applying the variational principle for the system total energy to the ground state electron density, the most fundamental equation which is the “non-interacting” SE-like equation within the framework of DFT, the Kohn-Sham equation, is then obtained to solve the wavefunction of those non-interacting fictitious electrons [58].

With the aid of DFT, a multitude of broad properties for materials can be computationally acquired, such as the binding energy of molecules, cohesive energy and equilibrium structure of solids, the vibrational properties of materials, the band structures for metals and semi-conductors and the dielectric/optical/magnetic properties for some functional materials. Moreover, DFT is capable of depicting the solid-liquid interface structure accurately and is also able to describe the molecular ad(de)sorption, dissociation process or other important electrochemical process on the electrolyte/electrode interface precisely. Therefore, it is rational to investigate the Mg aqueous corrosion mechanism at an atomic scale with DFT in our study because it could unravel some detailed atomic surface chemistry, such as charge transfer/redistribution near the interface and the adsorption pattern of water molecules or other clusters on the surface, which are difficult or less efficient to obtain by currently available experimental techniques. More importantly, the DFT calculation results could also be a credible theoretical benchmark or verification to guide the experiments or further support some significant experimental data, with relatively

less expenses but fairly essential atomic-scale views.

1.3 Significance of Current Research

During the past few decades, extensive experimental and theoretical studies on high purity Mg and Mg alloys' aqueous corrosion behaviour and mechanism have been performed with numerous novel findings reported and several new theories proposed in the literature. Nevertheless, there's still a lack of, or remaining debate on the underlying mechanism for Mg corrosion in aqueous electrolyte at the atomic scale. The most perplexing phenomenon of Mg corrosion under aqueous conditions is the negative difference effect (NDE), which corresponds to an enhanced hydrogen evolution reaction (HER) on Mg surfaces when the working electrode is under anodic polarisation. Multiple different theories have been proposed to demonstrate the mechanism of the NDE for Mg based on some experimental observations or calculation results. However, there is still no consensus on the implicit mechanism for the NDE of Mg currently. In addition, the atomic structure of the Mg/water interface or the detail of the electric double layer (EDL) is hard to be directly obtained by traditional experimental tools. The thermodynamic stability of Mg surfaces in different adsorption states under various pH and potentials, and the relevant reaction kinetics on these stable surfaces during Mg aqueous corrosion require for further investigation at the scale that the atomic and electronic principles and mechanisms of the corrosion reactions could be clearly unravelled.

In the current study, first-principles calculations within the DFT formalism are performed to investigate the Mg aqueous corrosion mechanism at the atomic scale. The most significant features of our atomic simulation work are as follows:

i) we use the experimental observations and results of Mg corrosion electrochemistry to construct our theoretical simulation model for the Mg/water interface, and then correlating our calculation results (essential interface properties, such as the geometry and the potential of zero charge) to the experimental conditions as a verification;

ii) we provide new insights into the corrosion product (hydride) formation of Mg and suggest a robust indicator for predicting stable adsorption sites of atoms/radicals on the Mg surfaces

during aqueous corrosion;

iii) we formulate a general thermodynamic model to capture the essential features of stable Mg surfaces in an aqueous environment and to determine the important corrosion reaction kinetics on these surfaces under different pH and potentials.

1.4 Overview of Chapters

The following is a summary of each chapter in this thesis. We start the thesis by introducing the background knowledge of Mg aqueous corrosion, the development of computational materials science and the significance of our research work in **Chapter 1**. In **Chapter 2**, we provide a literature review concerning the current understanding of the aqueous electrochemistry of Mg and its alloys, essential thermodynamics and kinetics for Mg corrosion and important theoretical electrochemistry theory and model. In **Chapter 3**, we discuss the general ab initio simulation method we use and revisit the fundamental theory and basic mathematical formalism for the density functional theory. We investigate the fundamental structure of the Mg (0001)/water interface in the aqueous condition with ab initio molecular dynamics, and also relate the theoretical-calculated potential of zero charge (PZC) for Mg basal plane in the explicit water to the experimental conditions in **Chapter 4**. In **Chapter 5**, we explore the mechanism of hydrogen adsorption and hydride formation in Mg surfaces under aqueous conditions. We also suggest that the electron localisation function (ELF) is a promising indicator for predicting thermodynamically stable adsorption sites for hydrogen in Mg surfaces. In **Chapter 6**, we study the electrochemical stability of Mg (0001) surfaces under different pH and potentials in liquid water, which is followed by further investigations of correlated corrosion reaction pathways and barriers on the stable surfaces across different electrode potentials. Finally, in **Chapter 7**, we end this thesis by summarizing our findings on the Mg aqueous corrosion mechanism through ab-initio methods and providing new insights on the future research roadmap of modelling Mg aqueous corrosion and metal/water interface with current atomic modelling techniques or some brand-new methods (such as machine learning-based methods) which have tremendous potential.

Chapter 2

Overview of Mg Corrosion

Electrochemistry

¶ *Chapter Synopsis*

This chapter revisits the current headway and challenge of Mg aqueous corrosion electrochemistry drawing from both experimental works and theoretical simulation studies. In the first place, the advantages/limitations and the widespread applications of Mg and its alloys are reviewed, followed by an introduction of their poor corrosion resistance in a humid environment. The aqueous corrosion (redox) reactions and some typical corrosion morphology and products of Mg are then discussed based on the experimental studies. This chapter also provides a comprehensive overview of proposed mechanisms for the negative difference effect (NDE) of Mg aqueous corrosion, which is an abnormal hydrogen evolution reaction distinguishing Mg corrosion and other metals' corrosion. The Mg corrosion kinetic models, the electrochemical stability of different corrosion products or various surface states, and the formation of the corrosion surface film of Mg are also reviewed herein. To provide more insights into theoretical modelling and understanding of Mg aqueous corrosion, a discussion of the essential electrochemical theory for the electrified metal/water interface and a review of the computational techniques for modelling significant electrochemical process, *e.g.*, Mg aqueous corrosion are included as the final parts in this chapter.

2.1 General Overview of Mg and its Alloys

Magnesium (Mg) is a lustrous gray-white alkaline earth metal with several notable characteristics. It possesses the lowest melting point (923 K) and boiling point (1363 K) among all the alkaline earth metals, making it highly versatile in various applications. Furthermore, it holds the distinction of being the lightest (with a density of 1.74 g/cm^3) among all engineering structural metals [59]. Therefore, as shown in Table 2.1, magnesium has superior specific stiffness and tensile strength compared with the widely-used aluminium and iron [1]. The exceptional lightness and high strength of magnesium renders it exceptionally well-suited for applications that necessitate significant weight reduction, such as aerospace industry and automobile industry [60].

Table 2.1: Comparison of physical properties of Mg, Al and Fe (as reproduced from [1]).

Physical Properties	Magnesium (Mg)	Aluminium (Al)	Iron (Fe)
Crystal Structure	hcp	fcc	bcc
Density at 298.15 K (g/cm^3)	1.74	2.70	7.86
Specific Stiffness ($\text{Mpa}/(\text{kg/m}^3)$)	25.4	25.5	26.9
Specific Strength ($\text{Mpa}/(\text{kg/m}^3)$)	0.140	0.120	0.0500
Elastic Modulus (10^6 Mpa)	44.1	68.9	206
Thermal Conductivity ($\text{W/m} \cdot \text{K}$)	159	237	52.0

Mg is an abundant metallic element found widely in nature (the eighth most abundant element in the earth's crust and the third most abundant in seawater) and is essential for numerous biological processes within the human body. Nevertheless, pure metallic magnesium (Mg) is rarely found in nature due to its high chemical reactivity, leading to the transformation of metallic Mg into a combination with other elements, such as mineral deposits (magnesite), oxides and chlorides [61]. In 1808, the Mg was initially isolated from the mixture of magnesia and mercuric oxide by electrolysis, but the coherent Mg metal was produced around 20 years later [62]. Following the early-stage electrolytic separation techniques of Mg, currently, there are three essential procedures for fabricating bulk Mg in industry, namely the silicothermic Pidgeon

process (a thermal reduction process of Mg oxides/minerals), the Dow process (electrolysis process of molten Mg chlorides) and the solid oxide membrane (SOM) process (reducing the Mg oxide with an electrolytic method on an yttria-stabilized zirconia membrane) [63, 64, 65].

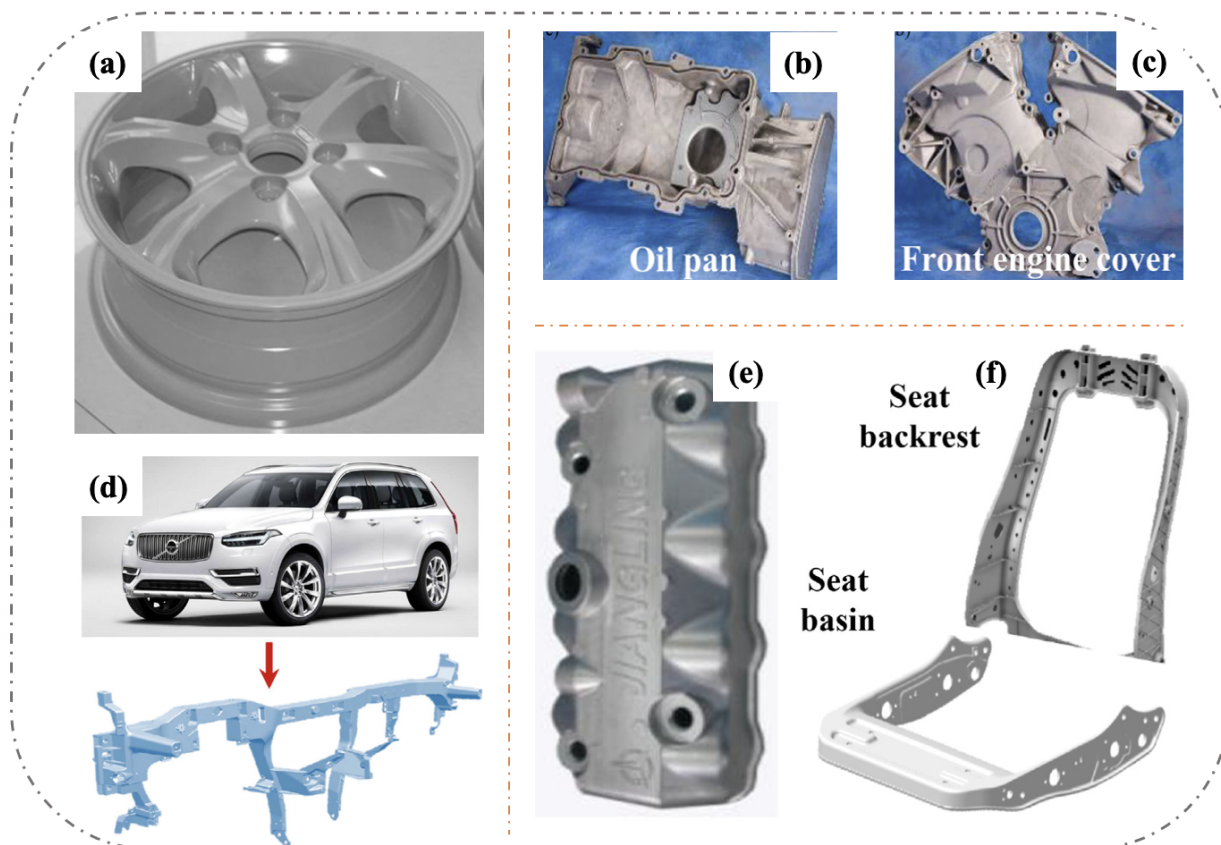


Figure 2.1: Different applications of Mg alloys in several car components: (a) Hollow Mg alloy wheel produced by billet extrusion; (b) Cast Mg-based oil pan; (c) Cast Mg alloy front engine cover made by the U.S. Automotive Materials Partnership for the Mg Intensive V6 Engine; (d) Mg-based (die-cast) central control bracket of the Volvo new XC90 K426 Model; (e) Mg cylinder head over of Changan 465Q; (f) Mg alloy seat frame. (as reproduced from [6])

Over the past decades, the need to address and mitigate the adverse effects of greenhouse gas emissions, particularly carbon dioxide (CO_2), on global warming and climate change has become increasingly imperative. This is especially true for the fossil fuels based transportation sector, which plays a significant role in contributing to these emissions (accounts for approximately 20 % of the total) [66]. The most cost-efficient method for reducing fuel consumption and greenhouse gas emission is to decrease the weight of vehicles, which requires the application of lightweight structural materials. Mg alloy, as the lightest engineering structural material with outstanding strength, is the undisputed candidate for weight reduction in the automobile

industry. Since first being used in the Beetle model of Volkswagen (each model containing approximately 22 kg Mg), Mg alloys have been widely applied in automobile manufacturing. From 2005 to 2015, the average weight of Mg used per car has increased from 3 kg to 50 kg [67]. In 1928, Porsche achieved a groundbreaking milestone by producing the first car engine that incorporated Mg. This innovative approach resulted in a substantial reduction in engine weight, typically ranging from 20% to 70% when compared to traditional steel-made engines [68]. Moreover, the substitution of cast iron or Al-based alloys with Mg alloys in various car components, including the engine block, gearbox, wheels, oil pan, and engine cradle, presents a significant opportunity for weight reduction [69]. In the case of replacing cast iron, this substitution alone could result in a total weight reduction of up to 50 kg. Similarly, substituting aluminum alloys with Mg alloys could contribute to a reduction in car mass by approximately 20 kg. Figure 2.1 demonstrates the utilization of magnesium (Mg)-based alloys in various critical components of a modern car model.

The most frequently used commercial Mg alloy series in automobile manufacturing is the magnesium-aluminium-manganese (Mg-Al-Mn) alloy system because of its excellent castability and favourable strength characteristics. The inclusion of Al results in improved mechanical properties of the Mg substrate, including increased strength and hardness, while also enhancing the fluidity and casting performance of the molten Mg alloy during the die-casting process. Introducing trace amounts of Mn (generally in the range of 0.3 - 1.5 *wt.%* due to the low solubility of Mn) into the Mg base, barely contributes to the improvement of the strength, however, alleviates the susceptibility of the Mg substrate to a corrosion environment. It is well recognized that AM50 (5 *wt.%* Al + 0.45 *wt.%* Mn) and AM60 (6 *wt.%* Al + 0.25 *wt.%* Mn) alloys are the most typical and widely used Mg-Al-Mn alloy. The microstructure of the die-casting AM50 is characterized by a solid solution with the dominated α -Mg phase, a fully divorced eutectic β -Mg₁₇Al₁₂ phase which mainly distributes at the grain boundaries, and the smaller Mn₅Al₈ precipitates that evenly locate both inside the grains and on the grain boundaries [70]. The tensile strength, yield limit and elongation rate of AM50 are superior to pure Mg, increasing from 165 MPa to 230 MPa, 69 MPa to 125 MPa and 8% to 15%, respectively [71]. Furthermore, the Brinell hardness of AM50 is approximately 60% higher than that of pure Mg,

which suggests that the hardness of Mg could be enhanced simultaneously with an increased ductility by doping Al and Mn. Therefore, the Mg-Al-Mn alloys are suitable for fabricating ductile components in car bodies which are used at a temperature lower than 400 K, such as the seat frame, bracket, steering wheel, radiator bracket and wheel hub. In addition to its extensive utilization in the automotive industry, the Mg-Al-Mn alloy with proper surface treatment could also be applied to some corrosive environments thanks to their better corrosion resistance provided by the Mn_5Al_8 precipitates. A recent study indicates that the AM50 alloy, with a moderate corrosion rate and excellent cytocompatibility, is an ideal choice for stent applications [72].

Another significant Mg alloy system which is massively implemented in the car-fabricating industry is the magnesium-aluminium-zinc (Mg-Al-Zn) ternary alloy. In a manner similar to the introduction of Al into the Mg substrate, the incorporation of Zn into the system is also able to enhance the overall mechanical performance through the second-phase strengthening mechanism, which is facilitated by the formation of MgZn precipitates. To date, the AZ series alloys, such as AZ31 (3 wt.% Al + 0.98 wt.% Zn), AZ61 (6.5 wt.% Al + 0.99 wt.% Zn) and AZ91 (9 wt.% Al + 0.8 wt.% Zn) are the most widely-used Mg-Al-Zn alloys due to a good combination of their enhanced strength and ductility. It has been revealed that the ultimate tensile strength, the proof stress and the hardness of the AZ91 alloy fabricated with the thixomolding process (leading to fewer defects and porous in the bulk) could reach levels near 280 MPa, 190 MPa and 70 (Brinell hardness) respectively [73]. By increasing the weight ratio of Zn within the Mg-Al-Zn system, the alloy's overall strength can be improved through the generation of additional MgZn precipitates [74]. However, it is important to note that an excessive amount of MgZn can lead to the formation of a network structure along the grain boundaries. This network structure acts as a cathode, thereby accelerating the occurrence of micro-galvanic corrosion within the matrix and reducing the corrosion resistance of the alloy significantly [75]. Therefore, it is important to control the amount of Zn added into the Mg matrix, and to balance different properties of the alloy. Mg-Al-Zn alloys with rational compositions are good candidates for the more ductile car components like central control bracket, transmission housing and cylinder header cover [76].

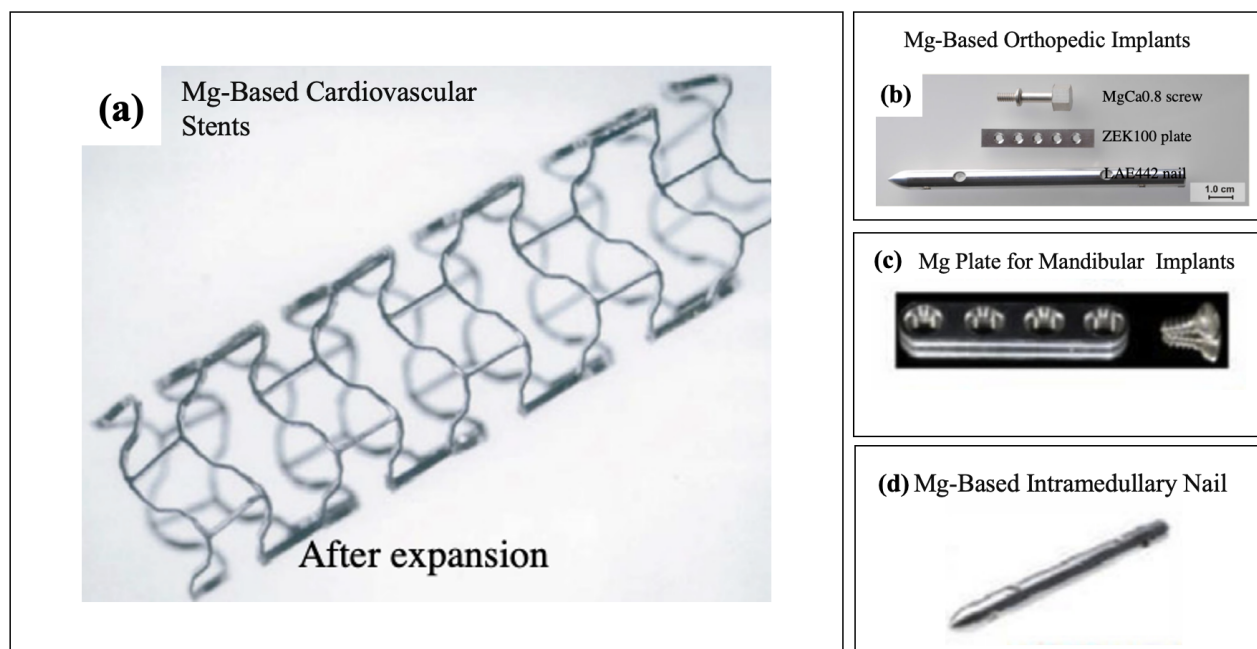


Figure 2.2: Current representative biomedical applications of Mg-based alloys: (a) Mg-based vascular stent implants, fabricated by BIOTRONIK; (b) Multiple biodegradable Mg alloy implants which are produced for orthopaedic applications; (c) Mg-based plate for mandibular implantation; (d) Mg-based intramedullary nail. (as reproduced from [7, 8])

Along with their outstanding mechanical properties and lightweight, Mg alloys are also crucial materials for a broad range of biomedical applications (as shown in Figure 2.2) thanks to their benign biocompatibility and biodegradability. The primary reason for applying Mg alloys into surgical implants is that they show non-toxicity and excellent histocompatibility (Mg implants are able to stimulate the formation of new bone) in the human body [77]. In addition, Mg is an important nutrition element for the human body (a recommended daily intake is estimated at 240 - 420 mg/day), which indicates that a slight electrochemical degradation of the implant Mg alloys is harmless to its nearby tissues. The elastic modulus of Mg alloys (generally approximately 45 GPa) is more comparable to that of bone (20 GPa) than other prospective biomedical alloys, such as Ti and Zn, with the elastic modulus of 120 and 90 GPa, respectively [8]. Such a smaller mechanical property (elastic modulus) mismatch between implant materials and bone inside the body could reduce the stress-shielding effect of the bone and avoid implant loosening or damage during the healing process. Ca, as an essential composition element of bones, is generally alloyed into pure Mg with an optimal content of 0.6 *wt.%* to improve the bending/compressive strength and the corrosion resistance of the metal [78]. Furthermore,

doping Sr into Mg could not only enhance the overall mechanical properties of the metal by grain size refinement but also increase the biocompatibility because Sr benefits bone tissue growth and reduces bone resorption [79]. Due to its biocompatible nature and exceptional strengthening properties, Zn is highly favored as another alloying element for Mg to upgrade the yield strength and the corrosion resistance in various biomedical applications.

At present, the two most popular biomedical applications of Mg alloys are the vascular stent implants and orthopaedic surgery. The first successful case of applying a Mg-based biodegradable vascular stent into the human body can be traced back to 2005 when it was placed into a 6-week-old baby's left pulmonary artery [80]. In the following decade, Mg stents, such as the WE43 stent (3.7 - 4.3 *wt.%* Y + 2.4 - 4.4 *wt.%* RE), were widely used in treating plaques in arteries or used as drug-eluting stent, and it was found that these Mg-based vascular stents are safe for nearby tissues with good mechanical performance and reasonable degradation rate during the therapy [81, 82]. Besides being implemented as vascular stents, Mg alloys are also promising candidates for orthopaedic applications in the form of screws, plates, nails and pins in light of their excellent biodegradation and bone generation capability. A recent study suggests that using a degradable Mg-based screw to treat anterior cruciate ligament rupture is better than applying other permanent implants because the implemented screw could degrade gradually thus avoiding some graft damages [83]. It has also been reported that a high-purity Mg screw was used to fix bone flaps in the frontal head of a Chinese patient who was suffering osteonecrosis in 2013 successfully, with significantly satisfactory therapeutic results and benign bone replacement [84].

Despite boasting several outstanding properties, including high specific strength, benign damping capability, superior thermal conductivity and desirable biocompatibility, Mg and its alloys face three critical limitations that hinder their further application and diminish their overall service life [85, 86, 87]. These limitations encompass low ductility at room temperature, poor creep resistance at elevated temperatures, and high chemical activity (inadequate corrosion resistance and poor flammability resistance) of Mg-based alloys [88, 89, 90].

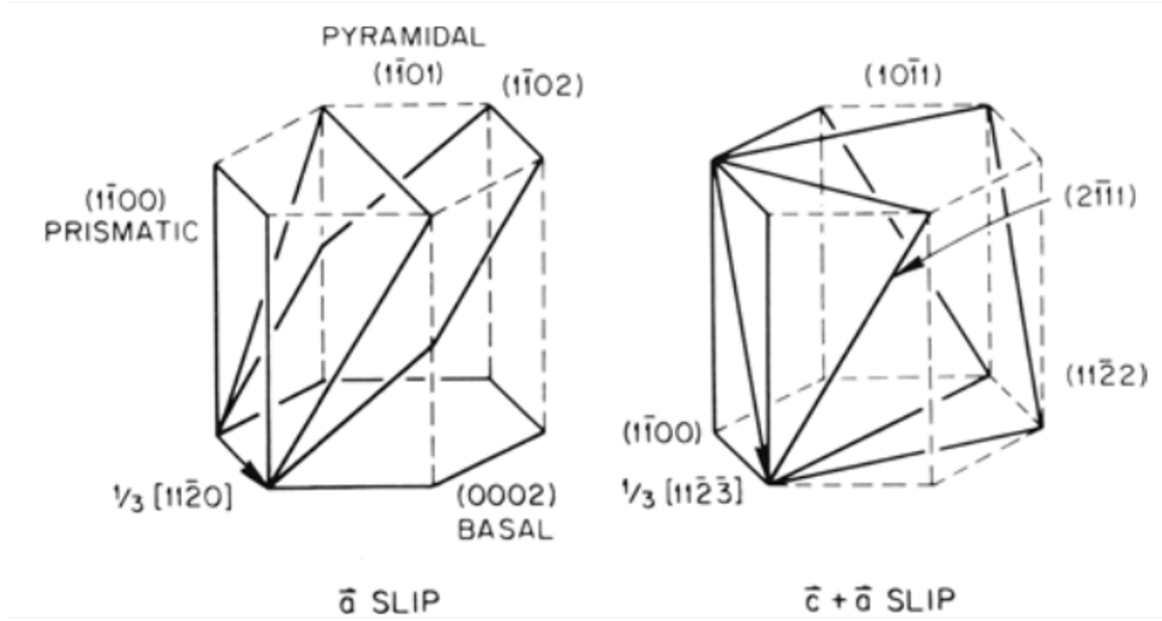


Figure 2.3: Typical hcp crystal's basal, prismatic and pyramidal slip systems with Burgers vector $\langle \mathbf{a} \rangle$ and $\langle \mathbf{c} + \mathbf{a} \rangle$. (as reproduced from [9])

It is widely recognized that the generalized plastic flow and the inherent ductility of the hcp Mg originates from the $\langle \mathbf{c} + \mathbf{a} \rangle$ dislocations occurring on the pyramidal planes ($\{10\bar{1}1\}$ and $\{11\bar{2}\bar{2}\}$ planes) [9, 91]. Nevertheless, this essential $\langle \mathbf{c} + \mathbf{a} \rangle$ dislocation that plays a crucial role in inducing significant strain along the c-axis of Mg is found to be meta-stable on the easy-glide pyramidal planes at room temperature. By employing molecular dynamics simulations, Wu and Curtin disclosed that this transient dislocation on the pyramidal plane exhibits a high tendency to transition under thermal activation, into one of three immobile dissociated dislocations with lower energies along the basal planes (the specific form of the resulting dislocation depends on the external stress) [92, 93]. As a result, this dislocation transition within hcp Mg effectively eliminates the primary slip systems responsible for c-axis strain, resulting in low ductility at room temperature. In light of the essence of the magnesium's limited room-temperature ductility, it becomes achievable to enhance its ductility by increasing the concentration of the $\langle \mathbf{c} + \mathbf{a} \rangle$ dislocations within the bulk metal. Liu *et al.* fabricated submicrometer-size Mg single crystals in a high-stress status, thus activating more stable $\langle \mathbf{c} + \mathbf{a} \rangle$ dislocations and elevating the ductility and plasticity of the samples [94]. Similarly, the utilization of a grain-refinement technique known as friction stir processing (FSP) was discovered to enhance the room-temperature ductility of the as-cast Mg-Zn-Ca alloy. [95]. Furthermore, the inclusion of rare-earth (RE) elements in the

Mg matrix, particularly those with a propensity for dislocation binding such as Y, can enhance the room-temperature ductility of Mg by promoting the activation of additional $\langle \mathbf{c} + \mathbf{a} \rangle$ slip systems within the metal [96].

While Mg and its alloys can maintain mechanical strength and perform normally at room temperature, the application of Mg-based components at elevated temperatures (above 393 K) under a long-term stress presents challenges due to the loss of strength and inherent susceptibility to creep deformation [97]. At present, there exists no universally acknowledged evidence indicating a direct correlation between the poor creep resistance of Mg alloys and the intrinsic properties of magnesium itself. Alternatively, the addition of other alloy constituents and the formation of low thermal stability secondary phases contributes to the poor mechanical properties of Mg alloys at elevated temperatures with external stress [98].

For the Mg-Al based alloys, such as AM60 and AZ91, the prominent creep mechanisms observed are diffusion-controlled dislocation climbing and grain boundary sliding [99, 100]. The existence of the typical metallic intermediate $\text{Mg}_{17}\text{Al}_{12}$ in the Mg-Al system seems to be the root cause for the low creep resistance of Mg-Al alloys [101, 102, 103]. As temperature elevated, $\text{Mg}_{17}\text{Al}_{12}$ particles become coarser and softer due to their intrinsic low melting point (731 K), thus prompting the grain boundary sliding and providing less inhibition to the dislocation climbing. As a result, the creep strain rate of the Mg-Al based alloys increases significantly at high temperatures, with softening intermetallic particles and other solutes segregation along grain boundaries, eventually contributing to an undesirable strength-loss and material failure [104]. By comprehending the fundamental factors that contribute to the inadequate creep resistance of Mg-Al alloys, numerous studies have discovered that augmenting the grain boundary or enhancing the pinning effect of second-phase particles within these alloys through the addition of supplementary elements (such as Ca, Si, Sr, and RE elements) can substantially enhance their resistance to creep [105, 106, 107, 108]. For instance, two typical Mg-Al-Si ternary alloys, AS21 and AS41, are observed to have lower creep strain rate than the AM60 and AZ91 alloys at 423 K, which is because of the inhibition of the grain boundary sliding by the Mg_2Si particles [109]. It has been discovered that RE elements exhibit a higher chemical affinity to magnesium compared to aluminium [110]. Consequently, the introduction of RE elements into the Mg-Al

systems can effectively impede the formation of the detrimental $\text{Mg}_{17}\text{Al}_{12}$ particles. Instead, it promotes the formation of Mg-RE intermetallic particles, which could hinder grain boundary sliding and enhance the creep resistance of the Mg-Al alloys [111].

In addition to the mechanical property limitations, there are also primary concerns regarding the high chemical reactivity of Mg and its alloys, particularly when employing Mg-based alloys in aggressive environments. Magnesium, especially in powder or strip form, exhibits a pronounced flammability when exposed to an open flame or heat source, resulting in the instantly ignition with deep-burning fires characterized by an elevated flame temperature of approximately 2800 K [112]. Research has revealed that the ignition tolerance of Mg is highly dependent on its form and size, leading to its ignition temperature varying in a range of approximately 90 K [113]. Specifically, finer Mg powders (6 μm particles with a ignition temperature of 650 K) or thinner Mg strips exhibit a lower ignition temperature compared to coarser powders (173 μm particles with a ignition temperature of 677 K) or thicker strips [114]. Although the bulk-form Mg requires a higher temperature for initiating the burning reaction compared to its powder/strip form, there are still increasing concerns about the flammability of bulk Mg, particularly in the high-temperature/pressure alloying process or the component manufacturing procedure, like hot rolling, welding and melting.

The ignition temperature (the lowest temperature to observe a flare on the surface) for pure Mg is in the range of 868 K–915 K, while that for common casting Mg alloys, such as AZ91D, in the air is approximately 920 K at the initial burning stage, which could then decrease gradually as the reaction is ongoing due to the formation of some liquid phases [115]. The combustion of Mg in the air typically begins with the interaction of oxygen, resulting in the formation of a nodular or porous layer of magnesium oxide [116]. Furthermore, the exothermic oxidation reaction of Mg ignition releases heat, enabling the reaction between magnesium and nitrogen in the air at temperatures exceeding 3300 K, generating the yellowish nitride phase (Mg_3N_2) [117]. To enhance the ignition resistance of Mg and its alloys, incorporating a minor amount of RE elements or calcium into the substrate Mg, along with a suitable heat treatment method, is found to raise the ignition temperature of Mg alloys by up to 300 K, which is due to the formation of a denser and more protective surface oxide layer [118, 119].

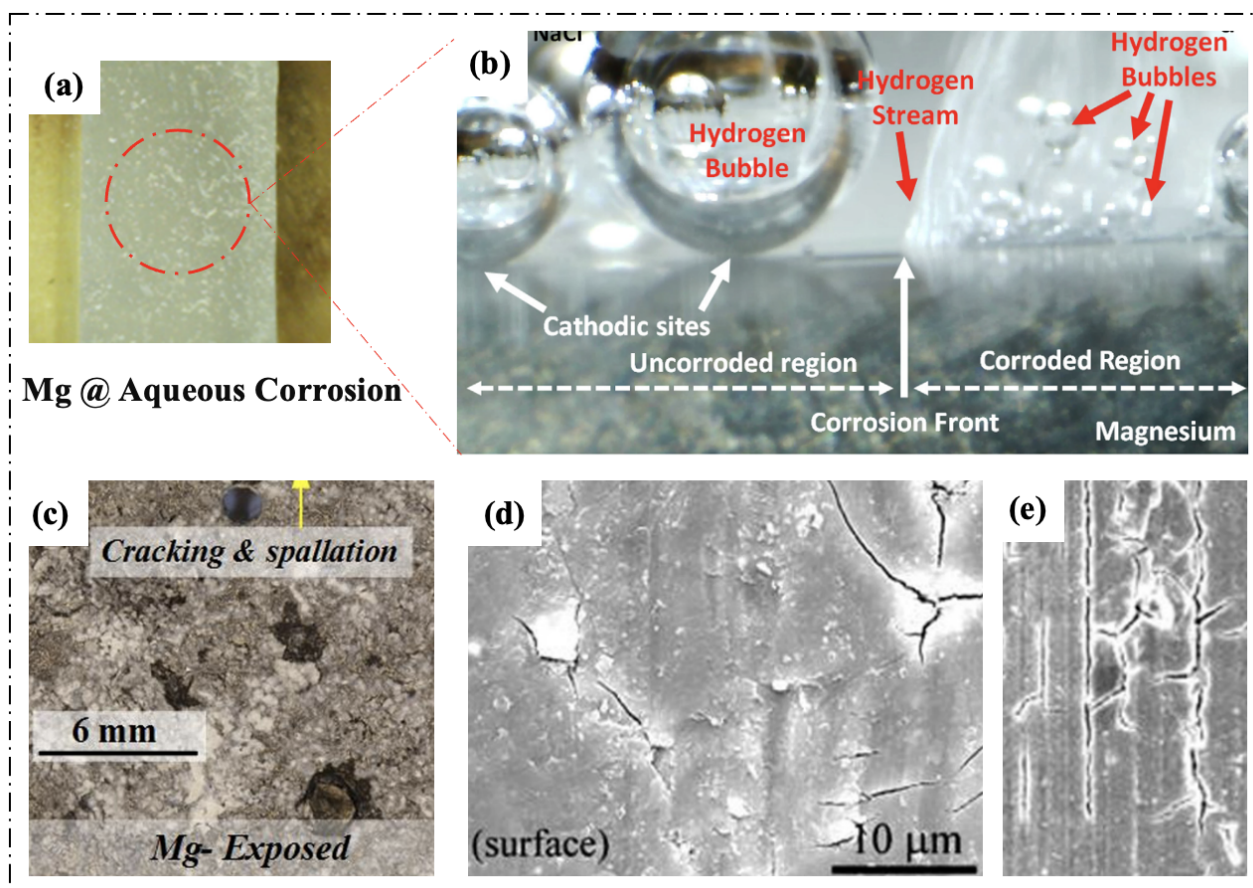


Figure 2.4: Mg Aqueous corrosion process and corrosion-induced surface morphology: (a) Mg specimen under aqueous corrosion in 0.01 M NaOH solution with additional 3.5 wt.% NaCl; (b) Magnified image of the Mg surface in (a) during corrosion; (c)-(e) Surface porous, spallation and multiple crevices of Mg alloys after exposure in a humid environment. (as reproduced from [10, 11])

Another primary limitation of Mg alloys due to the intrinsic high chemical reactivity of Mg is their poor corrosion resistance in a humid environment. When putting a piece of bulk Mg in moist air, the metal surface loses its luster because of the corrosion reaction with water/oxygen in the air, with developing a dark film with increased roughness and defects above the metal surface as the image shown in Figure 2.4(c)-(e) [26]. The aqueous corrosion reaction becomes more intense if immersing the Mg metal into the solution. The dark surface film forms rapidly as the aqueous corrosion of Mg initiates, accompanied by the release of hydrogen bubbles at the interface between the metal and the water solution [27]. The corrosion morphology of Mg in a solution is more intricate and varied compared to its corrosion in the air. When subjected to aqueous corrosion in different electrolytes or specimens with heterogeneous compositions, several distinct corrosion patterns emerge, including on-surface pittings, worm-like filaments

(also nominated as fliform), and crevices on the surface film [120, 121]. The surface film that develops on the Mg substrate during aqueous corrosion is commonly acknowledged to be porous and less compact than the surface film of other metals, like Al, only partially covering the metal as it has a low Pilling-Bedworth ratio (less than 1) [122]. As a result, this permeable film, which is susceptible to breaking in a corrosive environment that contains chloride, can only offer limited protection to the underlying metal in aqueous conditions, thus leading to the inadequate corrosion resistance of Mg. Furthermore, alloying some other elements into Mg to improve its mechanical property, however, could inadvertently accelerate the corrosion reaction rate with an essential increase in its electrochemical activity [123, 124].

Due to the significant impact of corrosion degradation on the service life of magnesium components, which can lead to unexpected structural failure and substantial economic losses, it is imperative to uncover the reaction kinetics, underlying mechanism and electrochemistry of magnesium aqueous corrosion at a more microscopic scale [125]. This knowledge is essential for developing more efficient corrosion prevention methods for Mg and its alloys in various applications so that they could keep their strength and serve normally in some corrosive environment. Accordingly, the subsequent section provides a more comprehensive revision of Mg corrosion electrochemistry and the corresponding atomic mechanisms.

2.2 Corrosion Electrochemistry of Mg under Aqueous Conditions

2.2.1 Electrochemistry Stability of Mg in Aqueous Environments

Like other alkaline earth metals, magnesium is highly chemically active and tends to transfer from its pure metal state to an oxidation state spontaneously when it contacts oxidants, such as halogens, oxygen and water. Thermodynamically, the reactive nature of metallic Mg is demonstrated by the significant negative chemical potential of the compounds or ions that contain oxidized state Mg at room temperature (298.15 K). As shown in Table 2.2, introducing a piece of Mg specimen in pure water could lead to a natural oxidation of Mg into solvated

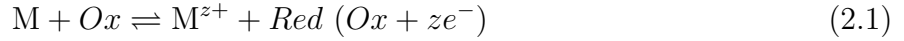
Mg ions, oxides, hydrides or hydroxides of magnesium owing to their more negative chemical potential comparing with Mg in the metallic states. Among these solvated ions and compounds, magnesium hydroxide possesses the most negative chemical potential, which is why the ions, oxide and hydride tend to convert into the most stable hydroxide phase during the aqueous corrosion of Mg. If there are some impurity ions, such as chloride ions in the solution, Mg ions and oxide from the surface film could react with these Cl^- , and form the thermodynamically more stable chloride phase. When Mg metal is placed in moist air which contains gaseous CO_2 , the (hydroxy) carbonate phase with a remarkable negative chemical potential has a natural tendency to form on top of the $\text{MgO}/\text{Mg}(\text{OH})_2$ film. It has been found that the existence of the non-conductive carbonate phase could block the anodic and cathodic sites on the surface, thus reducing the corrosion rate of Mg in the humid environment [126].

Table 2.2: Chemical potential, Gibbs formation enthalpy and magnesium oxidation states of pure Mg, Mg compounds and Mg ions at room temperature, 298.15 K (as reproduced from [2, 3]).

Species	μ° (kJ/mol)	$\Delta_f H^\circ$ (kJ/mol)	Oxidation State (Mg)
$\text{Mg}(s)$	0	0	0
$\text{Mg}^+(aq)$	-255.2	/	+1
$\text{Mg}^{2+}(aq)$	-456.1	/	+2
$\text{Mg}(\text{OH})^+(aq)$	-626.7	/	+2
$\text{Mg}(\text{OH})_2(s)$	-832.6	-924.5	+2
$\text{MgH}_2(s)$	-35.9	-75.3	+2
$\text{MgO}(s)$	-569.3	-601.6	+2
$\text{MgCO}_3(s)$	-1012.1	-1095.8	+2
$\text{MgCl}_2(s)$	-591.8	-641.3	+2

In general, the aqueous corrosion of metal is a typical electrochemical process, which indicates that the external potential and pH of the solution could have essential impacts on the type of corrosion products and the correlated corrosion mechanism. To better describe possible thermodynamically stable phases of an aqueous electrochemistry system under various conditions, the E (potential)-pH diagram, which is also known as the Pourbaix diagram, was proposed by

Marcel Pourbaix in 1963 and has been widely used in metal corrosion science and equilibrium electrochemistry studies. The Pourbaix diagram relates the electrode potential (which is referred to a standard electrode potential) and pH of the electrolysis with the famous Nernst equation, and constructs an equilibrium two-dimensional phase diagram of the electrochemical system under investigation. In the diagram, different predominated phases (solid or solvated ions) at certain pH and potentials are separated by the boundaries determined from the related Nernst equation of essential chemical species. For instance, for the following reversible redox reaction of a metal M (Ox refers to an oxidizer and Red indicates its reduction state by obtaining z electrons from the metal):



the Nernst equation could be expressed as:

$$E_H = E^\ominus - \frac{RT}{zF} \ln \frac{[M^{z+}][Red]}{[Ox]} = E^\ominus - \frac{RT \ln(10)}{zF} \log_{10} \frac{[M^{z+}][Red]}{[Ox]} \quad (2.2)$$

Here E_H and $E^\ominus$ are the voltage potential of the redox reaction at temperature T with respect to the SHE (4.44 ± 0.2 V) and the reaction potential under standard conditions (298.15 K and 101.325 kPa) respectively [127]. R is the gas constant, and F is the Faraday constant which measures the electric charge per mole of elementary charges. The redox reaction potential is also a measure of the chemical potential of electrons in the system and could be obtained by dividing the corresponding reaction free energy change (ΔG_r) with factor $-zF$. Referencing the reaction potential to the SHE not only sets a standard zero potential for different redox reactions but also establishes the foundation of constructing a Pourbaix diagram by introducing the pH dependence into the Nernst equation:

$$E_H = E^\ominus - \frac{RT \ln(10)}{zF} \left[\log_{10} \frac{[M^{z+}][Red]}{[Ox]} + \xi \text{pH} \right] \quad (2.3)$$

where ξ is a prefactor of pH depending on the number of electrons being transferred in the redox reaction and the number of hydronium involved in the reaction. Herein, the potential of

the previously mentioned redox reaction shows a linear correlation with pH, illustrating the boundary between the solid metal M and its oxidation states (M^{z+}) on the Pourbaix diagram.

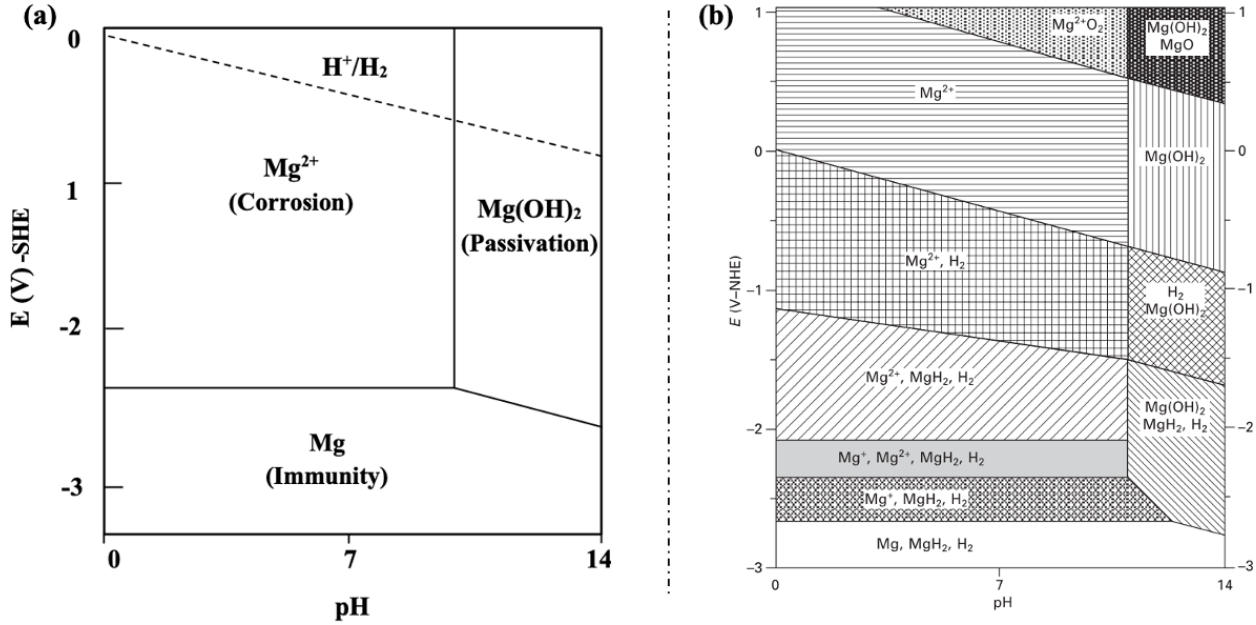


Figure 2.5: Pourbaix diagram for aqueous Mg system at 298.15 K and 1 atm: (a) Fundamental Mg Pourbaix diagram (referenced to the SHE) in water with the concentration of soluble Mg ions of approximately 10^{-6} M; (b) Mg Pourbaix diagram including meta-stable Mg univalent ions and Mg hydride phase. (as reproduced from [12, 2])

For an aqueous Mg system in thermodynamic equilibrium, three primary phases prevail: the aqueous Mg divalent ion, Mg hydroxide, and metallic Mg. Figure 2.5(a) illustrates that these three phases correspond to distinct regions on the Pourbaix diagram for Mg. The diagram highlights the immunity region, which promotes the stabilization of Mg metal, the corrosion region associated with dissolved Mg divalent ions, and the passivation region that facilitates the formation of a hydroxide surface layer (acts as a barrier and retards further Mg dissolution under aqueous conditions). The horizontal line in the diagram is the phase boundary between the metallic Mg and Mg^{2+} ions, which also indicates the dissolution potential for bulk Mg of approximately -2.38 V in reference to the SHE. This dissolution potential of Mg is significantly more cathodic than the SHE, thus suggesting a great thermodynamic driving force of eroding the metal Mg into an oxidized state. The vertical line refers to a critical pH value of 11 where soluble divalent Mg ions start to deposit and form the more stable hydroxide phase in the solution [128]. Furthermore, the phase boundary between the metallic Mg and its hydroxide phase is

determined by the Nernst equation of Mg-water reaction ($\text{Mg} + \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2 + 2\text{H}^+ + 2e^-$), which possesses the same slope as that of the water reduction reaction (dashed line in the diagram).

In comparison to the fundamental Mg Pourbaix diagram as shown in Figure 2.5(a), a more detailed diagram with all possible substances in the Mg-water electrochemical system is demonstrated in Figure 2.5(b). In this scenario, the Pourbaix diagram includes two intermediate species during the aqueous corrosion of Mg, namely the univalent Mg ion and Mg hydride. Notably, the hydride phase of Mg exhibits stability across a broad pH range, spanning approximately from 1 to 14, when the potential remains more negative (cathodic) than -1 V relative to the normal hydrogen electrode (NHE). This intermediate hydride phase can coexist alongside bulk Mg in the immunity region, both univalent and divalent Mg ions in the corrosion region, as well as the hydroxide phase of Mg in the passivation region. The cathodic potential plays an essential role in retaining the stability of the Mg hydride phase in an aqueous condition because the hydrogen anion requires extra electrons to stabilize itself. Once the potential of the system becomes more positive (or under anodic polarisation), the hydride phase of Mg tends to convert into the neutral hydrogen gas and Mg in their oxidation states through the following anodic reaction [129]:



The corresponding cathodic reaction and reaction products of Mg hydride oxidation depend on the pH of the solution, and suggest the phase boundary of the hydride phase and the soluble ions or hydroxide phase for Mg in Figure 2.5(b):



Interestingly, the anodic and cathodic reactions of Mg hydride oxidation by water both involve hydrogen evolution. This characteristic sets apart the Mg hydride oxidation from the general Mg-water reaction, as it results in double the production of hydrogen gas when the quantities

of Mg used are identical. According to this intensified hydrogen-production attribute, the Mg hydride phase is considered a significant intermediate substance during Mg aqueous corrosion. This hydride phase is deemed to be responsible for certain abnormal corrosion phenomena in Mg, such as the negative difference effect (NED), which is because the formation and decomposition of the Mg hydride can substantially alter the quantity of hydrogen gas generated under varying electrode potentials [130].

For the atypical Mg univalent ions with a short lifetime in the gaseous phase, the corresponding stable region in the Pourbaix diagram is remarkably narrower than that of the hydride phase though the aqueous univalent ion possesses a more negative chemical potential based on Table 2.2 [131]. A more cathodic potential window (less than -2.1 V to NHE) and less basic solution are required for thermodynamic stability (theoretically) of this partial-oxidized Mg ion under aqueous conditions, which indicates an extremely strict condition to find it in experiments. Up to date, there continues to be an ongoing debate on the presence of this univalent ion or equivalent species for Mg due to a lack of direct experimental evidence of their existence during Mg aqueous corrosion [132]. Therefore, unlike the experimentally observed hydride phase of Mg, it is rational to treat this theoretical aqueous ion as a secondary intermediate species during Mg corrosion and avoid illustrating Mg corrosion mechanism based on it.

Those above Pourbaix diagrams in Figure 2.5 successfully determine the most stable bulk phase of Mg in an aqueous environment under a certain potential and pH, thus constructing a thermodynamic blueprint of Mg aqueous corrosion on a macroscopic scale. Nevertheless, in reality, the corrosion reactions primarily begin at the metal-water interface, and the stability of the metal surface or its adsorption states play a crucial role in both the corrosion mechanism and reaction kinetics. Accordingly, Hansen *et al.* proposed the notion of a surface Pourbaix diagram to figure out the thermodynamically favourable surface state (with different adsorbates and surface coverage) under varying electrochemical conditions in 2008 [133]. Following this concept, Williams *et al.* firstly constructed a surface Pourbaix diagram of the hydroxylated Mg (0001) surface (with different coverages of the hydroxyl being adsorbed on the surface) based on first-principles calculation results as shown in Figure 2.6 (a) [13]. Herein, the surface diagram could also be separated into three main regions (corrosion, immunity and passivation) similar

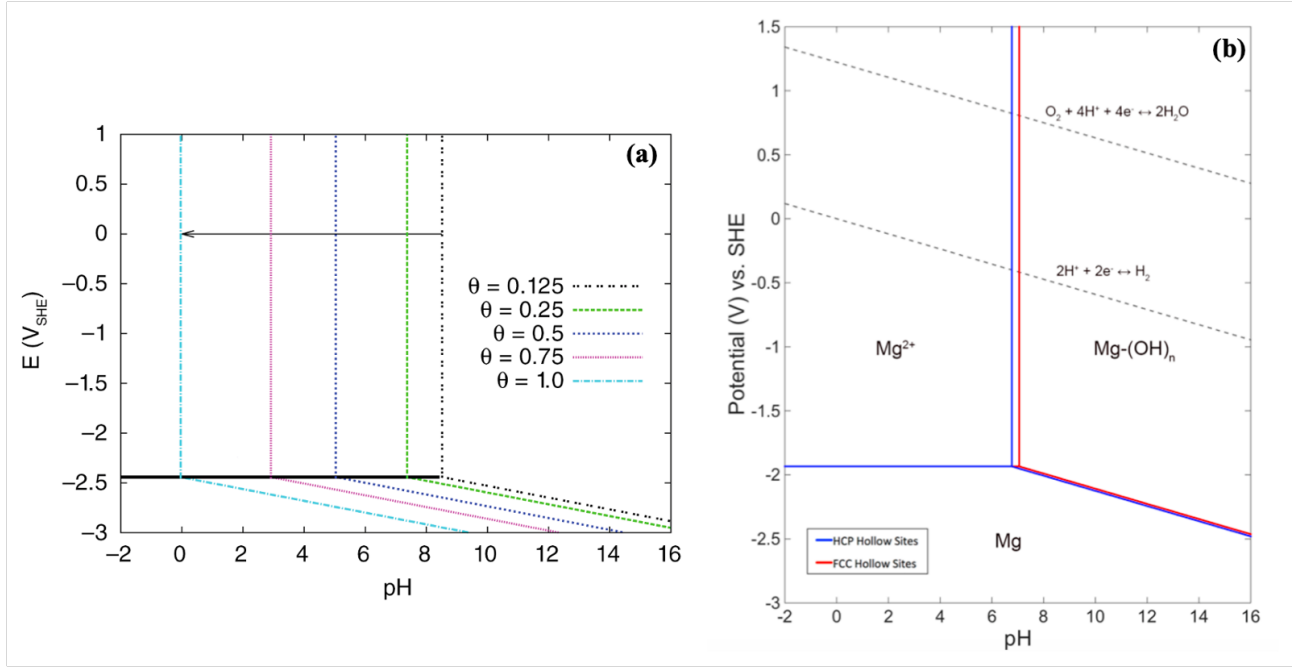


Figure 2.6: DFT-calculated surface Pourbaix diagram of Mg (0001) surface in an aqueous environment: (a) the Mg (0001) surfaces are covered by hydroxyls at fcc site with varying coverage (θ); (b) the Mg (0001) surface with hydroxyls ($\theta = 0.06$) adsorbed at fcc and hcp site respectively. (as reproduced from [13, 14])

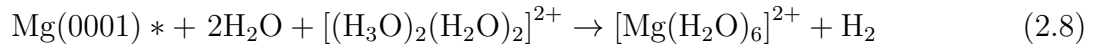
to those of the bulk Pourbaix diagram of Mg, but only replacing the bulk Mg phase and bulk hydroxide phase with a clean and a hydroxylated Mg surface. The phase boundary between the pristine Mg (0001) surface (area surrounded by the thick horizontal line and the colourful slash) and the hydroxylated surface (area enclosed by the vertical line and the slash) is identified from the Nernst equation of the following surface reaction between water and Mg:



It is clear that the surface coverage has an essential impact on the portion of each domain on the diagram: a higher coverage of surface hydroxyl tends to expand the area of the passivated Mg surface, thereby decreasing the stable region for the uncorroded Mg surface and that for the dissolved Mg. In this sense, this surface diagram indicates that a fully hydroxylated Mg (0001) surface has elevated corrosion resistance in comparison to a pristine or partially hydroxylated Mg surface, which agrees with the fact that surface hydroxide film could protect the subsurface metal from being corroded. Yuwono *et al.* further investigated the influence of the adsorption

site (fcc or hcp hollow site) on the hydroxylated Mg (0001) surface Pourbaix diagram, and found a limited adsorption-site dependence of the diagram as demonstrated in Figure 2.6(b) [14].

While the initial demonstration of the stability of the pristine and hydroxylated Mg (0001) surface under aqueous conditions is noteworthy, the aforementioned Mg surface Pourbaix diagrams can be considered rudimentary and possess notable limitations in accurately quantifying stable Mg surfaces during corrosion. Firstly, these surface Pourbaix diagrams only determine the phase boundary between the pristine surface and a hydroxylated surface with a specified coverage, yet lack a detailed description of the phase boundary (or relative stability) for these hydroxylated surfaces with distinct coverage or for Mg surfaces covered by other possible adsorbates (such as H and O atoms) from water. In addition, the inclusion of solvated Mg ions into a surface Pourbaix diagram through the Nernst equation-based method obfuscates the bulk reaction and surface reaction thus leading to a blurred definition of the phase boundary between the pristine Mg surface and a dissolving Mg. For instance, the related chemical reaction for the Mg surface dissolving into Mg divalent ions used by Williams *et al.* is as follows [13]:



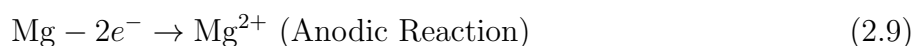
Here, the reactant encompasses a pristine Mg surface while the product is a water-solvated Mg ion (bulk phase), which leads to a discrepancy in depicting the status of Mg. The Mg dissolution reaction involves the formation of certain theoretical chemical species, such as the hydronium dication, which are used to simplify the calculation of reaction enthalpy. However, it is important to note that these theoretical species may not necessarily be present in experimental conditions. Therefore, these surface Pourbaix diagrams constructed from Nernst equation-based method significantly depend on the reactants and products selected for the reaction, which is not expected for empirically determining the most stable surface in an electrochemical system. In **Chapter 6**, instead of following the Nernst equation-based method, we construct the Mg surface Pourbaix diagram that includes all possible adsorption states (OH, O and H adsorption at different adsorption sites with varying coverage) in an aqueous environment based on a semiconductor defect-inspired method within a grand-canonical ensemble [134]. This method circumvents the

need to calculate the phase boundary between various surfaces based on perplexing surface reactions. Instead, it constructs the diagram by identifying the surface state with the lowest chemical potential relative to the species in a reservoir under specific electrochemical conditions, such as pH and potential, thus providing an intuitive insight into the electrochemical stability of various Mg surfaces during aqueous corrosion.

2.2.2 Mg Corrosion Kinetics

In the previous section, we discussed the electrochemical thermodynamics of Mg corrosion, highlighting the susceptibility of metallic Mg to undergo corrosion and transition into their oxidation states under specific conditions. However, when it comes to understanding the corrosion behaviour and reaction rate of Mg in aqueous environments, traditional thermodynamics investigations like the Pourbaix diagram fall short of providing comprehensive information. This limitation necessitates a closer examination of the electrochemical kinetics associated with Mg corrosion, which could unravel the atomic mechanism for some significant corrosion phenomena.

The corrosion reaction of Mg in water is characterized as a fundamental redox reaction, which can be expressed as two distinct half-cell reactions (Equation 2.9 and 2.10):



where the anodic process enables the dissolution and oxidation of metallic Mg into Mg divalent ions by losing two electrons, and the cathodic process is a normal hydrogen evolution reaction (HER) which is associated with water dissociation and reduction. When a piece of Mg metal is immersed in an aqueous electrolyte solution, electrons have a tendency to continuously transfer across the interface through the preceding redox reaction until an electrochemical equilibrium is established at the interface. Under equilibrium conditions, the rate of electronation and de-electronation process of each half-cell reaction at the electrode/solution interface cancel each other, thus building a reversible half-cell potential or the nominated equilibrium potential (E_{eq}) which is the absolute potential difference across the interface [135]. The current flows that

correspond to the forward and the reversible reaction of the half-cell reaction at equilibrium are equivalent to each other in magnitude but opposite in direction, with the name of equilibrium exchange current density (i_0), contributing to a zero net current flow across the interface [136]. This characteristic current density illustrates the intrinsic rate of the half-cell reaction, or the electron exchange rate between the electrode and substances in the solution, therefore reflecting the kinetics of a particular interfacial reaction. It has been revealed that the exchange current density (for the cathodic reaction, and vice versa for the anodic reaction) primarily depends on the surface reaction rate and concentrations of reactants (oxidants) as well as products (reductants) [137]:

$$i_0 = Fk_0 ([Ox]^{1-\beta}[Red]^\beta) \quad (2.11)$$

where k_0 is the reaction constant and β is a symmetry factor which refers to a dimensionless charge transfer coefficient. Once there is a net current flow across the electrode-electrolyte interface, the established equilibrium for the half-cell reaction gets disrupted. As a result, the interface potential (E) is biased from the equilibrium potential, leading to an overpotential ($\eta = E - E_{eq}$) directly correlated to the non-equilibrium drift-current density. The most famous mathematic expression describing the relationship between the overpotential and drift current density for an electrochemical interface reaction (*e.g.*, for an anodic reaction) is the Butler-Volmer equation [138]:

$$i_{\text{drift}} = \overrightarrow{i} - \overleftarrow{i} = i_0 \left[\exp\left(\frac{(1-\beta)F\eta}{RT}\right) - \exp\left(\frac{-\beta F\eta}{RT}\right) \right] \quad (2.12)$$

where $\overrightarrow{i}$ corresponds to the forward de-electronation (anodic) current density and $\overleftarrow{i}$ refers to the backward electronation (cathodic) current density. When the interface potential is strongly positive-biased from the equilibrium potential ($\eta \gg 0$), the electronation term in the Butler-Volmer equation becomes negligible, thus simplifying the equation to the anodic Tafel equation [139]:

$$i_{\text{drift}} \approx \overrightarrow{i} = i_0 \exp\left(\frac{(1-\beta)F\eta}{RT}\right) \quad (2.13)$$

while the potential is significantly cathodic ($\eta \ll 0$), the Butler-Volmer equation is approaching

the cathodic Tafel equation:

$$i_{\text{drift}} \approx \overleftarrow{i} = i_0 \exp\left(-\frac{\beta F \eta}{RT}\right) \quad (2.14)$$

Considering the polarisation of the interface is by definition small ($\eta \approx 0$), it is rational to approximate the exponential function of the overpotential as a function of $1 + \frac{(1-\beta)F\eta}{RT}$ or $1 - \frac{\beta F \eta}{RT}$, thereby leading to a linear relationship ($i_{\text{drift}} \approx i_0 \frac{F\eta}{RT}$) between the drift current and the overpotential. This linear relationship also demonstrates that the electrode reaction under low-field conditions, slightly off the equilibrium, shows an ohmic behaviour across the interface.

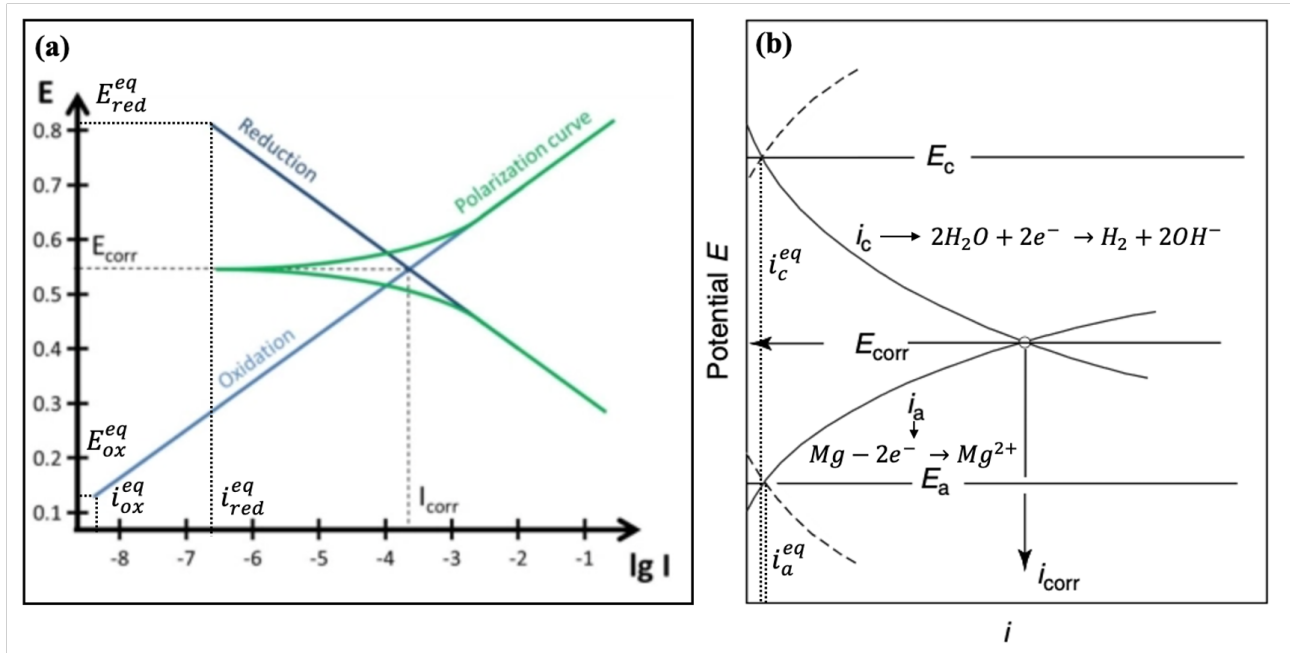


Figure 2.7: Schematic Evans diagram for (a) An arbitrary corrosion (redox) reaction with the potential as a function of the logarithm of the current density; (b) Mg aqueous corrosion reaction, with the cathodic reaction as the HER and anodic reaction as the Mg dissolution reaction. (as reproduced from [15])

As well as the half-cell reaction equilibrium, the overall redox reaction at the interface, including the anodic and cathodic reaction, should also reach equilibrium with the anodic current equal to the cathodic current to avoid an accumulation of charges on the electrode. Such an equilibrium establishment for the cathodic (reduction) and anodic (oxidation) reaction is shown in Figure 2.7, which is also known as the Evans diagram and essential for understanding the underlying redox reaction kinetics [140, 141]. In Figure 2.7(b), the Evans diagram depicts the intersection point where the cathodic HER rate (current density) aligns with the rate of the anodic Mg dissolution reaction. This point is referred to as the corrosion potential (E_{corr}),

or the open-circuit potential, and the corrosion current (i_{corr}) for Mg, whose values signify the initiation point and rate at which metallic Mg undergoes corrosion. The characteristic potential and current density of metal corrosion primarily rely on the standard equilibrium potentials and exchange current densities of the individual half-cell reactions. Moreover, they provide insights into the kinetic aspects of the redox reactions. It is worth noting that the corrosion potential deviates from the standard equilibrium potential for Mg dissolution as depicted in the Pourbaix diagram. This discrepancy arises because the former takes into account the equilibrium of the entire cell reaction, whereas the latter solely considers the equilibrium of the half-cell reaction.

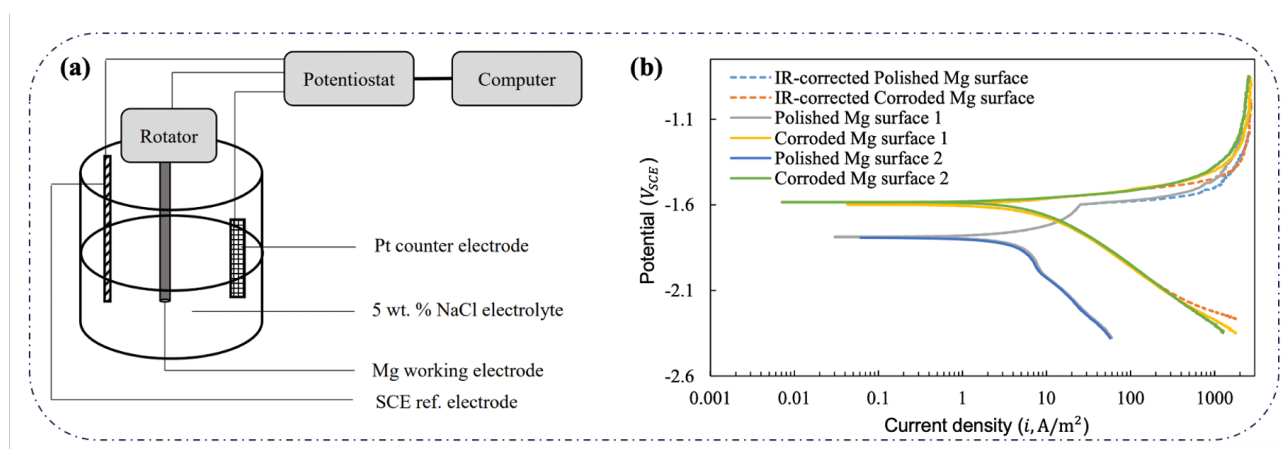


Figure 2.8: Potentiodynamic polarisation method for Mg aqueous corrosion rate measurement: (a) Basic set-up of the potentiodynamic polarisation experiments for Mg corrosion using a rotating disk electrode; (b) the corresponding polarisation curves for Mg specimens with different (polished or pre-corroded) surface states, with the electrolyte as 5 wt.% NaCl and the polarisation scanning rate of $1 \text{ mV} \cdot \text{s}^{-1}$. (as reproduced from [16])

The Evans diagram for Mg aqueous corrosion is typically determined experimentally using the potentiodynamic polarisation method [142]. This technique involves adjusting the potential of a metal electrode within a predetermined range, relative to a reference electrode, such as the standard hydrogen electrode (SHE) or the saturated calomel electrode (SCE). The process entails the measurement of current flows passing between the working electrode (the metal electrode under investigation) and an inert electrode (the counter electrode) immersed in a solution in response to the scanning voltage. A fundamental set-up of the potentiodynamic polarisation method for studying the polarisation behaviour of the Mg aqueous corrosion is displayed in Figure 2.8(a). Figure 2.8(b) shows the polarisation curves (potential *vs.* current density) for Mg samples with a polished surface or a corrosion-product-covered surface measured

by the aforementioned set-up [16]. Based on the Mg polarisation curves, it can be observed that the corrosion potential of the pre-corroded samples is more positive compared to the polished samples. This difference indicates a better corrosion resistance of the corroded Mg surface when compared to the polished or pristine Mg surface. This enhanced corrosion resistance on the corroded surfaces stems from the presence of a corrosion product which is a combination of Mg hydroxide and oxide forming a protective layer on the metal surface [143]. Additionally, these surface products improve the kinetics of the cathodic hydrogen evolution reaction (HER) because the presence of the hydroxide within the surface film disrupts the local ionic equilibrium (*i.e.*, Mg^{2+} ions precipitate in super-saturated conditions requires more OH^- from the solution), hence accelerating the water self-dissociation reaction and the hydrogen evolution process [144]. For the anodic reaction kinetics, the polarisation curves of the polished Mg samples witness an acceleration of the anodic corrosion reaction at approximately -1.6 (V_{SCE}), where the pitting corrosion of Mg initiates due to the lack of protection from the thick surface film, thereby boosting the anodic Mg dissolution reaction. To further investigate the polarisation curves of Mg corrosion by converting the current density into their logarithm, a Tafel characteristic curve could be determined, and the essential kinetic parameters for each half-cell reaction, like the exchange current density (i_0) and the charge transfer coefficient (β), are obtainable based on the Tafel equation.

Although experimental techniques, such as the potentiodynamic polarisation and the potentiostat polarisation method, are capable of assessing crucial kinetic parameters related to the aqueous corrosion of Mg, the explanation of certain peculiar corrosion phenomena for Mg solely based on experimental measurements remains challenging in the absence of a comprehensive understanding of the underlying corrosion mechanism at an atomic scale. Thanks to the development of computational materials science and theoretical modelling techniques during the last decades, numerous theoretical kinetic models for Mg aqueous corrosion have been constructed through the nudged-elastic-band (NEB) method within the DFT framework to estimate the corrosion reaction barrier and the reaction rate [18, 19, 35, 145, 146]. For a general heterogeneous chemical reaction, its catalytic rate constant is dominated by the traditional

Arrhenius equation:

$$v = A \exp \left(-\frac{E_a}{RT} \right) \quad (2.15)$$

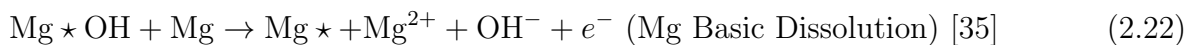
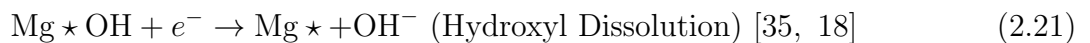
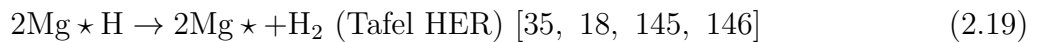
where A is the rate pre-factors (also named as the standard attempt frequency), and E_a refers to the reaction energy barrier which could be determined from the DFT calculations [147]. Nevertheless, the electrocatalytic rate constant of an electrochemical reaction also displays a potential dependence according to the Butler-Volmer equation (Equation 2.12) [136]:

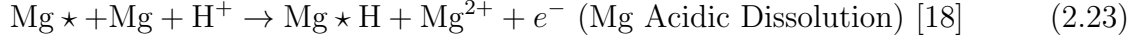
$$v'_{\text{anodic}} = \frac{i}{c_0 n F} = A \exp \left(-\frac{E_a}{RT} \right) \exp \left(\frac{\alpha_a F \eta}{RT} \right) \quad (2.16)$$

$$v'_{\text{cathodic}} = \frac{-i}{c_0 n F} = A \exp \left(-\frac{E_a}{RT} \right) \exp \left(-\frac{\alpha_c F \eta}{RT} \right) \quad (2.17)$$

with c_0 as the concentration of reactants, α as the charge transfer coefficient, F as the Faraday constant, and n referring to the number of electrons transferred in the reaction. Therefore, by acquiring knowledge of the reaction barrier for an interface electrochemical reaction through theoretical analysis, it becomes possible to reconstruct the potential-current density curve using Equation 2.16 and 2.17.

In the theoretically constructed kinetic model of Mg aqueous corrosion, extensive research has been conducted on four primary interface reactions occurring on the Mg (0001) surface. These include the water dissociation reaction, the hydrogen evolution reaction through the Tafel or Heyrovsky mechanism, the surface hydroxyl dissolution reaction, and the Mg dissolution reaction [148]:





The theoretical estimation of the reaction enthalpy and the associated reaction energy barriers for the aforementioned reactions has been conducted using both implicit and empirical solvation models with varying DFT parameters. The resulting values are presented in Table 2.3, showcasing the findings of the investigations:

Table 2.3: The reaction enthalpy and reaction energy barrier for some essential electrochemical surface reactions on the (0001) surface for Mg aqueous corrosion.

Interface Reaction	Reaction Enthalpy (eV)	Reaction Barrier (eV)
Water Dissociation ^{2.18}	$-1.78^{[145]}, -1.82^{[146]}$	$1.31^{[145]}, 0.66^{[146]}$
Tafel HER ^{2.19}	$0.14^{[145]}, 0.23^{[146]}$	$1.31^{[36]}, 1.04^{[145]}, 1.26^{[146]}$
Heyrovsky HER ^{2.20}	$-0.30^{[36]}, -1.07^{[146]}$	$1.08^{[36]}, 0.28^{[146]}$
Hydroxyl Dissolution ^{2.21}	$-0.83^{[35]}$	$1.90^{[35, 36]}, 1.06^{[18]}$
Mg Dissolution ^{2.23, 2.22}	$-2.83^{[36]}, -1.44^{[146]}$	$1.51^{[35]}, 0.97^{[146]}$

It is clear that, as the initial step for the Mg aqueous corrosion, the water dissociation reaction on the Mg (0001) surface possesses a significant negative reaction enthalpy and an applicable reaction barrier, suggesting a spontaneous dissociation and adsorption of water molecules on the metal surface. For the homolytic Tafel hydrogen evolution pathway, despite a moderate reaction barrier, the DFT calculation results indicate that this reaction is less prone to happen at the Mg (0001)/water interface due to its endothermic characteristic. It has also been found experimentally that the kinetic of Tafel HER is predominated by the surface coverage of the negatively charged hydrogen (θ_{H}), which could vary under different electrode overpotentials [149]. In comparison, the heterolytic HER through the Heyrovsky pathway with a negative reaction enthalpy and a lower reaction barrier is more likely to occur on the Mg surface in a solution, and has been proven to be the primary source of the cathodic-related hydrogen gas and the cathodic HER current densities [14, 150]. The thermodynamically favorable hydroxyl dissolution reaction on the Mg surface plays a crucial role in generating new adsorption/reaction sites, thereby ensuring the continuous occurrence of corrosion reactions, with a typically cathodic feature [35]. Being consistent with the thermodynamic study, the metallic Mg has a significant negative

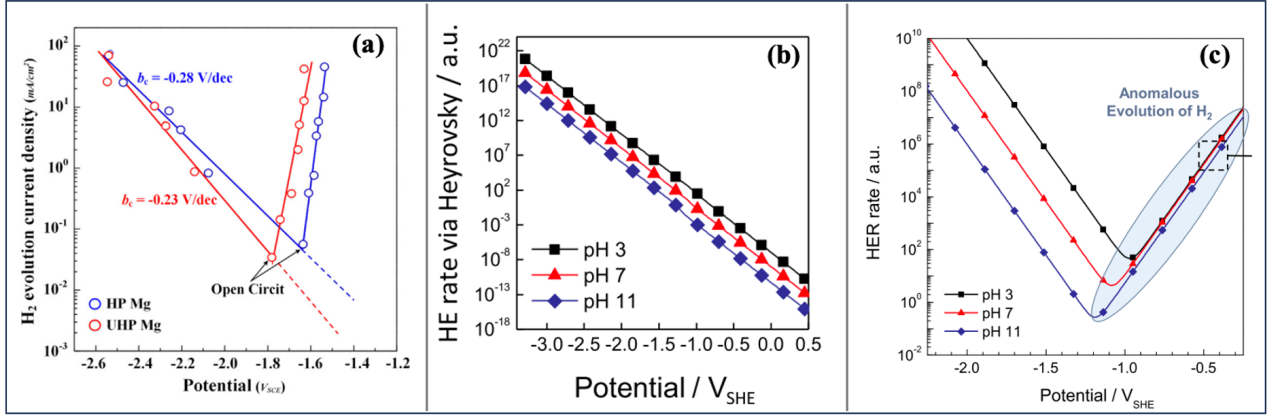
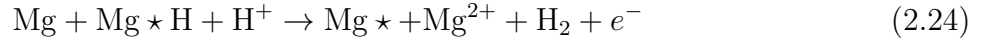


Figure 2.9: Polarisation curves for the HER of Mg aqueous corrosion: (a) HER current densities as a function of the electrode potential for the high-purity (HP) and ultra high-purity (UHP) Mg samples in 0.1 M NaCl solution measured from experiments; (b), (c) DFT-calculated HER rate (proportional to the current density) for the hydrogen gas evolved through the Heyrovsky pathway, and through the Heyrovsky as well as a proposed anodic HER pathway. (as reproduced from [17, 18])

standard electrode potential at room temperature (-2.38 eV), and it displays a high tendency to dissolve anodically as Mg^{2+} ions in the solution, with a reaction enthalpy of approximately -2 eV and a barrier of approximately 1 eV [36, 146].

Based on the DFT-calculated reaction barriers (constants) and the connection between the rate constant and the current density as demonstrated in Equation 2.16 and 2.17, the polarisation curve of Mg aqueous corrosion reactions are sketched with factoring the conservation of the concentrations for the surface reactants [18, 19, 35]. In Figure 2.9(a), the HER current density for Mg aqueous corrosion exhibits a distinct V-shape relationship concerning the electrode polarisation potential. This unique HER behaviour in Mg aqueous corrosion is referred as the negative difference effect (NDE), which signifies an unusually heightened hydrogen evolution rate when the electrode is subjected to anodic polarisation (*i.e.*, applying a positive potential). For the sake of brevity, a detailed discussion of this intriguing HER behavior in Mg aqueous corrosion is temporarily excluded from the current section, yet is accessible in the next section. The DFT-calculated HER rate in Mg aqueous corrosion for the Heyrovsky pathway in Figure 2.9(b) only captures the cathodic (the potential less than the open-circuit potential of Mg) feature according to the experiment data, while barely displaying the anodically enhanced hydrogen evolution behaviour. To better illustrate the experiment results, Yuwono *et al.* proposed a novel

HER pathway which depends on the anodic dissolution of Mg [18]:



By including this anodic HER pathway in their theoretical kinetic models for Mg aqueous corrosion, a more coincident polarisation curve for the HER was obtained as the schematic of Figure 2.9(c), which exhibits the increased hydrogen evolution rate under anodic potentials.

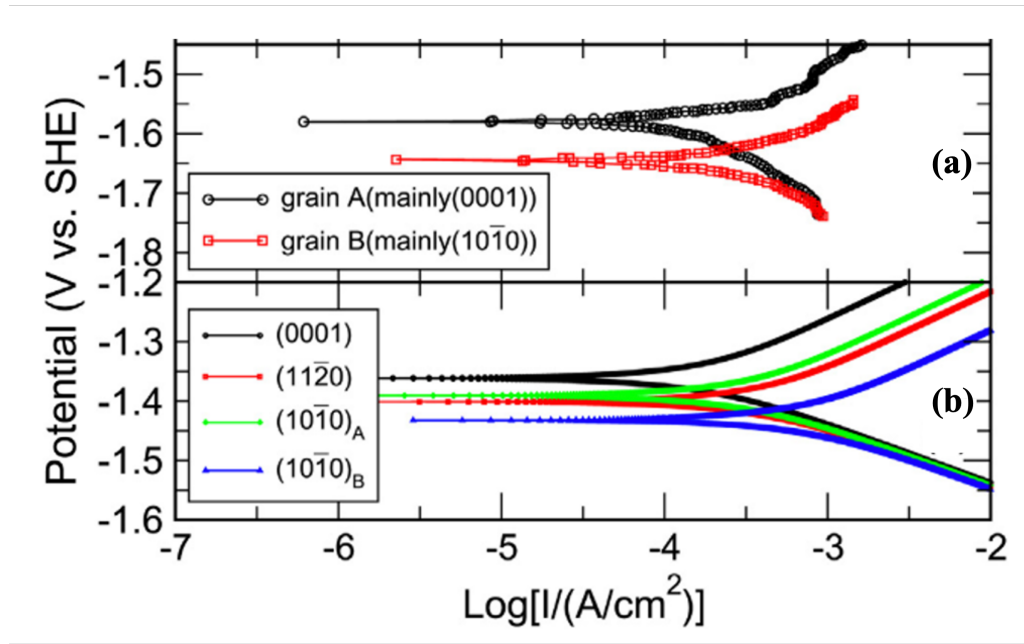


Figure 2.10: Polarisation curves for the anodic dissolution reaction on different Mg surfaces in Mg aqueous corrosion: (a) Experimental measurement of the Mg dissolution current densities under varying polarisation potential of the (0001) and (10 $\bar{1}$ 0) surface for AZ31 Mg alloys in a saturated Mg(OH)₂ solution; (b) Theoretical calculated polarisation curves for the anodic dissolution of the (0001), two terminated-type (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0) Mg surfaces. (as reproduced from [19])

In addition to the significant HER observed in the Mg aqueous corrosion, extensive calculations within the DFT framework are conducted to simulate the current densities of the typical anodic dissolution reaction in Mg [19]. In Figure 2.10, the simulated current densities for Mg dissolution exhibit good consistency with the experimental data. It is suggested that different Mg surfaces have distinct tendencies to dissolve in the solution, with the uniform (0001) surface having the most positive corrosion potential and a less robust anodic kinetics, which is in good agreement with the observations in other recent MD simulation works on

Mg aqueous corrosion [151, 152]. Nevertheless, the stepped (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0) surfaces possess further negative corrosion potentials, and their enhanced anodic dissolution kinetics imply a faster dissolution process for these rough surfaces in the solution due to the activity of those coordinatively unsaturated surface atoms. In this case, these theoretical kinetic models for Mg aqueous corrosion bridge the macroscopic experimental discoveries and the atomic-level reaction kinetics thereby benefiting further investigations which aims at unraveling the underlying mechanism of Mg aqueous corrosion.

2.2.3 Negative Difference Effect (NDE)

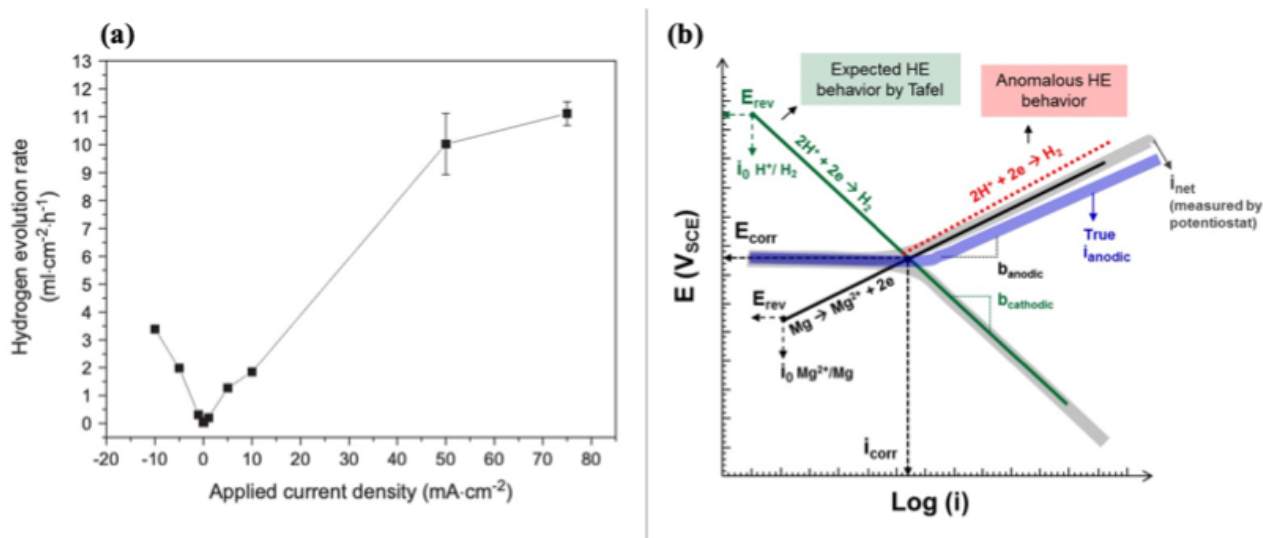


Figure 2.11: Negative difference effect of the HER in the aqueous corrosion of Mg: (a) Hydrogen evolution rate at different polarisation current densities in a 0.1 M NaCl solution; (b) Schematic Evans diagram for Mg aqueous corrosion highlighting the expected Tafel line for a general cathodic HER and that for the experimentally observed abnormal HER. (as reproduced from [20, 21])

As mentioned in the previous section, the hydrogen evolution behaviour in Mg aqueous corrosion exhibits an abnormal characteristic: as the electrode overpotential becomes more anodic (*i.e.*, positive), the hydrogen evolution rate and hydrogen gas production boost significantly, yet they are expected to increase with a cathodic polarisation according to the cathodic half-cell corrosion reaction (2.10) or the Heyrovsky reaction. This exceptional HER observed in Mg aqueous corrosion is also nominated as the negative difference effect (NDE), because it refers to a negative rate difference between the hydrogen evolution reaction occurring at an open-circuit

potential (*i.e.*, corrosion potential) and at an anodic polarized potential:

$$\Delta k = k_{\text{ocp}} - k_{\text{anodic}} < 0 \quad (2.25)$$

When the electrode is under anodic polarisation, the number of electrons in the system is reduced, with a promotion of de-electronation (anodic) reactions to generate more electrons while a suppression of electronation (cathodic) reactions due to the decrease of reactant concentrations. Therefore, the cathodic hydrogen evolution process that requires electrons to reduce the protons or water molecules in the solution is assumed to be inhibited by an anodic overpotential rather than accelerated.

Figure 2.11(a) displays the anomalous hydrogen evolution behaviour of the aqueous corrosion for Mg observed from experiments: at an anodic polarisation, the measured hydrogen evolution rate upturns nearly linearly concerning the increased applied current density, which is a similar case for the cathodic polarisation [20]. The schematic in Figure 2.11(b) describes the NDE of Mg from an electrochemical perspective. The solid black line and the solid green line represent the Tafel line of the anodic Mg dissolution reaction and the conventional cathodic HER (hydrogen evolution reaction) for metals, respectively, with the slope of each line corresponding to their reaction rate constants. Once the two half-cell reactions reach overall equilibrium (at the corrosion potential), the experimental standard polarisation curve of Mg aqueous corrosion can be obtained as shown by the right-part curves in the figure. Notably, the dashed red line suggests a proposed anodic hydrogen evolution that might contribute to the increased hydrogen production at anodic overpotentials during Mg aqueous corrosion. Although the schematic Tafel lines clearly depict the NDE for Mg with the aid of the hypothesized anodic HER line, the underlying reaction mechanism for this abnormal anodic hydrogen evolution is still a subject of debate. At present, there exist primarily four popular theories for explaining the NDE in the Mg aqueous corrosion, namely surface-film catalysis mechanism, impurity enrichment theory, uni-positive Mg^+ model, and subsurface hydride model.

The first potential underlying mechanism for the NDE is linked to the formation of a surface film during the corrosion process of Mg. When Mg undergoes aqueous corrosion, it has been

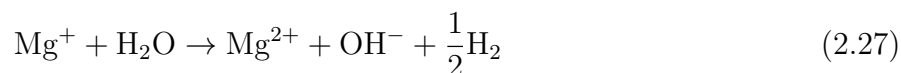
found that there tends to form a bi-layer surface film above the metal surface. This film consists of two distinct layers: an inner layer rich in MgO , which is thinner and more porous, and an outer layer rich in $\text{Mg}(\text{OH})_2$, which is thicker and less porous. This film partially covers the metal surface, offering modest protection against further corrosion. Despite retarding the subsequent metal dissolution after its formation, the surface film shows a catalysis characteristic on the hydrogen evolution of the Mg corrosion, thus being connected to the NDE. Salleh *et al.* found that the presence of a preformed $\text{Mg}(\text{OH})_2$ film on the Mg surface leads to higher HER kinetics (1 to 3 times more faster) compared to the pristine surface, especially when the pH of a solution is approximately at 11, which is the favourite value for the hydroxide precipitation [144]. They attributed the enhanced HER kinetics on the surface film to the catalysis effect of the on-surface hydroxides assisting the water dissociation near the interface hence providing more protons for the hydrogen evolution, according to a similar observation from a theoretical study [13]. Williams *et al.* also discovered that upon applying anodic polarisation to a Mg electrode, not only the anodic metal dissolution process is facilitated, but also the growth of the cathodic dark area, or the corroded surface film on the surface, increases rapidly with an increasing anodic current density [153]. Accordingly, these blooming cathodic surface films under anodic polarisation, which prompt the local water dissociation and provide more protons and cathodic sites for the HER during Mg aqueous corrosion, could be a potential origin of the NDE. However, this surface-film catalysis mechanism is still controversial because Fajardo *et al.* argued that the strong NDE could be found in the absence of the surface film where the corrosion of Mg occurs in a chloride-free citric acid solution [154]. Rather than the surface-catalysis mechanism, they accounted for the NDE with an observation that hydrogen bubbles mainly produce from the regions dominated by the anodic dissolution reaction.

Another prevalent theory explaining the NDE of Mg during anodic polarisation centres around the existence of additional impurity elements within the substrate, such as Ni, Al, Zn, Mn, and Cu. The mechanism of the impurities contributing to the NDE is as follows: with Mg dissolving into the solution during corrosion, certain noble impurities become dislodged from the substrate. These dissolved impurities subsequently tend to redeposit on the metal surface, creating new sites for the cathodic reaction. This process ultimately leads to an enhancement

of the cathodic hydrogen evolution reaction. It was found by Taheri *et al.* that applying anodic current upon the Mg electrode contributed to a higher enrichment of impurities (*e.g.*, Fe-rich particles) within the dark surface-film region, hence enhancing the cathodic activity of these corroded regions and boosting the cathodic hydrogen evolution [155]. However, the effectiveness of surface impurities in accelerating the hydrogen evolution rate is constrained. Lysne *et al.* discovered that the Fe impurity formed on the Mg surface is relatively inefficient in enhancing the hydrogen evolution rate, and it fails to account for the significant volume of released hydrogen gas under anodic polarisation [156]. Moreover, studies have revealed that there exists a concentration threshold for impurities (Fe, Ni, and Cu) in Mg, beyond which the corrosion rate of Mg experiences a sharp decrease [157]. To get rid of the influence of the impurities, Fajardo *et al.* used high purity Mg samples (with purity $> 99.98\%$) and ultra-high purity samples (with purity $> 99.9999\%$) for the anodic polarisation corrosion test. During the aqueous corrosion for those pure Mg samples, the intensive hydrogen evolution was still observed with the anodic polarisation, illustrating the NDE of Mg could not be fully explained by the impurity enrichment theory [17].

The aforesaid surface-film catalysis model and the impurity theory both elucidate the NDE by the enhanced cathodic HER with an expansion of the cathodic active sites on the metal surface during the anodic polarisation. Even so, a recent study done by Li *et al.* estimated the hydrogen evolution rate associated with the anodic reactions, or that related to the cathodic (HER) reactions, under various applied anodic current densities and found that the former is further higher than the later, which indicates the NDE to be an anodic hydrogen evolution process [158]. In this study, the apparent Mg valence was measured to be 1.2 ± 0.1 , thus supporting the theoretical uni-positive Mg^+ model that was initially proposed by Song and Atrens [159]. In this univalent model, rather than directly being oxidized to the Mg^{2+} , the Mg metal is assumed to form the partially oxidized univalent ions Mg^+ electrochemically at the first stage. Afterwards, this special uni-positive Mg ion could reduce water molecules into hydrogen gas molecules:





Such a HER process is typically anodic because the anodic current density could accelerate the partial oxidation (*i.e.* anodic dissolution) of metallic Mg as the reaction (2.26) to form the univalent ion, which subsequently reacts with water to generate hydrogen gas thus elevating the overall HER rate under the anodic polarisation. Despite having a negative formation free energy, as discussed in Table 2.2, the direct observation of these univalent Mg ions remains challenging and controversial in experiments due to their extremely short lifetime in aqueous electrolytes [36]. Initially, the existence of Mg^+ was demonstrated by Petty *et al.* through an oxidation experiment for Mg. In this experiment, a saturated sulfate solution flowed past a Mg anode into a separate cell containing an oxidizing agent MnO_4^{2-} which was reduced to MnO_2 after contacting the solution [28]. The reduction of the oxidizing agent in the separate cell was naturally attributed to the presence of the hypothetical reductive univalent Mg ion because the oxidizing agent could not directly react with the metal electrode. Nevertheless, in a recent study, Samaniego *et al.* found that in Petty's experiment, it was the SO_2 which reduced from the sulfate solution by the Mg electrode that reduced the aqueous MnO_4^{2-} in the separated cell, rather than the hypothetical Mg^+ ions [160]. As a result, the univalent Mg^+ model for the NDE remains inconclusive until precise experimental determination of the uni-positive ion is achieved.

Besides the cathodic catalysis models and the anodic univalent-ion expedited hypothesis, the abnormal HER of Mg under anodic polarisation during its aqueous corrosion could also be elaborated via the chemical reaction between water and the magnesium hydride (MgH_2) formed underneath the surface film. Referring to the Mg Pourbaix diagram in Figure 2.5(b), the hydride phase of Mg exhibits remarkable thermodynamic stability over a wide pH range, particularly when the electrode is subjected to cathodic polarisation. The formation of this hydride phase was also observed by Xu *et al.* according to the corresponding peaks of MgH_2 and Mg_2H_4 in the Raman spectra obtained from the cathodic polarisation of a high-purity Mg (99.995 *wt.*%) species in a 0.1 M NaCl solution, with a contribution to the total measured cathodic current density by the following cathodic reactions [161]:





Upon converting the applied cathodic potential to anodic, these (sub-surface) hydrides lost their stability as well as the protection provided by the dissolving on-surface film or the top-surface metal layer, and react with water intensively, as the reaction (2.4), leading to the anodic hydrogen evolution boosting. Binns *et al.* further confirmed the presence of this hydride phase beneath the surface film of a cathodically preprocessed Mg species through the analysis of X-ray diffraction spectra and dynamic secondary ion mass spectrometry (SIMS) maps [162]. Additionally, their findings revealed that the hydride phase not only facilitates the anodic hydrogen evolution through its decomposition but also compels the filaments on the surface to move, leaving behind a trail of $\text{Mg}(\text{OH})_2$. This phenomenon could contribute to the characteristic filiform corrosion morphology observed in the Mg aqueous corrosion. Several recent DFT studies on the sub-surface hydride for Mg also provide the rationale for this model to demonstrate the NDE. It has been found that a stable sub-surface hydride-like tri-layer structure (H–Mg–H) could form on the Mg (0001) surface in a hydrogen-rich environment, which is thought to be a potential precursor for the bulk hydride phase [163]. By executing an ab-initio MD calculations, Surendralal *et al.* discovered that the hydrogen dissociated from water molecules on the Mg (0001) surface has a high tendency diffuse into the sub-surface region of the metal at an open-circuit potential, with the adsorbed H carrying approximately an unit negative charge [151]. While this hydride model has provided valuable insights into the mysterious nature of NDE for Mg, it is still subject to questioning due to the following fact: the anomalous HER resulting from the decomposition of this hydride phase should cease at the point when the formation rate of the hydride becomes significantly slow (or when the applied potential exceeds the equilibrium potential for the bulk hydride, approximately $-1.2 V_{\text{SHE}}$). However, experimental evidence shows that NDE continues to occur even if the applied potential surpasses this equilibrium value for the hydride, thus leading to a flaw of this model.

In conclusion, the aforementioned theories aiming to explain the NDE of Mg each have their distinct strengths and weaknesses, but none of them provides a complete and comprehensive explanation for the phenomenon. Therefore, to unveil a clear atomic-scale picture of the mechanism behind this unique hydrogen evolution behavior during Mg aqueous corrosion, it

is crucial to conduct further detailed experiments and undertake more advanced theoretical studies.

2.2.4 Surface Film Formed on Mg during Aqueous Corrosion

Following the discussion in the section on Mg and its corresponding species' electrochemical stability under aqueous conditions, the metallic state of Mg or the pristine Mg surface tend to oxidise to form oxide or hydroxide, thus leading to a modification of the surface features and a formation of the surface film which could affect its corrosion behaviour. In contrast to the surface oxide films observed on Al, Fe, and Cu-based metals, the surface film that develops on Mg during its aqueous corrosion exhibits a notably higher degree of porosity and decreased compactness. Moreover, it possesses a low Pilling-Bedworth ratio of 0.8 (a value less than 1 refers to a non-protective scale), suggesting that the metallic surface of Mg is less likely to be coated by this particular surface layer completely [164]. Hence, the film on the surface of the Mg metal is less protective in corrosive environments, allowing for the easy infiltration of water molecules and other corrosive substances, which leads to accelerated corrosion of the metal.

While the specific composition of the Mg surface film formed during aqueous corrosion is based on corrosion conditions such as solution species and concentrations, it typically exhibits a dual-layer structure. This structure comprises a dense layer of MgO in proximity to the metal-film interface and an outer surface characterized by the porous Mg(OH)₂ [31, 122, 165]. Yao *et al.* have verified the detailed composition of the surface film on top of the high purity Mg ribbons which were immersed in the distilled water or 3% NaCl (saturated with Mg(OH)₂) solution respectively [31]. According to the depth profiling X-ray photoelectron spectroscopy (XPS) spectra, for Mg species corroded by two types of solutions, they both found that two distinct binding energy (BE) peaks of the O 1s signal existed as the immersion time increased, which refers to the hydroxide phase (higher BE component, of ~ 533.2 eV) and the oxide phase (lower BE peak, of ~ 531.1 eV) within the surface film separately. In comparison to the corrosion surface film that develops in distilled water, the film on the magnesium specimen submerged in a 3% NaCl solution exhibited significantly greater thickness and a more extensive degree of hydration. In addition, because of the presence of the Cl⁻ ions in the electrolyte, the

hydroxide and oxide film are much easier to be penetrated by this cation, with the incorporation of basic chloride salts into the surface film, ultimately accelerating the corrosion process. In subsequent research conducted by Zhao et al., it was discovered that the presence of chlorine ions, particularly at higher concentrations in the solution, significantly contributes to the degradation of the surface film, thus resulting in a notable expansion of the film-free surface area [166].

This typical surface film, characterized by its bi-layer structure, which develops during Mg aqueous corrosion, exhibits distinct features under varying corrosion potentials. At the open-circuit potential of Mg in corrosive solutions ($\sim -1.5 \text{ V}_{\text{SHE}}$), the corrosion of Mg is primarily driven by the surface micro-galvanic mechanism (*i.e.*, a severely corroded surface area can effectively protect its surrounding substrate from galvanic corrosion), thus contributing to non-uniform corrosion damage and the formation of a surface film with highly heterogeneous thickness [167]. When the Mg electrode undergoes an anodic polarisation, Mg dissolution from the surface occurs in a more uniform fashion, leading to the formation of a thicker and more consistently homogeneous surface film. Yet, as mentioned in the previous section, an anodic polarisation of the Mg electrode tends to expedite the rate of HER, thereby causing the anodic surface film to become more porous and develop additional cracks. During cathodic polarisation, the duplex corrosion surface film of Mg maintains its primary composition, consisting of an inner layer dominated by oxides and an outer layer primarily composed of hydroxides, similar to its composition under more anodic potentials. In addition to these two primary corrosion products, the cathodic surface film also contains a noteworthy concentration of hydride phase for Mg after immersion in ultra-pure water with cathodic charging, which indicates the potential occurrence of interactions between the MgH_2 (in the surface film) with the aqueous electrolyte during Mg corrosion [168, 169].

Based on an investigation conducted by Brady *et al.*, which employed secondary ion mass spectroscopy (SIMS) alongside an isotopic substitution technique, a comprehensive understanding of the corrosion surface film's growth mechanism on high purity Mg was unveiled [170]. This mechanism was found to encompass both the inward diffusion of H or O atoms from the aqueous solution to the metal substrate and the outward diffusion of dissolved metal ions. However, in cases where the Mg matrix incorporates impurity elements, such as Al, the development

of the corrosion surface film is primarily governed by the inward diffusion of hydrogen and oxygen, which results in a more uniform surface topology and a thinner film compared to the layer formed on the pristine Mg sample. Following the direct imaging results obtained from the FIB cross-sectioning STEM examination, the microstructure of the surface film formed on mechanically-polished Mg, which was immersed in pure water for 48 h under the corrosion potential, was found to be a composition of an inner nano-crystalline MgO-rich layer with high porosity and a less-porous Mg(OH)₂-rich plate-like outer layer [171]. The crystalline oxide-enriched inner layer of the surface film is thought to develop through the interaction between the Mg sample and the gaseous oxygen (O₂) present in the ambient air during the mechanical polishing process in the laboratory [172]. This air-formed thick MgO micro-crystalline layer on the metal surface can subsequently react with the atmospheric water vapour in the polishing procedure, thus leading to the formation of an ultra-thin hydroxide layer on its surface. After ageing the polished Mg sample in pure water, the outer micro-thin hydroxide layer undergoes continuous growth through a dissolution-precipitation reaction involving the corrosion of the Mg substrate (specifically, the dissolution of metallic Mg into Mg²⁺ ions). Over time, this process induces the gradual transformation of the micro-thin hydroxide layer into a thicker, platelet-shaped hydroxide layer that dominates the outer part of the corrosion surface film. Simultaneously, the inner native oxide layer suffers a chemical hydration-driven degradation process, with a partial transformation into the energetically more favourable hydroxide phase when exposed to aqueous conditions. This transformation results in a significant volume expansion at the interface between the inner and outer layers of the surface film, which plays a crucial role in the development of the observed porosity within the inner layer [173, 174].

The stability of the corrosion surface film on Mg can be modified significantly by incorporating specific alloying elements, *e.g.*, RE elements, into the matrix, hence subsequently influencing the corrosion behaviour of Mg under aqueous conditions [175, 176]. Leleu *et al.* found that the surface film developed on the commercial Mg alloys containing appropriate concentrations of Y elements experiences an enrichment of the doped RE elements within the surface layer of oxides and hydroxides, which contributes to the formation of a thinner surface film (hybrid with Mg/Y oxides and hydroxides) with a stronger coverage ability, or a higher Pilling-Bedworth

ratio compared with the film observed on pure Mg samples [177]. Consequently, the corrosion resistance provided by the RE-enriched Mg surface film is significantly enhanced than the pristine Mg surface film, thereby triggering a higher charge transfer resistance and impedance values of the RE elements doped Mg matrix when compared to those of pure Mg sample during aqueous corrosion. Likewise, Feng et al. have confirmed that the addition of Sm, which exhibits the highest solid solubility in Mg among the light RE elements, to a Mg substrate enhances the formation of a quasi-passivated surface film on the metal [178]. This dopant leads to improvements in both surface film resistance and charge transfer resistance at the interface between the film and substrate. The conversion of the solute element Sm into its oxide that exhibits exceptional electrochemical stability, contributes significantly to fortifying and densifying the oxide layer within the surface film by replenishing the vacancies left behind by the dissolved Mg atoms from the inner oxide-rich layer. This strengthened surface film, in turn, effectively prevents the inward diffusion of water molecules or other detrimental ions into the metal surface, and serves as a robust shield, safeguarding the Mg substrate from further corrosion within the solution. While the introduction of RE elements into the Mg substrate can enhance the stability of the corrosion surface film, it is essential to recognize that the presence of solid solute RE elements in Mg may also pose potential drawbacks to its corrosion resistance. These drawbacks could manifest as galvanic corrosion or localized breakdown of the sample, primarily due to the uneven distribution of RE elements within the material [179, 120, 180]. This underscores the imperative need to explore a more efficient approach for incorporating RE elements into Mg, aiming to fully maximize their potential benefits in bolstering Mg's corrosion resistance.

2.3 Theoretical Electrochemistry

2.3.1 Overview of Electric Double Layer (EDL)

In many electrochemical processes, including aqueous corrosion of metals, heterogeneous electrochemical reactions can occur at the interface between the bulk metal and the aqueous solution, which exhibits significant heterogeneity with regard to electronic density as well

as the spatial arrangements of ionic species and solvent molecules [181]. When the metal electrode, charged with external electric potential, interacts with the aqueous electrolyte, there is an accumulation of some counter-charged ions from the solution near the electrode surface to balance the excess surface charges, meanwhile repelling the co-ions in the surrounding regions of the electrolyte. As a consequence, a bilayer structure with opposing charges or polarities forms near the surface of the metal electrode. This phenomenon gives rise to the creation of a capacitor, commonly referred to as the electric double layer (EDL) at the interface between the metal electrode and electrolyte [182]. The intricate microstructures inherent in the EDL, which encompass factors such as the orientation and arrangement of solvent ions at the interface, as well as the adsorption states of the electrode surface, play a pivotal role in influencing the charge transfer process. Moreover, these microstructures significantly impact the mechanisms and thermodynamics governing interfacial electrochemical reactions. Therefore, a meticulous examination of the EDL becomes crucial for advancing our understanding of the various electrochemical processes that transpire at the metal/solution interface.

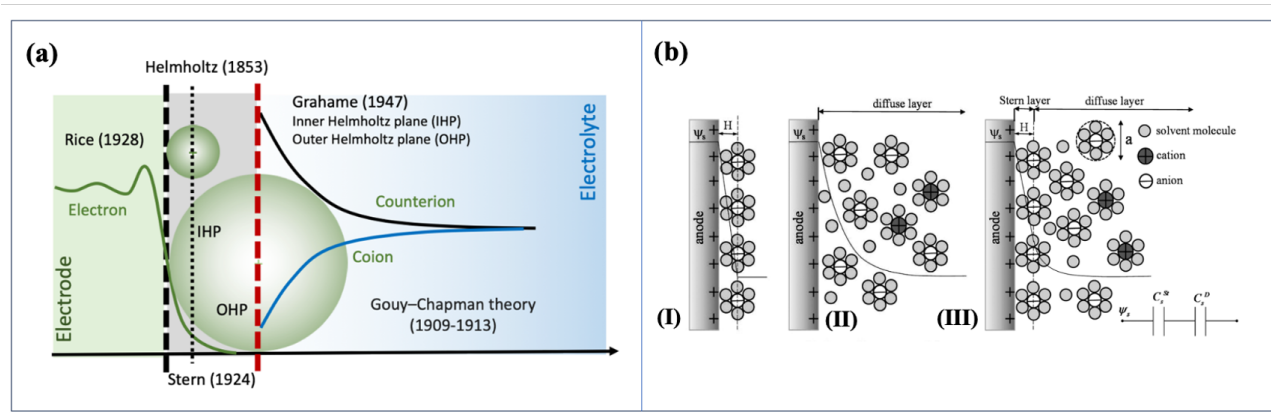


Figure 2.12: (a) Schematic of theoretical models for the EDL structure of metal/aqueous solution interface; (b) Detailed models for (I) the Helmholtz model, (II) the Gouy–Chapman model and (III) the Gouy–Chapman–Stern model. (as reproduced from [22, 23])

For over a century, numerous theoretical models have been crafted to mathematically describe the structure of the EDL [183, 184, 185, 186]. In 1853, Helmholtz introduced the earliest conceptual model for the EDL, which represented the double-layer structure as comprising two distinct layers of opposite charges. In this model, one of these layers is considered to be charged ions rigidly adhered to the electrode surface, or the excess surface charges, while the other layer,

composed of the network of counter ions, is situated at a fixed distance H from the surface within the solution [183]. As a result, the surface charge potential exhibits a linear decrease with increasing distance from the electrode (as demonstrated in Figure 2.12 (b)-(I)), rendering the double-layer structure akin to a capacitor with a consistent capacitance. Nevertheless, there are two significant limitations associated with this basic model which leads to departures from experimental observations [187]. Firstly, the counter ions are not firmly held in a stable position away from the electrode surface due to the thermal motion of the solvent ions or molecules. Secondly, the model does not adequately account for the structural changes in the EDL caused by variations in ion concentration (diffusion effect) or temperature.

To optimise the simple Helmholtz EDL model by accounting for the non-uniform distribution of ionic species in the electrolyte near the electrode surface, Gouy introduced a diffusive EDL model in 1909 [184]. This novel model was subsequently elaborated upon by Chapman through the Poisson-Boltzmann (PB) theory, and then nominated as the Gouy-Chapman model [185]. Herein, the EDL becomes less sharp when contrasted with the initial Helmholtz model due to the treatment of counter ions as diffusive and mobile within the electrolyte, thereby causing them to disperse with a concentration from the electrode surface into the bulk electrolyte following the Boltzmann distribution (under dilute conditions):

$$c_{\pm}(x) = c_0 \exp \left(\mp \frac{e(\phi(x) - \phi_0)}{k_B T} \right) \quad (2.30)$$

where $c_{\pm}$ and c_0 represent the concentrations of positive and negative (monovalent) ions within the EDL region and that of the bulk phase in the electrolyte respectively. $\phi(x)$ denotes the spatially varying electrostatic potential in the solution, and ϕ_0 indicates the potential for which the concentrations of positive and negative ions are the same. By substituting the Boltzmann distribution of the electrolyte ion concentrations into the fundamental Poisson equation, it is straightforward to get the Poisson-Boltzmann equation (here shows the one-dimensional case):

$$\frac{\partial^2 \bar{\phi}}{\partial x^2} = \frac{2ec_0}{\epsilon\epsilon_0} \sinh \left(\frac{e\bar{\phi}(x)}{k_B T} \right) \quad (2.31)$$

where $\bar{\phi} = \phi(x) - \phi_0$ and ϵ refers to the static dielectric constant of the solution. This essential

equation also defines the Debye length κ^{-1} of the EDL, which is generally expressed as:

$$\kappa^{-1} = \sqrt{\frac{\epsilon\epsilon_0 k_B T}{2e^2 c_0}} \quad (2.32)$$

hence signifies the spatial domain where the electrostatic potential of the EDL prevails within the aqueous electrolyte [188]. While the Gouy-Chapman diffusion model offers a more practical representation of the EDL structure compared to the rigid model, it tends to overestimate the characteristic thickness (*i.e.*, Debye length) of the EDL and may encounter challenges when dealing with highly charged counter ions within the electrolyte or high concentration electrolyte [189].

In 1924, Stern integrated the fundamental principles of the Helmholtz model and the Gouy-Chapman model, taking into account the size effect of the ionic species in the aqueous electrolyte, and dividing the EDL structure into two distinct layers as shown in Figure 2.12 (b)-(III): one counter-ion layer with a single-ion thickness which remains stuck to the electrode surface (Stern layer), and another diffuse layer which comprises compensating ions dispersed non-uniformly because of the thermal agitation (Gouy-Chapman layer) [186]. According to the Stern model, the capacitance of the EDL can be described as that of a series of interconnected capacitors, with two distinct components corresponding to the inner Stern layer and the outer diffusive layer:

$$\frac{1}{C_{\text{EDL}}} = \frac{1}{C_{\text{Stern}}} + \frac{1}{C_{\text{Diffuse}}} \quad (2.33)$$

which agrees well with the experimentally measured data of the EDL capacitance with rational assumptions of the local dielectric constants [190]. Approximately two decades later, Graham expanded upon the Stern model by introducing the concept of inner and outer Helmholtz planes (*i.e.*, IHP and OHP), thereby subdividing the Stern layer into two different segments based on the adsorption status of ionic species within the solution [191]. The locus of the IHP is determined by the electric centre of the ionic plane where the ions are directly adsorbed on the electrode surface, either through the formation of covalent bonds via chemical interactions or through physical adherence facilitated by van der Waals forces. For the OHP, its position is established by the electric centre for the solvated ions near the surface at the point of the

closest approach between these ions and the electrode.

In addition to the arrangement of ionic species within the EDL, the spatial configuration of the solvent molecules in proximity to the electrode surface was considered by Bockris *et al.* in the 1960s [192]. They suggested that some solvent molecules exhibit a tendency to undergo physical adsorption onto the charged electrode surface within the immediate vicinity of the IHP. These molecules display a pronounced preference for orientation or an alignment of their dipole moments in response to the electrostatic field generated by the additional charges present on the surface, which exerts a notable influence on the solvent's permittivity. Despite significant recent advancements in enhancing the theoretical model for the EDL structure based on the aforementioned models, it still possesses certain limitations and primarily applies to a broad, generalized context [193, 194]. Further refinement and investigation are necessary to address the limitations of these theoretical models and enhance their applicability.

2.3.2 *Ab initio* Study of Metal/Water Interface

So far, numerous advanced experimental probing techniques, including X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS), and the Kelvin probe force microscopy (KPFM)-AFM method, have been employed extensively to investigate the atomic-scale structure of the electric double layer (EDL) as a verification of the theoretical models and to conduct in-depth analysis of charge transport and reactions at the electrified solid-liquid interface [195, 196, 197, 198]. Nonetheless, the majority of these surface-sensitive techniques necessitate samples compatible with ultrahigh vacuum conditions or intricate differential-pumping systems, which presents numerous challenges when it comes to operation and obtaining precise data [199]. Additionally, the electrified interfaces comprise multiple layers within the EDL, potentially leading to complex electrochemical signals during experimental observations. As a consequence, achieving the extremely high nanometer-scale depth resolution for surface-sensitive spectroscopy to deeply understand the structure and properties of the EDL remains a challenging endeavour in laboratory settings at present [200].

To overcome the constraints imposed by current experimental techniques for investigating

the electrified solid/liquid interface and the associated EDL structure, cutting-edge computational methods, spanning from *ab initio* molecular dynamics (AIMD) simulations within the framework of DFT, as well as grand canonical Monte Carlo (GCMC) methods to the quantum mechanics/molecular mechanics (QM/MM) approach, have been widely applied in modelling electrochemical systems [201, 202, 203, 204, 205]. These computational tools enable the robust and precise unravelling of the atomic-level details of the EDL structure as well as disclosing a detailed mechanism for some essential interface phenomena for the electrochemical process. Among these methods, *ab initio*-based computational techniques are the most popular, as they have the unique capability to yield invaluable insights into both the atomic/electronic structure of the EDL and the dynamic characteristics of liquid electrolyte near the interface with a combination of numerical efficiency and sufficient accuracy.

An initial implementation of AIMD simulation for investigating the EDL structure (*i.e.*, the detailed geometry of the solvent molecules near the electrode surface) of the metal/water interface by the finite size of the unit cell and a limited number of solvent molecules could date back to the early years of this century. By employing *ab initio* Car–Parrinello molecular dynamics, Izvekov *et al.* studied the structure of the Cu (110)/water interface within the confines of a constant volume and temperature set at 300 K (NVT ensemble) [206]. Their research unveiled a distinctive bi-layer arrangement of water molecules near the Cu (110) surface: the first layer resembled a chemisorbed ice-like water network, tightly adhering to the surface, while the second layer comprised water molecules capable of greater mobility. A similar highly organized bi-layer structure of the water molecules near the (111) surface of Pt was then discovered by Meng *et al.* through AIMD simulations [207]. They additionally revealed that within the well-arranged water bi-layer network, two distinct types of hydrogen bonds exist—comprising a robust hydrogen bond alongside two less robust ones. These variations in H bonds stem from the varying charge redistribution among water molecules oriented differently. To deeply investigate the stability of this ordered ice-like water bi-layer structure in proximity to typical hcp metal surfaces at room temperature, Schnur *et al.* performed AIMD simulations for the water bi-layers situated on surfaces including Au (111), Ag (111), Pt (111), Pd/Au (111) and Ru (0001) [208]. It has been demonstrated that for the noble metal surface, like Au (111) and

Ag (111) surface, this hexagonal water bi-layer structure undergoes significant disordering at a temperature of 300 K. This disorder is evident in the wall-oxygen distribution function, which shows only one broad peak at a distance farther from the equilibrium distance of an adsorbed water monomer from the surface of Au (111) and Ag (111), which indicates the presence of water molecules with an open character near the noble metal surface. However, the bi-layer water network retains its stability at the same temperature when adhered to the late transition metal surfaces with stronger interactions (with water molecules), such as the Pt (111), Pd/Au (111), and Ru (0001) surfaces. Yet, it's noteworthy that the orientation of the water molecules within the hexagonal ice-like structure often undergoes frequent reversals, transitioning from a H-down configuration to a H-up orientation, and vice versa. This dynamic behaviour contributes to fluctuations in the work function of these more reactive transition metal surfaces, which can be attributed to the thermal motion of the near-surface water molecules. According to DFT total energy calculations conducted by Michaelides *et al.* on various hexagonal surfaces of $3d$, $4d$, and $5d$ transition and noble metals with adsorption of either the intact water bi-layer network or the dissociated water-OH-H overlayer, it was observed that the strength of the bonds between water and the metal surface significantly influences the stability and arrangement of ice-like bi-layers [209]. A more intense interaction between the O-H radical (or that originating from the water molecule) and the surface metal atoms is more prone to lead to the separation of water molecules within the bi-layer, resulting in a more complex EDL structure.

In addition to offering valuable insights into the atomic-scale intricacies of the EDL structure, *ab initio* simulations also have the potential to reveal essential characteristics of the electrified metal/electrolyte interface, such as the potential of zero charge (PZC), interface capacitance and the charging behaviour, with precision and reliability [210]. Recently, Le *et al.* have pioneered a remarkably efficient computational SHE-based method for determining the PZC of diverse transition metal surfaces, exclusively relying on the associated AIMD simulations, thus eliminating the need for experimental data or input in estimating the metal's PZC [211]. In this work, they discovered that the primary contributor to the potential deviation between the PZC for transition metal surfaces and their work function obtained through *ab initio* calculations is the interface dipole potential, rather than being predominantly influenced by the overall

water dipole potential. This interface dipole potential is primarily caused by the redistribution of charges on the surface induced by the chemisorbed water molecules. In subsequent AIMD simulations conducted by Kelly *et al.*, they explored the PZC of various transition metal-water interfaces, including the surfaces of (111), (100), (0001) and (211) covered by liquid water molecules [212]. The results revealed a strong correlation between the PZC of transition metals and the water coverage on the metal surface. Moreover, they found that the water coverage could be accurately predicted based on the vacuum adsorption energies of water molecules or OH radicals on the metal surfaces, further suggesting the correlated PZC values.

As mentioned in the previous section, the differential capacitance is an essential property for the EDL, and could be fundamentally calculated based on the Gouy-Chapman model ($C_d^{GC} = \epsilon\kappa \cosh\left(\frac{e_0\varphi_s}{2k_B T}\right)$, with φ_s representing the surface potential) or the Debye capacitance model ($C_d^{DB} = \epsilon\kappa$) in the limit of low electrolyte concentrations [213]. Nonetheless, at higher electrolyte concentrations, it becomes evident that the differential capacitance of the EDL is primarily influenced by an additional factor to the Gouy-Chapman capacitance: the Helmholtz capacitance (C_d^H), which is fundamentally contingent on the charge density of the electrode surface, and thus contains the information on the microscopic structure of the electrified interface that is missing in the Gouy-Chapman part [193].

Preliminary findings from impedance spectra experiments on transition metal surfaces, such as the (111) surfaces of Pt, Ag, and Au, in aqueous electrolyte, reveal a noteworthy sharp peak maximum in the differential EDL (Helmholtz) capacitance [214]. This peak emerges at the potential close to the PZC and can be qualitatively explained by the dielectric saturation effect. Using a combination of DFT simulations and the continuum solvation model, Fang *et al.* conducted a comprehensive analysis of the Pt (111)/water interface [215]. They determined the PZC to be 0.31 V_{SHE} and found the interface capacitance to be 20 $\mu\text{F}/\text{cm}^2$ when operating at potentials away from the PZC, both of which agree well with experimentally measured values [216]. However, because the continuum model ignores the intricate interactions between water molecules and the metal surface, as well as the precise configurations of water molecules within the EDL, the EDL capacitance derived from these ab initio simulations failed to accurately reproduce the peak maximum near the PZC. By treating the water molecules within the

electrolyte explicitly, Le *et al.* delved into the Pt (111)/water electrified interface deeply using the AIMD simulations, and replicated the characteristic bell-shaped differential Helmholtz capacitance for the EDL (with a peak maximum at the PZC), which is significantly influenced by the interface dipole potential controlled by the potential-dependent coverage of chemisorbed water molecules on the surface [217]. A similar result was observed in the context of the Helmholtz capacitance for the Pt (111)/water electrified interface by Bouzid *et al.* using AIMD simulations, with the electrode potential set using the constant Fermi-level method [202]. They further revealed an evolution of the water orientation in the vicinity of the Pt surface as the potential fluctuated around the PZC: at potentials more anodic than the PZC, the dipole moment of water molecules predominantly points away from the surface; at the potential more cathodic than the PZC, most of the interface water molecules exhibit a distinct orientation preference, with both hydrogen atoms aligning toward the electrode.

Despite the robustness and precision in modelling atomic structures and deriving essential properties of electrified metal/liquid interfaces through ab initio simulation methods, certain limitations persist within these techniques. Firstly, due to the high computational expense associated with the most commonly used techniques in simulating the electrified metal/liquid interface, namely AIMD, certain simplifications for the electrolyte are imperative. These include employing a limited-size unit cell and reducing the number of solvent molecules in calculations to expedite computations and enhance efficiency. However, it's worth noting that such simplifications may introduce some degree of systematic inaccuracy or error (*e.g.*, finding some unrealistic configurations of the interface) when estimating certain properties of the EDL [218, 219, 220]. Besides, the majority of contemporary simulation works on modelling the EDL structure for the electrified interface are within a constant charge scheme of the DFT framework, which is inconsistent with the actual constant potential status in experiment conditions [221, 222]. Therefore, it is expected to develop and benchmark innovative, efficient techniques to address the aforementioned limitations of current ab initio simulation methods for modelling the EDL, thus enhancing our precise comprehension of the impact of the EDL on electrocatalysis and achieving accurate determination of reaction thermodynamic and kinetic parameters.

2.4 Summary & Knowledge Gap

In this chapter, a concise overview of Mg aqueous corrosion and the associated fundamental electrochemistry theory are presented. In doing so, we notice that despite numerous experimental and theoretical studies on Mg corrosion during the past centuries, there is still a lack of a comprehensive understanding of the atomic-scale mechanisms underlying certain crucial corrosion phenomena, like the negative difference effect and corrosion product formation during Mg aqueous corrosion. This is due to the constraints of current experimental techniques and the limited efficiency or accuracy in modelling the metal/water interface from *ab initio* approaches.

Magnesium and its alloys have seen widespread utilization in the automotive, aerospace, and clinical medicine fields, owing to their exceptional specific stiffness, high tensile strength, as well as their remarkable biocompatibility and biodegradability. Even so, the broader utilization of this superior metal in extended industry sectors is hindered by its mechanical shortcomings and its pronounced chemical reactivity in aggressive environments. The aqueous corrosion of Mg in humid environments or a solution was discovered approximately 20 years after its initial isolation, which involved the observation of metallic Mg dissolving into an aqueous solution, accompanied by the passivation of its lustrous metal surface through the formation of oxides and hydroxides, as well as the robust evolution of hydrogen gas.

Thermodynamic studies of magnesium and its various chemical compounds reveal that the distinctive magnesium oxide, hydroxide, hydride, and solvated divalent ion all display a notably negative chemical potential, thus suggesting a simultaneous transition from pure metal to a range of its oxidation states when in contact with oxygen agents like water. To include the impact of external potential or the electrolyte pH on the stability of metallic Mg and its compounds under electrochemical conditions, the classical Nernst equation along with the pH-potential diagram (*i.e.*, Pourbaix diagram) is extensively applied in the context of the Mg-water system. The insights gained from the bulk Pourbaix diagram of the aqueous Mg system imply that maintaining electrochemical stability and effective passivation of metallic Mg in aqueous conditions necessitates both alkaline or neutral pH conditions and cathodic external potentials. Furthermore, a modification of the bulk Pourbaix diagram to a surface one could unravel the

most stable surface adsorption states of numerous Mg surfaces in different corrosion conditions, hence providing in-depth comprehension of the mechanism behind significant interface corrosion reactions. In addition to thermodynamic studies of Mg aqueous corrosion, several kinetic models and fundamental theories, such as the Butler-Volmer equation and transition state theory, have been extensively employed to elucidate the connection between overpotential and the drift current densities pertaining to crucial corrosion reactions of Mg, and to estimate the reaction rate constant. Through an analysis of the current density associated with the HER with respect to the applied potentials during the aqueous corrosion of Mg, it is surprising to find that the hydrogen evolution rate during Mg corrosion, typically considered a cathodic-characteristic reaction, experiences an abnormal enhancement under anodic polarisation, which is a phenomenon commonly referred to as the negative difference effect. While various prominent theories have been put forth to clarify the unconventional hydrogen evolution behaviour observed during Mg aqueous corrosion, including the surface-film catalysis mechanism, impurity enrichment theory, uni-positive Mg^+ model, and subsurface hydride model, there is currently in a notable absence of a thorough and all-encompassing explanation for the atomic-scale mechanism underlying this phenomenon. Further to the vital HER, the formation of the surface film on the Mg surface during its aqueous corrosion has also undergone extensive explorations, which illustrate that the primary constituents of the corrosion surface film are the oxide and hydroxide of Mg.

With the support of the underpinning theories regarding the electric double layer of the metal/water interface, theoretical modelling techniques, including state-of-the-art *ab initio* simulation methods, have been extensively integrated into modern supercomputer clusters for determining the atomic-scale structure for the EDL and a variety of critical characteristics, such as the potential of zero charge and the differential capacitance of the interface, constructing the basis of understanding the corrosion reactions occurring at the electrified solid/water interface. Nevertheless, owing to the high computational costs and some naive but unavoidable hypothesis or simplifications made in the theoretical modelling works, there remains some inaccuracies as well as flaws in the depiction of the structure and attributes for the electrified interface, thus requiring continued refinement and the establishment of benchmarks for the associated theory and modelling techniques.

Herein, we introduce a brief summary of the gaps identified from the extensive literature on the Mg aqueous corrosion. First, experimental observation on the Mg/water interface, where multiple electrochemical reactions take place throughout aqueous corrosion simultaneously at OCP or under polarisations, demands advanced electrochemical characterisation techniques with stringent operating conditions. However, due to the rapid corrosion rate and the significant alterations in local pH and interface morphology resulting from hydrogen gas evolution and surface film formation in the Mg and aqueous electrolyte interface, a thorough examination and comprehensive understanding of the fundamental structural information of the EDL for Mg, *e.g.*, surface adsorption states and near-surface water orientations, as well as the associated properties, such as the PZC and the differential capacitance, remain unclear at present. Second, while there has been extensive research on the formation of the primary corrosion products of Mg, namely oxide and hydroxide, through both experimental and simulation studies, the generation mechanism of another crucial degradation byproduct, Mg hydride (MgH_2), which arises from the interaction between Mg and hydrogen, and is believed to significantly influence the hydrogen evolution behaviour during the aqueous corrosion of Mg, has received less empirical attention due to its high chemical reactivity in aqueous conditions. Finally, and most importantly, the negative difference effect (*i.e.*, the abnormal hydrogen evolution behaviour under anodic polarisation) of Mg, initially observed approximately a century and a half ago, continues to be a topic of extensive debate within the realm of Mg aqueous corrosion, with a variety of explanations regarding the mechanism or origin of this phenomenon yet each of which accompanied by its own set of limitations. As a result, the most paramount focus in the study of Mg aqueous corrosion remains the development of a comprehensive theory and thermodynamic/kinetic models, based on experimental observations or theoretical modelling to elucidate the atomic-scale mechanism of the NDE for Mg.

Chapter 3

Method and Theory

¶ *Chapter Synopsis*

Over the course of scientific and engineering history, theoretical modelling has been employed to comprehend the behaviour of intricate systems, or to further demonstrate experimental observations. By leveraging sophisticated theoretical models, we can gain insights into complex physical phenomena that prove challenging to directly measure through experiments, and elucidate the underlying mechanisms governing these physical behaviours. Ab initio materials simulation, founded on electronic structure calculations, is widely used in current materials science research with the aid of enhanced computing power and the evolution of super-computing clusters over the past few decades. In this thesis, we apply density functional theory (DFT), a cornerstone of atomic simulations, as our primary theoretical framework for modelling the electrochemical behaviour and interface reactions of magnesium under aqueous conditions because of its exceptional efficiency and precision. In this chapter, we first review the fundamental formalism and basic theory of DFT, followed by a recap of its application to periodic systems, such as periodic crystals. Next, we briefly revisit critical computational theories used to model the electrochemical system (*e.g.*, Mg/water interface) and estimate energy barriers for interface reactions within the framework of DFT. These include the implicit (continuum) solvation model and the nudged elastic band theory.

3.1 Density Functional Theory (DFT)

3.1.1 From Many Body Schrödinger Equation to Density Functional Theory

By depicting how the wave function (Ψ) of a quantum particle evolves with time in the region of interest, the Schrödinger equation is central to modern quantum chemistry [223]:

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \left[-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}, t) \right] \Psi(\mathbf{r}, t) \quad (3.1)$$

Here, $\Psi(\mathbf{r}, t)$ refers to the wave function of a non relativistic quantum particle with a mass of m at time t and a position of $\mathbf{r}$, $V(\mathbf{r}, t)$ indicates the external potential energy landscape surrounding the quantum particle, $\hbar$ is the reduced Planck constant and i is $\sqrt{-1}$. If we consider our studied quantum particle in a stationary (electronic) state, we can then simplify the aforementioned time-dependent Schrödinger equation into its special case, known as the time-independent Schrödinger equation, by separating the time variable (t) from the wave function:

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) \cdot e^{-iEt/\hbar} \quad (3.2)$$

Thus, we can substitute the separated wave function back into Equation 3.1 to derive the fundamental time-independent Schrödinger equation in quantum mechanics:

$$\left[-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}) \right] \psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (3.3)$$

In the bracket, these two terms combine into the general Hamiltonian ($\hat{H}$) of the system, which represents the total energy (kinetic energy plus potential energy) of the system. The expectation value of the total energy for the system could hence be estimated from:

$$\langle H \rangle = \int \psi^*(\mathbf{r}) \hat{H}(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} = E \int |\psi(\mathbf{r})|^2 d\mathbf{r} = E \quad (3.4)$$

and $|\psi(\mathbf{r})|^2$ is the probability of finding the particle at position $\mathbf{r}$, with its integration to be

normalised to the value of one.

Rather than dealing with a simple, one-particle system, the focus of interest for condensed matter physicists and quantum chemists typically revolves around complex many-body systems, specifically systems consisting of numerous electrons and multiple nuclei. As a result, it becomes necessary to introduce the wave function of a many-body system, which is a function of the spatial coordinates of every nucleus and each individual electron within the system. For instance, the many-body wave function describing a system in a stationary state that contains M electrons with positions of $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_M$ and N nuclei having coordinates of $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N$ could be expressed as:

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_M; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) \quad (3.5)$$

Similarly to the one-particle system, we can determine the total energy of the system by applying the many-body Hamiltonian to the wave function that has been introduced. In this case, the Hamiltonian ($\hat{H}_{\text{tot}}$) becomes more complicated because it involves the interactions between electrons and nuclei:

$$\begin{aligned} \hat{H}_{\text{tot}} = & - \sum_I \frac{\hbar^2}{2M_I} \nabla_{\mathbf{R}_I}^2 + \frac{1}{2} \sum_{\substack{I, J \\ I \neq J}} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \\ & - \sum_i \frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 + \frac{1}{2} \sum_{\substack{i, j \\ i \neq j}} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \\ & - \sum_{I, i} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} \end{aligned} \quad (3.6)$$

Here, the summation indices i, j and I, J indexes the electrons and nuclei in the system, and will always run from 1 to M and from 1 to N , respectively. M_I and Z_I correspond to the mass and atomic number of the nucleus I , and m_e indicates the mass of an electron. ϵ_0 is the vacuum permittivity. In Equation 3.6, the first two terms account for the kinetic energy of the nuclei and the Coulomb interaction between them. The following two terms similarly describe the kinetic energy of electrons and the Coulomb interactions among them. The final term accounts for the interaction between the electrons and the nuclei within the system.

When describing solids or molecules adsorbed on a solid surface, it is reasonable to assume that the nuclei in the system remain clamped in a known position because of their heavier mass and slower movement compared with electrons. This assumption leads to the famous Born-Oppenheimer (BO) approximation, proposed by Max Born and J. Robert Oppenheimer in 1927, which treated the wave function of nuclei and electrons in the system separately:

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) = \phi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \Phi\{\mathbf{R}_I\} \quad (3.7)$$

In this context, the wave function of the nuclei, denoted as $\Phi\{\mathbf{R}_I\}$, solely depends on the positions of the nuclei in the system. Nevertheless, the wave function of the electrons, represented as $\phi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})$, is influenced not only by the positions of the electrons but also by the positions of the ions. Due to the significant mass of the nuclei, they are presumed to be stationary at fixed positions within the system. As a result, their kinetic energy is considered negligible, and the Coulomb repulsion energy among the ions remains constant (in a periodic system, *i.e.*, a solid crystal, this nucleus-nucleus interaction needs to be included to avoid an infinite energy). This definition hence allow us to simplify the total Hamiltonian of the system as:

$$\hat{H}'_{\text{tot}} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{I,i} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} \quad (3.8)$$

It's important to emphasise that the energy derived from this Hamiltonian represents the total energy of the system, excluding the Coulomb energy of the ions ($E = E_{\text{tot}} - E_{\text{col}}(\{\mathbf{Z}_I\}, \{\mathbf{R}_I\})$).

If we further regard the nuclear coordinates ($\mathbf{R}_I$) as an external parameter for the electron's wave function, and state the Coulomb potential generated by nuclei and experienced by electrons as:

$$V_n(\mathbf{r}) = - \sum_I \frac{e^2}{4\pi\epsilon_0} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}|} \quad (3.9)$$

we can eliminate the nuclear dependency completely from the many-body Schrödinger equation, and obtain the fundamental equation of electronic structure theory which looks somewhat similar to the single-particle Schrödinger equation in Hartree atomic units:

$$\left[-\sum_i \frac{\nabla_{\mathbf{r}_i}^2}{2} + \sum_i V_n(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi(\{\mathbf{r}_i\}) = E \Psi(\{\mathbf{r}_i\}) \quad (3.10)$$

The primary distinction between Equation 3.10 and the single-particle Schrödinger equation lies in the inclusion of an extra term in the many-electron equation that depicts the mutual Coulomb repulsion effect of electrons. In order to deal with this complicated Coulomb repulsion (between electrons) term explicitly, several approximations have been proposed since the late 1920s. With a combination of the independent electrons approximation ($\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1) \cdots \phi_N(\mathbf{r}_N)$), where interactions between electrons are neglected, and the mean-field approximation (treating the electrostatic potential generated by electronic charge from a classical Poisson's equation), we can readily express the single-electron Schrödinger equation by converting the electron repulsion effect into an 'average' potential, which is created by all electrons and experienced by each individual electron:

$$\left[-\frac{\nabla^2}{2} + V_n(\mathbf{r}) + V_H(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \quad (3.11)$$

where $\phi_i(\mathbf{r})$ is the independent wave function for the i -th electron, with an energy state of ε_i . $V_H(\mathbf{r})$ is the average electrostatic potential, *i.e.*, the Hartree potential energy which satisfies the Poisson equation:

$$\nabla^2 V_H(\mathbf{r}) = -4\pi n(\mathbf{r}) \quad (3.12)$$

and $n(\mathbf{r})$ refers to the electronic charge density, which could be calculated from the summation of probabilities of finding electrons in each occupied state i :

$$n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2 \quad (3.13)$$

While the single-electron Schrödinger equation based on the mean-field approximation effectively describes the behaviours of independent electrons, this model falls short in capturing the correlations between the electrons. One of the key characteristics of atomic electrons as typical fermions is their possession of half-integer spin, which leads them to follow Pauli's

exclusion principle, *i.e.*, no two identical electrons can occupy the same electronic state. By considering the exclusion principle of electrons with the aid of the Slater determinant, we can utilize the variational principle on the total energy ($E = \langle \Psi | \hat{H} | \Psi \rangle$) of the system to determine the solution for the single-electron wave function ϕ_i (with the requisite condition of orthogonality), thereby deriving the renowned Hartree-Fock equation [224]:

$$\left[-\frac{\nabla^2}{2} + V_n(\mathbf{r}) + V_H(\mathbf{r}) \right] \phi_i(\mathbf{r}) + \int d\mathbf{r}' V_X(\mathbf{r}, \mathbf{r}') \phi_i(\mathbf{r}') = \varepsilon_i \phi_i(\mathbf{r}) \quad (3.14)$$

The additional non-local potential $V_X(\mathbf{r}, \mathbf{r}')$, which is called the Fock exchange potential, has an explicit expression of:

$$V_X(\mathbf{r}, \mathbf{r}') = - \sum_j \frac{\phi_j^*(\mathbf{r}') \phi_j(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \quad (3.15)$$

and introduces Pauli's exclusion effect to the independent electrons, yet complicates enormously the practical solution of the Hartree-Fock equations.

Although the Born-Oppenheimer approximation proves valuable in removing nuclear dependencies of the many-particles Schrödinger equation, for a system containing N electrons (characterized by a wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$), the complexity remains at $3N$ due to the necessity of dealing with the $3N$ Cartesian coordinates. In 1964, Hohenberg and Kohn introduced a pivotal simplification for the intricate many-electron Schrödinger equation, as the most essential pillar of the density functional theory [57]. They proposed that the ground state wave function of a many-electron system, when influenced by an external potential, can be uniquely determined as a functional of its electronic charge density ($n(\mathbf{r})$). This insight was summarised through the two Hohenberg-Kohn theorems. The first theorem suggests that the external potential (V_n) of the nuclei, is uniquely dependent on the electron density in its ground state (with the lowest possible energy of the system), thus establishing the total Hamiltonian of the many-electron system. Despite that the first theorem underlines the significance of the ground-state electronic density of the electrons, it does not offer a solution for determining this crucial system quantity. The second theorem solves this problem by dictating that one can find a universal functional of the ground-state electronic density, $n(\mathbf{r})$, which solely relies on

the number of electrons within the system, such that the global minimum value of the energy functional:

$$E[n(\mathbf{r})] = \int V_n(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})] \quad (3.16)$$

is exactly the ground state energy of the system, and could be minimised by the ground state electronic density $n_0(\mathbf{r})$. Hence, the precise ground state energy and density are entirely dictated by the energy functional of the electronic density $E[n(\mathbf{r})]$. In addition, it worth noting that the functional, $F[n(\mathbf{r})]$, includes the kinetic energy of electrons ($\hat{T} = -\sum_i \frac{1}{2}\nabla_i^2$) and the Coulomb energy of electrons ($\hat{W} = \frac{1}{2}\sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$). Therefore, we can rewrite Equation 3.16 in a symbolic form:

$$E = \int d\mathbf{r}n(\mathbf{r})V_n(\mathbf{r}) + \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle \quad (3.17)$$

Though the Hohenberg-Kohn theorem demonstrates that the ground state energy of a many-electron system is a functional of the electronic density in its ground state, the precise form of this crucial functional $F[n(\mathbf{r})]$ concerning the electron density remains hidden, and has not been described by the theorem. The Hohenberg-Kohn theorems were made practically applicable by Kohn and Sham in 1965, who introduced the Kohn-Sham equations [225]. These equations cleverly transformed the implicit kinetic energy and Coulomb energy terms (as shown in Equation 3.17) into explicit expressions based on the electron density. Building upon Kohn and Sham's concept, the total energy functional pertaining to the electronic density of a many-electron system can be articulated as follows:

$$E[n(\mathbf{r})] = \underbrace{-\sum_i \int d\mathbf{r} \phi_i^*(\mathbf{r}) \frac{\nabla^2}{2} \phi_i(\mathbf{r})}_{\text{Kinetic Energy}} + \underbrace{\int d\mathbf{r} n(\mathbf{r}) V_n(\mathbf{r})}_{\text{External Energy}} + \underbrace{\iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}}_{\text{Hartree Energy}} + \overbrace{E_{xc}[n(\mathbf{r})]}^{\text{XC Energy}} \quad (3.18)$$

Here the electronic density $n(\mathbf{r})$ can be computed using a set of orthogonal electron wave functions $\phi(\mathbf{r})$ as:

$$n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2 \quad (3.19)$$

In Equation 3.18, the first term represents the cumulative kinetic energies of a set of non-interacting, subsidiary single electrons which share the same ground-state electronic density as the corresponding many-electron system. The second term, also referred to as the external energy term, characterises the energy resulting from the interaction between the nuclei and electrons. The Hartree energy term indicates the classical electron-electron Coulomb interaction. The last, yet very significant component, the so-called exchange-correlation energy ($E_{xc}[n(\mathbf{r})]$), accounts for the remaining many-body effects, such as the electronic energy not included in the non-interacting kinetic and electrostatic terms, and can be used to generate the exchange-correlation potential:

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \quad (3.20)$$

Nevertheless, the exact form of this functional remains unknown, necessitating a rational approximation to enhance the accuracy of the calculation results. The most basic approximation for the exchange-correlation function is the local density approximation (LDA), where the $E_{xc}[n(\mathbf{r})]$ is approximated point by point in real space (*i.e.*, from each infinitesimal volume in the system) by the exchange-correlation energy of the homogeneous electron gas of density $n(\mathbf{r})$ [57]. While LDA serves as a useful initial approximation for the exchange-correlation functional in many-electron systems, it falls short in capturing certain critical material characteristics, such as metallic and insulating behaviour. This limitation arises from its inability to account for the inhomogeneous electronic density and its variations in spatial dimensions near the atomic nuclei. Incorporating considerations for electron density variations near the atomic nuclei, the generalized gradient approximation (GGA) is introduced, resulting in enhanced accuracy when calculating binding energies, atomisation energies, and structural energy differences. These functionals treat the exchange-correlation energy of electrons as a function of both the local electron density $n(\mathbf{r})$ and the corresponding density gradient $\nabla n(\mathbf{r})$. Several renowned GGA functionals are widely employed in DFT calculations, including the Perdew-Burke-Ernzerhof

(PBE), Becke-Lee-Yang-Parr (BLYP) functionals, and the innovative Bayesian Error Estimation Functional (BEEF) [226, 227, 228]. By introducing the exchange-correlation energy (potential) functional, the Schrödinger equation of the single-electron wave function can be reformulated into the Kohn-Sham equation, forming the basis of the Kohn-Sham theory:

$$\left[-\frac{1}{2}\nabla^2 + V_n(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \quad (3.21)$$

The practical procedure for solving the Kohn-Sham equations is as follows: the first task is to determine the external potential $V_n(\mathbf{r})$ from the nuclear coordinates in the system; second, an initial guess of the electronic density $n(\mathbf{r})$ is needed, often derived from a rough summation of the isolated atoms' electronic densities, to determine both the Hartree potential $V_H(\mathbf{r})$ and the exchange-correlation potential $V_{xc}(\mathbf{r})$, which in turn enables the construction of the initial Kohn-Sham Hamiltonian; third, solving the Kohn-Sham equations yields a new set of single-electron wave functions $\phi'_i(\mathbf{r})$, allowing us to construct an improved estimation of the electronic density and hence the total potential. This process is iteratively executed until the new density converges to match the old density within a predetermined tolerance, which is also called 'self-consistency' in DFT calculations.

3.1.2 Pseudopotentials and PAW Formalism

In general, it is widely accepted that valence electrons within atoms exhibit greater sensitivity to alterations in the chemical bonding environment than core electrons that are located near the Coulomb singularity, thus playing a more prominent role in the process of forming chemical bonds in materials. As a result, the core electrons can be treated as they appear in the isolated atoms and are assumed to remain frozen in the vicinity of atomic nuclei, leading to an effective ion with a screened ionic potential, commonly referred to as a pseudopotential [229]. The introduction of pseudopotentials, utilizing the frozen core approximation, enables DFT calculations to be conducted with greater efficiency. This is due to the reduced number of nodes in the core regions for valence electrons (as they are no longer required to be orthogonal to the core electrons), resulting in the need for smaller basis set expansions to adequately represent. To effectively

implement the use of pseudopotentials in DFT calculations, it is crucial to establish a radial cutoff r_c . Within this cutoff radius, the all-electron wave function is substituted with a smooth, nodeless function. Beyond the radial cutoff, the pseudo-wave function must accurately reproduce the electron density of the all-electron function. One of the frequently used pseudopotentials in DFT calculations was proposed by Hamann, Schlüter, and Chiang in 1979, known as the norm-conserving pseudopotential (the norm of the pseudo-wave function is identical to the corresponding all-electron wave function within r_c) [230]:

$$\hat{V}_{ps}(r) = \sum_l \sum_m |Y_{lm}\rangle V_{lm}(\mathbf{r}) \langle Y_{lm}| \quad (3.22)$$

Here the $|Y_{lm}\rangle$ projects the one-electron wave function (*i.e.*, Kohn-Sham orbital) onto the angular momentum states defined by the quantum numbers of l and m . $V_{lm}(\mathbf{r})$ refers to the pseudopotential that operates on the projected wave function. An alteration of the norm-conserving pseudopotential is the ultra-soft pseudopotential, which reduces the required basis-set size by relaxing the norm-conserving constraint with the introduction of a generalized eigenvalue problem [231].

Based on the Vanderbilt-type ultra-soft pseudopotential (USP) and the linearised augmented-plane-wave (LAPW) method, Blöchl initially proposed the projector-augmented-wave (PAW) formalism in 1994 [232]. The essence of this formalism lies in its ability to transform the rapidly oscillating wave functions of valence electrons into smoother representations within the core regions while also offering a means to retrieve the information of the all-electron wave function within the core region. Within the PAW formalism, an efficient linear transformation converts the pseudo-wave function, characterized by a wave vector $\mathbf{k}$, of an individual electron, $\tilde{\psi}_{n\mathbf{k}}$ into the corresponding one-electron Kohn-Sham orbital $\psi_{n\mathbf{k}}$ as follows:

$$|\psi_{n\mathbf{k}}\rangle = |\tilde{\psi}_{n\mathbf{k}}\rangle + \sum_i \left(|\phi_i\rangle - |\tilde{\phi}_i\rangle \right) \langle \tilde{p}_i | \tilde{\psi}_{n\mathbf{k}} \rangle \quad (3.23)$$

It's important to highlight that the pseudo-wave function $\tilde{\psi}_{n\mathbf{k}}$ coincides with the exact orbital $\psi_{n\mathbf{k}}$ within the interstitial regions between the PAW spheres. However, it represents an inaccurate approximation of the true wave function within the confines of the spheres. $|\phi_i\rangle$ and $|\tilde{\phi}_i\rangle$

respectively refer to the PAW all-electron partial waves and PAW pseudo partial waves, which are associated by the set of projector functions $|\tilde{p}_i\rangle$. The PAW method is highly efficient and robust when it comes to computing and incorporating supplementary augmentation quantities into the pseudo-valence wave functions, thus leading to its popularity in several modern DFT packages, such as the Vienna ab initio software package (VASP) used in our works [233, 234].

3.1.3 Reciprocal Lattice and Periodic DFT

The DFT framework is a versatile tool applicable to a wide range of quantum mechanical systems comprising electrons and nuclei. Condensed matter physics is primarily concerned with applying the DFT formalism to periodic crystal systems, with a specific focus on materials like metallic Mg, which is the central focus of our research. For the periodic crystals, atoms are arranged in patterns which replicate themselves periodically, thus the system can be treated as a collection of unit cells repeating themselves in space infinitely. The fundamental unit cell, also known as the primitive unit cell, is the smallest part of a crystal that can be used to construct the entire solid through rigid translations. Generally, it takes the form of a parallelepiped with edges labelled as $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$, which also form the primitive lattice vectors. These primitive vectors are used to define the crystal direct (or translation) vectors:

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \quad (3.24)$$

with n_1 , n_2 and n_3 as integers. To effectively solve the Kohn-Sham equation in conjunction with periodic boundary conditions, electron wave functions are often expressed using a Fourier series. This approach involves applying Fourier transformations to the primitive lattice vectors, yielding the reciprocal lattice vectors denoted as $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$. For instance, the reciprocal lattice vector $\mathbf{b}_1$ is generated from the following equation:

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \quad (3.25)$$

Likewise, the same procedure is applied to $\mathbf{b}_2$ and $\mathbf{b}_3$ by cyclically permuting the indices. The

selection of the primitive vectors for the reciprocal lattice is made to achieve the following characteristic:

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij} \quad (3.26)$$

Here δ_{ij} represents the Kronecker delta. Therefore, the reciprocal lattice can be defined as the collection of all vectors $\mathbf{G}$ that serve as wave vectors for plane waves within the Fourier series of a spatial function exhibiting the same periodicity as the direct lattice:

$$\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3 \quad (3.27)$$

with m_1 , m_2 and m_3 as integers. Similar to the real-space unit cell, the reciprocal lattice can be subdivided into Wigner-Seitz cells, with the smallest one known as the first Brillouin zone, which encapsulates all the lattice's essential information.

Taking into account the periodic nature of crystals, the solutions to the Kohn-Sham equations can be described as plane waves that are modulated by periodic functions, a principle commonly referred to as the Bloch theorem [235]:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \quad (3.28)$$

where $u_{n\mathbf{k}}(\mathbf{r})$ represents a periodic function that mirrors the periodicity of the crystal's direct lattice, such that $u_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r} + N \cdot \mathbf{a}_j)$, with a wave vector denoted as $\mathbf{k}$ (crystal momentum vector) confined within the boundaries of the first Brillouin zone. Utilizing the Bloch theorem, rather than simulating an infinite number of electrons within an infinite crystal, we can confine our DFT simulation to a finite number of electrons which are contained within a periodic unit cell of the crystal. Nonetheless, as the complete periodic information is incorporated within the first Brillouin zone (contains a restricted set of values of $\mathbf{k}$ with the property that each distinct from the others), simulating the entire infinite crystal requires an impractical infinite number of $\mathbf{k}$ -points within this zone. In practical DFT simulations, a finite number of points are sampled within the first Brillouin zone to make the problem computationally manageable.

3.2 Implicit (Continuum) Solvation Model

The most critical electrochemical reactions associated with magnesium corrosion occur at the interface between the magnesium surface and an aqueous solution. To theoretically investigate such an electrochemical process, it is essential to employ a computational model that effectively incorporates the solvent effect. One of the commonly employed approaches for modelling the solvent effect at a solid/liquid interface is to explicitly consider all solvent molecules, including water molecules. This is achieved by utilizing *ab initio* molecular dynamics to relax both the electronic and ionic degrees of freedom of both the solute and the solvent molecules. The explicit solvent model in DFT calculations is resource-intensive. It demands a significant amount of computational time to reach an equilibrium state when dealing with numerous solvent molecules. Furthermore, substantial computational resources (*i.e.*, increasing number of computational nodes or cores) are necessary for the statistical averaging of critical properties at the solid/liquid interfaces.

To decrease the need for explicit calculations of solvent molecules at the metal/water interface while still capturing the crucial solvent effects, such as electrostatic interactions with the solute, an alternative approach called the implicit (continuum) solvent model is introduced [236]. In this model, the solvent is treated as a continuous medium with a defined dielectric constant (function), which implies that the solute is immersed in a solvent bath and the averaging over solvent degrees of freedom becomes inherently implicit in the properties of this solvent medium. Fattebert and Gygi originally introduced the implicit solvent model into plane wave Car-Parrinello molecular dynamics by resolving the Poisson problem through a compact finite difference method [237]. Subsequently, Marzari *et al.* extended the implicit solvent model in the DFT code by introducing non-electrostatic solvent effects like cavitation and dispersion, achieved through a combined utilisation of quantum volume and quantum surface [238].

Herein, we provide a brief overview of the implicit solvent model utilised in VASP calculations. For a combined solute/solvent system, the free energy of the system can be described as a sum of a functional F , concerning the total electron density and the averaged atomic densities $N_i(\mathbf{r})$

of the solvent species with the atomic number of Z_i , and an electrostatic contribution term:

$$A = F [n_{\text{tot}}, \{N_i(\mathbf{r})\}] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) \left(\sum_i Z_i N_i(\mathbf{r}) - n_{\text{tot}}(\mathbf{r}) \right) \quad (3.29)$$

Here the total electron density n_{tot} includes the electron density of the solute n_{solute} and the solvent n_{solv} . V_{ext} is the external potential generated by the solute nuclei. To determine the ground state free energy of the system using a computationally feasible approach, the initial step involves minimising the free energy over the solvent electron density n_{solv} , hence yielding the following outcome:

$$\tilde{A} = G [n_{\text{solute}}(\mathbf{r}), \{N_i(\mathbf{r})\}, V_{\text{ext}}(\mathbf{r})] - \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n_{\text{solute}}(\mathbf{r}) \quad (3.30)$$

where $G [n_{\text{solute}}(\mathbf{r}), \{N_i(\mathbf{r})\}, V_{\text{ext}}(\mathbf{r})]$ refers to a universal functional of the electron density of the solute, the average atomic densities of the various species in the solvent and the external potential of the solute nuclei, which could be further expanded as:

$$\begin{aligned} & G [n_{\text{solute}}(\mathbf{r}), \{N_i(\mathbf{r})\}, V_{\text{ext}}(\mathbf{r})] \\ &= \min_{n_{\text{solv}}} \left\{ F [n_{\text{tot}}, \{N_i(\mathbf{r})\}] - \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) \left(\sum_i Z_i N_i(\mathbf{r}) - n_{\text{solv}}(\mathbf{r}) \right) \right\} \\ &= A_{\text{KS}} [n_{\text{solute}}(\mathbf{r}), V_{\text{ext}}(\mathbf{r})] + A_{\text{diel}} [n_{\text{solute}}(\mathbf{r}), \{N_i(\mathbf{r})\}, V_{\text{ext}}(\mathbf{r})] \end{aligned} \quad (3.31)$$

A_{KS} refers to the general Kohn-Sham density functional for the solute, and A_{diel} includes all interactions between the solute and solvent along with the internal energy for the solvent, which could be further optimized by minimising it over the averaged atomic densities of solvent species. By further introducing the cavitation and dispersion effect in the total free energy of the system, and decoupling the electrostatic term from the Kohn-Sham functional, we can reformulate the free energy of the solute/solvent as [236]:

$$\begin{aligned} A [n_{\text{solute}}(\mathbf{r}), \phi(\mathbf{r})] &= A_{\text{TXC}} [n_{\text{solute}}(\mathbf{r})] + \int d\mathbf{r} \phi(\mathbf{r}) (N_{\text{solute}}(\mathbf{r}) - n_{\text{solute}}(\mathbf{r})) \\ &\quad - \int d^3\mathbf{r} \epsilon(\mathbf{r}) \frac{|\nabla \phi(\mathbf{r})|^2}{8\pi} + \tau \int d^3\mathbf{r} |\nabla S(\mathbf{r})| \end{aligned} \quad (3.32)$$

with A_{TXC} as the free energy density functional describing the electron kinetic and exchange-correlation energy for the solute. N_{solute} represents the nuclear charge density for solute, and its combination with the electronic density leading to the formation of an integrated electrostatic potential $\phi(\mathbf{r})$ in a polarisable medium. $\epsilon(\mathbf{r})$ is the relative permittivity of the solvent, and $S(\mathbf{r})$ refers to the cavity shape function. τ is the effective surface tension term. The relative permittivity for the solvent is generally treated as a function of the shape of the diffuse dielectric cavity, which is in turn determined as a functional of the solute electronic density [239]:

$$\epsilon[n_{\text{solute}}(\mathbf{r})] = 1 + (\epsilon_{\text{b}} - 1) S[n_{\text{solute}}(\mathbf{r})] \quad (3.33)$$

$$S[n_{\text{solute}}(\mathbf{r})] = \frac{1}{2} \operatorname{erfc} \left\{ \frac{\log(n_{\text{solute}}/n_{\text{c}})}{\sigma\sqrt{2}} \right\} \quad (3.34)$$

where ϵ_{b} is the relative permittivity of the bulk solute. n_{c} is the critical electronic density where the dielectric cavity starts to form and σ determines the width of the cavity. Therefore, the solvation energy for a metal slab immersed in a continuum solvent is greatly dependent on both the electronic density of the solute and the shape function of the dielectric cavity in this model, which can be efficiently computed within the framework of DFT.

3.3 Nudged Elastic Band Theory

A significant challenge in theoretical chemistry and condensed matter physics lies in the computation of transition rates (which depend on energy barriers) for some essential reactions, for instance the hydrogen evolution reaction during Mg aqueous corrosion. Nevertheless, the transition events are labelled as ‘rare events’ in typical dynamic simulations due to their slower occurrence compared to atom vibrations, necessitating an unaffordably long simulation time. Assuming a Boltzmann distribution can be established in the reactant state, the transition rate can be determined through a purely statistical approach, commonly referred to as transition state theory [240]. For crystals, the atoms are tightly bound at their equilibrium positions in the unit cell when the temperature is significantly below the melting point, in which case

the harmonic approximation to the transition state theory (hTST) is capable of simulating the reactions happening in the bulk crystals or crystal surfaces [241]. The transition rate k^{hTST} within the harmonic approximation is then obtained by estimating the free energy and frequencies of the normal modes for the lowest few saddle points, perched at the edge of the potential energy basin, and for the initial state:

$$k^{\text{hTST}} = \frac{\prod_i^{3N} \nu_i^{\text{init}}}{\prod_i^{3N-1} \nu_i^\ddagger} e^{-(E^\ddagger - E^{\text{init}})/k_B T} \quad (3.35)$$

where $\nu_i^\ddagger$ and $E^\ddagger$ refer to the normal mode frequency and energy for the saddle point. ν_i^{init} and E^{init} represent the frequency and energy for the initial state. To search for saddle points, it is essential to find a path with the greatest statistical weight that connects the initial and final state for a designated chemical reaction, which is also called the minimum energy path (MEP). This path possesses a series of points (each akin to a distinct state) wherein forces acting upon the atoms are exclusively oriented along the path direction, and its maxima refer to the saddle points on the potential surface.

There exist various methods for discerning the possible MEPs and saddle points of given chemical reactions [242]. One of the most effective methods that have been widely used in conjunction with electronic structure calculations is called the nudged elastic band theory (NEB), which constructs a set of replicas of the system that are interconnected by a spring interaction, effectively emulating the behaviour of an elastic band [243]. The optimization of atomic forces within each replica propels the band toward gradual convergence, culminating in its eventual attainment of the MEP. In the NEB method, each replica (image) is subject to a total force comprising the spring force along the local tangent and the actual force (on the potential energy surface) perpendicular to the local tangent:

$$\mathbf{F}_i = \mathbf{F}_i^s|_{\parallel} - \nabla E(\mathbf{R}_i)|_{\perp} \quad (3.36)$$

Here $\mathbf{F}_i^s|_{\parallel}$ is the spring force, which is calculated by the spring constant k , the coordinates of images $\{\mathbf{R}_i\}$, and the normalized local tangent at image i , labelled as $\hat{\boldsymbol{\tau}}_i$:

$$\mathbf{F}_i^s|_{\parallel} = k (|\mathbf{R}_{i+1} - \mathbf{R}_i| - |\mathbf{R}_i - \mathbf{R}_{i-1}|) \hat{\boldsymbol{\tau}}_i \quad (3.37)$$

The second term in Equation 3.36 indicates the actual force of image i , and can be obtained from the gradient of the free energy for the system:

$$\nabla E(\mathbf{R}_i)|_{\perp} = \nabla E(\mathbf{R}_i) - \nabla E(\mathbf{R}_i) \cdot \hat{\boldsymbol{\tau}}_i \quad (3.38)$$

Based on these equations, an optimisation algorithm of the total forces on the reaction images, such as the projected velocity Verlet algorithm can be employed to ease the elastic band into the MEP. To improve the efficiency and accuracy of the traditional NEB method, Henkelman *et al.* introduced the climbing image NEB (CI-NEB) method in 2000 [244]. This new method (involving a small modification to the general NEB method), still runs a few iterations with the regular method and then identifies the image with the highest total energy along the reaction pathway. The force on this specific image is redefined as follows:

$$\begin{aligned} \mathbf{F}_{i_{\max}} &= -\nabla E(\mathbf{R}_{i_{\max}}) + 2\nabla E(\mathbf{R}_{i_{\max}})|_{\parallel} \\ &= -\nabla E(\mathbf{R}_{i_{\max}}) + 2\nabla E(\mathbf{R}_{i_{\max}}) \cdot \hat{\boldsymbol{\tau}}_{i_{\max}} \hat{\boldsymbol{\tau}}_{i_{\max}} \end{aligned} \quad (3.39)$$

By incorporating this method into DFT-based codes, the determination of transition states and reaction energy barriers becomes achievable with a reduced number of interpolation images and diminished difference from the exact value.

Chapter 4

Atomic Structure and Potential of Zero Charge for Mg Surfaces

¶ *Chapter Synopsis*

A thorough comprehension of the structure at the metal/bulk water interface on a molecular level is crucial for various processes, especially in the aqueous corrosion of metals. However, the buried nature of this interface makes experimental exploration challenging, necessitating a heavy reliance on theoretical simulations. In this chapter, we employed second-generation Car-Parrinello molecular dynamics to investigate the structural characteristics of the water/Mg (0001) interface. This molecular dynamic simulation was subsequently coupled with static density functional theory calculations to delve into the atomic interaction between water molecules and Mg atoms at the interface, allowing us to further scrutinize the pivotal attribute of the electrochemical interface, namely the potential of zero charge. Through conducting a detailed structural analysis of the interface configurations generated from ab initio simulation, we discovered that water adsorption on the Mg (0001) surface significantly roughens the surface by lifting upward the top-layer Mg atoms firmly bound with water molecules. Further electronic structure evaluation of the water/Mg (0001) interface reveals that the difference in potential energy for removing an electron to the vacuum level through the electrified interface (which directly connects to the potential of zero charge) and the work function of the basal Mg surface

primarily stems from the redistribution of electron density at the interface and the overall dipole moment of the water molecules within the electric double layer. Note that this chapter is part of a published peer-reviewed journal article in the Journal of Chemical Physics [DOI: 10.1063/5.0093562]. The molecular dynamic simulation work (obtaining the basic structure of the Mg/water interface) presented in this chapter is primarily led by Dr. Richard Fogarty, and the analysis along with the statistic DFT calculations for determining the potential of zero charge was done by me.

4.1 Introduction

Metal/water interfaces play an essential role in numerous significant electrochemical processes, including battery charge/discharge cycles, electrocatalysis, and metal's aqueous corrosion [11, 245, 246]. Understanding the interfacial structure and atomic interactions occurring at these interfaces is of remarkable importance for a comprehensive grasp of these processes and searching for an effective controlling approach. In this chapter, the reason for our particular focus on the Mg/water interface lies in its significance within the context of Mg aqueous corrosion. Thanks to their outstanding mechanical properties and benign biocompatibility, magnesium alloys have found extensive applications across diverse industries, including the automotive sector, medical implant technology, and aqueous air batteries [247, 248, 249]. Nonetheless, insufficient corrosion resistance of Mg and its alloys under aqueous environments limits their further applications. As an initial step to unravel the mechanism of Mg aqueous corrosion, gaining insight into the structure and interactions occurring at the Mg/water interface (where numerous pivotal corrosion reactions take place) is particularly crucial.

Despite the utilisation of several cutting-edge experimental techniques, such as shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) and Kelvin probe force microscopy (KPFM)-AFM, probing the atomic structure of the metal/water interface continues to be challenging, primarily due to the demanding experimental conditions and the intricate nature of the electric double layer [195, 196]. Theoretical simulations, such as *ab initio* molecular dynamics (AIMD), offer valuable insights into essential questions about metal/water interfaces

that are challenging to investigate in experiments with less effort. For instance, previous AIMD simulations on the metal/water interfaces for the *d*-electron metals, like the (111) surface for Pt, Cu and Pd, have uncovered that near-surface water monomers exhibit two distinct orientation preferences: one with the dipole moment directed toward the bulk water, and the other oriented in the opposite direction [4, 250]. Yuwono *et al.* investigated the interaction between water molecules and the stepped pristine Mg (311) surface with AIMD simulations, and further discovered that both the water dissociation reaction and the metal dissolution reaction are highly likely to occur near the region of step Mg atoms [18]. Through ab initio simulations conducted under carefully controlled potentiostat conditions at the electrified Mg (0001)/water interface, Surendralal *et al.* observed that the hydrogen evolution reaction (HER) on the Mg (0001) surface proceeds via a Heyrovsky-like reaction pathway, characterized by the interaction between water molecules and on-surface negative hydrogen ions (H^-) [151]. It is important to note in this context that the inherent reactivity of Mg causes the metallic Mg/water interface becoming a metastable phase. This is supported by the experimental observation of the formation of a hybrid surface film composed of magnesium oxide and hydroxide that begins to develop on the metal surface upon its exposure to water [167]. However, this film offers limited protection to the underlying metal due to its high porosity and the presence of cracks within its structure, which leads to the reasonable assumption that there are regions on the surface where water can effectively access the bare metal. Hence, it is apt to use the bare metal/water interface model for calculating the pathways for some essential interface reactions [18, 36, 145, 251]. Consequently, it becomes imperative to acquire insights into the metastable structure and interactions taking place at the Mg/water interface, as this interface essentially serves as the initial structure for a multitude of significant reactions within the aqueous corrosion process.

Beyond the fundamental structural details of the magnesium/water interface, other crucial interface characteristics, such as the potential of zero charge (PZC), hold considerable significance in establishing a connection between the reaction energy barriers calculated through DFT (typically computed at the PZC) and actual experimental conditions [35, 252]. The fundamental concept of the potential of zero charge (PZC) in an electrified metal/water interface pertains

to the condition of the electrode surface where no excess charge prevails freely. According to the theory proposed by Trasatti, the PZC of metal electrodes could be correlated to the work function of metals through the following expression [253]:

$$E_{\text{PZC}} = \Phi + \delta\chi^{\text{M}} - g_{\text{dipole}}^{\text{S}} + K \quad (4.1)$$

where Φ refers to the work function of metal electrodes in a vacuum, and $\delta\chi^{\text{M}}$ is the difference of metal surface potential in contact with a vacuum and with a solution. $g_{\text{dipole}}^{\text{S}}$ is the sum of surface potential of water (χ^{S}) exposed to air and the potential difference ($\delta\chi^{\text{S}}$) when water is in contact with the metal electrode and constant K indicates the potential drop at the reference electrode/solution interface. This equation suggests that the PZC for metal/water interfaces shows some linear associations with respect to the correlated work function, which was further confirmed by experimental measurements for a range of metal surfaces [253]. While several experimental methods, including the surface tension method, the capacitance measurement method and the CO charge-displacement method, have been devised to enhance the precision of PZC measurements for electrodes, persistent uncertainties in these measurements arise from challenges in sample preparation, particularly in crafting single crystal electrodes, as well as the intricacy of the measurement techniques [254, 255, 256]. As a result, first principles simulations of metal surfaces in aqueous environments have emerged as a potent and efficient alternative for determining the PZC [218]. Sakong *et al.* simulated the Pt (111)/water system explicitly by modelling the system with AIMD and revealed that the PZC for the Pt slab covered by an ion-free water film is approximately 4.96 eV, with a standard deviation of around 0.23 eV [257]. Le *et al.* determined the PZC for several transition metals (Pt, Au, Pd, Ag) concerning the computational standard hydrogen electrode (c-SHE) using AIMD simulations and found that the results closely align with experimental data [211]. However, we lack knowledge of an experimental value for Mg, and there is no appropriate experimental method available to determine the PZC solely for the Mg(0001)/bulk water interface, excluding contributions from other interfaces, owing to its inherently metastable nature.

In this chapter, we aim to obtain a detailed picture of the Mg(0001)/bulk water interface

through AIMD calculations and estimate the potential of zero charge for the surface (*i.e.*, the difference between the potential energy required to move an electron from the electrode into the vacuum beyond the water/metal interface and the metal’s work function). Our initial focus centres on reporting the orientations of water molecules near the Mg surface and the morphological changes of the metal surface induced by the presence of aqueous water molecules. Utilising static DFT calculations, we subsequently partition the Volta potential difference at the interface into three separate components: the contribution from the water dipole, the electron density component, and the geometric aspect. Finally, we compare the significant structural characteristic for the Mg (0001)/water interface and for other different metals, thus demonstrating the essential discrepancy in the Volta potential difference between the typical *sp*-electron metal, Mg and other *d*-electron metals primarily stems from the water-introduced surface roughening, and providing valuable insights into the aqueous corrosion of Mg.

4.2 Method

4.2.1 Ab initio Molecular Dynamics (AIMD)

We conducted ab initio molecular dynamics (MD) simulations of the Mg(0001)/water interface within a hexagonal cell of six atomic layers, denoted as a $p(6 \times 6)$ cell, containing a total of 216 Mg atoms and accompanied by 144 water molecules. These simulations were performed using the NVT ensemble, as depicted in Figure 4.1. The lattice parameters used were $19.26 \times 19.26 \times 43.41$ Å, with the a and b parameters being determined from optimisation of the bulk Mg cell ($a = b = 3.21$ Å). These settings led to a water thickness of approximately 12 Å and a vacuum region of approximately 15 Å. We ran the simulation for a total of approximately 24 *ps* with the first 3.5 *ps* being considered the equilibration period. We used a target temperature of 300 K and a timestep of 0.5 *fs*. Due to the large size of our cell, we used only the Γ point for the k-point sampling for this simulation. We used the optB88-vdW functional for the AIMD calculations due to its good description of bulk water and its previous use in studying metal/water interfaces, thereby making comparisons to literature simpler [146, 258]. Herein, we carried out our molecular dynamic simulation using second-generation Car-Parrinello dynamics

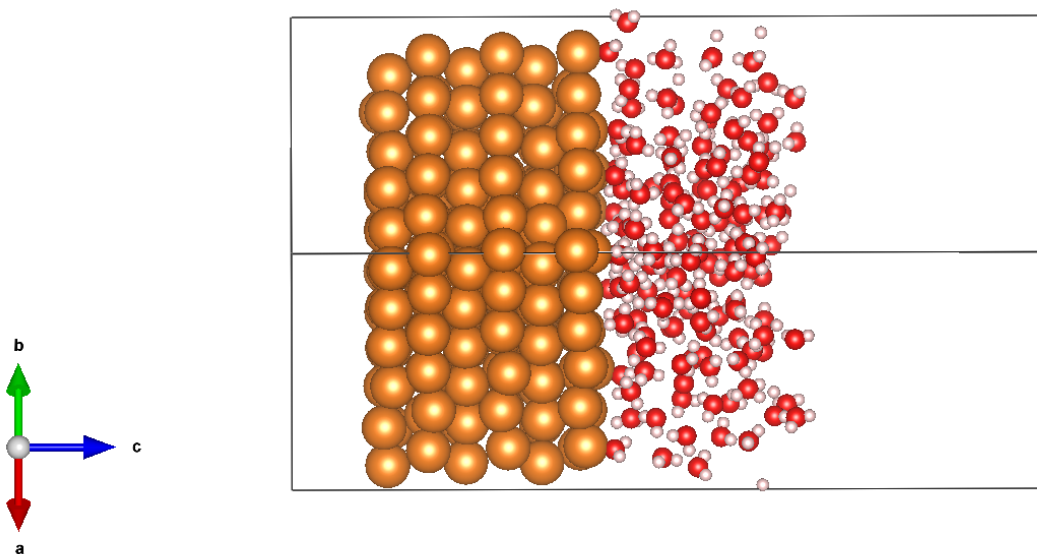


Figure 4.1: Configuration of the Mg (0001)/water system at 9.5 ps. The orange atom refers to Mg atom, red one is the oxygen atom and H is represented by the white atom.

(SGCP) for speeding up *ab initio* MD while maintaining considerable accuracy, except for the initial 630 fs where we used Born-Oppenheimer molecular dynamics (BOMD). More details about the techniques of the SGCP dynamics can be found in the original paper which is the foundation of this chapter, and the main MD simulation work was led by Dr. Richard Fogarty [152].

4.2.2 Potential of Zero Charge (PZC) Calculations

Turning to the potential of zero charge (PZC) calculations of Mg in aqueous conditions, we carried out single-point energy calculations of the Mg (0001)/water interface using the structure from *ab initio* molecular dynamics (AIMD) trajectories: we started after 4.5 *ps* to ensure the system is in equilibrium, and then took structures every 200 steps thereafter. We carried out these calculations using both the plane-wave DFT based Vienna *ab initio* software package (VASP) and the Gaussian-plane-wave based DFT code CP2K.

For the VASP calculations, we used an energy cut-off of 600 eV to make sure the total energy, Fermi energy and work function of the system converge [233, 234]. The projector augmented-wave method (PAW) which generalizes the pseudopotential and linear augmented-plane-wave

(LAPW) methods was used to improve the calculation efficiency by transforming the rapidly oscillating wave-functions near ion cores into more smooth ones [259]. The PBE functional within the generalised gradient approximation (GGA) was used in the calculations to approximate the exchange-correlation interactions of electrons [226]. This is because other calculations suggest that PBE leads to calculated PZC and work function values in good agreement with experiments for several metals [260, 250]. Using this functional also allows more direct comparisons to others results as PBE is commonly used for calculating both work functions and PZC. To deal with the asymmetric nature of our system, the dipole correction method was carried out for obtaining an accurate vacuum level [261].

For the PZC calculations using CP2K, the Goedecker-Teter-Hutter (GTH) pseudopotentials with core charges of +2, +6 and +1 for Mg, O and H were used [262]. The exchange-correlation interaction of electrons is approximated by the PBE functional. The Gaussian-type basis sets in the calculations for Mg, O and H are the rc-7pt5-sspd+s basis set, the molopt-TZV2P basis set (*q6*) and the molopt-TZV2P basis set (*q1*) respectively [152]. The absolute and relative grid cutoff for the single-point energy calculation was 8000/800 eV, with the SCF converging to the tolerance of 10^{-6} .

The model we used for the PZC calculation is the vacuum/metal/liquid/vacuum (VMLV) model and is the same as the model we used for the AIMD calculation. The PZC is thus defined relative to the vacuum level, and is the difference between the electron electrochemical potential in the metal (Fermi energy, ϵ_F) and the vacuum level outside the water. The potential energy difference between the PZC (U_{PZC}) and the work function (Φ_{M}) is thus calculated as follows:

$$\begin{aligned}\Delta\phi_{\text{total}} &= eU_{\text{PZC}} - \Phi_{\text{M}} \\ &= E_{\text{water/vacuum}} - E_{\text{metal/vacuum}}\end{aligned}\tag{4.2}$$

where $E_{\text{water/vacuum}}$ corresponds to the potential energy of the vacuum level outside the water, and $E_{\text{metal/vacuum}}$ is that of the vacuum level outside the metal. The difference in potential energy ($\Delta\phi_{\text{total}}$) can be decomposed into three parts with respect to different contributions:

$$\Delta\phi_{\text{total}} = \Delta\phi_{\text{e}} + \Delta\phi_{\text{ori}} + \Delta\phi_{\text{geom}} \quad (4.3)$$

$\Delta\phi_{\text{e}}$ is the contribution that stems from the electron density redistribution at the water/metal interface and $\Delta\phi_{\text{ori}}$ refers to the orientation contribution from the total water dipole moment. In our setup of the metal/water interface, the metal is asymmetric with one side in contact with vacuum and the other side with water molecules. Consequently, the geometry of the metal slab at the two sides can be different, thus contributing to a potential energy difference $\Delta\phi_{\text{geom}}$. We now describe how these are computed, and hence defined.

To determine the magnitude of different contributions to $\Delta\Phi_{\text{total}}$, further single-point energy calculations were carried out; these involved dividing the total system into metal and water parts at fixed geometries and finding the energies of the individual parts. First, the orientation contribution ($\Delta\phi_{\text{ori}}$) was calculated by separating the water molecules from the AIMD trajectories of the total system for individual single-point energy calculations. The difference in the potential energy of the vacuum level between the two sides of the water slab corresponds to the contribution from the water dipole moment. Similarly, the Mg slab was extracted from the total system for a further single-point energy calculation to estimate the geometry effect $\Delta\phi_{\text{geom}}$, which is the potential energy difference of the vacuum at the two sides of the metal slab. Finally, the contribution of the electron density redistribution ($\Delta\phi_{\text{e}}$) was calculated from the difference in $x - y$ planar average electrostatic potential along the z -axis between the system and separated parts:

$$V_{\text{diff}} = V_{\text{total}} - V_{\text{water}} - V_{\text{metal slab}} \quad (4.4)$$

where V_{total} is the planar average electrostatic potential along the z -axis of the whole interface, and V_{water} and $V_{\text{metal slab}}$ are the corresponding average electrostatic potentials of the water molecules and the Mg slab respectively. These were all obtained from single-point energy calculations.

4.3 Results

4.3.1 Mg (0001)/Water Interface Structure

Herein, we focus on the structure of the Mg (0001)/water interface generated from our MD calculations. In the following section, we spot that the atomic arrangement of the Mg surface submerged in aqueous surroundings, along with the collective orientation of water molecules, significantly influences the potential of zero charge for the Mg(0001) surface. Therefore, we delve deeply into these two crucial aspects of the interface’s structural information here (further details of the water dynamics and hydrogen bonding of water clusters within the interface region are available in the original paper as mentioned previously).

Figure 4.2 illustrates the distributions of tilt and roll angles for different category of water molecules. Defining the direction of the water dipole as extending from the oxygen atom to the midpoint between the two hydrogen atoms, a positive (negative) tilt indicates that the dipole points away from (towards) the surface. In the case of the strongly adsorbed water molecule (labelled as solAds, with distance of oxygen from water to the Mg slab, $r_{\min}(\text{O} - \text{Mg}) < 3 \text{ \AA}$), the tilt distribution indicates that the water dipole predominantly orients itself away from the surface, with a notable degree of freedom evident in a broad distribution spanning from 0° to $+90^\circ$. The physisorbed water molecule (solPhys, with $3 < r_{\min}(\text{O} - \text{Mg}) < 5 \text{ \AA}$ and at most one donated hydrogen bond), on the other hand, exhibits nearly the inverse behavior, with the water dipole predominantly directed toward the surface. This observation aligns with the representation of the solPhys group as physisorbed water, given that the dipole typically requires orientation towards the surface to facilitate an interaction with Mg-H. However, in cases where the absolute roll angle is large, one hydrogen may still be able to engage in interactions. For the water molecules that near the Mg surface yet not interacting directly (solNonAds, with $3 < r_{\min}(\text{O} - \text{Mg}) < 5 \text{ \AA}$ and two or more donated hydrogen bond), they exhibit a notably wide distribution of tilt angles, displaying a slight inclination toward positive tilt angles.

In Figure 4.2 (d), the roll angle distributions for near-surface water are presented. A roll angle near zero, regardless of the orientation angles, implies that each hydrogen atom is at a similar distance from the surface. Conversely, large roll angles generally indicate variations in

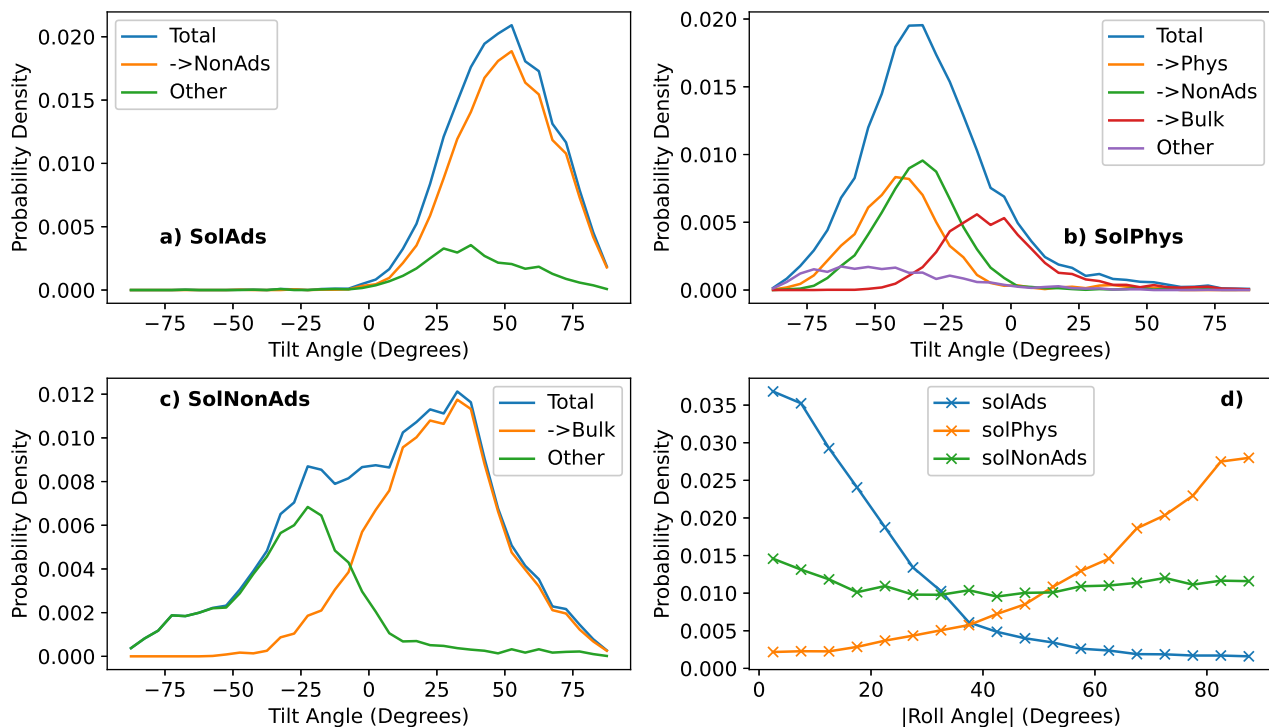


Figure 4.2: Probability distributions for a) solAds tilt angle, b) solPhys tilt angle, c) solNonAds tilt angle and d) the absolute values for roll angles.

the z-coordinates of the hydrogen atoms, as the surface normal aligns along the z-axis. However, as the tilt angle approaches 90° , the gap between hydrogen z-coordinates tends to approach zero, irrespective of the roll angle. SolAds exhibits a strong preference for small roll angles, indicating that each hydrogen atom maintains a relatively consistent interaction with the surface. In contrast, solPhys demonstrates a predilection for larger roll angles, which stems from the fact that generally only one hydrogen atom interacts with the surface. The absence of a strong preference for solNonAds is likely due to their lack of direct interactions with the surface.

Concerning the morphology of the Mg surface, Figure 4.3 displays the planar distribution function for the Mg atoms in the surface layer, which is defined using the average planar value of the third atomic layer of Mg as the reference point for distance measurement. The planar distribution of Mg atoms exhibits two distinct peaks: the dominant peak corresponds to Mg atoms that do not have solAds water molecules within $3 \text{ \AA}$ radius, denoted as MgFree; the smaller peak represents Mg atoms with solAds water molecules within $3 \text{ \AA}$, referred to as MgSol hereafter. The mean position of MgFree has experienced only a slight change, approximately $+0.1 \text{ \AA}$ when compared to the equivalent atoms at the metal/vacuum interface. Consequently, it

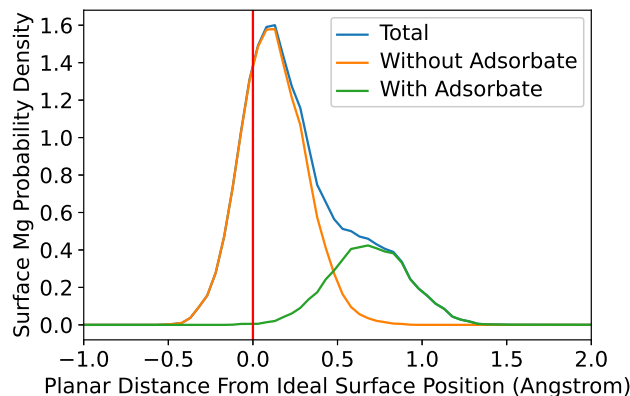


Figure 4.3: Planar distribution of Mg atoms in the outer surface layer (*i.e.*, the 36 atoms closest to water). The value of zero is 5.27 Å from the average planar position of the third atomic layer (this value comes from the separation of first and third layers in vacuum). The “With Adsorbate” group refers to Mg atoms with $r_{\min}(\text{Mg} - \text{O}) < 3$ Å. Note the red vertical line marks the zero on the x-axis.

is evident that the water environment has had a minimal impact on the planar spacing of Mg-Mg for the majority of surface atoms. Conversely, the MgSol species are displaced by approximately +0.7 Å, moving towards the bulk water. This distinct behaviour exhibited by MgFree and MgSol substantially contributes to the surface’s increased roughness.

4.3.2 Potential of Zero Charge for Mg (0001) Surface

Figure 4.4 shows the difference in potential energy for removing an electron (to the vacuum level) through the Mg(0001)/water interface minus the work function ($\Delta\phi_{\text{total}}$) for Mg calculated using both VASP and CP2K. For the VASP result, the average $\Delta\phi_{\text{total}}$ is -1.00 eV with a standard deviation of 0.44 eV. The work function calculated with VASP is 3.60 ± 0.02 eV, which is close to the value of 3.79 ± 0.07 eV recommended by Kawano based on a range of experimental measurements [263]. Therefore, referencing the VASP-calculated potential to the vacuum level leads to an absolute value for the PZC of 2.60 V for the Mg (0001) surface.

For the calculated result of CP2K, $\Delta\phi_{\text{total}}$ is -1.06 eV (with a standard deviation of 0.41 eV), which differs from the VASP result by 0.06 eV. However, the work function calculated by CP2K is smaller than the reference value by 0.27 eV, with a value of 3.39 ± 0.02 eV. The underestimated work function of CP2K is due to the nature of the localized Gaussian basis sets of Mg, which cannot depict the density far from the surface accurately because they decay too

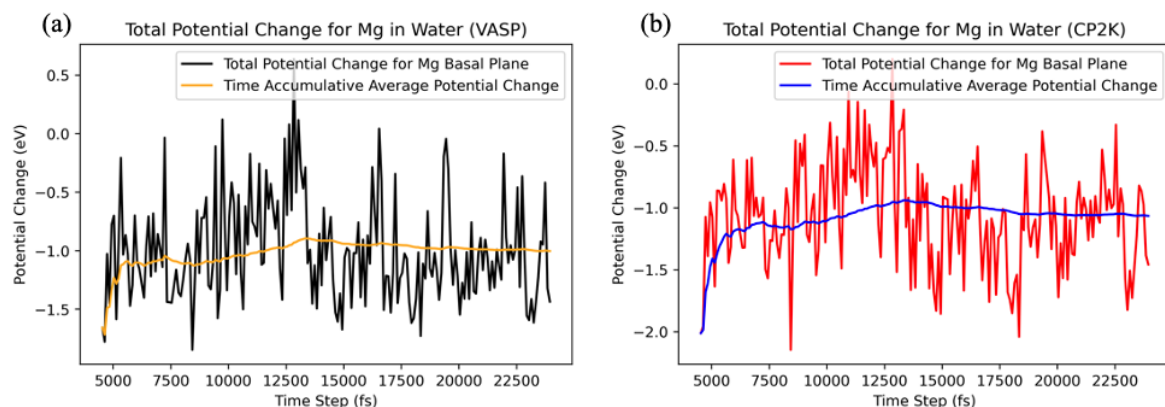


Figure 4.4: Potential energy for removing an electron from Mg through the metal/water interface minus the Mg work function ($\Delta\phi_{\text{total}}$) with respect to time calculated with a) VASP, and b) CP2K. Note that data in a) has a mean of -1.0 eV and standard deviation of 0.44 eV. Data in b) has a mean of -1.06 eV and standard deviation of 0.41 eV.

rapidly with distance. To improve the accuracy of the work function calculated in CP2K, it is possible to add extra basis functions (ghost atoms) at the interface of Mg/vacuum: with one layer of ghost atoms, the work function of the Mg basal plane is improved to 3.55 eV. However, introducing ghost atoms in the system only at the Mg/vacuum interface will lead to an extra basis set error (approximately -0.15 eV) in the calculation of the $\Delta\phi_{\text{total}}$ because it is impossible to add them in a similar way at the Mg/water interface (to each side of the metal slab). In addition, without using the ghost atom setup, the $\Delta\phi_{\text{total}}$ value calculated using CP2K is close to that of VASP. These results suggest that errors from basis-set incompleteness (for calculating changes in potentials across interfaces) are similar between metal/water and metal/vacuum interfaces when using Gaussian basis sets. This can therefore be exploited to calculate PZC values by i) calculating $\Delta\phi_{\text{total}}$ using the (inaccurate) Gaussian-basis functions and ii) adding $\Delta\phi_{\text{total}}$ to an accurate work function value (this could be obtained using either ghost atoms, or from an experimental source). Using this method leads to a calculated PZC of 2.49 V relative to the vacuum level; a value in good agreement with the plane-wave results.

In experiments, the reference electrode potential is often chosen as the standard hydrogen electrode (SHE), which has an absolute value of 4.4 ± 0.2 V [127]. Subtracting the experimental estimate of the SHE from our calculated PZC leads to a result of -1.8 V vs SHE for the Mg

Table 4.1: Results of the PZC calculations for Mg in water using different codes/basis set (VASP and CP2K). PW refers to the plane-wave basis and GPW refers to the mixed Gaussian and plane-wave approach used in CP2K. Note that for CP2K results the bracketed results are where ghost-atoms were used to calculate the pure metal work function value (Φ_M). The value of PZC is $\frac{\Phi_M + \Delta\phi_{\text{total}}}{e}$

Code/Basis	PZC (V)	Φ_M (eV)	$\Delta\phi_{\text{total}}$ (eV)	$\Delta\phi_e$ (eV)	$\Delta\phi_{\text{geom}}$ (eV)	$\Delta\phi_{\text{ori}}$ (eV)
VASP (PW)	2.60	3.60	-1.00	-0.41	-0.05	-0.54
CP2K (GPW)	2.33 (2.49)	3.39 (3.55)	-1.06	-0.48	-0.04	-0.54

(0001) surface using the VASP results. The moving average data in Figure 4.4 suggests this value would not change significantly if a longer simulation time was used. We can gain an estimate of the reliability of this PZC value from previous studies calculating the PZC for surfaces where reliable experimental values were available [4, 211, 257]. These studies found errors were generally below 0.2 V using the same functional (PBE for PZC calculations) and similar (often shorter) simulation times. Combining this error estimate with the ± 0.2 V estimate for the absolute SHE value leads to a total error estimate of between ± 0.2 V and ± 0.4 V for our PZC values.

To understand the nature of $\Delta\phi_{\text{total}}$ we decompose it into three different parts as listed in Table 4.1. The contribution of the water dipole moment ($\Delta\phi_{\text{ori}}$) in our Mg (0001) surface/water system, which is -0.54 eV from both VASP and CP2K results, provides a significant contribution to $\Delta\phi_{\text{total}}$. This result suggests that the net dipole moment of all water molecules tends to point from the surface to the vacuum. This kind of dipole moment refers to the water molecule orientation with a positive tilt angle (larger than 0 degrees and smaller than 90 degrees), indicating that the overall orientation of water molecules in our system has a preference. Another main contribution to the total potential energy difference is made by the electron density redistribution ($\Delta\phi_e$) that occurs on forming the metal/water interface, which is -0.41 eV from VASP (-0.48 eV from CP2K). This contribution stems from the induced dipole introduced by the interaction between the Mg surface and the adsorbed water molecules, which causes electrons to accumulate near the metal surface while they are depleted at the adsorbed water layer. Negative values of $\Delta\phi_e$ are common for neutral molecules, including noble gas atoms, adsorbed at metal surfaces [264, 265, 266]. This has previously been rationalised as an effect of Pauli repulsion between the surface and adsorbate densities, with surface electron density tails

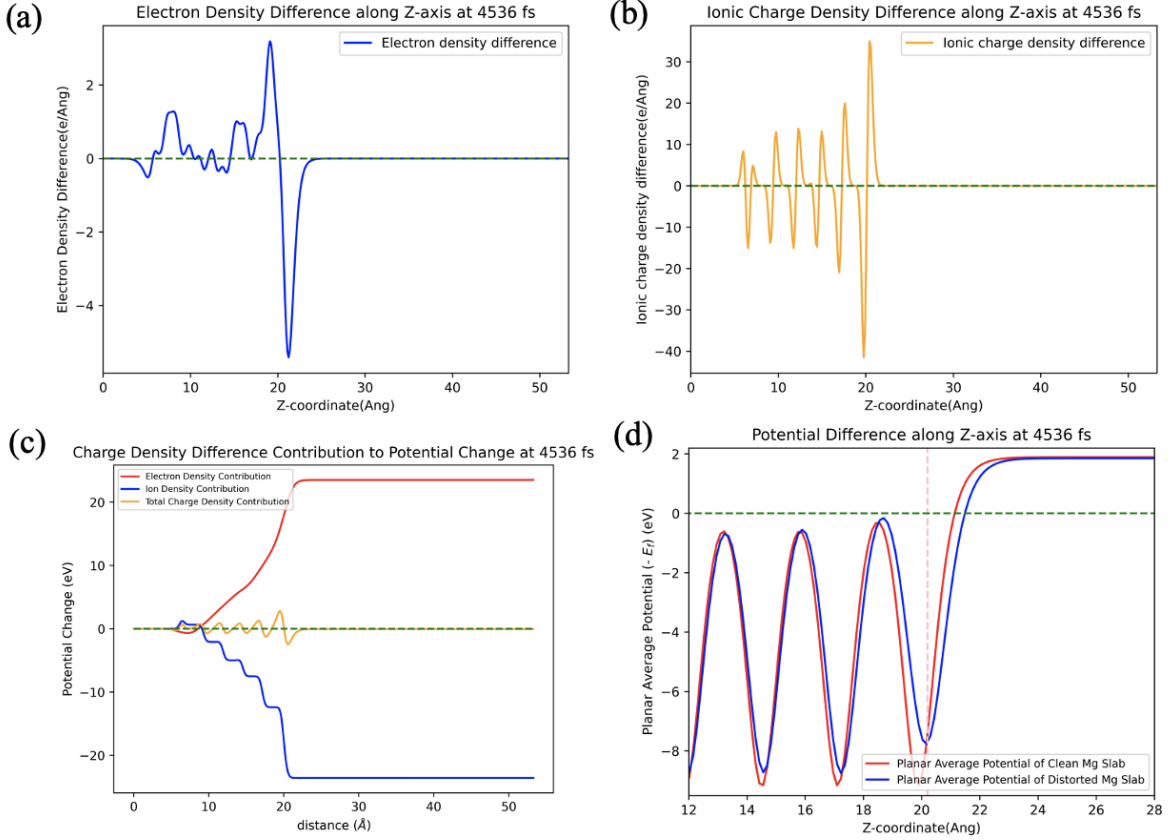


Figure 4.5: (a) Planar average electron density difference between the clean surface and distorted surface along the z-axis (CP2K results); (b) Planar average ionic charge density difference between the clean surface and distorted surface along the z-axis (CP2K results); (c) X-Y plane integrated electrostatic potential energy from the electron/ion density difference between the clean surface and the distorted surface; (d) Planar average electrostatic potential of the clean surface and the distorted surface.

effectively being pushed into the metal in order to orthogonalise the resultant wave function. This electron pushback (sometimes referred to as the pillow effect) decreases the surface dipole and hence the work function; a more detailed discussion of this mechanism can be found in the cited works [264, 265, 266]. The final contribution is from the change in geometry of the metal slab when it interacts with water: some surface Mg atoms in the Mg(0001)/water interface are pulled out slightly, thus forming an asymmetric metal slab. The contribution to the potential energy difference is -0.05 eV for both codes.

We attempted to gain further insight into the small geometric contribution ($\Delta\phi_{\text{geom}}$) by calculating the potential difference and the charge density difference between a p(6×6×3) clean surface and a distorted surface from the MD simulation (at ≈ 4.5 ps). The results are shown in

Figure 4.5. The X-Y plane integrated total electrostatic potential (which is integrated from the electron/ionic density difference) suggests that the surface distortion introduces a small potential energy change (approximately -0.05 eV) for this geometry. This agrees with the result of $\Delta\phi_{\text{geom}}$ which was calculated from the vacuum potential difference of a distorted Mg surface averaged over a large number of geometries. The Hirshfeld charges of the top layer Mg atoms in the clean surface and distorted surface are nearly the same, with differences of only approximately 0.01 e , which indicates that individual atoms charge densities of top layer Mg atoms are not affected by the surface distortion significantly. Therefore, the distortion-related interface dipole and the potential energy change should be insignificant. Figure 4.5 (d) shows that the obvious difference of the planar average electrostatic potential between the clean surface and the distorted surface appears at the last peak (approximately 20 Å). The last peak of the distorted surface is shorter and broader comparing with that of the clean surface, which demonstrates that the electron density is more evenly spread out due to the surface distortion. Consequently, the surface distortion induced electron redistribution could also lead to a small interface dipole and potential energy change.

4.3.3 Comparisons with Other Water/Metal Surfaces

We can contrast a restricted set of computed properties derived from our AIMD experiment with corresponding simulations for other metal/water interfaces. A potentially significant distinction between the Mg (0001)/water interface and previously investigated d -electron metal/bulk water interfaces lies in the notable surface distortion and consequent increase in effective roughness observed in our present study. We could not locate any references to analogous effects in AIMD simulations of d -electron metals [208, 267, 268, 257]. However, similar distortions have been reported for metal surface + monomer calculations for Be(0001) and Al(111), while the lack of significant distortion has been explicitly reported for Rh(0001) and Ag(111) [269, 270, 271]. In summary, significant surface ΔZ distortions seem to be a distinctive feature of sp metal/water interfaces. This leads to the question: why do sp metals exhibit a greater susceptibility to water-induced surface distortion when contrasted with d -electron metals? Below, we propose a potential explanation.

We suggest that the difference in behaviour is due to a larger penalty for ΔZ surface distortions in d -electron metals compared to sp metals. The penalty for this distortion is the loss of favorable bonding between (mainly) nearest neighbour atoms. Using a surface with a nearest neighbour distance of 3.21 Å (the Mg lattice parameter) as an example, a ΔZ distortion of +0.7 Å will lead to an increase of only 0.08 Å ($\approx 2\%$) for nearest-neighbour bond lengths, but shifts the Mg-Mg-Mg bond angle by 12° . For a system with non-directional bonding (*e.g.*, where s - s bonding dominates) this is expected to lead to only a small decrease in the bonding interaction, while for directional bonds (*e.g.*, d - d) the change in bonding angle may significantly weaken bonding interactions. Thus, the energy cost of a ΔZ distortion is expected to be much smaller for sp metals compared to d -electron metals due to lower directionality of bonding. A smaller energy cost for a ΔZ distortion will then lead to a larger level of distortion for the same driving force; thus, sp metals are expected to be more prone to this distortion than d -electron metals.

Our calculated $\Delta\phi_{\text{total}}$ value of -1.00 eV (-1.06 eV) from VASP (CP2K) indicates that the presence of water decreases the energy required to remove an electron from Mg. This negative $\Delta\phi_{\text{total}}$, in aqueous conditions is also observed for other metal surfaces; examples of values from the literature are shown in Table 4.2 [4]. Although $\Delta\phi_{\text{total}}$ varies significantly between different metals, the main contribution to $\Delta\phi_{\text{total}}$ is the electron density redistribution ($\Delta\phi_e$) at the metal/water interface for the listed six metals. The contribution of the water dipole orientation is quite small (no more than 0.2 eV) compared with that of electron redistribution. In this case, we can say that the work function decrease of a metal in aqueous conditions mainly stems from the electron redistribution at the interface within the Water/Metal/Water (WMW) calculations.

However, in our Mg(0001)/water calculations, the contribution of the water dipole orientation (-0.54 eV) is larger than that of interface electron redistribution (-0.41 eV from VASP or -0.48 eV from CP2K). This significant increase of water orientation contribution stems from the setup of the system. In the referenced calculations, a symmetric WMW system is used. The bulk water in this system has two similar metal/water interfaces, thus the orientation of water molecules should show some symmetric features which leads to a nearly zero net total dipole moment; the physical origin of non-zero $\Delta\phi_{\text{ori}}$ in these systems is then unclear to us. In contrast, our

Table 4.2: Calculated potential difference between the PZC and the work function of 6 metal surfaces through DFT calculations based on a Water/Metal/Water model. The contribution of the water orientation and the electron redistribution to the total potential difference are also shown. All values are taken from the work of Li *et. al* [4].

Metal Surfaces	Φ_M (eV)	$\Delta\phi_{\text{total}}$ (eV)	$\Delta\phi_e$ (eV)	$\Delta\phi_{\text{ori}}$ (eV)
Pt (111)	5.8	-1.2	-1.3	0.1
Pd (111)	5.1	-1.2	-1.0	-0.2
Cu (111)	5.3	-1.1	-1.0	-0.1
Zn (0001)	4.4	-0.9	-0.7	-0.2
Ag (111)	4.7	-0.8	-0.7	-0.1
Pb (111)	3.9	-0.4	-0.2	-0.2

VMLV model involves two different interfaces of the bulk water: a metal/water interface and a water/vacuum interface. This leads to a strong water orientation effect in the total potential difference. Thus our $\Delta\phi_{\text{ori}}$ and $\Delta\phi_{\text{total}}$ values are not directly comparable to the values in Table 4.2; however, our $\Delta\phi_e$ values should have the same physical origin.

By studying 11 metal/water interfaces through AIMD, Li *et al.* found that the calculated $\Delta\phi_e$ could be linearly correlated with both water monomer adsorption energies (E_{ads}) and a measure for coverage of chemisorbed water (θ) on the metal surfaces [4]. To see if the Mg(0001)/water interface fit the observed trend we calculated the expected $\Delta\phi_e$ value using our adsorption energy and θ . The value of θ , as defined by Li *et al.*, is estimated by counting the number of water molecules per unit surface area within 3.5 Å above the top surface layer from our AIMD calculations. Because some Mg atoms on the surface top layer are pulled further towards water than others in our AIMD calculations, the position of the top surface layer, which acts as the zero-point plane for determining the water coverage, has an upper layer limit given by the average position of the MgSol atoms which are pulled +0.7 Å towards the bulk water, and a lower layer limit given by the average position of MgFree atoms. According to the AIMD results, the upper layer limit of the coverage of the chemisorbed water molecules (θ_{up}) on the Mg basal plane is 0.0410 Å⁻², while the lower layer limit (θ_{low}) is 0.0138 Å⁻².

Based on the referenced correlations of those 11 metal/water interfaces, the lower limit of the coverage θ_{low} would be expected for a metal with a monomer adsorption energy (E_{ads}) of -0.31 eV, and a contribution of the electron redistribution ($\Delta\phi_e$) of -0.71 eV. By comparison, the upper layer limit θ_{up} corresponds to a metal with an adsorption energy (E_{ads}) of -0.76 eV, and a

$\Delta\phi_e$ of -1.79 eV. As listed in Table 4.1, the calculated ($\Delta\phi_e$) for the Mg (0001)/water interface by DFT codes is -0.41 eV (VASP) or -0.48 eV (CP2K), which is smaller than the values in either the upper or lower layer limit cases. This overestimation of the model $\Delta\phi_e$ is because we assume that the position of all Mg atoms in the layer is at the upper or the lower position, thus leading to an over-interaction between the Mg top layer and water molecules. In reality Mg atoms at different positions (upper layer or lower layer) tend to play different roles in the interaction with water molecules. Therefore, we can expect that at the Mg (0001)/water interface the interaction between the distorted top-surface atoms and the water molecules plays a dominant role in the electronic interactions between the metal and water. Consequently, in estimating $\Delta\phi_e$ for the Mg(0001)/water interface, we can define an effective coverage of chemisorbed water θ_{eff} on the surface by only considering the upper layer limit coverage θ_{up} and the fraction of the distorted Mg atoms on the top layer (w_{disMg}):

$$\theta_{\text{eff}} = \theta_{\text{up}} \times w_{\text{disMg}} \quad (4.5)$$

Therefore, the effective coverage of chemisorbed water θ_{eff} on the Mg surface of our AIMD calculations is approximately $0.0103 \text{ \AA}^{-2}$, which could be related to a metal with a monomer adsorption energy (E_{ads}) of -0.25 eV, and the $\Delta\phi_e$ of -0.56 eV. This θ_{eff} -related electron redistribution contribution agrees well with our DFT-calculated value (-0.41 eV or -0.48 eV), thus suggesting that the surface morphology of different metals (coarse or flat) in contact with water will influence the metal-water interaction significantly.

In the referenced 11 metal/water calculations, most metals are *d*-electron metals whose surface is relatively flat under aqueous conditions, with no significant displacement of the surface atoms being reported from previous AIMD simulations or monomer water adsorption calculations. As a result, the electron density of all surface atoms of the *d*-electron metals could be influenced by the water molecules equally as their surfaces are not distorted. However, Mg shows a significant surface distortion in aqueous conditions based on our AIMD simulations. This significant surface distortion will lead to a coarser surface, with only the electron density of those distorted surface atoms being affected by water molecules, thus decreasing the overall interface electron redistribution contribution $\Delta\phi_e$. This morphology-dependent water-metal

interaction is exemplified by comparing the interface of Mg (0001)/water and Pt (111)/water. The monomer adsorption energy of the Pt (111) surface is approximately -0.40 eV, which is similar to that of the Mg (0001) surface (-0.41 eV of an atop-flat water monomer) [260]. Nevertheless, Li *et al.* found a far larger $\Delta\phi_e$ contribution for Pt (111) surface ($\Delta\phi_e = -1.3$ eV) compared to our result for the Mg(0001) surface ($\Delta\phi_e = -0.4$ eV), which likely stems from the top surface morphology. Thus, we expect that $\Delta\phi_{\text{total}}$ will generally be smaller for *sp*-metals compared to *d*-electron metals, which is consistent with previous experimental works [253].

4.4 Conclusion

In summary, we have explored the atomic structure of the Mg (0001)/water interface and the correlated potential of zero charge through ab initio molecular dynamics and statistic DFT calculations. For the detailed picture of water molecules within the electrified Mg (0001)/water interface, we have discovered the following orientation patterns for water from their tilt angle distribution: the overall (dipole) orientation of the strongly adsorbed water molecules points away from the metal surface; while the physisorbed water molecules exhibit an inverse orientation preference, with the dipole moment pointing towards the surface; the water molecules near the surface yet without direct interaction with Mg atoms show a more random orientation, with slightly more monomers pointing towards the bulk water region. In addition, a slight roll angle exhibited by the strongly adsorbed water molecules signifies an approximately equal interaction of the two hydrogen atoms with the Mg surface; a pronounced roll angle observed in the physisorbed water molecules suggests a singular hydrogen interaction with the surface atoms; an indistinct inclination for the roll angle of the non-interacting water molecules confirms the absence of interactions with the surface.

For the Mg surface, the Mg atoms experiencing a substantial influence from the adsorbed water molecules are elevated by roughly +0.7 Å from their initial position, hence leading to roughening of the Mg (0001) surface when exposed to aqueous conditions. Compared to other *d*-electron metals, this large degree of surface roughening appears to be a distinctive characteristic of *sp* metals, such as Mg, which we rationalise as an effect of their less directional *s-s* bonding

in contrast to the highly directional d - d bonding.

The current study has determined a potential of zero charge for the Mg (0001) surface relative to the standard hydrogen electrode (SHE) at -1.8 ± 0.2 V. We have unravelled that the Volta potential difference $\Delta\phi_{\text{total}}$ (*i.e.*, the potential difference between the PZC and the work function-related potential) of the Mg (0001) surface arises from three components: the contribution from the water dipole moment ($\Delta\phi_{\text{ori}}$), the contribution arising from the redistribution of electron density due to the metal-water interaction ($\Delta\phi_{\text{e}}$), and the contribution originating from geometric effects ($\Delta\phi_{\text{geom}}$) attributable to the asymmetric configuration of the metal slab. Despite the magnitude of the water dipole contribution ($\Delta\phi_{\text{ori}}$) to the overall Volta potential difference of Mg is less comparable with that of other metals owing to our calculation settings for the Mg slab, our calculated electron density contribution ($\Delta\phi_{\text{e}}$), the most essential constituent to the total potential difference, aligns well with the estimated values derived from linear correlations (between the $\Delta\phi_{\text{e}}$ and the water monomer adsorption energy as well as the adsorption coverage) of other 11 metal/water interfaces. Furthermore, we have confirmed that the geometric component ($\Delta\phi_{\text{geom}}$), stemming from our unique calculation model, leads to a minimal distortion-related interface dipole and therefore exerts a negligible impact on the overall Volta potential difference.

We anticipate that the findings outlined in this chapter will hold great importance in comprehending magnesium corrosion because the interface between Mg/water essentially marks the inception of several crucial reactions. The structural data presented indicates that the rearrangement of both water and the metal surface will play a substantial role in altering the barriers associated with dissolution reactions. In terms of building kinetic models, the value of the PZC at this interface is a necessary parameter for deriving reaction rates at varying conditions from barriers calculated at the PZC (as is the standard in DFT).

Chapter 5

H adsorption and Hydride Formation in Mg

¶ *Chapter Synopsis*

The interaction between atomic H and a Mg surface is a key process for the formation of sub-surface Mg hydride, which may play an important role in Mg aqueous corrosion. In this chapter we describe first-principles DFT calculations to study the mechanisms for hydrogen adsorption and crystalline Mg hydride formation under aqueous conditions. The Electron Localisation Function (ELF) is found to be a promising indicator for predicting stable H adsorption in the Mg surface. It is found that sub-surface H adsorption and hydride layer formation is dominated by high ELF adsorption sites. Our calculations suggest that the on-surface adsorption of atomic H, OH radicals and atomic O could enhance the electron localisation at specific sites in the sub-surface region, thus forming effective H traps locally. This is predicted to result in the formation of a thermodynamically stable sub-surface hydride layer, which is a potential precursor of the crucial hydride corrosion product of magnesium. This chapter has been published as a peer-reviewed journal article in the Physical Chemistry Chemical Physics [DOI:10.1039/D2CP05242C].

5.1 Introduction

The interaction of reactive atomic or molecular hydrogen with various metal surfaces has spawned great interest as a result of its significance in numerous industries and applications [272, 273, 274]. Understanding the basic principle of H adsorption, dissociation and desorption on metal surfaces is of high priority for improving the efficiency of H-related heterogeneous catalytic reactions and enhancing the productivity of hydrogen fuel cells or hydrogen storage [275, 276]. Among a large number of metals, the hydrogen-Mg interaction has been extensively investigated because Mg is a promising inexpensive material for large scale hydrogen storage [277, 278, 279]. In addition, it has been suggested that the study of the interplay between H atoms or H_2 molecules and the Mg surfaces also has a practical significance in revealing the mechanism of Mg aqueous corrosion [18, 145].

Mg, as the lightest engineering metal, is widely used in the automobile sectors (Mg-Al based alloys, such as AM50) and clinical medicine (Mg-Zn binary alloys) thanks to its high mechanical strength and benign biocompatibility [74, 85]. However, further applications of Mg and its alloys have been restricted by their poor corrosion resistance in a humid environment. Under aqueous conditions, Mg rapidly corrodes and reacts with water molecules, generates hydrogen gas and forms a dark corrosion film on the metal surface [280]. This surface film is generally a porous bi-layer structure which is composed of an inner MgO layer with a $Mg(OH)_2$ -rich outer layer [122, 155]. Due to a large number of pores and cracks in the corrosion film, it only provides limited protection to the bulk Mg from further corrosion. Several observed corrosion phenomena of Mg, such as the negative difference effect (NDE) and the hydrogen evolution reaction (HER) kinetics, have been attributed to the on-surface corrosion product formed during aqueous corrosion [144, 281].

In addition to the basic corrosion product (MgO and $Mg(OH)_2$) in the surface film, crystalline Mg hydride, which is produced initially from the H-Mg surface interaction, also forms and plays a role in aqueous Mg corrosion. Liu *et al.* observed the presence of this Mg hydride underneath the surface layer of high purity Mg after being corroded by distilled water [282]. A crystalline Mg hydride structure is also found enriched in the β -phase of Mg-Al based alloys,

whose formation could be attributed to atomic H adsorption and diffusion into the bulk Mg [130]. Because the calculated energy barrier for H atoms diffusing from the top surface of Mg to the bulk phase is smaller (0.7 eV) than that of the hydrogen evolution reaction (approximately 1.04 eV) on the Mg basal plane, the adsorbed H atoms are highly mobile and could penetrate the surface to form a crystalline Mg hydride or a hydride-like structure underneath the metal surface [145, 151, 283]. Moreover, the Pourbaix diagram of Mg-H₂O shows that this Mg hydride phase could form in the whole pH range under a cathodic potential [284]. This finding is supported by some previous studies: under cathodic polarisation, the corrosion-related current density (I_c) of Mg is composed of the cathodic hydrogen evolution density (I_h) and the MgH₂-formation current density (I_m) [161]. Binns *et al.* also verified that the MgH₂ layer is found underneath the top surface of the Mg sample that is pre-treated cathodically, and concluded that MgH₂ might have the ability to enhance the anodic hydrogen evolution during aqueous corrosion through its decomposition, and thus form a filiform corrosion morphology [162]. In a previous *ab initio* study, Jiang *et al.* found a stable sub-surface hydride-like tri-layer structure (H-Mg-H) in a hydrogen environment (Mg surface interacting with hydrogen gas), which could be the structure of a precursor to MgH₂[163].

Although various experimental and simulation results demonstrate the existence of crystalline MgH₂, or a hydride-like layer, underneath the Mg surface during aqueous corrosion, the atomic scale formation mechanism of this Mg hydride structure under aqueous conditions at the open circuit potential (OCP) is still unclear. Furthermore, the influence of the surface adsorption state (with different surface adsorbates, such as atomic H, OH radicals and atomic O) on the formation of the sub-surface hydride structure also requires further detailed investigation. In this chapter, we applied first-principles calculations (in the density functional framework) to explore the hydrogen adsorption and hydride formation mechanisms at Mg surfaces with different adsorption states. Finding low energy structures formally involves searching the very large phase space of all possible surface compositions and structures. We discovered that the electron localisation function (ELF) is a good indicator that can be used to predict the energetically favourable positions for H adsorption within Mg surfaces, and the formation of sub-surface hydride structures is dominated by this ELF-oriented H adsorption. We also found

that the on-surface adsorption could influence the ELF pattern of the surface, thus altering the sub-surface H adsorption.

5.2 Theory and Methods

5.2.1 Theory of the Electron Localisation Function (ELF)

Herein, we demonstrate that the electron localisation function (ELF) can be a good predictor for the possible adsorption sites of small adsorbates on Mg surfaces.

The ELF was introduced by Becke and Edgecombe to identify covalent bonds in simple molecular systems [285]. As a measure of the degree of Pauli exclusion at a point in space, the ELF is calculated as the probability of finding an electron in the vicinity of another like-spin electron [286]. The formula of the ELF proposed by Becke and Edgecombe can be written as:

$$\text{ELF}_\sigma = \frac{1}{1 + \chi_\sigma^2} \quad (5.1)$$

with the dimensionless localisation index χ_σ being [285, 287]:

$$\begin{aligned} \chi_\sigma &= \frac{2(\tau_\sigma - \tau_\sigma^W)}{\tau_\sigma^{\text{UEG}}} \\ &= \frac{\sum_i f_{\sigma,i} |\nabla \psi_{\sigma,i}|^2 - \frac{1}{4} \frac{|\nabla n_\sigma|^2}{n_\sigma}}{\frac{3}{5} (6\pi^2)^{2/3} n_\sigma^{5/3}} \end{aligned} \quad (5.2)$$

The numerator in Equation 5.2 describes the kinetic energy density difference between a Fermionic system and a Bosonic system. τ_σ is the positively defined kinetic energy density of the electrons, calculated from the wave functions $\psi_{\sigma,i}$ weighted by the occupation number $f_{\sigma,i}$. τ_σ^W , on the other hand, is the von Weizsäcker kinetic energy density, and describes the same positively defined kinetic energy density as the first term, but assumes electrons are Bosons (no Pauli exclusion) [288, 289]. The von Weizsäcker kinetic energy density can be easily obtained from the one-body charge density n_σ as $\tau_\sigma^W = \frac{1}{8} \frac{|\nabla n_\sigma|^2}{n_\sigma}$. The denominator in Equation 5.2, τ_σ^{UEG} , is the same as the numerator but calculated for a uniform electron gas with the same local density.

The numerator in Equation 5.2 is sometimes also called the Pauli kinetic energy density D_σ for it signifies the degree of Pauli exclusion at a point in space [290]. A small D_σ indicates a small probability of finding a second like-spin electron near the reference point (high Pauli exclusion) thus suggesting that the electron is highly localised around that particular region in the space. The employment of the kinetic energy density of the uniform electron gas (D_σ^0) serves as a reference to D_σ , and the final form of Equation 5.1 restricts the value of ELF to be between 0 and 1. The upper limit of 1 of the ELF denotes complete electron localisation (such as a point charge in space), and an ELF value of 0.5 corresponds to having the same degree of localisation as a homogeneous electron gas with the same local density. Therefore, the higher the ELF value, the more localised the electrons. The position of a local ELF maximum is sometimes also denoted as an attractor. Such attractors behave like electrophiles, such as protons [291].

The ELF has been demonstrated to be a powerful tool to differentiate the nature of chemical bonds for many materials [291, 292]. At the same time, the ELF has also been used to investigate the electron distribution of metal surfaces with different packing patterns [293, 294]. The chemisorption bonds between metal surfaces and some isoelectronic species can also be investigated using the ELF [295]. There have been reports showing that the ELF can be used to predict the position of hydrogen atoms in hydrides [296, 297]. For instance, the ELF pattern of the pure Ca substructure can be used to predict the possible H positions in its hydride form CaH_2 , indicating that high ELF regions have a high probability of attracting hydrogen atoms [291]. It has also been found recently that removing the on-surface hydrogen from the (110) surface of Mg hydride could form a high ELF region which is localised at the position of the H vacancy [298]. Furthermore, the ELF has been shown to be independent of the particular computational method used, such as basis sets and pseudopotentials [299]. As a result, the ELF is a promising and reliable instrument for analysing the possible H adsorption sites in metal surfaces.

5.2.2 Computational Methods

To simulate the chemisorption processes on a Mg surface, first-principles calculations based

on the DFT formalism were performed as implemented in the Vienna Ab Initio Software Package (VASP) [233, 234]. The Projector Augmented-Wave (PAW) method with the frozen core approximation was employed to model the electronic wavefunctions where Mg’s 3s, O’s 2s and 2p, and H’s 1s are treated as valence electrons [232, 259]. A kinetic-energy cutoff of 700 eV was used for the plane-wave expansion of the valence wavefunctions of systems that contain Mg and H. For systems that have Mg, H and O, a tighter 750 eV cutoff was used to ensure the total energy converges within 1 meV/atom. Electronic exchange and correlation were described using the Perdew–Burke–Ernzerhof (PBE) variant of the generalized gradient approximation (GGA) [226]. For the Mg (0001) surface, the Brillouin-zone was sufficiently sampled by a Γ -centred $8 \times 8 \times 1$ Monkhorst-Pack k -point mesh with the total energy per unit cell converges within 5 meV [300]. The electronic minimisation process was deemed converged when a total energy difference of 0.01 meV (per unit cell) between two steps was achieved. The atomic positions were fully relaxed to a force tolerance of 1 meV/Å.

The Mg (0001) surface was modelled by a $p(2 \times 2)$ slab prototype. The slab is selected as 11 layers thick so that the interaction between both sides of the slab becomes negligible and the surface energy converges within 0.1 meV/Å². This periodic surface unit cell is also large enough along the x and y directions to allow the simulation of chemisorbtion with surface coverages ranging from 0.25 monolayer (ML) to 1 monolayer (ML). The lattice parameters of the slab were $6.40 \times 6.40 \times 45.83$ Å³, which were determined from the cell optimization of the bulk Mg cell. To eliminate spurious interactions between image structures due to periodic boundary conditions, a vacuum of 20 Å was added in the z-direction (surface normal direction). We added H, O, and OH as adsorbates to the available surface adsorption sites and sub-surface interstitial sites (Figure 5.1) on one side of the slab. This asymmetric configuration leads to a dipole moment in the unit cell, which was countered by adding a dipole layer in the vacuum [261]. For the on-surface adsorption, the surface fcc and hcp hollow sites were considered to be potentially occupied by H, O and OH radicals. For the sub-surface interstitial sites, we took only H uptake into account because of the small size of H and its high mobility in the Mg substrate [301].

For the surface with a sub-monolayer coverage of H, OH, or O, we chose a consistent reference (an H₂ molecule, a clean Mg basal plane, and a water molecule) when calculating the adsorption

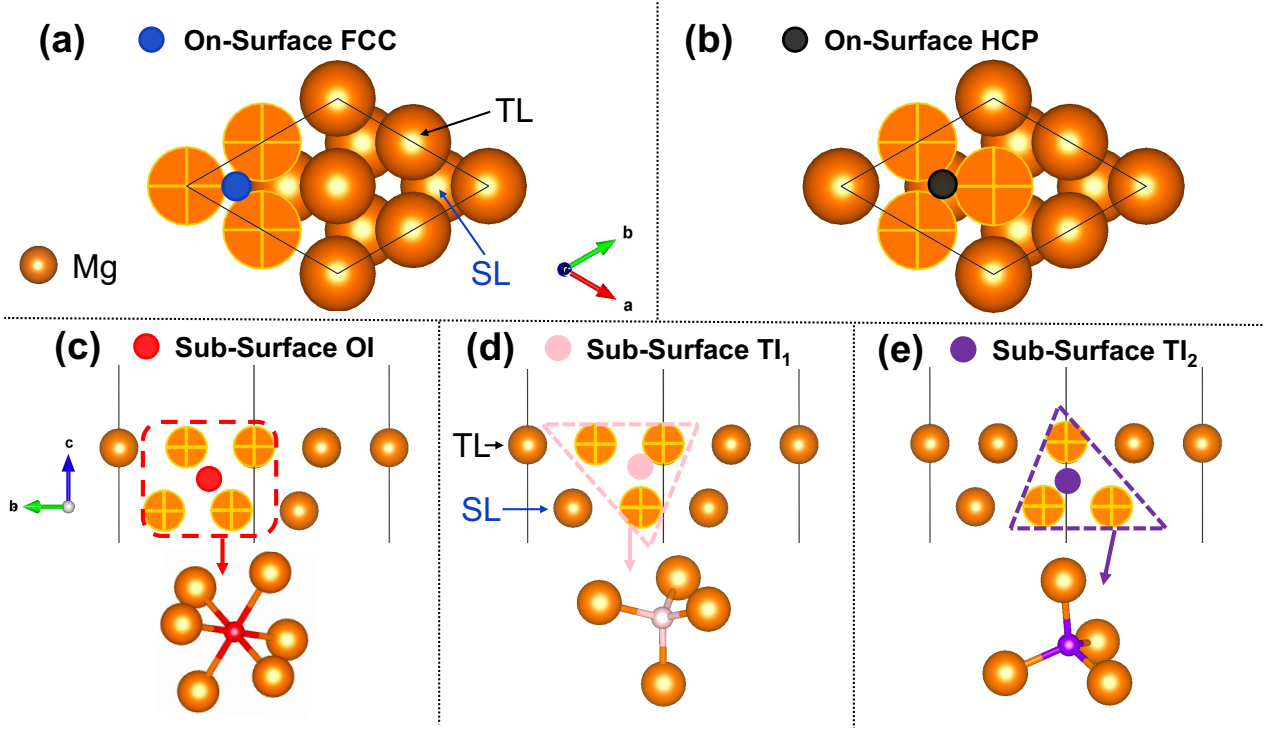


Figure 5.1: Schematic diagram of available on-surface and sub-surface adsorption sites at the Mg (0001) surface. Images (a) and (b) correspond to the top view of the Mg (0001) surface. The on-surface fcc and hcp sites are represented by the blue and black circles respectively. Top layer (TL) Mg atoms and second layer (SL) ones are indicated in the figure. Panels (c)-(e) demonstrate the octahedral (OI), tetrahedral-I (TI₁) and tetrahedral-II (TI₂) interstitial sites within the sub-surface region of the Mg basal plane from the side view.

energy per adsorbate. The adsorption energy $E_{\text{Mg}^*\text{H}_m\text{O}_n}^{\text{ad}}$ is given by

$$E_{\text{Mg}^*\text{H}_m\text{O}_n}^{\text{ad}} = \frac{1}{k} [E_{\text{Mg}^*\text{H}_m\text{O}_n} - E_{\text{Mg}^*} - m\mu_{\text{H}} - n\mu_{\text{O}}] \quad (5.3)$$

with the energy of H and O obtained from DFT calculations

$$\mu_{\text{H}} = \frac{1}{2} E_{\text{H}_2(\text{g})} \quad (5.4)$$

$$\mu_{\text{O}} = E_{\text{H}_2\text{O}(\text{g})} - 2\mu_{\text{H}} \quad (5.5)$$

where k refers to the number of adsorbates on the surface per unit cell, and $E_{\text{Mg}^*\text{H}_m\text{O}_n}$, E_{Mg^*} , $E_{\text{H}_2(\text{g})}$ and $E_{\text{H}_2\text{O}(\text{g})}$ are DFT-calculated total energies of different adsorption surfaces, the clean Mg (0001) surface, a H₂ gas molecule and a H₂O gas molecule respectively. Herein, the energy

(chemical potential) of oxygen is controlled by water rather than oxygen gas because we assumed that our system exists in hydrogen-rich conditions [134]. In the case of the H sub-surface adsorption into Mg surfaces fully covered with H, OH, or O, we estimated the H adsorption energy E_{H}^{ad} through

$$E_{\text{H}}^{\text{ad}} = \frac{1}{l} [E_{\text{Mg(1ML)*H}_l} - E_{\text{Mg(1ML)*}} - l\mu_{\text{H}}] \quad (5.6)$$

Here $E_{\text{Mg(1ML)*H}_l}$ is the total energy of the Mg (0001) surfaces (fully covered with H, OH, or O) whose sub-surface interstitial sites are occupied by H atoms, and $E_{\text{Mg(1ML)*}}$ is the energy of the reference fully covered Mg surfaces. l is the number of sub-surface H atoms per unit cell. A negative H adsorption energy indicates that the sub-surface hydrogen adsorption, at a certain interstitial site within the fully covered Mg surfaces, is exothermic compared with a H_2 gas molecule, thus suggesting a stable H sub-surface structure in the Mg basal plane.

We note that the zero-point energy (ZPE) was not included in our adsorption energy calculations. A previous study has demonstrated that for the hydrogen dissociative adsorption on the Mg basal plane, the difference in ZPE between one H atom in the H_2 gas and adsorbed on to the Mg (0001) surface is less than 2 meV [163]. This insignificant ZPE change for H thus contributes little to the total adsorption energy. Similarly, it has been found that the ZPE difference between O and OH adsorption on the metal surface is approximately 15 meV, suggesting that it has negligible influence on the adsorption energy differences reported here [302, 303]. Based on these findings, we deemed that it is unnecessary to include ZPE correction in the current study. We also verified that introducing the solvent effect in our calculations barely alters the adsorption patterns and the most stable adsorption phases (see Appendix). Thus, ignoring the solvent effect in our calculations does not change the conclusions.

5.3 Results and discussion

5.3.1 H Adsorption on or below the Mg (0001) Surface

In this section, we investigate H adsorption on a Mg (0001) surface from our DFT calculations.

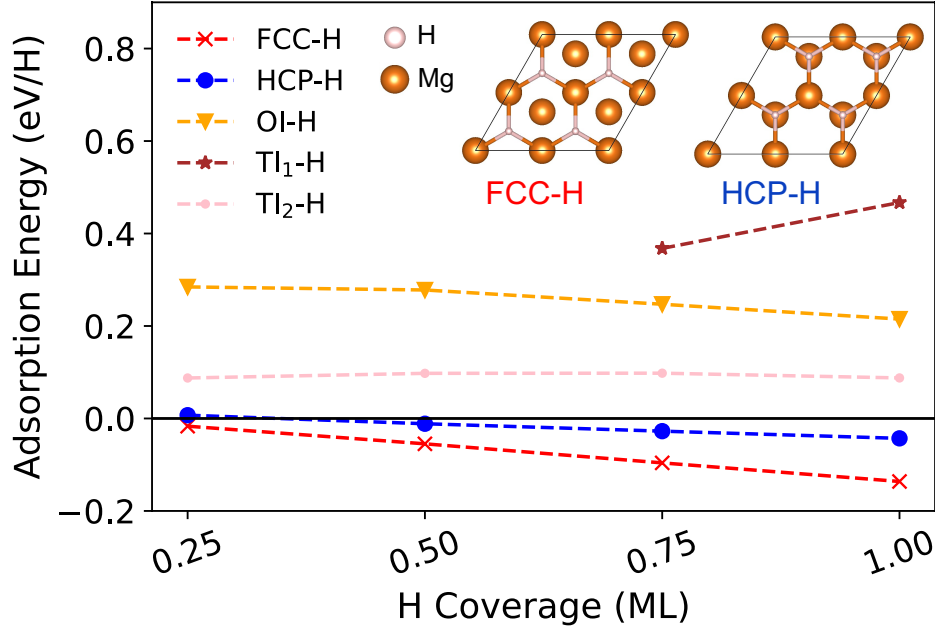


Figure 5.2: Adsorption energy (per adsorbed atom) of H on Mg(0001) surfaces or in the sub-surface interstitial sites when the H coverage is less than 1 ML. A negative adsorption energy corresponds to an energetically favourable adsorption referring to the clean surface and H_2 gas molecule. Insets are the stable on-surface fcc and hcp H adsorption structures.

At low H coverage (less than 1 ML), the favourable adsorption sites for H are on-surface fcc and hcp sites. For the surfaces pre-covered with 1 ML H, sub-surface H adsorption becomes thermodynamically stable. By analysing the ELF pattern for the clean Mg surface and for the H pre-covered surface, we find that ELF is a promising indicator for determining the possible stable adsorption sites for H in a Mg surface.

In Figure 5.2 we plot the adsorption energy of H at the different adsorption sites of the Mg (0001) surface with a hydrogen coverage ranging from 0 to 1 ML. Across all H coverages the fcc adsorption site appears to be the most energetically favourable. Although less stable than the fcc site, the hcp site has negative adsorption energies for all coverages considered (with the exception of 0.25 ML when the adsorption energy is very small at approximately 7 meV) and these energies are more negative than all other sub-surface adsorption sites (octahedral, tetrahedral-I and II). This suggests the hcp site provides an additional (meta-)stable adsorption site on the Mg basal plane for H.

Using the pristine surface and H_2 gas as reference, the adsorption energies of H in three sub-surface sites considered are all positive for all H coverages. This demonstrates that sub-

surface H adsorption is thermodynamically unfavourable at low H concentrations under the Mg (0001) surface. The tetrahedral-I adsorption configuration is only stable for a H coverage larger than 0.75 ML, below which it automatically relaxed into the surface hcp configuration after geometry optimisation. Therefore, only the adsorption energies for higher coverage are shown for the tetrahedral-I adsorption in Figure 5.2. The H adsorption energy suggests that when the surface H concentration is low, H preferentially adsorbs onto the Mg (0001) surface instead of penetrating into the sub-surface. This finding of selective H adsorption preference based on H concentration is consistent with previous works [163, 304].

Table 5.1: Distortion energy E_{dis} (meV/H) for the Mg (0001) surfaces with H at different adsorption sites when the total H coverage is no more than 1 ML. For comparison, the corresponding total H adsorption energy (meV/H) is marked within the parentheses.

θ_H (ML)	fcc	hcp	OI	TI ₁	TI ₂
0.25	8.6 (-16.7)	13.4 (7.1)	3.7 (284.5)	/	21.1 (87.5)
0.50	5.3 (-54.8)	9.1 (-11.4)	6.3 (277.9)	/	21.4 (97.6)
0.75	2.6 (-96.0)	4.4 (-27.4)	11.7 (247.0)	33.6 (367.9)	23.2 (97.9)
1.00	2.1 (-136.3)	3.4 (-43.0)	18.0 (215.0)	79.4 (467.0)	29.0 (87.7)

To understand why a hydrogen atom tends to bind to the on-surface hollow sites rather than the sub-surface interstitial sites, we considered four different energy components that contribute to the total adsorption energy, namely the H₂ dissociation energy, the lattice distortion energy, the ELF-related energy and the Coulomb interaction energy, and estimated the individual contribution of each component. Because the H₂ molecule is set as the reference, the dissociation energy of the H₂ molecule is a dominating constituent that increases the adsorption energy. The DFT-calculated value for the H₂ bond (breaking an H₂ molecule into two H atoms) is approximate 3.36 eV/H, which is close to the value calculated by Kresse of 3.40 eV/H [305]. In addition to the energy penalty caused by breaking the H-H bond, inserting H into the Mg surface requires a distortion of the surface structure due to the non-negligible size of the H atoms. The energy of this distortion (sometimes also called the deformation energy) can be calculated as [306]

$$E_{dis} = \frac{1}{n}(E_{Mg*}^{H_n} - E_{Mg*}) \quad (5.7)$$

where $E_{\text{Mg}^*}^{\text{H}_n}$ is the energy of the distorted (by n H atoms) Mg slab computed without the H atom(s) present and E_{Mg^*} is the total energy of a relaxed pristine Mg (0001) slab. Table 5.1 shows the calculated distortion energy for the Mg (0001) surface with H at certain coverages in different sites. For the on-surface adsorptions, the distortion energy per H atom decreases with an increase of H coverage, and the contribution of the distortion energy to the total adsorption energy is diminished. The distortion energy of fcc adsorption is larger than that for hcp at all coverages. This distortion energy difference between fcc and hcp plays a more significant role in the total adsorption energy difference at low H coverage (less than 0.50 ML). At higher coverage, the difference in total adsorption energy between fcc and hcp is far larger than the difference in distortion energy (at 1 ML, the difference in total adsorption energy is approximately 93 meV while the difference in distortion energy is only 1.3 meV), indicating that there are other energy components that dominate the overall difference. The distortion energy for the sub-surface tetrahedral adsorption increases with a larger H coverage, and is significantly larger than that of the on-surface and octahedral interstitial (OI) adsorptions. For the H adsorbed in the OI site, the distortion energy is relatively low when the coverage is less than 0.5 ML. However, the total adsorption energy of OI adsorption is much more positive than the on-surface adsorption, where the distortion energy is larger than the OI adsorption at 0.25 ML and 0.5 ML. This significant positive adsorption energy of the OI adsorption could be attributed to the lack of other essential energy lowering contributions, such as the H-electron interaction, and will be explained specifically in the following.

For hydrogen adsorption on Mg surfaces, the H-electron interaction contributes negatively to the H adsorption energy. This is caused by the fact that H has a higher electronegativity (2.1) than Mg (1.3) [307]. When put in Mg cages, H atoms tend to form H^- and leave Mg in positively charged states [146]. As one might expect the magnitude of the H-electron attractive interaction in the Mg surfaces is position sensitive: i.e. this interaction is more prominent at the positions where electrons are more localised. Figure 5.3 shows the electron localisation function distribution within the Mg (0001) surface. The planar average ELF along Z-axis and the side-view contour both indicate a higher ELF value (a maximum of 0.68 on the planar averaged plot) near the on-surface region compared to the sub-surface and bulk regions. This

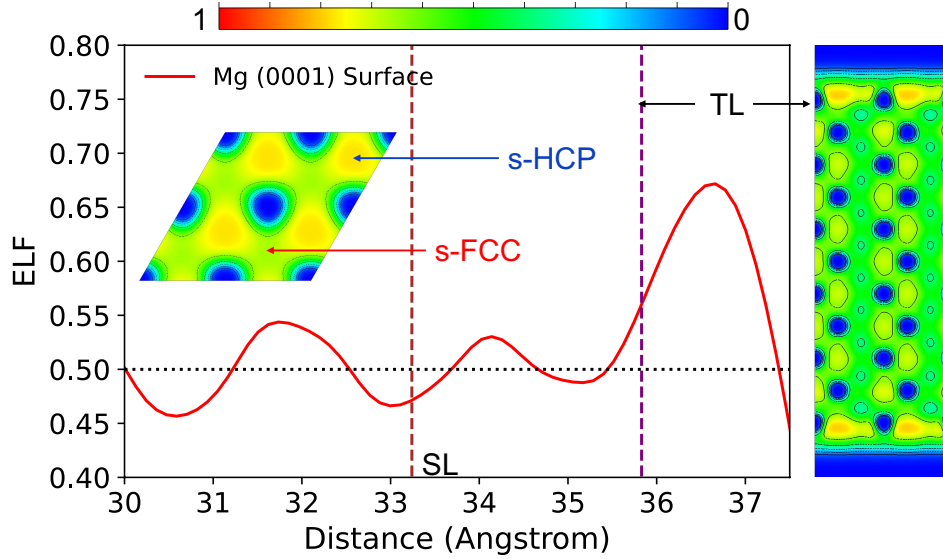


Figure 5.3: Planar (XY-Plane) average ELF of Mg (0001) surface along Z-axis. Inset is the top-view ELF contour of the surface top-layer (a warmer colour region indicates electrons are more localised within this region). The side-view ELF contour is shown at the right of the figure. The vertical dashed lines (the purple line and the brown line) mark the average atomic position of the top layer (TL) and second layer (SL) respectively.

on-surface electron localisation enhancement of a Mg (0001) surface stems from the changes in local coordination of the top-layer atoms. Due to this enhanced electron localisation near the on-surface region, a stronger H-electron interaction is to be expected, and thus H atoms are more likely to be located in the on-surface adsorption sites than the sub-surface and bulk regions under low concentration. This conclusion is consistent with the calculated H adsorption energies: the H adsorption energies of the on-surface fcc and hcp adsorption sites are more negative than other sub-surface adsorptions. We thus deduce that the H-electron interaction energy should be positively correlated to the local ELF value.

Table 5.2: Onsite ELF value at different adsorption sites (on-surface fcc, hcp and sub-surface OI, TI₁ and TI₂ sites) of a clean Mg (0001) surface. An ELF value approaching 0.5 means the local electron localisation is similar to a uniform electron gas. A higher ELF value indicates that electrons are highly localised onsite.

Mg (0001) Surface	fcc	hcp	OI	TI ₁	TI ₂
ELF Value	0.666	0.785	0.349	0.687	0.673

Table 5.2 shows the ELF value at different H adsorption sites of Mg (0001) surfaces. The onsite ELF values of the on-surface fcc, hcp and the sub-surface TI₁ and TI₂ sites are all larger

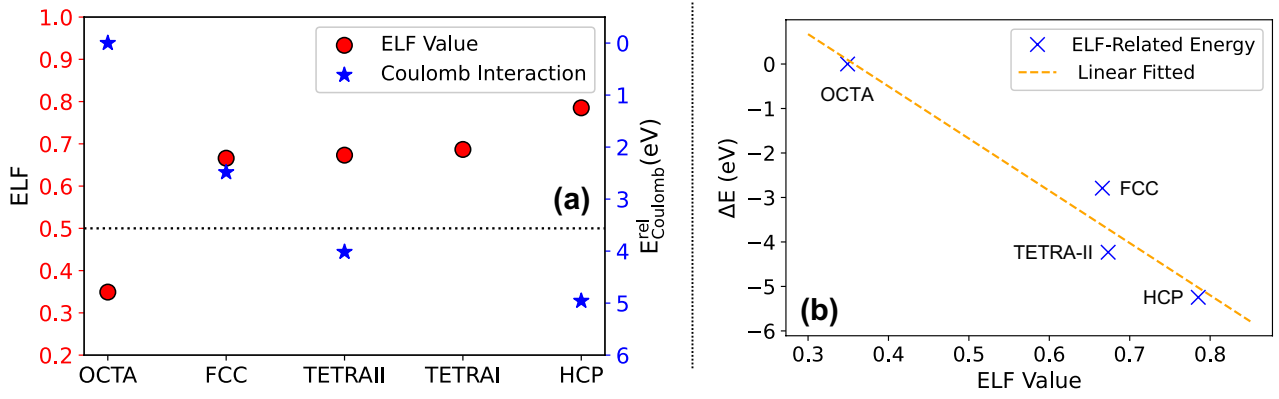


Figure 5.4: (a) Relative Coulomb interaction energy (calibrated by the Coulomb interaction energy of the octahedral adsorption) and ELF values at different sites for Mg (0001) surface with 0.25 ML H. A more positive relative Coulomb interaction energy suggests a weaker Coulomb interaction at the correspondent adsorption site. (b) Linear fit of the estimated ELF-related energy with respect to the onsite ELF value. The ELF-related energy is calculated as the energy remainder of the total adsorption energy subtracting the H_2 dissociation energy, distortion energy and the Coulomb interaction energy, then calibrated by the highest value (the energy remainder of the octahedral adsorption is set as zero) to demonstrate the relationship between the ELF and the correlated energy. The Coulomb interaction energy and the ELF-related energy of the tetrahedral-I adsorption are excluded here because the 0.25 ML Tl_1 adsorption is energetically unfavourable.

than 0.5, confirming that electrons at these positions are more localised than those in the uniform electron gas (free electrons). These localised electrons at specific adsorption sites act as proton-attractors and lower the adsorption energy by increasing the local H-electron attractive interaction. For the OI site, the small local ELF value suggests that electrons are as delocalised and metallic-like as in the free-electron gas. Therefore, the H-electron interaction at the OI site is weaker than other sites, which leads to a notable positive adsorption energy of the OI adsorption even though the related distortion energy is relatively small.

Although it is clear that the ELF is an indicator of the local H-electron interaction, and thus of the low energy adsorptions sites within the Mg surface, it is a local property and does not provide an estimate of the long-range Coulomb interactions. Consequently, the relationship between the ELF value at an adsorption site and the total adsorption energy do not have a perfect one-to-one correspondence for systems with ionic-character: the Mg-H bond is closer to an ionic bond according to a previous study of the Mg-H system [308]. For instance, the H adsorption energy of the fcc site is more negative than that of the hcp site despite the ELF value at the fcc site being smaller than that of the hcp site. This apparent discrepancy is due to

the long-range Coulomb interactions between the hydride and Mg ions, which is an additional energy-lowering constituent for the total adsorption energy. We opted to estimate the long-range Coulomb interaction through the Ewald method which splits the electrostatic energy into the real-space and the reciprocal-space terms respectively [309]. The charge-charge interaction energy $E_{q_{ij}}$ is calculated using the Bader charges of ions and estimated through the Pymatgen library [310, 311].

Figure 5.4(a) shows the relative Coulomb interaction energies (which are calibrated by the Coulomb energy of the octahedral adsorption, with a value of -10.89 eV) of the Mg-H (0.25 ML) system with H at different adsorption sites. Although the ELF of the on-surface fcc is smaller than that of hcp (but of similar magnitude), the Coulomb interaction energy of one H at the fcc site of the Mg (0001) surface is greater than for one H in the hcp case, which results in a more negative adsorption energy. Likewise, despite the sub-surface TI_2 site possessing the third largest ELF value among all adsorption sites, the total adsorption energy for H at this site is still energetically unfavourable due to the small Coulomb interaction. We conclude that the Coulomb interaction plays a dominant role in determining the most stable H-adsorption site on the Mg surface when the ELF values for the candidate sites are of similar magnitude. However, a high Coulomb interaction is not a sufficient condition for a stable H adsorption if the ELF value is smaller than 0.5. For the OI adsorption, the large coulomb interaction fails to cancel the larger energy penalty which is due to the lack of electron localisation at this site.

To demonstrate the connection between the ELF value and the energy, we estimated the ELF-related energy from the adsorption energy remainder found by subtracting from the total adsorption energy the H_2 dissociation energy, lattice distortion energy and the Coulomb interaction energy. Because the calculated Coulomb interaction energy only includes the contribution from the monopole-monopole interaction, ignoring the dipole-dipole and dipole-monopole interactions, the estimated long-range interaction energy carries an error. Consequently, instead of focusing on the absolute adsorption energy remainder, we calibrated the energy remainder for different adsorption sites with the most positive one (that of the OI adsorption) to underline the variation of the ELF with its energy contribution. Figure 5.4(b) illustrates the relationship between the calibrated adsorption energy remainder and the correspondent

ELF value. The linear regression with a negative slope indicates that a higher onsite ELF value leads to a more negative energy term, thus suggesting a stronger H-electron interaction locally. This observation supports our observation that the H-electron interaction energy and the local ELF value are correlated positively, and the localised electrons can reasonably be treated as a proton-attractor.

Overall, the ELF is a reliable indicator for predicting the possible stable adsorption site for H in the Mg (0001) surface. This is because the ELF value is positively correlated to the adsorption energy, with the higher the value the larger the H-electron interaction, and thus the more negative the corresponding energy. To fully determine the most energetically favourable site we also need to consider the structure distortion energy and the Coulomb interaction. However, the position with the largest ELF value within the Mg surface has a high probability of being stable adsorption site, which could also be thought as an effective trap for capturing H from the environment. In addition to predicting the position of H traps in a pristine Mg (0001) surface, we also demonstrated that the ELF could forecast the possible adsorption sites for H in a defective Mg surface in the Appendix.

In previous sections we found that the Mg (0001) on-surface fcc site is the most energetically favourable adsorption site for H when the H coverage is less than 1 ML. The sub-surface H adsorption at low H coverage is unfavourable due to the lack of electron localisation or efficient Coulomb interactions. However, a hydride-like structure has been found underneath the Mg surface both experimentally and by means of simulation, which suggests that sub-surface H adsorption can be thermodynamically feasible under some conditions [162, 151, 274]. We explored this further by investigating the thermodynamic stability of sub-surface H adsorption at a higher H coverage within the Mg surface ($1\text{ML} \leq \Theta_{\text{H}} \leq 2\text{ML}$) by pre-adsorbing 1 ML H atoms at the on-surface fcc sites initially. Then the available sub-surface interstitial sites are subsequently occupied by H atoms until the total H coverage reaches 2 ML.

Figure 5.5 illustrates the sub-surface H adsorption energy at different interstitial sites in the 1 ML H (fcc) covered Mg (0001) surface. To demonstrate the influence of the surface adsorption state on the sub-surface H adsorption, we chose the H covered Mg (0001) surface and H_2 gas molecule as the references for calculating the H adsorption energy. As the sub-surface H

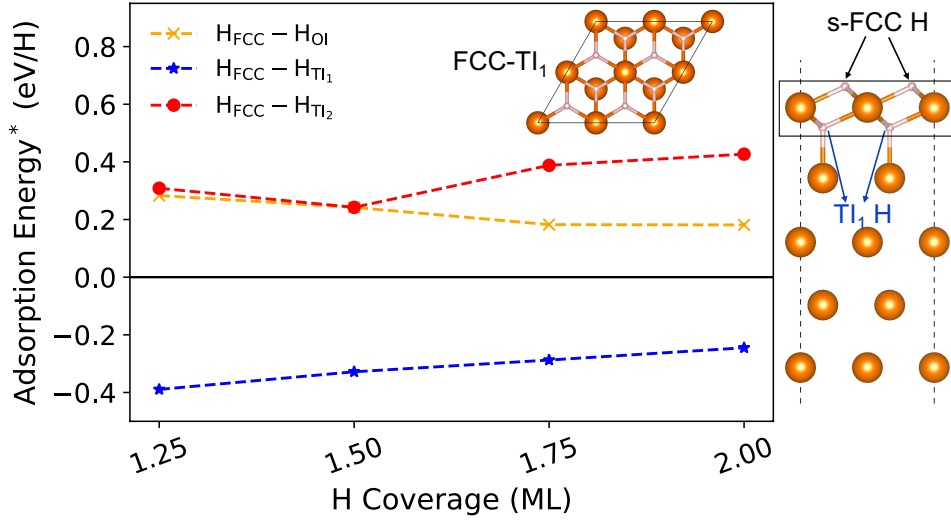


Figure 5.5: Adsorption energy per adsorbed atom (* suggests that the reference is no longer the clean Mg surface) of H in the sub-surface interstitial sites of the Mg (0001) surface when the H coverage is larger than 1 ML: 1 ML H is pre-adsorbed on the on-surface fcc sites. A negative adsorption energy corresponds to an energetically favourable adsorption, and is evaluated relative to the 1 ML H (fcc) covered surface and an H_2 gas molecule. The inset is the top view of the stable sub-surface tetrahedral-I (TI_1) H adsorption structure for the 1 ML fcc-H covered Mg basal plane. The side view of the 4FCC- TI_1 adsorption structure shows the position of two types of H within the surface.

coverage increases, the TI_1 adsorption remains energetically favourable having the most negative adsorption energy among three sub-surface adsorption sites. The adsorption energies of the OI and TI_2 adsorption are positive across all coverages, indicating an unstable H adsorption site, as compared with the H covered Mg surface and gaseous H_2 . This adsorption energy pattern demonstrates that when the Mg (0001) surface is covered by 1 ML H at the most energetically favourable on-surface site (fcc), the sub-surface H adsorption in the TI_1 site could be feasible, thereby forming a stable H-Mg-H tri-layer structure at 2 ML H coverage. This H(fcc)-Mg(TL)-H(TI_1) tri-layer structure (shown in the Figure 5.5) was also discovered in a previous theoretical study, and is considered a prospective precursor of the magnesium hydride which forms underneath the Mg surface [163]. Moreover, the presence of the sub-surface Mg hydride structure was also detected experimentally in the cathodically charged Mg specimen during its aqueous corrosion [162]. The x-ray diffraction spectra of the corroded specimen monitored the presence of the crystalline Mg hydride by detecting additional peaks that are expected for MgH_2 . The secondary ion mass spectrometry image further located the Mg hydride

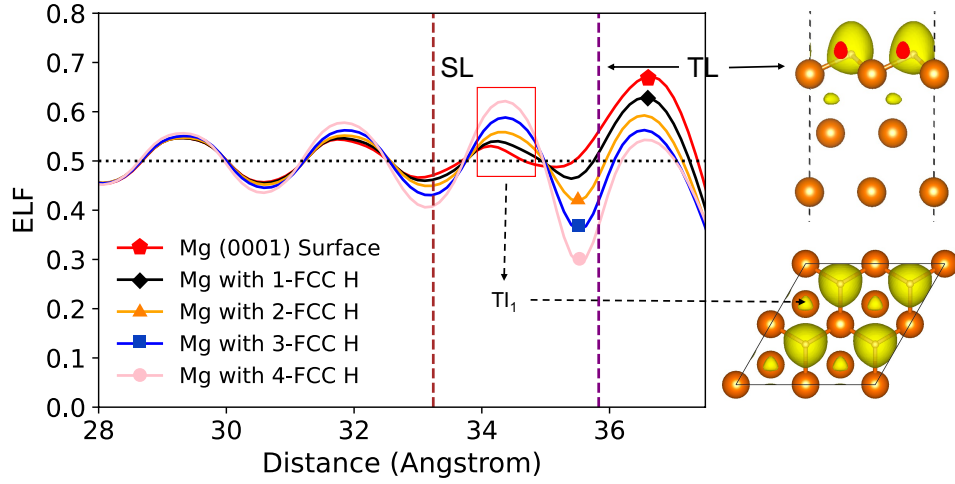


Figure 5.6: Planar (XY-Plane) average ELF of the H (fcc) covered Mg (0001) surface along Z-axis as the increase of the H coverage from 0 to 1 ML. The side-view and the top-view of the ELF isosurface plot (isosurface level = 0.80) for the 1 ML H (fcc) covered Mg surface are shown at the right of the figure. A newly formed ELF maximum (small size yellow circles) could be found at the sub-surface tetrahedral-I (TI_1) sites, which corresponds to the labelled peak in the planar average plot.

in the sub-surface region of the specimen. In this sense, the pre-adsorbed on-surface fcc H could enhance the stability of the sub-surface H adsorption at some particular regions within the Mg basal plane, thus forming a sub-surface hydride-like structure.

Table 5.3: Onsite ELF value changes at different sub-surface interstitial sites as the on-surface fcc H coverage increases from 0 to 1 ML.

fcc-H Coverage (ML)	0	0.25	0.50	0.75	1.00
Octahedral (OI)	0.349	0.493	0.465	0.420	0.367
Tetrahedral-I (TI_1)	0.687	0.734	0.743	0.805	0.816
Tetrahedral-II (TI_2)	0.673	0.691	0.711	0.712	0.740

As mentioned previously, the ELF could be a rational indicator for predicting the stable H adsorption sites in the Mg surface. We now investigate the mechanism of the stabilizing of the sub-surface TI_1 H adsorption by the on-surface H layer in the Mg surface by studying the evolution of the ELF in the sub-surface region of the Mg (0001) surface with the increase of the fcc H coverage from 0 to 1 ML. Figure 5.6 shows the planar average ELF of the Mg (0001) surface with different fcc H coverage along the Z-axis. With the increase of the on-surface fcc H coverage, the planar average ELF peak which is located above the top surface gradually

decreases. In contrast, the ELF peak in between the top layer and the second layer of the Mg surface is enhanced significantly due to the introduction of the on-surface fcc H. This enhanced ELF peak in the planar-average plot can be correlated with a newly formed ELF maximum (as shown in the Figure 5.6 isosurface plot) at the sub-surface TI_1 sites.

Table 5.3 demonstrates that the onsite ELF value changes at different sub-surface interstitial sites during the formation of the 1 ML on-surface fcc H layer. For the two tetrahedral interstitial sites, the onsite ELF values both increase from the pristine Mg surface to a surface with the fcc sites fully covered with H. The onsite ELF value of the octahedral interstitial site reaches a maximum of 0.493 when the on-surface H coverage is 0.25 ML, and finally drops to a similar value as that of the clean surface when the fcc H ML forms. This indicates that the on-surface fcc H is incapable of enhancing the electron localisation above the critical value (0.5) at the octahedral site. Across all on-surface H coverages, the TI_1 site possesses the largest ELF value among three sub-surface interstitial sites, which is consistent with the local ELF maximum found in the ELF isosurface plot. On the basis of the ELF augmentation at the TI_1 site, the H-electron interaction is strengthened significantly at this interstitial site. Accordingly the H adsorption energy at the TI_1 sites of a Mg (0001) surface is presumed to be negative because of the on-surface H adsorption, which agrees with the aforementioned result in Figure 5.5. In this regard, ELF provides a reliable insight into predicting the stable H adsorption sites within Mg surfaces.

Figure 5.7 shows the ELF contour map for the Mg (0001) surface with the fcc sites occupied by H and with different H coverages in the sub-surface TI_1 sites. When the sub-surface sites lack H atoms, the pre-adsorbed H atoms at fcc sites consume the electrons spread on the top surface, promoting the formation of a new ELF maximum in the sub-surface TI_1 site. The subsequent occupation of these interlayer ELF maxima with H is thus energetically favourable and modifies the surface ELF pattern further. Before the sub-surface TI_1 sites are fully occupied, H uptake at one TI_1 site (ELF maximum position) can enhance the electron localisation at the neighbour TI_1 sites. Once the sub-surface TI_1 sites are completely occupied by H, the entire H(fcc)-Mg(TL)-H(TI_1) tri-layer structure forms with electrons in the sub-surface region being depleted. This electron depletion is shown in the rightmost schematic in Figure 5.7: the

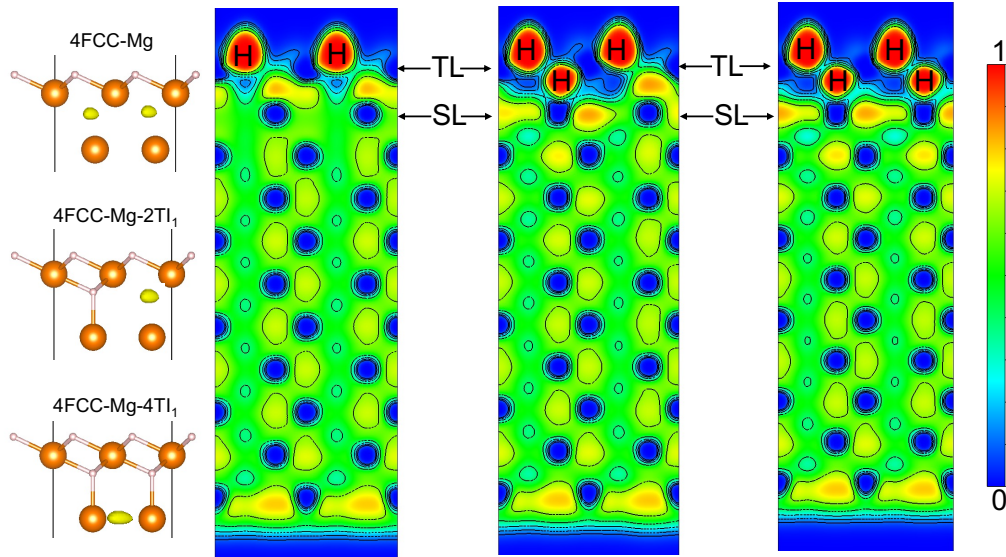


Figure 5.7: ELF contour map of the side view of the fcc H covered Mg (0001) surface with different H coverage in the sub-surface TI_1 sites (from the left to the right, the sub-surface H coverage is 0, 0.50 and 1 ML). The leftmost schematic demonstrates the correspondent adsorption structures with the ELF maximum tagged as yellow oval. The H positions are also labeled in the contour figures.

ELF value between the top layer and the second layer is approximately 0. We also note that a newly-created ELF maximum is located at the hcp hollow site of the second layer, which is similar to the position of the ELF maximum on a clean Mg (0001) surface. The ELF pattern of the stoichiometric H-Mg-H tri-layer structure indicates that ionic Mg-H bonds are built within the tri-layer, thus leading to a chemically complete structure which could be separated from the bulk Mg. Therefore, a novel almost-clean Mg surface is created underneath the tri-layer structure, with the ELF maximum positioned in the regular hcp sites. A newly formed ELF maximum in the second Mg layer is a reactive site for subsequent H adsorption, thus providing an energetically feasible path for continuously forming more H-Mg-H tri-layer structures within the Mg surface. This ELF-driven H adsorption in the Mg (0001) surface could be a possible mechanism for the growth of bulk phase MgH_2 within the bulk of Mg.

5.3.2 H Adsorption below the hydroxylated or oxidised Mg (0001) Surface

In the previous section, we demonstrated that the ELF maximum and high ELF sites within

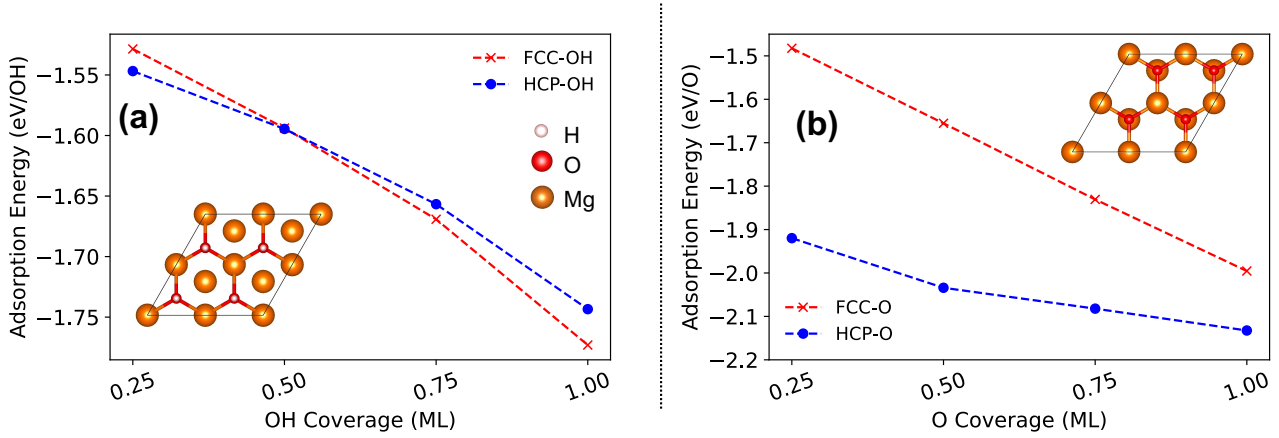


Figure 5.8: (a) Adsorption energy per adsorbed radical of OH on the Mg (0001) surface. When the coverage is larger than 0.50 ML, the absorption of OH at hcp sites is more stable than at fcc sites. The inset shows the fcc adsorption pattern, with the Mg, O and H atoms represented by the orange, red and white spheres, respectively. (b) Adsorption energy per adsorbed O atom for O on the Mg (0001) surface. The hcp site is more energetically favourable for O adsorption at all surface coverages. The inset presents the stable hcp O adsorption structure.

the Mg surface are potential adsorption sites for H. The on-surface H adsorption alters the ELF pattern of the underlying Mg surface with new ELF maxima developing within the sub-surface region, leading to thermodynamically stable H adsorption at the sub-surface interstitial sites. However, during aqueous corrosion of Mg, a hydrogen atom is more likely to escape from the surface as H_2 rather than being adsorbed on the surface [35]. In a humid environment, the bare Mg surface tends to be covered by oxygen atoms or hydroxyl groups produced by water dissociation at the surface. We now explore the ELF pattern evolution and the sub-surface H adsorption of the hydroxylated and oxidised Mg (0001) surfaces. We found that the on-surface fcc and hcp sites are the most energetically favourable for OH and O adsorption, respectively. The on-surface OH or O adsorption can enhance the ELF value at a sub-surface interstitial site, resulting in stable sub-surface H adsorption in the hydroxylated or oxidised Mg (0001) surface.

Figure 5.8 shows the adsorption energy of OH groups and O atoms on the on-surface fcc and hcp sites of the Mg (0001) surface. Overall, the on-surface adsorption of O and OH on the fcc and hcp sites of the Mg (0001) surface are all energetically favourable with negative adsorption energies. For OH adsorption, the hcp site is more energetically favourable at coverages below 0.50 ML. At higher OH coverage (0.50 to 1 ML), the on-surface fcc site becomes more stable for OH groups. Because the neutral hydroxyl radical requires one extra electron to form a

more stable chemical state (hydroxide), the on-surface OH groups tend to remove electrons from the top layer Mg atoms in the same manner as the on-surface H. The hydroxyl group and H atom both require one electron to form a fully-filled electron shell, thus leading to a similar adsorption pattern (stable fcc adsorption) for these two adsorbates. For the on-surface adsorption of O (requires two extra electrons to form oxide), the hcp site adsorption has a more negative adsorption energy than the fcc adsorption site at all coverages. In this case, the adsorption pattern for O perfectly corresponds to the ELF pattern of the Mg (0001) surface, which indicates that the ELF-related O-electron interaction energy plays a more important role in the total adsorption energy for O than for OH and H adsorption. This more significant ELF-related energy for O adsorption could be attributed to the electronegativity difference between O and H (3.5 and 2.1, respectively) [312]. Compared with H adsorption on the Mg surface, O is more electrophilic with a larger electronegativity, which leads to an enhanced adsorbate-electron interaction. As a result, the ELF-related energy of the O adsorption is more significant than that of the H adsorption, and the adsorption pattern of the O adsorption coincides well with the ELF distribution within the Mg (0001) surface.

Despite the OH radical having a similar electronegativity to the O atom (with a value in the range from 2.2 to 3.2, with the precise value depending on the structure and strength of the H bonding), the OH adsorption on the Mg (0001) surface shows an identical pattern to the H adsorption rather than the O adsorption, with the fcc site being more favourable than the hcp site [313]. The enhanced ELF-related energy in the OH adsorption case narrows the difference in adsorption energy between the fcc and hcp sites, but does not play an equally significant role in the total adsorption energy as in O adsorption. This indicates that the energetically favourable hcp adsorption for the O atom is not only stabilized by the increased O-electron interaction (enhanced electronegativity of the adsorbate) but also settled by other important contributions.

To determine additional causes for the stabilisation of the O hcp adsorption, we investigated the lattice distortion energy for the Mg surface with O and OH radicals at hcp and fcc sites, respectively. Figure 5.9 (a) shows that the distortion energy for O adsorption at both hcp and fcc sites is larger than that for OH adsorption at all coverages. This is because the OH radical is adsorbed above the top layer of the surface with a distance of approximately 1 Å, which

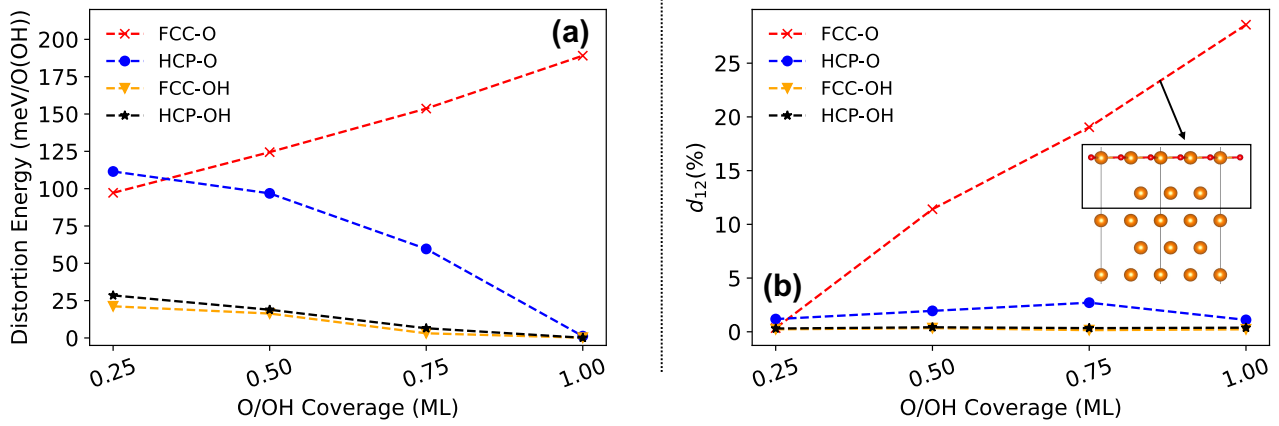


Figure 5.9: (a) Distortion energy (meV per adsorbate) of the on-surface adsorption at fcc and hcp sites on the Mg (0001) surface for O atoms and OH radicals. (b) Variations of the spacing between the top and second layers of the Mg surface with O and OH adsorbed at the fcc and hcp sites at different coverages. Here the layer spacing is the percent change of the layer distance for the hydroxylated or oxidised Mg surface with respect to the distance for the clean Mg surface.

introduces limited lateral lattice distortion. The O adsorption on the Mg (0001) surface is generally an in-plane adsorption with O just located in the top layer, and induces a larger lateral lattice distortion and an enhanced distortion energy. For the OH adsorption, the distortion energies for the fcc and the hcp adsorption sites both decrease with the increase of the coverage. In addition, the OH adsorption at the hcp site possesses a slightly higher distortion energy than the OH adsorption at the fcc site when the coverage is smaller than 1 ML. At 1 ML coverage, the distortion energy for OH adsorption reduces to approximately zero because of the high symmetry of the fully covered surface, which is similar to H adsorption. The distortion energy for O adsorption at an hcp site is 4-5 times larger than that of the OH hcp/fcc adsorption at 0.25 ML coverage and decays to zero rapidly as the coverage increases. By contrast, the O adsorbed at the on-surface fcc site introduces a strongly increasing distortion energy with respect to the increasing coverage. According to the distortion energy difference between O adsorption at the hcp and fcc sites shown in Figure 5.9 (a), this distortion energy difference for the O adsorption contributes significantly to the total adsorption energy difference between these two sites. Unlike the H adsorption and the OH adsorption, the hcp adsorption for O results in a smaller lattice distortion energy compared with the fcc adsorption, which also stabilises the onsite hcp O adsorption in addition to the enhanced adsorbate-electron interactions.

The remarkable distortion energy for the O adsorption at fcc sites could contribute to the

large layer spacing between the top layer (TL) and the second layer (SL) of the surface. Figure 5.9 (b) shows the variation of the TL-SL spacing (distance change referenced to the clean surface) for the Mg surface with O and OH adsorbed at different sites. The O adsorption at fcc sites induces a significant layer separation between the top layer and the second layer of the Mg (0001) surface with increased coverage. At 0.25 ML, the TL-SL layer spacing for O and OH adsorption at both hcp and fcc sites is at a similar small level. As the coverage increases, the subsequent adsorption for the OH radicals at hcp and fcc sites and O at hcp sites alters the layer spacing by 5% or less. However, the layer spacing for the Mg surface with O adsorbed at fcc sites increases significantly as more O is adsorbed onto the surface, reaching a maximum of 28% at 1 ML coverage: this indicates a significant layer separation between the top Mg-O layer and the substrate. Such a large layer spacing results in a distortion energy that is far larger than for O adsorption at hcp sites. Therefore, for O adsorption, the hcp sites are more stable as a consequence of a higher onsite ELF value (larger O-electron interaction) and a negligible lattice distortion (layer separation) compared with the fcc sites.

The ELF pattern of the hydroxylated and oxidised Mg (0001) surface suggests a possible explanation for the unique layer separation (large layer spacing) for O adsorption at fcc sites. As shown in Figure 5.10, the ELF contour patterns for the OH adsorption demonstrate that the on-surface OH radicals partially consume the electrons of the top layer Mg both for the fcc and hcp sites: OH only requires 1 electron and it is slightly above the top atomic layer. Thus, there are still numerous electrons distributed in the sub-surface region underneath the top layer. These remaining electrons can connect the top layer Mg atoms with the second layer by forming chemical bonds, thus restricting the TL-SL spacing and diminishing the related distortion energy. However, for the O adsorption, the on-surface O depletes more electrons within the top layer because one O atom requires two electrons to form a stable anion and the O is adsorbed just in the top layer with an insignificant vertical displacement. The ELF contour map for O adsorption at a hcp site demonstrates the decrease of the sub-surface electrons compared with OH adsorption. Although the sub-surface electrons are depleted more completely by the adsorbed hcp O atoms, a chemical bond between the adsorbed O and the Mg atom directly underneath is visible in the contour map. This O-Mg bond plays a similar role as the

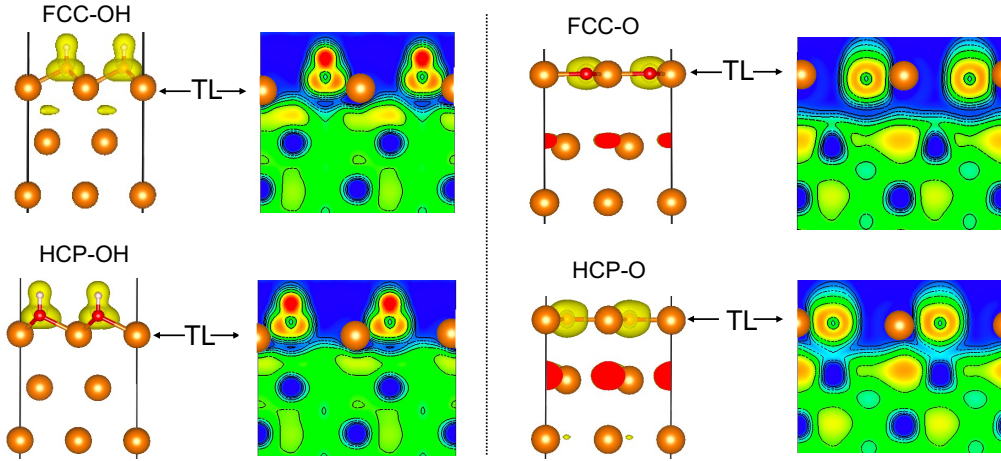


Figure 5.10: ELF contour map and the isosurface (level=0.76) plot for the side view of the Mg (0001) surface with 1 ML of OH and O on the fcc and hcp sites. In the ELF contour maps, the position of the top layer atoms is indicated by the space-filling sphere model.

inter-layer electrons, which connect the top layer atoms to the substrate and reduces the layer spacing, thus clarifying the small layer spacing for the O adsorption at hcp sites. However, the O adsorption at fcc sites lacks this essential Mg-O bond because of the layer configuration. The ELF contour map shows that the topmost Mg-O layer interacts weakly with the second layer Mg atoms, with fewer electrons remaining in the sub-surface region and no evident chemical bonding between the O and SL Mg atoms. In this case, the weak electronic interaction between the atoms in the top layer and the second layer contributes to the large layer separation when O is adsorbed on fcc sites, and the lattice distortion energy is related to this lattice distortion, thereby destabilising the O adsorption at this site.

In addition, the on-surface OH radicals and O atoms also modify the ELF pattern of the pristine Mg (0001) surface and generate new ELF maxima in the sub-surface region in the same way that the on-surface H atoms do. Considering the two most stable adsorption patterns for the OH and O adsorption on the Mg surface (adsorption at fcc and hcp sites), the isosurface plot and the ELF contour map illustrate that OH at an on-surface fcc site introduces a new ELF maximum at the sub-surface TI_1 site, whereas the O at an hcp site creates a new maximum at the sub-surface TI_2 site (also close to the hcp site in the second Mg layer). These novel sub-surface ELF maxima are possible locations within the hydroxylated or oxidised Mg surface for adsorbing additional H atoms. Thus, in a humid environment, where the Mg surface is generally covered by OH and O groups, sub-surface H adsorption and the formation of a Mg

hydride-like layer could occur.

To better understand the H sub-surface adsorption in the hydroxylated or oxidised Mg (0001) surface, we adsorbed H atoms in the available interstitial sites (OI, TI₁ and TI₂) in the 1 ML OH and O covered Mg surface in the most stable adsorption state, and calculated the H sub-surface adsorption energy for different adsorption configurations.

Figure 5.11 (a) illustrates the adsorption energy for the sub-surface H within the Mg (0001) surface covered with 1 ML of OH at fcc sites. At all H coverages in the sub-surface region, the TI₁ interstitial is the most stable site among three sub-surface sites, with a negative adsorption energy for placing H atoms at this site of the hydroxylated surface. For H adsorption at the OI and TI₂ sites, the positive adsorption energy indicates an unstable H uptake at these interstitial sites in the OH covered Mg surface. This sub-surface H adsorption energy pattern agrees well with the ELF pattern within the Mg (0001) surface covered by OH at fcc sites: the electron localisation at the sub-surface TI₁ site is enhanced significantly by the on-surface OH radicals at fcc sites, thereby suggesting a potentially spontaneous H adsorption. Therefore, a stable OH(fcc)-Mg-H(TI₁) tri-layer that has an identical configuration to the aforementioned H(fcc)-Mg-H(TI₁) tri-layer structure forms within the Mg substrate. This can be understood because the adsorption of OH at fcc sites on the Mg surface has an equivalent influence on the ELF distribution in the surface as the H adsorption at fcc sites. Likewise, the OH(fcc)-Mg-H(TI₁) tri-layer is also a chemically completed structure, with the inter-layer electrons depleted adequately by the on-surface OH radicals and the sub-surface H atoms. After adding H atoms at the TI₁ site of the Mg surface covered with OH at fcc sites, a novel ELF maximum could be found at the hcp hollow site within the second Mg surface layer, which suggests that more H atoms are likely to be adsorbed at the reconstructed pristine Mg surface underneath the tri-layer structure.

For the sub-surface H adsorption in the Mg (0001) surface covered with O at hcp sites, the OI and the TI₂ sites are both thermodynamically stable locations for H atoms at all coverages up to 1 ML. H adsorption at the TI₁ site is energetically favourable at a H coverage less than 0.60 ML. Amongst three sub-surface H adsorption sites in the oxidised Mg (0001) surface, the TI₂ site is the most stable with the most negative adsorption energy. This active H adsorption site is just

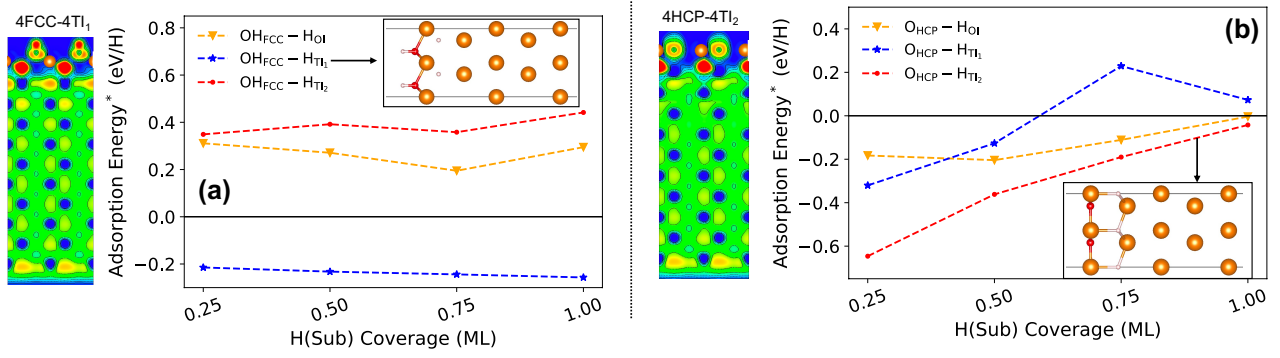


Figure 5.11: (a) Adsorption energy per H atom of H in sub-surface interstitial sites within the Mg (0001) surface covered by 1 ML OH radicals at fcc sites. Negative adsorption energy suggests stable sub-surface H adsorption with respect to the hydroxylated Mg surface and H₂ gas. The inset shows the structure of the most energetically favourable sub-surface H adsorption site (TI₁), with the corresponding ELF contour map on the left. (b) Adsorption energy of H in the sub-surface region with the Mg (0001) surface covered by 1 ML of O at hcp sites. The inset shows the structure of the most stable H sub-surface adsorption in the oxidised surface (TI₂). The related ELF contour map is also shown on the left.

the ELF maximum generated by the on-surface O atoms at hcp sites in the Mg (0001) surface, thus confirming again that the ELF is a good indicator for predicting possible adsorption sites for H in the Mg surface. Based on the ELF contour map for the O(hcp)-Mg-H(TI₂) structure, the sub-surface H further consumes the remaining inter-layer electrons within the Mg surface, and also weakens the chemical bond between the O and the underneath Mg. However, the adsorbed H at the TI₂ site connects to the top Mg atom with a H-Mg bond, and prevents the separation of the topmost Mg-O layer from the bulk phase. In addition, the introduction of the sub-surface H in the hcp-O covered Mg surface establishes a new ELF maximum at the TI₂ interstitial between the second and the third Mg layer. This ELF evolution within the oxidised Mg surface thus indicates the possible energetically favourable pathway of forming the H-Mg-H layers within the bulk phase. Consequently, we conclude that the sub-surface Mg hydride-like layer (H-Mg-H structure) could form during Mg aqueous corrosion within the Mg surface covered by O and OH (from water dissociation) following an ELF-driven H adsorption mechanism.

5.4 Conclusion

In conclusion, we have studied hydrogen adsorption and hydride layer formation mechanism within the Mg (0001) surface using density functional theory calculations. We discovered that atomic H tends to be adsorbed in the high Electron Localisation Function (ELF) adsorption site within the Mg surface. By decomposing the total H adsorption energy in the Mg (0001) surface, we found that the onsite ELF value at each adsorption site is linearly correlated to the ELF-related adsorption energy. This confirms that the ELF is a reliable predictor of the H adsorption structure. The ELF maxima region within the surface could also be treated as an effective hydrogen trap. At low H coverage, fcc sites are the most stable adsorption sites on the Mg basal plane due to the joint effect of the ELF (H-electron interaction) and the Coulomb interactions. When the surface is pre-adsorbed with 1 ML of H at fcc sites, the electron localisation at the sub-surface TI_1 is significantly enhanced, leading to energetically favourable sub-surface H adsorption and a stable $\text{H}(\text{fcc})\text{-Mg-H}(\text{TI}_1)$ tri-layer structure.

For the on-surface adsorption of OH radicals and atomic O, both the ELF (adsorbate-electron interaction) and the lattice distortion can influence the stable adsorption pattern (fcc sites and hcp sites are the most stable on-surface adsorption sites for OH and O, respectively). The ELF pattern in the sub-surface region of the Mg-basal plane could also be modified by the on-surface OH and O atoms, thus stabilising the sub-surface H adsorption and resulting in the formation of similar $\text{OH}(\text{fcc})\text{-Mg-H}(\text{TI}_1)$ structure for the hydroxylate Mg surface and $\text{O}(\text{hcp})\text{-Mg-H}(\text{TI}_2)$ structure for the oxidised Mg surface.

The adsorbate generated ELF variation within the Mg (0001) surface drives sub-surface H adsorption and the formation of the hydride layer (or its precursor) underneath the topmost Mg layer, thus illustrating the underlying mechanism for the Mg hydride formation during the aqueous corrosion at the open circuit potential. Because the formation of the sub-surface hydride is dominated by the electron localisation within the Mg surface, it is possible to control the electron localisation thereby modulating the formation of the hydride. For instance, modifying the metal surface state by doping, introducing defects or adsorbing other radicals could change the electron localisation of the metal with the formation of new ELF maxima, which could

further prompt the hydride formation. Furthermore, charging the surface or applying external strain/stress on the metal could also alter the electron localisation, thus tuning the formation of the hydride. This finding lays a foundation for understanding the significance of the Mg hydride crystalline structure in Mg aqueous corrosion, and for further revealing the nature of some enigmatic phenomena in the Mg corrosion, such as the negative difference effect.

Chapter 6

Electrochemical Stability of Mg Surfaces & Corrosion Reaction Pathways

¶ *Chapter Synopsis*

In the previous chapter, we confirmed that the sub-surface hydride layer formation during Mg aqueous corrosion is a spontaneous chemical process, with hydrogen atoms trapped in the electron-localised interstitial sites within the bulk Mg. While some theoretical hypotheses and experimental observations suggest a potential role that this sub-surface hydride could play in hydrogen evolution-related phenomena during Mg aqueous corrosion (e.g., the enhanced HER over anodic polarization), there still exists controversy and ambiguity regarding the underlying mechanism through which this hydride enhances hydrogen evolution at a significant anodic overpotential. Here we investigate the electrochemical stability of the Mg (0001) surfaces with on-surface adsorptions (*e.g.*, H, O and OH) and sub-surface H adsorptions under varying pH and potentials by constructing the surface Pourbaix diagram based on DFT calculation results. The surface Pourbaix diagram suggests a notable electrochemical stability of the sub-surface hydride phase at a considerable anodic overpotential of 0.3 V_{SHE} when the pH is approximately 8, thereby elucidating the thermodynamic stability of this hydride phase and its

prospective contribution to the enhanced hydrogen evolution under anodic polarisation. To gain a deeper understanding of how this hydride phase enhances the HER anodically, we conducted extensive reaction kinetic investigations on various stable surface conditions. We discovered that the presence of sub-surface H could contribute to extra hydrogen evolution through a Heyrovsky-pathway reaction, with its rate-limiting step showing an anodic characteristic and significantly favouring external anodic polarisation. Furthermore, we have elucidated that the surface adsorption condition, contingent on the pH and potential, exerts a significant influence on both the mechanism and kinetics of the water dissociation reaction and hydrogen evolution reaction (HER) during the corrosion process.

6.1 Introduction

As one of the important engineering materials for modern industries, Mg-based alloys, with outstanding specific strength, are of fundamental importance in the application scenarios that require significant weight reduction, like the automobile and aerospace industry [60]. At present, Mg is in urgent demand for aqueous Mg-air battery fabrication because of their high gravimetric energy density, which plays an essential role in the future sustainable energy landscape [314]. Mg-air batteries employ metallic Mg as the anode material and rely on atmospheric oxygen as the cathodic reactant. To enhance safety and prolong service-life, these batteries incorporate an aqueous electrolyte into the cell before charging [315]. Despite their remarkable characteristics like great natural abundance, low cost and non-toxicity compared with the widely used lithium batteries, aqueous Mg-air batteries are less rechargeable and possess a shorter servicing lifespan than the prevalent Li-air batteries with a remarkable capacity loss and a significant increased discharge voltage after several charge cycles [316]. These primary limitations of Mg-based aqueous batteries stem from the inadequate corrosion resistance of Mg in aqueous environments. After contacting with a corrosive battery electrolyte, such as a NaCl solution, Mg electrodes tend to be continuously corroded by the aggressive oxygen agents in the solution, and eventually passivated by MgO and MgO₂ layers on the surface, which partly blocks ion transport, reducing the faradaic efficiency and decreasing the output energy density [317, 318]. Even worse, the

corrosion rate along with the hydrogen evolution of the Mg electrode increases drastically with an enhanced anodic polarisation, thereby leading to some unexpected detriments to the battery's overall structure. Unlike the conventional cathodic promoted hydrogen evolution reaction ($\text{H}^+ + e^- \rightarrow \frac{1}{2}\text{H}_2$), this puzzling anodic condition boosting hydrogen evolution of Mg is enhanced by a positive increase of the electrode potential and is also known as the negative difference effect (NDE): this describes a negative difference between the rate of the hydrogen evolution reaction for Mg under the open circuit condition (OCP) and that under an anodic polarisation [2]. Despite numerous methods proposed to mitigate the corrosion of Mg-batteries under aqueous conditions, such as modifying the compositions of the Mg matrix through alloying with other elements (Al, Zn, Pb, Ga, RE, etc.) or applying anodised thin films as coatings on the Mg electrode, the origins and mechanisms of the anodic accelerating corrosion (i.e., the NDE) continue to be an open question [319, 320]. A thorough understanding of this phenomenon is essential if we are to design more efficient corrosion prevention techniques for Mg-based batteries.

As discussed in Chapter 2, over the past few decades, several assumptions and theories based on experimental observations and theoretical simulations have emerged to interpret the NDE of Mg. These include theories such as the surface-film or impurity-enrichment enlarged cathodic activity theory, the univalent Mg^+ theory, the passive film devastation assumption, and the hydride (MgH_2) formation theory, each of which holds its rationality yet has some limitations. Lately, a mounting collection of empirical data and simulation results provides compelling support for the notion that the creation and dissolution of the hydride phase beneath the surface, during the aqueous corrosion of Mg, hold significant promise in elucidating the anomalous hydrogen evolution observed in pure Mg under anodic polarization. When a high-purity (99.995 wt.%) Mg species is immersed in an aqueous NaCl electrolyte with a cathodic polarisation, the existence of the MgH_2 and Mg_2H_4 phases was determined by the corresponding peaks in the Raman spectra [161]. A subsequent study executed by Binns *et al.* also located this hydride phase which forms under cathodic polarisation during Mg corrosion mainly distributing in the sub-surface region of the metal according to the dynamic secondary ion mass spectrometry (SIMS) maps, and found its decomposition at anodic potentials, which supplies additional hydrogen evolution [162]. Theoretical results based on DFT and ab initio MD simulations have

provided further insight into the hydride formation process: hydrogen, once dissociated from water molecules at the surface of Mg, exhibits a strong propensity to penetrate the uppermost layer and become ensnared by the interstitial localised electrons, which culminates in the creation of thermodynamically favourable sub-surface hydride-like layers within the metal (a detailed investigation of the sub-surface hydride formation mechanism has been given in Chapter 5) [151, 163, 321].

Despite numerous pieces of evidence highlighting the role of this sub-surface hydride phase in the NDE of Mg, two pivotal questions persist, demanding immediate clarification. First, theoretical studies have verified the thermodynamic stability of the hydride-like layer under open circuit conditions without considering the impact of electrode potential and pH for the electrolyte, which is not equivalent to the experimental conditions. According to the experimentally measured Pourbaix diagram of Mg, the equilibrium potential for the bulk hydride formation is approximately $-1.2 \text{ V}_{\text{SHE}}$ at a neutral pH, at which point hydride-induced NDE ceases, and the hydride model no longer applies [2]. In addition, electrochemical reactions invariably occur in the interface region, which suggests the thermodynamic stability of the surface phase could be more important than the bulk phase at the interface. Hence, it is crucial to further ascertain the stability of the sub-surface hydride layer (assumed to be a potential precursor of the bulk hydride) under specific electrode potentials and across diverse pH solutions, as this is essential for a comprehensive validation of the theory’s correctness. Second, the distinct reactions at the Mg/electrolyte interface and the molecular-level mechanisms driving the intensified hydrogen evolution, mediated by the sub-surface hydride during anodic polarisation, are still not well understood, and so require clarification, particularly considering the complex influence of pH and potential.

In this chapter, we investigated the electrochemical stability of Mg (0001) surfaces in different adsorption states under various potentials and pH by constructing surface Pourbaix diagrams using a grand-canonical framework. Specifically, the stability of the surfaces with hydrogen adsorption as sub-surface interstitials is determined and subsequently included in the overall surface diagram. We noticed that the Mg (0001) surfaces with sub-surface hydride-like structure are remarkably stable at anodic potentials (*e.g.*, the equilibrium potential of the sub-surface

hydride in an oxygen-covered Mg surface could reach 0.38 V_{SHE} at pH around 8). This relatively anodic stability of the hydride-like structure facilitates a cycle of formation and dissolution of the hydride layer in conjunction with H₂ evolution under anodic conditions in a steady-state scenario, thereby playing a dominant role in enhancing the NDE of Mg. Moreover, according to the surface Pourbaix diagram, the surface (adsorption) state in an electrochemical environment is predominantly influenced by the electrode potential and pH of the solution. As a consequence, an interface reaction that involves identical reactants or products but occurs under distinct conditions (*i.e.* on various surface states characterised by specific potential and pH values) might exhibit disparate reaction pathways and kinetics [322]. We thus studied the typical water dissociation reaction, HER and the sub-surface hydride formation on the Mg (0001) surface at different stable adsorption states. Through kinetic investigations utilising an implicit solvent model, it becomes evident that the process of water dissociation can be notably expedited by on-surface oxygen/hydrogen, primarily through the O-H and H-H interaction, which consequently leads to a barrier-free kinetics for water dissociation on the preliminarily corroded Mg (0001) surface. Similar to previous kinetic studies, we also found that the general HER on the Mg surface tends to follow the Heyrovsky reaction pathway because of the lower energy barrier and more negative reaction free energy compared with the Tafel pathway, with a water molecule in the solution reacting with the on-surface H, OH or the sub-surface hydride. Moreover, we further found that the rate-limiting step, namely the outward diffusion of the sub-surface hydrogen, for the HER that consumes the sub-surface hydride, could be accelerated significantly by the anodic polarisation, thus exhibiting an anodic-favourable behaviour. As a result, the application of anodic potentials to the Mg electrode assists the transformation of sub-surface hydrides, and accelerates the HER rate under anodic conditions. Along with the aforementioned electrochemical stability of the sub-surface hydride layer at anodic polarisation, this dynamic process sheds light on the kinetic characteristics of the NDE for Mg resulting from the presence of hydride.

6.2 Methods

6.2.1 Grand-canonical approach extending method

To identify the thermodynamically stable state of the Mg (0001) surface under specific electrochemical circumstances, we constructed a comprehensive surface Pourbaix diagram for the Mg basal plane. This diagram was developed using the grand canonical approach which was inspired by defect chemistry calculations. It links the results of ab initio calculations directly with experimental parameters, such as the pH scale and the electrode potential, both pivotal in defining the electrochemical system's state [134, 323]. Within this grand-canonical framework, the electrochemical system naturally segregates into three fundamental domains: the bulk electrode, the aqueous electrolyte (reservoir), and the interface region. Because the electrochemical system is assumed to be in thermal equilibrium, the electrochemical potentials ($\tilde{\mu}$) of the species in the system remain constant across the system. The excess Gibbs free surface energy for the surface (or the interface region) state α with adsorption of species i , could therefore be expressed as:

$$\Delta G^\alpha(T, U) = G^\alpha(T, U) - G^\circ(T, U) - \sum N_i \tilde{\mu}_i(T, U) \quad (6.1)$$

Here $G^\alpha(T, U)$ is the free energy of the surface α with N_i adsorbates of species i at a temperature of T and electrode potential U , $G^\circ(T, U)$ is the corresponding free energy of the surface in its pristine state, and $\tilde{\mu}_i(T, U)$ is the electrochemical potential of the solvated species i in the electrolyte under the same conditions. Within the scope of this grand-canonical approach, the electrochemical potential of the solvated species is generally related to the chemical potential of their gas phase via the corresponding redox potential. In this sense, the need for computationally demanding calculations to evaluate the solvation energy of species within the electrolyte can be circumvented, aligning with the concepts on which the computational hydrogen electrode (CHE) is based [133]. For the hydrogen adsorption at the electrode/electrolyte interface, the electrochemical potential of hydrogen can be expressed as a function of the electrode potential (normally calibrated to a reference electrode, *e.g.*, the standard hydrogen electrode (SHE)) and

the pH of the electrolyte:

$$\tilde{\mu}_H = \mu_H^\circ - eU_{SHE} - k_B T \ln(10) \text{pH} \quad (6.2)$$

with μ_H° as the chemical potential of hydrogen at a standard condition, here taken to be half of the chemical potential for a hydrogen gas molecule at standard ambient temperature (298 K) and pressure (1 atm). U_{SHE} is the electrode potential measured relative to the SHE, which also refers to the electron electrochemical potential difference between the (working) electrode and the standard one:

$$\tilde{\mu}_e - \tilde{\mu}_e^{SHE} = -eU_{SHE} \quad (6.3)$$

Equation 6.2 describes the adsorption of a neutral hydrogen atom at an interface. It can also be interpreted as the adsorption of a solvated proton $H^+(aq)$, accompanied by the uptake of an electron from the Fermi level of the metallic electrode at the electrified interface, thereby leading to a more practical application of it in describing the ion adsorption procedure of an electrochemical system. The presence of bulk water within the electrolyte under conditions rich in hydrogen (resulting in H_2 evolution) ensures the electrochemical potential of oxygen is set by the formation energy of water ($\Delta_f G^\circ[H_2O]$). That is, it can be determined from the electrochemical potential of H, and thus be expressed as a function of pH and potential:

$$\tilde{\mu}_O = \mu_O^\circ + \Delta_f G^\circ(H_2O) - 2[-eU_{SHE} - k_B T \ln(10) \text{pH}] \quad (6.4)$$

For the Mg (0001) surface immersed in an aqueous solution, the excess Gibbs free surface energy for the surface with adsorption of H atoms, O atoms or OH radicals can be expressed by the following equation according to the grand-canonical approach:

$$\begin{aligned} \Delta G[\text{Mg}^\beta(0001)](\text{pH}, U_{SHE}) &= G[\text{Mg}^\beta(0001)] - G[\text{Mg}^\circ(0001)] - N_O \mu_O^\circ - N_H \mu_H^\circ \\ &\quad - N_O \Delta_f G^\circ(H_2O) + (2N_O - N_H)[-eU_{SHE} - k_B T \ln(10) \text{pH}] \end{aligned} \quad (6.5)$$

where $G[\text{Mg}^\beta(0001)]$ corresponds to the free energy of the Mg basal plane with adsorption of N_O oxygen atoms and N_H hydrogen atoms, while $G[\text{Mg}^\circ(0001)]$ refers to that of the Mg surface in its pristine state. A negative excess Gibbs free surface energy (ΔG) for a surface

adsorption state signifies its favorable electrochemical stability under the specified pH and electrode potential. Hence, the conceivable surface state at a specific electrode potential and solution pH is ascertained by identifying the surface possessing the most negative excess surface energy within those electrochemical circumstances.

6.2.2 Electronic structure modelling with DFT

To estimate the excess Gibbs free surface energy of Mg (0001) surface in different electrochemical states along with determining the energy barrier of crucial interface reactions, we performed first-principles calculations within the DFT formalism as implemented in the Vienna Ab Initio Software Package (VASP), where the Perdew–Burke–Ernzerhof (PBE) functional was used to describe the electronic exchange and correlation [233, 234, 226]. The core electrons of Mg, O, and H were modelled using the Projector Augmented-Wave (PAW) technique, employing the frozen core approximation [232]. Meanwhile, the $3s$, $2s$ and $2p$, $1s$ electrons of Mg, O, and H respectively were considered as valence electrons and treated accordingly [259]. The electronic convergence criteria and the force tolerance were set to 10^{-7} eV and 10^{-3} eV/Å for the ionic relaxation computations, with a kinetic-energy cutoff of 700 eV for the system containing Mg and H, or a cutoff of 750 eV for the Mg-O-H ternary system to ensure the total energy converges within 10^{-3} eV/atom. All surface calculations were executed using a Γ -centred $8 \times 8 \times 1$ Monkhorst-Pack k -point mesh so that the total energy could converge within 5×10^{-3} eV per unit cell [300]. For the calculations including water molecules or hydrogen molecules interacting with on-surface H/O atoms or hydroxyl radicals, the van der Waals (vdW) interactions were considered by treating the dispersion energy correction term with the DFT-D3 method proposed by Grimme *et al.* [324]. In addition, the solvation of Mg (0001) surfaces under aqueous conditions was simulated with a self-consistent implicit solvation model that describes the dielectric screening of the solute. A dielectric constant of water, *i.e.*, 78.3, was used. The model has been implemented in the VASPsol package [236, 325]. The Gibbs free energy correction for the gas references H_2 and O_2 , including the zero-point energy (ZPE), the enthalpy and entropy correction contributed by the vibration, rotation and translation modes, was obtained from frequency calculations, which give total corrections of -0.043 and -0.45 eV for

the hydrogen and oxygen gas respectively, in good agreement with experimental values [326].

The climbing image nudged elastic band (CI-NEB) method as implemented in the VASP-Transition State Theory (TST) tools was used to search for saddle points (*i.e.*, transition states) across the energy landscape linking specified initial reactant states to eventual product states [244, 327]. To determine the initial and final geometries of the water dissociation reaction or the HER on Mg (0001) surfaces across diverse adsorption states, the most energetically favourable structures were derived from previous works, or discovered by performing local geometry relaxation for various configurations with the reactant (product) molecules or radicals adsorbed on different surface adsorption sites in different orientations and eventually selecting the relaxed geometries with the lowest energy [152, 328]. Intermediate images positioned between the initial and final states along a designated reaction pathway were acquired using a linear interpolation technique. The force convergence criteria for these intermediate images along the reaction band was set as 5×10^{-2} eV/Å. As indicated by a prior investigation, variations in electrode potential do not substantially alter the energy barrier for the water dissociation and hydrogen (de)adsorption processes on the metal surface [329]. Hence, in this study, it is justifiable to overlook the potential dependence of the computed reaction energy barrier.

For the Bader charge analysis of essential atoms in the images along a certain reaction pathway, the program developed by Henkelman *et al.* that is based on an efficient approach to partition a charge density grid into Bader volumes was used here [330, 331]. The crystal orbital Hamilton populations (COHP) analysis as implemented in the LOBSTER program was employed to estimate the bonding or anti-bonding contributions to the band-structure energy. Furthermore, the integration of the COHP (ICOHP) aided in quantifying the bond strength of critical bonds within the system, including O-H bonds [332].

The Mg (0001) surface was simulated by an 11-layer $p(2 \times 2)$ slab prototype with a unit cell dimension of $6.40 \times 6.40 \times 45.83$ Å³. A vacuum region with a length of 20 Å was added in the Z direction to eliminate spurious interactions between image structures because of the periodic boundary conditions. The setup of the on-surface adsorption site (*e.g.*, fcc and hcp hollow site) for H, O or OH and the sub-surface adsorption interstitial (*e.g.*, octahedral and tetrahedral interstitial) for H on the Mg (0001) was the same as that in Chapter 5 (see Figure

5.1). Both the on-surface and sub-surface adsorption coverage fall within the range of 0.25 to 1.00 monolayer (ML). In addition to the single species adsorption on the Mg surface, a hybrid on-surface adsorption case such as H with OH and OH with O, was also considered in this study. Because the adsorbates were selectively added to single side of the Mg (0001) surface, resulting in an inherent asymmetry in the geometries and an additional dipole moment within the unit cell, a dipole correction method, which introduced a counteracting dipole layer in the vacuum region, was employed in the surface calculations [261]. Scanning tunneling microscopy (STM) images of the Mg (0001) surfaces across different adsorption states, were simulated in constant height mode using the Tersoff-Hamann (TF) model, incorporating the calculated partial charge density of the surfaces [333].

6.3 Probing Mg Surfaces-states under Aqueous Conditions

The aqueous corrosion of Mg is a typical electrochemical phenomenon occurring at the interface of Mg and water, which is significantly influenced by both the external electrical potential and the pH level of the surrounding solution. Given the unique mechanisms and kinetics exhibited by the fundamental corrosion reactions across various adsorption states on the Mg surface, it is important to estimate the thermodynamically stable surface conditions across a range of proposed electrochemical scenarios, which necessitates the construction of a comprehensive surface Pourbaix diagram. Previous studies have primarily examined the electrochemical stability of Mg (0001) surfaces with specific coverage of OH radicals or O atoms being adsorbed separately at certain surface sites [13, 14, 334]. Nevertheless, this earlier research constructed the surface Pourbaix diagram of the Mg (0001) surface using limited adsorption instances, thus leading to the neglect of some stable surfaces. Furthermore, it relied on a Nernst equation based approach, which may result in an indistinct representation of the phase boundaries between different adsorption states. In this section, we explore the electrochemical stability of 120 configurations of the Mg (0001) surface with the on-surface adsorption of H, O atoms and OH radicals or the sub-surface adsorption of H. Initially, the

surface Pourbaix diagrams of the Mg (0001) surface with only 64 distinct on-surface adsorption configurations (without considering the effect of solvent) were constructed via the aforementioned grand-canonical approach. To comprehensively assess the stability and selectivity of surfaces hosting sub-surface hydrogen, an additional 56 surface configurations were introduced into the surface ensemble. These configurations included adsorbed H or O atoms, or OH radicals on on-surface sites, alongside H situated within the sub-surface interstitial. Subsequently, an all-encompassing surface Pourbaix diagram was developed, incorporating the entirety of these conceivable configurations.

6.3.1 Electrochemical stability of Mg (0001) on-surface adsorption configurations

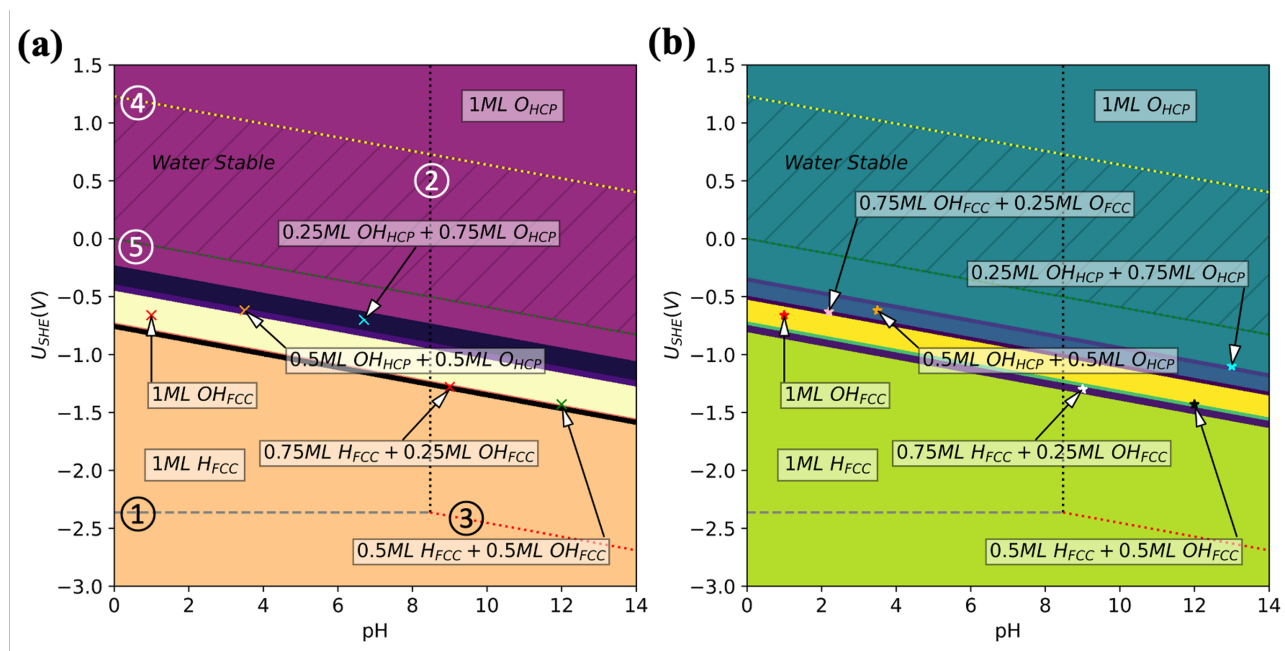


Figure 6.1: Surface Pourbaix diagram of the Mg (0001) surface with on-surface adsorptions of H, OH and O under thermodynamic equilibrium: (a) surfaces without solvent; (b) surfaces in aqueous conditions modelled by the implicit solvent model. The dashed line labelled from ① to ③ indicates the phase boundary of bulk Mg/aqueous Mg^{2+} , aqueous Mg^{2+} /bulk $Mg(OH)_2$ and bulk Mg/bulk $Mg(OH)_2$ respectively. The grey hashed region indicates the water stability region, with the boundary ④ of water/ O_2 and ⑤ of water/ H_2 .

In Figure 6.1 we show the surface Pourbaix diagram of the Mg (0001) surface primarily focusing on the on-surface adsorption configurations with or without a solvent. For the Mg

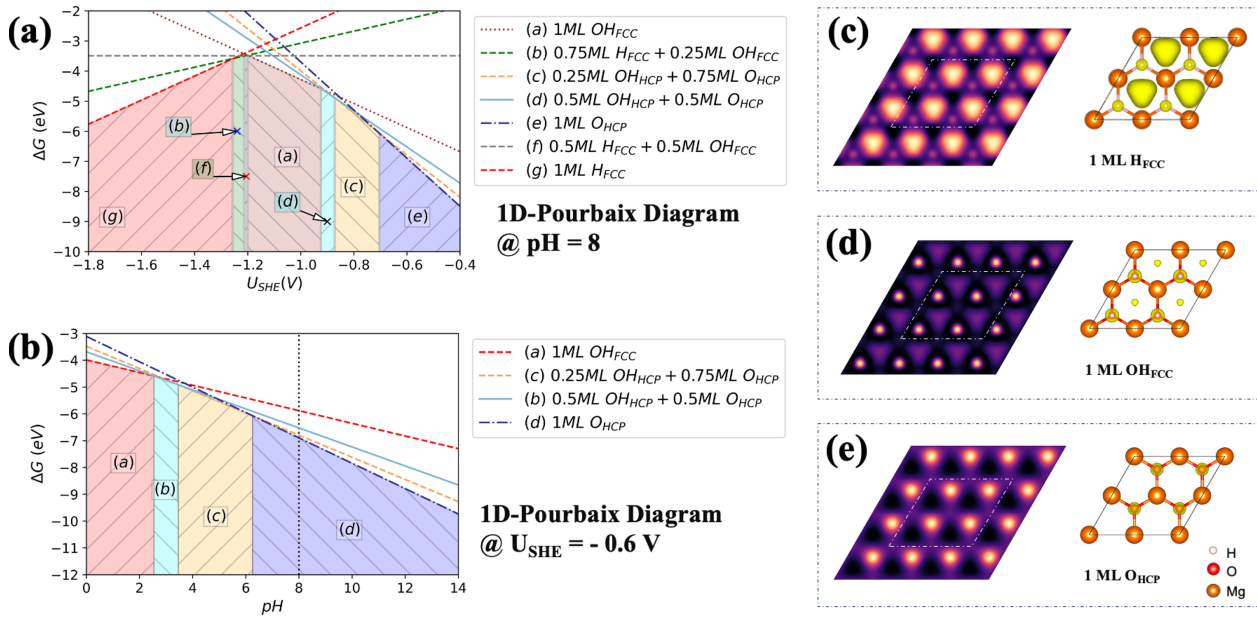


Figure 6.2: (a) Excess Gibbs free surface energy (without solvent) of the stable Mg (0001) on-surface adsorption configurations as a function of electrode potential at pH = 8; (b) excess Gibbs free surface energy (without solvent) of the stable Mg (0001) on-surface adsorption configurations as a function of pH when the electrode potential is $-0.6 V_{SHE}$; (c)-(e) simulated STM images of the three lowest energy Mg (0001) surface states which are covered with 1 ML H at fcc sites, 1 ML OH at fcc sites and 1 ML O at hcp sites. The yellow circles (isosurface plot) refer to a partition charge accumulation onsite.

(0001) surfaces, when excluding the effect of solvent, there are predominantly seven distinct surface adsorption states within the potential range of -3.0 to $1.5 V_{SHE}$, across a solution pH spanning from 0 to 14. Among these electrochemically stable adsorption configurations, the three most prevalent surface states are: 1 ML coverage of H adsorbed at the fcc site, 1 ML coverage of OH radicals at the fcc site, and 1 ML coverage of O at the hcp site. The simulated STM images of these three surface configurations are displayed in Figure 6.2 (c)-(e). In slightly alkaline conditions (pH = 8), as demonstrated in Figure 6.2 (a), the pristine Mg (0001) surface tends to become covered by a 1 ML of H at cathodic potentials, up until the electrode potential reaches approximately $-1.26 V_{SHE}$. As the electrode potential increases anodically, the electrochemical potential of H within the reservoir decreases according to Equation 6.2 (*i.e.* the H becomes more stable), resulting in a diminishing likelihood of aqueous H^+ adsorption on the surface. Conversely, the electrochemical potential of O in the electrolyte solution increases with a more positive potential, which enhance the on-surface OH or O adsorption accordingly. Consequently,

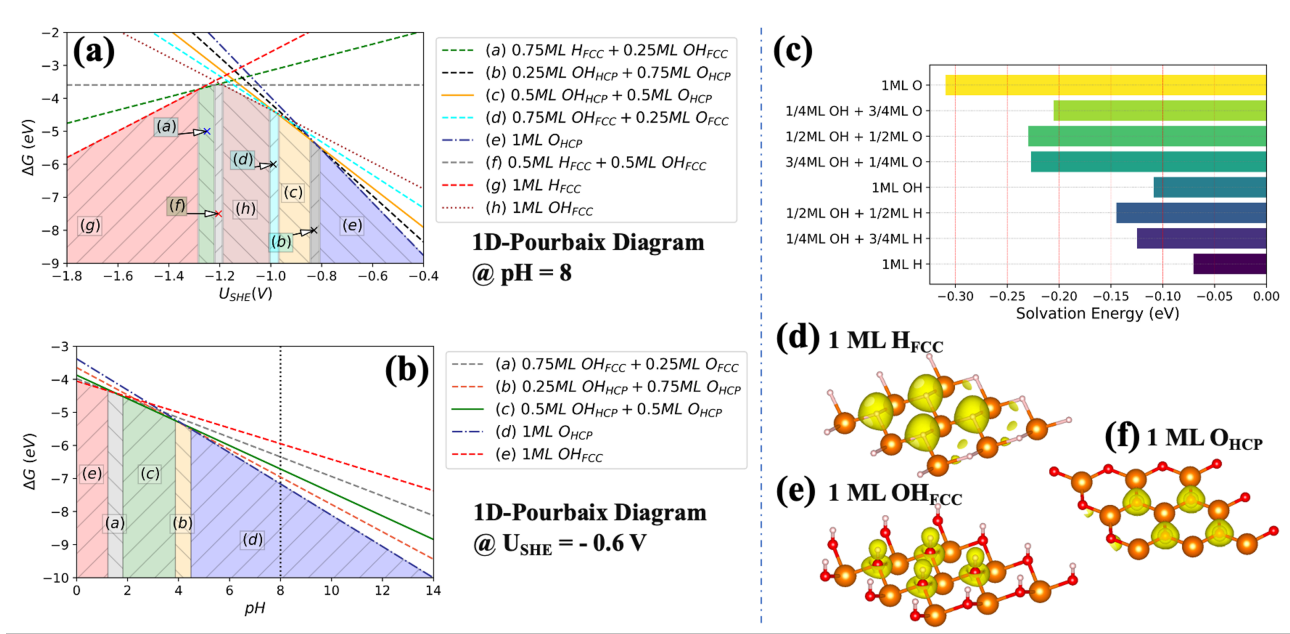


Figure 6.3: (a) Excess Gibbs free surface energy (with solvent effect) of the stable Mg (0001) on-surface adsorption configurations as a function of electrode potential at pH = 8; (b) excess Gibbs free surface energy (with solvent effect) of the stable Mg (0001) on-surface adsorption configurations as a function of pH when the electrode potential is -0.6 V_{SHE}; (c) solvation energy of the stable Mg (0001) on-surface adsorption configurations; (d)-(f) isosurface plot of localised (excess) electrons above the Mg (0001) surface covered with 1 ML H (fcc), 1 ML OH (fcc) and 1 ML O (hcp), respectively.

the Mg surfaces convert from a high hydrogen coverage state to a high hydroxyl adsorption configuration when the electrode potential shifts positively from -1.26 to -0.92 V_{SHE}, with some hybrid adsorption states (*e.g.*, 0.75 ML H + 0.25 ML OH at fcc sites and 0.5 ML H + 0.5 ML OH at fcc sites) become electrochemically stable in a narrow potential window. As the electrode potential continues to rise anodically, the fully hydroxylated Mg (0001) surface experiences a gradual reduction in surface hydrogen. It undergoes a sequential transformation: initially transitioning to a configuration with 0.5 ML OH + 0.5 ML O at the hcp sites, followed by further oxidation resulting in a state with 0.25 ML OH + 0.75 ML O at the hcp sites. Ultimately, at an electrode potential of approximately -0.7 V_{SHE}, the surface completes its conversion into a fully oxidised state, with 1 ML O atoms adsorption at hcp sites.

As the pH of the electrolyte solution varies from acidic to alkaline, the electrochemical potential of H within the electrolyte becomes increasingly negative. This heightened stability of aqueous H makes the deposition of H onto the Mg surface more challenging. To destabilise the H within the reservoir and enhance on-surface H adsorption at alkaline conditions, a more

cathodic electrode potential is thus required to increase the electrochemical potential of H. Hence, the domain encompassing surface configurations covered by higher coverage of H or OH undergoes a shift towards a more negative potential as the pH is increased, thereby ensuring the preservation of their electrochemical stability. Moreover, under experimental anodic conditions for Mg aqueous corrosion (e.g., pH = 8 and electrode potential of $-0.6 V_{SHE}$), the Mg (0001) surface exhibits a propensity to be covered by a monolayer of oxygen, as illustrated in the diagrams presented in Figure 6.1. This circumstance leads to a deficiency in the availability of hydrogen resources for the anodically enhanced HER, thus leaving the enigma of the negative difference effect for Mg unresolved.

We now explore the impact of solvent on the electrochemical stability of various adsorption configurations of the Mg surface. For the solvated Mg (0001) surface Pourbaix diagram, as displayed in Figure 6.1 (b), the previously mentioned seven stable adsorption configurations retain their electrochemical stability when the solvent is included: 1 ML coverage of adsorbed H, OH and O on the Mg (0001) surface remain the three lowest energy configurations. In addition to these surface states, a novel adsorption arrangement emerges on the phase diagram under aqueous conditions, characterised by 0.75 ML OH + 0.25 ML O at the fcc sites. Compared with the solvent-free surface Pourbaix diagram, nearly all of the regions of surface configurations with more O adsorption (except for the adsorption state of 0.25 ML OH + 0.75 ML O at the hcp site) expand by encroaching upon the stable area of the adsorption states with more OH radicals, which indicates that solvation favours the oxidised Mg surface more than the hydroxylated one. Similarly, the surface state featured by high H coverage is stabilised less by the implicit solvent medium than the hydroxylated surface. Therefore, the hybrid adsorption states of H and OH, such as 0.75 ML H + 0.25 ML OH at the fcc sites and 0.5 ML H + 0.5 ML OH at the fcc sites, invade certain stability regions of the H-covered surface, as can be seen in Figure 6.1 (b). This intrusion also broadens the potential window, within which their electrochemical stability can be extended, relative to the solvent-free condition.

To further investigate the effect of solvation on the Mg (0001) surface with distinct adsorption of H, OH and O, we plot the solvation free energy (which is calculated as the energy difference between the DFT total energy of the surface in a vacuum and that in an implicit solvent

environment) of the electrochemically stable surface configurations under aqueous conditions in Figure 6.3 (c). Consistent with our earlier observations concerning the alterations in the surface Pourbaix diagram prompted by the presence of solvent, the solvation energy resulting from O, OH, and H adsorption follows a descending pattern. Specifically, the surface featuring O adsorption displays a higher preference for the wetting (solvation) process compared to the OH-covered surface, which in turn binds more robustly with the solvent than the H-covered surface.

This solvation phenomenon of Mg (0001) surfaces in different adsorption configurations can be elucidated from the following two observations. First, conforming to the Born solvation model which is used for estimating the electrostatic component of the solvation Gibbs free energy for a solvated ion, the electrostatic-related solvation energy is proportional to the square of the net charge carried by the ion; *i.e.*, a greater net charge of the solvated ion contribute to further negative solvation energy ($\Delta G_{solv} \propto -q_{net}^2$) [335]. As the implicit solvent model inherently captures the essence of electrostatic interactions between the solute and the surrounding continuum solvent medium, we can simply assess the solvation energy of adsorbed OH radicals, as well as O and H atoms, on the Mg surfaces by applying the Born equation. The Bader charge analysis indicates that the net charge of the O, OH radical and H adsorbed on the Mg (0001) surface exhibit values of approximately -1.7 *e*, -1.0 *e* and -0.9 *e*, respectively. Consequently, the solvation energy estimated by the Born equation of the Mg (0001) surface with adsorption of O, OH and H shows a declining trend, aligning with our findings from DFT calculations.

In addition, Yoo *et al.* found that the effect of (implicit) solvation is less on metallic surfaces (*i.e.*, surfaces with a greater number of unpaired electrons at the top layer) than surfaces with nonmetallic features [336]. This solvation effect alleviation of metallic surfaces stems from their high intrinsic electronic polarisability, which is able to screen the electrostatic charges efficiently and reduce the solvation energy. For the nonmetallic surface, the efficient electrostatic screening is reduced due to their less diffusive and polarisable surface electrons, which could be compensated significantly by introducing the implicit solvent. In our case, the Mg surfaces covered by hydrogen possess apparent metallic attributes. This outcome arises from the fact

that a hydrogen atom can only consume a single electron from the surface, resulting in an excess of electrons remaining on the surface subsequent to hydrogen adsorption (refer to Figure 6.3 (d), with the average Bader charge of the top-layer Mg atoms being about +1.1), and thereby reducing the solvation effect. Conversely, O adsorption on the Mg (0001) surface depletes more electrons from the surface (leads to the average Bader charge of the top-layer Mg atoms of +1.6), with electrons tightly bonded (localised) around O atoms as shown in Figure 6.3 (e). The nonmetallic nature of O adsorption surfaces results in a diminished capacity for effective electrostatic screening. Consequently, compared to the metallic surfaces covered with hydrogen, these surfaces exhibit a stronger affinity for the implicit solvent to enhance the electrostatic screening.

6.3.2 Electrochemical stability of Mg (0001) sub-surface (H) adsorption configurations

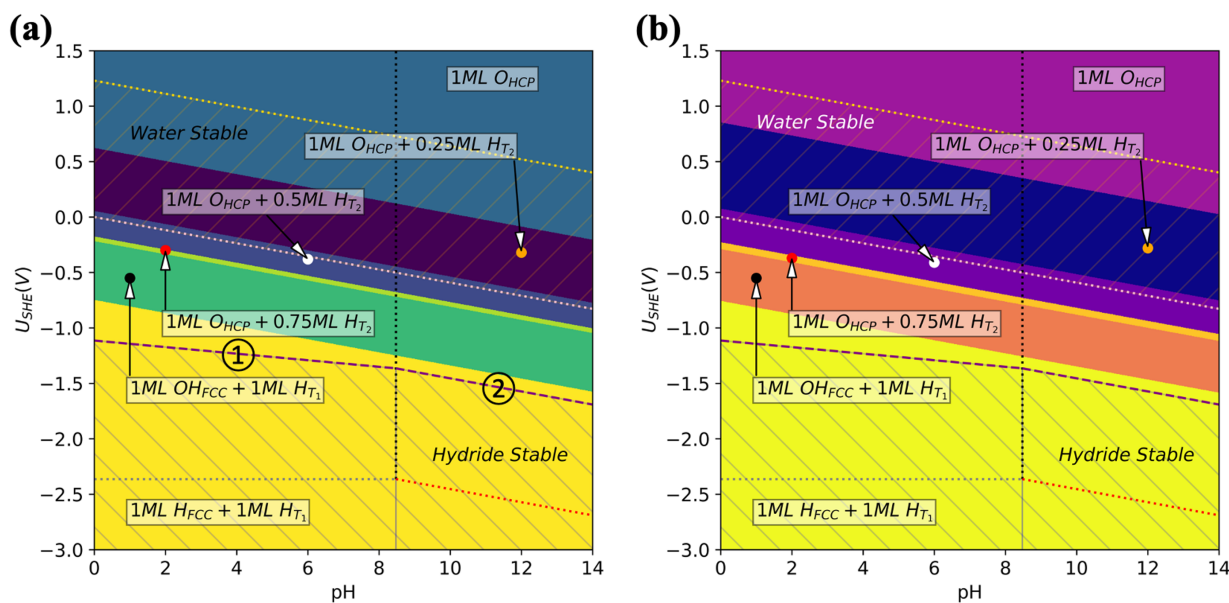


Figure 6.4: (Sub)-Surface Pourbaix diagram of the Mg (0001) surface with on-surface adsorption of H, OH and O, along with sub-surface adsorption of H under thermodynamic equilibrium: (a) surfaces without solvent; (b) surfaces under aqueous conditions modelled by the implicit solvent model. The dashed line labelled of ① and ② suggests the phase boundary of bulk Mg hydride (MgH_2) / aqueous Mg^{2+} , and bulk MgH_2 / bulk $Mg(OH)_2$ respectively. The lower grey hashed region indicates the bulk hydride phase stability region [24].

For the surface Pourbaix diagram of the Mg basal plane that incorporates various on-surface

adsorption configurations for H, OH and O, it is observed that under anodic polarisation the surface predominantly adsorbs monolayer O atoms at hcp sites. However, this phenomenon alone fails to provide a rational explanation for the observed NDE behavior of Mg. To ascertain the electrochemical stability of the surfaces featuring the sub-surface hydride phase, which is being investigated as a potential factor responsible for the anodically enhanced HER, we reconstruct the surface Pourbaix diagram of the Mg (0001) surface. This involved extending the on-surface adsorption phase diagram to include surface configurations with sub-surface hydrogen adsorption in addition to the on-surface adsorption ensemble. The resulting sub-surface Pourbaix diagrams (with or without the solvent) are illustrated in Figure 6.4.

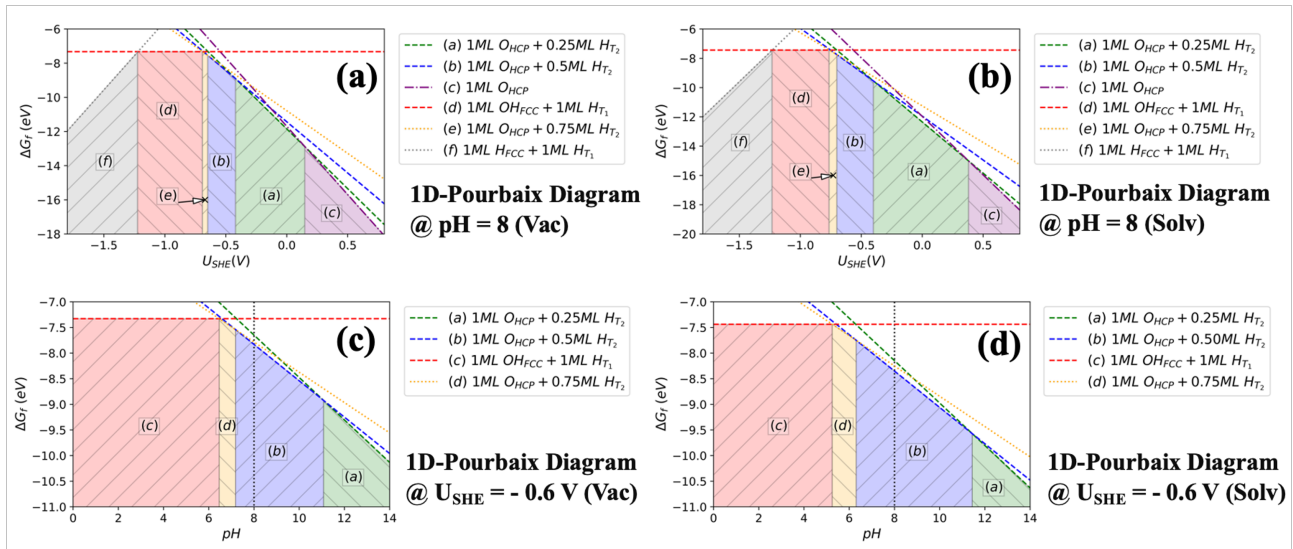


Figure 6.5: (a)-(b) Excess Gibbs free surface energy (without and with solvent) of the stable Mg (0001) on-surface and sub-surface adsorption configurations as a function of electrode potential at $\text{pH} = 8$; (c)-(d) excess Gibbs free surface energy (without and with solvent) of the stable Mg (0001) on-surface and sub-surface adsorption configurations as a function of pH when the electrode potential is -0.6 V_{SHE} .

After introducing the sub-surface hydrogen adsorption configurations into the surface Pourbaix diagram, regardless of the solvent effect, it is apparent that the surfaces featuring a combination of on-surface adsorption and sub-surface hydrogen adsorption exhibit significantly enhanced electrochemical stability compared to configurations reliant solely on on-surface adsorptions. This modification of the surface phase diagram hence renders a total of six distinct and stable (on-surface and sub-surface) hybrid adsorption surface configurations under the given electrochemical conditions: 1 ML H (on-surface fcc sites) + 1 ML H (sub-surface tetrahedral-1

sites), 1 ML OH (on-surface fcc sites) + 1 ML H (sub-surface tetrahedral-1 sites), 1 ML O (on-surface hcp sites) + 0.75 ML H (sub-surface tetrahedral-2 sites), 1 ML O (on-surface hcp sites) + 0.5 ML H (sub-surface tetrahedral-2 sites), 1 ML O (on-surface hcp sites) + 0.25 ML H (sub-surface tetrahedral-2 sites), and 1 ML O at on-surface hcp sites. It is worth noting that the inclusion of hydrogen within sub-surface interstitials retains the underlying trend in the potential and pH-based variations of on-surface adsorption structures on the Mg (0001) surface. In other words, as we move from cathodic potentials towards more anodic potentials at a fixed pH value (see Figure 6.5(a)-(b)), the preferred on-surface adsorption state of the Mg surface undergoes a similar sequence of phase transitions as mentioned previously: starting from a highly hydrogen-covered state, transitioning to an OH-covered configuration, and finally culminating in a fully oxidised state with a diminishing presence of surface-adsorbed hydrogen due to the stabilisation of hydrogen in the electrolyte by the increasing potential. This decrease in hydrogen coverage under increased electrode potential could also be observed in the sub-surface hydride phase development with varying potentials, *e.g.*, in the absence of solvent, the 1 ML sub-surface hydride diminishes to 1/4 ML as the electrode potential ascends to $-0.41 V_{SHE}$ at a solution pH of 8. Moreover, the elevated alkaline pH level of the solution requires more electrons (*i.e.*, more cathodic potential) to sustain the electrochemical stability of the hydrogen adsorption on the Mg surfaces, thus shifting the surface configurations with increased hydrogen coverage towards a region of more negative potentials.

The substitution of the hybrid on-surface and sub-surface adsorption configurations with only on-surface adsorption states in the phase diagram demonstrates a strong thermodynamic affinity of the sub-surface hydrogen incorporation into the Mg surfaces, which stems from the significant electron localisation within the sub-surface interstitials of the surfaces (as discussed in Chapter 5). These localised electrons accumulated within the surface behave as an efficient hydrogen trap and captures hydrogen from the environment to form a hydride with a considerable thermodynamic driving force, accordingly consolidating the sub-surface hydride configurations in the electrolyte. The tagged dashed lines in Figure 6.4 distinguishes the experimentally measured phase boundaries between the bulk MgH_2 phase and the aqueous Mg^{2+} (indicated by line ①), or the bulk $Mg(OH)_2$ (indicated by line ②), leaving a stable region for the Mg hydride phase

under a cathodic potential range, which is in good accordance with previous observations of the crystalline hydride formation under cathodic potentials [161, 162]. As indicated by our computed sub-surface Pourbaix diagram, the stability region for the bulk hydride phase extensively overlaps with the electrochemically robust area corresponding to the surface configuration featuring 1 ML of hydrogen at the on-surface fcc sites and an additional 1 ML of hydrogen within the sub-surface tetrahedral-1 sites. This essential tri-layer H (on-surface)-Mg (top-layer)-H (sub-surface) structure has been discovered in earlier ab initio studies of hydrogen adsorption in the Mg basal plane, and is postulated to serve as a potential precursor for the development of the bulk hydride phase within Mg due to its notable parallels in both structural and electronic characteristics with MgH_2 [163, 321]. Therefore, the stability region overlap between the bulk Mg hydride and the tri-layer hydride phase in the sub-surface Pourbaix diagram not only underscores the shared electrochemical stability characteristics of the bulk hydride and its precursor but also serves as empirical validation for our simulation findings against experimental data.

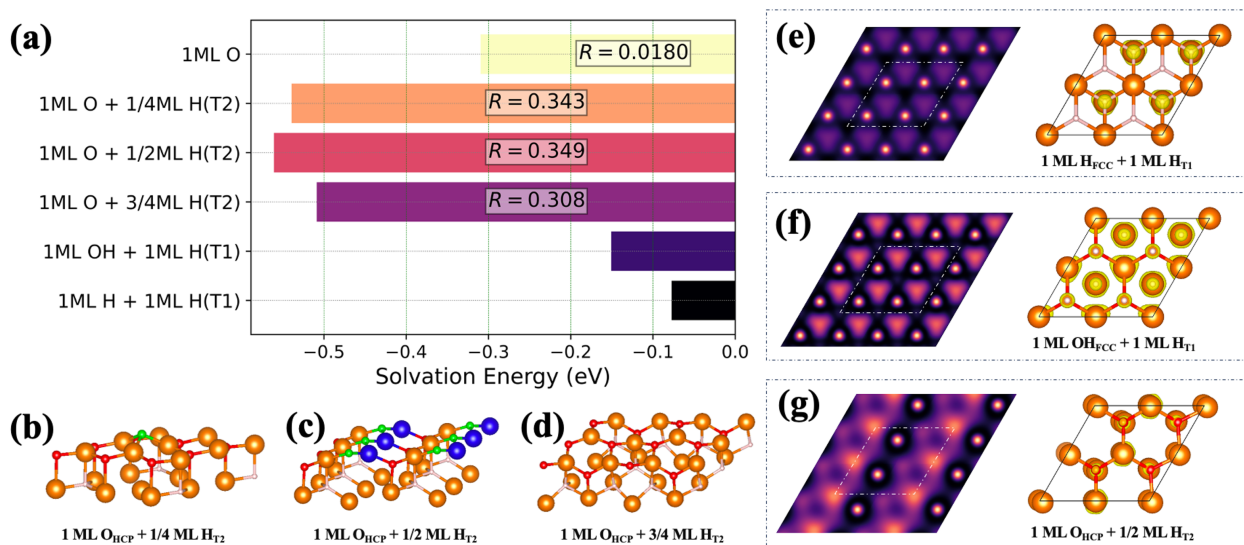


Figure 6.6: (a) Solvation energy of the electrochemically stable configurations of the Mg (0001) surface with sub-surface hydrogen adsorption; (b)-(d) side view of the surface geometries for the Mg (0001) surface with 1 ML O at hcp sites and different coverages of H (ranges from 1/4 ML to 3/4 ML) at sub-surface tetrahedral-2 site; (e)-(g) simulated STM images of three typical on-surface and sub-surface hybrid adsorption configurations: 1 ML H at fcc sites + 1 ML H at tetrahedral-1 sites, 1 ML OH at fcc sites + 1 ML H at tetrahedral-1 sites and 1 ML O at hcp sites + 1/2 ML H at tetrahedral-2 sites.

In Figure 6.6 (e)-(g), the simulated STM images of the Mg (0001) surfaces with on-surface

adsorption of H, OH and O plus the sub-surface H adsorption, exhibit significant differences from the corresponding images (see Figure 6.2) for the surfaces solely featuring on-surface adsorption. For the Mg surfaces in the state of on-surface adsorption of H and OH radicals, the subsequent sub-surface adsorption of H reshapes the electron distribution pattern of the surface, resulting in further contrast modifications to the STM images of the surface exhibiting the identical on-surface adsorption configuration yet incorporating these sub-surface hydrides. Adding sub-surface hydrogen into the O-covered Mg surface not only leads to an electron redistribution but also introduces a major geometry change of the surface, *e.g.*, the insertion of sub-surface hydrogen results in a conspicuous unevenness on the surface's top layer, as illustrated in Figure 6.6 (b)-(d), achieved by elevating specific atoms within the uppermost layer. Therefore, the STM images of the surfaces experiencing co-adsorption of on-surface O and sub-surface H undergo a significant reconfiguration when compared to images of the oxidized surfaces: both the contrast and fundamental patterns exhibit striking differences. In this scenario, the presence of the subsurface hydride phase can be ascertained through experimental detection of STM image variations on the Mg (0001) surface across a range of electrochemical conditions.

The alteration in surface geometry resulting from sub-surface hydrogen adsorption also significantly influences the effect of solvation on the surfaces. Figure 6.6 (a) shows the solvation energy for the six electrochemically stable surface configurations identified in the sub-surface Pourbaix diagrams. Evidently, introducing hydrogen into the sub-surface interstitials of the Mg surfaces featuring on-surface adsorption of H or OH has minimal impact on their solvation energy within the implicit solvent, which is due to the smaller surface geometry reconfiguration induced by the sub-surface hydride in these cases. However, the solvation energy of the oxidised Mg surface with an inclusion of the sub-surface H, which experiences significant surface geometry reconstruction and possesses rougher surface morphology, increases tremendously in contrast with the oxidised surface lacking sub-surface hydrides. The surface roughness (R) of these oxidised surfaces was estimated by measuring the variance in the heights of the top-layer atoms, and the value is indicated on the bar charts in Figure 6.6 (a). It is clear that the surface exhibiting the highest roughness (with 1 ML on-surface O adsorption at the hcp sites and 1/2 ML sub-surface H adsorption at the tetrahedral-2 sites) acquires the most negative solvation

energy. A recent ab initio study carried out by Aziz *et al.* attributes this roughness-enhanced (implicit) solvation effect to the presence of the anisotropic surface charge, which results in the solvation cavity approaching the surface more closely, hence increasing the solvent-solute interaction and boosting the solvation energy [337].

As discussed in the previous section, the on-surface Pourbaix diagram highlights fully oxidised surface configurations of Mg that lack a hydrogen source for the NDE under experimental anodic conditions, such as the electrolyte pH of 8 under an electrode potential in the range of -1.6 to -0.6 V_{SHE} . However, when the sub-surface H adsorption surface configurations are included in the surface ensemble, Mg surfaces hosting the sub-surface hydride phase manage to uphold their electrochemical stability even under extremely anodic potentials. For instance, the surface featuring 1 ML O at the on-surface hcp site and 1/4 ML H at the sub-surface tetrahedral-2 site keeps its stability until the potential exceeds 0.38 V_{SHE} (higher than the H_2 stable potential, 0 V_{SHE}) when the solution pH is 8 with the inclusion of the solvent. As the electrode potential varies from cathodic to anodic windows in a weak alkaline solution (as depicted in Figure 6.5 (a)-(b)), regardless of shifts in on-surface adsorption patterns, the sub-surface hydrogen consistently maintains its electrochemical stability, yet the gaseous H_2 phase is less stable than the aqueous water phase at significant anodic potential.

This essential observation from our calculated sub-surface Pourbaix diagram strongly supports the hydride model for the Mg NDE from the thermodynamic aspect: at cathodic polarisation, a Mg hydride bulk-like tri-layer structure forms in an aqueous condition; with an anodically increasing electrode potential, the on-surface hydrogen atoms are progressively lost, transforming into hydrogen gas, while the sub-surface hydride phase retains its electrochemical stability even within the stabilising conditions of bulk water; the stable sub-surface hydride phase consequently acts as an auxiliary hydrogen reservoir for the HER under anodic conditions, contributing to the anodically enhanced hydrogen evolution; the formation and consumption of this sub-surface hydride phase tend to reach an equilibrium at specific electrochemical conditions ultimately, thereby resulting in a consistent anodic hydrogen evolution rate as observed in experiments.

6.4 Micro-kinetic Modelling for Surface-dependent Corrosion Reactions

Until this point, we have investigated the stable configurations of the Mg (0001) surface across different electrochemical conditions. At a specific electrode potential within a solution possessing a specific pH value, the Mg basal plane exhibits a unique adsorption pattern, featuring either solely on-surface adsorption of H, OH and O species from the electrolyte or a hybrid combination of on-surface adsorption along with sub-surface H adsorption. This surface configuration variation concerning the electrochemical conditions further implies a possible potential-pH dependency of the kinetics and mechanism for the corrosion reactions occurring at the Mg/electrolyte interface. Prior research focusing on the reaction pathway and kinetics for the essential aqueous corrosion reaction of Mg, such as the water dissociation reaction and the HER, implicitly assumed a pristine Mg surface as the initial reaction state for the surface, which practically ignores the surface stability under different electrochemical circumstances and consequently introduces bias in analysing the reaction barriers [13, 18, 145, 146]. To evaluate the impact of the surface configurations (resulting from various electrochemical conditions) on the kinetics or mechanism of Mg aqueous corrosion reactions, we estimate the reaction energy barrier of various reaction pathways for water dissociation and the hydrogen evolution process on the electrochemically stable Mg (0001) surfaces featuring typical adsorption patterns in different electrode potential ranges, *e.g.*, single species on-surface H, OH and O adsorption. Moreover, it has been suggested in the previous section that the sub-surface hydride phase could keep its stability under highly anodic polarisation conditions, and contributes to the abnormal anodic hydrogen evolution reaction. We now delve deeper into the reaction pathway leading to the creation of this vital sub-surface hydride phase which is subsequent to the water dissociation reaction and examine the anodic hydrogen evolution reaction which involves the consumption of the sub-surface hydrogen atoms.

6.4.1 Water dissociation reaction pathways on Mg (0001) surfaces

As a necessary preliminary stage for the HER, the interaction between water molecules and the

Mg (0001) surface, as well as the subsequent dissociation of water (also known as the Volmer step), both play pivotal roles in the process of aqueous corrosion of Mg. Earlier kinetic investigations have confirmed that water dissociation on the pristine Mg basal plane is a spontaneous process, characterized by a markedly negative reaction free energy. Moreover, the energy barrier associated with this dissociation process is contingent upon the configuration of the dissociated water molecules: the dissociation of water from a bi-layer water structure necessitates less activation energy compared to that of a water monomer, owing to the intermolecular interactions between water molecules [145, 146]. Similarly, under varying electrochemical conditions, the Mg surfaces featuring different adsorption states interact with water molecules differently, thereby leading to various water dissociation kinetics and energy barriers. In this case, we investigate the water monomer dissociation reaction pathway on three distinct Mg (0001) surfaces: the pristine surface (as a reference for other surface states), the hydrid surface (stable under cathodic conditions), and the entirely oxidised surface (stable under anodic conditions). It is important to note that we do not address the water dissociation reaction on the hydroxylated surface state in this context because it involves a complex HER simultaneously, which will be demonstrated in more details later.

In Figure 6.7 (a), the minimum energy pathway, which defines the reaction coordinates for the water monomer dissociation reaction originating on the pristine Mg (0001) surface, reveals a reaction energy barrier of 0.88 eV. This computationally derived energy barrier aligns correspondingly with previous DFT calculations and is found to be less dependent on solvation [145, 146]. During the reaction, one of the O-H bonds within the water monomer undergoes cleavage, with a subsequent co-adsorption of the dissociated H and OH onto the surface fcc sites. The Bader charge analysis in Figure 6.7(b) indicates that the positively charged H from the water molecule converts to a hydride after being adsorbed on the Mg (0001) surface, thus leading to the monomer dissociation reaction on the pristine surface becoming a typical cathodic reaction:



which could be potentially boosted when the surface is negatively charged, *i.e.*, cathodically polarised.

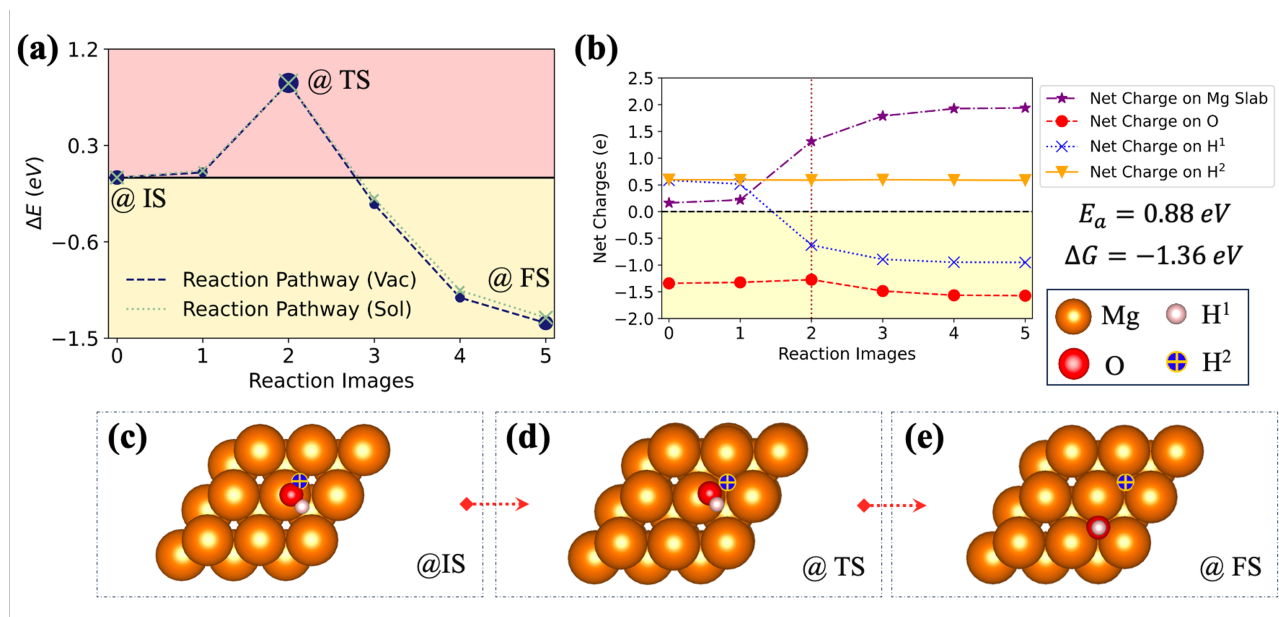


Figure 6.7: Water monomer dissociation reaction on the pristine Mg (0001) surface: (a) the minimum energy pathway of the water dissociation reaction on the clean Mg (0001) surface, as derived from the CI-NEB DFT calculations without/with the implicit solvent model; (b) Bader charge analysis of the dissociated water molecule on the surface; (c)-(e) initial state, transition state and final state of the system.

Based on our calculated surface Pourbaix diagram for the Mg (0001) surface, under cathodic potentials, the basal plane of Mg experiences stabilisation due to the adsorption of 1 ML hydrogen atoms at fcc sites. The presence of this hydride layer on the surface has the potential to significantly influence the interaction between the water monomer and the surface, hence playing a pivotal role in shaping the behaviour of water dissociation. Figure 6.8 (a) shows that the water monomer dissociation process on the Mg (0001) surface featuring on-surface H adsorption experiences a two-step energy climbing procedure, with different reaction energy barriers of 0.27 eV and 0.30 eV respectively, and finally forms a thermodynamically stable sub-surface hydride phase (the reaction free energy is -2.12 eV). Referring to the essential surface geometry configurations along the reaction pathway as demonstrated in Figure 6.8 (b)-(e), the initial transition state (TS₁) of the water monomer dissociation on the hydride surface involves a H-O-H bond angle torsion for water molecule of 109.33°, and the second transition state (TS₂) indicates the O-H bond breaking procedure, along with one on-surface fcc H (labelled as H₁) diffusing into the sub-surface tetrahedral-1 site.

It is evident that the water dissociation process on the Mg (0001) surface benefits from the

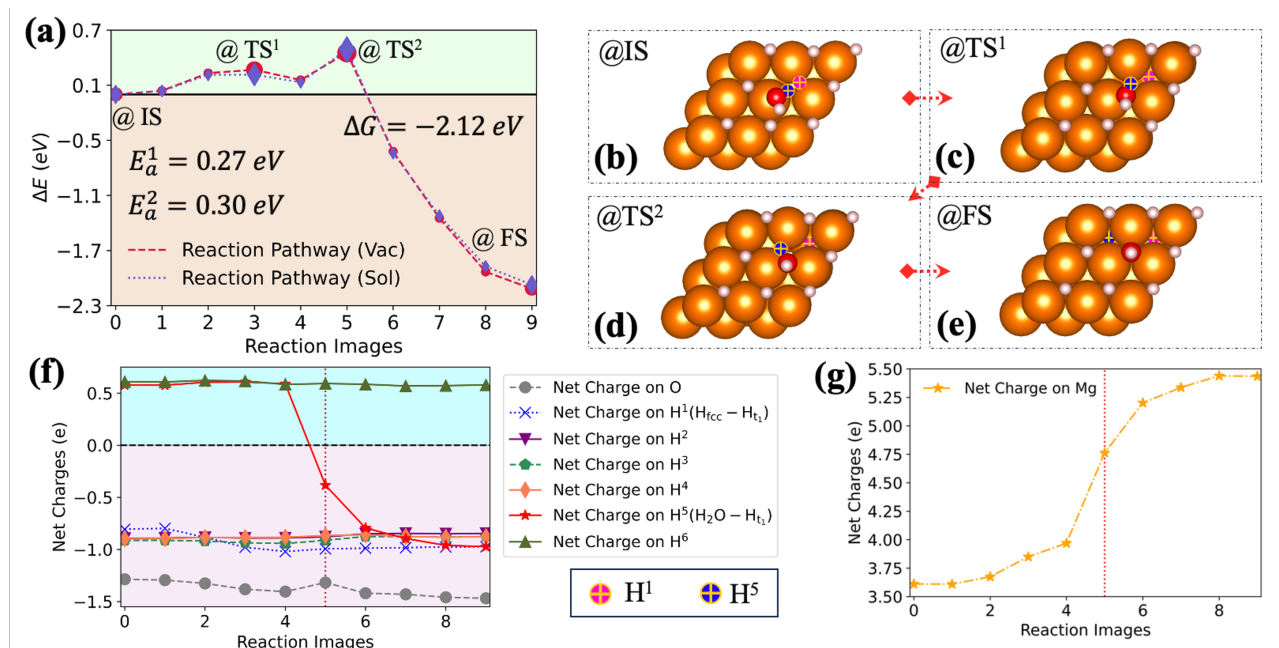


Figure 6.8: Water monomer dissociation reaction on the 1 ML H-covered Mg (0001) surface: (a) the minimum energy pathway of the water dissociation reaction on the hydride Mg (0001) surface, as derived from the CI-NEB DFT calculations without/with the implicit solvent model; (b)-(e) initial state, transition state 1, transition state 2 and final state of the system; (f)-(g) Bader charge analysis of the dissociated water molecule and Mg atoms within the surface.

on-surface hydrogen atoms because of the intricate interplay between the positively charged H (H₅) within the water molecule and the negatively charged H (H₁) located on the surface. This H⁻ – H⁺ interaction is validated through Bader charge analysis of the system: the on-surface H which interacts with the H of the water molecule exhibits a marginally more positive net charge in comparison to the other surface H atoms. Hence, on the hydride Mg surface, the energy barrier for the dissociation of a water monomer decreases by almost a third compared with that on a pristine Mg surface.

Furthermore, to accommodate the dissociated OH and H from the water monomer, the surface eventually arranges itself into a more stable sub-surface hydride phase with the dissociated H and the corresponding interacting on-surface H located at a tetrahedral-1 site. This reaction pathway unveils a potential mechanism for the creation of sub-surface hydride phases within Mg surfaces exposed to aqueous conditions, further supporting their presence during Mg aqueous corrosion, but now from a kinetic perspective. During the water dissociation and hydride formation process, the overall net charge of the Mg slab (excluding all adsorbates) becomes more positive as it approximately donates two electrons to the adsorbed OH (on-surface fcc

site) and H (sub-surface tetrahedral-1 site), which demonstrates a charge-transfer that is similar between this case and the situation where water dissociates on the pristine surface.

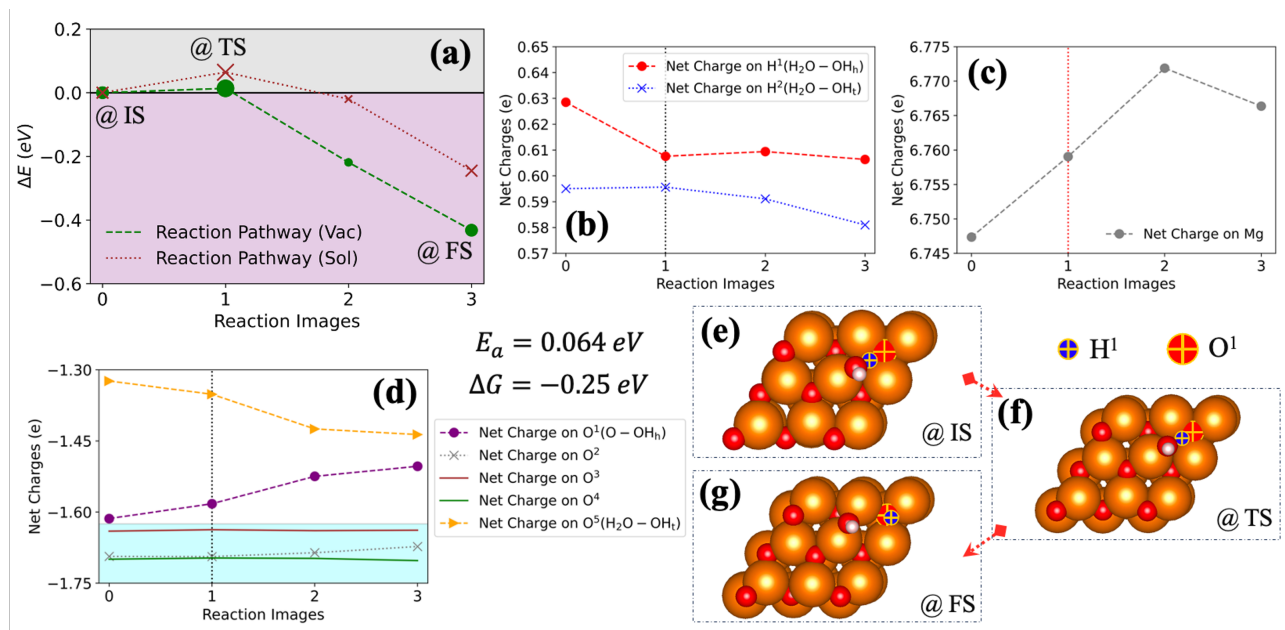


Figure 6.9: Water monomer dissociation reaction on the 1 ML O-covered Mg (0001) surface: (a) the minimum energy pathway of the water dissociation reaction on the oxidised Mg (0001) surface, as derived from the CI-NEB DFT calculations without/with the implicit solvent model; (b)-(d) Bader charge analysis of the H atoms from the dissociated water molecule, the Mg atoms within the surface, and the O atoms from the water monomer or on the surface. OH_t labels the on-top adsorbed hydroxyl groups directly dissociated from the water molecule, and OH_h labels the hydroxyl in a hollow site converted from the surface oxygen; (e)-(g) surface geometries of the initial state, transition state and final state along the reaction pathway.

In the previous section, we found that the interaction between the on-surface hydrogen (negatively charged) and the hydrogen within the water molecule have a remarkable ability to diminish the dissociation energy of water monomers by weakening the strength of the O-H bond. This catalytic effect provided by the on-surface adsorbates for the water dissociation reaction is also available on the O-covered Mg (0001) surface. Illustrated in Figure 6.9 (e)-(g), the initial stages of water monomer dissociation on the oxidised Mg basal plane encompass a series of events: the cleavage of the O-H bond, the acquisition of the H atom by the on-surface O atom (forms the OH_h), and the subsequent surface hydroxylation which leads to the deposition of additional hydroxyl groups (OH_t) onto the surface. The minimum energy pathway in Figure 6.9 (a) demonstrates that the water dissociation reaction on the oxidised Mg (0001) surface is nearly barrier-free, with an exceptionally low energy barrier of 0.064 eV when solvation is

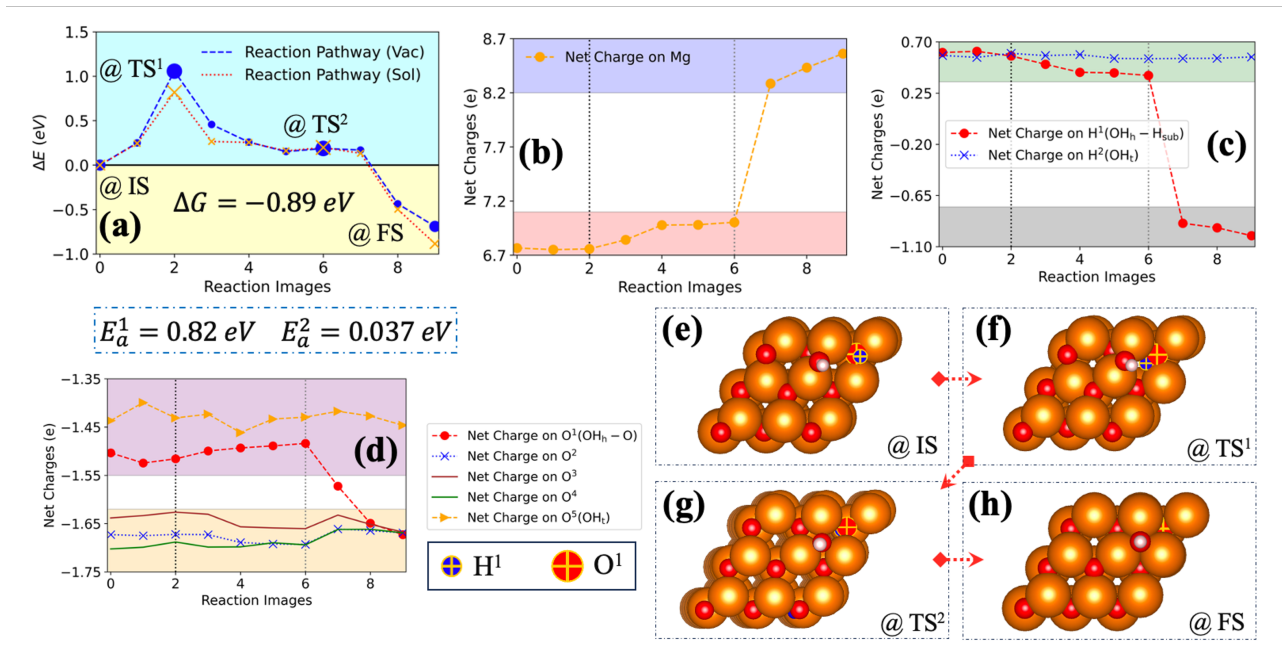


Figure 6.10: Sub-surface hydride formation reaction following the water dissociation reaction on the 1 ML O-covered Mg (0001) surface: (a) the minimum energy pathway of the sub-surface hydrogen formation reaction; (b)-(d) Bader charge analysis of the Mg atoms within the surface, the on-surface and sub-surface H atoms and the O atoms on the surface; (e)-(h) surface geometries of the initial state (which is the final state of the preceding water dissociation reaction), two transition states and final state along the reaction pathway.

considered. This low barrier of water monomer splitting on the oxidised surface stems from the interplay between the surface oxygen and hydrogen within the water monomer, and enhances the probability of water dissociation on the oxidised Mg surface, providing more available hydrogen atoms for the HER. The oxygen atoms located on the surface is more negatively charged than the on-surface hydrogen atoms, thereby leading to a more intense connection to the positively charged hydrogen within the water molecule. Consequently, this interaction between the surface oxygen and water hydrogen sets the stage for an almost effortless water dissociation reaction, with the transformation of a surface oxygen into a surface hydroxyl accompanied by the capture of the dissociated hydrogen atom. Furthermore, this water dissociation reaction has a minimal impact on the overall charges retained by the Mg surface, as indicated by Bader charge analysis. This is primarily because this reaction predominantly revolves around the interaction between the water monomer and the surface oxygen atoms, rather than involving Mg atoms directly.

It is also worth noting that the reaction pathway is influenced significantly by solvation, *i.e.*, the energy of the subsequent reaction states referenced to the initial state are shifted

more positively within the implicit solvent environment. This is because this reaction pathway involves an essential surface state conversion from a fully oxidised configuration to a hybrid adsorption of O and OH. As discussed previously, the oxidised surface is more stabilised by the solvent than by the hydroxylated surface, resulting in a more negative solvation energy of the initial reaction state (fully oxidised) than that of the following images (less oxidised yet more hydroxylated).

Like water monomer dissociation on the hydride Mg (0001) surface, the dissociated hydrogen atom from the water molecule exhibits the potential to migrate into the subsurface interstitials following its adsorption onto the on-surface oxygen of the oxygen-covered surface. Figure 6.10 (a) reveals that this sub-surface hydride formation reaction encompasses two distinct energy barriers, which refer to the rotation of the O-H bond (with a barrier of 0.82 eV), and the breaking of the O-H bond within the sub-surface region (with a barrier of 0.037 eV) respectively. This sub-surface hydride formation process, which is subsequent to the water dissociation reaction on the O-covered Mg surface, happens simultaneously thanks to its favourable negative reaction free energy (-0.89 eV), and requires the metal surface supplying two electrons to stabilise the negatively charged sub-surface hydride phase. Hence, applying a cathodic potential promotes the creation of sub-surface hydrogen within the Mg surface. This observation aligns with the experimental conditions (*i.e.*, negatively charged Mg electrode) required to stabilise the hydride phase within Mg while undergoing aqueous corrosion.

6.4.2 General HER pathways with on-surface hydrogen atoms on Mg (0001) surfaces

The hydrogen evolution reaction (HER) is an essential reaction during the aqueous corrosion of Mg, closely associated with some important corrosion phenomena, such as the NDE and the formation of filaments on the surface [162]. Theoretically, the hydrogen evolution process on the Mg (0001) surface could either follow the Tafel reaction pathway:



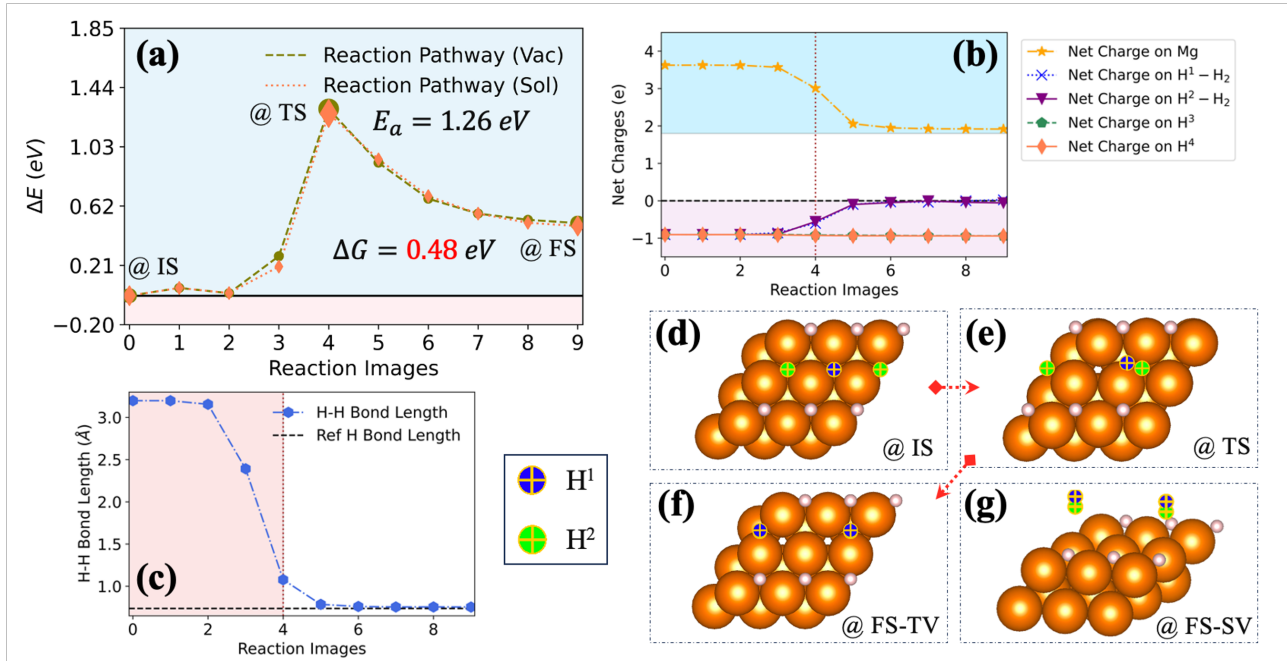


Figure 6.11: Tafel-mechanism hydrogen evolution reaction on the 1 ML H-covered Mg (0001) surface: (a) the minimum energy pathway of the Tafel-mechanism hydrogen evolution from the hydride Mg (0001) surface; (b) Bader charge analysis of the Mg atoms within the surface and the on-surface H atoms; (c) The H-H (desorbed from the surface) distance evolution along the reaction pathway, with the dashed line corresponding to the referenced bond length of H₂ [25]; (d)-(g) surface geometries of the initial state, transition states and top-view (TV) or side-view (SV) of the final state along the reaction pathway.

or the Heyrovsky pathway:



However, recent ab initio studies have found that the HER on the Mg basal plane is more likely to happen by the Heyrovsky mechanism because of its lower reaction energy barrier and more negative reaction free energy relative to the Tafel mechanism [18, 35, 145, 146]. To further determine the influence of the surface states (*i.e.*, electrochemical conditions) on the HER mechanism and kinetics on the Mg (0001) surface, here we investigate the general HER (only involves the on-surface H atoms) through the Tafel or Heyrovsky-like (we use water molecules rather than the hydronium to react with on-surface hydride to circumvent the introduction of complex ions into the system) pathway on the stable Mg surface configurations in different electrochemical environments, *e.g.*, the 1 ML H-covered surface and the 1 ML OH-covered

surface.

Under cathodic potentials, the Mg (0001) surface exhibits a high propensity for being covered by 1 ML hydrogen atoms positioned at the on-surface fcc sites, thus leading to the HER possibly occurring on the surface either through the Tafel or the Heyrovsky mechanism. Figure 6.11 (a) shows the minimum energy pathway of the Tafel HER on the completely hydride Mg (0001) surface. This Tafel HER on the Mg surface with 1 ML H atoms involves the detachment of two hydrogen atoms from the fcc hollow sites on the surface, followed by their recombination into a neutral H₂ molecule. Consistent with the preceding DFT computations, we note a parallel observation that the Tafel-based HER on the hydride Mg basal plane presents itself as an endothermic process, featuring a reaction free energy of 0.48 eV [18, 146]. Furthermore, this scenario is characterised by a relatively elevated energy barrier, amounting to 1.26 eV. These results hence indicate the significant impracticality of the Tafel-based HER on the Mg (0001) surface under aqueous conditions, despite a high hydrogen coverage on the metal surface. According to the Bader analysis of the system in Figure 6.11 (b), this Tafel-mechanism HER is a typical anodic HER rather than a charge-free reaction:



The desorption process of the on-surface H atoms requires the de-electronation of the H atom which is energetically unfavourable (according to the H adsorption studies in Chapter 5), thus leaving two electrons within the Mg surface and leading the surface Mg atoms to become less positively charged. While this reaction pathway displays an anodic characteristic, which could be potentially prompted by the anodic polarisation of the Mg electrode, the prospect of HER through this mechanism remains unfeasible on the Mg surfaces even at anodic potentials. This is because the surface configuration featuring adsorption of the on-surface hydrogen atoms, which provides the on-surface reactant H atoms for the Tafel HER, is observed to be electrochemically unstable at anodic potentials as suggested by our calculated surface Pourbaix diagram.

Unlike the energetically unfavourable Tafel HER on the hydride Mg (0001) surface, the Heyrovsky-like HER as shown in Figure 6.12, exhibits a negative reaction free energy (-1.35

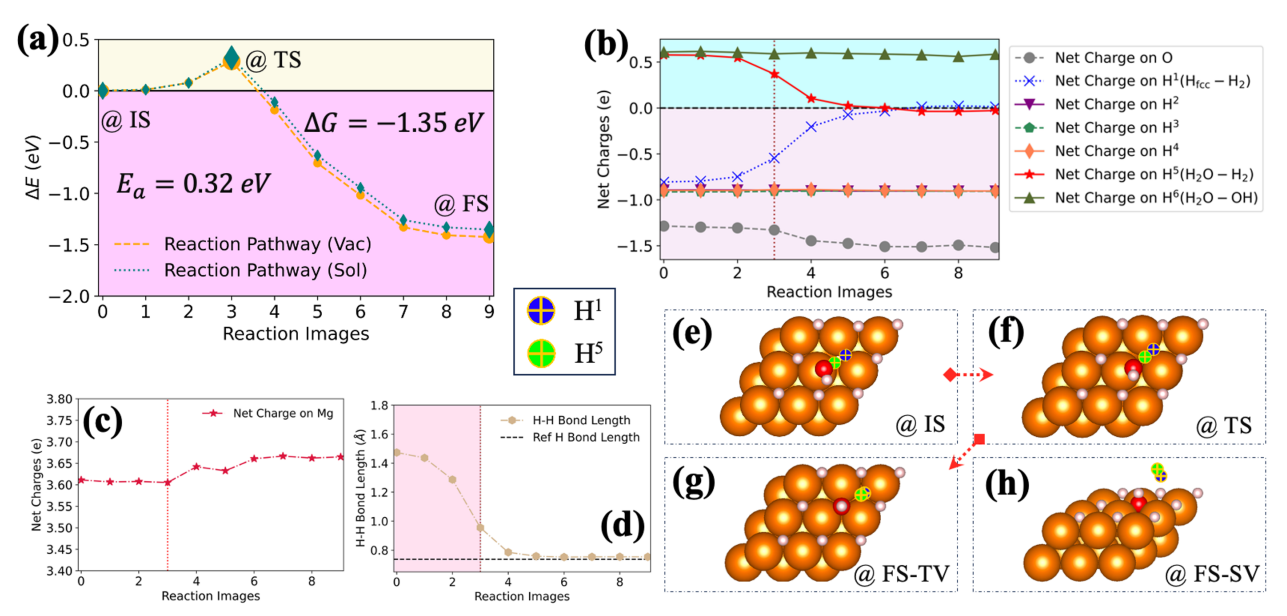


Figure 6.12: Heyrovsky-like hydrogen evolution reaction on the 1 ML H-covered Mg (0001) surface: (a) the minimum energy pathway of the Heyrovsky-like hydrogen evolution from the hydride Mg (0001) surface; (b)-(c) Bader charge analysis of the water molecule, the on-surface H atoms and the Mg atoms within the surface; (d) The H-H distance evolution along the reaction pathway; (e)-(h) surface geometries of the initial state, transition states and top-view (TV) or side-view (SV) of the final state along the reaction pathway.

eV), and a modest reaction energy barrier (0.32 eV). The outcomes obtained here align well with earlier DFT investigations on the Heyrovsky HER happening on the Mg (0001) surface [18, 146]. Akin to the water dissociation reaction followed by the sub-surface hydride formation on the hydride Mg (0001) surface, this Heyrovsky-like HER in conjunction with the water dissociation is also efficiently activated by the presence of on-surface hydrides, which contributes to a notably low energy barrier for the reaction. During the progression of the reaction, a hydrogen atom within the water molecule engages with the on-surface hydride, initiating a sequence wherein the $\text{H}^+ - \text{H}^-$ pair subsequently recombines to form a neutral H_2 molecule above the surface. Additionally, the dissociated hydroxyl from this process adsorbs onto the fcc site of the surface. As indicated by the Bader charge analysis (Figure 6.12 (b)-(c)) of the system, during the Heyrovsky-like hydrogen evolution process, the net charge of the Mg surface barely changes, thus rendering the following reaction mechanism:



This reaction pathway highlights that the surplus electrons needed for the Heyrovsky HER are not sourced from the electrode (as shown in Equation 6.8), but rather are directly furnished by the on-surface hydride [151]. Although it relies less on the electrons supplied by the electrode, the Heyrovsky-like HER on the Mg (0001) surface remains a cathodic-potential favorable process. This is because that the concentration (coverage) of the crucial reactant, specifically the hydride phase on the surface, is notably influenced by the electrochemical conditions, *i.e.*, the electrode potential and the pH of the solution. Under cathodic potentials, the on-surface hydrogen atoms exhibit enhanced electrochemical stability, resulting in elevated reactant coverage and an acceleration of the reaction rate. Conversely, under anodic potentials, the stability of the on-surface hydride on the Mg surface diminishes, with a decrease of the H coverage on the surface, impeding the progression of this HER process.

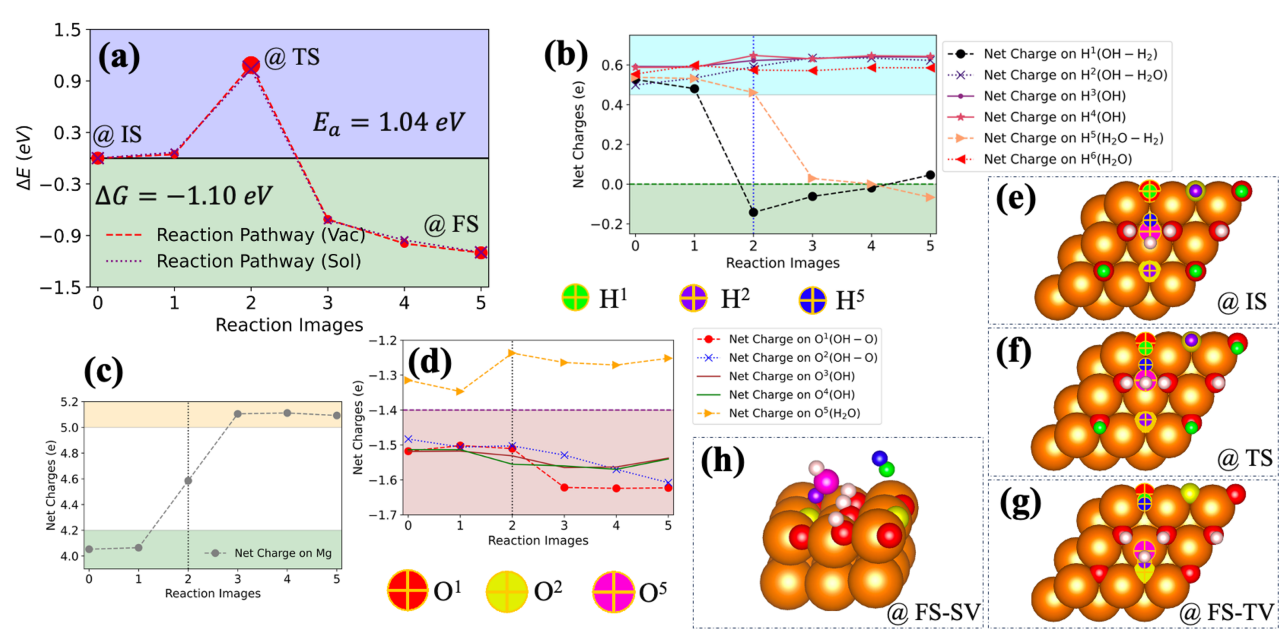


Figure 6.13: Water-catalysis HER on the 1 ML OH-covered Mg (0001) surface: (a) the minimum energy pathway of the hydrogen evolution with water molecule as catalyst from the hydroxylated Mg (0001) surface; (b)-(d) Bader charge analysis of the H atoms of water molecule or on-surface OH radicals, the Mg atoms within the surface and the O from the OH groups; (e)-(h) surface geometries of the initial state, transition states and top-view (TV) or side-view (SV) of the final state along the reaction pathway.

As the electrode potential shifts from an intensely cathodic range to less negative potentials, the hydride Mg (0001) surface undergoes a gradual transformation. During this process, the dominant phase of the Mg surface shifts from the on-surface hydrides towards the on-surface

hydroxides. The hydroxylated Mg (0001) surface demonstrates a simultaneous dissociation of water monomers alongside an unconventional hydrogen evolution process. This atypical HER involves a unique combination of hydrogen atoms originating from both water molecules and the on-surface OH groups, with the presence of water monomers significantly facilitating this intricate reaction. In Figure 6.13(a), we present the minimum energy pathway of this HER on the 1 ML OH-covered Mg (0001) surface, which exhibits a reaction free energy of -1.10 eV and an energy barrier of 1.04 eV under aqueous conditions. At the early stage of the reaction, a water monomer is initially adsorbed at the bridge site between two on-surface OH groups (see Figure 6.13 (e)), with an observable interaction between the water's oxygen and hydrogen atoms from the hydroxyls. Subsequently, the influence of the nearby H atom (denoted as H¹) from another hydroxyl on the surface causes a gradual weakening of one of the O-H bonds within the water molecule. This attraction effect leads to the eventual rupture of the O-H bond, facilitating the release of a dissociated hydrogen atom from the water monomer, which combines with the hydrogen from the adjacent hydroxyl group to form a stable H₂ molecule. Simultaneously, the dissociated OH radical originating from the water molecule locates itself close to the center of three on-surface hydroxyls as shown in Figure 6.13 (g), from where it can easily capture a hydrogen atom from the underneath hydroxyl radicals to stabilise itself, thus restoring itself to a water-like geometry above the surface (see Figure 6.13 (h)). As a result, throughout the hydrogen evolution process occurring above the hydroxylated Mg (0001) surface, the water monomer presents a catalytic-like behaviour. Its initial dissociation plays a pivotal role in facilitating the onsite HER, followed by the subsequent capture of hydrogen (by the dissociated OH group) which serves to restore both stability and the geometric configuration resembling a water molecule. Based on the Bader charge analysis for this unique HER, the entirely hydroxylated Mg (0001) surface undergoes an electron loss of approximately 1 e^- over the reaction, finally converts to a 0.5 ML O-covered and 0.5 ML OH-covered surface, with the release of two hydrogen atoms from the surface to form a H₂ molecule and the reconstituted water molecule:



Thus the process of HER taking place on the hydroxylated Mg (0001) surface requires not only

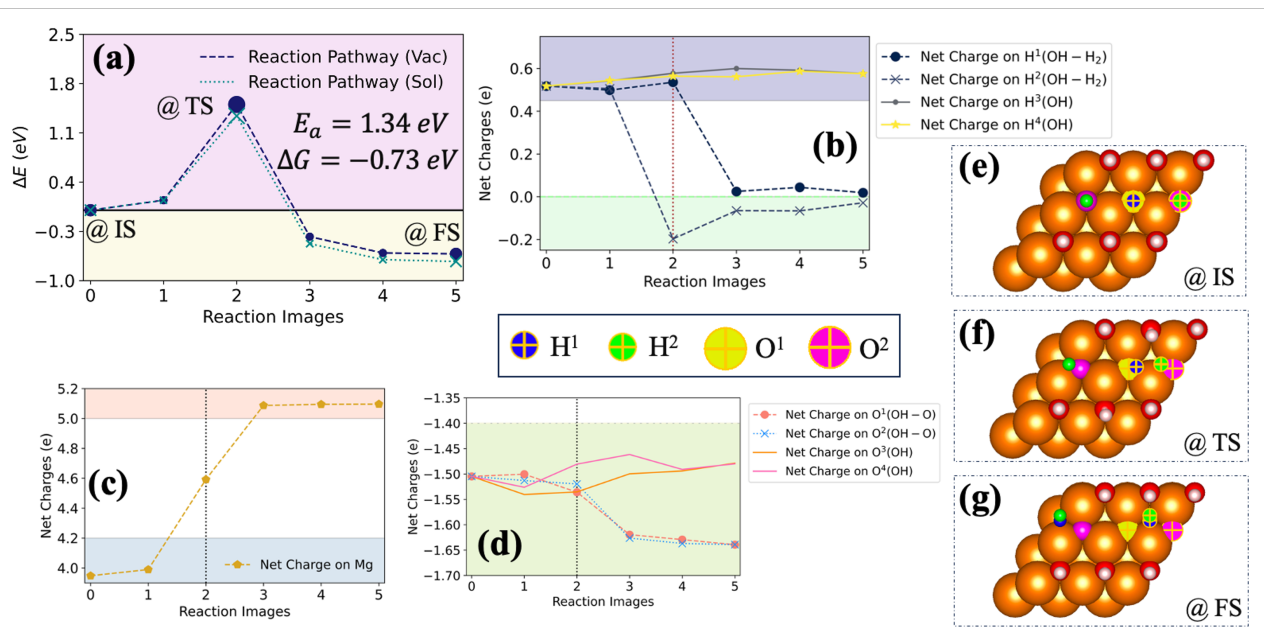


Figure 6.14: HER on the 1 ML OH-covered Mg (0001) surface: (a) the minimum energy pathway of the hydrogen evolution directly from the hydroxylated Mg (0001) surface; (b)-(d) Bader charge analysis of the H atoms of the on-surface OH radicals, the Mg atoms within the surface and the O from the OH groups; (e)-(g) surface geometries of the initial state, transition states and the final state along the reaction pathway.

the initiation facilitated by water monomer dissociation but also cathodic polarisation of the electrode, which ensures the availability of a surplus of electrons contributing to the progression of the reaction.

To further verify the catalytic effect of the water monomer for the HER initiating from the hydroxylated Mg (0001) surface, we investigate the HER occurring on the 1 ML OH-covered Mg (0001) surface without the aid of the adsorbed water molecule. As shown in Figure 6.14, the inherent charge transfer (augmented by cathodic conditions) that underlies the HER process in the absence of water on the hydroxylated Mg surface parallels what is observed when the water monomer is present. However, an intriguing distinction emerges: with the water molecule absent from the surface, there is a rise of approximately 0.3 eV in the energy barrier, along with a corresponding reduction of 0.4 eV in the free energy of the HER. This insight confirms the significance of the presence of the water monomer in catalysing the HER on the hydroxylated Mg surface, whose dissociation both stabilises the final state of the reaction and substantially diminishes the energy barrier associated with the reaction. Compared with the O-H bonds within brucite, the O-H bonds for the hydroxyl groups on the Mg (0001) surface exhibit an

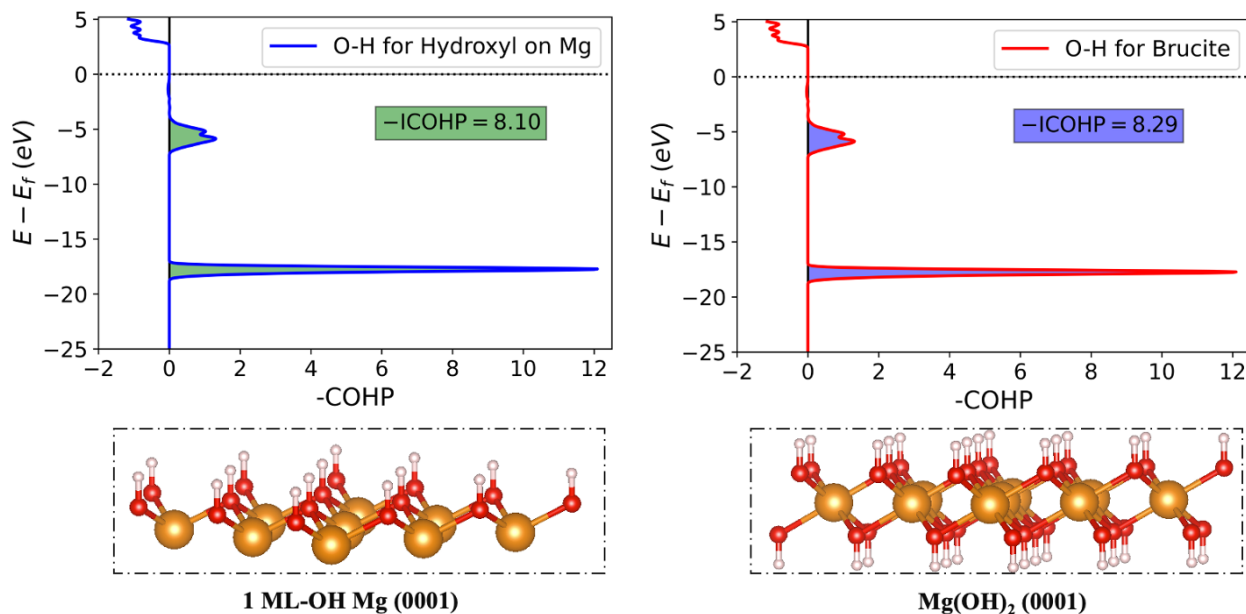


Figure 6.15: COHP analysis of the O-H bond for the hydroxyl groups on the Mg (0001) surface, or for those of the brucite (0001) surface. Higher value of the -ICOHP indicates a stronger bond strength.

elongated bond with reduced strength, according to the COHP analysis (see Figure 6.15). This divergence is attributed to the stronger Mg-O interaction on the metal surface than that on the hydroxide surface. Specifically, the Mg atoms on the metallic surface possess a surplus of electrons, thereby engendering stronger interactions with the oxygen atoms from the hydroxyl groups (meanwhile weakening the O-H interaction) in comparison to those originating from the brucite structure. Consequently, water molecules are more prone to dissociate and cleave the O-H bonds of the hydroxyl radicals on the Mg (0001) surface compared with those on the brucite surface, thereby increasing the possibility of the occurrence of the aforementioned water-catalysed HER.

In addition, unlike the H or the O-covered Mg surfaces, we find that on the OH-covered Mg (0001) surface, the dissociated hydrogen atoms from the water molecule encounter notable challenges in diffusing into the sub-surface region and forming the hydride phase. Conversely, the hydrogen atoms within the on-surface OH radicals tend to capture and react with the dissociated hydrogen atoms easily, indicating the role of the on-surface OH layer as a hindrance to the hydrogen penetration and sub-surface hydride formation within the Mg surface.

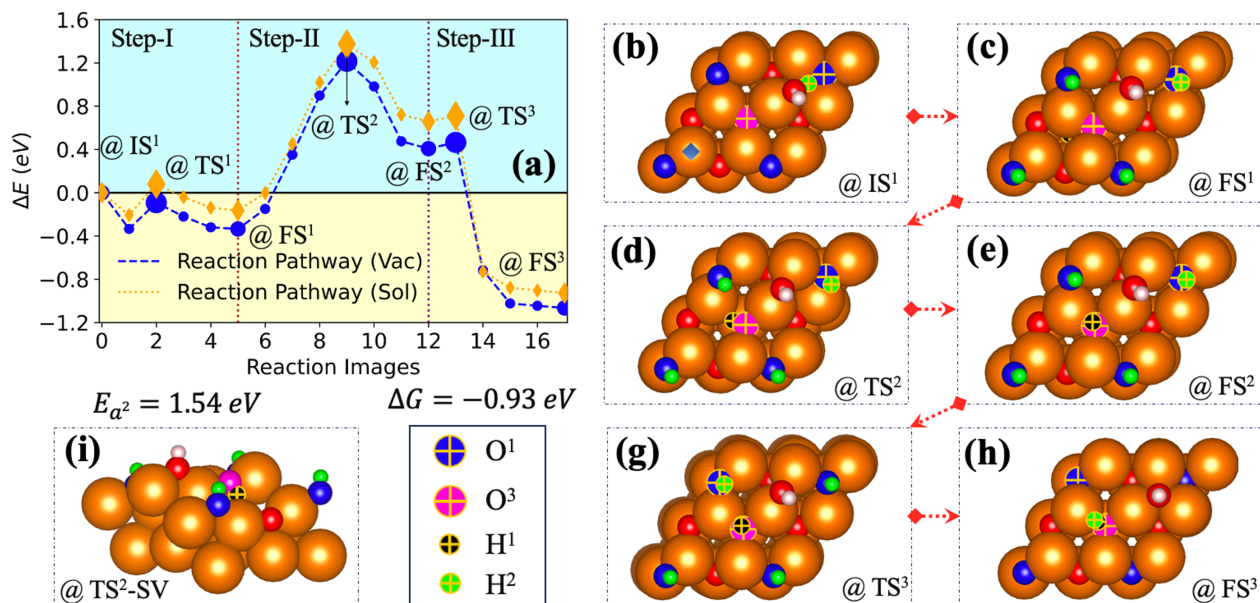


Figure 6.16: HER on the 1 ML O + 0.25 ML H_{sub} -covered Mg (0001) surface: (a) the minimum energy pathway of the hydrogen evolution involving the sub-surface hydride within the oxidised Mg (0001) surface. This complex reaction pathway is composed of three essential steps: the water dissociation process (with sub-surface hydrogen interior diffusion), sub-surface outward diffusion with its combination with on-surface oxygen, and the hydrogen evolution reaction from the H of hydroxyls; (b)-(h) surface geometries of the initial state for step I (the blue diamond indicates the starting position underneath the top surface layer of the sub-surface hydrogen), final state for step I (initial step for step II), transition state for step II, final state for step II (initial step for step III), transition state for step III and the final state for step II along the reaction pathway; (i) Side-view (SV) of the transition state for the step II for the overall reaction.

6.4.3 HER pathways with sub-surface hydrides in Mg (0001) surfaces

In the previous section we uncovered the reaction pathway for the HER on the Mg basal plane, with the participation of the on-surface hydrogen atoms either through the Tafel or the Heyrovsky-like mechanism. However, with an increase of the electrode potential from cathodic to anodic ranges, these on-surface hydrogen atoms continue to be consumed, hence curtailing the on-surface HER and ultimately leading to the formation of an oxide surface at significantly anodic polarisation. To further elucidate the experimental observation of the anodically enhanced HER (NDE) during Mg aqueous corrosion, we need to search for an alternative HER pathway that is feasible under anodic potentials with an available surface phase capable of supplying hydrogen for the reaction. Based on the calculated Mg (0001) surface Pourbaix diagram that includes sub-surface hydrogen adsorption, the sub-surface hydride phase, which potentially

serves as a source for the hydrogen evolution, maintains its electrochemical stability even under conditions of high anodic polarisation. At present, owing to the absence of both experimental and theoretical investigations, it remains unclear what the reaction pathway and mechanism of the HER involving the sub-surface hydride phase is at anodic potentials. We thus explore the detailed reaction pathway for the Heyrovsky-like HER with depletion of the sub-surface hydride from the most thermodynamically stable surface configuration at a strongly anodic potential (*e.g.*, at 0.38 V_{SHE}), namely the surface with adsorption of 1 ML O at on-surface hcp sites and 0.25 ML H at sub-surface tetrahedral-2 sites as suggested by the calculated Pourbaix diagram. We also inspect the charge state evolution for the key reactant species throughout the reaction.

In Figure 6.16, we present the reaction pathway for the Heyrovsky-like HER that incorporates the sub-surface hydride, taking place on the fully oxidised Mg (0001) surface. This illustration showcases a complex minimum energy pathway for this remarkable HER, which includes three distinct sub-steps crucial for accomplishing the ultimate hydrogen evolution, with a reaction free energy of -0.93 eV. The initial sub-step within the overall reaction pertains to a water dissociation process occurring on the surface, coupled with the internal diffusion of sub-surface hydrogen through the sub-surface interstitials. Akin to the water dissociation reaction observed on the 1 ML O-covered Mg (0001) surface, when a water monomer splits on the Mg surface in an identical on-surface adsorption state yet with the presence of additional sub-surface hydrogen, it displays a barrier-free and spontaneous reaction. This results in the formation of energetically more stable dissociation radicals that readily adsorb to the surface. The significant energy barrier noted in the first sub-step reaction (0.29 eV) mainly arises from the migration of the sub-surface hydrogen, originally located at the sub-surface tetrahedral-2 site, to the sub-surface position beneath an on-surface oxygen atom at the end of the sub-step reaction (as shown in Figure 6.16 (c)). The subsequent reaction includes the outward diffusion of the sub-surface hydrogen to an on-surface state, facilitated by the presence of the on-surface oxygen atom where they combine into a hydroxyl radical. This sub-step reaction pathway is shown in Figure 6.16 (c)-(e): initially the sub-surface hydrogen gradually approaches the contiguous upward oxygen atom till a pointing-down covalent O-H bond forms; in the following reaction there is a rotation of the freshly generated O-H bond from a downward orientation to an upward orientation, successfully

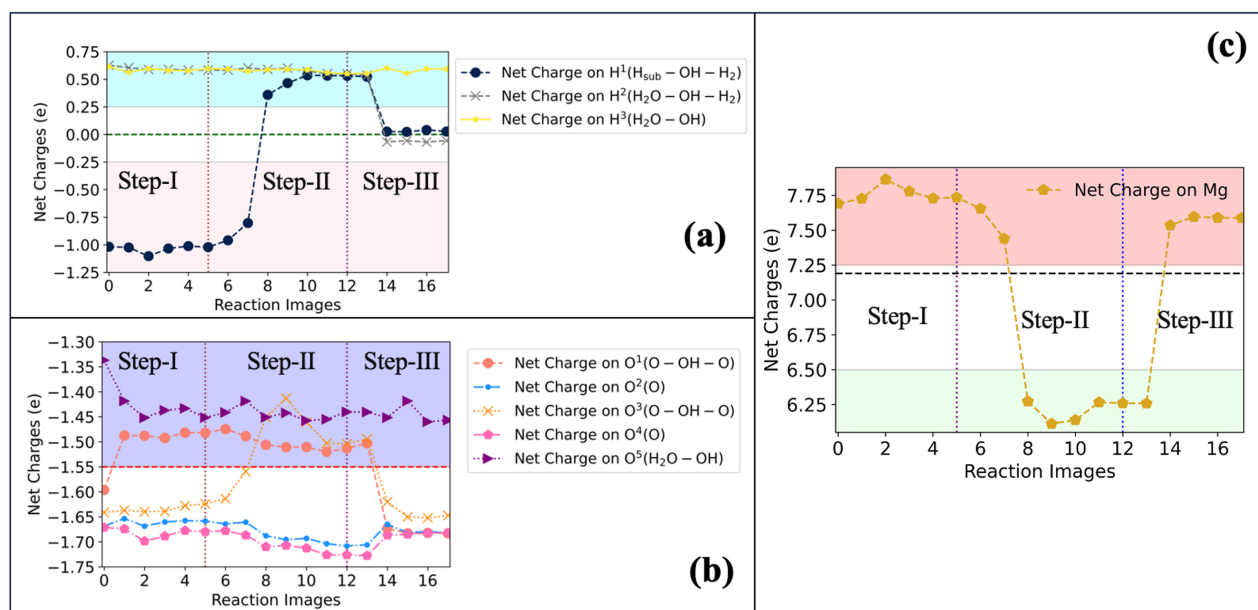


Figure 6.17: Bader charge analysis of the HER on the 1 ML O + 0.25 ML H_{sub} -covered Mg (0001) surface: (a) Net charges on H atoms that form sub-surface interstitials and on H atoms from the water monomer; (b) Net charges on O atoms adsorbed at the surface hcp hollow sites and on those from water molecules; (c) Net charges on the Mg (0001) surface.

transporting the sub-surface hydrogen to on-surface hydrogen within a hydroxyl group. It is worth noting that this specific process of hydrogen outward diffusion and hydroxyl recombination can be considered the reverse procedure of the hydride formation reaction previously discussed on the fully oxidised Mg surface. However, the energy barrier associated with this sub-step reaction is high, having a value of 1.54 eV, indicating that this particular process might serve as the rate-determining step for the overall HER involving sub-surface hydrogen. In the final sub-step reaction, the newly formed hydroxyl radical undergoes a reaction with a neighbouring hydroxyl, resulting in the evolution of a hydrogen molecule from the surface, characterised by an energy barrier less than 0.1 eV. It is crucial to emphasise that, instead of the intuitive perspective of the direct interaction between the positively charged on-surface hydrogen and the negatively charged sub-surface hydrogen in the sub-surface hydride involved hydrogen HER, the pivotal role in transporting the sub-surface hydrogen to the top of the Mg surface is played by the on-surface oxygen atom.

The Bader charge analysis (see Figure 6.17) shows that in the first sub-step reaction, the water dissociation reaction along with the sub-surface hydrogen diffusion within the surface

barely alters the net charges on the hydrogen atoms or those on the Mg surface. However, the water dissociation process induces a marginal alteration of the charge on the oxygen atom within the water molecule and one of the surface-adsorbed oxygen atoms that captures the dissociated hydrogen atom from the water monomer. As the oxygen atom within the water monomer dissociates from the molecule into a hydroxyl group, it acquires an elevated negative charge and engages in a more intensive interaction with the Mg surface. On the contrary, when the on-surface oxygen combines with the dissociated hydrogen, it weakens its bond with the surface, resulting in a more positive charge on the oxygen atom.

For the outward diffusion of the hydrogen from the sub-surface interstitial locations to the on-surface sites, accompanied by the recombination with the on-surface oxygen atom, the net charge on the sub-surface hydrogen varies drastically from a significant negative state ($-1\ e$) to a positive value ($0.5\ e$). Meanwhile, the oxygen atom on the surface, which seizes the sub-surface hydrogen to form a hydroxyl, undergoes a fractional reduction in its negative charge because of its reduced interaction with the Mg surface. As a consequence, this particular transition process from sub-surface hydrogen to on-surface hydrogen displays a noteworthy anodic feature:



Thus is challenging under open circuit conditions because of both reaction thermodynamics and kinetics (*i.e.*, with a remarkably positive reaction free energy and an exceedingly high energy barrier), effectively limiting the decomposition of the sub-surface hydride phase. To counterbalance the surplus of electrons mainly generated by the sub-surface hydride during this sub-step reaction, the metal surface shifts to a less positively charged state, with an overall reduction of the surface net charge from $+7.75\ e$ to $+6.25\ e$. When the Mg electrode experiences anodic polarisation, electrons in the system are being constantly pumped out from the metal, thereby promoting the anodic sub-step of the sub-surface hydride transformation reaction, which acts as the rate-limiting step for the entire HER. Consequently, this charge state modification of the slab accelerates the subsequent hydrogen evolution process by boosting the conversion of sub-surface hydrogen to an on-surface state, making a significant contribution

to the enhancement of the anodic HER rate, or the experimentally observed NDE during Mg aqueous corrosion. The last sub-step reaction of this distinctive sub-surface hydrogen HER requires a cathodic-featured hydrogen aggregation reaction relying upon the combination of two surface hydroxyl radicals, with a pair of positively charged hydrogen atoms ($+0.5 e$) transitioning into a neutral hydrogen molecule. Alongside the reduction of surface hydroxyl groups into hydrogen gas molecules and the bare surface oxygen atoms, the Mg surface turns into a more positive state by losing approximately $1.3 e$ electrons as it donates electrons to compensate for the loss of the original O-H bonding in the adsorbed oxygen atoms. Despite the charge transfer during the overall HER between the Mg electrode and the adsorbates being finite, the crucial sub-step reaction with the maximum energy barrier, namely the outward diffusion of the sub-surface hydrogen, displays a pronounced tendency to favour an anodic external potential, thus significantly contributing to this special hydrogen evolution under anodic conditions.

6.5 Conclusion

By employing first-principles calculations, we demonstrate the electrochemical stability of the Mg (0001) surface in various adsorption states and further elucidate the impact of its surface conditions on the kinetics of key corrosion reactions. Based on the grand-canonical approach in DFT calculations, where the influence of pH and potential on the electrochemical stability of the Mg (0001) surface is accounted for, we observe a notable transformation in the surface configuration under aqueous conditions, which progresses from an initial fully hydride adsorption state to a hydroxylated surface and culminates in a fully oxidized surface upon anodic increase of the electrode potential. Furthermore, we extend the conventional surface Pourbaix diagram, which primarily focuses on on-surface adsorption patterns of the Mg basal plane, by incorporating multiple sub-surface hydrogen adsorption configurations. It is worth highlighting that Mg (0001) surfaces with sub-surface hydride adsorption exhibit remarkable electrochemical stability when the Mg electrode is under anodic polarisation. To be more precise, at a pH level of approximately 8, the equilibrium potential for the sub-surface hydride phase within the Mg (0001) surface, covered by a monolayer of oxygen, attains an exceptionally high anodic value of

0.38 V_{SHE}. Hence, this anodically stable sub-surface hydride phase could potentially serve as the essential hydrogen source for the anodic hydrogen evolution as it is observed experimentally.

In addition, we discover that the mechanisms and kinetics of crucial corrosion reactions of Mg, such as the water dissociation reaction and the hydrogen evolution process, significantly depend on the surface adsorption condition that is determined by the electrode potential or pH level of the solution. For Mg surfaces coated with hydrogen or oxygen atoms, a noteworthy interaction occurs between the on-surface species and the hydrogen atom within a water monomer, thereby facilitating water dissociation on the Mg (0001) surface by reducing the energy barrier for the reaction. Followed by these water dissociation reactions on the hydride or oxidised Mg (0001) surface, the dissociated hydrogen atoms become kinetically available to diffuse into the sub-surface interstitial spaces and generate the sub-surface hydrides. Consistent with previous studies, we also find that under cathodic electrode potentials, the HER on the Mg basal plane covered with hydrogen atoms prefers the Heyrovsky-like mechanism over the Tafel mechanism due to a notable lower reaction energy barrier. As the electrode potential rises anodically, the Mg (0001) surface undergoes a stepwise transformation into a hydroxylated surface, where hydrogen gas molecules evolve through the dissociation of surface hydroxyls, catalysed by the presence of water monomers. In addition to the regular HER consuming on-surface hydrogen of the Mg (0001) surface, the HER under anodic conditions, which is likely to deplete the sub-surface hydrogen, displays a distinctive three-step process. The rate-limiting step of this HER, which involves the outward diffusion of sub-surface hydrogen to on-surface sites, necessitates a substantial shift in the charge on sub-surface hydrogen from $-1 e$ to $+0.5 e$, thereby exhibiting a significant anodic nature. Accordingly, the sub-surface hydrogen contributed HER could be enhanced with an external anodic potential. This mechanism potentially explains the experimentally observed increase in the HER rate when the Mg electrode is subjected to anodic conditions, *i.e.*, the NDE of Mg.

This work provides new insights into the ongoing debate surrounding the puzzling phenomenon of the anodically enhanced HER during magnesium aqueous corrosion. Stemming from the current deficient hydride model for demonstrating the NDE of magnesium, our investigation delves deeper to unveil the thermodynamic driving forces and the microscopic

kinetic mechanisms behind the sub-surface hydride's role in the abnormal HER of Mg under anodic polarisation. Unlike the bulk hydride phase of Mg, the sub-surface hydride-like structure maintains its electrochemical stability in experimental anodic conditions and consistently serves as a reliable source for the hydrogen evolution process at positive potentials. The pivotal rate-limiting step of the HER, with the involvement of the sub-surface hydrogen, shows a pronounced anodic characteristic and can be substantially accelerated under anodic polarisation, thus lending theoretical support to the atomistic mechanism of the hydride model. Finally, one more crucial insight to glean from this study is that, in addition to the electrode potential, the surface conditions determined by the electrochemical environment have a significant impact on the interface reaction mechanism and its microscopic kinetics, which should be given careful consideration in future investigations of interface reactions.

Chapter 7

Conclusion and Future Work

7.1 Conclusion

To conclude, in this thesis, we have studied the fundamental mechanism of Mg aqueous corrosion at the atomic scale via first-principles calculation within the framework of DFT. Magnesium, recognized as the most promising lightweight metal among engineering metals, has found extensive applications across diverse sectors of modern industries, spanning from automobile manufacturing to clinical medicine. However, the widespread utilisation of Mg and its alloys in electrochemical environments, such as air batteries and aviation industries, faces significant impediments due to its notably poor corrosion resistance, particularly in aqueous conditions. Several experimental studies have unveiled the fundamental corrosion characteristics of magnesium in a moist environment, with a crucial observation on the development of a porous and inadequately protective surface film, which is further accompanied by the evolution of hydrogen bubbles from the metal/water interface. Nevertheless, the mechanism underlying certain critical corrosion phenomena in Mg subjected to an applied voltage bias (*e.g.*, anodic polarization), such as the negative difference effect (NDE) associated with an abnormal hydrogen evolution reaction, continues to be a subject of debate and requires a comprehensive understanding at the atomic level of aqueous Mg electrochemistry and the interface reactions. The first-principles method, based on the DFT formalism, has demonstrated its efficacy in modelling and accurately predicting the thermodynamic and kinetic properties of Mg aqueous corrosion

behaviour herein. This success not only opens up avenues for efficient exploration of diverse reaction pathways but also enables a thorough investigation of the corresponding mechanisms at the Mg/water interface through theoretical computations. The acquisition of insights from our DFT calculations hence proves advantageous in the exploration and validation of novel or existing theories of the Mg aqueous corrosion mechanism, especially those foundational to the utilisation of Mg alloys in both structural and functional material applications.

As an initial, but very significant, stride in comprehending the mechanisms underlying numerous electrochemical reactions occurring at the interface during magnesium aqueous corrosion, in Chapter 4 we investigate the detailed structural characteristics and an intrinsic property, namely the potential of zero charge (PZC), of the Mg (0001)/water interface. Using ab initio molecular dynamics (AIMD) simulations, we confirm that within the electrified double layer region of the Mg basal plane, water molecules interacting with the metal surface significantly (*i.e.*, chemisorbed) exhibit a pronounced dipole orientation pointing away from the surface yet physisorbed water molecules display a contrasting preference with an inverse orientation. At the initial stage of aqueous corrosion, the pristine Mg surface undergoes increased roughness as a result of water-metal interactions, causing certain Mg atoms (those that directly interact with chemisorbed water monomers) to be elevated by approximately $+0.7 \text{ \AA}$ due to the less directional nature of s - s bonding in typical sp metals. By performing statistical DFT calculations on the equilibrium structure of Mg (0001)/water derived from AIMD trajectories, our analysis reveals that the PZC, an essential parameter for deriving reaction rates for metal surfaces, for the Mg (0001) surface is determined to be $-1.8 \pm 0.2 \text{ V}$ relative to the standard hydrogen electrode. This finding significantly contributes to bridging the existing gap in experimental data for the Mg (0001) surface, which is because of the inherent challenges in accurately measuring such a reactive surface under aqueous conditions. An extended examination of the potential difference between the PZC and the work function-associated potential of the Mg (0001) surface, commonly referred to as the Volta potential difference, reveals three discernible contributing factors: the contribution from the water dipole moment ($\Delta\phi_{\text{ori}}$), the contribution arising from electron density redistribution ($\Delta\phi_{\text{e}}$), and the contribution stemming from geometric effects ($\Delta\phi_{\text{geom}}$). Despite the magnitude of the water dipole contribution and the geometric contribution

closely relates to the configuration of the system and is less comparable with those of others' calculations, the electron density redistribution contribution in our analysis, which is considered a crucial factor in determining the Volta potential difference of metals, aligns seamlessly with the estimated values obtained through linear correlations between $\Delta\phi_e$ and the water adsorption energy across 11 other metal/water interfaces.

With a foundational understanding of the structure and characteristics of the Mg/water interface, in Chapter 5, we then explore the hydrogen adsorption procedure during Mg aqueous corrosion, which serves as the prerequisite step for the essential hydrogen evolution reaction of Mg. Furthermore, the formation mechanism of the sub-surface hydride of Mg, a promising corrosion product that might play a role in the abnormal hydrogen evolution under anodic polarisation (*i.e.*, NDE), is also investigated. We discover that the electron localisation function (ELF) is a pivotal indicator for predicting the potential adsorption sites for hydrogen in the Mg surfaces: the ELF maxima within the surface create effective hydrogen traps, significantly enhancing the probability of capturing hydrogen atoms on-site. Upon analysing the total adsorption energy of hydrogen on the Mg (0001) surface, we observe a linear correlation between the on-site ELF value at each adsorption site and the corresponding ELF-related adsorption energy. At hydrogen coverage below 1 monolayer (ML), the on-surface fcc sites emerge as the most energetically favourable adsorption sites on the Mg (0001) surface, which is attributed to the combined influence of hydrogen-electron interaction (ELF) and Coulomb interaction. In addition, our computations indicate that the on-surface adsorption of atomic H, OH radicals, and atomic O on the Mg surface has the potential to amplify electron localisation at specific sites within the sub-surface region, hence benefiting the formation of the sub-surface Mg hydride structure. Specifically, the presence of 1 ML pre-adsorbed hydrogen atoms at the on-surface fcc sites of the Mg (0001) surface particularly enhances the ELF level at the sub-surface tetrahedral-I (TI₁) sites, thereby leading to the formation of the previously observed H(fcc)-Mg-H(TI₁) tri-layer structure, which is considered a vital precursor for the bulk hydride of Mg. In the case of on-surface adsorption of OH radicals or O atoms, the ELF patterns in the sub-surface region undergo modifications as well, which in turn, facilitates the creation of the OH(fcc)-Mg-H(TI₁) structure for the hydroxylate Mg surface and O(hcp)-Mg-H(TI₂) structure for the oxidised Mg

surface. This discovery establishes a fundamental basis for comprehending the importance of the crystalline structure of Mg hydride in aqueous corrosion, and it also contributes to unravelling the underlying nature of certain perplexing phenomena observed in Mg corrosion, including the negative difference effect.

While the chemical stability and formation mechanism of the sub-surface hydride phase of Mg under aqueous corrosion have been affirmed in Chapter 5, the electrochemical stability of this hydride phase—taking into account the impact of electrode potential and solution pH—and its specific role in the negative difference effect for Mg, are presently not fully elucidated. In Chapter 6, we employ the grand-canonical approach within DFT calculations to construct the surface Pourbaix (*i.e.*, E-pH) diagram of Mg basal planes in diverse adsorption states under aqueous conditions. In the scenario where only on-surface adsorptions are taken into account, as the electrode potential increases from cathodic to anodic values, the Mg (0001) surface experiences a transition in surface states, from an entire hydride state at cathodic potentials to a hydroxylated surface, and eventually converting to a completely oxidised surface under highly anodic conditions, which indicates the significance of the potential and pH in impacting the surface configurations. Incorporating several sub-surface hydrogen adsorption states into the surface Pourbaix diagram of the Mg (0001) surface highlights the electrochemical stability of sub-surface hydride phases in an alkaline solution when the electrode is under anodic polarisation. Therefore, the presence of the anodically stable Mg sub-surface hydride phase emerges as a promising candidate for facilitating the hydrogen evolution reaction under anodic potentials. This observation supports the hypothesis linking the negative difference effect of Mg to the existence of the hydride phase, consequently giving rise to an unconventional hydrogen evolution process at anodic conditions.

To gain a deeper understanding of the kinetics and mechanisms underlying crucial electrochemical reactions in Mg aqueous corrosion and to elucidate the impact of the sub-surface hydride phase on the hydrogen evolution reaction, we conducted barrier calculations using the CI-NEB method. Specifically, our focus is on the water dissociation reaction and hydrogen evolution reaction on Mg surfaces, by exploring various adsorption configurations of the surface (under the influence of pH and potential) to provide comprehensive insights into these processes.

Our calculations reveal that the on-surface hydrides, hydroxyl radicals, or oxygen atoms play a pivotal role in accelerating both the water dissociation reaction and the hydrogen evolution process. This acceleration occurs through the interaction between on-surface hydrogen/hydrogen in the hydroxyl/oxygen and the hydrogen in water molecules, thereby aiding in the cleavage of the O-H bond within the water molecule and lowering the reaction energy barrier. We further find that, following the water dissociation reactions on the hydride or oxidised Mg (0001) surface, the dissociated hydrogen atoms gain kinetic availability for diffusion into the sub-surface interstitial spaces, thus leading to the formation of sub-surface hydrides. Besides exploring the cathodic hydrogen evolution reaction following the Heyrovsky pathway, we also delve into the hydrogen evolution reaction involving sub-surface hydrogen under anodic conditions, unveiling it as a discernible three-step process. The pivotal stage (*i.e.*, rate-limiting step) governing the sub-surface hydrogen evolution reaction herein pertains to the outward diffusion of sub-surface hydrogen toward on-surface sites, which mandates a pronounced alteration in the charge state of sub-surface hydrogen, transitioning from a negatively charged hydride to a proton. This procedure exhibits a significant anodic feature and could be further accelerated through the application of an externally imposed anodic voltage bias to the Mg electrode. Therefore, the kinetic analysis of the sub-surface hydride-involved hydrogen evolution process could provide a logical explanation for the observed increase in the rate of the hydrogen evolution reaction when the Mg electrode subjected to anodic conditions, *i.e.*, the negative difference effect of Mg, and initially validates the previously proposed hydride-related hypothesis of the abnormal hydrogen evolution behaviour.

7.2 Future Work

Despite the fact that this thesis extensively explores the atomic structure of the Mg/water interface and establishes comprehensive kinetic and thermodynamic models for the sub-surface hydride hypothesis to elucidate the negative difference effect during Mg aqueous corrosion, there are still additional tasks ahead, which involve calculations for further validating the hydride hypothesis and refining the existing calculations to enhance their accuracy. First, in the

calculations wherein we simulated the Mg/water interface with ab initio molecular dynamics and modelled the barrier for essential corrosion reactions at the interface, we performed the DFT calculations in a constant electron condition (*i.e.*, canonical ensemble) rather than in a constant potential mode (*i.e.*, grand-canonical ensemble) that mimics the real experimental conditions. In experimental conditions, the negative difference effect of Mg becomes apparent during anodic polarisation, indicating an electron-deficient state within the Mg electrode. This external potential results in a voltage bias from the potential of zero charge of the surface, consequently prompting the modification of the electrified double-layer structure and a shift in the energy barrier for the typical corrosion reaction, such as the hydrogen evolution reaction. Therefore, for subsequent phases of the research, it is imperative to conduct ab initio calculations on the aqueous Mg system under controlled potentiostat conditions, employing either the constant Fermi-level method or the hair-probe model [221, 338]. These models establish an open-boundary condition for electrons, allowing for an in-depth exploration of the impact of applied voltage on the thermodynamics and kinetics of corrosion reactions.

Secondly, in Chapter 6, we formulated the surface Pourbaix diagram specifically for the basal plane of Mg. However, this analysis omitted consideration for other Mg surfaces, such as the (10 $\bar{1}$ 0) surface, with distinct crystal orientations that could be present under aqueous conditions. Additionally, we did not account for the potential impact of defects on the electrochemical stability of Mg surfaces. Hence, it would be compelling to incorporate orientation effects and consider defective surface states in future calculations, aiming to develop a more comprehensive surface Pourbaix diagram for Mg under electrochemical conditions. Furthermore, in the selection of potential adsorption states for the computation of the surface Pourbaix diagram, we opted for calculating a limited set of surfaces with specific coverage and empirical adsorption sites and established a finite database due to the restriction of the computation resources. Failing to explore all potential adsorption sites and coverages may result in overlooking crucial surface states, thus introducing inaccuracies to the surface Pourbaix diagram. To augment the database without performing an infinite number of expensive DFT calculations, a rational approach that involves training the limited data using innovative machine-learning techniques to generate a more comprehensive database is expected to be employed in the future.

Appendix A

Appendix

A.1 Electron Localisation Function (ELF) and Charge Density (CD)

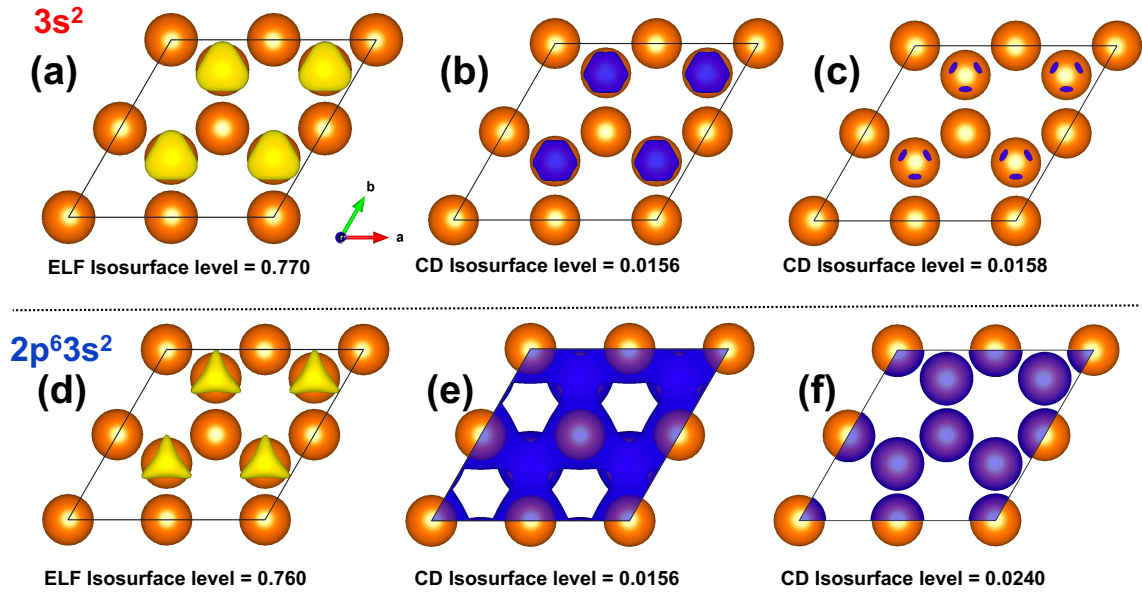


Figure A.1: ELF and Charge density (CD) of Mg (0001) surface calculated from DFT calculations with different treatment of the valence electrons for Mg atoms ($3s^2$ and $2p^63s^2$ respectively). (a)-(c) ELF and CD isosurface plots of the Mg (0001) surface (Mg atoms with $3s^2$ as the valence electrons). (d)-(f) ELF and CD isosurface plots of the Mg (0001) surface (Mg atoms with $2p^63s^2$ as the valence electrons). The unit of the ELF isosurface level is 1 and that of the charge density isosurface level is e/Bohr^3 .

The electron localisation function (ELF) reflects the probability of finding an electron near

the location of another like-spin electron, thus demonstrating the degrees of localisation of an electron at a point in space [291]. The usual interpretation of a local ELF maximum is that there's likely to be an occupied orbital peaked at the point. One advantage of using the ELF maxima to predict the stable local hydrogen adsorption site of a metal surface is that the ELF depends on the local kinetic energy density that is relatively less prone to be washed out by the occupation of other orbitals.

As shown in Figure A.1 (a) and (d), the ELF plots of the Mg (0001) surface obtained from calculations with different treatments of the Mg valence electrons ($3s^2$ and $2p^63s^2$) both indicate an ELF maximum at the on-surface hcp hollow site, confirming the robustness of the ELF. Although the charge density could also illustrate the electron distribution within a metal surface, the topological shape of the charge density on the other hand, strongly depends on the occupation of not only the interstitial localised orbital but all other orbitals too. As shown in Figure A.1 (b), the pseudo charge density calculated using only Mg's $3s$ electrons looks almost identical to the ELF plot [Figure A.1 (a)] with local maxima at the on-surface hcp hollow sites. However, when Mg's $2p$ electrons are also taken into consideration as valence electrons, the local maxima are washed out by the occupied $2p$ orbitals [see Figure A.1 (e) and (f)]. Therefore, the charge density cannot be used directly to find the potential hydrogen adsorption sites. As a result, for Mg surface, we chose the ELF to determine the position of the hydrogen trap.

A.2 Defect-induced ELF Modification and H adsorption on the Mg (0001) Surface

In this section, we study the ELF of a defective Mg (0001) surface with an atomic vacancy at the top layer and investigate the H adsorption on this defective surface. Removing one Mg atom from the topmost surface layer forces the charge density redistribution, thus leading to a significant change in the onsite electron localisation. As shown in Figure A.2 (b), the absence of one Mg atom at the top layer leads to the formation of a new ELF maximum at the on-surface fcc hollow site adjacent to the atomic vacancy (labelled as FCC*). In addition, this atomic vacancy also enhances the electron localisation of the neighbouring hcp hollow site (labelled as

HCP* in the figure), which was the previous ELF maximum on the pristine Mg (0001) surface.

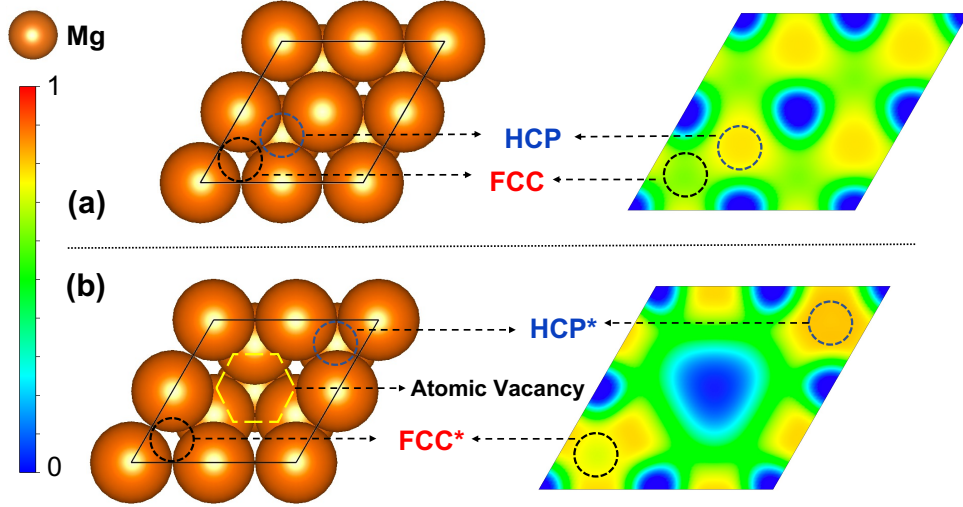


Figure A.2: Pristine Mg (0001) surface and defective Mg (0001) surface (with an atomic vacancy) with the corresponding top-view ELF contours. (a) The pristine Mg (0001) surface structure and the ELF contours. The on-surface hcp and fcc sites are also indicated by the circles and labelled as HCP and FCC. (b) The defective Mg (0001) surface structure with a point defect and the ELF contour. The atomic vacancy is demonstrated by the yellow hexagon. HCP* and FCC* indicate the general on-surface hcp and fcc adsorption sites of the defective Mg (0001) surface.

Table A.1: Onsite ELF value/Hydrogen adsorption energy (eV per H) at the on-surface adsorption sites of the pristine and the defective Mg (0001) surface. The H adsorption energy at the atomic vacancy site (position for the removed Mg atom) is also demonstrated in the table.

Adsorption Site	FCC	HCP	FCC*	HCP*	Atomic Vacancy
On-site ELF	0.666	0.785	0.837	0.860	/
H Adsorption Energy (eV/H)	-0.0167	0.00707	-0.0523	-0.0681	0.0460

Table A.1 shows the ELF value of the on-surface fcc/hcp adsorption sites for the pristine and defective Mg (0001) surface. Consistent with the ELF contours, these ELF values also show that introducing an atomic vacancy on the Mg (0001) surface increases the onsite ELF value of the hcp and fcc hollow site significantly. The H adsorption energy at the hcp/fcc sites of the imperfect Mg surface becomes more energetically favourable because of the enhanced onsite electron localisation and the improved correlative hydrogen-electron interaction. However, instead of accumulating locally, electrons are less localised at the atomic vacancy of the defective Mg surface according to the ELF contour in Figure A.2 (b). Therefore, placing a hydrogen atom at the vacancy is thermodynamically unfavourable due to the lack of localised electrons,

with notable positive adsorption energy (see Table A.1). Based on the geometry optimisation of the defective Mg (0001) surface with a hydrogen atom at the Mg vacancy, the adsorbed H tends to be adsorbed at the second-layer hcp hollow site (with a higher ELF value compared with the Mg vacancy), rather than staying at the vacancy during the relaxation.

To conclude, the existence of the atomic vacancy on the Mg (0001) surface could modify the electron localisation pattern of the surface. New ELF maxima tend to form at the on-surface hcp/fcc hollow sites in the vicinity of the atomic vacancy rather than at the atomic vacancy, thus contributing to a more robust trap on the surface Mg for hydrogen. As an indicator, the ELF is also able to predict the possible adsorption site for hydrogen on the defective Mg surface. This finding enlightens us that the hydrogen adsorption on the Mg surface during the aqueous corrosion could be impacted by the Mg dissociation reaction (with the point defects forming and the onsite electron localisation changing), which might further influence the sub-surface hydride formation and dissociation.

A.3 Influence of the Solvent Effect

To investigate the influence of the solvent effect on the surface adsorption of the Mg (0001) surface during aqueous corrosion, we employ the implicit solvent method with VASPsol to calculate the adsorption energy of atomic H, O and OH radical in aqueous conditions [236, 325]. As illustrated in Figure A.3, the adsorption energy of H, O and OH on the Mg basal plane in an implicit water environment becomes more negative compared to the adsorption energy in the vacuum. This suggests that the solvent effect could stabilize the adsorbed species on the Mg (0001) surface. Nevertheless, including the solvent effect in the calculation does not change the adsorption patterns in all adsorption cases (i.e. the order of the adsorption energy for H/OH/O at different adsorption sites for all coverage resist change by the solvent). As we are interested in the most stable adsorption structure, we conclude that it is rational to use the adsorption energy in the vacuum to determine the most stable adsorption phase in our calculations.

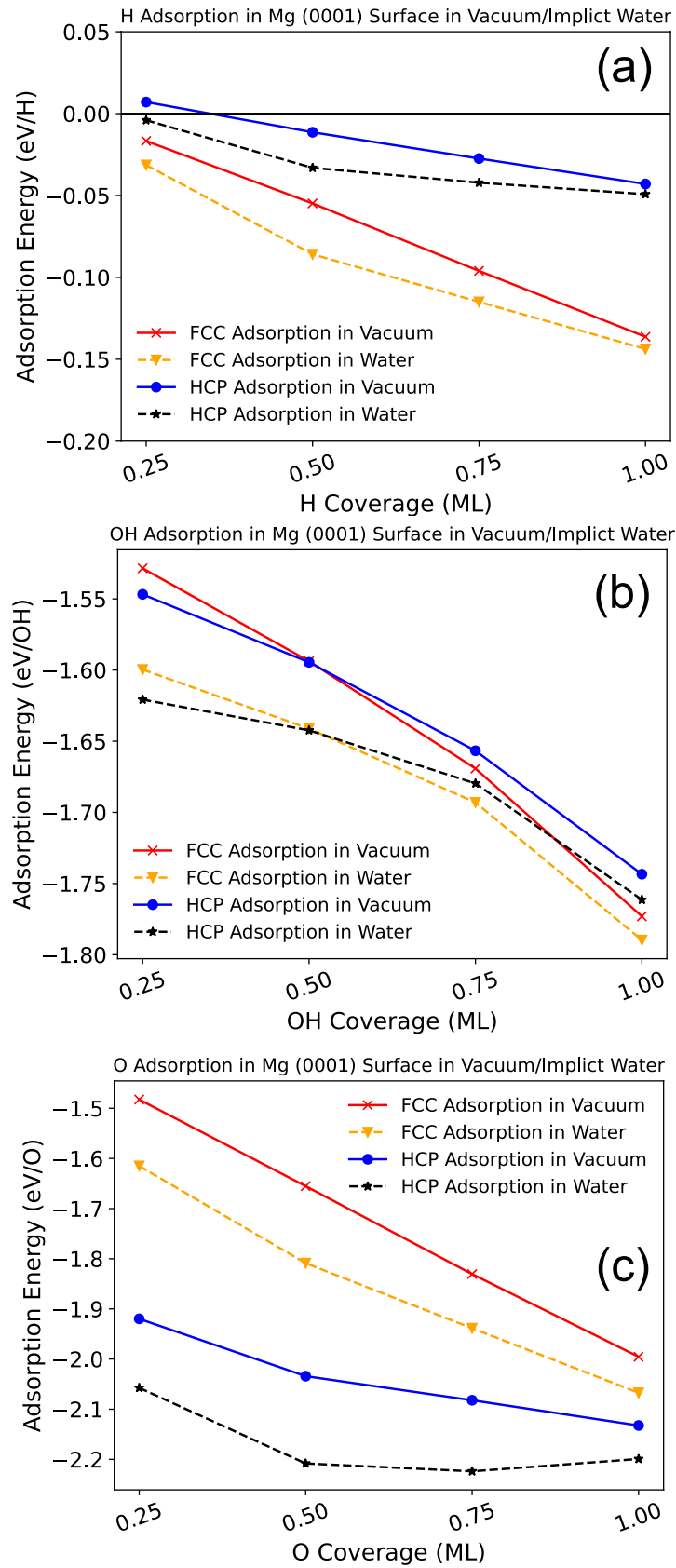


Figure A.3: H/OH/O adsorption energy (eV per adsorbate) at different on-surface adsorption sites (hcp and fcc) of the Mg (0001) surface in the vacuum/implicit water.

References

- [1] M. Kulekci. Magnesium and its alloys applications in automotive industry. *The International Journal of Advanced Manufacturing Technology*, 39:851–865, 2008.
- [2] G. Song. *Corrosion of magnesium alloys*. Elsevier, 2011.
- [3] D. Lide. *CRC handbook of chemistry and physics*, volume 85. CRC press, 2004.
- [4] X. Li, A. Chen, X. Yang, J. Zhu, J. Le, and J. Cheng. Linear correlation between water adsorption energies and volta potential differences for metal/water interfaces. *The Journal of Physical Chemistry Letters*, 12(30):7299–7304, 2021.
- [5] J. Lee. *Computational materials science: an introduction*. CRC press, 2016.
- [6] B. Liu, J. Yang, X. Zhang, Q. Yang, J. Zhang, and X. Li. Development and application of magnesium alloy parts for automotive OEMs: A review. *Journal of Magnesium and Alloys*, 2023.
- [7] Y. Sun, H. Wu, W. Wang, R. Zan, H. Peng, S. Zhang, and X. Zhang. Translational status of biomedical Mg devices in china. *Bioactive Materials*, 4:358–365, 2019.
- [8] Y. Chen, Z. Xu, C. Smith, and J. Sankar. Recent advances on the development of magnesium alloys for biodegradable implants. *Acta Biomaterialia*, 10(11):4561–4573, 2014.
- [9] M. Yoo. Slip, twinning, and fracture in hexagonal close-packed metals. *Metallurgical transactions A*, 12:409–418, 1981.
- [10] Y. Yang and M. Scenini, F. and Curioni. A study on magnesium corrosion by real-time

- imaging and electrochemical methods: relationship between local processes and hydrogen evolution. *Electrochimica Acta*, 198:174–184, 2016.
- [11] M. Esmaily, J. Svensson, S. Fajardo, N. Birbilis, G. Frankel, S. Virtanen, R. Arrabal, S. Thomas, and L. Johansson. Fundamentals and advances in magnesium alloy corrosion. *Progress in Materials Science*, 89:92–193, 2017.
- [12] K. Ryoo. Metal oxide particle removal using electrolyzed anode water. *Journal of the Electrochemical Society*, 152(11):G885, 2005.
- [13] K. Williams, J. Labukas, V. Rodriguez-Santiago, and J. Andzelm. First principles modeling of water dissociation on Mg (0001) and development of a Mg surface pourbaix diagram. *Corrosion*, 71(2):209–223, 2015.
- [14] J. Yuwono, N. Birbilis, K. Williams, and Nikhil V. Medhekar. Electrochemical stability of magnesium surfaces in an aqueous environment. *The Journal of Physical Chemistry C*, 120(47):26922–26933, 2016.
- [15] N. Sato. Basics of corrosion chemistry. *Green Corrosion Chemistry and Engineering*, 1, 2012.
- [16] D. R. Banjade. *Fundamental investigation of magnesium corrosion using experiments and simulation*. Brigham Young University, 2018.
- [17] S. Fajardo and G. Frankel. Effect of impurities on the enhanced catalytic activity for hydrogen evolution in high purity magnesium. *Electrochimica Acta*, 165:255–267, 2015.
- [18] J. Yuwono, C. Taylor, G. Frankel, N. Birbilis, and S. Fajardo. Understanding the enhanced rates of hydrogen evolution on dissolving magnesium. *Electrochemistry Communications*, 104:106482, 2019.
- [19] H. Ma, X. Chen, R. Li, S. Wang, J. Dong, and W. Ke. First-principles modeling of anisotropic anodic dissolution of metals and alloys in corrosive environments. *Acta Materialia*, 130:137–146, 2017.

- [20] G. Frankel, A. Samaniego, and N. Birbilis. Evolution of hydrogen at dissolving magnesium surfaces. *Corrosion Science*, 70:104–111, 2013.
- [21] Aline. Gabbardo. *New Approaches to Study Magnesium Corrosion Behavior*. The Ohio State University, 2019.
- [22] J. Wu. Understanding the electric double-layer structure, capacitance, and charging dynamics. *Chemical Reviews*, 122(12):10821–10859, 2022.
- [23] R. Burt, G. Birkett, and X. Zhao. A review of molecular modelling of electric double layer capacitors. *Physical Chemistry Chemical Physics*, 16(14):6519–6538, 2014.
- [24] G. Perrault. The potential-pH diagram of the magnesium-water system. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 51(1):107–119, 1974.
- [25] H. Yang and J. Whitten. Dissociative adsorption of H_2 on ni (111). *The Journal of Chemical Physics*, 98(6):5039–5049, 1993.
- [26] A. Bussy. Mémoire sur le radical métallique de la magnésie. *Ann. Chim*, 46:434–437, 1831.
- [27] W. Beetz. On the development of hydrogen from the anode. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 32(216):269–278, 1866.
- [28] R. Petty, A. Davidson, and J. Kleinberg. The anodic oxidation of magnesium metal: evidence for the existence of unipositive magnesium. *Journal of the American Chemical Society*, 76(2):363–366, 1954.
- [29] S. Splinter, N. McIntyre, W. Lennard, K. Griffiths, and G. Palumbo. An AES and XPS study of the initial oxidation of polycrystalline magnesium with water vapour at room temperature. *Surface Science*, 292(1-2):130–144, 1993.
- [30] J. Nordlien, S. Ono, N. Masuko, and K. Nis. Morphology and structure of oxide films formed on magnesium by exposure to air and water. *Journal of the Electrochemical Society*, 142(10):3320, 1995.

- [31] H. Yao, Y. Li, and A. Wee. An XPS investigation of the oxidation/corrosion of melt-spun Mg. *Applied Surface Science*, 158(1-2):112–119, 2000.
- [32] K. Gusieva, C. Davies, J. Scully, and N. Birbilis. Corrosion of magnesium alloys: the role of alloying. *International Materials Reviews*, 60(3):169–194, 2015.
- [33] R. Zeng, Y. Hu, S. Guan, H. Cui, and E. Han. Corrosion of magnesium alloy AZ31: The influence of bicarbonate, sulphate, hydrogen phosphate and dihydrogen phosphate ions in saline solution. *Corrosion Science*, 86:171–182, 2014.
- [34] N. Kirkland, G. Williams, and N. Birbilis. Observations of the galvanostatic dissolution of pure magnesium. *Corrosion Science*, 65:5–9, 2012.
- [35] C. Taylor. A first-principles surface reaction kinetic model for hydrogen evolution under cathodic and anodic conditions on magnesium. *Journal of the Electrochemical Society*, 163(9):C602, 2016.
- [36] J. Yuwono, N. Birbilis, C. Taylor, K. Williams, A. Samin, and N. Medhekar. Aqueous electrochemistry of the magnesium surface: Thermodynamic and kinetic profiles. *Corrosion Science*, 147:53–68, 2019.
- [37] D. Tawil. Corrosion and surface protection developments, magnesium technology. In *Proceedings of the Conference*, volume 66, 1986.
- [38] J. Meng, W. Sun, Z. Tian, X. Qiu, and D. Zhang. Corrosion performance of magnesium (Mg) alloys containing rare-earth (RE) elements. In *Corrosion Prevention of Magnesium Alloys*, pages 38–60. Elsevier, 2013.
- [39] X. Guo, G. Song, J. Hu, and D. Huang. Corrosion inhibition of magnesium (Mg) alloys. In *Corrosion Prevention of Magnesium Alloys*, pages 61–84. Elsevier, 2013.
- [40] W. Innes. Electroplating and electroless plating on magnesium and magnesium alloys. In *Modern Electroplating*, page 601. Wiley-Interscience, 1974.

- [41] J. Zhu, H. Jia, K. Liao, and X. Li. Improvement on corrosion resistance of micro-arc oxidized AZ91D magnesium alloy by a pore-sealing coating. *Journal of Alloys and Compounds*, 889:161460, 2021.
- [42] J. Liang, P. Srinivasan, C. Blawert, M. Störmer, and W. Dietzel. Electrochemical corrosion behaviour of plasma electrolytic oxidation coatings on AM50 magnesium alloy formed in silicate and phosphate based electrolytes. *Electrochimica Acta*, 54(14):3842–3850, 2009.
- [43] A. Jangde, S. Kumar, and C. Blawert. Influence of glycerol on plasma electrolytic oxidation coatings evolution and on corrosion behaviour of coated AM50 magnesium alloy. *Corrosion Science*, 157:220–246, 2019.
- [44] T. Jin, F. Kong, R. Bai, and R. Zhang. Anti-corrosion mechanism of epoxy-resin and different content Fe_2O_3 coatings on magnesium alloy. *Frontiers of Materials Science*, 10:367–374, 2016.
- [45] C. Chang, T. Huang, C. Peng, T. Yeh, H. Lu, W. Hung, C. Weng, T. Yang, and J. Yeh. Novel anticorrosion coatings prepared from polyaniline/graphene composites. *Carbon*, 50(14):5044–5051, 2012.
- [46] Y. Tarzanagh, D. Seifzadeh, and R. Samadianfard. Combining the 8-hydroxyquinoline intercalated layered double hydroxide film and sol—gel coating for active corrosion protection of the magnesium alloy. *International Journal of Minerals, Metallurgy and Materials*, 29(3):536–546, 2022.
- [47] J. Hafner. Atomic-scale computational materials science. *Acta Materialia*, 48(1):71–92, 2000.
- [48] N. Cheimarios, G. To, D. Kokkoris, G. Memos, and A. Boudouvis. Monte carlo and kinetic monte carlo models for deposition processes: a review of recent works. *Frontiers in Physics*, 9:631918, 2021.
- [49] I. Steinbach. Phase-field models in materials science. *Modelling and Simulation in Materials Science and Engineering*, 17(7):073001, 2009.

- [50] A. Karma. Phase-field formulation for quantitative modeling of alloy solidification. *Physical Review Letters*, 87(11):115701, 2001.
- [51] J. Eiken. Dendritic growth texture evolution in Mg-based alloys investigated by phase-field simulation. *International Journal of Cast Metals Research*, 22(1-4):86–89, 2009.
- [52] N. Zhou, C. Shen, M. Mills, and Y. Wang. Phase field modeling of channel dislocation activity and γ' rafting in single crystal Ni – Al. *Acta Materialia*, 55(16):5369–5381, 2007.
- [53] B. Alder and T. Wainwright. Studies in molecular dynamics. i. general method. *The Journal of Chemical Physics*, 31(2):459–466, 1959.
- [54] H. Andersen. Molecular dynamics simulations at constant pressure and/or temperature. *The Journal of Chemical Physics*, 72(4):2384–2393, 1980.
- [55] Wilfred F. Van G. and H. Berendsen. Computer simulation of molecular dynamics: methodology, applications, and perspectives in chemistry. *Angewandte Chemie International Edition in English*, 29(9):992–1023, 1990.
- [56] F. Giustino. *Materials modelling using density functional theory: properties and predictions*. Oxford University Press, 2014.
- [57] P. Hohenberg and W. Kohn. Inhomogeneous electron gas. *Physical Review*, 136(3B):B864, 1964.
- [58] W. Kohn and L. Sham. Self-consistent equations including exchange and correlation effects. *Physical Review*, 140(4A):A1133, 1965.
- [59] B. Mordike and T. Ebert. Magnesium: properties—applications—potential. *Materials Science and Engineering: A*, 302(1):37–45, 2001.
- [60] J. Tan and S. Ramakrishna. Applications of magnesium and its alloys: A review. *Applied Sciences*, 11(15):6861, 2021.
- [61] E. Emley. *Principles of magnesium technology*. Pergamon Press, 1966.

- [62] H. Davy. *The Collected Works of Sir Humphry Davy, Bart: Bakerian lectures and miscellaneous papers from 1806 to 1815*, volume 5. Smith, Elder and Company, 1840.
- [63] M. Halmann, A. Frei, and A. Steinfeld. Magnesium production by the pidgeon process involving dolomite calcination and MgO silicothermic reduction: thermodynamic and environmental analyses. *Industrial & Engineering Chemistry Research*, 47(7):2146–2154, 2008.
- [64] D. Eliezer, E. Aghion, and F. Froes. Magnesium science, technology and applications. *Advanced Performance Materials*, 5:201–212, 1998.
- [65] E. Gratz, J. Milshtein, and U. Pal. Determining yttria-stabilized zirconia (YSZ) stability in molten oxy-fluoride flux for the production of magnesium with the SOM process. *Journal of the American Ceramic Society*, 96(10):3279–3285, 2013.
- [66] R. Pachauri, M. Allen, V. Barros, J. Broome, W. Cramer, R. Christ, J. Church, L. Clarke, Q. Dahe, and P. Dasgupta. *Climate change 2014: synthesis report. Contribution of Working Groups I, II and III to the fifth assessment report of the Intergovernmental Panel on Climate Change*. Ipcc, 2014.
- [67] S. Golroudbary, I. Makarava, E. Repo, A. Kraslawski, and P. Luukka. Magnesium life cycle in automotive industry. *Procedia CIRP*, 105:589–594, 2022.
- [68] S. Schumann. The paths and strategies for increased magnesium applications in vehicles. In *Materials Science Forum*, volume 488, pages 1–8. Trans Tech Publ, 2005.
- [69] E. Aghion, B. Bronfin, and D. Eliezer. The role of the magnesium industry in protecting the environment. *Journal of Materials Processing Technology*, 117(3):381–385, 2001.
- [70] A. Kiełbus, T. Rzychoń, and R. Cibis. Microstructure of AM50 die casting magnesium alloy. *Journal of Achievements in Materials and Manufacturing Engineering*, 18(1-2):135, 2006.

- [71] S. Pantelakis, N. Alexopoulos, and A. Chamos. Mechanical performance evaluation of cast magnesium alloys for automotive and aeronautical applications. *Journal of Engineering Materials and Technology*, 129, 2007.
- [72] D. Dvorsky, J. Kubasek, E. Jablonska, J. Lipov, and D. Vojtech. High strength AM50 magnesium alloy as a material for possible stent application in medicine. *Materials Technology*, 34(14):838–842, 2019.
- [73] M. Okayasu and T. Fukui. A study of the mechanical properties of a Mg – Al – Zn alloy (AZ91) produced via thixomolding. *International Journal of Material Forming*, 14:271–280, 2021.
- [74] S. Zhang, X. Zhang, C. Zhao, J. Li, Y. Song, C. Xie, H. Tao, Y. Zhang, Y. He, and Y. Jiang. Research on an Mg – Zn alloy as a degradable biomaterial. *Acta Biomaterialia*, 6(2):626–640, 2010.
- [75] S. Cai, T. Lei, N. Li, and F. Feng. Effects of Zn on microstructure, mechanical properties and corrosion behavior of Mg – Zn alloys. *Materials Science and Engineering: C*, 32(8):2570–2577, 2012.
- [76] Y. Liu, Z. Huang, H. Ding, M. Fang, and S. Xiong. Study on pressure variations in the mold of magnesium alloy die castings. In *Key Engineering Materials*, volume 353, pages 1614–1616. Trans Tech Publ, 2007.
- [77] F. Witte, J. Fischer, J. Nellesen, H. Crostack, V. Kaese, A. Pisch, F. Beckmann, and H. Windhagen. In vitro and in vivo corrosion measurements of magnesium alloys. *Biomaterials*, 27(7):1013–1018, 2006.
- [78] Y. Wan, G. Xiong, H. Luo, F. He, Y. Huang, and X. Zhou. Preparation and characterization of a new biomedical magnesium-calcium alloy. *Materials & Design*, 29(10):2034–2037, 2008.
- [79] X. Gu, X. Xie, N. Li, Y. Zheng, and L. Qin. In vitro and in vivo studies on a Mg – Sr

- binary alloy system developed as a new kind of biodegradable metal. *Acta Biomaterialia*, 8(6):2360–2374, 2012.
- [80] P. Zartner, R. Cesnjevar, H. Singer, and M. Weyand. First successful implantation of a biodegradable metal stent into the left pulmonary artery of a preterm baby. *Catheterization and Cardiovascular Interventions*, 66(4):590–594, 2005.
- [81] B. Heublein, R. Rohde, V. Kaese, M. Niemeyer, W. Hartung, and A. Haverich. Biocorrosion of magnesium alloys: a new principle in cardiovascular implant technology? *Heart*, 89(6):651–656, 2003.
- [82] C. Di Mario, H. Griffiths, O. Goktekin, N. Peeters, J. Verbist, M. Bosiers, K. Deloose, B. Heublein, R. Rohde, and V. Kasese. Drug-eluting bioabsorbable magnesium stent. *Journal of Interventional Cardiology*, 17(6):391–395, 2004.
- [83] B. Song, W. Li, Z. Chen, G. Fu, C. Li, W. Liu, Y. Li, L. Qin, and Y. Ding. Biomechanical comparison of pure magnesium interference screw and polylactic acid polymer interference screw in anterior cruciate ligament reconstruction—a cadaveric experimental study. *Journal of Orthopaedic Translation*, 8:32–39, 2017.
- [84] D. Zhao, S. Huang, F. Lu, B. Wang, L. Yang, L. Qin, K. Yang, Y. Li, W. Li, and W. Wang. Vascularized bone grafting fixed by biodegradable magnesium screw for treating osteonecrosis of the femoral head. *Biomaterials*, 81:84–92, 2016.
- [85] R. Wang, A. Eliezer, and E. Gutman. An investigation on the microstructure of an AM50 magnesium alloy. *Materials Science and Engineering: A*, 355(1-2):201–207, 2003.
- [86] G. Song and S. Song. A possible biodegradable magnesium implant material. *Advanced Engineering Materials*, 9(4):298–302, 2007.
- [87] H. Hermawan, D. Dubé, and D. Mantovani. Developments in metallic biodegradable stents. *Acta Biomaterialia*, 6(5):1693–1697, 2010.
- [88] S. Agnew. Deformation mechanisms of magnesium alloys. In *Advances in wrought magnesium alloys*, pages 63–104. Elsevier, 2012.

- [89] S. Vagarali and T. Langdon. Deformation mechanisms in hcp metals at elevated temperatures—ii. creep behavior of a Mg – 0.8%Al solid solution alloy. *Acta Metallurgica*, 30(6):1157–1170, 1982.
- [90] A. Atrens, G. Song, F. Cao, Z. Shi, and P. Bowen. Advances in mg corrosion and research suggestions. *Journal of Magnesium and Alloys*, 1(3):177–200, 2013.
- [91] S. Agnew, D. Brown, and C. Tomé. Validating a polycrystal model for the elastoplastic response of magnesium alloy AZ31 using in situ neutron diffraction. *Acta Materialia*, 54(18):4841–4852, 2006.
- [92] Z. Wu and W. Curtin. The origins of high hardening and low ductility in magnesium. *Nature*, 526(7571):62–67, 2015.
- [93] Z. Wu and W. Curtin. Mechanism and energetics of $\langle c + a \rangle$ dislocation cross-slip in hcp metals. *Proceedings of the National Academy of Sciences*, 113(40):11137–11142, 2016.
- [94] B. Liu, F. Liu, N. Yang, X. Zhai, L. Zhang, Y. Yang, B. Li, J. Li, E. Ma, and J. Nie. Large plasticity in magnesium mediated by pyramidal dislocations. *Science*, 365(6448):73–75, 2019.
- [95] H. Wang, D. Zhang, G. Cao, and C. Qiu. Improving room-temperature ductility of a Mg – Zn – Ca alloy through friction stir processing. *Journal of Materials Research and Technology*, 17:1176–1186, 2022.
- [96] S. Sandlöbes, S. Zaefferer, I. Schestakow, S. Yi, and R. Gonzalez-Martinez. On the role of non-basal deformation mechanisms for the ductility of Mg and Mg – Y alloys. *Acta Materialia*, 59(2):429–439, 2011.
- [97] N. Mo, Q. Tan, M. Bermingham, Y. Huang, H. Dieringa, N. Hort, and M. Zhang. Current development of creep-resistant magnesium cast alloys: A review. *Materials & Design*, 155:422–442, 2018.

- [98] K. Athul, A. Pillai, U. and Srinivasan, and B. Pai. A review of different creep mechanisms in Mg alloys based on stress exponent and activation energy. *Advanced Engineering Materials*, 18(5):770–794, 2016.
- [99] S. Agnew, K. Liu, E. Kenik, and S. Viswanathan. Tensile and compressive creep behavior of die cast magnesium alloy AM60B. *Magnesium Technology 2000*, pages 285–290, 2000.
- [100] K. Asl, A. Tari, and F. Khomamizadeh. The effect of different content of Al, RE and Si element on the microstructure, mechanical and creep properties of Mg – Al alloys. *Materials Science and Engineering: A*, 523(1-2):1–6, 2009.
- [101] A. Luo. Recent magnesium alloy development for elevated temperature applications. *International Materials Reviews*, 49(1):13–30, 2004.
- [102] B. Mordike. Creep-resistant magnesium alloys. *Materials Science and Engineering: A*, 324(1-2):103–112, 2002.
- [103] K. Maruyama, M. Suzuki, and H. Sato. Creep strength of magnesium-based alloys. *Metallurgical and Materials Transactions A*, 33:875–882, 2002.
- [104] Y. Huang, H. Dieringa, N. Hort, T. Leil, K. Kainer, and Y. Liu. Effects of segregation of primary alloying elements on the creep response in magnesium alloys. *Scripta Materialia*, 58(10):894–897, 2008.
- [105] A. Srinivasan, U. Pillai, and B. Pai. Microstructure and mechanical properties of Si and Sb added AZ91 magnesium alloy. *Metallurgical and Materials Transactions A*, 36:2235–2243, 2005.
- [106] A. Luo and M. Powell, B. and Balogh. Creep and microstructure of magnesium-aluminum-calcium based alloys. *Metallurgical and Materials Transactions A*, 33:567–574, 2002.
- [107] M. Pekguleryuz and E. Baril. Creep resistant magnesium diecasting alloys based on alkaline earth elements. *Materials Transactions*, 42(7):1258–1267, 2001.

- [108] J. Zhang, P. Yu, K. Liu, D. Fang, D. Tang, and J. Meng. Effect of substituting cerium-rich mischmetal with lanthanum on microstructure and mechanical properties of die-cast Mg – Al – RE alloys. *Materials & Design*, 30(7):2372–2378, 2009.
- [109] W. Blum, P. Zhang, B. Watzinger, B. Grossmann, and H. Haldenwanger. Comparative study of creep of the die-cast Mg-alloys AZ91, AS21, AS41, AM60 and AE42. *Materials Science and Engineering: A*, 319:735–740, 2001.
- [110] L. Wei, G. Dunlop, and H. Westengen. Development of microstructure in cast Mg – Al–rare earth alloys. *Materials Science and Technology*, 12(9):741–750, 1996.
- [111] G. Pettersen, H. Westengen, R. Høier, and O. Lohne. Microstructure of a pressure die cast magnesium—4wt.% aluminium alloy modified with rare earth additions. *Materials Science and Engineering: A*, 207(1):115–120, 1996.
- [112] E. Dreizin, C. Berman, and Edward P. Vicenzi. Condensed-phase modifications in magnesium particle combustion in air. *Combustion and Flame*, 122(1-2):30–42, 2000.
- [113] Y. Chunmiao, H. Dezheng, L. Chang, and L. Gang. Ignition behavior of magnesium powder layers on a plate heated at constant temperature. *Journal of Hazardous Materials*, 246:283–290, 2013.
- [114] I. Hartmann, J. Nagy, and H. Brown. *Inflammability and explosibility of metal powders*. US Department of the Interior, Bureau of Mines, 1943.
- [115] N. Mebarki, N. Kumar, J. Blandin, M. Suery, F. Pelloux, and G. Khelifati. Correlation between ignition and oxidation behaviours of AZ91 magnesium alloy. *Materials Science and Technology*, 21(10):1145–1151, 2005.
- [116] F. Czerwinski. The oxidation behaviour of an AZ91D magnesium alloy at high temperatures. *Acta Materialia*, 50(10):2639–2654, 2002.
- [117] P. Boris. A study of the flammability of magnesium. Technical report, Federal Aviation Administration Washington DC Systems Research and Development Service, 1964.

- [118] B. Bobryshev and Y. Aleksandrova. Ignition of magnesium and its alloys. *Metal Science and Heat Treatment*, 30(3):219–222, 1988.
- [119] H. Watarai. Trend of research and development for magnesium alloys-reducing the weight of structural materials in motor vehicles. Technical report, NISTEP Science & Technology Foresight Center, 2006.
- [120] Y. Song, D. Shan, and E. Han. Pitting corrosion of a rare earth Mg alloy GW93. *Journal of Materials Science & Technology*, 33(9):954–960, 2017.
- [121] Y. Song, D. Shan, R. Chen, and E. Han. Corrosion characterization of Mg – 8Li alloy in nacl solution. *Corrosion Science*, 51(5):1087–1094, 2009.
- [122] M. Taheri, M. Danaie, and J. Kish. TEM examination of the film formed on corroding Mg prior to breakdown. *Journal of the Electrochemical Society*, 161(3):C89, 2013.
- [123] A. Samaniego, N. Birbilis, X. Xia, and G. Frankel. Hydrogen evolution during anodic polarization of Mg alloyed with Li, Ca, or Fe. *Corrosion*, 71(2):224–233, 2015.
- [124] J. Kruger, G. Makar, and K. Sieradzki. A fundamental understanding of the effect of alloying elements on the corrosion resistance of rapidly solidified Mg alloys. Technical report, Johns Hopkins University, 1989.
- [125] D. Xia, C. Deng, D. Macdonald, S. Jamali, D. Mills, J. Luo, M. Strebl, M. Amiri, W. Jin, and S. Song. Electrochemical measurements used for assessment of corrosion and protection of metallic materials in the field: A critical review. *Journal of Materials Science & Technology*, 112:151–183, 2022.
- [126] M. Shahabi-Navid. *Atmospheric corrosion of Mg and MgAl alloys—characterization and mechanisms*. Chalmers Tekniska Hogskola (Sweden), 2015.
- [127] S. Trasatti. The absolute electrode potential: an explanatory note (Recommendations 1986). *Pure and Applied Chemistry*, 58(7):955–966, 1986.

- [128] A. Pardo, M. Merino, A. Coy, R. Arrabal, F. Viejo, and E. Matykina. Corrosion behaviour of magnesium/aluminium alloys in 3.5 wt.% NaCl. *Corrosion Science*, 50(3):823–834, 2008.
- [129] C. Chao and T. Jen. Reaction of magnesium hydride with water to produce hydrogen. *Applied Mechanics and Materials*, 302:151–157, 2013.
- [130] J. Chen, J. Dong, J. Wang, E. Han, and W. Ke. Effect of magnesium hydride on the corrosion behavior of an AZ91 magnesium alloy in sodium chloride solution. *Corrosion Science*, 50(12):3610–3614, 2008.
- [131] C. Van Der Linde, A. Akhgarnusch, C. Siu, and M. Beyer. Hydrated magnesium cations $\text{Mg}^+(\text{H}_2\text{O})_n$, $n \approx 20 - 60$, exhibit chemistry of the hydrated electron in reactions with O_2 and CO_2 . *The Journal of Physical Chemistry A*, 115(36):10174–10180, 2011.
- [132] J. Huang, G. Song, A. Atrens, and M. Dargusch. What activates the Mg surface—A comparison of Mg dissolution mechanisms. *Journal of Materials Science & Technology*, 57:204–220, 2020.
- [133] H. Hansen, J. Rossmeisl, and J. Nørskov. Surface pourbaix diagrams and oxygen reduction activity of Pt, Ag and Ni(111) surfaces studied by DFT. *Physical Chemistry Chemical Physics*, 10(25):3722–3730, 2008.
- [134] M. Todorova and J. Neugebauer. Extending the concept of defect chemistry from semiconductor physics to electrochemistry. *Physical Review Applied*, 1(1):014001, 2014.
- [135] B. Popov. *Corrosion engineering: principles and solved problems*. Elsevier, 2015.
- [136] J. Bockris. *Modern Electrochemistry: an introduction to an interdisciplinary area*, volume 1. Springer Science & Business Media, 2012.
- [137] D. Tang, J. Lu, L. Zhuang, and P. Liu. Calculations of the exchange current density for hydrogen electrode reactions: A short review and a new equation. *Journal of Electroanalytical Chemistry*, 644(2):144–149, 2010.

- [138] J. Butler. The mechanism of overvoltage and its relation to the combination of hydrogen atoms at metal electrodes. *Transactions of the Faraday Society*, 28:379–382, 1932.
- [139] J. Tafel. Über die polarisation bei kathodischer wasserstoffentwicklung. *Zeitschrift für Physikalische Chemie*, 50(1):641–712, 1905.
- [140] U Evans and C. King. The corrosion and oxidation of metals. *Journal of The Electrochemical Society*, 108(4):94C, 1961.
- [141] P. Pedferri. Evans diagrams. *Corrosion Science and Engineering*, pages 103–118, 2018.
- [142] S. Esmailzadeh, M. Aliofkhazraei, and H. Sarlak. Interpretation of cyclic potentiodynamic polarization test results for study of corrosion behavior of metals: a review. *Protection of Metals and Physical Chemistry of Surfaces*, 54:976–989, 2018.
- [143] C. Li, Z. Tong, Y. He, H. Huang, D. Yong, and P. Zhang. Comparison on corrosion resistance and surface film of pure Mg and Mg – 14Li alloy. *Transactions of Nonferrous Metals Society of China*, 30(9):2413–2423, 2020.
- [144] S. Salleh, S. Thomas, J. Yuwono, K. Venkatesan, and N. Birbilis. Enhanced hydrogen evolution on $\text{Mg}(\text{OH})_2$ covered Mg surfaces. *Electrochimica Acta*, 161:144–152, 2015.
- [145] K. Williams, V. Rodriguez-Santiago, and W. Andzelm. Modeling reaction pathways for hydrogen evolution and water dissociation on magnesium. *Electrochimica Acta*, 210:261–270, 2016.
- [146] T. Würger, C. Feiler, G. Vonbun-Feldbauer, M. Zheludkevich, and R. Meißner. A first-principles analysis of the charge transfer in magnesium corrosion. *Scientific Reports*, 10(1):15006, 2020.
- [147] T. Vegge. Locating the rate-limiting step for the interaction of hydrogen with Mg (0001) using density-functional theory calculations and rate theory. *Physical Review B*, 70(3):035412, 2004.

- [148] T. Tang, X. Liu, Y. Ji, J. Norskov, and K. Chan. Modeling hydrogen evolution reaction kinetics through explicit water-metal interfaces. *The Journal of Physical Chemistry C*, 124(51):28083–28092, 2020.
- [149] M. Chialvo and A. Chialvo. Kinetics of hydrogen evolution reaction with frumkin adsorption: re-examination of the Volmer – Heyrovsky and Volmer – Tafel routes. *Electrochimica acta*, 44(5):841–851, 1998.
- [150] A. Benbouzid, M. Gomes, I. Costa, O. Gharbi, N. Pébère, J. Rossi, M. Tran, B. Tribollet, M. Turmine, and V. Vivier. A new look on the corrosion mechanism of magnesium: an EIS investigation at different ph. *Corrosion Science*, 205:110463, 2022.
- [151] S. Surendralal, M. Todorova, M. Finnis, and J. Neugebauer. First-principles approach to model electrochemical reactions: Understanding the fundamental mechanisms behind mg corrosion. *Physical Review Letters*, 120(24):246801, 2018.
- [152] R. Fogarty, B. Li, N. Harrison, and A. Horsfield. Structure and interactions at the Mg (0001)/water interface: an ab initio study. *The Journal of Chemical Physics*, 156(24), 2022.
- [153] G. Williams, N. Birbilis, and H. McMurray. The source of hydrogen evolved from a magnesium anode. *Electrochemistry Communications*, 36:1–5, 2013.
- [154] S. Fajardo, C. Glover, G. Williams, and G. Frankel. The evolution of anodic hydrogen on high purity magnesium in acidic buffer solution. *Corrosion*, 73(5):482–493, 2017.
- [155] M. Taheri, J. Kish, N. Birbilis, M. Danaie, E. McNally, and J. McDermid. Towards a physical description for the origin of enhanced catalytic activity of corroding magnesium surfaces. *Electrochimica Acta*, 116:396–403, 2014.
- [156] D. Lysne, S. Thomas, M. Hurley, and N. Birbilis. On the Fe enrichment during anodic polarization of Mg and its impact on hydrogen evolution. *Journal of the Electrochemical Society*, 162(8):C396, 2015.

- [157] J. Hanawalt. Corrosion studies of magnesium and its alloys. *Trans Aime*, 147:273–299, 1942.
- [158] Y. Li, Z. Shi, X. Chen, and A. Atrens. Anodic hydrogen evolution on Mg. *Journal of Magnesium and Alloys*, 9(6):2049–2062, 2021.
- [159] G. Song and A. Atrens. Corrosion mechanisms of magnesium alloys. *Advanced Engineering Materials*, 1(1):11–33, 1999.
- [160] A. Samaniego, B. Hurley, and G. Frankel. On the evidence for univalent Mg. *Journal of Electroanalytical Chemistry*, 737:123–128, 2015.
- [161] S. Xu, J. Dong, and W. Ke. Effect of magnesium hydride on the corrosion behavior of pure magnesium in 0.1 M NaCl solution. *International Journal of Corrosion*, 2010, 2010.
- [162] W. Jeffrey, F. Zargarzadah, V. Dehnavi, J. Chen, J. Noël, and D. Shoesmith. Physical and electrochemical evidence for the role of a Mg hydride species in Mg alloy corrosion. *Corrosion*, 75(1):58–68, 2019.
- [163] T. Jiang, L. Sun, and W. Li. First-principles study of hydrogen absorption on Mg (0001) and formation of magnesium hydride. *Physical Review B*, 81(3):035416, 2010.
- [164] P. Pedferri and M. Ormellese. *Corrosion science and engineering*, volume 720. Springer, 2018.
- [165] K. Unocic, H. Elsentriecy, M. Brady, H. Meyer, G. Song, M. Fayek, R. Meisner, and B. Davis. Transmission electron microscopy study of aqueous film formation and evolution on magnesium alloys. *Journal of the Electrochemical Society*, 161(6):C302, 2014.
- [166] M. Zhao, M. Liu, G. Song, and A. Atrens. Influence of ph and chloride ion concentration on the corrosion of mg alloy ZE41. *Corrosion Science*, 50(11):3168–3178, 2008.
- [167] G. Song and K. Unocic. The anodic surface film and hydrogen evolution on Mg. *Corrosion Science*, 98:758–765, 2015.

- [168] J. Chen, J. Wang, E. Han, J. Dong, and W. Ke. States and transport of hydrogen in the corrosion process of an AZ91 magnesium alloy in aqueous solution. *Corrosion Science*, 50(5):1292–1305, 2008.
- [169] A. Seyeux, M. Liu, P. Schmutz, G. Song, A. Atrens, and P. Marcus. ToF – SIMS depth profile of the surface film on pure magnesium formed by immersion in pure water and the identification of magnesium hydride. *Corrosion Science*, 51(9):1883–1886, 2009.
- [170] M. Brady, M. Fayek, H. Elsentriecy, K. Unocic, L. Anovitz, J. Keiser, G. Song, and B. Davis. Tracer film growth study of hydrogen and oxygen from the corrosion of magnesium in water. *Journal of the Electrochemical Society*, 161(9):C395, 2014.
- [171] M. Taheri, R. Phillips, J. Kish, and G. Botton. Analysis of the surface film formed on mg by exposure to water using a FIB cross-section and STEM – EDS. *Corrosion Science*, 59:222–228, 2012.
- [172] J. Nordlien, S. Ono, N. Masuko, and K. Nisancioglu. A TEM investigation of naturally formed oxide films on pure magnesium. *Corrosion Science*, 39(8):1397–1414, 1997.
- [173] J. Mejias, A. Berry, K. Refson, and D. Fraser. The kinetics and mechanism of MgO dissolution. *Chemical Physics Letters*, 314(5-6):558–563, 1999.
- [174] O. Fruhwirth, G. Herzog, I. Hollerer, and A. Rachetti. Dissolution and hydration kinetics of MgO. *Surface Technology*, 24(3):301–317, 1985.
- [175] Q. Luo, Y. Guo, B. Liu, Y. Feng, J. Zhang, Q. Li, and K. Chou. Thermodynamics and kinetics of phase transformation in rare earth-magnesium alloys: A critical review. *Journal of Materials Science & Technology*, 44:171–190, 2020.
- [176] G. Wu, C. Wang, M. Sun, and W. Ding. Recent developments and applications on high-performance cast magnesium rare-earth alloys. *Journal of Magnesium and Alloys*, 9(1):1–20, 2021.

- [177] S. Leleu, B. Rives, J. Bour, N. Causse, and N. Pébère. On the stability of the oxides film formed on a magnesium alloy containing rare-earth elements. *Electrochimica Acta*, 290:586–594, 2018.
- [178] Y. Feng, Q. Li, T. Zhao, and F. Pan. A quasi-passivated film formed on as-solutionized Mg – Sm – Zn – Zr alloy in NaCl solution. *Corrosion Science*, 198:110136, 2022.
- [179] M. Liu, P. Schmutz, P. Uggowitzer, G. Song, and A. Atrens. The influence of yttrium (Y) on the corrosion of Mg – Y binary alloys. *Corrosion Science*, 52(11):3687–3701, 2010.
- [180] H. Azzeddine, A. Hanna, A. Dakhouche, L. Rabahi, N. Scharnagl, M. Dopita, F. Brisset, A. Helbert, and T. Baudin. Impact of rare-earth elements on the corrosion performance of binary magnesium alloys. *Journal of Alloys and Compounds*, 829:154569, 2020.
- [181] M. Dunwell, Y. Yan, and B. Xu. Understanding the influence of the electrochemical double-layer on heterogeneous electrochemical reactions. *Current Opinion in Chemical Engineering*, 20:151–158, 2018.
- [182] J. Bockris, A. Reddy, and M. Gamboa-Adelco. *Modern Electrochemistry 1, 2A, and 2B*. Springer, 2006.
- [183] H. Helmholtz. Studien über electrische grenzschichten. *Annalen der Physik*, 243(7):337–382, 1879.
- [184] M. Gouy. Sur la constitution de la charge électrique à la surface d’un électrolyte. *J. Phys. Theor. Appl.*, 9(1):457–468, 1910.
- [185] D. Chapman. Li. a contribution to the theory of electrocapillarity. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 25(148):475–481, 1913.
- [186] O. Stern. Zur theorie der elektrolytischen doppelschicht. *Zeitschrift für Elektrochemie und Angewandte Physikalische Chemie*, 30(21-22):508–516, 1924.
- [187] B. Conway, J. Bockris, and I Ammar. The dielectric constant of the solution in the diffuse and helmholtz double layers at a charged interface in aqueous solution. *Transactions of the Faraday Society*, 47:756–766, 1951.

- [188] F. Fogolari, A. Brigo, and H. Molinari. The Poisson – Boltzmann equation for biomolecular electrostatics: a tool for structural biology. *Journal of Molecular Recognition*, 15(6):377–392, 2002.
- [189] G. Torrie and J. Valleau. Electrical double layers. 4. limitations of the Gouy – Chapman theory. *The Journal of Physical Chemistry*, 86(16):3251–3257, 1982.
- [190] X. Wang, K. Liu, and J. Wu. Demystifying the Stern layer at a metal-electrolyte interface: Local dielectric constant, specific ion adsorption, and partial charge transfer. *The Journal of Chemical Physics*, 154(12), 2021.
- [191] D. Grahame. The electrical double layer and the theory of electrocapillarity. *Chemical Reviews*, 41(3):441–501, 1947.
- [192] J. Bockris, M. Devanathan, and K. Müller. On the structure of charged interfaces. In *Electrochemistry*, pages 832–863. Elsevier, 1965.
- [193] W. Schmickler. Electronic effects in the electric double layer. *Chemical Reviews*, 96(8):3177–3200, 1996.
- [194] K. Sakaushi, T. Kumeda, S. Hammes-Schiffer, M. Melander, and O. Sugino. Advances and challenges for experiment and theory for multi-electron multi-proton transfer at electrified solid–liquid interfaces. *Physical Chemistry Chemical Physics*, 22(35):19401–19442, 2020.
- [195] N. Ottosson, M. Faubel, S. Bradforth, P. Jungwirth, and B. Winter. Photoelectron spectroscopy of liquid water and aqueous solution: Electron effective attenuation lengths and emission-angle anisotropy. *Journal of Electron Spectroscopy and Related Phenomena*, 177(2-3):60–70, 2010.
- [196] S. Shin, D. Kim, G. Bae, S. Ringe, H. Choi, H. Lim, C. Choi, and H. Kim. On the importance of the electric double layer structure in aqueous electrocatalysis. *Nature Communications*, 13(1):174, 2022.

- [197] C. Li, J. Le, Y. Wang, S. Chen, Z. Yang, J. Li, J. Cheng, and Z. Tian. In situ probing electrified interfacial water structures at atomically flat surfaces. *Nature materials*, 18(7):697–701, 2019.
- [198] L. Collins, J. Kilpatrick, I. Vlassiouk, A. Tselev, S. Weber, S. Jesse, S. Kalinin, and B. Rodriguez. Dual harmonic kelvin probe force microscopy at the graphene-liquid interface. *Applied Physics Letters*, 104(13), 2014.
- [199] E. Strelcov, C. Arble, H. Guo, B. Hoskins, A. Yulaev, I. Vlassiouk, N. Zhitenev, A. Tselev, and A. Kolmakov. Nanoscale mapping of the double layer potential at the graphene-electrolyte interface. *Nano Letters*, 20(2):1336–1344, 2020.
- [200] O. Magnussen and A. Groß. Toward an atomic-scale understanding of electrochemical interface structure and dynamics. *Journal of the American Chemical Society*, 141(12):4777–4790, 2019.
- [201] M. Hansen, A. Nilsson, and J. Rossmeisl. Modelling pH and potential in dynamic structures of the water/Pt(111) interface on the atomic scale. *Physical Chemistry Chemical Physics*, 19(34):23505–23514, 2017.
- [202] A. Bouzid and A. Pasquarello. Atomic-scale simulation of electrochemical processes at electrode/water interfaces under referenced bias potential. *The Journal of Physical Chemistry Letters*, 9(8):1880–1884, 2018.
- [203] K. Yang, S. Yiacoumi, and C. Tsouris. Monte carlo simulations of electrical double-layer formation in nanopores. *The Journal of Chemical Physics*, 117(18):8499–8507, 2002.
- [204] C. Hou, P. Taboada-Serrano, S. Yiacoumi, and C. Tsouris. Monte carlo simulation of electrical double-layer formation from mixtures of electrolytes inside nanopores. *The Journal of Chemical Physics*, 128(4), 2008.
- [205] T. Jang, D. Paik, Seung-J. Shin, and H. Kim. Density functional theory in classical explicit solvents: Mean-field QM/MM method for simulating solid–liquid interfaces. *Bulletin of the Korean Chemical Society*, 43(4):476–483, 2022.

- [206] S. Izvekov, A. Mazzolo, K. VanOopdorp, and G. Voth. Ab initio molecular dynamics simulation of the Cu(110) – water interface. *The Journal of Chemical Physics*, 114(7):3248–3257, 2001.
- [207] S. Meng, L. Xu, E. Wang, and S. Gao. Vibrational recognition of hydrogen-bonded water networks on a metal surface. *Physical Review Letters*, 89(17):176104, 2002.
- [208] S. Schnur and A. Groß. Properties of metal-water interfaces studied from first principles. *New Journal of Physics*, 11(12):125003, 2009.
- [209] A. Michaelides, A. Alavi, and D. King. Insight into H₂O-ice adsorption and dissociation on metal surfaces from first-principles simulations. *Physical Review B*, 69(11):113404, 2004.
- [210] P. Li, Y. Jiao, J. Huang, and S. Chen. Electric double layer effects in electrocatalysis: Insights from ab initio simulation and hierarchical continuum modeling. *JACS Au*, 2023.
- [211] J. Le, M. Iannuzzi, A. Cuesta, and J. Cheng. Determining potentials of zero charge of metal electrodes versus the standard hydrogen electrode from density-functional-theory-based molecular dynamics. *Physical Review Letters*, 119(1):016801, 2017.
- [212] S. Kelly, H. Heenen, N. Govindarajan, K. Chan, and J. Nørskov. OH binding energy as a universal descriptor of the potential of zero charge on transition metal surfaces. *The Journal of Physical Chemistry C*, 126(12):5521–5528, 2022.
- [213] A. Bard, L. Faulkner, and H. White. *Electrochemical methods: fundamentals and applications*. John Wiley & Sons, 2022.
- [214] T. Pajkossy and D. Kolb. Double layer capacitance of Pt (111) single crystal electrodes. *Electrochimica Acta*, 46(20-21):3063–3071, 2001.
- [215] Y. Fang, G. Wei, and Z. Liu. Theoretical modeling of electrode/electrolyte interface from first-principles periodic continuum solvation method. *Catalysis Today*, 202:98–104, 2013.

- [216] N. Garcia-Araez, V. Climent, E. Herrero, J. Feliu, and J. Lipkowski. Thermodynamic approach to the double layer capacity of a Pt(111) electrode in perchloric acid solutions. *Electrochimica Acta*, 51(18):3787–3793, 2006.
- [217] J. Le, Q. Fan, J. Li, and J. Cheng. Molecular origin of negative component of helmholtz capacitance at electrified Pt(111)/water interface. *Science Advances*, 6(41):eabb1219, 2020.
- [218] V. Tripkovic, M. Björketun, E. Skúlason, and J. Rossmeisl. Standard hydrogen electrode and potential of zero charge in density functional calculations. *Physical Review B*, 84(11):115452, 2011.
- [219] J. Rossmeisl, E. Skúlason, M. Björketun, V. Tripkovic, and J. Nørskov. Modeling the electrified solid-liquid interface. *Chemical Physics Letters*, 466(1-3):68–71, 2008.
- [220] M. Björketun, Z. Zeng, R. Ahmed, V. Tripkovic, K. Thygesen, and J. Rossmeisl. Avoiding pitfalls in the modeling of electrochemical interfaces. *Chemical Physics Letters*, 555:145–148, 2013.
- [221] N. Bonnet, T. Morishita, O. Sugino, and M. Otani. First-principles molecular dynamics at a constant electrode potential. *Physical Review Letters*, 109(26):266101, 2012.
- [222] M. Melander. Grand canonical rate theory for electrochemical and electrocatalytic systems i: General formulation and proton-coupled electron transfer reactions. *Journal of The Electrochemical Society*, 167(11):116518, 2020.
- [223] E. Schrödinger. Quantisierung als eigenwertproblem. *Annalen der Physik*, 385(13):437–490, 1926.
- [224] V. Fock. Näherungsmethode zur lösung des quantenmechanischen mehrkörperproblems. *Zeitschrift für Physik*, 61:126–148, 1930.
- [225] W. Kohn and L. Sham. Density functional theory. In *CONFERENCE PROCEEDINGS-ITALIAN PHYSICAL SOCIETY*, volume 49, pages 561–572. EDITRICE COMPOSITORI, 1996.

- [226] J. Perdew, K. Burke, and M. Ernzerhof. Generalized gradient approximation made simple. *Physical Review Letters*, 77(18):3865, 1996.
- [227] A. Becke. Density-functional exchange-energy approximation with correct asymptotic behavior. *Physical Review A*, 38(6):3098, 1988.
- [228] J. Wellendorff, K. Lundgaard, A. Møgelhøj, V. Petzold, D. Landis, J. Nørskov, T. Bligaard, and K. Jacobsen. Density functionals for surface science: Exchange-correlation model development with bayesian error estimation. *Physical Review B*, 85(23):235149, 2012.
- [229] P. Schwerdtfeger. The pseudopotential approximation in electronic structure theory. *ChemPhysChem*, 12(17):3143–3155, 2011.
- [230] D. Hamann, M. Schlüter, and C. Chiang. Norm-conserving pseudopotentials. *Physical Review Letters*, 43(20):1494, 1979.
- [231] D. Vanderbilt. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Physical Review B*, 41(11):7892, 1990.
- [232] P. Blöchl. Projector augmented-wave method. *Physical Review B*, 50(24):17953, 1994.
- [233] G. Kresse and J. Furthmüller. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B*, 54(16):11169, 1996.
- [234] G. Kresse and J. Furthmüller. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science*, 6(1):15–50, 1996.
- [235] F. Bloch. Über die quantenmechanik der elektronen in kristallgittern. *Zeitschrift für Physik*, 52(7-8):555–600, 1929.
- [236] K. Mathew, R. Sundararaman, K. Letchworth-Weaver, T. Arias, and R. Hennig. Implicit solvation model for density-functional study of nanocrystal surfaces and reaction pathways. *The Journal of Chemical Physics*, 140(8), 2014.

- [237] J. Fattebert and F. Gygi. First-principles molecular dynamics simulations in a continuum solvent. *International Journal of Quantum Chemistry*, 93(2):139–147, 2003.
- [238] O. Andreussi, I. Dabo, and N. Marzari. Revised self-consistent continuum solvation in electronic-structure calculations. *The Journal of Chemical Physics*, 136(6), 2012.
- [239] S. Petrosyan, A. Rigos, and T. Arias. Joint density-functional theory: Ab initio study of Cr_2O_3 surface chemistry in solution. *The Journal of Physical Chemistry B*, 109(32):15436–15444, 2005.
- [240] H. Eyring. The activated complex in chemical reactions. *The Journal of Chemical Physics*, 3(2):107–115, 1935.
- [241] A. Voter and J. Doll. Dynamical corrections to transition state theory for multistate systems: Surface self-diffusion in the rare-event regime. *The Journal of Chemical Physics*, 82(1):80–92, 1985.
- [242] G. Henkelman, G. Jóhannesson, H. Jónsson, and S. Schwartz. Progress on theoretical chemistry and physics. *Kluwer Academic Publishers*, pages 269–300, 2000.
- [243] G. Mills and H. Jónsson. Quantum and thermal effects in H_2 dissociative adsorption: Evaluation of free energy barriers in multidimensional quantum systems. *Physical Review Letters*, 72(7):1124, 1994.
- [244] G. Henkelman, B. Uberuaga, and H. Jónsson. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *The Journal of Chemical Physics*, 113(22):9901–9904, 2000.
- [245] D. Chao, W. Zhou, F. Xie, C. Ye, H. Li, M. Jaroniec, and S. Qiao. Roadmap for advanced aqueous batteries: From design of materials to applications. *Science Advances*, 6(21):eaba4098, 2020.
- [246] S. Nitopi, E. Bertheussen, S. Scott, X. Liu, A. Engstfeld, S. Horch, B. Seger, I. Stephens, K. Chan, C. Hahn, J. Nørskov, T. Jaramillo, and I. Chorkendorff. Progress and perspectives

- of electrochemical CO₂ reduction on copper in aqueous electrolyte. *Chemical Reviews*, 119(12):7610–7672, 2019.
- [247] T. Abbott. Magnesium: industrial and research developments over the last 15 years. *Corrosion*, 71(2):120–127, 2015.
- [248] N. Sezer, Z. Evis, S. Kayhan, A. Tahmasebifar, and M. Koç. Review of magnesium-based biomaterials and their applications. *Journal of Magnesium and Alloys*, 6(1):23–43, 2018.
- [249] R. Dominko, J. Bitenc, R. Berthelot, M. Gauthier, G. Pagot, and V. Di Noto. Magnesium batteries: Current picture and missing pieces of the puzzle. *Journal of Power Sources*, 478:229027, 2020.
- [250] J. Le, A. Cuesta, and J. Cheng. The structure of metal-water interface at the potential of zero charge from density functional theory-based molecular dynamics. *Journal of Electroanalytical Chemistry*, 819:87–94, 2018.
- [251] K. Limmer, K. Williams, J. Labukas, and J. Andzelm. First principles modeling of cathodic reaction thermodynamics in dilute magnesium alloys. *Corrosion*, 73(5):506–517, 2017.
- [252] E. Skúlason, G. Karlberg, J. Rossmeisl, T. Bligaard, J. Greeley, H. Jónsson, and J. Nørskov. Density functional theory calculations for the hydrogen evolution reaction in an electrochemical double layer on the Pt (111) electrode. *Physical Chemistry Chemical Physics*, 9(25):3241–3250, 2007.
- [253] S. Trasatti. Work function, electronegativity, and electrochemical behaviour of metals: II. potentials of zero charge and “electrochemical” work functions. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 33(2):351–378, 1971.
- [254] B. Fitchett, J. Rollins, and J. Conboy. Interfacial tension and electrocapillary measurements of the room temperature ionic liquid/aqueous interface. *Langmuir*, 21(26):12179–12186, 2005.

- [255] A. Cuesta. Measurement of the surface charge density of CO-saturated Pt (111) electrodes as a function of potential: the potential of zero charge of Pt (111). *Surface Science*, 572(1):11–22, 2004.
- [256] A. Auer, X. Ding, A. Bandarenka, and J. Kunze-Liebhauser. The potential of zero charge and the electrochemical interface structure of Cu (111) in alkaline solutions. *The Journal of Physical Chemistry C*, 125(9):5020–5028, 2021.
- [257] S. Sakong and A. Groß. The electric double layer at metal-water interfaces revisited based on a charge polarization scheme. *The Journal of chemical physics*, 149(8), 2018.
- [258] M. Gillan, D. Alfe, and A. Michaelides. Perspective: How good is DFT for water? *The Journal of Chemical Physics*, 144(13), 2016.
- [259] G. Kresse and D. Joubert. From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical Review B*, 59(3):1758, 1999.
- [260] J. Carrasco, J. Klimeš, and A. Michaelides. The role of van der waals forces in water adsorption on metals. *The Journal of Chemical Physics*, 138(2), 2013.
- [261] J. Neugebauer and M. Scheffler. Adsorbate-substrate and adsorbate-adsorbate interactions of Na and K adlayers on Al(111). *Physical Review B*, 46(24):16067, 1992.
- [262] M. Krack. Pseudopotentials for H to Kr optimized for gradient-corrected exchange-correlation functionals. *Theoretical Chemistry Accounts*, 114:145–152, 2005.
- [263] H. Kawano. Effective work functions of the elements: Database, most probable value, previously recommended value, polycrystalline thermionic contrast, change at critical temperature, anisotropic dependence sequence, particle size dependence. *Progress in Surface Science*, 97(1):100583, 2022.
- [264] P. Bagus, V. Staemmler, and C. Wöll. Exchangelike effects for closed-shell adsorbates: Interface dipole and work function. *Physical Review Letters*, 89(9):096104, 2002.

- [265] X. Crispin, V. Geskin, A. Crispin, J. Cornil, R. Lazzaroni, W. Salaneck, and J. Bredas. Characterization of the interface dipole at organic/metal interfaces. *Journal of the American Chemical Society*, 124(27):8131–8141, 2002.
- [266] H. Vázquez, Y. Dappe, J. Ortega, and F. Flores. A unified model for metal/organic interfaces: Idis, ‘pillow’ effect and molecular permanent dipoles. *Applied Surface Science*, 254(1):378–382, 2007.
- [267] L. Pedroza, A. Poissier, and M. Fernández-Serra. Local order of liquid water at metallic electrode surfaces. *The Journal of Chemical Physics*, 142(3), 2015.
- [268] L. Bellarosa, R. García-Muelas, G. Revilla-López, and N. López. Diversity at the water-metal interface: metal, water thickness, and confinement effects. *ACS Central Science*, 2(2):109–116, 2016.
- [269] Y. Yang, Y. Li, S. Wang, and P. Zhang. Adsorption structure of water molecules on the Be (0001) surface. *Journal of Applied Physics*, 115(21), 2014.
- [270] V. Ranea, A. Michaelides, R. Ramirez, J. Verges, P. De Andres, and D. King. Density functional theory study of the interaction of monomeric water with the Ag 111 surface. *Physical Review B*, 69(20):205411, 2004.
- [271] V. Ranea. Potential energy surface of H₂O on Al 111 and Rh 111 from theoretical methods. *The Journal of Chemical Physics*, 137(20), 2012.
- [272] K. Christmann. Interaction of hydrogen with solid surfaces. *Surface Science Reports*, 9(1-3):1–163, 1988.
- [273] M. Hofman, D. Wang, Y. Yang, and B. Koel. Interactions of incident H atoms with metal surfaces. *Surface Science Reports*, 73(4):153–189, 2018.
- [274] P. Sprunger and E. Plummer. The interaction of hydrogen with simple metal surfaces. *Surface Science*, 307:118–123, 1994.

- [275] J. Guo and P. Chen. Interplay of alkali, transition metals, nitrogen, and hydrogen in ammonia synthesis and decomposition reactions. *Accounts of Chemical Research*, 54(10):2434–2444, 2021.
- [276] B. Sakintuna, F. Lamari-Darkrim, and M. Hirscher. Metal hydride materials for solid hydrogen storage: a review. *International Journal of Hydrogen Energy*, 32(9):1121–1140, 2007.
- [277] I. Jain, C. Lal, and A. Jain. Hydrogen storage in mg: a most promising material. *International Journal of Hydrogen Energy*, 35(10):5133–5144, 2010.
- [278] Q. Luo, J. Li, B. Li, B. Liu, H. Shao, and Q. Li. Kinetics in mg-based hydrogen storage materials: Enhancement and mechanism. *Journal of Magnesium and Alloys*, 7(1):58–71, 2019.
- [279] Y. Shang, C. Pistidda, G. Gizer, T. Klassen, and M. Dornheim. Mg-based materials for hydrogen storage. *Journal of Magnesium and Alloys*, 2021.
- [280] S. Fajardo, C. Glover, G. Williams, and G. Frankel. The source of anodic hydrogen evolution on ultra high purity magnesium. *Electrochimica Acta*, 212:510–521, 2016.
- [281] Z. Shi, G. Song, and A. Atrens. Corrosion resistance of anodised single-phase Mg alloys. *Surface and Coatings Technology*, 201(1-2):492–503, 2006.
- [282] M. Liu, P. Schmutz, S. Zanna, A. Seyeux, H. Ardelean, G. Song, A. Atrens, and P. Marcus. Electrochemical reactivity, surface composition and corrosion mechanisms of the complex metallic alloy Al_3Mg_2 . *Corrosion Science*, 52(2):562–578, 2010.
- [283] Z. Han, H. Chen, and S. Zhou. Dissociation and diffusion of hydrogen on defect-free and vacancy defective Mg (0001) surfaces: A density functional theory study. *Applied Surface Science*, 394:371–377, 2017.
- [284] J. Chen, J. Dong, J. Wang, E. Han, and W. Ke. Effect of magnesium hydride on the corrosion behavior of an AZ91 magnesium alloy in sodium chloride solution. *Corrosion Science*, 50(12):3610–3614, 2008.

- [285] A. Becke and K. Edgecombe. A simple measure of electron localization in atomic and molecular systems. *The Journal of Chemical Physics*, 92(9):5397–5403, 1990.
- [286] A. Savin, O. Jepsen, J. Flad, O. Andersen, H. Preuss, and H. von Schnering. Electron localization in solid-state structures of the elements: the diamond structure. *Angewandte Chemie International Edition in English*, 31(2):187–188, 1992.
- [287] R. Clements, J. Womack, and C. Skylaris. Electron localisation descriptors in onetep: a tool for interpreting localisation and bonding in large-scale dft calculations. *Electronic Structure*, 2(2):027001, 2020.
- [288] C. Weizsäcker. Zur theorie der kernmassen. *Zeitschrift für Physik*, 96(7):431–458, 1935.
- [289] F. Della Sala, E.o Fabiano, and L. Constantin. Kohn-sham kinetic energy density in the nuclear and asymptotic regions: Deviations from the von weizsäcker behavior and applications to density functionals. *Physical Review B*, 91(3):035126, 2015.
- [290] B. Patra, S. Jana, L. Constantin, and P. Samal. Relevance of the pauli kinetic energy density for semilocal functionals. *Physical Review B*, 100(15):155140, 2019.
- [291] A. Savin, R. Nesper, S. Wengert, and T. Fässler. ELF: The electron localization function. *Angewandte Chemie International Edition in English*, 36(17):1808–1832, 1997.
- [292] A. Savin, A. Becke, J. Flad, R. Nesper, H. Preuss, and H. Von Schnering. A new look at electron localization. *Angewandte Chemie International Edition in English*, 30(4):409–412, 1991.
- [293] L. De Santis and R. Resta. Electron localization at metal surfaces. *Surface Science*, 450(1-2):126–132, 2000.
- [294] R. Rousseau and D. Marx. Exploring the electronic structure of elemental lithium: from small molecules to nanoclusters, bulk metal, and surfaces. *Chemistry–A European Journal*, 6(16):2982–2993, 2000.

- [295] F. Ample, D. Curulla, F. Fuster, A. Clotet, and J. Ricart. Adsorption of CO and CN^- on transition metal surfaces: a comparative study of the bonding mechanism. *Surface Science*, 497(1-3):139–154, 2002.
- [296] J. Lang, D. and Zaikina, D. Lovingood, T. Gedris, and S. Latturner. $\text{Ca}_2\text{LiC}_3\text{H}$: A new complex carbide hydride phase grown in metal flux. *Journal of the American Chemical Society*, 132(49):17523–17530, 2010.
- [297] R. Nesper and S. Wengert. Localization patterns in interstitial space: A special property of the electron localization function (ELF). *Chemistry—A European Journal*, 3(6):985–991, 1997.
- [298] S. Dong, C. Li, J. Wang, H. Liu, Z. Ding, Z. Gao, W. Yang, W. Lv, L. Wei, and Y. Wu. The “burst effect” of hydrogen desorption in MgH_2 dehydrogenation. *Journal of Materials Chemistry A*, 2022.
- [299] P. Fuentealba, E. Chamorro, and J. Santos. Understanding and using the electron localization function. In *Theoretical and Computational Chemistry*, volume 19, pages 57–85. Elsevier, 2007.
- [300] H. Monkhorst and J. Pack. Special points for Brillouin-zone integrations. *Physical Review B*, 13(12):5188, 1976.
- [301] J. Renner and H. Grabke. Determination of diffusion coefficients in the hydriding of alloys. *Zeitschrift für Metallkunde*, 69(10):639–642, 1978.
- [302] M. Yan, Z. Huang, Y. Zhang, and C. Chang. Trends in water-promoted oxygen dissociation on the transition metal surfaces from first principles. *Physical Chemistry Chemical Physics*, 19(3):2364–2371, 2017.
- [303] A. Anderson, J. Uddin, and R. Jinnouchi. Solvation and zero-point-energy effects on OH (ads) reduction on Pt(111) electrodes. *The Journal of Physical Chemistry C*, 114(35):14946–14952, 2010.

- [304] G. Wu, S. Liu, J. Zhang, Y. Wu, L. Qian, K. Chou, and X. Bao. Density functional theory study on hydrogenation mechanism in catalyst-activated Mg (0001) surface. *Transactions of Nonferrous Metals Society of China*, 19(2):383–388, 2009.
- [305] G. Kresse. Dissociation and sticking of H₂ on the Ni (111),(100), and (110) substrate. *Physical Review B*, 62(12):8295, 2000.
- [306] R. Staub, M. Iannuzzi, R. Khaliullin, and S. Steinmann. Energy decomposition analysis for metal surface–adsorbate interactions by block localized wave functions. *Journal of Chemical Theory and Computation*, 15(1):265–275, 2018.
- [307] A. Allred. Electronegativity values from thermochemical data. *Journal of Inorganic and Nuclear Chemistry*, 17(3-4):215–221, 1961.
- [308] T. Noritake, M. Aoki, S. Towata, Y. Seno, Y. Hirose, E. Nishibori, M. Takata, and M. Sakata. Chemical bonding of hydrogen in MgH₂. *Applied Physics Letters*, 81(11):2008–2010, 2002.
- [309] D. Wang, J. Liu, J. Zhang, S. Raza, X. Chen, and C. Jia. Ewald summation for ferroelectric perovskites with charges and dipoles. *Computational Materials Science*, 162:314–321, 2019.
- [310] W. Tang, E. Sanville, and G. Henkelman. A grid-based bader analysis algorithm without lattice bias. *Journal of Physics: Condensed Matter*, 21(8):084204, 2009.
- [311] S. Ong, W. Richards, A. Jain, G. Hautier, M. Kocher, S. Cholia, D. Gunter, V. Chevrier, K. Persson, and G. Ceder. Python materials genomics (pymatgen): A robust, open-source python library for materials analysis. *Computational Materials Science*, 68:314–319, 2013.
- [312] R. Ouellette and J. Rawn. *Principles of Organic Chemistry*. Academic Press, 2015.
- [313] T. Krygowski and H. Szatyłowicz. Varying electronegativity of OH/O-groups depending on the nature and strength of H-bonding in phenol/phenolate involved in H-bond complexation. *The Journal of Physical Chemistry A*, 110(22):7232–7236, 2006.

- [314] F. Cheng and J. Chen. Metal–air batteries: from oxygen reduction electrochemistry to cathode catalysts. *Chemical Society Reviews*, 41(6):2172–2192, 2012.
- [315] J. Gao, X. Li, Q. Liu, H. Fan, S. Gao, Y. Song, and E. Wang. A chloride-free electrolyte to suppress the anodic hydrogen evolution corrosion of magnesium anode in aqueous magnesium air batteries. *Chemical Engineering Journal*, 464:142655, 2023.
- [316] Y. Wang, Y. Sun, W. Ren, D. Zhang, Y. Yang, J. Yang, J. Wang, X. Zeng, and Y. NuLi. Challenges and prospects of Mg-air batteries: A review. *Energy Materials*, 2(200024):10–20517, 2022.
- [317] C. Li, Y. Sun, F. Gebert, and S. Chou. Current progress on rechargeable magnesium-air battery. *Advanced Energy Materials*, 7(24):1700869, 2017.
- [318] M. Deng, D. Höche, S. Lamaka, L. Wang, and M. Zheludkevich. Revealing the impact of second phase morphology on discharge properties of binary Mg – Ca anodes for primary Mg-air batteries. *Corrosion Science*, 153:225–235, 2019.
- [319] X. You, X. Zhang, C. Yu, Y. Chen, H. Li, Y. Hou, L. Tian, N. Yang, and G. Xie. Corrosion protection of magnesium alloys anode by cerium-based anodization coating in magnesium-air battery. *Journal of Rare Earths*, 41(3):471–476, 2023.
- [320] X. Zhao, J. Su, G. Li, J. He, S. Chen, G. Wang, and A. Liu. The electrochemical behavior of Mg – 9Al – 0.5Zn, Mg – 9Al – 0.7Zn, and Mg – 9Al – 1.0Zn in a NaCl solution. *Materials and Corrosion*, 70(11):2082–2087, 2019.
- [321] B. Li, C. Xiao, N. Harrison, R. Fogarty, and A. Horsfield. Role of electron localisation in H adsorption and hydride formation in the Mg basal plane under aqueous corrosion: a first-principles study. *Physical Chemistry Chemical Physics*, 25(8):5989–6001, 2023.
- [322] H. Liu, X. Jia, A. Cao, L. Wei, C. D’agostino, and H. Li. The surface states of transition metal X-ides under electrocatalytic conditions. *The Journal of Chemical Physics*, 158(12), 2023.

- [323] A. Groß. Reversible vs standard hydrogen electrode scale in interfacial electrochemistry from a theoretician’s atomistic point of view. *The Journal of Physical Chemistry C*, 126(28):11439–11446, 2022.
- [324] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT – D) for the 94 elements H – Pu. *The Journal of Chemical Physics*, 132(15), 2010.
- [325] K. Mathew, V. Kolluru, S. Mula, S. Steinmann, and R. Hennig. Implicit self-consistent electrolyte model in plane-wave density-functional theory. *The Journal of Chemical Physics*, 151(23), 2019.
- [326] M. Chase and National Information Standards Organization (US). NIST – JANAF *thermochemical tables*, volume 9. American Chemical Society Washington, DC, 1998.
- [327] G. Henkelman and H. Jónsson. Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. *The Journal of Chemical Physics*, 113(22):9978–9985, 2000.
- [328] R. Fogarty and A. Horsfield. Molecular dynamics study of structure and reactions at the hydroxylated Mg(0001)/bulk water interface. *The Journal of Chemical Physics*, 157(15), 2022.
- [329] D. Cheng, Z. Wei, Z. Zhang, P. Broekmann, A. Alexandrova, and P. Sautet. Restructuring and activation of Cu(111) under electrocatalytic reduction conditions. *Angewandte Chemie*, 135(20):e202218575, 2023.
- [330] G. Henkelman, A. Arnaldsson, and H. Jónsson. A fast and robust algorithm for bader decomposition of charge density. *Computational Materials Science*, 36(3):354–360, 2006.
- [331] M. Yu and D. Trinkle. Accurate and efficient algorithm for bader charge integration. *The Journal of Chemical Physics*, 134(6), 2011.
- [332] R. Nelson, C. Ertural, J. George, V. Deringer, G. Hautier, and R. Dronskowski. LOBSTER: Local orbital projections, atomic charges, and chemical-bonding analysis from projector-

- augmented-wave-based density-functional theory. *Journal of Computational Chemistry*, 41(21):1931–1940, 2020.
- [333] J. Tersoff and D. Hamann. Theory and application for the scanning tunneling microscope. *Physical Review Letters*, 50(25):1998, 1983.
- [334] M. Ng, D. Blackwood, H. Jin, and T. Tan. First-principles investigation into the contributions of ORR and HER in magnesium corrosion. *Journal of The Electrochemical Society*, 2023.
- [335] M. Born. Volumen und hydrationswärme der ionen. *Zeitschrift für Physik*, 1(1):45–48, 1920.
- [336] S. Yoo, M. Todorova, and J. Neugebauer. Selective solvent-induced stabilization of polar oxide surfaces in an electrochemical environment. *Physical Review Letters*, 120(6):066101, 2018.
- [337] A. Aziz and J. Carrasco. Modeling magnesium surfaces and their dissolution in an aqueous environment using an implicit solvent model. *The Journal of Chemical Physics*, 156(17), 2022.
- [338] M. Zauchner, A. Horsfield, and T. Todorov. Efficient electron open boundaries for simulating electrochemical cells. *Physical Review B*, 97(4):045116, 2018.