

**Ab Initio Theoretical Studies of Electrocatalysis for
Oxygen and Carbon Dioxide Reduction Reactions**

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A thesis submitted for the degree of Doctor of Philosophy

Statement of originality

I, Ruixuan Chen, confirm that the research included within this thesis is my work or that where it has been carried out in collaboration with or supported by others, this is duly acknowledged below, and my contribution is indicated. Previously published material is also acknowledged below. This thesis has not been previously submitted for the award of a degree by this or any other university.

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Abstract

The present PhD thesis focuses on the investigation of model catalysts, primarily Fe-N-C macrocycles, in two key electrochemical processes: the oxygen reduction reaction (ORR) and the carbon dioxide reduction reaction (CO₂RR). Additionally, the nitrogen-doped carbon material in ORR is also studied. The main motivation behind this research is to lay the groundwork for the rational design of catalysts that can be effectively employed in electrochemical cells. Such catalysts have the potential to significantly mitigate CO₂ emissions, contribute to the closure of the carbon cycle, and facilitate the utilisation of renewable energy sources.

By employing DFT calculations, this thesis explores the electronic structures, binding energies, and thermodynamic considerations of the model catalysts. In the first project, the theoretical computations are combined with experimental data to comprehensively unravel the mechanisms of Fe-N-C macrocycles for the ORR. In the following project, the transition metal carbon M-N-C (M=Fe, Co, Ni, Cu) with the same macrocycle structures in the previous study are applied to screen for selective and efficient CO₂RR catalyst. It turns out the Fe-N-C is also a promising CO₂RR catalyst and further analysis is conducted. For the last project, the nitrogen doped carbon model catalysts are employed to understand a long-standing contentious issue: origin of their ORR active site. The insights gained from these studies shed light on the underlying mechanisms and key factors governing the catalytic performance of these materials.

The research outcomes presented in this thesis contribute to the advancement of catalyst design strategies for the ORR and CO₂RR, highlighting the potential for achieving sustainable energy conversion processes. The reduction of CO₂ emissions and the establishment of a closed carbon cycle can be facilitated, promoting a greener and more sustainable future.

List of Publications

Publications related to this thesis:

Chen R., Favero S., Wang M., Luo H., Barrio J., Higgins L., Cheung J., Bagger A., Stephens I. & Titirici M. Kinetics of oxygen reduction on Fe macrocycles. In preparation (It includes most of the results in chapter 4)

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Table 4.4 Scaling relations of the intermediates. OLS stands for ordinary least square, β is the fitted slope and α is the intercept. Fixed β is the scheme that *O has the double bond hence $\beta=2$ while for the rest *OOH and *OH $\beta=1$. The μ and σ are the mean and standard deviation values for the intercept.

Table 4.5 Binding Energies (G) of oxygenated ORR intermediates species (*O, *OH, *OOH) on the selected Fe macrocycles with water on its back side, for spin relaxed magnetic moments m=0 and m=2.

Table 5.1 Spin relaxed and fixed configurations for different metal atoms of macrocycles. HS is noted for high spin, IS for intermediate spin and LS for low spin.

Table 5.2 DFT energy of raw Fe macrocycles with different magnetic moment *(m=2), *(m=0) and intermediates H*, CO*, COOH*. Binding energy E(H*), E(CO*) and E(COOH*) are shown for the spin relaxed *(m=2) configuration. Notation of AABB and ABAB are defined in chapter 4.3.2.

Table 5.3 DFT energy of raw Co macrocycles with different magnetic moment *(m=1), *(m=0.5) and intermediates H*, CO*, COOH*. Binding energy E(H*), E(CO*) and E(COOH*) are shown for the spin relaxed *(m=1) configuration.

Table 5.4 DFT energy of raw Ni macrocycles with different magnetic moment $^*(m=0)$, $^*(m=0.5)$ and intermediates H^* , CO^* , $COOH^*$. Binding energy $E(H^*)$, $E(CO^*)$ and $E(COOH^*)$ are shown for the spin relaxed $^*(m=0)$ configuration.

Table 5.5 DFT energy of raw Cu macrocycles with different magnetic moment $^*(m=0.5)$, $^*(m=0)$ and intermediates H^* , CO^* , $COOH^*$. Binding energy $E(H^*)$, $E(CO^*)$ and $E(COOH^*)$ are shown for the spin relaxed $^*(m=0.5)$ configuration.

Table 5.6 Energy corrections, ZPE is zero-point energy, the integral is the heat capacity, $-TS$ is the entropy contribution, μ is the chemical potential.

Table 5.7 DFT and binding energies of the charged molecules. The charge $Q(-3)$ is the total charge of the entire molecule. The values in red are outliers.

Table 5.8 DFT and binding energies of the charged molecules. The charge $Q(-2)$ is the total charge of the entire molecule.

Table 5.9 DFT and binding energies of the charged molecules. The charge $Q(-1)$ is the total charge of the entire molecule.

Table 5.10 DFT and binding energies of the charged molecules. The charge $Q(+1)$ is the total charge of the entire molecule

Table 5.11 DFT and binding energies of the charged molecules. The charge $Q(+2)$ is the total charge of the entire molecule.

Table 5.12 DFT and binding energies of the charged molecules. The charge $Q(+3)$ is the total charge of the entire molecule.

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Table 5.14 Summary of magnetic moment of Fe for charged molecules without any absorbates.

Table 6.1 DFT energies of the molecules and OH on nitrogen of the molecules marked with $*$ and $^*OH$ (N) respectively. $G(^*OH)$ (N) are the free energies of OH on nitrogen.

Table 6.2 On zigzag (4, 4) graphene, DFT energies of the molecules and OH on nitrogen of the molecules marked with * and *OH (N) respectively. C1 means OH bind on the closest non-quaternary carbon near the nitrogen, and C2 are carbon atoms sampled on the graphene plane. Columns starts with G are the free energies of the corresponding configurations.

Table 6.3 On zigzag (9, 3) graphene, DFT energies of the molecules and OH on nitrogen of the molecules marked with * and *OH (N) respectively. C means OH bind on the closest non-quaternary carbon near the nitrogen. Columns starts with G are the free energies of the corresponding configurations.

Table 6.4 Parallel to zigzag (4, 4) graphene, DFT energies of the molecules and OH on nitrogen of the molecules marked with * and *OH (N) respectively. C means OH bind on the closest non-quaternary carbon near the nitrogen. Columns starts with G are the free energies of the corresponding configurations.

Table 6.5 DFT energies of the molecules and OH on nitrogen of the molecules marked with * and *OH (N) respectively. C means OH bind on the closest non-quaternary carbon near the nitrogen. Columns starts with G are the free energies of the corresponding configurations. Molecules are either bonded through a carbon atom with gold (Bonded) or parallel to the gold plane (Parallel).

Acronyms

CHE	Computational Hydrogen Electrode
CO ₂ RR	CO ₂ reduction reaction
CV	Cyclic Voltammogram
BO	Born-Oppenheimer
DFT	Density Functional Theory
FFT	Fast Fourier Transform
GGA	Generalised Gradient Approximation
GTO	Gaussian Type Orbital
HER	Hydrogen Evolution Reaction
HF	Hartree-Fock
HK	Hohenberg-Kohn
HOPG	Highly Oriented Pyrolytic Graphite
HSE06	Heyd-Scuseria-Ernzerhof 2006
KS	Kohn-Sham
LCAO	Linear Combination of Atomic Orbitals
LDA	Local Density Approximation
LSDA	Local Spin Density Approximation
LSV	Linear Sweep Voltammogram
ORR	Oxygen Reduction Reaction
OER	Oxygen Evolution Reaction
PBE	Perdew-Burke-Ernzerhof
RHE	Reversible Hydrogen Electrode
RPBE	Revised Perdew-Burke-Ernzerhof
SHE	Standard Hydrogen Electrode
SWV	Square Wave Voltammetry
XANES	X-ray Adsorption Near Edge Spectroscopy
XAS	X-ray Adsorption Spectroscopy
XPS	X-ray Photoelectron Spectroscopy

Objectives and outlines of this thesis

The objectives of this thesis are:

- (1) Elucidate fundamental mechanisms of Fe-macrocycles in ORR by utilising density functional theory (DFT) and computational hydrogen electrode (CHE) model. Explain the anomalies in the corresponding experiments.
- (2) Reveal underlying mechanisms of transition-metal-macrocycles in CO₂RR with DFT and binding energy classification model. Screen the possible candidates as efficient CO₂RR catalysts for future experiments.
- (3) Explore the potential mechanisms of ORR activity for metal free nitrogen doped carbon materials with DFT and CHE.

The main novelties in relevant project:

- (1) In Fe-macrocycles, the primary categories are Fe-phthalocyanine and Fe-porphyrin. Upon examining their cyclic voltammograms for ORR, it was observed that they displayed either a single peak or double peaks during the scanning process. All the Fe-porphyrins show single peak while except 4NH₂FePC all Fe-phthalocyanines show double peaks. Notably, the group exhibiting double peaks demonstrated significantly improved ORR performance for the 4-electron pathway. This thesis begins by calculating the binding energies to validate the scaling relation within the Fe-macrocycle system, followed by demonstrating that *OH desorption acts as the rate-limiting step. It is found that the single peak group exhibits excessive binding of *OH, which reduces its favourability. Additionally, the single peak group shows a higher tendency for peroxide selection, resulting from a higher binding energy of *O compared to *OOH, further reducing its efficiency for ORR to water. The valence of Fe corresponding to the peaks is investigated, revealing that both Fe²⁺ and Fe³⁺ are possible under different solvation energies. For the samples displaying a single peak only, it is proposed that an electrochemical reaction occurs where the electron is not released, rendering it undetectable by CV but instead

absorbed by the catalyst to accommodate its spin as per thermodynamics. This proposal also fits into the scheme of modelled XANES spectrum.

- (2) In transition-metal-macrocycles (M-N-C, M=Fe, Co, Ni, Cu) for CO₂RR, single metal catalytic site is of particular interest due to the potential ability to hinder the HER. This thesis starts by calculating the binding energy of the intermediates H*, CO*, and COOH* with different spins. It is found that the Fe-macrocycles with relaxed spin exhibit promising CO₂RR performance with suppressed HER. Further study with charge variation indicates that 4NH₂FePC is the most promising one due to its higher affinity toward H* compared to COOH*. This material is also the outlier in ORR study where it is Fe-phthalocyanine but only show single peak.
- (3) Differentiating the contributions of various nitrogen types to the ORR in metal-free nitrogen-doped carbon poses challenges. In this thesis, models for different catalysts are constructed based on experimental data, and their binding energies are investigated. However, the use of CHE is limited by the requirement for conductive materials, whereas the experimental materials exhibit semiconducting properties. Therefore, substrates are substituted to fulfil the conductive criteria of CHE. The origin of electroactivity can be partially attributed to the quaternary nitrogen, whereas the rest nitrogen species demonstrate no activity in the modelled system. This could be attributed to deviations from the intended synthesis process or the significant influence of entangled configurations and material defects. In such cases, a single molecule model may underfit.

Chapter 1 provides an introduction to the landscape of climate change and increasing energy demands, as well as an electrochemical solution to these challenges.

Chapter 2 delves into the fundamentals of DFT for electronic structure modelling and calculation.

Chapter 3 introduces the fundamentals of electrochemical cells and CHE for theoretical modelling.

Chapter 4 presents a brief review of the research on the ORR and then proceeds to investigate the mechanisms of Fe-macrocycles in depth. I conducted all the modelling and theoretical analysis, while Silvia Favero performed all the experiments.

Chapter 5 briefly reviews the research on the CO₂RR and subsequently investigates its mechanisms in transition metal nitrogen carbon (M-N-C) materials. Utilising the models and theoretical analysis developed, a screening of promising materials for the reaction was conducted.

Chapter 6 gives an overview of metal free nitrogen doped carbon materials for ORR, followed by a study of the reaction mechanisms. I constructed various models to understand the origin of the electrocatalytic activity while Yue Xu conducted all the experiments.

Chapter 7 summarises the main conclusions of this PhD work and provides an outlook for future research.

Chapter 1

Introduction

In this chapter, I will present the motivations and objectives of my research. It begins with the worldwide concerns of climate change and rising energy consumption, moves on to explore renewable energy and electrochemical solution, and ultimately lands on the catalysts.

1.1 Climate change and escalating energy demand

After the first industrial revolution, coal became a primary source of energy. Following the second industrial revolution, oil and gas joined this queue as well. However, the utilisation of these fossil fuels has resulted in the accumulation of large amounts of greenhouse gases in the atmosphere, particularly carbon dioxide (CO₂), which contributes to global warming and climate change, posing a threat to the entire ecosystem.^{25,26} For example, as global temperatures increase, the polar icebergs are melting, causing sea levels to rise.²⁵ This can lead to flooding in coastal areas²⁷ and the displacement of people who live in these regions. Except for human, some marine organisms are unable to adapt to changes in temperature resulting in death and disruption of biodiversity that have drastic impacts on food webs.²⁵ Furthermore, climate change indicates the increasing frequency of extreme weather conditions, such as scorching droughts and frigid blizzards which bring about disastrous loss.²⁶

The harmful environmental effects have been recognised globally. In 2015, 196 countries signed the Paris Agreement, a legally binding international treaty on climate change that aims to limit the global temperature increase to below 2°C and pursue efforts to limit it further down to 1.5°C.²⁸ The past and the future regarding the amount of CO₂ emission and potential global temperature increase are summarised in **Figure 1.1**.

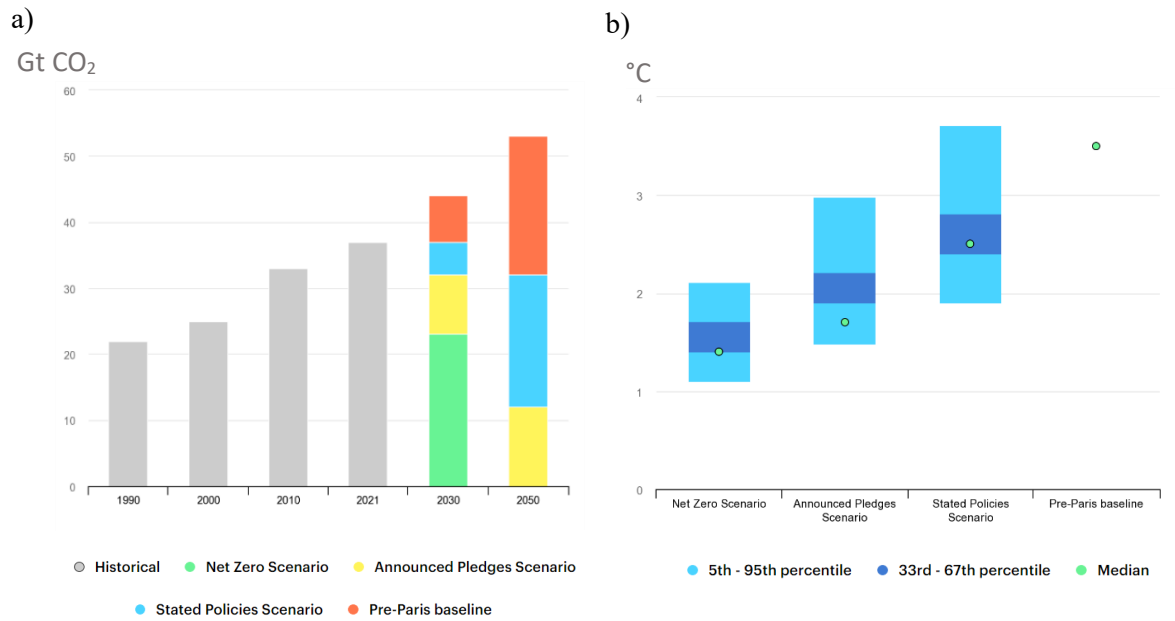


Figure 1.1 a) Global energy related CO₂ emissions (Gt Gigaton) by scenario, 1990-2050.¹ The coloured bar is stacked from bottom to top depending on the scenario stated. b) Peak temperature rises in the IEA World Energy Outlook-2022 by scenarios.²

It is discouraging that even if all countries continue their current policies after the Paris Agreement, with a CO₂ emission level dropping back to that of 2010 in 2050, the projected temperature will still rise by approximately 2.5°C, missing the basic 2°C target. Therefore, enormous efforts are needed to achieve the announced pledges or even to appeal for net zero emissions.

Besides the environmental concern, the fossil fuels are not renewable in the long run due to their finite nature. From the trend in world annual energy consumption in **Figure 1.2**, except for major events, for instance 1979 oil crisis, 2008 financial crisis and Covid 2019, the demand for energy is always increasing. The compound effect will exhaust the non-renewable energy sources inevitably at an exponential rate. Thus, the need for renewable energy that will potentially address the challenges as described is unprecedented high.

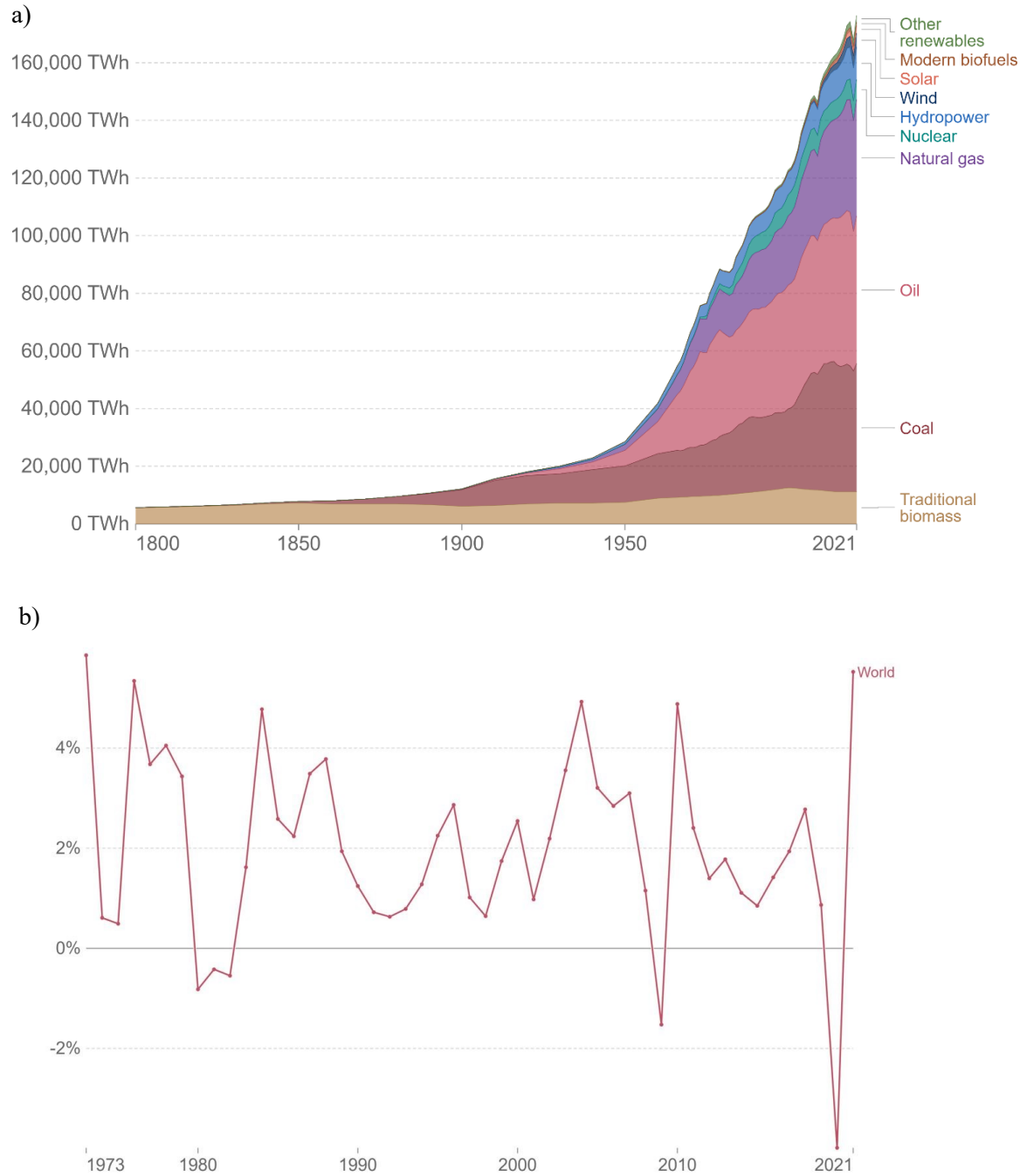


Figure 1.2 a) Global primary energy consumption by source ~1800-2021. b) Annual percentage change in world energy consumption 1973-2021.³

1.2 Electrochemical approach

Renewable energy sources come from naturally replenished sources and can be replenished within a human lifecycle. Many renewable energy sources like solar, wind, and hydropower produce no direct CO₂ emissions at all during operation. It is noted that a tiny number of indirect emissions during construction and installation do exist but negligible. In 2020, 29% of the world's electricity was generated from renewable sources, up from 27% in 2019.²⁹ While the statistics may be inspiring, the main challenge facing renewable energy such as those mentioned above is their intermittency. Electricity generated can be tremendously wasted due to the mismatch between supply and demand. Hence, advanced energy storage and conversion devices are of vital importance to the development of renewable energy techniques.

Electrochemical approach has attracted extensive attention, since it is promising for closing the carbon cycle and achieving net zero emissions.^{4,30} Electricity that is difficult to integrate into the power grid can be stored as chemical energy or more valuable chemical feedstock by using CO₂ as a reactant. This approach has the benefit of reducing CO₂ levels in the atmosphere, a primary greenhouse gas that is actively sought to be removed. Energy conversion can be achieved using hydrogen (H₂) as chemical fuel, a completely carbon-free and clean source of energy with water (H₂O) as the sole product, or other hydrocarbons that are reduced from CO₂. And the electricity will be converted from the chemical energy via fuel cell. H₂ and O₂ can be evolved from the H₂O by electrolysis making a closed energy loop. These are illustrated in **Figure 1.3**.

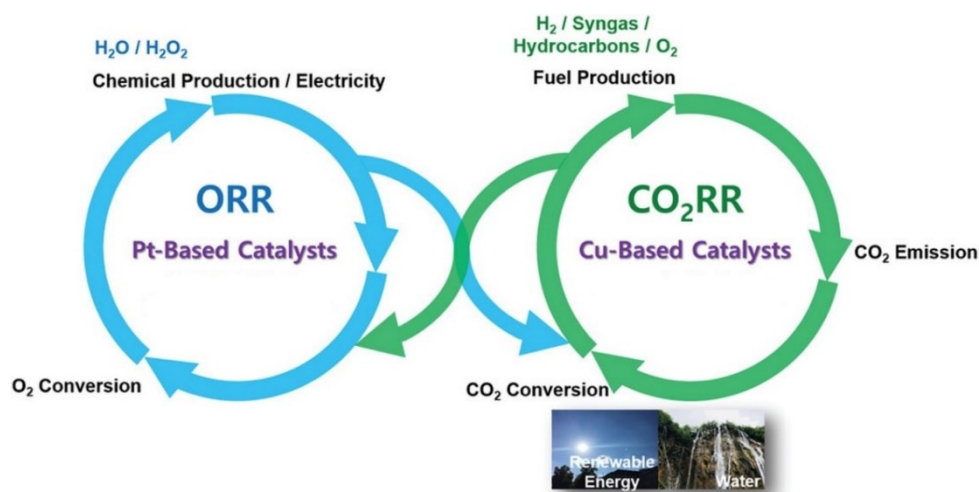


Figure 1.3 Schematic illustration of the renewable energy utilisation vision via electrochemical approach for carbon and energy cycle. Currently the core catalysts for both ORR and CO₂RR require alternatives or improvements.⁴

The working principle of hydrogen proton exchange membrane fuel cell (PEMFC), an important electrochemical device to convert the chemical energy into electricity, is shown below.

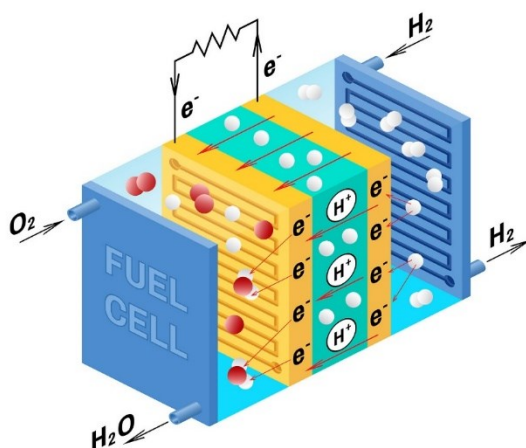


Figure 1.4 Proton exchange membrane fuel cell working principle diagram.⁵

The anode of the fuel cell receives fuel H₂, where it undergoes a chemical reaction with a catalyst, causing it to split into protons and electrons. The cathode, on the other hand, receives oxygen from the air. The protons move through a permeable electrolyte membrane towards the cathode, while the electrons flow out of the fuel cell, generating an electrical current. The only by-product is water at the cathode from the protons and oxygen. There are alternative fuel sources and different types of fuel cells that can serve a similar purpose, albeit with varying specifications to accommodate different scenarios.³¹

However, the overall efficiency of fuel cell is greatly reduced due to the sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode. Despite it has been demonstrated that the use of platinum (Pt) and its alloys can enhance the performance of the ORR, their limited availability and high cost impose a constraint on their wider application.^{12,32,33} Additionally, Pt is prone to rapid deactivation because of the occurrence of methanol crossover, which refers to the diffusion of the methanol fuel from the anode

to the cathode. This can result in two factors that can decrease the efficiency of the ORR: the electro-oxidation of the crossed-over methanol at the cathode, and the poisoning effect caused by carbon monoxide (CO) resulting from incomplete methanol oxidation.³⁴

As for the electrochemical systems for CO₂ reduction, it consists of four components, as depicted in **Figure 1.5**: a cathode, an anode, an electrolyte containing CO₂, and a membrane. The cathode serves as the electrocatalyst for the reduction of CO₂, while the anode provides a site for oxidation, such as the oxygen evolution reaction (OER). State-of-art materials for anode are precious metals and their oxides such as Ir, Ru, IrO₂ and RuO₂.³⁵ The electrolyte is essential to facilitate transport of charged species, transport CO₂ to the surface of the electrocatalyst. The membrane, such as polytetrafluoroethylene (PTFE) or perfluoro sulfonic acid (PFSA) separates the products of oxidation and reduction while maintaining charge balance.³⁶ Typical electrochemical reactions at the electrode are shown inside the figure. The OER at the anode will not be discussed in detail as it is less critical to the overall performance and is outside the scope of this thesis. However, its correlation to ORR will be revealed in **Chapter 3**. For the CO₂RR at the cathode, except for CO which costs two electrons per molecule, there are a range of products containing one (C1) or two (C2) carbon atoms that can be generated at different potentials (**Table 1.1**) The list is not exhausted, other species are possible as well.

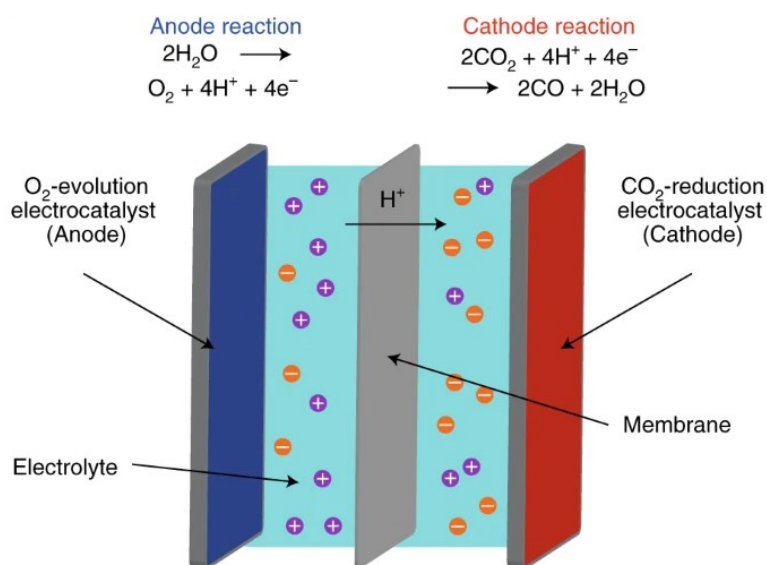


Figure 1.5 A typical electrochemical CO₂ recycling system.⁶

Half reactions of CO ₂ reduction	Electrode potentials, E^0 (V vs SHE, pH = 7)
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O}$	-0.33
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}$	-0.35
$2\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-0.38
$(2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2)$	-0.42
$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$	-0.51
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.53
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$	-0.61
$\text{CO}_2 + \text{e}^- \rightarrow \text{CO}_2^{\cdot-}$	-1.90

Table 1.1 Standard electrode potentials of CO₂ conversions to C1 and C2 products in aqueous solutions.²⁴

Nonetheless, The electrochemical reduction of CO₂ (CO₂RR) is both energetically and atomically inefficient due to high kinetic overpotentials and challenges in selectively producing desired chemical products, especially in competition with the hydrogen evolution reaction (HER) in aqueous environments.⁴ Cu-based catalysts are potential solutions to the issue, but they suffer from low efficiency and selectivity.^{37,38}

1.3 Objectives and outlines of this thesis

This chapter introduces the motivation for CO₂ reduction and energy conversion device integrated with renewable energy harvester. Electrochemical approach is promising but hindered by the appropriate catalysts. To overcome this issue, it is important to develop low-cost, efficient, and selective catalysts for CO₂RR and ORR. However, the reaction mechanisms for these novel catalysts have yet to be

understood, posing a significant challenge for catalysts screening and performance optimisation. Therefore, the objectives of this thesis are:

- (4) Elucidate fundamental mechanisms of Fe-macrocycles in ORR by utilising density functional theory (DFT) and computational hydrogen electrode (CHE) model. Explain the anomalies in the corresponding experiments.
- (5) Reveal underlying mechanisms of transition-metal-macrocycles in CO₂RR with DFT and binding energy classification model. Screen the possible candidates as efficient CO₂RR catalysts for future experiments.
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Chapter 1 provides an introduction to the landscape of climate change and increasing energy demands, as well as an electrochemical solution to these challenges.

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Chapter 7 summarises the main conclusions of this PhD work and provides an outlook for future research.

Chapter 2

Electronic Structure Calculations

The macroscopic properties of the materials are determined by their microscopic electronic structures. The Schrödinger equation³⁹ describes the fundamental principles that govern the behaviour of atoms and electrons thus mapping the electronic interactions. However, an inherent obstacle arises when attempting to solve it in the presence of chaos resulting from many-body interactions. Density functional theory (DFT) offers an approximate solution to the ab initio method in solving the non-relativistic and time-independent Schrödinger equation of a many-body system.

2.1 Wavefunction Method

The wavefunction method is a fundamental approach in quantum mechanics that could describe the probabilistic behaviour of the wave-particle duality. By solving the Schrödinger equation, the necessity of DFT is introduced seamlessly.

2.1.1 Schrödinger Equation

The dynamics of a nonrelativistic quantum mechanical system can be described by the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi \quad (2-1)$$

Where Ψ is the many-body wave function and $\hat{H}$ is the Hamiltonian operator.

For a system consisting of M nuclei and N electrons, when taking the atomic units ($4\pi\epsilon_0 = \hbar = e = m_e = 1$), the Hamiltonian has the form

$$\begin{aligned}\hat{H} = & -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{k=1}^M \frac{1}{M_k} \nabla_k^2 - \sum_{i=1}^N \sum_{k=1}^M \frac{Z_k}{|\mathbf{r}_i - \mathbf{R}_k|} \\ & + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{k=1}^M \sum_{l \neq k}^M \frac{Z_k Z_l}{|\mathbf{R}_k - \mathbf{R}_l|}\end{aligned}\quad (2-2)$$

The first and second terms are kinetic energy of the nuclei and electrons, respectively. The third term is the electrostatic attraction between the electrons and nuclei, and the fourth and fifth terms are the electrostatic repulsion within electrons and nuclei themselves.

The wavefunction Ψ is a function of nuclei position $\mathbf{R}$, electrons position $\mathbf{r}$, and spin state σ . As the Hamiltonian is independent of time variable t, considering equation (2-1), factorisation can be applied:

$$\Psi(\mathbf{R}, \mathbf{r}, \sigma, t) = \Phi(\mathbf{R}, \mathbf{r}, \sigma) A(t) \quad (2-3)$$

Insert (2-3) back to equation (2-1):

$$A(t) = \exp(-iEt) \quad (2-4)$$

$$\hat{H}\Psi(\mathbf{R}, \mathbf{r}, \sigma) = E\Psi(\mathbf{R}, \mathbf{r}, \sigma) \quad (2-5)$$

Therefore, the nonrelativistic time-dependent Schrödinger equation reduces to its time-independent form where E is the energy associated with the time-independent wavefunction Ψ .

However, even for the time-independent Schrödinger equation, the solution becomes intractable except for hydrogen atom or hydrogen-like systems. As the interaction terms are cyclic dependent when there are more than two particles inside the system. This is referred to as the many-body problem. Besides, the dimension for the representation of the system is too high for practical computation.

2.1.2 The Born-Oppenheimer Approximation⁴⁰

Since the nuclei are much heavier than the electrons, electrons move much faster than nuclei such that the electrons can be viewed as moving in the field of stationary nuclei. The assumption of fixed nuclei not only makes nuclei kinetic energy zero but also nuclei potential energy a constant. Therefore, the Hamiltonian for many-body given in (2-2) has been reduced to the one for many electrons. The updated many electrons Hamiltonian is given by:

$$\hat{H}_e = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i) + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + E_{kn} \quad (2-6)$$

Where $V_{\text{ext}}(\mathbf{r}_i)$ is external potential created by the nuclei as stated before

$$V_{\text{ext}}(\mathbf{r}_i) = \sum_{k=1}^M \frac{Z_k}{|\mathbf{r}_i - \mathbf{R}_k|} \quad (2-7)$$

With BO approximation we simplified the Hamiltonian as the kinetic energy of the electrons, potential energy of the electrons in the field of nuclei, potential energy due to electron-electron interaction. It can be written in the following compact form:

$$\hat{H}_e = \hat{T}_e + \hat{V}_{ext} + \hat{V}_{ee} \quad (2-8)$$

2.2 Density Functional Theory

The wavefunction method we have developed so far requires $4N$ coordinates with $3N$ position-space and N spin coordinates given N electrons. The linear scaling relationship with the number of electrons prohibitively hinders its application. Ever since the Thomas and Fermi's "electron gas" proposal,^{41,42} it occurs to people that one may acquire the experiment observables without knowing the complete N -electron wavefunction. Instead, the role used to play by the wavefunction can be replaced by the ground state electron density $\rho(\mathbf{r})$ which is given by:

$$\int \rho(\mathbf{r}) d\mathbf{r} = N \quad (2-9)$$

2.2.1 The Hohenberg-Kohn Theorems

The first Hohenberg-Kohn theorem⁴³ states that the external potential $V_{ext}(\mathbf{r})$ is (up to a constant) a unique functional of $\rho(\mathbf{r})$. Therefore, together with the definition of electron density in (2-9), the ground state is a unique functional of $\rho(\mathbf{r})$. We can write the energy functional as following:

$$E[\rho(\mathbf{r})] = \int \rho(\mathbf{r})V_{ext}(\mathbf{r})d\mathbf{r} + F_{HK}[\rho(\mathbf{r})] \quad (2-10)$$

Where $F_{HK}[\rho(\mathbf{r})]$ is called *universal functional* that is independent of $V_{ext}(\mathbf{r})$

$$F_{HK}[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})] \quad (2-11)$$

This theorem proves the existence of $\rho(\mathbf{r})$ while the next theorem introduces a path to find the $\rho(\mathbf{r})$. The second Hohenberg-Kohn theorem states that the electron density $\tilde{\rho}(\mathbf{r})$ that minimises the total energy of the system is the true ground state density. Again, it is the variational principle that leads to the ground state density $\rho_0(\mathbf{r})$. And such scheme is the Density Functional Theory (DFT). If we know the form of universal functional, the Schrödinger equation is solved exactly under BO approximation. But this is not the reality, and further approximations need to be employed.

2.2.2 The Kohn-Sham Methods⁴⁴

Following the second HK theorem and the electron numbers constraint we have: the variation of electron density around ground state is zero.

$$\frac{\delta}{\delta\rho(\mathbf{r})} \left\{ E[\rho(\mathbf{r})] - \mu \left(\int \rho(\mathbf{r})d\mathbf{r} - N \right) \right\} = 0 \quad (2-12)$$

If we inspect $E[\rho(\mathbf{r})]$, it contains the external potential, kinetic energy and electron-electron interactions term which includes classic Coulombic potential $V_C(\mathbf{r})$ (the Hartree energy), and quantum exchange and correlation effect $E_{xc}[\rho(\mathbf{r})]$. Neglecting the higher order changes in $\delta\rho(\mathbf{r})$:

$$\frac{\delta T}{\delta \rho} + V_{ext}(\mathbf{r}) + V_c(\mathbf{r}) + \frac{\delta E_{xc}'}{\delta \rho} = \mu \quad (2-13)$$

To solve this equation Kohn and Sham came up with a brilliant idea which makes it a norm for follow-up research. They suppose there exists a fictitious system of N non-interacting electrons that have the same density and energy with the interacting system we are interested in. To accomplish such assumption the non-interacting electrons must move in an effective external field $V_{KS}(\mathbf{r})$:

$$\frac{\delta T_0}{\delta \rho} + V_{KS}(\mathbf{r}) = \mu \quad (2-14)$$

$$V_{KS}(\mathbf{r}) = \frac{\delta T}{\delta \rho} - \frac{\delta T_0}{\delta \rho} + V_{ext}(\mathbf{r}) + V_c(\mathbf{r}) + \frac{\delta E_{xc}'}{\delta \rho} \quad (2-15)$$

The Hamiltonian for the artificial system is trivial:

$$\hat{H}_{KS} = -\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r}) \quad (2-16)$$

Then the kohn-Sham equation is:

$$\hat{H}_{KS}\phi_i = \epsilon_i\phi_i \quad (2-17)$$

the electron density is given by:

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2 \quad (2-18)$$

However, there are terms unknown in (2-29) which are called exchange-correlation energy and potential:

$$V_{xc}(\mathbf{r}) \equiv \frac{\delta E_{xc}}{\delta \rho} \equiv \frac{\delta T}{\delta \rho} - \frac{\delta T_0}{\delta \rho} + \frac{\delta E'_{xc}}{\delta \rho} \quad (2-19)$$

If we know the exact E_{xc} then the Kohn-Sham equation would be solved exactly. Therefore, one of the main tasks for modern density functional theory is to find better approximations of these quantities.

To this point, the Kohn-Sham approach provides a density functional alternative that significantly reduces the variable dimensions and make them independent of the number of electrons. It creates a reference system and explicitly define all the known quantities, leaving the unknowns into an exchange-correlation functional that is remained to be derived.

2.3 Exchange-Correlation Functionals

2.3.1 Local Density Approximation

The quality of the DFT is determined by the exchange-correlation functional $E_{xc}[\rho(\mathbf{r})]$. For local density approximation (LDA), the assumption is that the electrons are distributed uniformly and locally in each small volume element. LDA treats the $E_{xc}[\rho(\mathbf{r})]$ exactly as the Tomas-Fermi homogeneous gas model⁴⁵.

2.3.2 Generalised Gradient Approximation

The LDA gives a comparable or better result compared to Hartree-Fock approximation, but it is still crude in terms of its use in chemistry. Taylor expansion is a neat tool and easy to come up with when fitting. GGA extends the LDA by incorporating information about the spatial gradients of the electron density which makes it possible to be applied in chemical problems.

$$E_{XC}^{GGA}[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) \epsilon_{XC}[\rho(\mathbf{r}), \nabla \rho(\mathbf{r})] d\mathbf{r} \quad (2-22)$$

PBE⁴⁶ is one of the most popular functionals of this type. Later these functionals are further improved. For example, RPBE⁴⁷ is parameter free and provides a more accurate description of exchange-correlation effects for a wide range of systems. It is natural to include the Laplacian for higher precision, and that is called meta-GGA which is computationally more demanding. Besides, there exist hybrid functionals that are the mixture of different proportions of other functionals' exchange and correlation energy with the intention to accentuate the merit and avoid the drawback. HSE06⁴⁸ is the hybrid functional that includes part of the exact exchange energy and parameterised PBE functional.

One of the main challenges in computational catalysis is accurately predicting adsorption energies of molecules on surfaces. RPBE has been found to yield better predictions of adsorption energies for many systems, compared to other functionals.^{12,13,32} This is essential for understanding the mechanisms of electrocatalytic reactions and for designing better catalysts. HSE06 has been considered as an even more precise version of RPBE but with much heavier computation loading.²¹ Other hybrid functionals show worse predictions of binding energies for macrocycle systems with initial trials. Considering the balance between computational cost and precision, this thesis will use the RPBE functional throughout.

2.4 X-ray Absorption Spectroscopy

2.4.1 Introduction

X-ray absorption is a process in which a core electron in an atom is excited to an unoccupied orbital by an incoming x-ray with sufficient energy. By measuring the intensity of the absorption with the varying energy of the incident photon, a spectrum of the absorption cross section can be generated to determine the unoccupied density of states. The probability of an excitation increases sharply when the energy of the incident photon matches the binding energy of a core electron, which is known as an edge. It is named based on the shell of the core electron being excited (e.g., K-edge for 1s electron, L-edge for 2s or 2p electrons M-edge to 3s, 3p, 3d electrons etc.). XAS is element-specific due to the distinct binding energies of different elements, and XANES (X-ray Absorption Near Edge Structure) is a subset of XAS that focuses on the absorption within 50-100 eV of an edge to study the local electronic structure as shown in the figure below:

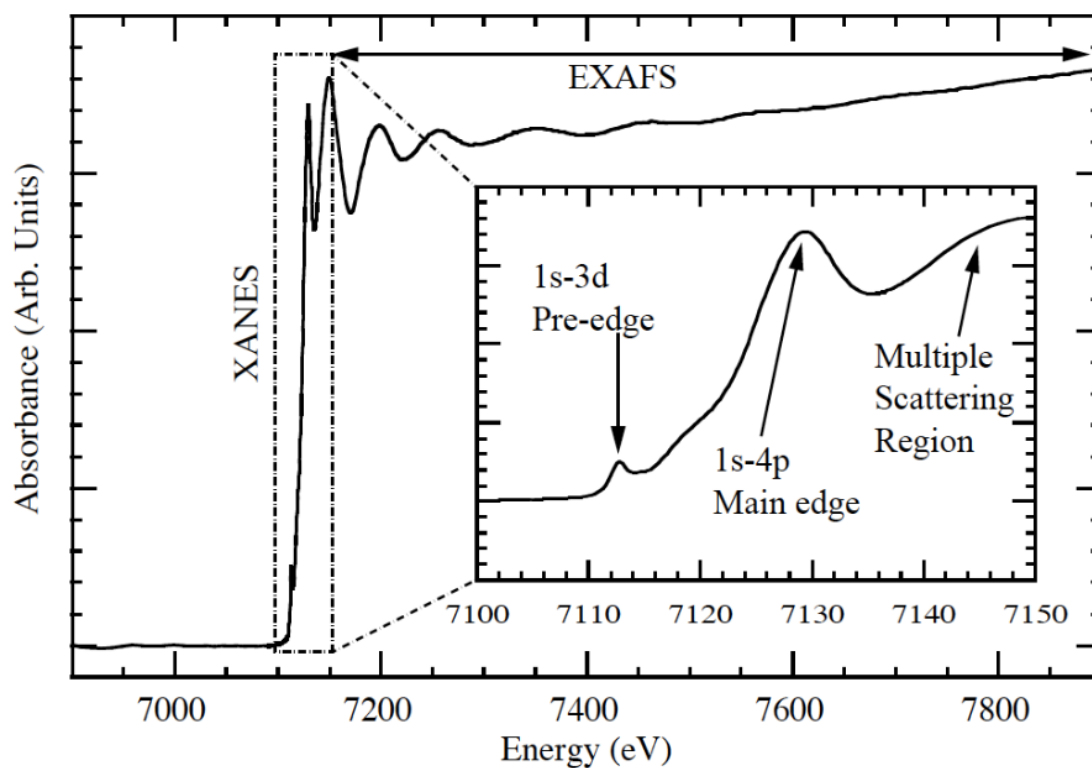


Figure 2.1 Illustration of XAS that includes XANES and EXAFS of Fe.⁷

XANES investigates the characteristics right before and right after the edge, covering roughly 1% of the main edge energy on both sides. This study focuses on aspects such as the edge's location (which primarily signifies the oxidation level), the existence and form of minor features immediately preceding the main edge ("pre-edge" features), and the intensity, quantity, placement, and form of peaks found at the main edge's summit.

2.4.2 Fermi's Golden Rule

Fermi's Golden Rule⁴⁹ estimates the transition rates between quantum states due to time-dependent perturbation. The transition rate is the probability of a transition per unit time.

$$I(\omega) \propto \sum_f |\langle \Psi_f | D | \Psi_i \rangle|^2 \delta(\omega - E_{fi}) \quad (2-23)$$

Where D is the time-dependent perturbation or dipole operator. f stands for the final state and i is the initial state, E_{fi} is the energy emitted over the transition. Delta symbol is the Dirac delta function whose value is zero everywhere except at zero, and whose integral over the entire real value is one. In the context of XAS, the intensity as a function of the incident photon's frequency is proportional to the transition rate of the initial state to the final state and the corresponding energy difference. However, the finite lifetime of the excited state leads to the broadening of its energy according to the Heisenberg's uncertainty principle. The Dirac delta function is the limit of the following Lorentzian function⁵⁰:

$$\delta(\omega - E_{fi}) \rightarrow \frac{4\Gamma}{(E_{fi} - \omega)^2 + \Gamma^2} \quad (2-24)$$

Where Γ is the half width at half maximum (HWHM) of the peak.

If the initial state is the core orbital and final state is the unoccupied orbital, then the energy difference will be the difference of their eigenvalue. But for many-body wavefunctions, the relaxation effects come in and the energy difference will deviate. It is still possible to optimise the molecule to ground and excited states to get the energy difference with DFT. However, the Kohn-Sham scheme will produce a non-interacting fictitious system with the same electron density in which the determination of the exact occupations of the excited state's orbital will be a problem. In practice, these parameters can be calibrated with experiment data.

2.5 Conclusion

The framework of the DFT is introduced to understand the electronic structures of materials. It is indispensable for interpreting the macroscopic properties of materials and is applied throughout the thesis. In addition, the method to simulate XANES spectrum is presented to provide insights when compared with the experiment result.

Chapter 3

Principle of electrochemical cells

This chapter focuses on the fundamentals of electrochemistry and the derivation of the computational model that is employed in the subsequent chapters. It consists of thermodynamics, general introductions for electrocatalysis, a concise derivation of computational hydrogen electrode (CHE) and its applications.

3.1 Thermodynamics

The change in Gibbs free energy ΔG can be used to predict the direction of the chemical or electrochemical reaction. For reaction that needs catalyst, normally $\Delta G > 0$ which indicates the reaction is not spontaneous and external energy is required for it to proceed. In electrocatalysis, the energy source is the electricity.

The potential of the electrochemical cell in general conditions is calculated from the reduction potentials of the two half-reactions. The half-reaction with a higher reduction potential will work as E_{red} , and the other one will be E_{ox} .

$$E_{cell} = E_{red} - E_{ox} \quad (3-1)$$

For a general half reaction where v_i is the coefficient, n is the stoichiometric number of electrons transferred in the process, and O_i and R_i are the oxidised reactant and reduced product respectively:



The potential of the half reaction is obtained from the Nernst equation:

$$E = E^\circ - \frac{RT}{nF} \ln \frac{\Pi a_{red}^{v_i}}{\Pi a_{ox}^{v_i}} \quad (3-3)$$

E° is the standard electrode potential whose value is relative to the standard hydrogen electrode (SHE), while $a_{red}^{v_i}$ and $a_{ox}^{v_i}$ are the activities of R_i and O_i . Activity measures the effective concentration of a species under non-ideal conditions:

$$a = e^{\frac{\mu - \mu^\circ}{RT}} \quad (3-4)$$

μ is the chemical potential and μ° is in standard state. It's the partial derivative of the Gibbs free energy with respect to the composition.

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,N_{j \neq i}} \quad (3-5)$$

A simple explanation for the necessity of activity for concentrated solution is that the ion migrations will be hindered or potentially be promoted compared to its diluted counterpart as the interionic interactions become significant. SHE is declared to be a reference electrode with zero volts potential under standard conditions: pressure of H_2 gas at 1 bar or 0.1 MPa, environment temperature at 298.15 K and the activity of H^+ protons at 1.

Thermodynamically, the change in free energy associated with the cell potential in an electrochemical reaction is summarised in the following equation:

$$\Delta G = -nFE_{cell} \quad (3-6)$$

where n is the number of electrons transferred per mole product.

3.2 Electrocatalysis

3.2.1 Electrochemical cell

A common electrochemical cell, as shown below, comprises an electrolyte, an anode and a cathode serving as two electrodes, an ion conductor and an electron conductor as two conductors, and a controller for imposing the potential bias. It should be noticed that often there is a reference electrode with stable electrode potential besides the two electrodes. The ion conductor shown in the figure is schematic, the ions could be other sensible ones. The anode is where the oxidation happens, and the cathode is for the reduction.

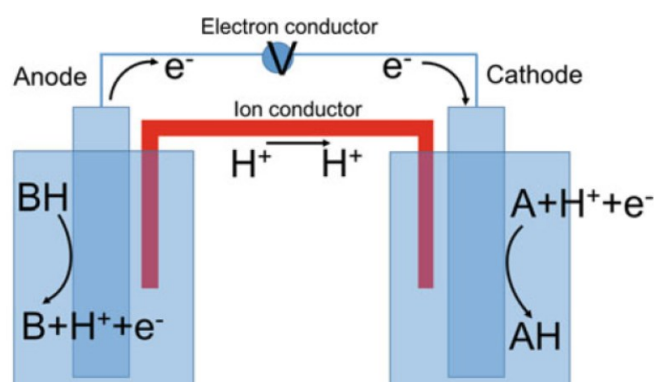


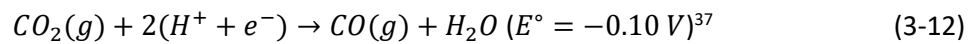
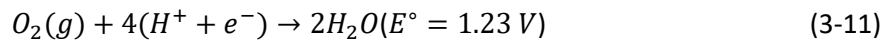
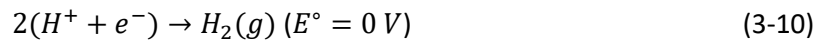
Figure 3.1. Illustration of an electrochemical cell with separated electron and ion conductor. At the cathode the reactant is reduced and receives a proton electron pair while at the anode the reactant is oxidised and releases a proton electron pair.⁸

3.2.2 Electrochemical catalytic reaction

The electrochemical catalytic reactions such as hydrogen evolution reaction (HER)⁵¹, the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER)^{10,12,13,32,52} and the CO₂ reduction reaction (CO₂RR)^{17,18,53} can be described by the equations in **Figure 3.1**:



And more specifically in the reduction form for the reactions of interest:



For ORR (3-10) is the reaction on the cathode and (3-11) on the anode. And according to (1-6) the free energy barrier of the entire electrochemical reaction is 4.92 eV. For CO₂RR, the anode remains the same, but at the cathode as it is aware that the potential difference between the (3-10) and (3-12) is too small to retain the thermodynamic advantage. Therefore, there exists two competitive routes for CO₂RR. To

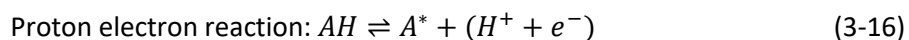
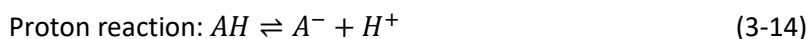
quantify the effect of multiple products, Faradaic efficiency (FE) is used as a metric that represents the proportion of the total current utilised to produce a particular product. An increase in FE for a specific product indicates better selectivity, and its computation can be done by applying the following formula:

$$FE = \frac{\alpha n F}{Q} \times 100\% \quad (3-13)$$

where α , n , F , and Q are the number of electrons transferred, the number of moles for the desired product, Faraday's constant, and the total charge passed, respectively.

Back to the reactions, multiple proton-electron transfers imply the importance of intermediate step to the study of reaction mechanisms. The intermediates that vary from atomic compositions to binding sites significantly increase the complexity of the problem.

Generally, electrochemical reactions can be categorised into three types as shown in the equations below, where A is the reactant, $*$ denotes a surface site and A^* stands for its binding on the electrode surface:



In the next section we will discuss these reactions with their electrochemical prototypes.

3.2.3 Electrochemical interface

The electrochemical interface is critical for the mechanism of the electrochemical reaction as the intermediate can extend into the electrolyte. Measured by the distance to the working electrode, there

are three different regions: the surface region, the interface region, and the electrolyte region. The surface region is closest to the electrode; thus, the intermediate would be least affected by the electrolyte environment and the reaction would be a pure proton electron reaction. Towards the electrolyte is the interface region where some of the reaction intermediates are affected by the electrolyte due to the dipole. In this scenario, the reaction is not a simple proton electron reaction, and the electrostatic potential would be sum of the absolute potential and the potential induced by the dipole from the intermediates. The electrolyte region, by its name is inside the electrolyte in which the reaction is no longer related to the working electrode potential. Instead, it would only depend on the pH.

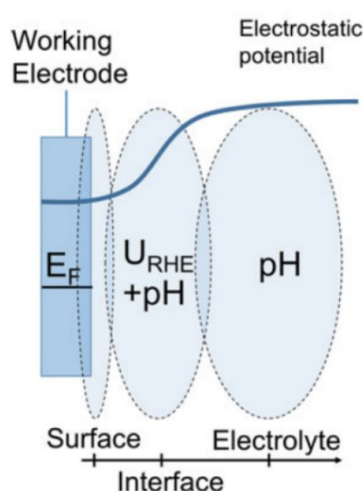


Figure 3.2. Illustration of regions near the electrode: the surface, the interface, and the electrolyte. Electrical potential dominates the reactions in the surface region, while far away from the electrode, it becomes the pH. The interface region is a combination of the surface and the electrolyte, i.e., potential and pH.⁸

3.2.4 Pourbaix diagram

Pourbaix diagram is a phase diagram that maps the different stable redox species in the aqueous solutions typically. The electrochemical reactions above can also be understood in this scheme:

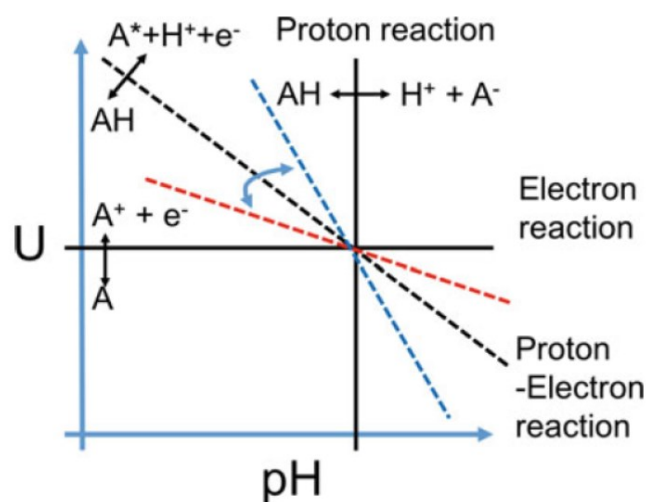


Figure 3.3. The Pourbaix diagram characterise relations between the electrode potential U and pH that divides the electrochemical reactions into three different types: proton reaction (3-13), electron reaction (3-14), and proton-electron reaction (3-16, dashed lines).⁸

Perpendicular to the pH axis is the proton reaction that depends on pH alone. An example is the buffer reaction. Correspondingly, electron reaction, typically as ionisation reaction, only depends on external potential. Naturally, there is a proton-electron reaction in between with a constant slope due to its constant RHE potential.

One of the difficulties for the electrocatalytic reaction studies is that the intermediates may undergo separate electron or proton or unpaired electron-proton process where experimentally electron transfer of the intermediates are not observable. This can be alleviated via DFT by calculating the work function or measuring the dipole of the interface. However, this is beyond the scope of this thesis and will not be discussed.

3.2.5 Simulation challenge

At atomic scale, electrocatalysis is determined by the electronic structure of the interface between the electrode and the electrolyte. A routine approach for DFT simulations to model the process would lead to a fixed number of ions and electrons that fail to match the experimental observables where pH and potential are often constant.

With DFT calculations, the binding energy of an intermediate or adsorbate is⁸:

$$\Delta E_A = E_{slab,A*} - E_{slab} - E_{A(g)} \quad (3-17)$$

$E_{slab,A*}$ is the energy of the slab with A adsorbed, E_{slab} is the slab energy alone and $E_{A(g)}$ is the gas phase reference. Although it is not an easy task to select a functional independent reference, Christensen et al. proposed a method to eliminate the systematic errors.

Given the binding energy ΔE_A , the Gibbs free energy for a reaction is derived as⁸:

$$\Delta G_A = \Delta E_A - T\Delta S + \int_0^T C_p dT + \Delta ZPE \quad (3-18)$$

ΔS is the electronic and vibrational entropy of the system, $\int_0^T C_p dT$ is the heat capacity and ΔZPE is the zero-point energy correction of the reaction. This equation, however, only applies for the metals where there is no proton and electron involved. A more elaborate model is introduced for electrochemical reaction where the proton and the electron make a significant impact.

3.3 Computational Hydrogen Electrode

3.3.1 Derivation

Rossmeisl, Hansen and their co-workers proposed the computational hydrogen electrode (CHE)^{54,55} that combined the chemical potential of protons and electrons for simplification. The assumptions are the following:

- (1) The bulk of the electrolyte is in equilibrium.
- (2) The surface where the reactions take place is in equilibrium with the electrodes and the bulk of the electrolyte.
- (3) The adsorption energy is independent on the electrostatic field.

The thermodynamic equilibriums are sound conditions in simplification of the model. The third assumption couples the proton and electron with a minor discrepancy in practice. As discussed earlier in the interface region, the interaction between the intermediates and electrostatic field depends on the dipole nature of the intermediates. Ignore the idiosyncrasy, the electrochemical free energy can then be derived as:

$$\Delta G = \Delta E - T\Delta S + \int_0^T C_p dT + \Delta ZPE - n \cdot (\mu_{H^+} + \mu_{e^-}) \quad (3-19)$$

where μ_{H^+} and μ_{e^-} are the chemical potentials of the protons in solution and the electrons at the Fermi level of the working electrode. Notice the electron proton pair is in equilibrium under standard conditions with hydrogen that can work as the reference electrode:

$$\frac{1}{2}\mu_{H_2} = \mu_{H^+}^{ref} + \mu_{e^-}^{ref} \quad (3-20)$$

where μ_{H_2} is the chemical potential of hydrogen gas at standard conditions and the ref in the superscript refers to the reference electrode. This scheme is depicted in **Figure 3.1**

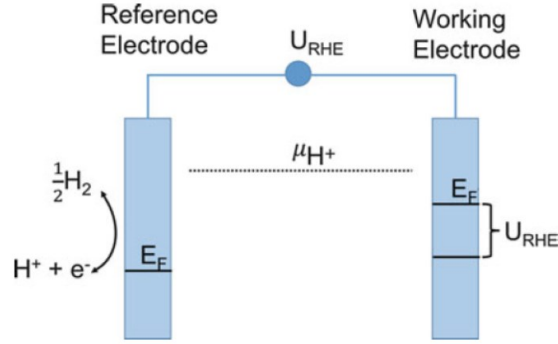


Figure 3.4. Schematic diagram of the computational hydrogen electrode (CHE). The hydrogen reaction is in equilibrium with the reference electrode. The protons for both the working and the reference electrode have the same chemical potential, while the electrons at the working electrode are affected by external potential U_{RHE} .⁸

Assuming that protons at the reference electrode are in equilibrium with protons in the electrolyte as dashed line suggests in **Figure 3.4**:

$$\mu_{H^+}^{ref} = \mu_{H^+} \quad (3-21)$$

The relation between the chemical potential of the electron at two electrodes is given by:

$$\mu_{e^-}^{ref} = \mu_{e^-} + eU_{RHE} \quad (3-22)$$

The hydrogen molecule energy is easy to calculate, so the total energy is:

$$E_{CHE}(n, U_{RHE}) = E(n) - E(n = 0) - n \cdot \left(\frac{1}{2} \mu_{H_2} - eU_{RHE} \right) \quad (3-23)$$

And the free energy as a function of electron transfer number n and potential U_{RHE} is:

$$\Delta G_{CHE} = \Delta E - T\Delta S + \int_0^T C_p dT + \Delta ZPE - n \cdot \left(\frac{1}{2}\mu_{H_2} - eU_{RHE}\right) \quad (3-24)$$

3.3.2 Free energy calculation

Given the derivation of CHE, the free energy diagram of the electrocatalysis can be constructed within the framework. For ORR or OER, there are four coupled proton electron reactions that are exactly the reverse of each other. In terms of ORR, the intermediates are OOH^* , O^* and OH^* :



Mark the chemical potential of a single proton electron pair as:

$$\mu_{(H^+ + e^-)} = \frac{1}{2}\mu_{H_2} - eU_{RHE} \quad (3-29)$$

Then for reactions (3-25) to (3-28), their free energies are:

$$\Delta G_1 = G_{OOH^*} - G_{O_2} - \mu_{(H^+ + e^-)} \quad (3-30)$$

$$\Delta G_2 = G_{O^*} + G_{H_2O^*} - G_{OOH^*} - \mu_{(H^+ + e^-)} \quad (3-31)$$

$$\Delta G_3 = G_{OH^*} - G_{O^*} - \mu_{(H^+ + e^-)} \quad (3-32)$$

$$\Delta G_4 = G_{H_2O^*} - G_{OH^*} - \mu_{(H^+ + e^-)} \quad (3-33)$$

The free energy diagram can be drawn from those quantities:

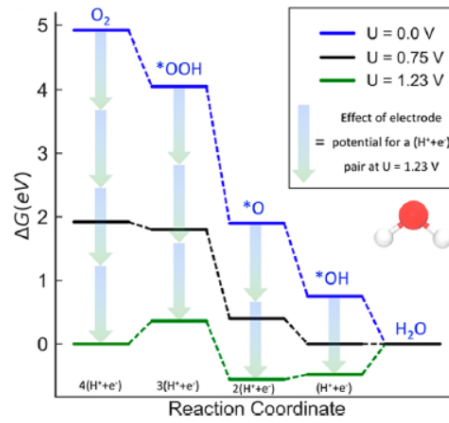


Figure 3.5. Illustration of free energy diagram at three different potentials: pristine 0 V, equilibrium 1.23 V and limiting potential 0.75 V.⁹

As the thermodynamic driving force is a min-max of the four intermediate reactions, the ideal catalyst would have four equal free energies, i.e., $\Delta G_1 = \Delta G_2 = \Delta G_3 = \Delta G_4 = 1.23 \text{ eV}$. But in practice, this is

never achieved. **Figure 3.5** shows at 1.23 V the most uphill reaction is from *OH to H₂O which suggest that the *OH will stay on the surface at the theoretical equilibrium potential. The potential can be adjusted to its maximum where all reactions are downhill. That maximum value is named limiting potential, and the potential difference to make all the steps downhill is called overpotential:

$$\eta = |U - U^{theoretical}| \quad (3-34)$$

It is an important metric to bridge the theoretical calculations with experiments. Although the onset potential in experiment is not well defined, the overall trend can provide valuable insights in understanding the underlying mechanisms. However, low current density is required in experiment when comparing these two results as in the CHE the thermodynamic equilibrium is the precondition.

3.3.3 Scaling relations

The scaling relations are the linear relations of the Gibbs free energy between the adsorbates. It has been empirically proved to be correct in a broad range of materials and systems, and a wide range of adsorbates.⁵⁶ It is pronounced in reactions with the intermediates that bind through the same atom and on the same active site. On the one hand, the scaling relation provides an easy approach to predict the binding energy of the correlated intermediates. On the other hand, it could be a major obstacle in finding the efficient catalyst. Given the circumstances, a vital task is to find or design the catalyst beyond this constraint.^{57,58}

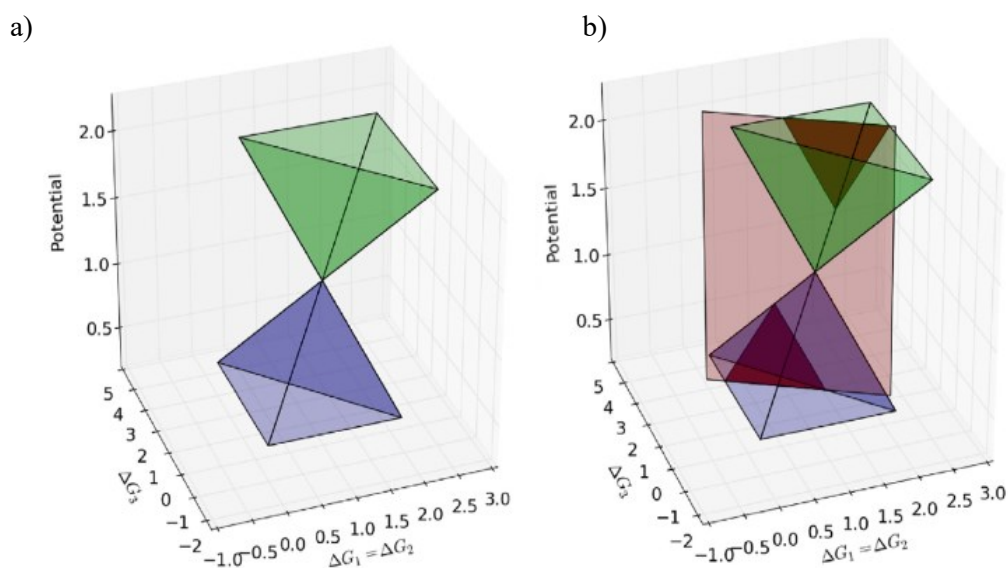
Specifically for ORR or OER, the OOH* and OH* are the intermediates that satisfy the condition mentioned above, and their scaling relation is¹³:

$$\Delta G_2 + \Delta G_3 = 3.2 \pm \sigma \text{ [eV]} \quad (3-35)$$

Where σ is the standard deviation in the fitting.

3.3.4 Volcano plots

To further elucidate the scaling relation in ORR or OER, Busch and co-workers¹⁰ first proposed a plot in **Figure 3.6a** consist of two pyramids with the only empirical constraint as the binding of *O is double of the *OH or equivalently to $\Delta G_1 = \Delta G_2$ as suggested in **Figure 3.6c**. Notice the ΔG_k now are in reverse order as the **Figure 3.6** is based on OER. Due to the symmetry of OER and ORR, ΔG_1 now stands for previous ΔG_4 and ΔG_2 stands for previous ΔG_3 . And the unique apex of the pyramids corresponds to ideal catalyst free from the scaling relation that has an optimal potential of U_{RHE} 1.23 eV for both reactions. When the scaling relation is imposed as the red plane in **Figure 3.6b**, which are the two red triangle slices, two apexes indicate two different suboptimal catalysts for ORR and OER correspondingly. It is worth to note that in such case the best ORR catalyst is not good for OER and vice versa.



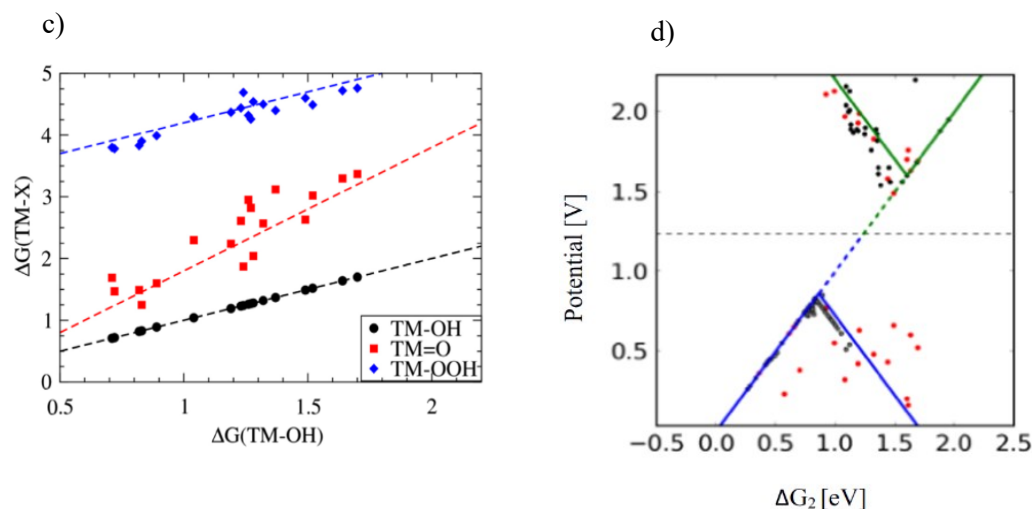


Figure 3.6. a) The plot shows two energy landscapes for the ORR and OER. The blue pyramid corresponds to the optimal potential for the ORR, while the green one is for the OER. b) The red plane indicates a constraint imposed by a constant energy offset between $\ast\text{OH}$ and $\ast\text{OOH}$ which divides the pyramids into two separate regions, forming darkened volcanoes for the ORR and OER. c) Predictions based on linear scaling for free energy of $\ast\text{-OH}$, $\ast\text{=O}$, and $\ast\text{-OOH}$ intermediates with respect to $\ast\text{OH}$ from various transition-metal nitrogen-carbon (TM-N-C) sites, (TM = Fe, Co, Mn) d) 2D cross-section represented by the red plane that intersects the ORR (blue) and OER (green) volcanoes. The black dotted line indicates the optimal potential of 1.23 eV for both reactions.¹⁰

Sabatier Principle states that an ideal catalyst should bind the molecules that participate in the chemical reaction neither too strongly nor too weakly. The scaling relation enriches the general Sabatier Principle in a quantitative perspective known as the volcano plot shown in **Figure 3.6d**. The horizontal axis is normally the binding energy of the intermediates, and the vertical axis is the theoretical overpotential for the reaction. With the volcano plot, it is straightforward to understand the limiting factor for the catalytic reaction.

3.3.5 Solvation effect

Water is ubiquitous in the ORR, but it is a tremendously challenging task to quantify the role of water in the electrochemical catalytic reaction. In terms of computational model, the water molecules can be embedded as the solvent model or explicitly added into the system or even involved into the reaction as the intermediates. The binding sites of the intermediates are critical for all the catalytic reactions. The choice of DFT functionals also leads to enormous variations for the solvation effect. Complicated as it is, a considerable number of efforts have been made to understand the characteristics.

The solvation energy is calculated by:

$$\Delta E_{sol} = E_{sol} - E_{vacuum} \quad (3-36)$$

Which is the total energy difference between the system with and without solvation.

Possible binding sites are shown in the **Figure 3.7**.

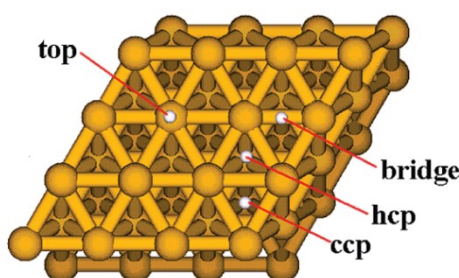


Figure 3.7. Different binding sites on closest-packed Pt(111) surface¹¹

Zhang and Asthagiri⁵⁹ summarised the work in understanding the solvation effect in the table below. It is observed that the solvation energy depends heavily on the factors mentioned in the beginning. The imprecise estimation will be accumulated to (3-19) and the volcano plot needs to be adjusted which

adds more variance or uncertainty for interpretation of the electrocatalysis. In addition, the solvation energy for Pt(111) is likely not the same for other materials as they have distinct atomic environment which further complicates the problem. This will be discussed in depth in chapter 4.

Species	RPBE-D3/ RPBE ⁵⁹	RPBE-D3 (JDFTx) ⁶⁰	PBE (VASPsol) ⁵⁹	PBE [VASPsol] ⁶¹	PBE [VASPsol] ⁶²
OOH*					
top	-0.13/-0.17	–	-0.17	–	–
O*					
fcc	0.01/0.02	-0.02	0.03	0.03	-0.02
hcp	0.01/0.02	-0.02	0.03	–	0.05
top	0.01/-0.05	-0.11	-0.02	–	-0.07
OH*					
bridge	-0.06/-0.08	–	-0.09	–	-0.17
fcc	-0.06/-0.10	-0.12	-0.16	–	-0.35
atop	-0.08/-0.09	–	-0.11	-0.10	-0.29

Table 3.1 Solvation energy in eV for ORR intermediates on Pt(111) with different methods or models.

3.4 Conclusion

The computational hydrogen electrode is the bridge that connects the theoretical simulation and practical experiment in electrochemical cell. With such scheme, electrochemical reactions could be probed from atomic views that are presented in last chapter. The development along the scheme such as the scaling relations and the volcano plot are substantial in understanding the electrocatalytic behaviour of the materials.

Chapter 4

DFT study on the mechanisms of Fe-N-C materials for ORR

This chapter will first introduce the motivation for the DFT study over the Fe-N-C materials as we review the research progress of electrocatalysts for ORR. Then the experiment setup from my collaborator will be briefly informed. Finally, my research from DFT perspective on interpretation of the mechanism will be discussed in detail.

4.1 Literature review

4.1.1 Foundation of scaling relations

Since studying the kinetics of electrochemical reactions and probing reaction intermediates experimentally can be extremely challenging, researchers have been developing alternative modelling-based methods to assist in the understanding of reaction mechanisms and trends in catalysts' activity. Nørskov *et al.* demonstrated an effective volcano model that became the cornerstone and the norm of the field: within the context of DFT, the overpotential of the electrocatalytic reactions could be correlated directly to the binding energies of the intermediates. Although the original paper only showed the performance of pure metal, it successfully predicted the alloy strategy to improve the ORR performance.¹²

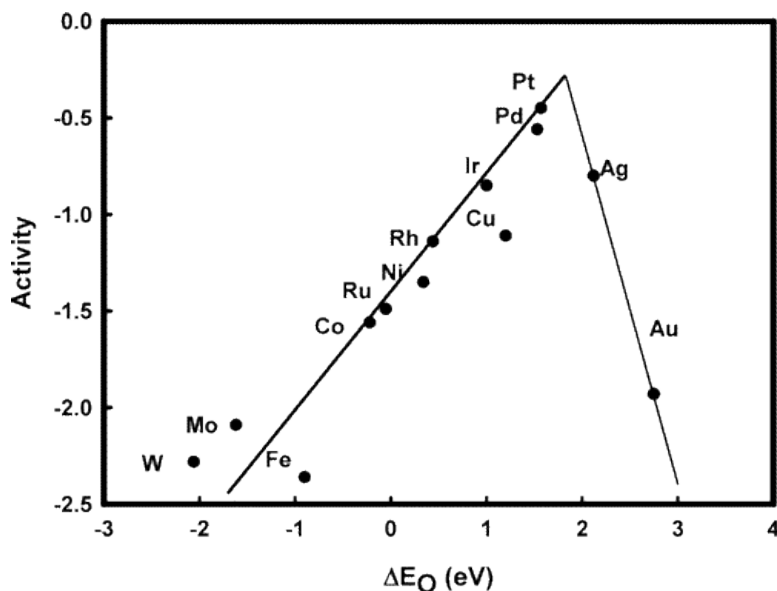


Figure 4.1 The electrocatalytic activity with respect to $\ast\text{O}$ intermediate binding energy for ORR on metal surface.¹²

The linearity or formally known as the scaling relations have been observed repeatedly in a range of different materials for different electrocatalytic process. It indicates that only one free parameter is allowed to determine the activity of the multi-step reactions. To further verify the hypothesis, Man et al. investigated the rutile, perovskite, spinel, rock salt, and bixbyite oxides computationally and found the scaling relations in OER or equivalently ORR.¹³ It should be noticed that the unity scaling relation is between $\ast\text{OOH}$ and $\ast\text{OH}$ since they have the same type of the binding site. For $\ast\text{O}$ it is not unity as different bond order leads to different binding sites.

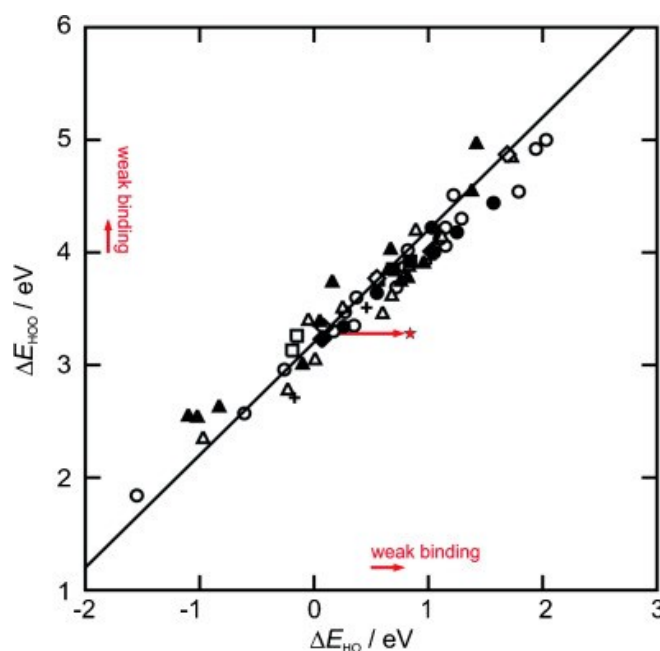


Figure 4.2 Adsorption energy of HOO^* plotted against the adsorption energy of HO^* on perovskites, rutiles, anatase, Mn_xO_y , Co_3O_4 , and NiO oxides. Hollow symbols represent the adsorption energy on the clean surfaces: perovskites ($\circ$), rutiles (Δ), Mn_xO_y ($\square$), anatase ($\diamond$), Co_3O_4 ($+$), NiO . The solid symbols represent the adsorption energies on high coverage surfaces, with oxygen atoms representing nearest neighbors. The best fit of all the points is $\Delta E_{\text{HOO}^*} = \Delta E_{\text{HO}^*} + 3.20 \text{ eV}$. The red star indicates the point at which the binding energies need to be for an ideal electrocatalyst. The relation for the perfect catalyst is:

$$\Delta E_{\text{HOO}^*} = \Delta E_{\text{HO}^*} + 2.46 \text{ eV}.^{13}$$

The constant residual observed when regressing the binding energy of *OOH and *OH is referred to the universality on oxide surface. As introduced in the fundamentals the fixed intercept term will apply a constraint to the volcano thus limiting the electrocatalytic performance of the materials. And the best materials in respect of the performance will have a residual of 2.46 eV.

4.1.2 ORR electrocatalyst materials

4.1.2.1 Pt

Pt is highly active for ORR as indicated by the theoretical volcano in **Figure 4.1** and experimental reports.⁶³ Nevertheless, the cost and the sustainability prevent its widespread implementation. There are two ways to deal with the intractable problem: enhance or replace. To enhance the electrocatalytic performance for ORR or reach the summit of the volcano for metal alloys, Ifan et al. suggested Pt alloy Pt₅La with approximately four times improvement in activity over Pt in 0.87-0.9 V,³² then proposed a systematic lanthanide contraction alloy strategy with six times higher current density 11 mA/cm² at 0.9 V using Pt₅Tb.³³ It should be aware that alloying can increase the activity but the lanthanide elements, also known as rare earth elements, are even more expensive than Pt, despite the high performance cost ratio. Crystal engineering can be utilised to achieve the selective exposure of crystallographic facets that are favorable for ORR. The selective exposure leads to the generation of unsaturated coordinated sites due to the exposure of well-characterised surfaces and modified local atomic environments. These unsaturated coordinated sites are known to enhance the ORR performance of Pt crystals. For instance, Wang et al. showed that Pt(111) is about 10 times more active for ORR than Pt(110) and Pt(100) facets.⁶⁴ Besides, the design of a specific nanostructure can lead to reduced particle agglomeration and migration during electrochemical operations, resulting in enhanced activity and stability. Li et al. reported that the jagged Pt NWs with 2–3 nm diameter and electrochemical surface area of 118 m² g⁻¹, presented an extraordinary mass activity of 13.6 A mg⁻¹. Even though numerous strategies¹⁴ have been proposed to improve the Pt-based catalyst, the cost and scarcity are still too high to bear.

4.1.2.2 Beyond Pt

Economically, Fe is around four orders of magnitude cheaper and eight orders more abundant than Pt regarding the production. It would be the ideal candidate for industrial-scale generalisation if materials synthesised from the metal are comparable to the performance of Pt or Pt group materials (PGMs) and free from degradation.

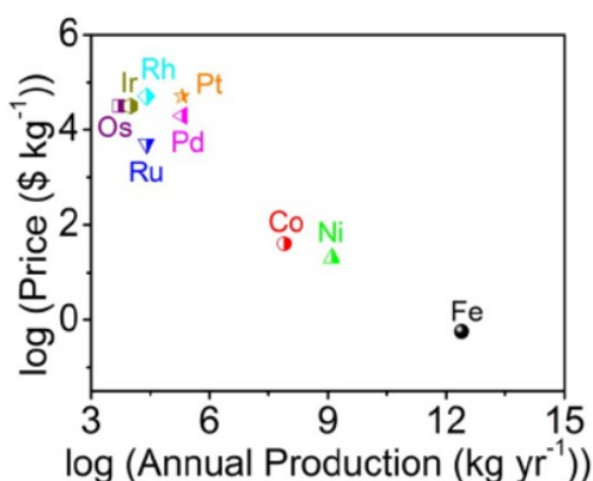


Figure 4.3 shows the price and scarcity of potential metals as electrocatalysts.¹⁴

Given the consideration, the transition-metal based non-precious metal catalysts (NPMCs) become the major interests of the research for ORR. Transition metal compounds including oxides and sulfides were studied with a high ORR performance in alkaline condition.⁶⁵ However, they cannot operate under the acidic environment due to corrosion.^{66–68} Instead, transition metal carbon materials are slightly more resilient in acidic conditions and show competitive performance. Metal-nitrogen-carbon (M-N-C) framework are held high expectations for ORR among all the transition metal carbon catalysts.^{69–71} The inspiration is from the biochemistry, where heme found in cytochrome c oxidase works as the active centre, which as an enzyme is responsible for catalysing the reduction of oxygen in both prokaryotes and mitochondria.⁷² For the metal centre, the Fe is generally considered the most active one among the reasonable choices Fe, Co and Mn with the activity ranking Fe > Co > Mn.⁶³ However, due to a lack of comprehensive understanding of the active sites and corresponding reaction mechanisms, it is difficult

to improve the Fe-N-C catalysts systematically. Thus, to enhance the overall efficiency of the catalysts, it is essential to acquire a profound understanding of the catalyst's nature in the active sites and the reaction mechanisms.

4.1.3 Fe-N-C as ORR electrocatalyst

Fe-N-C catalysts are appealing substitutes to platinum catalysts for the ORR due to their cost-effectiveness and sustainability. Among these catalysts, pyrolyzed Fe-N-C catalysts have demonstrated stunning potential in alkaline conditions. Nevertheless, it is still challenging to improve these catalysts in a systematic manner because of the presence of numerous iron species, making it difficult to characterise the active site and perform fundamental studies of the catalyst. However, tremendous efforts have been put to understand the complications. The common viewpoints on the active centres include nitrogen doped carbon that will be elaborated in chapter 6, Fe-N_x-C, iron oxide particles FeO_x-C exposed in electrolyte and iron particles embedded in nitrogen doped carbon Fe@N-C.⁷³⁻⁷⁷ Fe-N_x-C centres outperform the others in terms of the ORR performance and stability, thus receiving more attention.^{78,79} For FeN_x moieties, the x can be ranged from 2-6, making at least five configurations for the smallest unit without considering the spin. FeN₂ sites were examined to exhibit superior ORR performance.⁸⁰ FeN₃ sites are not preferred as ORR catalysts due to their increased resistance.⁸¹ FeN₅ was reported to have a lower adsorption energy for *OH and showed better ORR performance than FeN₄ with a similar preparation process.⁸² FeN₆ was also considered to be active for ORR despite the existence of different phases that are not active.⁸³ Although FeN_x moieties generally demonstrated high ORR activity, FeN₂ and FeN₃ suffer from the stability because of the demetallisation and aggregation of the iron atom, FeN₅ and FeN₆ have many more degrees of freedom that are challenge to characterise experimentally and simulate theoretically. Therefore, the FeN₄ moiety has emerged as the primary focus of research.

Model materials that are less stable for commercial use but with defined active site are utilised. The extensively studied one is macrocyclic FeN₄ complex, in which the FeN₄ unit represents a large

molecule with a Fe ion coordinated by four pyrrolic nitrogen atoms in a structure. Within this family, most research has centred on Fe phthalocyanines and Fe porphyrins with carbon materials as the support shown in **Figure 4.4**.

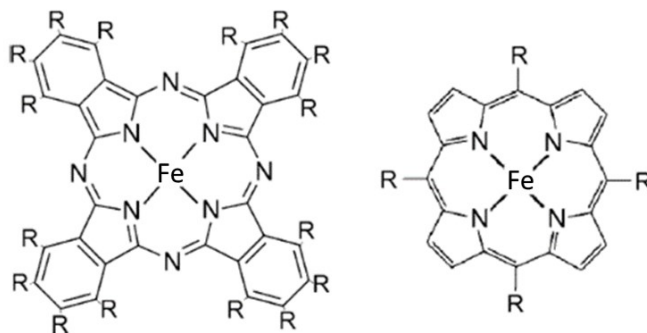


Figure 4.4 Structure of the most studied FeN_4 complexes for the ORR. Left: Fe phthalocyanine. Right: Fe porphyrin. Reproduced with permission from ref¹⁵.

The most intriguing yet unsolved problem can be simply presented with the cyclic voltammograms below, where OPG is ordinary pyrolytic graphite electrode, and above the dividing line are family of Fe phthalocyanines and under the line are Fe porphyrins. Despite various hypothesis having been presented, a universal on the cause of these peaks has still not been reached.

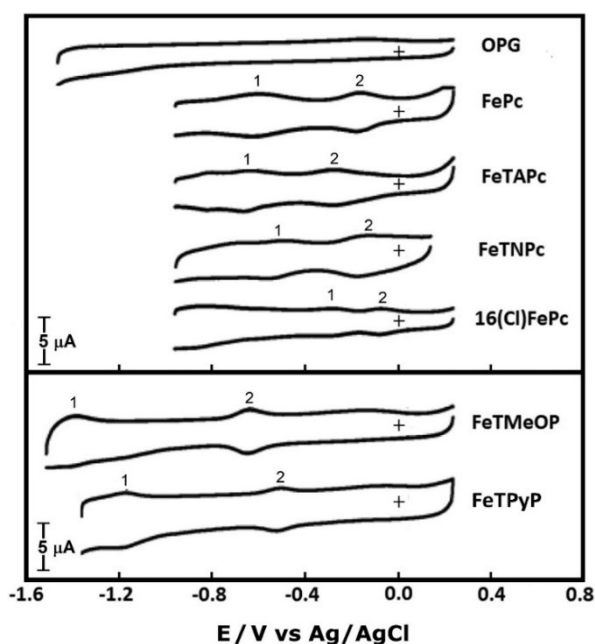


Figure 4.5 Cyclic voltammograms of a OPG electrode modified with Fe phthalocyanines and Fe porphyrins and recorded in deaerated, N₂ saturated 0.1 M NaOH, scan rate 0.1 V s⁻¹.¹⁶

Silva et al. believed that the marked peaks separate the region from high potential to low potential as Fe³⁺, Fe²⁺ and Fe⁺. And both the transitions from Fe³⁺ to Fe²⁺ and Fe²⁺ to Fe⁺ are possible to be the catalytic mechanism due to the fitting result.¹⁶ Alsudairi et al. argued that the low potential peak for plain Fe phthalocyanines was a hybrid interaction from the macrocycle ring and Fe²⁺/Fe⁺ redox transition.⁸⁴ Under the same separation scheme Zúñiga et al. also found that the Fe³⁺/Fe²⁺ redox transition to be linearly correlated with ORR onset potential, and they suggested that Fe-O₂ binding was important in the whole process.^{85,86} Wagner et al. probed the existence of a ferrous five-fold low spin heme-type FeN₄, a ferric five-fold high spin site and a ferrous intermediate spin Fe phthalocyanine type site.⁸⁷ Lingmei et al. studied porphyrin-based catalyst and found that the onset of 0.8 V vs RHE seemed responsible for the O₂ reduction while at below 0.6 V vs RHE another form of Fe was associated with the indirect reduction.⁸⁸

Even though the picture regarding the reaction mechanism is becoming increasingly lucid, there are plenty of inconsistencies that are difficult to explain. Firstly, not all the macrocycles have two peaks in a reasonable range ($E > -0.87$ V vs Ag/AgCl, ~ 0 V vs RHE) for ORR. Secondly, if the high potential peak is due to OH desorption, then it is abnormal that the onset potential for two peaks group is much higher than the single peak group below. Driven by these anomalies, an investigation was carried out to understand the underlying mechanisms.

4.2 Experiment result

Thanks Silvia Favero, my collaborator who conducted all the experiments.

4.2.1 Introduction

This study utilises a collection of Fe macrocycles to examine the active site and assess the impact of substituent groups on the activity of Fe-N-C catalysts. The research focuses on Fe, as FeN₄ sites have been predicted to be the most efficient for oxygen reduction⁸⁹, which has made Fe-N-C the most extensively researched catalysts. Despite the presence of numerous empirical results, there is still a lack of systematic and fundamental understandings that are of substantial importance towards the rational design of the ORR catalysts.

Square-wave voltammetry (SWV) is employed in N₂ (**Figure 4.6b**) to accurately identify the position of OH desorption peaks without recording the ORR activity. This technique is better at filtering the capacitive current thus providing better resolution to Faradaic processes compared to ordinary cyclic voltammetry. Linear sweep voltammetry (LSV) imposes a linearly shifting voltage to the catalysts in O₂ to depict the ORR responses, which are shown in **Figure 4.6c**. As is obvious they can simply be divided into two groups: 4PhFeP, 8EtFeP, 4NH₂FePC and FePC, 16ClFePC, 4COOHFePC. However, such clustering is different from the chemical characteristics of the materials where the porphyrins and phthalocyanines are the determinants. The CV peaks SWV characterises under N₂ (**Figure 4.6d**) indicate potentially more complicated mechanisms: FePC, 4COOHFePC, and 16ClFePC demonstrate two peaks in the scanned potential range, whereas 4PhFeP, 8EtFeP, and 4NH₂FePC only show a single peak. **Figure 4.6e** and **6f**. show the difference between the start of the ORR current and the position of the CV peak.

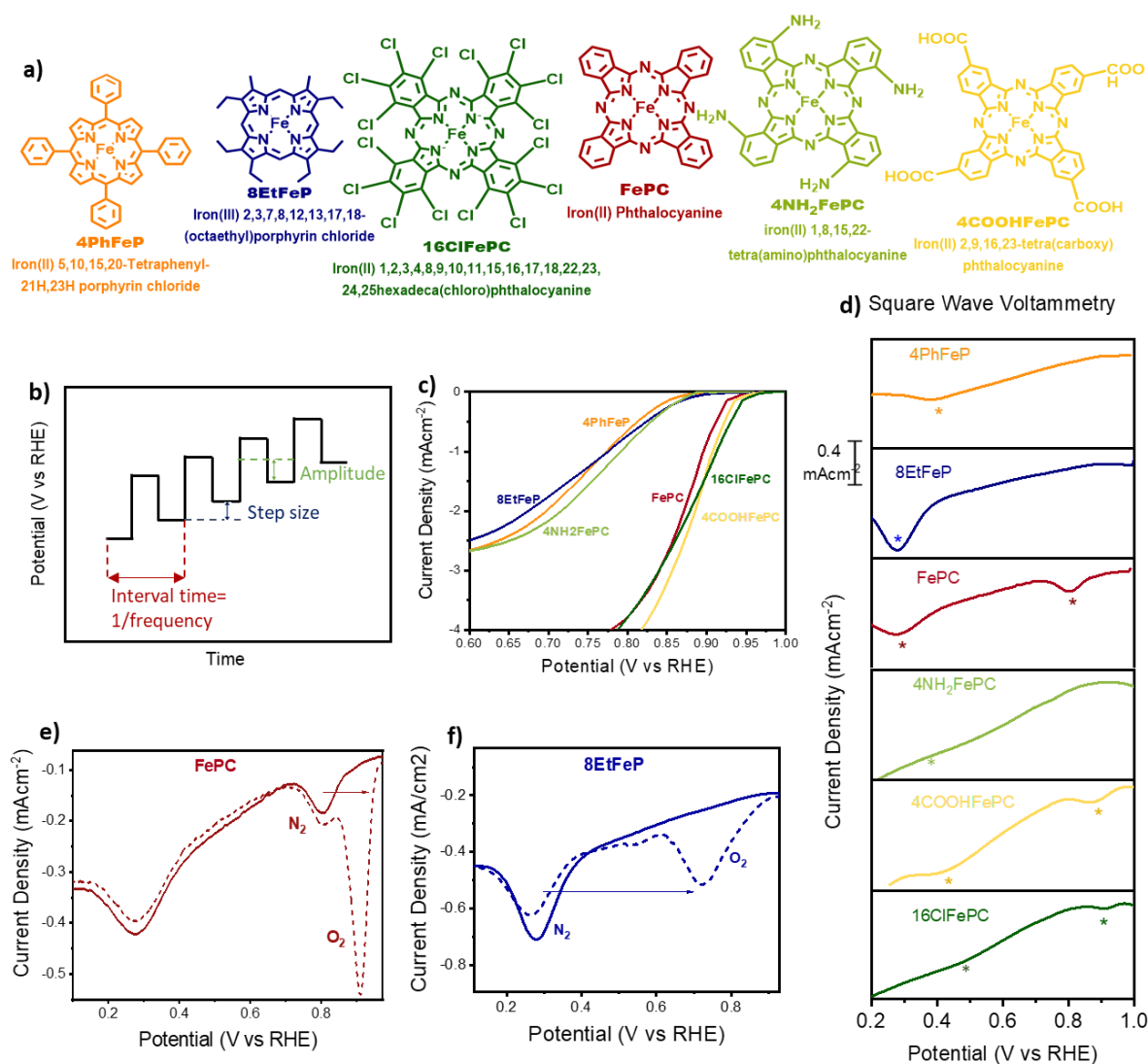


Figure 4.6 a) Structure and abbreviation of Fe macrocycles used in this work. b) Schematic representation of a square wave voltammogram c) Linear sweep voltammogram of the selected Fe macrocycles, obtained in oxygen-saturated 0.1M KOH, at a scan rate of 10mVs⁻¹ d) Square wave voltammograms of 4PhFeP (orange), 8EtFeP (blue), FePC (red), 4NH₂FePC (light green), 4COOHFePC (yellow), Data were collected in N₂-saturated 0.1M KOH, in static conditions, using a cathodic scan, composed of a potential step of 4mv, modulation amplitude of 20mV and a frequency of 2Hz, resulting in a scan-rate of 8mVs⁻¹. The peak position has been highlighted by an asterisk. e) Square wave voltammogram of FePC in nitrogen saturated (full line) and oxygen-saturated (dashed line) 0.1M KOH. Data were collected in static conditions, using a cathodic scan, composed of a potential step of 4mv, modulation amplitude of 20mV and a frequency of 2Hz, resulting in a scan-rate of 8mVs⁻¹. f) e) Square wave voltammogram of 8EtFeP in nitrogen saturated (full line) and oxygen-saturated (dashed line) 0.1M KOH. Data were collected in static conditions, using a cathodic scan, composed of a potential step of 4mv, modulation amplitude of 20mV and a frequency of 2Hz, resulting in a scan-rate of 8mVs⁻¹.

It is clear from the **Figure 4.6d** that the porphyrins with only one CV peak have a low potential vs. RHE in N₂ saturated electrolyte. That seems unlikely to be the onset potential for ORR on account of their high potential counterpart in O₂ saturated electrolyte. If we examine those with two CV peaks, the high potential peak in O₂ is slightly more positive than in N₂. For these molecules, there is a great mismatch between the position of the N₂ peak and the onset potential for oxygen reduction. This seems to suggest that whatever process causes the CV peak, it is not a necessary step for oxygen reduction. This is in contrast with the general understanding that the CV peak is caused by *OH desorption. In fact, if this was the case, above 0.4 V vs RHE the catalyst should be poisoned by adsorbed *OH and no ORR current should be recorded. On the other side, if we examine the molecules with two CV peaks, there is a much closer relationship between the ORR onset potential and the CV peak in N₂. To further understand these anomalies, some fundamental questions need to be answered.

4.2.2 Identification of active site

One of the fundamental questions is whether Fe is the active site. To appraise the feasibility, the comparison experiments of the porphyrins with or without Fe centre are set (**Figure 4.7a**). It is noticeable from **Figure 4.7b** that the low potential peak is from the Fe. Although the performance for pristine porphyrins is slightly better than porphyrins in absence of Fe, which implies both could be active, it is uncertain whether the active site is Fe from the LSV curves in **Figure 4.7c**. That the Fe is the active site will be confirmed with the characterisations of XAS.

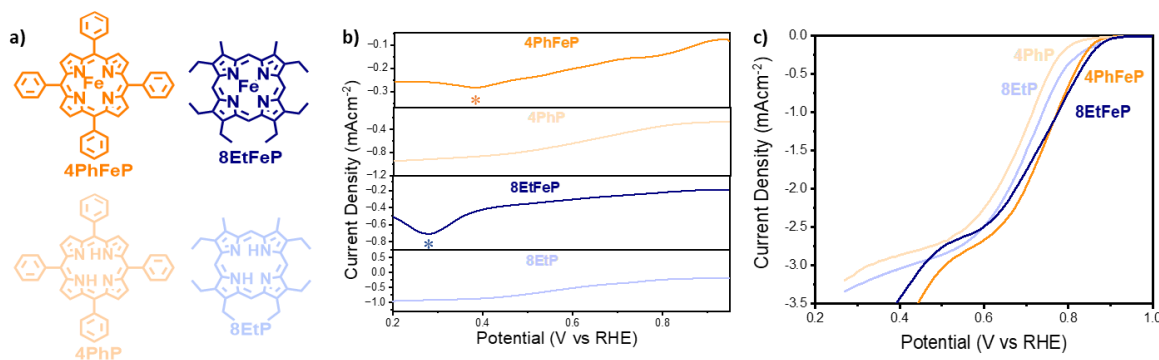


Figure 4.7 a) structure and abbreviation of the macromolecules 8EtFeP (blue), 8EtP (light blue), 4PhFeP (orange) and 4PhP (light orange) b) Square wave voltammogram of 8EtFeP (blue), 8EtP (light blue), 4PhFeP (orange) and 4PhP (light orange), in N₂-saturated 0.1M KOH. Data were collected in static conditions, using a potential step of 4mv, modulation amplitude of 20mV and a frequency of 2Hz, resulting in a scan-rate of 8mVs⁻¹. The position of the identified peaks is shown with an asterisk c) Linear Sweep Voltammogram of 8EtFeP (blue), 8EtP (light blue), 4PhFeP (orange) and 4PhP (light orange) obtained in O₂ saturated electrolyte, with a scan rate of 10 mVs⁻¹ at a rotational speed of 1600 rpm.

4.2.3 Tafel analysis

The Tafel analysis is applied experimentally to extrapolate the high potential CV peak that is missing for some molecules. Since a change in the Tafel slope indicates a change in the rate determining step, it is proposed that the crossing point is the place where OH desorption is no more limiting. As is can be seen that the values fit well for those who show two peaks.

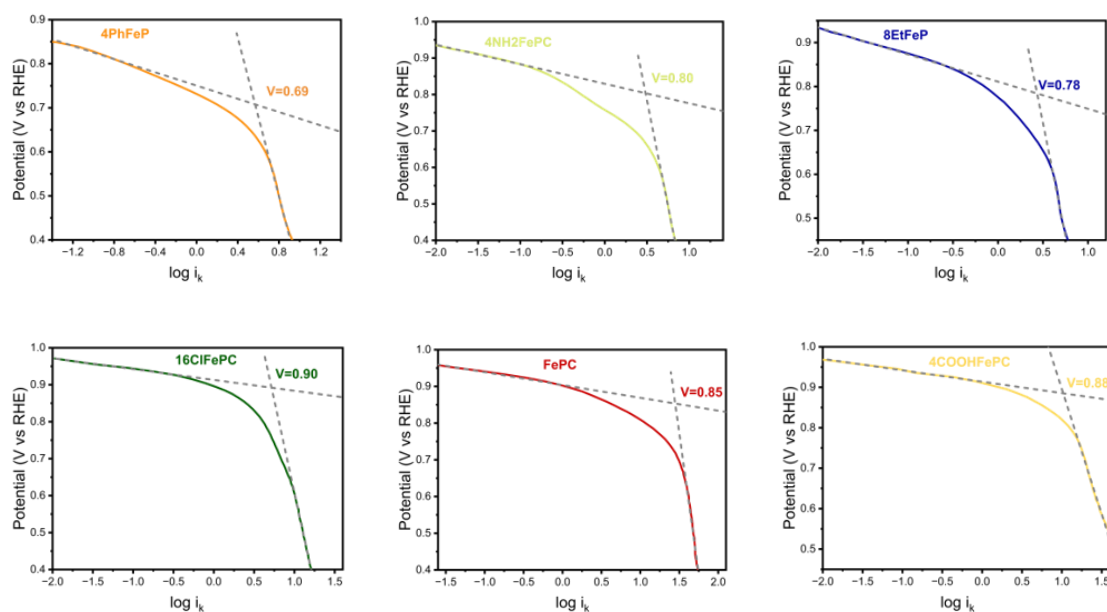


Figure 4.8 Tafel plot of the selected macrocycles. On the x-axis is the logarithm of the kinetic current density (in mAcm⁻²). The kinetic current density was extracted from the measured current density (*i*) using the Koutecky-Levich equation: $i_k = (i^{-1} - i_d^{-1})^{-1}$. Where i_d is the theoretical diffusion-limited current density, as determined by the Levich equation: $i_L = 0.62nFAD^{2/3}\omega^{1/2}\nu^{-1/6}S$. The dashed lines show the linear of high and low overpotential linear region of the Tafel plot. The value displayed on the graphs represent the potential at which the two linear fits intercept.

4.2.4 Pourbaix diagrams

The CV peaks can be a charge transfer process or a proton-electron pair transfer process. To study the nature of these peaks the Pourbaix diagrams can be plotted with the shift of the pH. To circumvent the introduction of more cations that could lead to more unknowns, the pH is adjusted by changing the KOH concentration within a small range 13-14.6. For molecule with two peaks e.g., FePC (**Figure 4.9a**), their positions of low potential peak are invariant with respect to pH, while the high potential peak shifts to lower potential as pH increases. For those with only one peak e.g., 8EtFeP, at the low potential (**Figure 4.9b**), their positions are also fixed with varied pH. These can be clearly summarised in the Pourbaix diagrams **Figure 4.9c** and **9d**. Within the experiment error of 0.059 V/pH, the high potential peak represents the proton-electron pair transfer process while the low potential peak indicates an electron transfer process as the independence from pH is pronounced.

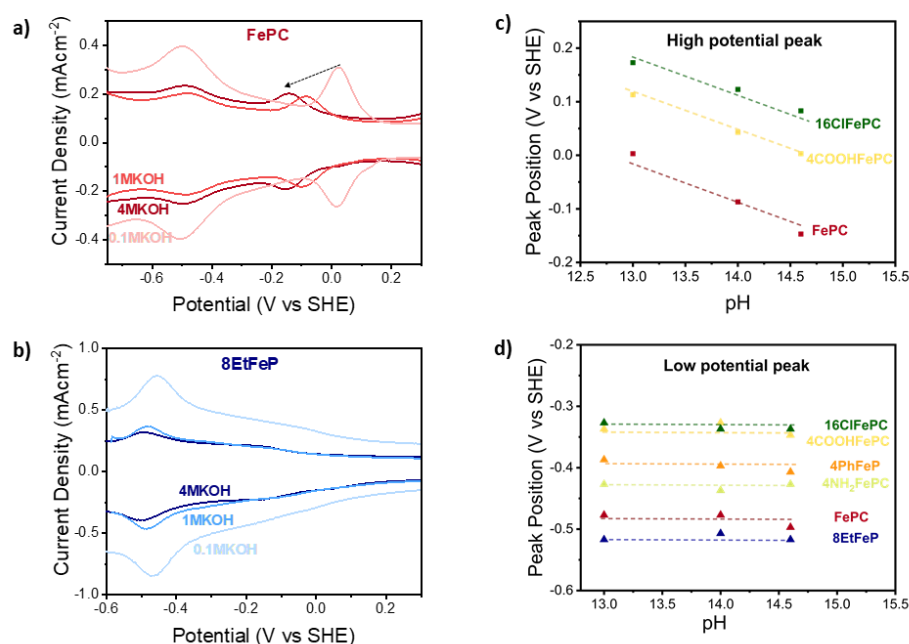


Figure 4.9 a) square wave voltammogram of FePC at different pH: from light to dark red data have been recorded in 0.1M KOH, 1M KOH and 4M KOH. b) square wave voltammogram of 8EtFeP at different pH: from light to dark blue data have been recorded in 0.1M KOH, 1M KOH and 4M KOH c) Position of the low potential peak as a function of pH, for the selected Fe macrocycles d) Position of the high potential peak, as a function of pH, for the selected Fe macrocycles.

4.2.5 Peroxide selectivity

Molecules in the same group also share the characteristic of peroxide efficiency. **Figure 4.10** shows that molecules with two peaks have low peroxide selectivity (less than 0.5% over the entire potential range), while single peak molecules are more effective at producing hydrogen peroxide (with a selectivity of 2 to 12%).

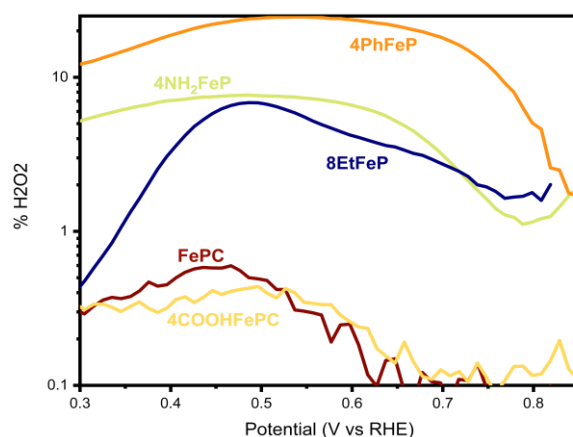


Figure 4.10 Percentage of peroxide generated versus potential applied in RHE. Data were collected using a RRDE set-up, at 1600rpm, in O₂-saturated 0.1M KOH.

4.2.6 Operando X-ray absorption spectroscopy (XAS)

The results of operando XAS measurements for selected samples (FePC, 4PhFeP, 8EtFeP, 4NH₂FePC) are displayed in **Figure 4.11**. FePC, which is part of the group exhibiting a high potential peak, displays a potential-dependent alteration in the HERFD XANES spectra under N₂ (**Figure 4.11a**). This alteration causes a shift in the white line towards higher energy values, a decrease in white line intensity, and an increase in the pre-edge peak intensity situated at 7118 eV, upon application of a reducing potential. However, all the molecules in the second group (4NH₂FePC – **Figure 4.11e**, 4PhFeP – **Figure 4.11g**, 8EtFeP – **Figure 4.11i**) exhibit no alteration in the HERFD XANES spectra in N₂ unless the O₂ is used instead (**Figure 4.11f, 11h, 11l**), confirming that the iron centre is the active site. For FePC, the spectral shifts can be attributed to *OH desorption occurring at higher potential in O₂ compared to N₂. According

to **Figure 4.6e**, it is likely that the O_2 will destabilise the $*OH$ resulting in a mildly higher potential CV peak. However, this reasoning cannot be applied to the rest of molecules that show single peak.

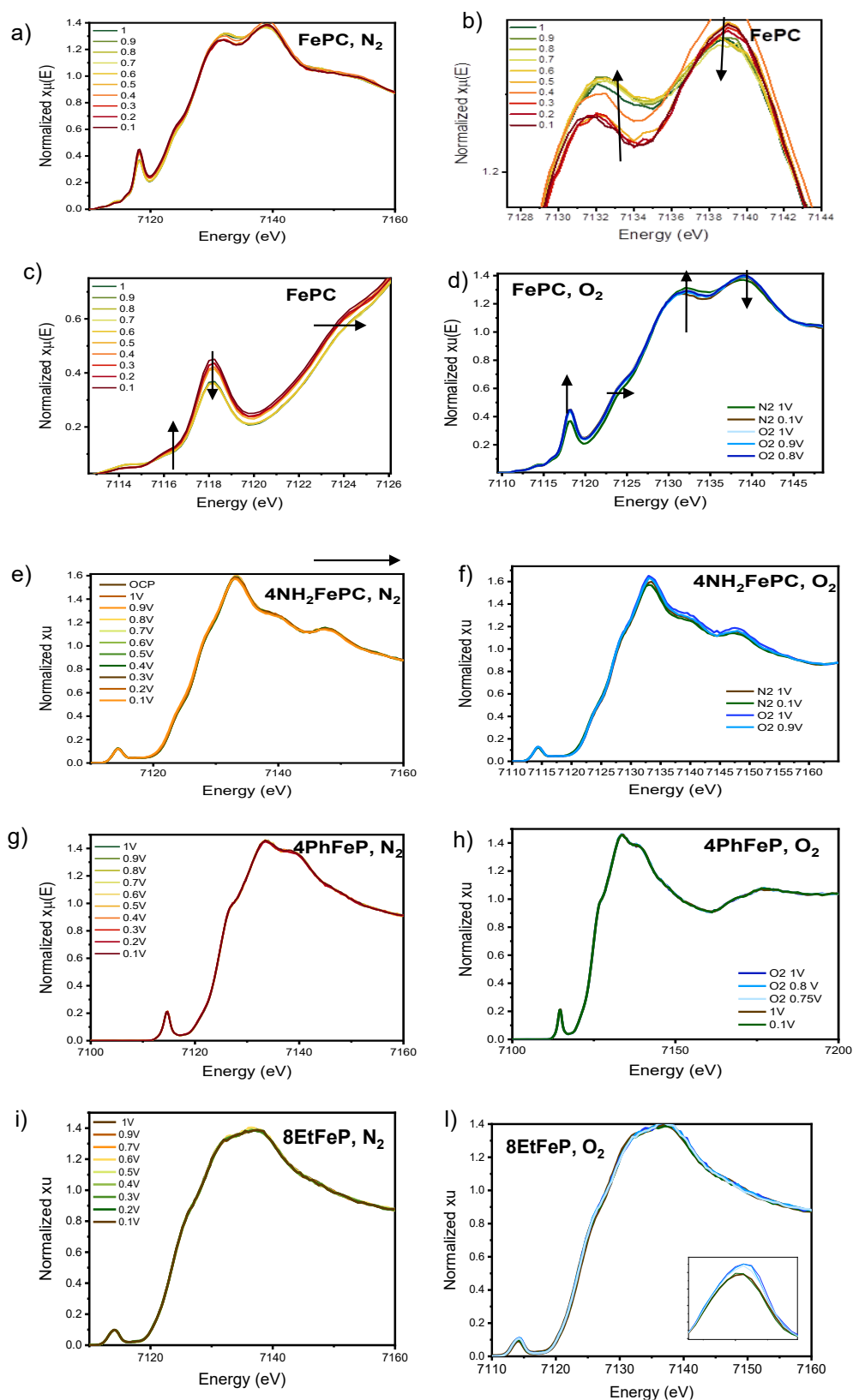


Figure 4.11 operando HERFD XANES of: a) FePC in N₂-saturated electrolyte b) and c) are zoom ins of the same spectra, d) FePC in O₂-saturated electrolyte, e) 4NH₂FePC in N₂-saturated electrolyte, f) 4NH₂FePC in O₂-saturated electrolyte, g) 4PhFeP in N₂-saturated electrolyte, h) 4PhFeP in O₂-saturated electrolyte, i) 8EtFeP in N₂-saturated electrolyte, l) 8EtFeP in O₂-saturated electrolyte.

4.2.7 Experiment summary

From the result of electrochemical characterisations there exist two groups of materials that show either a high potential peak plus a low potential peak or solely a low potential peak in the CV. The low potential peak is pH independent, which indicates it bears no resemblance to *OH desorption. This conclusion is in contrast to what has previously been reported⁹⁰. The group with two peaks has a low peroxide selectivity or a high ORR efficiency while the single peak group exhibits the opposite.

If the observable peak for those only show single low potential peak is not correlated to ORR performance, which is sensible when an ORR current has already been captured at 0.8 V while the peak lies at 0.3 V (vs. RHE, Fig. f), then a major task is to understand why the OH* desorption high potential peak is missing from the CV. In-situ XAS result possibly explains the mismatch of high potential peak in CV for FePC in different atmosphere, but the remaining curves are almost static which could possibly indicate that the valence of Fe stays constant thus no high potential peak can be detected for these materials.

The results are summarised in the **Table 4.1** below:

Molecule	High potential peak	Change in XAS spectra	Peroxide selectivity	ORR activity
4NH ₂ FePC	No	No	High	Low
4PhFeP	No	No	High	Low
8EtFeP	No	No	High	Low
4COOHFePC	Yes	-	Low	High
FePC	Yes	Yes	Low	High
16ClFePC	Yes	-	Low	High

Table 4.1 Summary of the characteristics of the Fe macrocycles. The change in XAS spectra was observed when a potential was applied in-situ from 1V vs RHE to 0.1V vs RHE in GDE configuration. Only certain molecules were analysed using in-situ XAS. High peroxide selectivity was defined as being above 2% in most of the potential region, and low otherwise. High ORR activity was defined as having a logarithm of the ORR current (in mAcm⁻²) above 0.4 at 0.75V vs RHE, while low ORR activity was defined as anything below this threshold.

It may seem to be counter-intuitive to have the oxidation state of Fe fixed with the ORR going on. The soundest conclusion I draw is that the single-peak molecules follow a different mechanism during the ORR, which I call as spin accommodation, will deliver all the experimental observables without involving the transfer of electrons.

4.3 DFT study on macrocycles for ORR

These are my contributions to the project.

4.3.1 Introduction

The well-defined macrocycles offer an ideal system for studying Fe-N-C catalysts, as the structural motif can be used directly in DFT simulations to obtain a correlation between experiments and simulations, providing a detailed and accurate representation of the system. From the perspective of the catalytic theory, DFT study over this system can be utilised to further verify the scaling relations. As for the experiment, the simulations will help to understand the fundamental mechanisms of the anomalies encountered.

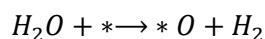
4.3.2 Fe macrocycles binding energy

DFT calculations were carried out using RPBE functional under Atomistic Simulation Environment (ASE)⁹¹ with the GPAW code^{92,93} applying finite-difference approximation. Unit k-points were set in

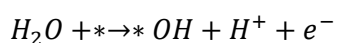
three orthogonal directions with a grid-spacing of 0.18 and a vacuum of minimal 5 Å. The geometry optimisations were performed with spin polarisation and relaxation on, and the convergence criterion was satisfied once the force was below 0.05 eV Å⁻¹. Periodic boundary conditions were considered along the xyz axes using both TTF (True True False) and FFF (False False False) conditions, where True indicates the periodicity is introduced and the FeN₄ plane coincides with the xy plane. There is a negligible difference for the spin relaxed states (Appendix **Table 2**). Therefore, only TTF data were shown here.

The simulations carried out on the pristine macrocycle (i.e., without any intermediates) suggest that two structures are stable in each iron macrocycle after undergoing spin-relaxed optimisations. One represents Fe²⁺ as it has a magnetic moment of zero, while the other structure has a magnetic moment close to two and can be identified as Fe³⁺ which will be explained in detail below. It is worth noting that despite having different spins in the original species, the intermediates only show one spin state, which is evident from the convergence of different initial states. Additionally, it is important to mention that the ethyl group's arrangements in 8EtFeP are indicated by isomers labelled AABB and ABAB as shown in the Appendix **Figure 1**. AABB indicates half of the amino groups are on the one side while the rest on the other side. ABAB stands for the alternating amino groups in the backbone. Both sets of data are included but are represented as a single entity, i.e., 8EtFeP, in the figures to avoid complexity.

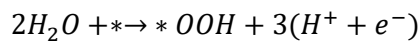
The free energies were calculated with the following three equations that includes the binding energy, thermal corrections and solvation effect:



$$\Delta G(*O) = E(*O) - E(*) + E(H_2) - E(H_2O) + 0.05 \quad (4-1)$$



$$\Delta G(*OH) = E(*OH) - E(*) + \frac{1}{2}E(H_2) - E(H_2O) + 0.35 - 0.3 \quad (4-2)$$



$$\Delta G(*OOH) = E(*OOH) - E(*) + \frac{3}{2}E(H_2) - 2E(H_2O) + 0.4 - 0.3 \quad (4-3)$$

Where the positive constant in the equation represents the zero point energy corrections and entropic contributions to the free energies and the negative number incorporates the implicit water solvation into the system considering its stabilisation effect.¹²

ΔG (eV) Name	*O (m=0)	*OH (m=0)	*OOH (m=0)	*O (m=2)	*OH (m=2)	*OOH (m=2)
4PhFeP	1.18	0.22	3.49	1.72	0.77	4.04
AABB_8EtFeP	1.17	0.31	3.40	1.70	0.85	3.93
ABAB_8EtFeP	1.19	0.33	3.48	1.73	0.88	4.02
FePC	1.41	0.44	3.70	1.91	0.95	4.20
16ClFePC	1.49	0.50	3.71	1.96	0.98	4.19
4NH ₂ FePC	1.42	0.43	3.68	1.86	0.89	4.12
4COOHFePC	1.45	0.48	3.69	1.95	0.99	4.19

Table 4.2 Binding Energies (G) of oxygenated ORR intermediates species (*O, *OH, *OOH) on the selected Fe macrocycles, for spin relaxed magnetic moments m=0 and m=2. The solvation energy is 0.3 eV in the table.

The simulations were run from m=0 and m=2 as the initial states and they converged to the same species *X (X= O, OH, OOH) without further variations in spin.

The calculated results were summarised in the tables where m is the spin relaxed magnetic moment that can be related to Fe²⁺ (m=0) and Fe³⁺ (m=2). First for m=0, considering its highly symmetric geometry

structure and paired electrons, it is reasonable to conclude that the valence is Fe^{2+} ($m=0$, low spin). As not only Fe^{4+} is too energy demanding to exist in our system, but also the spin relaxation is not compromised for the lowest energy optimisation purpose in a highly symmetric structure. Namely, $m=0$ is exact, it is not the approximation for $m=0.5$.

On the flip side, this is not the case for $m=2$. And it is supported by the charged simulations. As is shown in the **Figure 4.12**, by adding or subtracting electrons in previous charge neutral modelling system for $m=2$, the m shifted from 2 to near 1.5 or 2.5. However, the direction for binding energy change is not the same as the sign of charge for the system: the positive charge with magnetic moment around 2.5 has the weakest $^*\text{OH}$ binding, the neutral has the strongest binding and the negative is in between. The only exception is 4COOHFePC with two electrons added (**Figure 4.13**), which can be interpreted as the formation of a new phase. It suggests that the actual thermodynamically stable species correspond to $m=2$ could be Fe^{2+} ($m=2$, high spin), Fe^{3+} ($m=1.5$, intermediate spin) or Fe^{3+} ($m=2.5$, high spin). As the reference for the charged and uncharged systems are unknown, it is difficult to make an assertion. To simplify the following discussion, the $m=2$ is noted as Fe^{3+} .

Name	$m(+1)$	$m(0)$	$m(-1)$	$m(-2)$	$^*\text{OH}(+1)$	$^*\text{OH}(0)$	$^*\text{OH}(-1)$	$^*\text{OH}(-2)$
4PhFeP	2.21	2.00	1.61	1.63	1.07	0.88	0.97	0.92
AABB_8EtFeP	2.13	2.00	1.63	1.59	1.06	0.98	1.02	0.82
ABAB_8EtFeP	2.07	2.00	1.63	1.59	1.03	0.89	0.96	0.92
FePC	2.2	2.00	1.65	1.72	1.06	0.99	1.03	0.81
16ClFePC	2.46	1.98	1.71	1.71	0.92	0.77	0.8	0.79
4NH ₂ FePC	2.46	1.96	1.71	1.72	0.92	0.76	0.79	0.81
4COOHFePC	2.44	2.00	1.74	1.75	0.81	0.77	0.8	0.53

Table 4.3 Spin relaxed magnetic moment m and $^*\text{OH}$ binding energy (eV) with different number of charges in the bracket for the system.

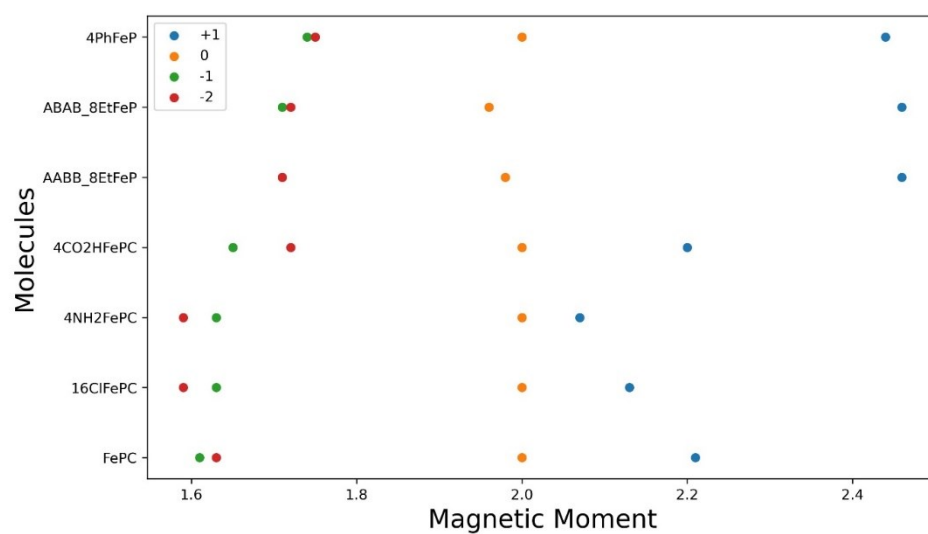


Figure 4.12 Magnetic moment of the molecules with different input charges.

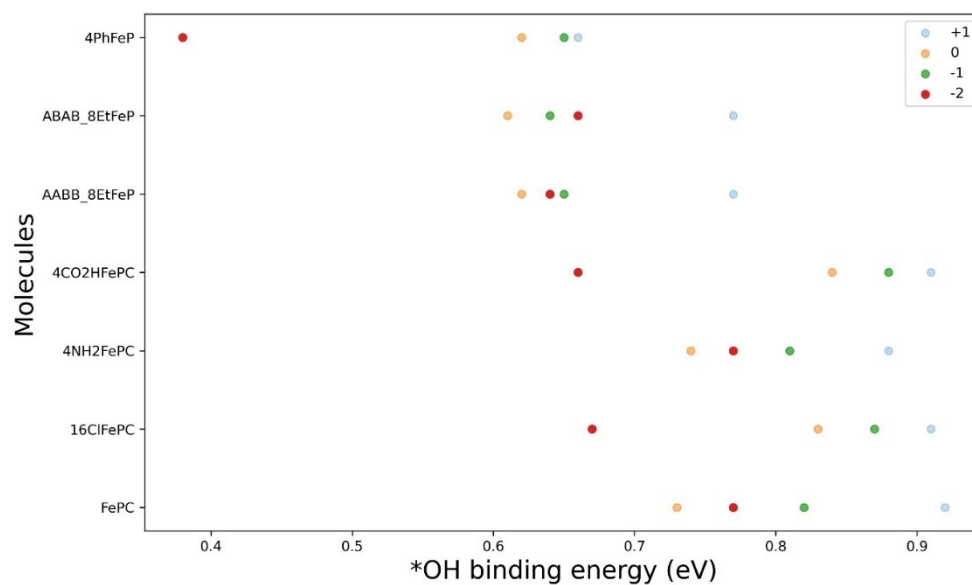
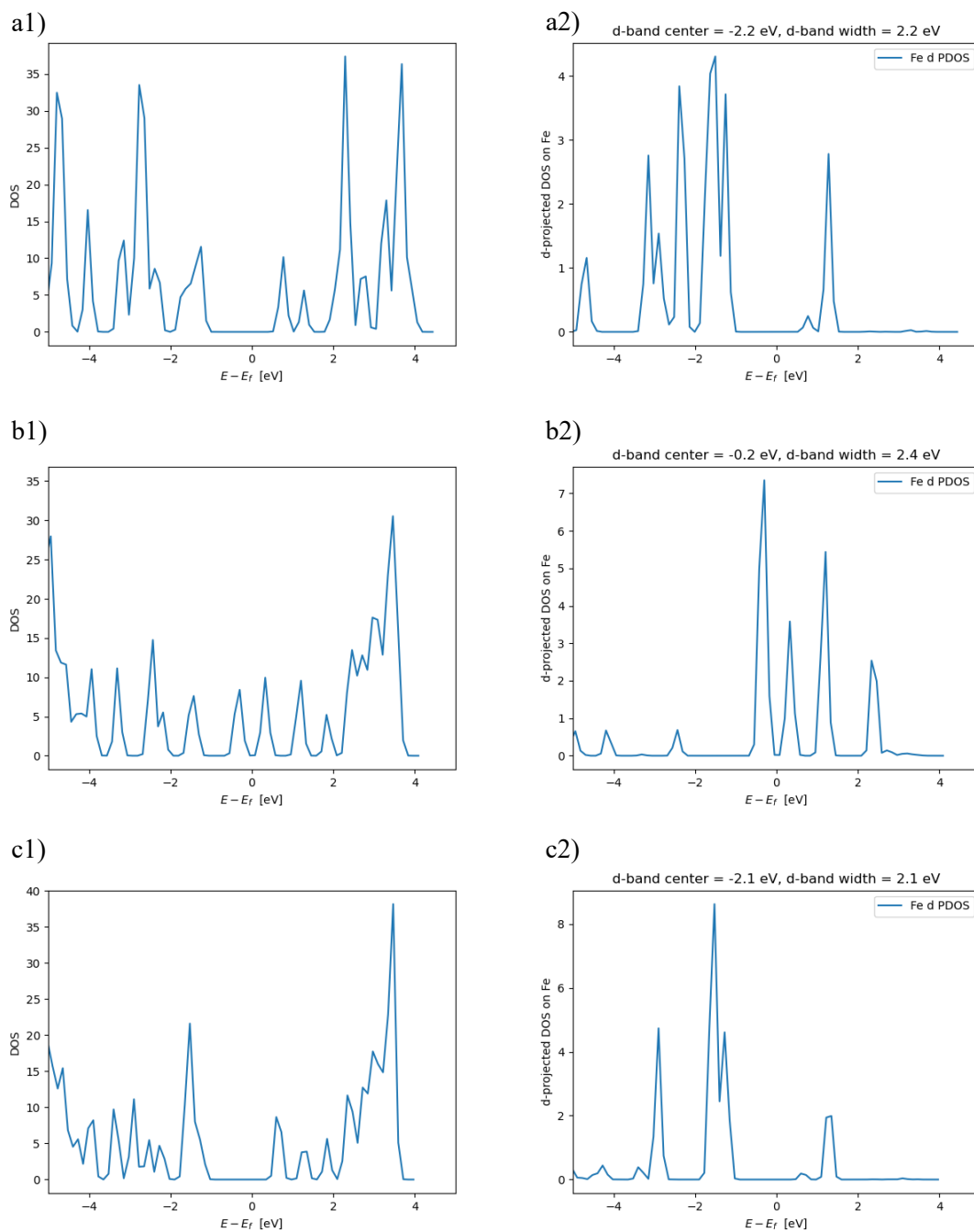


Figure 4.13 *OH binding energies of the molecules with different input charges. The solvation energy is 0.45 eV.

4.3.3 Fe macrocycles electronic structures

To further examine the electronic structures of the catalysts, their density of states (DOS) and projected density of states (PDOS) for Fe atom are shown below.



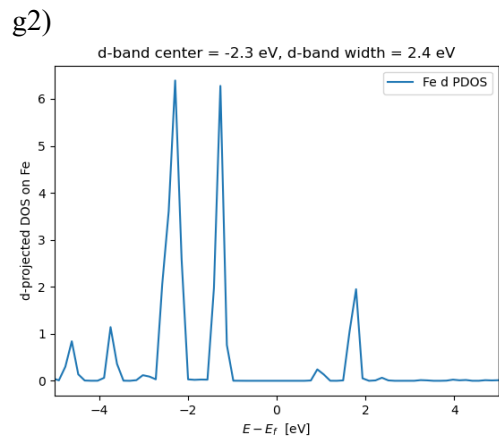
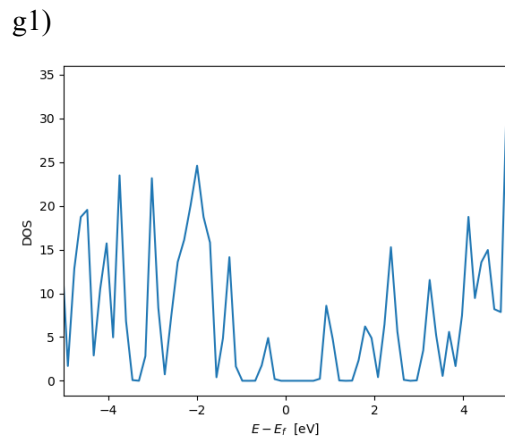
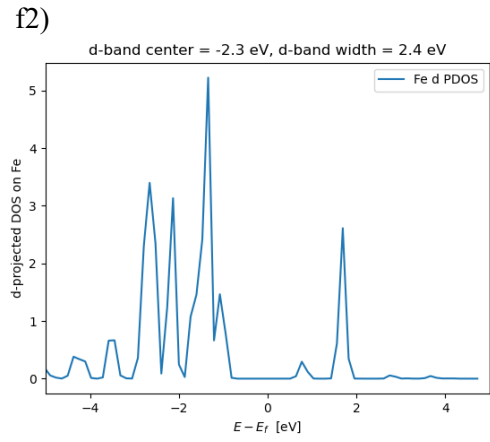
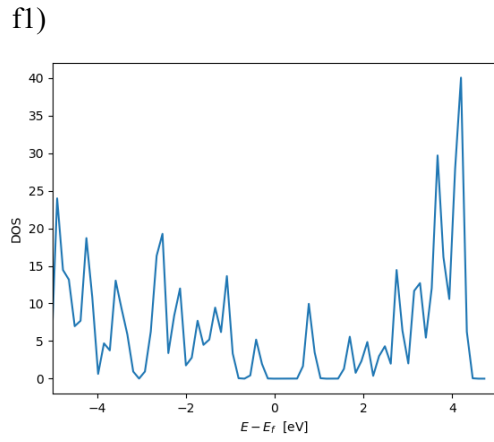
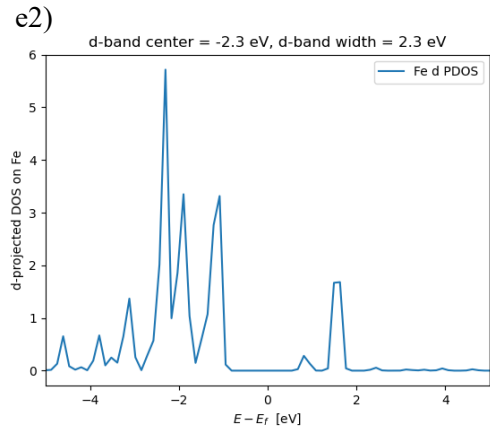
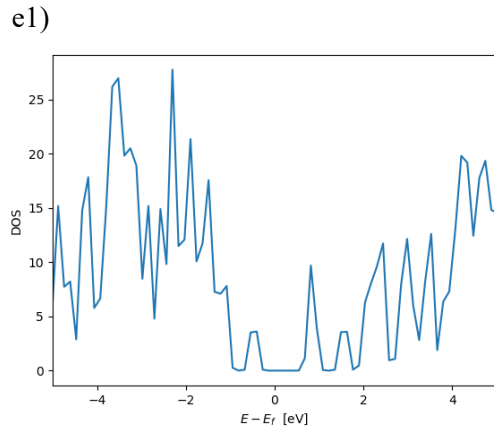
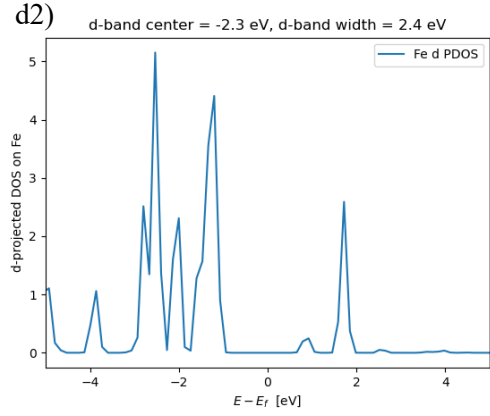
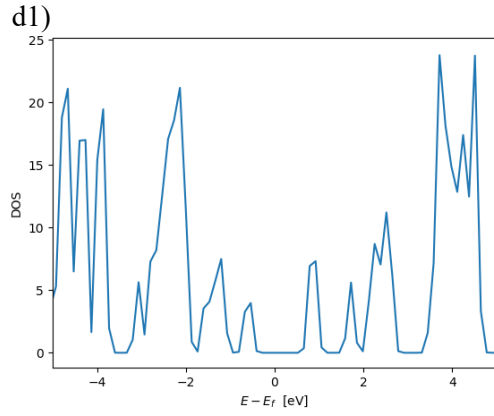
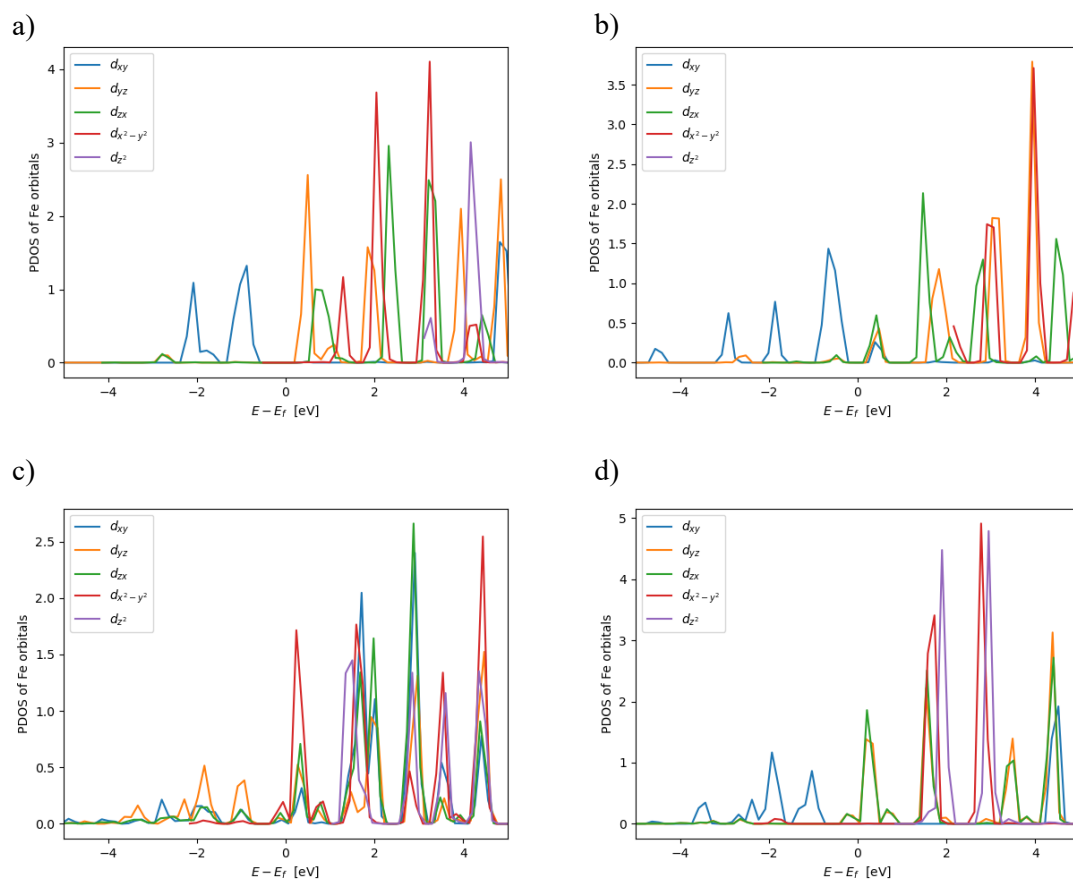


Figure 4.14 DOS and PDOS of Fe d band for pristine charge neutral macrocycles. The alphabetical orders are correspond to the sequence in **Table 4.2**, 1 is for density of states plot while 2 represents projected density of states. The energies are aligned with the Fermi level E_F and truncated within -5 to 5 eV. d-band is the weighted average of the density of states for d band. The d-band width is calculated as the square root of the second moment of the d band with respect to the Fermi level.

AABB_octa is the outlier in terms of the band structure. It has the d-band centre that situates at the Fermi level. It is this feature that makes it slightly more conductive than the rest of the molecules, as the d orbital from Fe contributes to the total DOS near the Fermi level. However, this does not contribute to the optimal *OH binding. The band gap for rest of the molecules is small (~ 1 eV), making conductivity not a significant issue. The d-band width is consistent, ~ 2.4 eV for all the macrocycles. These observations suggest that the d-band metrics are not informative enough to determine the catalytic properties of macrocycles. A further investigation for the d orbitals of Fe is conducted:



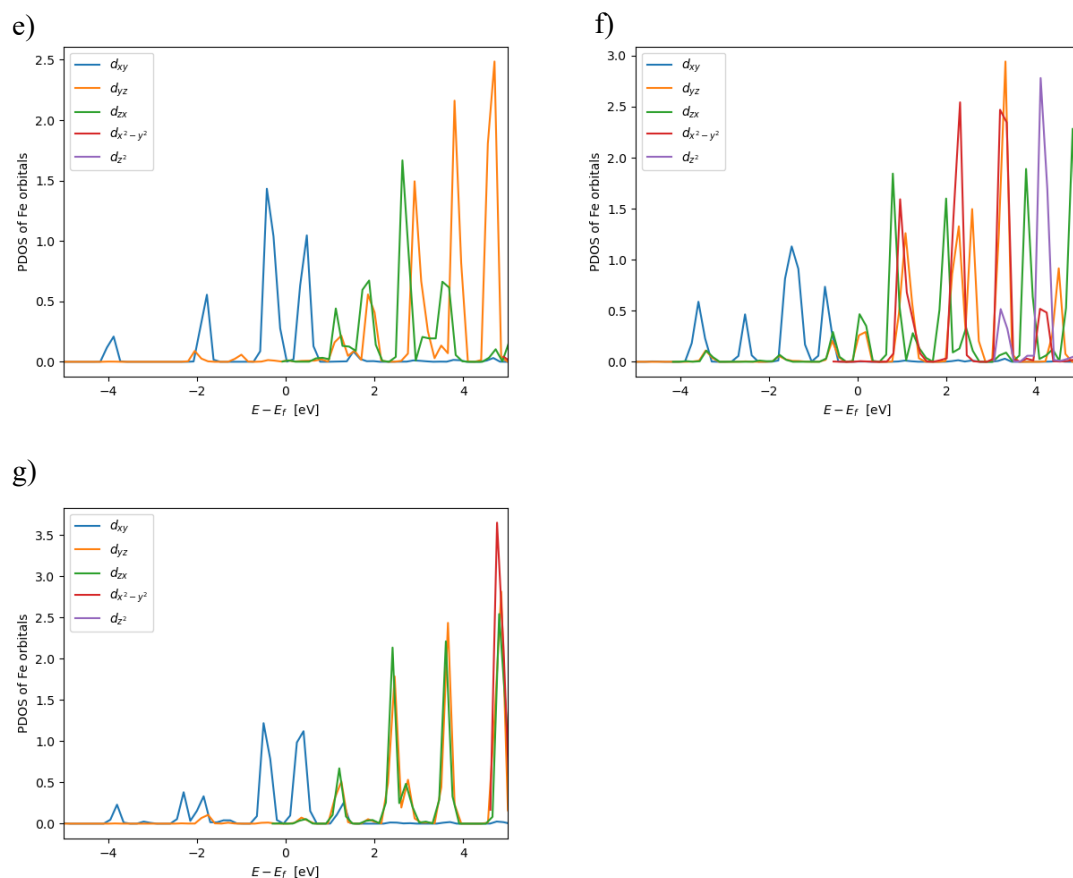
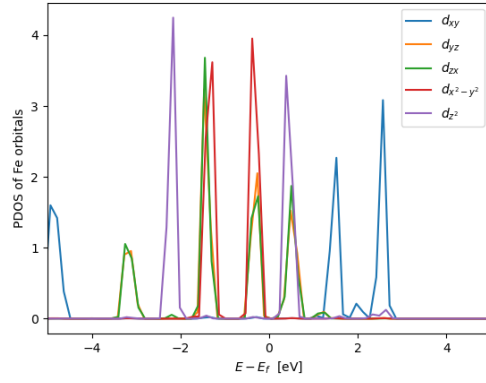


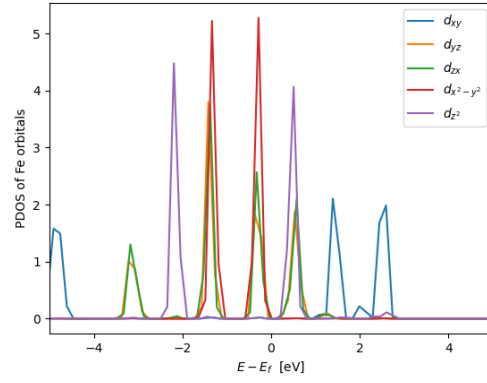
Figure 4.15 PDOS of Fe d orbitals for pristine charge neutral macrocycles. The alphabetical orders are correspond to the sequence in **Table 4.2**. The energies are aligned with the Fermi level E_f and truncated within -5 to 5 eV.

Most of the d_{xy} states are below the Fermi level as the xy plane coincides with rigid FeN_4 backbone. The higher energy parts are either perpendicular to the xy (d_{yz} , d_{xz} , d_{z2}) plane or with different orientations in xy plane (d_{x2-y2}). This result fits the chemical intuition of the chelation of FeN_4 . The ABAB_octa isomer in **Figure 4.15 c)** shows considerable amount of d_{xy} states above the Fermi level, suggesting the alternating ethyl side groups have impacts on the redistribution of Fe d orbitals. However, this does not overthrow the landscape of the occupation of the states, leading to similar binding energies of $^*\text{OH}$ for the compounds. And it is difficult to distinguish the materials from the plots, indicating a complex electronic interaction during the electrocatalysis. To understand how the charges affect the d orbital of Fe, charged simulations are carried and the results are demonstrated below.

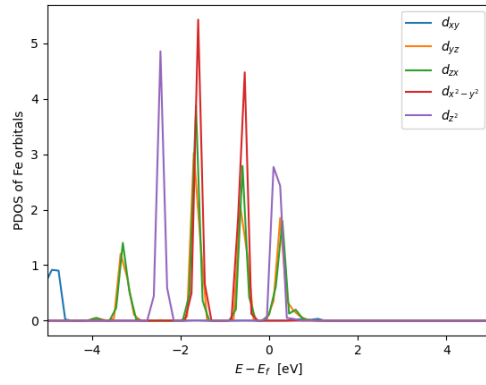
a1)



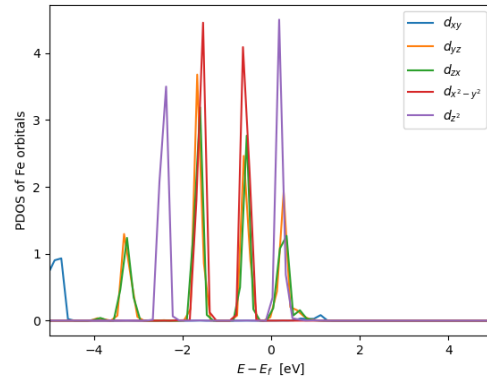
a2)



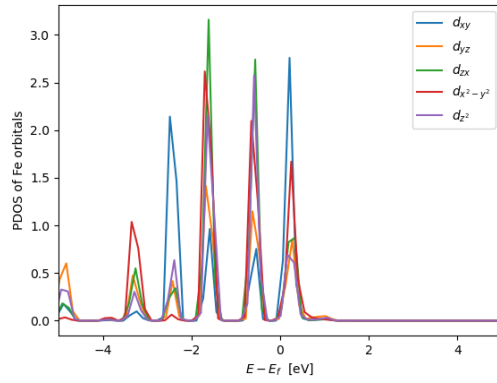
b1)



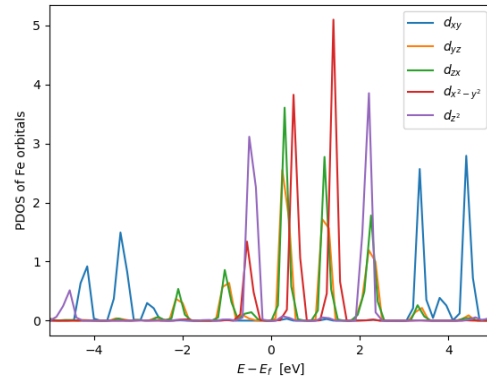
b2)



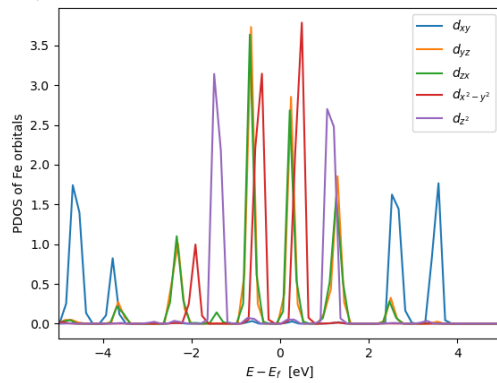
c1)



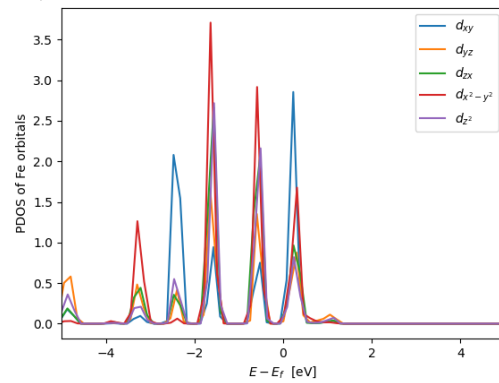
c2)



d1)



d2)



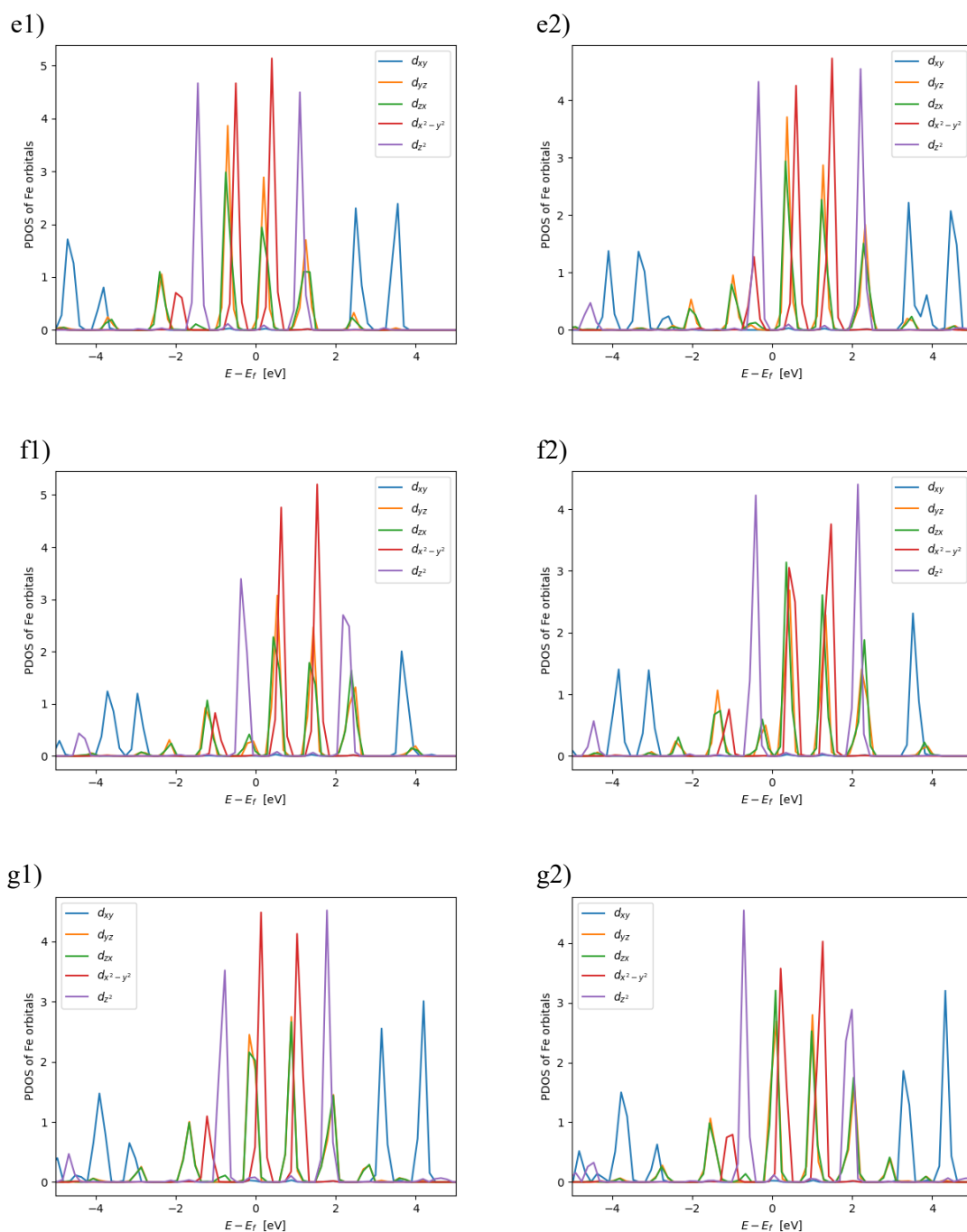


Figure 4.16 PDOS of Fe d orbitals for pristine charged macrocycles. The alphabetical orders are correspond to the sequence in **Table 4.2**. 1 means the system is charge (+1) and 2 is charge (-1). The energies are aligned with the Fermi level E_f and truncated within -5 to 5 eV.

There is not a single criterion that can separate the molecules into groups clearly. With a positive charge added, AABB/ABAB_octa (b1, c1) show no states above the Fermi level, potentially indicating a paired electron with lowest energy in d orbital. However, this is not case when adding an electron. For rest of

the molecules, the states are spread around the Fermi level, which further confirms that these molecules show good conductivities.

4.3.4 Scaling relations in Fe macrocycles

The scaling relations in Fe macrocycles are summarised in the **Figure 4.17** and **Table 4.4** below. The dashed lines were fitted with the ordinary least square (OLS) method while for solid lines their slopes were fixed to be what reported for other systems, i.e., 1 for *OH, *OOH and 2 for *O. In the latter case the intercept terms would have the mean μ and the standard deviation σ . The scaling relation between the *OOH and *OH once again proves the universality of $G(*\text{OOH}) = G(*\text{OH}) + 3.2 \text{ eV}$.¹³ The intriguing thing is the binding of *O, where the slope is 2 as a result of bond order in other materials.¹⁰ In Fe macrocycles, the fitted OLS slope is far away from 2 (**Table 4.4**). It can be understood that the bond between the oxygen atom and active site which is Fe is no longer the double bond, or the data points are not enough to demonstrate robust statistics, or there exists large perturbation of the electronic structures.

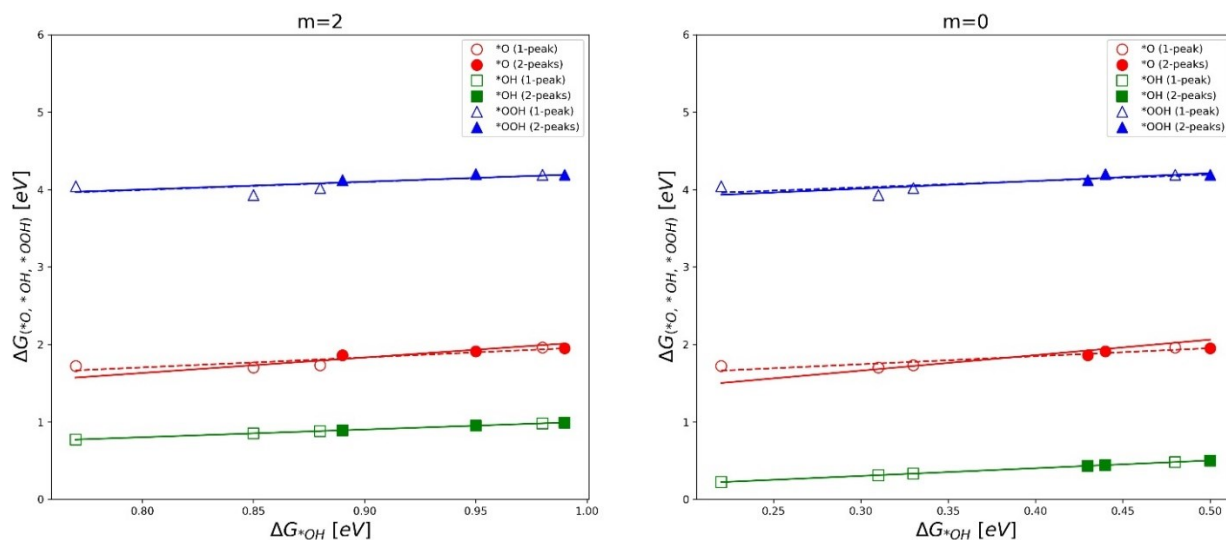


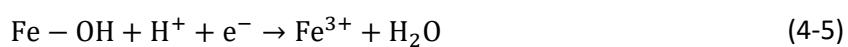
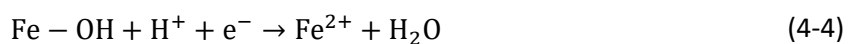
Figure 4.17 Scaling relationship between the binding energies of *OH, *O and *OOH, for $m=2$ and $m=0$. Data points relative to the only showing one CV peak are presented as empty symbols, while full symbols refer to 2-peaks molecules.

Scaling relation [eV]		OLS (dashed line)		Fixed β	
		α	β	μ	σ
m=2	G(*OH) vs. G(*O)	0.67	1.29	0.03	0.07
	G(*OH) vs. G(*OOH)	3.17	1.03	3.2	0.06
m=0	G(*OH) vs. G(*O)	1.43	1.03	1.06	0.1
	G(*OH) vs. G(*OOH)	3.78	0.83	3.71	0.06

Table 4.4 Scaling relations of the intermediates. OLS stands for ordinary least square, β is the fitted slope and α is the intercept. Fixed β is the scheme that *O has the double bond hence $\beta=2$ while for the rest *OOH and *OH $\beta=1$. The μ and σ are the mean and standard deviation values for the intercept.

4.3.5 Volcano plots

The volcano plot is a better sketch of the scaling relations. Since the original macrocycles could have multiple spin states but two valences that are responsible for the ORR, and the *OH intermediates only possess one, it is possible to calculate *OH desorption for both cases.



The state of the macrocycles (Fe^{2+} or Fe^{3+}) after *OH desorption is unknown. However, the subsequent electron transfer occurring at the low potential peak would correspond to either Fe^{2+} to Fe^+ or Fe^{3+} to Fe^{2+} , with a one-to-one mapping from the initial state. This is concluded from the invariance of the potential for the low potential peak with respect to the shift of pH, which suggested that peak is caused by a simple electron transfer and does not involve the adsorption or desorption of oxygenated intermediates there was only electron transfer (**Figure 4.9d**).

With all the DFT data in the **Table 4.2** and experimental data obtained or fitted, the raw volcano plots were shown in the **Figure 4.18**.

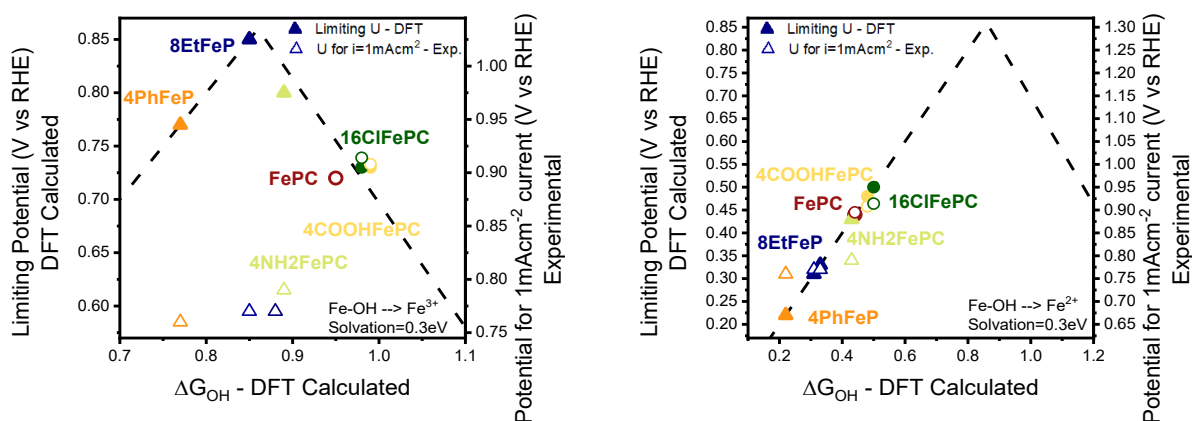


Figure 4.18 The volcano plot: on the left y-axis shows the DFT-limiting potential (represented by full symbols) for oxygen reduction, while the one on the right y-axis shows the experimentally determined potential required to achieve a current density of 1 mA cm^{-2} . Both datasets are plotted against the DFT predicted *OH binding energy. The solvation energy is 0.3 eV.

It can be spotted that for Fe^{3+} the experimental data are in disagreement with the DFT prediction while for Fe^{2+} the potentials offer a better match with the low potential peak in CV. There are two main reasons for the discrepancy. One is that the solvation energy applied in the plots are acquired from the Pt (111).¹² However, Fe macrocycles are remarkably different from Pt. The other is the intrinsic error from DFT, in which the absolute energy values are usually poorly described while the relative energetics are much better defined.

For the solvation energy, it was shifted into a variable that was modified to obtain the best fitting. For the DFT absolute error, improvements were made by fixing the position of FePC value from DFT on the volcano and plotting the relative energy values of the rest molecules compared to FePC. The updated volcanos are shown below.

Figure 4.19b and **16d** present similar volcano plots that use the DFT-calculated *OH binding energy from Fe-OH to Fe²⁺ (m=0) and Fe-OH to Fe³⁺ (m=2), respectively. The left y-axis of the graph shows the DFT-predicted overpotential (represented by full symbols) as a function of the DFT-predicted *OH binding energy, while the right y-axis shows the experimental ORR activity (represented by empty symbols) as a function of the DFT-predicted *OH binding energy, scaled to the potential at 1mAcm⁻² current for FePC. This allows for a reliable comparison between the calculated DFT energetics and experimental performance.

This analysis reveals three observations in both figures. Firstly, all the molecules are on the left side of the volcano indicating the rate determine step is *OH desorption. Secondly, the calculated *OH bonds from DFT allow us to distinguish the two types of catalysts experimentally. The ones with two peaks are active with optimal *OH binding energies for ORR, while the ones with one peak have weaker *OH binding energy and are also much less active in experiments. Thirdly, the match between the *OH prediction and the overlay of the experimental performance shows that the group of active catalysts are predicted relatively accurately on the volcano plot, while the less active catalysts are less precisely described. This observation suggests that the single peak molecules may follow a different activity mechanism.

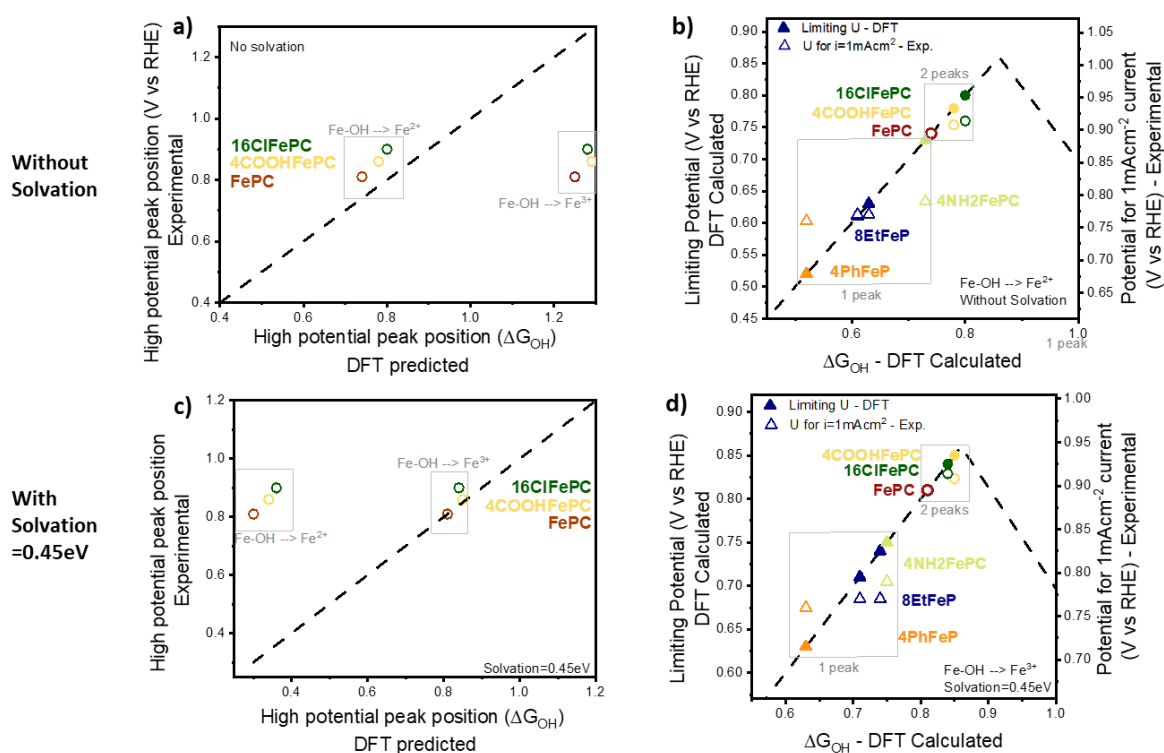


Figure 4.19 a) The positions of high-potential peaks obtained from experimental measurements and DFT calculations, without taking into account any additional solvation effects. The experimental peak position is only shown for molecules that exhibit two peaks, and it was determined as the average of the cathodic and anodic CV high peak positions. b) The volcano plot: on the left y-axis shows the DFT-limiting potential (represented by full symbols) for oxygen reduction, while the one on the right y-axis shows the experimentally determined potential required to achieve a current density of 1 mA cm^{-2} . Both datasets are plotted against the DFT predicted $^*\text{OH}$ binding energy. The DFT calculations assume that OH desorption occurs with a change in Fe oxidation state: $\text{Fe-OH} \rightarrow \text{Fe}^{2+}$, and without solvation corrections. The experimental data is adjusted to fit the prediction for FePC. c) The high-potential peak positions obtained from experimental measurements and DFT calculations, with a solvation correction of 0.45 eV . The value of 0.45 eV was chosen to fit the DFT-calculated peak position for $\text{Fe-OH} \rightarrow \text{Fe}^{3+}$ with the experimental one, for the case of FePC. The experimental peak position is only shown for molecules that exhibit two peaks, and it was determined as the average of the cathodic and anodic CV high peak positions. d) The volcano plot on the left y-axis shows the DFT-limiting potential (represented by full symbols) for oxygen reduction, while the one on the right y-axis shows the experimentally determined potential required to achieve a current density of 1 mA cm^{-2} . Both datasets are plotted against the DFT predicted $^*\text{OH}$ binding energy. The DFT calculations assume that OH desorption occurs without a change in Fe oxidation state: $\text{Fe-OH} \rightarrow \text{Fe}^{3+}$, and include a solvation correction of 0.45 eV . The experimental data is adjusted to fit the prediction for FePC.

4.3.6 Peroxide Selectivity

Another feature that could noticeably distinguish the two groups of the materials is peroxide selectivity. Regarding the reaction mechanisms, after the peroxide $^*\text{OOH}$ intermediate is formed, the reaction can proceed through two different pathways: one involving the desorption of HOO^- and the other involving the dissociation of the O-O bond, which leads to the $4e^-$ reduction to water (**Figure 4.20**).

We have previously discussed how the relation between the binding energies of oxygenated intermediates leads to the formation of a Sabatier volcano. The volcanos help predict the minimum overpotential required for a reaction to occur, and the catalytic activity and selectivity are mainly controlled by electronic effects. In the case of water production, the activity on the strong binding side of the volcano is limited by $^*\text{OH}$ desorption, while on the opposite side, the limiting factor is O_2 reduction to $^*\text{OOH}$. Similarly, peroxide production is limited by $^*\text{OOH}$ desorption on the left side of the volcano and O_2 reduction to $^*\text{OOH}$ on the right side. Since the potential for $^*\text{OH}$ desorption is always more positive than that of $^*\text{OOH}$, water production is favoured over peroxide production on the left side of the volcano. On the right side, the limiting step for both reactions is the same, and the limiting potentials overlap. The molecules tested in this study are predicted to be on the left side of the Sabatier volcano, which means that they are expected to have low peroxide selectivity. This means that the observed differences in selectivity among the molecules cannot be explained by their position on the volcano alone. This suggests that selectivity is not solely controlled by electronic effects but may also be correlated to the presence of a high potential peak: the molecules with a single peak, 4PhFeP, 8EtFeP, and 4NH₂FePC, were found to have higher peroxide production efficiencies.

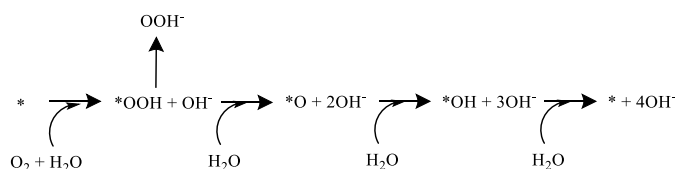


Figure 4.20 Reaction mechanisms for the ORR in alkaline environment.

A straightforward explanation from **Figure 4.20** could be the destabilisation of the $^*O$ intermediate with respect to $^*OOH$, which would drive the reaction towards OOH^- instead of $^*O$. To investigate this proposal, $^*O$ and $^*OOH$ binding energies are plotted below.

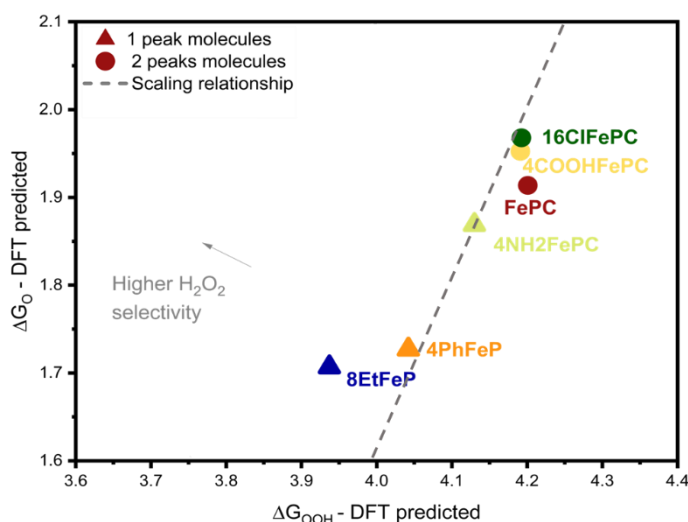
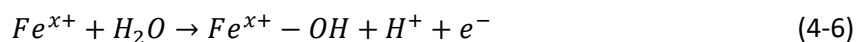


Figure 4.21 $^*O$ free energies, as a function of $^*OOH$ free energies, as predicted by DFT calculations. The dashed line shows the free energy predicted by the scaling relationship $\Delta G_O = 2\Delta G_{OOH} - 6.36$ [eV].

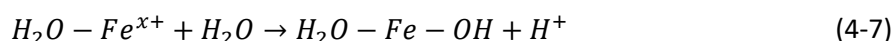
From **Figure 4.21**, it is clear that the predicted line separates the molecules into two groups that exactly match their peroxide selectivity. 4PhFeP and 8EtFeP have notably weaker $^*O$ bond compared to the $^*OOH$ leading to a more peroxide favoured route. Although it is less significant for 4NH₂FePC, it is still slightly above the line and peroxide is expected. On the contrary, there is no relative destabilisation of $^*O$ for the rest phthalocyanines which give rise to their high selectivity for oxygen reduction to water.

4.3.7 Spin accommodation

A simple yet tricky question is why the high potential CV peaks are missing from a particular group of materials that share loads of similarities? To understand it, we need to dig into the fundamental reaction mechanisms. If there exists a high potential peak, then the reaction mechanism is in equation (4-6) where the x stands for the valence and x is either 2 or 3 as the two volcanos we discussed before.



To meet the requirement of the missing peak, the electron cannot be in the product. According to the result of experiment XANES, there is no shift for molecules missing the peak which indicates that there could be no oxidation state change or there could be coordination change such that the shift is masked. No valence change is unlikely as the ORR current is observed. To simultaneously satisfy these two conditions, equation (4-7) is proposed:



In such configuration, the water is attached to the molecule explicitly to have a five-fold coordination environment. And the electron which is supposed be the product that causes the peak is captured by Fe as a result of the thermodynamics. Recall that no matter for Fe^{2+} or Fe^{3+} they converge to the identical Fe-OH. Therefore, in the proposed mechanism the reason that the electron can be absorbed by Fe is that the reduction of energy for the system to accommodate the spin of Fe is larger than that of releasing. And to facilitate this, the prerequisite is the stationary water on the Fe. Then it is apparent that the ORR performance for molecules undergo such mechanism will be poor as only one side of Fe is allowed to go through the ORR cycle. This seems to fit with the experimental observations in **Table 4.1** To verify the hypothesis, the thermodynamics are calculated in the table below. Now the asterisk stands for the stationary water on the back side of Fe.

ΔG (eV) Name	*O (m=0)	*OH (m=0)	*OOH (m=0)	*O (m=2)	*OH (m=2)	*OOH (m=2)
4PhFeP	1.26	0.28	3.42	1.75	0.77	4.04
AABB_8EtFeP	1.24	0.26	3.41	1.75	0.77	3.93
ABAB_8EtFeP	1.20	0.24	3.40	1.72	0.76	4.02
FePC	1.44	0.41	3.78	1.91	0.88	4.25
16ClFePC	1.50	0.62	3.94	1.98	1.10	4.42

4NH ₂ FePC	1.45	0.53	3.76	1.91	0.99	4.22
4COOHFePC	1.47	0.40	3.51	1.95	0.89	3.99

Table 4.5 Binding Energies (G) of oxygenated ORR intermediates species (*O, *OH, *OOH) on the selected Fe macrocycles with water on its back side, for spin relaxed magnetic moments $m=0$ and $m=2$.

With the data in **Table 4.2** and **Table 4.5**, the respective solvation energy of 0 and 0.45 eV for Fe^{2+} and Fe^{3+} as discussed in the two volcanos, the following two plots were plotted to show whether it is thermodynamically favourable for the peak to miss as equation (4-7) indicates for Fe^{2+} and Fe^{3+} . The intermediate *OH spin is also included to check whether it can be applied directly as a descriptor.

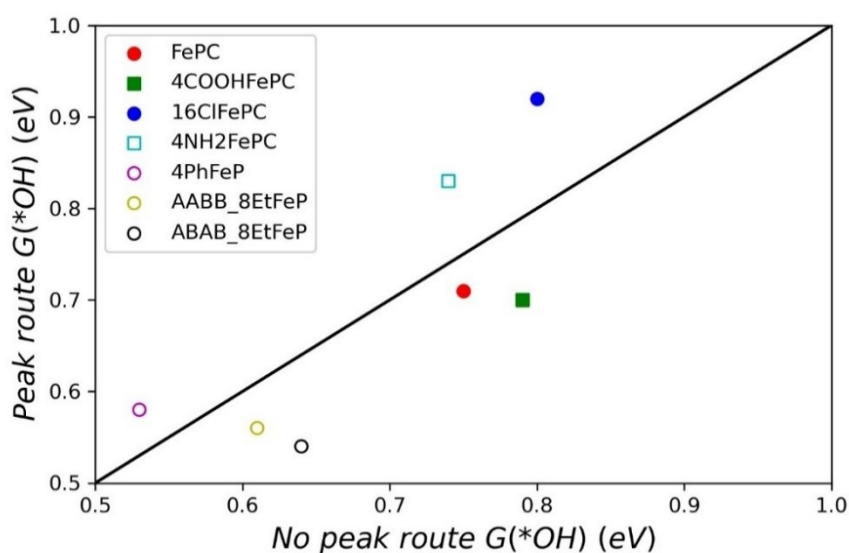


Figure 4.22 Free energy comparison of reaction (4-6) that suggests a peak and reaction (4-7) for missing peak if the high potential peak corresponds to Fe^{2+} . The full symbol represents the group with two CV peaks while the empty stands for single peak. Those with the sphere marker have the intermediate *OH magnetic moment close to 1 while for the square marker its around 2.5.

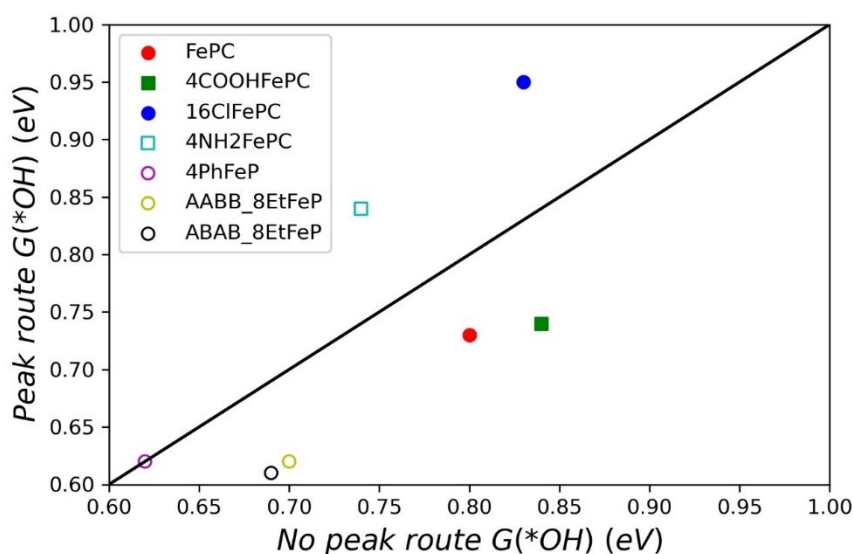


Figure 4.23 Free energy comparison of reaction (4-6) that suggests a peak and reaction (4-7) for missing peak if the high potential peak corresponds to Fe^{3+} . The full symbol represents the group with two CV peaks while the empty stands for single peak. Those with the sphere marker have the intermediate $*OH$ magnetic moment close to 1 while for the square marker its around 2.5.

It is not straightforward to draw a clear conclusion from both figures as it depends on a few assumptions and constrained on the precision of the calculations. The ideal condition or equivalently the proposed mechanism is that all the molecules show the peak (full symbol) lie on the top of the dividing line while the missing ones (empty symbol) on the bottom. However, the first difficulty is the whether the adsorption of the water molecule is spontaneous. This may seem easy if we simply calculate the binding energy of water for the molecules from **Table 4.2** and **Table 4.5**. However, the result is too small ca. 0.23kcal/mol that is below the chemical accuracy of 1kcal/mol to be confirmative, which suggests that some of the molecules may well not support the stationary water binding. As analysed before these molecules are within the group with better ORR efficiency, i.e., the full symbol ones. If this is the case the FePC and 4COOHFePC that lie below the line can be eliminated and the conflict is resolved. However, except for the 4PhFeP that has the precision issue, there is still a mystery for 4NH₂FePC. The insight is from the spin of the intermediate $*OH$. As is seen that 4NH₂FePC has a magnetic moment of ~ 2.5 while other porphyrins are ~ 1 , which indicates a fundamentally different mechanism for

4NH₂FePC. And the mechanism could be complicated considering the binding of *H with four amino groups and Fe as potential sites. There are two choices for the valence of Fe and five positions for hydrogen to bind which makes up $2 \times 2^5 = 64$ configurations.

Up to now it can be concluded that all the porphyrins lack the high potential peak can possibly be explained by the proposed mechanism. All the phthalocyanines except for 4NH₂FePC show the high potential peak because they may not bind the stationary water. 4NH₂FePC is the outlier that has completely different reaction mechanism. Although this conclusion seems to fit all the observations it requires more proofs. And it will be elaborated in the following discussion.

4.3.8 X-ray absorption near edge structure (XANES) simulation

In addition to the geometry optimisation settings as mentioned in chapter 4.3.2, the hch1s (half core-hole in the 1s orbital) setup is utilised for the Fe atom. The absolute energy scale is determined by calculating the difference between the total energy of the first core excited state and the ground state of hch1s. To generate the spectrum, the Haydock recursion method⁹⁴ is applied with unit k-points and default parameters recommended by GPAW. Due to the large size of the molecules, it was not feasible to increase the k-points for a delta Kohn-Sham calculation of the gamma point using the recursion method. As a result, the total energy difference of hch1s is used as the scale. Because of the lack of sampling k-points, and from the chapter 2 that the fictitious non-interacting Kohn-Sham orbital will cause errors, the simulation spectrum should be aligned with the experiment data.

Since there is no Fe⁺ in DFT spin relaxed optimised structure, only Fe³⁺ that relates to high potential CV peak, and Fe³⁺ to Fe²⁺ as low potential CV peak scheme will be discussed here.

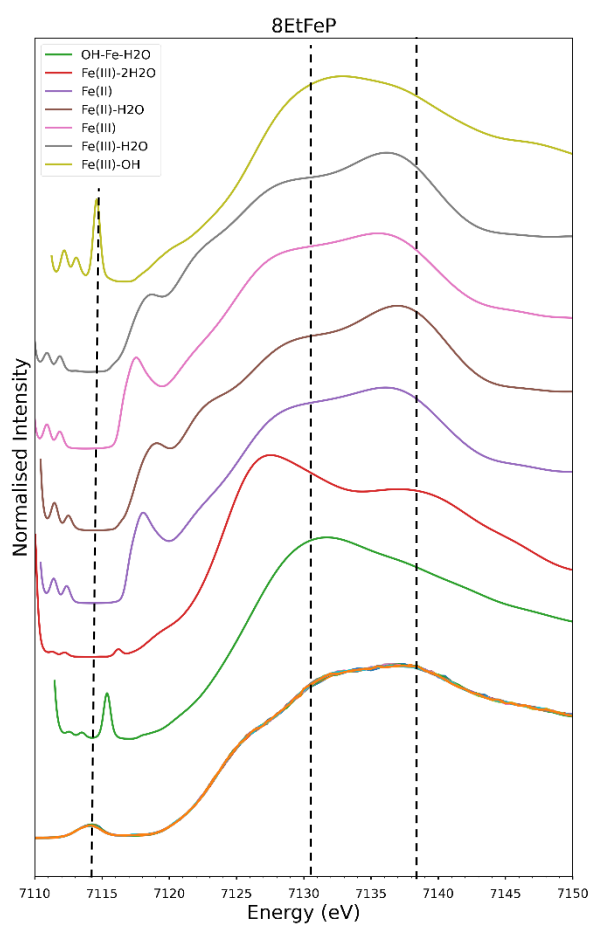
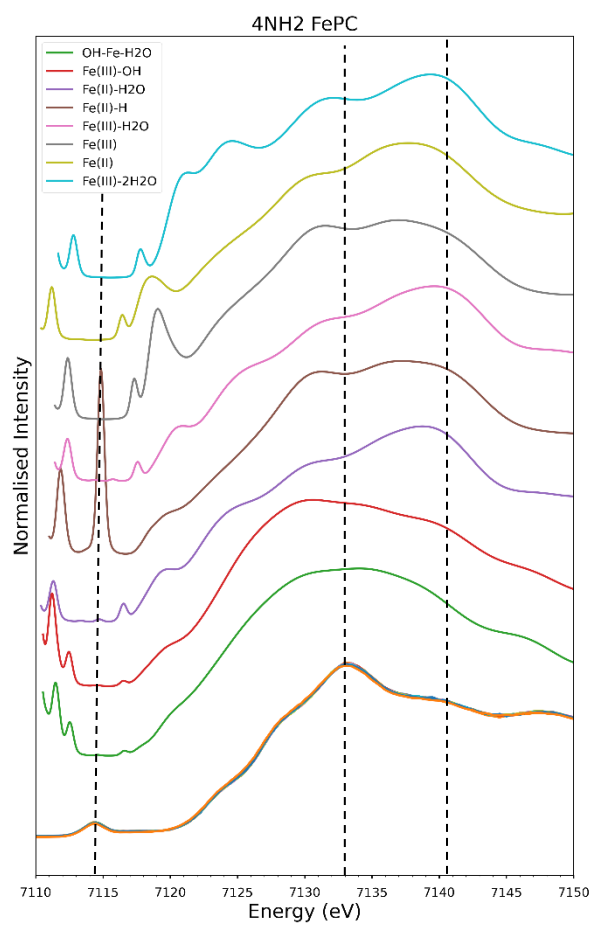
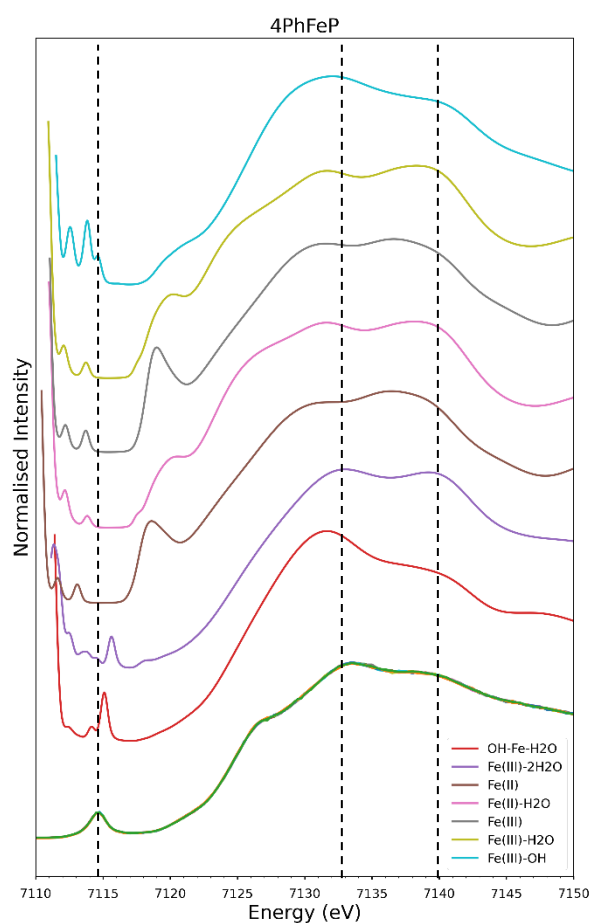
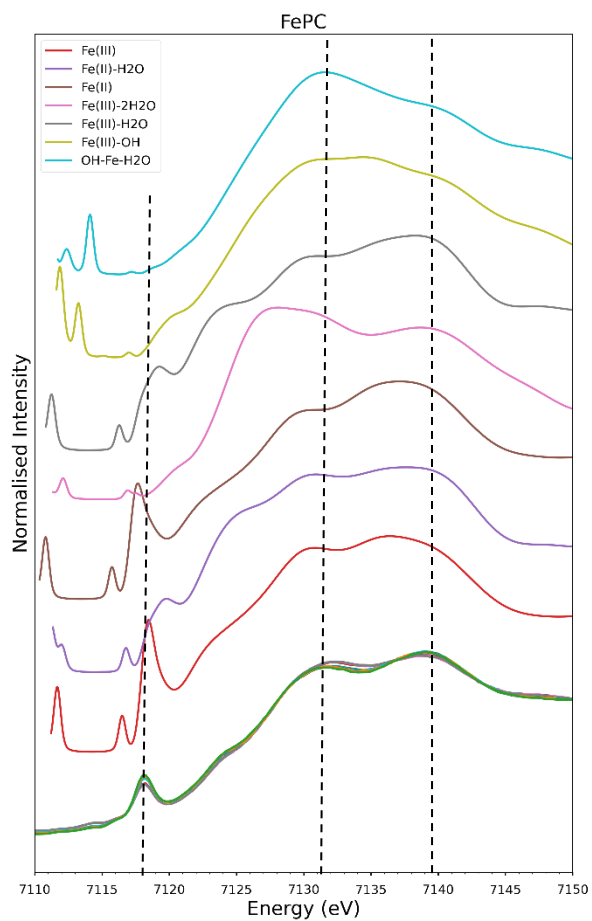


Figure 4.24 The XANES spectra for molecules FePC, 4PhFeP, 8EtFeP, and 4NH₂FePC with various adsorbed oxygenated species were simulated using DFT. The experimental data is shown at the bottom for comparison. The dashed black lines are possible peaks in experiment data and DFT simulations are aligned to them.

The simulated intermediates are related to the proposed mechanisms discussed in 4.3.6. For FePC, the pre-edge at 7118 eV is attributed to the existence of Fe(II)-N₄,⁹⁵ however, the difference between the calculated Fe²⁺ and Fe³⁺ spectrums is barely recognisable, leaving all the possibilities open. But there is no contradiction with the proposed mechanism which would allow the existence of all the intermediates.

For two porphyrins, they have significantly similar trend. Fe(II) and Fe(III) can be excluded at first glance when considering the their pre-edge peaks, as they have sharp peaks near 7118 eV that is difficult to be convoluted to have a flat curve when compared to the experiment data. And this is also the reason for their counterparts with water to survive as the they have remarkably blunt peaks. Then the intermediates that correspond to the pre-edge peak can only be OH-Fe-H₂O and Fe(III)-OH for 8EtFeP, and including Fe(III)-2H₂O for 4PhFeP. Once more, there is no contradiction with the spin accommodation hypothesis. Although neither can it be proved, the stationary water makes it better to fit into the offered scheme.

As for the outlier 4NH₂FePC, it is not a surprise that all the intermediates except for Fe(II)-H can be responsible for the pre-edge peak. And Fe(II) and Fe(III) can also be ruled out due to the same reason. Since the underlying mechanism for this molecule could be drastically complicated, which is analysed before that the adsorption *H could have 64 possibilities, here it is just presented that it could be the combination of spin accommodation and the binding of hydrogen or more entangled situations.

4.4 Conclusion

In this chapter, the research progress for efficient and inexpensive ORR electrocatalysts were briefly reviewed, which introduced the need to focus on Fe-N-C materials as the catalyst. Experimentally, Fe-macrocycles with well-defined structures were utilised to examine the oxygen reduction mechanisms.

There was an anomaly in the CV that two groups of materials either showed a single peak or two peaks. From the experiment result, the low potential peak was proved to be the electron transfer process and the high potential peak was related to the proton electron transfer. The single peak group had higher peroxide selectivity or lower ORR efficiency and exhibited no spectra change in XAS, while the double peaks group showed the opposite.

In the perspective of the simulations, first the scaling relations are proved to be correct in Fe phthalocyanine and porphyrin system, suggesting the validity of the methodology. The proton electron transfer is attributed to $^*OH$ desorption that could happen while keeping the Fe oxidation state at 3+ or 2+. Both possibilities are supported by accurate peak position predictions based on DFT calculations with different solvation corrections. With respect to peroxide selectivity, two groups can be evidently separated by the binding energy of $^*O$ vs. $^*OOH$, making the reaction path hypothesis solid. The DFT calculations indicate that molecules with two peaks are more active than those with a single peak, regardless of the final oxidation state, indicating a different mechanism for the latter group. This mechanism is closely related to the missing high potential peaks that should be the $^*OH$ desorption for the single peak group. Combining the evidence from the XAS and analysis from DFT data, a self-consistent hypothesis is proposed: the water may bind on the back side of the molecule such that the electron would act to accommodate the spin during the desorption of $^*OH$.

Chapter 5

DFT study on the selectivity of M-N-C materials for CO₂RR

This chapter will provide a short state of the art on CO₂RR using metals and motivation for transitioning towards metal-nitrogen-carbon (M-N-C) materials as electrocatalysts. I will present my own result on theoretical aspects for different transition metal in macrocycles. Finally, the Fe macrocycles that show high potential as highly efficient CO₂RR electrocatalysts are studied with DFT in detail.

5.1 Literature review

5.1.1 Metallic electrocatalysts

Hori et al. reported the first quantitative study in 1985 that measured both gaseous and liquid products from CO₂RR.⁹⁶ They conducted constant-current electrolysis on polycrystalline metal electrodes using CO₂-saturated 0.5 M KHCO₃ at 5 mA cm⁻² for up to an hour as a batch experiment. Following this and similar studies,^{97–100} metal electrodes were classified into four groups. The first group, consisting of Pb, Hg, Tl, In, Sn, Cd, and Bi, mainly produced formate (HCOO⁻). The second group, comprising Au, Ag, Zn, Pd, and Ga, primarily generated carbon monoxide (CO). The third group, consisting of Ni, Fe, Pt, and Ti, had minimal reduction of CO₂ but reduced water to H₂. Finally, the fourth group, which was copper, produced various hydrocarbons, aldehydes, and alcohols, making it the only pure metal to produce products beyond C1 that require more than two electrons transfer with considerable Faradaic efficiency. Bagger et al. provided a sound theoretical explanation for the division of the metals¹⁷. They correlated the macroscopic products of the metals with their microscopic binding energy H*, COOH* and CO*, which stands for the selectivity of competitive HER or the formic acid, or further reduction to CO. Cu's unique capability to reduce CO₂ into products beyond CO could be attributed to its distinctive property of having a positive adsorption energy for H* while possessing a negative adsorption energy for CO* that is not found in any other metal.

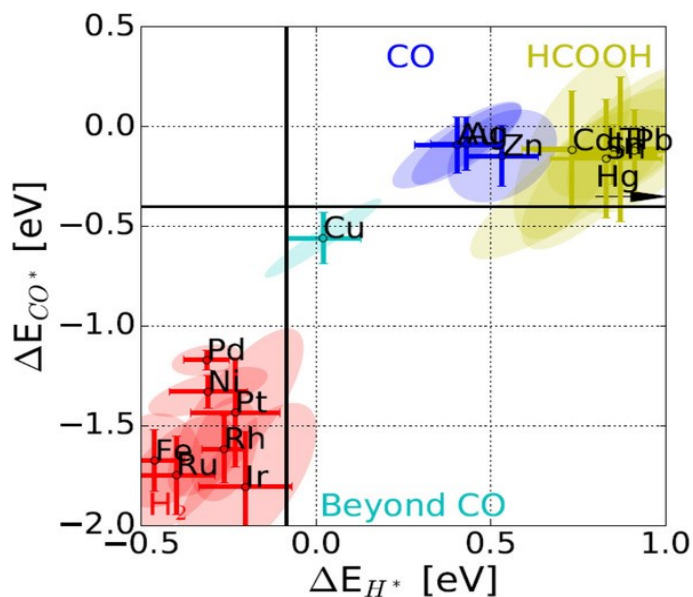


Figure 5.1 CO₂ reduction metal classification. the solid black lines show the thermodynamics of adsorbed or none-adsorbed H₂, i.e. $\Delta G_{H^*} = 0$, for $1/2H_2 \leftrightarrow H^*$ or CO $\Delta G_{CO^*} = 0$, for $CO \leftrightarrow CO^*$.¹⁷

In **Figure 5.2**, Metals that generate H₂ can be categorised as having hydrogen underpotential deposition H_{upd} . Metals that generate CO can be categorised as having a hydrogen coverage but not due to underpotential deposited hydrogen. Metals that produce formic acid can be characterised as having minimal hydrogen coverage, as indicated by $\Delta E_{H^*} - \Delta E_{COOH^*}$ values approximately equal to or greater than 0 eV. However, the boundary line between CO and formic acid is obscured as the Zn produce a small amount of formic acid and Cd produce a small amount of CO.¹⁷

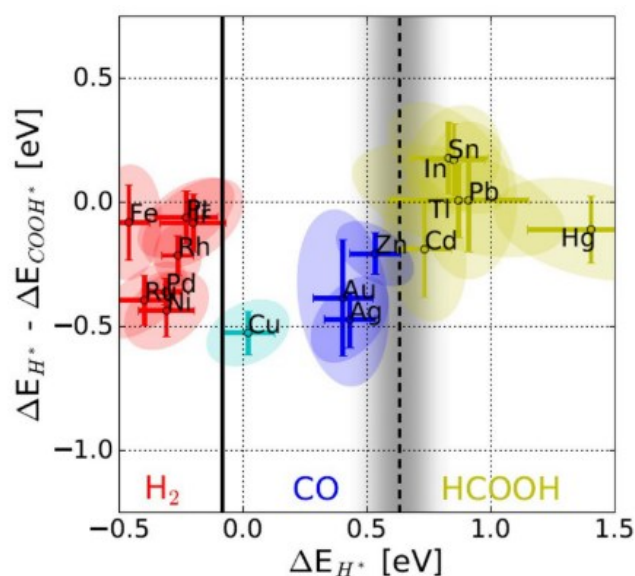


Figure 5.2 Experimental product classification by ΔE_{H^*} and $\Delta E_{H^*} - \Delta E_{COOH^*}$. The solid black lines show the thermodynamics of adsorbed or none-adsorbed H_2 , dashed black line with equidistance to Zn and Cd as the boundary for CO and HCOOH.¹⁷

5.1.2 Beyond Metals

Despite the flexibility of Cu, there are no catalysts that exhibit complete selectivity towards the CO_2RR due to the existence of HER, which reduces the efficiency for practical application. Besides, To find materials that possess higher selectivity, Bagger et al. studied porphyrin-like materials using DFT.¹⁸ The advantage of a single metal site in a porphyrin-like structure is that it can restrict the competing HER (**Figure 5.3**). In contrast to a metal catalyst surface, where hydrogen binds to a hollow site, the single metal site in a porphyrin-like structure requires ontop site binding of hydrogen (**Figure 3.7, Figure 5.3**). This difference in binding site structure results in an energy shift of about 0.3 eV between the $COOH^*$ and H^* intermediate, which are involved in CO_2RR and HER, respectively. Consequently, porphyrin-like catalysts can suppress HER and improve CO_2RR selectivity more effectively than metal catalysts.

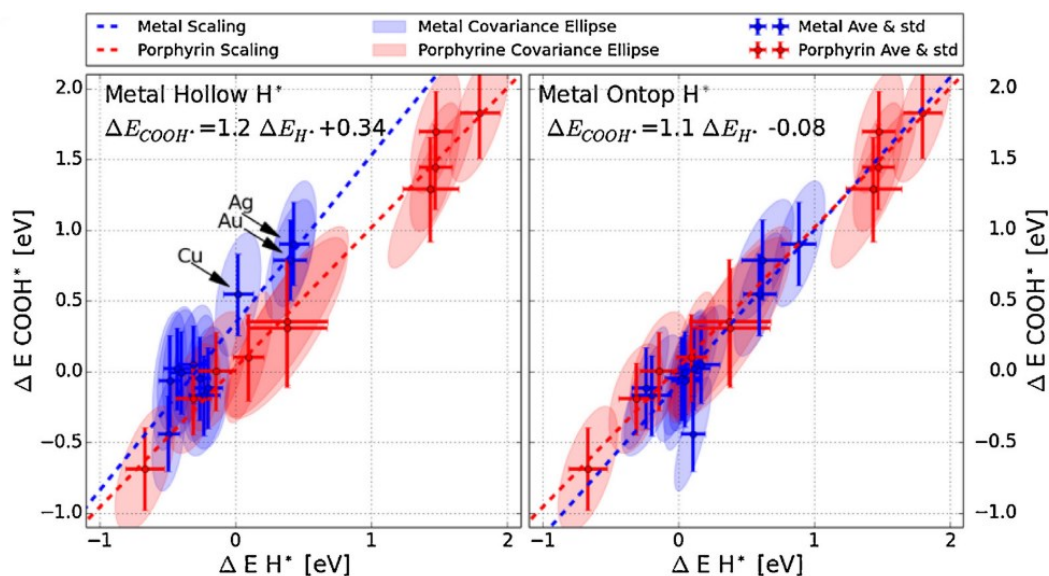


Figure 5.3 The DFT energy relation between H^* and $COOH^*$. The H^* binding is located at the hollow site in the left plot for the metal catalyst, whereas in the right one, it is forced onto the metal atom's ontop position ($E_{COOH^*} = 1.0 E_{H^*} + 0.03$ for the porphyrin-like structure). The porphyrin-like structure has a scaling relation advantage over the metal scaling relation.¹⁸

The binding energy comparison is in **Figure 5.3** Porphyrin-like structure with centre atom Fe or Mn shows better selectivity towards the products that are beyond CO.

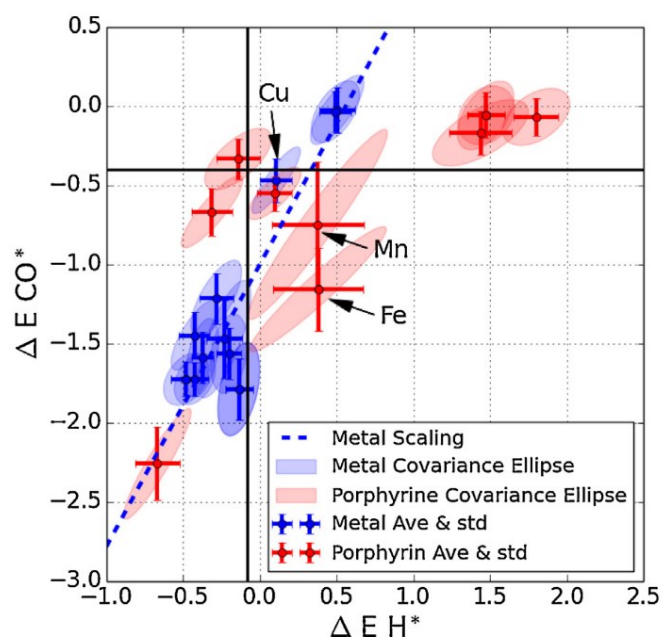


Figure 5.4. The DFT energy relation between $^*H$ and $^*CO$. The solid black lines show the thermodynamics of adsorbed or none-adsorbed H_2 or CO that correspond to $\Delta G_{H^*} = 0$ or $\Delta G_{CO^*} = 0$. Only the Cu metal, along with the Fe and Mn porphyrine-like structure, resides within the thermodynamically favourable region located in the lower right quadrant. Error bars represent the standard deviation of ensemble energies obtained from the BEEF-vdW functional, while the covariance ellipses depict the σ confidence intervals derived from the BEEF ensemble.¹⁸

However, as it can be seen from **Figure 5.4** that the binding strength of CO is too strong. This is not a merit for a catalyst, as excessively strong binding will lead to a poison of the active site. Nevertheless, experimental results suggested CO could be produced and no substantial degradation observed,^{101,102} which indicated a potential lack of precision of the computation. Vijay et al. studied a series of Fe-N_x-C for CO₂RR on graphene with different DFT functionals.²¹ They demonstrated that standard GGA functionals such as semi-local RPBE underestimates the binding energies of the intermediates. Instead, non-local hybrid functional HSE06 exhibits the accurate descriptions for $^*CO$, although at a much higher computational cost. DFT results of motifs with different defects and nitrogen coordination on graphene plane and experimental method temperature-programmed desorption (TPD) results are shown

in **Figure 5.5**. The calculations from HSE06 are more consistent with the TPD experimental results without excessively strong binding of CO*.

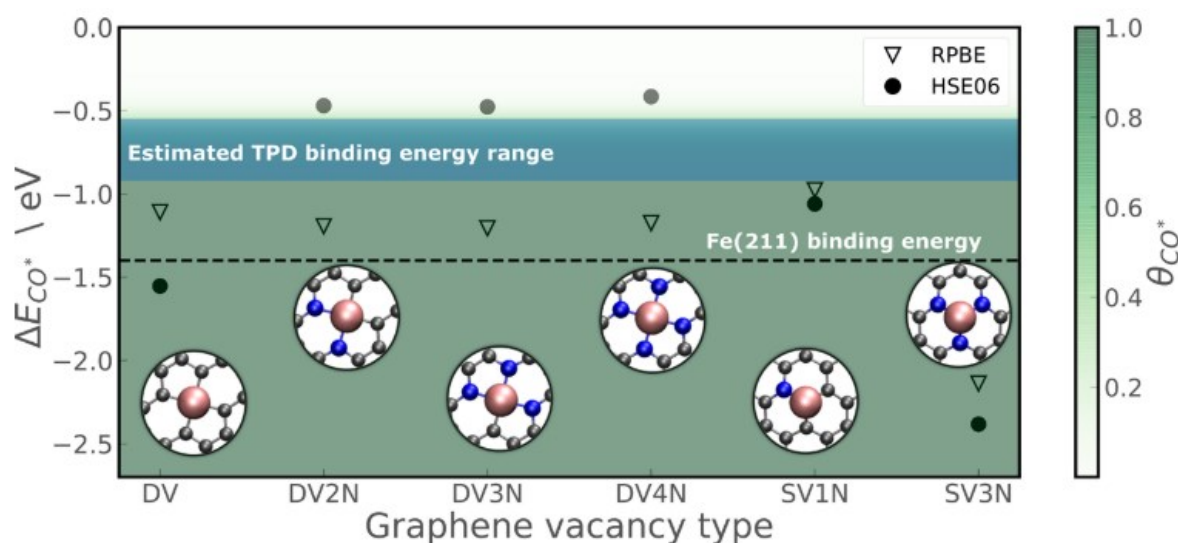


Figure 5.5. Comparison of adsorption energies of CO on iron-doped vacancies.¹⁹ Triangles stand for calculations with the GGA-RPBE functional and the circles represent hybrid HSE06 functional. D/S/V/N are abbreviations for double, single, vacancy, and nitrogen. Experimental estimate from TPD spectra²⁰ is marked by the blue band. The background fill indicates the coverage of CO predicted by the kinetic model using RPBE energetics. Fe(211) binding energies are shown with the dashed black line as a reference.²¹

5.2 DFT study on macrocycles for CO₂RR

5.2.1 Introduction

The merit of macrocycles as stationary models to unravel the fundamentals has been discussed in the last chapter. In addition, the regularised ontop binding, which could potentially lead to a better rejection of HER, is a direction that worth exploring. Moreover, as seen in last chapter, the spin of the transition metal that has not been yet fully understood, although it is believed to play a vital role in electrocatalysis. Understanding the different spin states of transition metals in macrocycles for CO₂RR could lead to materials with better selectivity while unrevealing important fundamental insight.

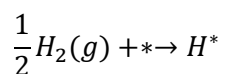
5.2.2 Transition metal macrocycles binding energy

The setup for DFT simulations is the same as described in chapter 4.3.2. Additionally, besides the spin relaxed configurations that are thermodynamically most favourable, spin fixed configurations that are one electron away from them are also considered. These are summarised in the **Table 5.1**. Except for the Fe as discussed that could have multiple possibilities when it comes to spin relaxed configurations considering the charged system, the rest show robust convergence without further deviations in spin. The periodic boundary conditions are set to be false along x, y and z directions to reduce the computation cost and examine the intrinsic catalytic response of the materials.

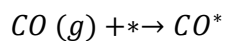
Name	Spin relaxed magnetic moment	d-subshell configuration	Spin fixed magnetic moment	d-subshell configuration
Fe 3d ⁶ 4s ²	2 2.5/1.5	Fe(II) 3d ⁶ (HS) Fe(III) 3d ⁵ (HS)/ 3d ⁵ (IS)	0	Fe (II) 3d ⁶ (LS)
Co 3d ⁷ 4s ²	1	Co(III) 3d ⁶ (IS)	0.5	Co(II) 3d ⁷ (LS)
Ni 3d ⁸ 4s ²	0	Ni(II) 3d ⁸	0.5	Ni(III) 3d ⁷
Cu 3d ¹⁰ 4s ²	0.5	Cu(II) 3d ⁹	0	Cu(I) 3d ¹⁰

Table 5.1 Spin relaxed and fixed configurations for different metal atoms of macrocycles. HS is noted for high spin, IS for intermediate spin and LS for low spin.

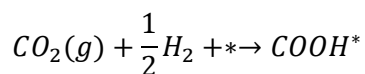
The binding energies were calculated with the following three equations. The unit is eV unless otherwise stated.



$$\Delta E(H^*) = E(H^*) - E(*) - \frac{1}{2}E(H_2) \quad (5-1)$$



$$\Delta E(CO^*) = E(CO^*) - E(*) - E(CO) \quad (5-2)$$



$$\Delta E(COOH^*) = E(COOH^*) - E(*) - E(CO_2) - \frac{1}{2}E(H_2) \quad (5-3)$$

ΔE (eV) Name	H* (m=0)	CO* (m=0)	COOH* (m=0)	H* (m=2)	CO* (m=2)	COOH* (m=2)
AABB_8EtFeP	-0.14	-1.51	-0.13	0.45	-0.92	0.45
ABAB_8EtFeP	-0.12	-1.52	-0.08	0.48	-0.92	0.53
16ClFePC	-0.15	-1.39	0.00	0.41	-0.83	0.55
4CO2HFePC	-0.17	-1.42	-0.02	0.42	-0.84	0.57
4NH2FePC	-0.15	-1.37	0.00	0.37	-0.84	0.53
FePC	-0.16	-1.42	-0.01	0.42	-0.84	0.57
4PhFeP	-0.29	-1.48	-0.05	0.24	-0.96	0.47

Table 5.2 Binding energy of Fe macrocycles with different magnetic moment m=0 (spin fixed), m=2 (spin relaxed) and intermediates H*, CO*, COOH*. Notation of AABB and ABAB are defined in chapter 4.3.2.

ΔE (eV) Name	H* (m=0.5)	CO* (m=0.5)	COOH* (m=0.5)	H* (m=1)	CO* (m=1)	COOH* (m=1)
AABB_8EtCoP	0.06	0.06	0.06	0.17	0.06	0.22
ABAB_8EtCoP	0.57	0.57	0.57	0.17	-0.45	0.27
16ClCoPC	0.00	0.00	0.00	0.21	0.05	0.39
4CO ₂ HCoPC	-0.01	-0.01	-0.01	0.18	0.06	0.38
4NH ₂ CoPC	-0.07	-0.07	-0.07	0.21	0.09	0.42
CoPC	-0.04	-0.04	-0.04	0.18	0.07	0.39
4PhCoP	0.35	0.35	0.35	-0.06	-0.19	0.00

Table 5.3 Binding energy of Co macrocycles with different magnetic moment m=0.5 (spin fixed), m=1 (spin relaxed) and intermediates H*, CO*, COOH*.

ΔE (eV) Name	H* (m=0.5)	CO* (m=0.5)	COOH* (m=0.5)	H* (m=0)	CO* (m=0)	COOH* (m=0)
AABB_8EtNiP	-1.06	-1.06	-1.06	1.30	0.06	1.41
ABAB_8EtNiP	-1.06	-1.06	-1.06	1.30	0.04	1.40
16ClNiPC	-1.48	-1.48	-1.48	1.62	0.08	1.71
4CO ₂ HNiPC	-1.56	-1.56	-1.56	1.73	0.07	1.81
4NH ₂ NiPC	-1.58	-1.58	-1.58	1.70	0.09	1.79
NiPC	-1.47	-1.47	-1.47	1.73	0.10	1.80
4PhNiP	-1.15	-1.15	-1.15	1.35	0.06	1.14

Table 5.4 Binding energy of Ni macrocycles with different magnetic moment m=0.5 (spin fixed), m=0 (spin relaxed) and intermediates H*, CO*, COOH*.

ΔE (eV) Name	H* (m=0)	CO* (m=0)	COOH* (m=0)	H* (m=0.5)	CO* (m=0.5)	COOH* (m=0.5)
AABB_8EtCuP	-1.77	-1.77	-1.77	1.77	0.07	1.65

ABAB_8EtCuP	-1.78	-1.78	-1.78	1.93	0.06	1.88
16ClCuPC	-1.88	-1.88	-1.88	2.03	0.06	1.97
4CO ₂ HCuPC	-1.90	-1.90	-1.90	2.05	0.08	1.99
4NH ₂ CuPC	-1.85	-1.85	-1.85	2.00	0.08	1.98
CuPC	-1.89	-1.89	-1.89	2.04	0.08	2.00
4PhCuP	-1.79	-1.79	-1.79	1.94	0.06	1.84

Table 5.5 Binding energy of Cu macrocycles with different magnetic moment $m=0$ (spin fixed), $m=0.5$ (spin relaxed) and intermediates H^* , CO^* , $COOH^*$.

The free energies were calculated from the binding energy in the table and the zero-point energy, entropy and enthalpic temperature correction from Varley et. al.¹⁰³ As Peterson et al. suggested that the RPBE functional has a systematic error for OCO backbone ~ 0.45 eV.⁵³ The corrections are summarised in the table below. In addition, the solvation energies for metals were calculated by Peterson and Nørskov, for $COOH \sim -0.25$ eV and for $CO \sim -0.1$ eV.¹⁰⁴ These values should be further calibrated by experimental data no matter what system the model applies.

Molecule	ZPE	$\int C_p dT$	-TS	E_{OCO}	μ
CO ₂	0.31	0.10	-0.66	0.45	0.20
CO	0.13	0.09	-0.61	-	-0.39
H ₂	0.28	0.09	-0.40	-	-0.03
Adsorbate					
*CO	0.19	0.08	-0.16	-	0.11
*COOH	0.62	0.10	-0.19	-	0.53
*H	0.18	0.01	-0.01	-	0.18

Table 5.6 Energy corrections, ZPE is zero-point energy, the integral is the heat capacity, -TS is the entropy contribution, μ is the chemical potential.¹⁰³

With the data in table the selectivity for CO₂RR of the macrocycles can be predicted by plotting the free energy of CO^* vs. H^* and H^* vs. $COOH^*$.

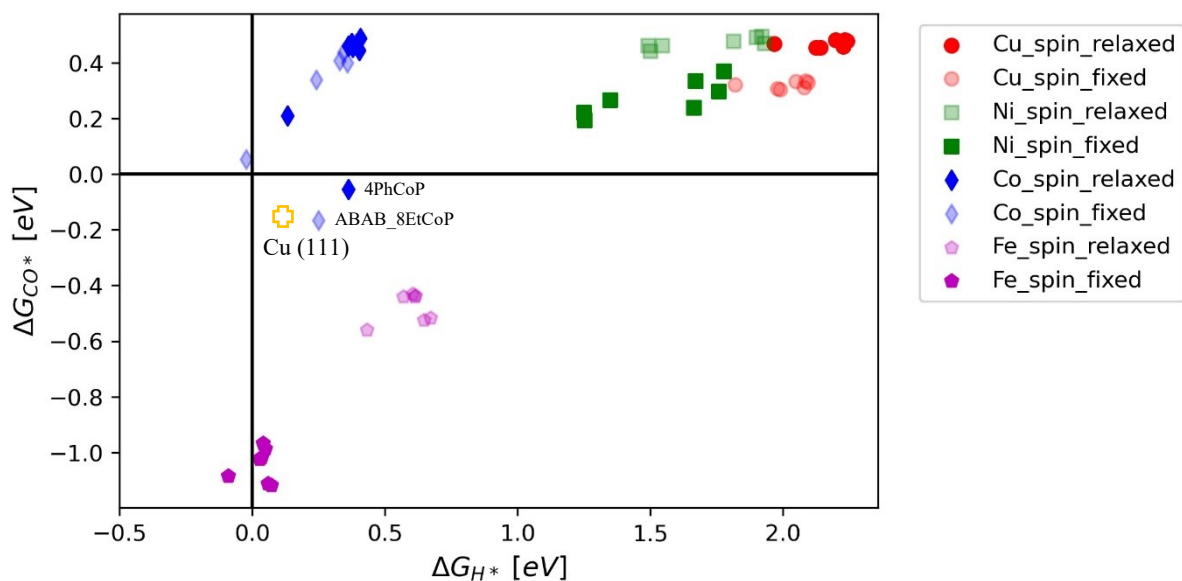


Figure 5.6 Binding energy of CO* vs. H* for different spins of the metal in macrocycles with different guest groups. The light-coloured markers represent the spin relaxed species while the solid ones are spin fixed as introduced in **Table 5.1**. The solid black lines show the thermodynamics of adsorbed or none-adsorbed H₂ or CO that correspond to $\Delta G_{H^*} = 0$ or $\Delta G_{CO^*} = 0$. The Cu metal data point is adjusted from ref ¹⁷

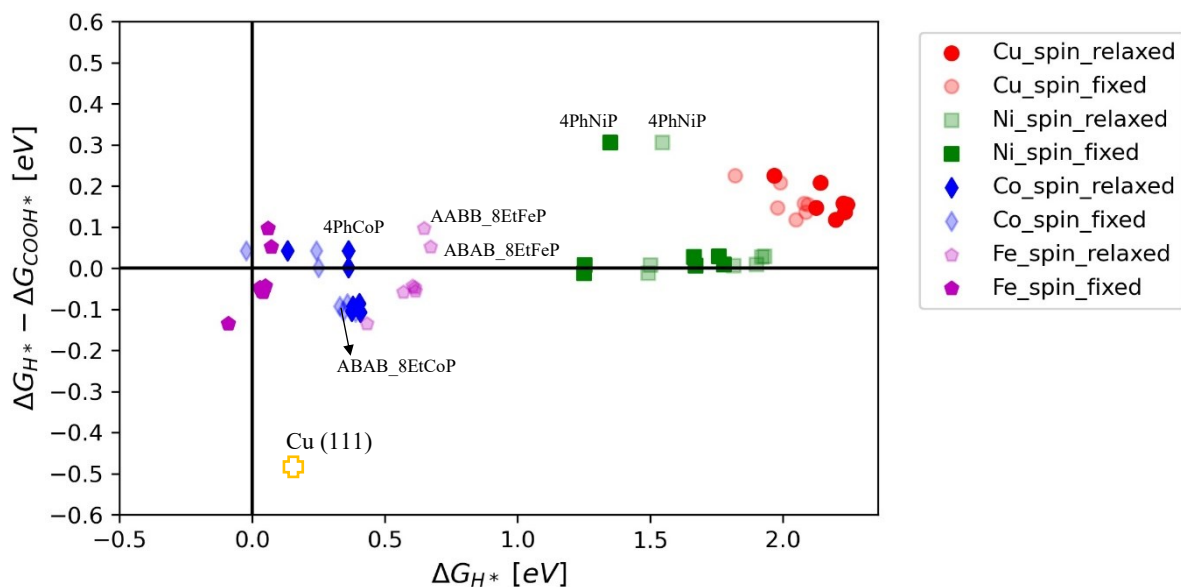


Figure 5.7 Binding energy of H* - COOH* vs. H* for different spins of the metal in macrocycles with different guest groups. The light-coloured markers represent the spin relaxed species while the solid ones are spin fixed as introduced in **Table 5.1**. The vertical solid black lines show the thermodynamics of adsorbed or none-adsorbed H₂ that correspond to $\Delta G_{H^*} = 0$, and the

horizontal one is the boundary of the thermodynamic preference over H^* (bottom) or $COOH^*$ (top). The Cu metal data point is adjusted from ref¹⁷

While Cu is not as expensive as Pt, the prospect of achieving a cost reduction of several times by replacing Cu with Fe remains highly attractive. The Fe macrocycles demonstrate great potential as a highly effective catalyst to replace metallic Cu for CO_2RR .

In **Figure 5.6**, The spin fixed Fe ($m=0$) macrocycles have an overly strong CO^* binding which indicates that the active site could be poisoned by CO. On the other hand, all the Cu/Ni macrocycles and most of the Co macrocycles bind CO too weakly, suggesting they are not suitable catalysts to reduce CO_2 to CO. Instead that they will mainly produce formic acid as their $\Delta G_{H^*} - \Delta G_{COOH^*} > 0$ (**Figure 5.7**). Among all the formic acid producers, 4PhNiP could present highest Faraday efficiency. And Cu macrocycles theoretically exhibit notably different behaviour than metallic Cu. The exceptions for CO binding of Cu/Ni/Co macrocycles are two Co porphyrins ABAB_8EtCoP and 4PhCoP that show negative ΔG_{CO^*} . Considering their positions in **Figure 5.7**, where ABAB_8EtCoP favours hydrogen coverage while 4PhCoP does not, it can be possible that ABAB_8EtCoP is a promising catalyst that will generate products beyond CO while 4PhCoP will produce a mixture of CO and formic acid.

The spin-relaxed Fe ($m=2$) macrocycles, excluding both 8EtFePs, are the most promising materials for CO_2RR . They are located in the lower right quadrant of **Figure 5.6** and allow for hydrogen coverage (**Figure 5.7**), enabling further reduction of CO. However, this perspective is static, as the spin configurations of the materials are unknown during electrocatalysis. The more flexible approach is to include all the Fe macrocycles as candidates for CO_2RR . In view of the charge and spin change during the electrocatalysis, further analysis is needed to understand the dynamics. Besides, an interesting phenomenon is that porphyrins appear to be outliers in all aspects, whether it is the formation of formic acid, CO, or other compounds beyond CO.

From all the macrocycles explored, the spin relaxed Fe macrocycles are optimistic to outperform metal Cu, which is promising taking cost into consideration. Nevertheless, it is not an easy task to control the spin of the catalyst during the catalytic reaction and an in-depth study about the dynamics of the

catalysts is needed. This will be discussed in chapter 5.2.3, where the simulations for spin relaxed charged Fe macrocycles will be presented.

5.2.3 Fe macrocycles

The simulation parameters are identical in chapter 4.3.2 except for the charge of the system that changes from -3 to 4. For charged system, the potential energy surface seems to be unimodal locally as all the molecules converge to the same structure even with different initial magnetic moments. The calculated DFT energies and magnetic moment are concluded in the tables below. It can be observed that in **Table 5.7** there are energies (marked in red) which significantly deviates from the clustering of the corresponding values. It suggests that these molecules may have transformed into another phase that bear little resemblance to what are interested with over-saturated electrons. Considering the complication, the plots will not illustrate this table.

Q = -3 Name	$\Delta E(H^*)$	$\Delta E(CO^*)$	$\Delta E(COOH^*)$
AABB_8EtFeP	2.12	1.15	1.95
ABAB_8EtFeP	2.14	1.13	2.00
16ClFePC	0.32	-0.51	0.30
4CO ₂ HFePC	0.27	-0.58	0.26
4NH ₂ FePC	0.22	-0.54	0.10
FePC	3.20	2.48	3.18
4PhFeP	4.95	3.87	4.70

Table 5.7 Binding energies of the charged molecules. The charge Q(-3) is the total charge of the entire molecule. The values in red are outliers.

Q = -2 Name	$\Delta E(H^*)$	$\Delta E(CO^*)$	$\Delta E(COOH^*)$
AABB_8EtFeP	0.27	-0.72	-0.02
ABAB_8EtFeP	0.23	-0.76	0.09
16ClFePC	0.29	-0.48	0.29
4CO ₂ HFePC	0.27	-0.55	0.27
4NH ₂ FePC	0.23	-0.54	0.07
FePC	0.23	-0.51	0.21
4PhFeP	0.30	-0.80	0.03

Table 5.8 Binding energies of the charged molecules. The charge Q(-2) is the total charge of the entire molecule.

Q = -1 Name	$\Delta E(H^*)$	$\Delta E(CO^*)$	$\Delta E(COOH^*)$
AABB_8EtFeP	0.23	-0.73	0.01
ABAB_8EtFeP	0.23	-0.75	0.09
16ClFePC	0.24	-0.45	0.31
4CO ₂ HFePC	0.24	-0.49	0.31
4NH ₂ FePC	0.21	-0.52	0.19
FePC	0.21	-0.49	0.25
4PhFeP	0.25	-0.78	0.07

Table 5.9 Binding energies of the charged molecules. The charge Q(-1) is the total charge of the entire molecule.

Q = +1 Name	$\Delta E(H^*)$	$\Delta E(CO^*)$	$\Delta E(COOH^*)$
AABB_8EtFeP	0.49	-0.48	0.67
ABAB_8EtFeP	0.51	-0.48	0.68
16ClFePC	0.24	-0.45	0.31
4CO ₂ HFePC	0.24	-0.49	0.31
4NH ₂ FePC	0.48	-0.74	0.73

FePC	0.53	-0.68	0.68
4PhFeP	0.51	-0.56	0.62

Table 5.10 Binding energies of the charged molecules. The charge Q(+1) is the total charge of the entire molecule.

Q = +2 Name	$\Delta E(H^*)$	$\Delta E(CO^*)$	$\Delta E(COOH^*)$
AABB_8EtFeP	0.50	-0.35	0.74
ABAB_8EtFeP	0.50	-0.36	0.62
16ClFePC	0.52	-0.64	0.63
4CO ₂ HFePC	0.54	-0.62	0.64
4NH ₂ FePC	0.51	-0.66	0.82
FePC	0.52	-0.59	0.63
4PhFeP	0.52	-0.47	0.58

Table 5.11 Binding of the charged molecules. The charge Q(+2) is the total charge of the entire molecule.

Q = +3 Name	$\Delta E(H^*)$	$\Delta E(CO^*)$	$\Delta E(COOH^*)$
AABB_8EtFeP	0.51	-0.37	0.77
ABAB_8EtFeP	0.52	-0.38	0.53
16ClFePC	0.51	-0.51	0.57
4CO ₂ HFePC	0.53	-0.58	0.56
4NH ₂ FePC	0.52	-0.54	0.85
FePC	0.51	-0.39	0.51
4PhFeP	0.81	-0.14	0.82

Table 5.12 Binding energies of the charged molecules. The charge Q(+3) is the total charge of the entire molecule.

Q = +4 Name	$\Delta E(H^*)$	$\Delta E(CO^*)$	$\Delta E(COOH^*)$
AABB_8EtFeP	0.51	-0.37	0.77
ABAB_8EtFeP	0.52	-0.38	0.53
16ClFePC	0.51	-0.51	0.57
4CO ₂ HFePC	0.53	-0.58	0.56
4NH ₂ FePC	0.52	-0.54	0.85
FePC	0.51	-0.39	0.51
4PhFeP	0.81	-0.14	0.82

Table 5.13 Binding energies of the charged molecules. The charge Q(+4) is the total charge of the entire molecule.

Charge Q Name	-3	-2	-1	0	1	2	3	4
AABB_8EtFeP	1.71	1.63	1.61	2.00	2.21	2.51	2.51	2.51
ABAB_8EtFeP	1.71	1.59	1.63	2.00	2.13	2.51	2.51	2.51
16ClFePC	1.60	1.59	1.63	2.00	2.07	2.20	2.33	2.38
4CO ₂ HFePC	1.75	1.72	1.65	2.00	2.20	2.27	2.32	2.40
4NH ₂ FePC	1.64	1.71	1.71	1.98	2.46	2.15	2.28	2.35
FePC	1.61	1.72	1.71	1.96	2.46	2.29	2.44	2.58
4PhFeP	1.74	1.75	1.74	2.00	2.44	2.49	2.47	2.51

Table 5.14 Summary of magnetic moment of Fe for charged molecules without any absorbates.

The visualisation of **Table 5.14**, **Figure 5.8** is an expansion of **Figure 4.12**, with the complements for charge smaller than -1 and larger than 2. For the complements, the variation in Fe magnetic moment is negligible, which suggests that the majority of the charge added in the beginning (-1, +1, +2) will be captured by Fe. On the contrary, only a small fraction of the charge in the successive additions has an effect on Fe's spin. In other words, they are dispersed throughout the rest of the macrocycles. The outliers are 4NH₂FePC and FePC, which have a reduced magnetic moment when the charge is two. This

indicates that electron absorbed by the Fe atom can be redistributed into the macrocycles, and for 4NH₂FePC it is presumably related to its amino groups as electron acceptor.

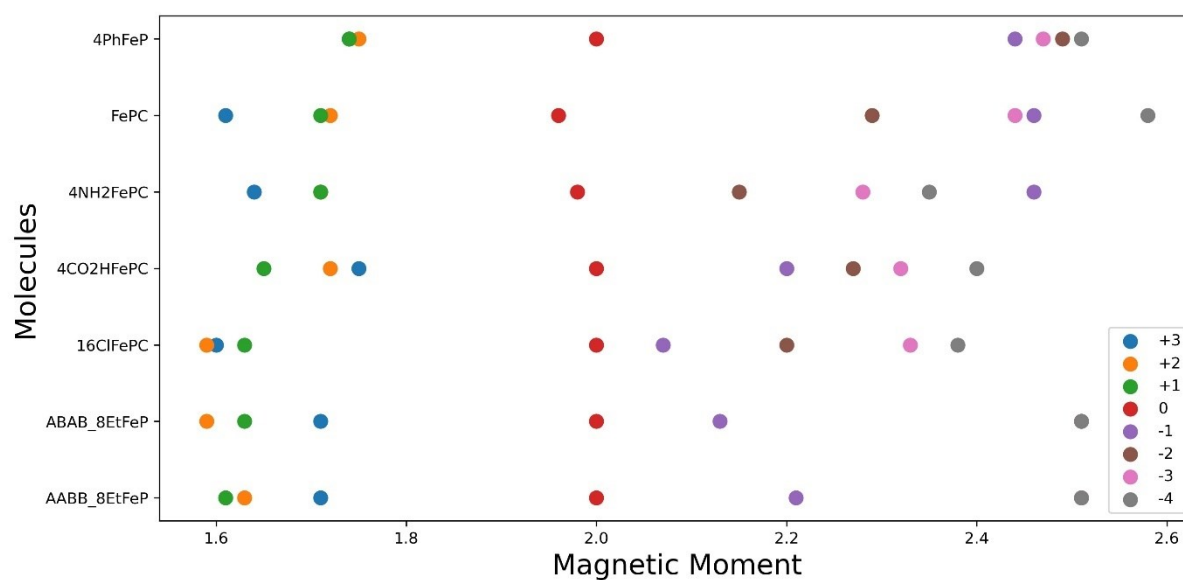
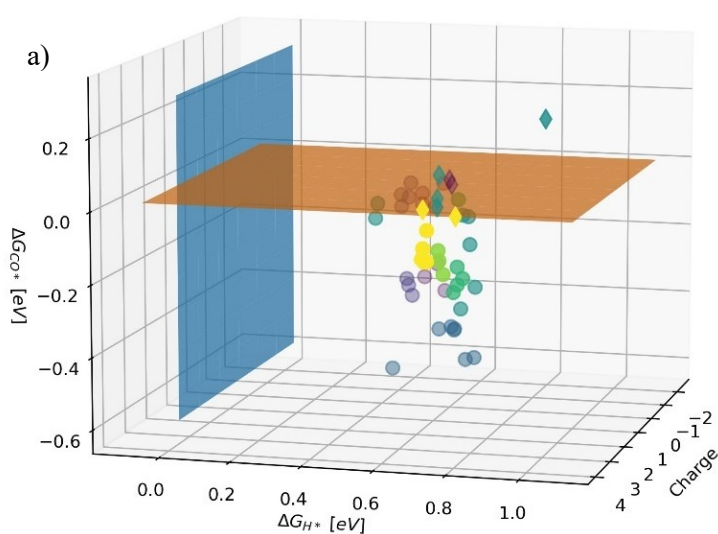


Figure 5.8 Magnetic moment of the molecules with different input charges.

With the addition of the third-dimension charge Q , their relation can be visualised below.



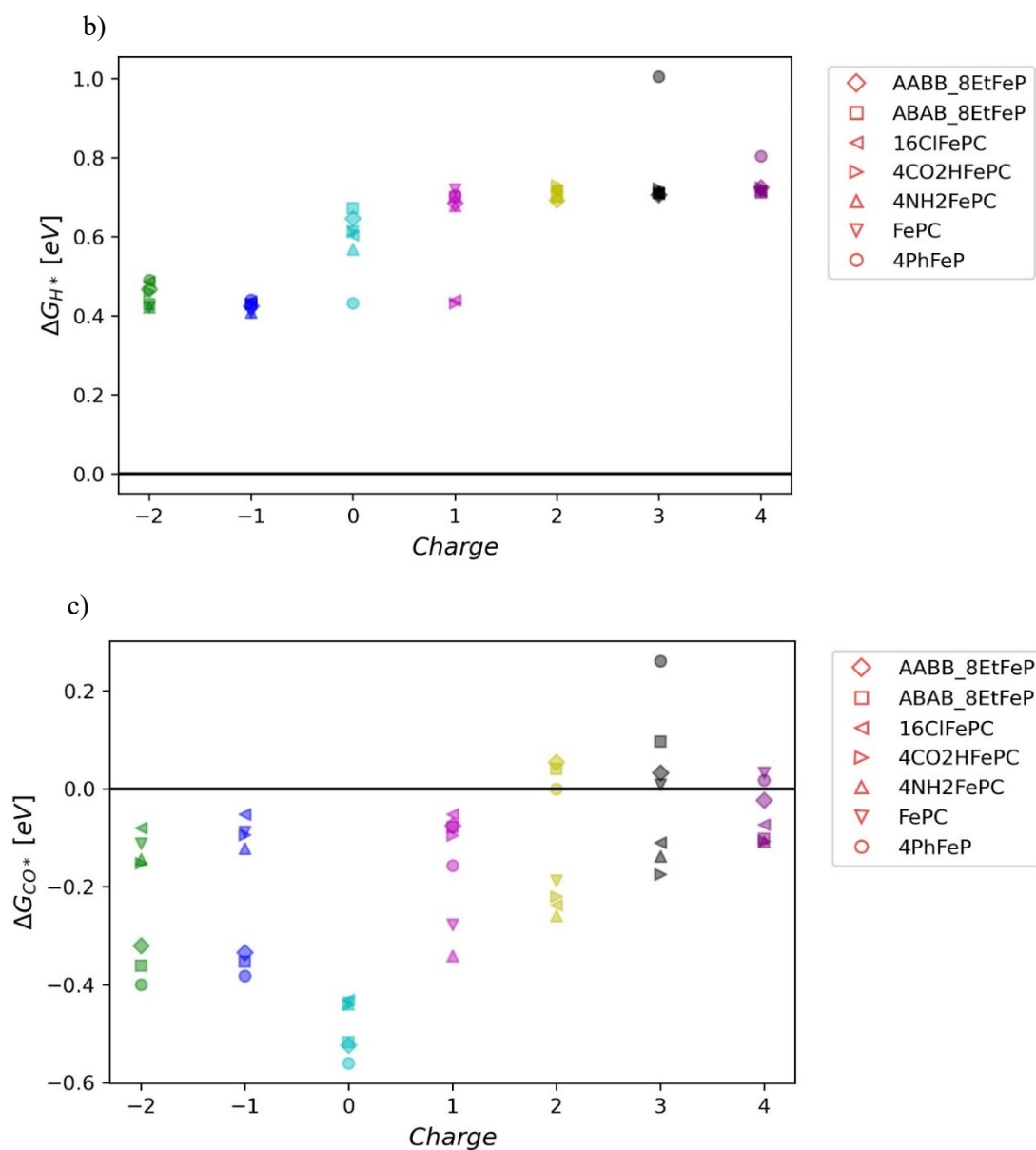


Figure 5.9 a) 3D view of free energies of H^* and CO^* and molecule charge variations. The blue and orange plane represent $\Delta G_{H^*} = 0$ and $\Delta G_{CO^*} = 0$. The diamond markers are for $\Delta G_{CO^*} > 0$ while the circle markers are for $\Delta G_{CO^*} < 0$. b) H^* free energy vs. charge, the blackline indicates $\Delta G_{H^*} = 0$. c) CO^* free energy vs. charge, the blackline indicates $\Delta G_{CO^*} = 0$. Colours are indicators of different charges and markers represent different macrocycles.

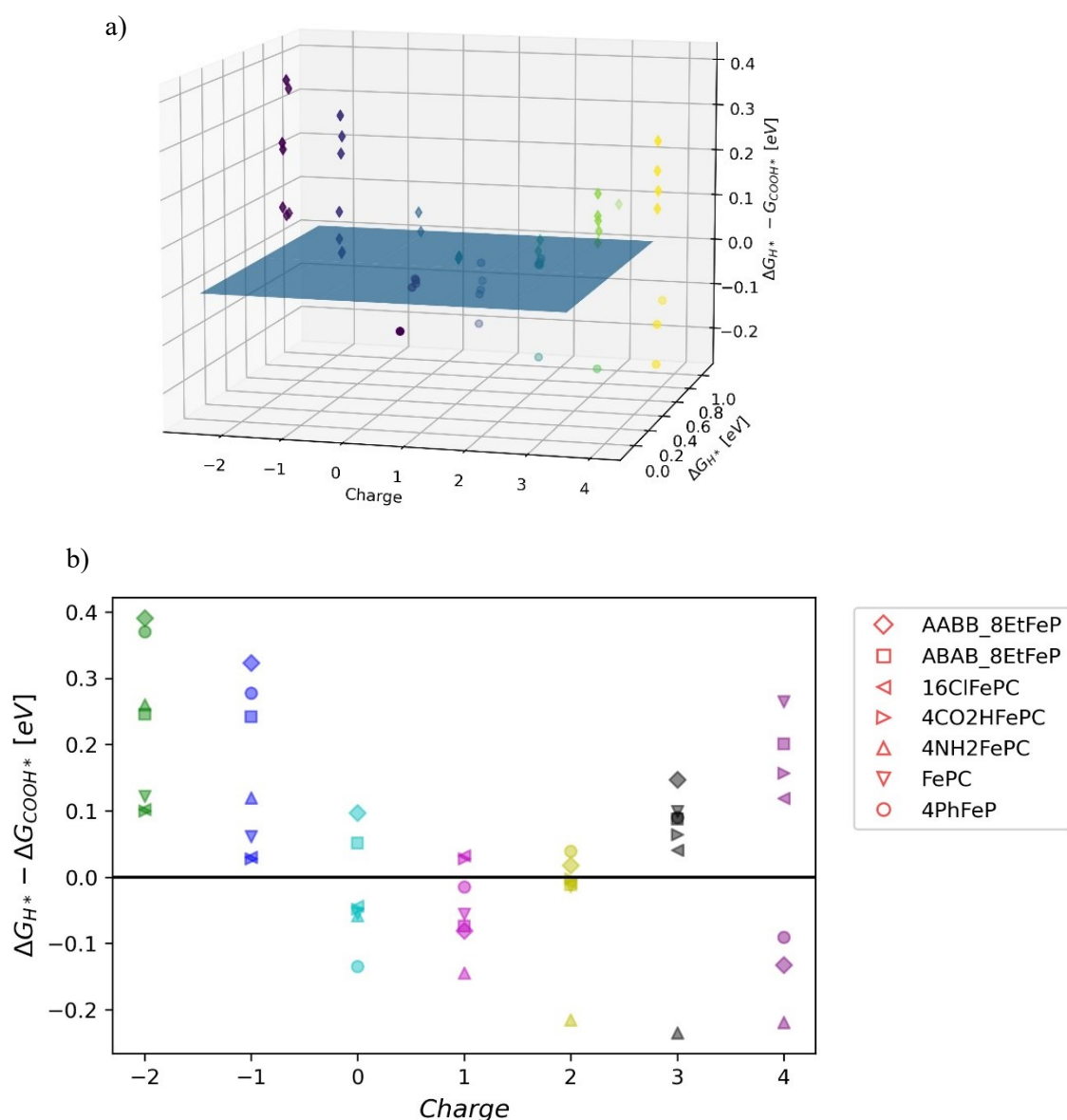


Figure 5.10 a) 3D view of binding energies H* and difference of H* and COOH* with molecule charge variations. The blue plane represents $\Delta G_{H^*} = \Delta G_{COOH^*}$. The circle markers are $\Delta G_{H^*} < \Delta G_{COOH^*}$ while the diamond markers are the reverse. b) H* and COOH* binding energy difference vs. charge, the blackline indicates $\Delta G_{H^*} = \Delta G_{COOH^*}$. Colours are indicators of different charges and markers represent different Fe macrocycles.

In **Figure 5.9**, ΔG_{H^*} is always positive by a large margin regardless how the charge shifts suggesting the HER is suppressed to a large extent. For the binding of CO*, as **Figure 5.9c** shows, the charge zero species have the strongest binding, but it weakens towards both the positive and the negative ends. With the addition of positive charges porphyrins will not bind CO* spontaneously, but the redistribution of electron density due to excessive positive charge conversely bring them back to the separation line. It

suggests that porphyrins are not stable and efficient CO₂RR catalyst. Apart from that, it seems that the porphyrins and the phthalocyanines make up two groups when the charge is negative: the porphyrins have a stronger CO* binding while for phthalocyanines it is relatively weaker. In **Figure 5.10**, $\Delta G_{H^*} - \Delta G_{COOH^*}$ displays a V shape trend with respect to the charge. It favours the formation of COOH* when charge is negative for all species. If it is believed that the ground state corresponds to a charge of zero, then this will not pose an issue for further reduction of CO. When charge is positive, only 4NH₂FePC demonstrates a consistent affinity towards H. In fact, the dynamic of this affinity could be even more complicated as has been discussed in chapter 4.3.6. This distinctive characteristic renders it highly promising as a catalyst for CO₂ reduction, facilitating the production of diverse carbon-based products beyond CO. Except 4NH₂FePC, the remaining molecules may also have the capability to reduce CO₂ to CO. However, their catalytic activity is possibly limited to C1 products. Nevertheless, the energies calculated are close to the boundary line and may suffer from the bias of the corrections and the variance of the structures. The robust conclusion apart from these bias and variance is the V trend of the $\Delta G_{H^*} - \Delta G_{COOH^*}$ and the special H* binding of 4NH₂FePC. This could be related to the dense states of 4NH₂FePC Fe d orbital as shown in **Figure 4.15 f**).

5.3 Conclusion

In this chapter, the research on metallic CO₂RR electrocatalysts was reviewed, with a focus on the theoretical foundations for why Cu stands out. Further DFT studies with porphyrin-like materials were introduced due to their restricted ontop H* binding, which increases the binding energy by ~0.3 eV. Given the advance in controlling the hydrogen binding energy, macrocycles with different transition metal centres were simulated, predicting Fe macrocycle as promising alternatives to replace Cu as electrocatalyst for CO₂RR. In-depth analysis with variation of charges further screens 4NH₂FePC as the most promising catalyst that could produce more valuable C2 products.

Chapter 6

DFT study on the mechanisms of nitrogen doped carbon for ORR

This chapter will begin by reviewing the development of nitrogen doped carbon as electrocatalyst for ORR. Next, a brief overview of the experimental setup by my collaborator will be introduced. Finally, a DFT exploration for the mechanisms will be presented.

6.1 Literature review

6.1.1 Metal-free nitrogen doped carbon

In 2009, Dai et al. reported that the metal-free nitrogen doped carbon (NC) nanotubes exhibit high ORR electrocatalytic activity in alkaline medium, comparable to the Pt.¹⁰⁵ Since then, a new research hotspot for ORR has been ignited. However, a major divergence in the research is whether the synthesised materials are truly metal-free. Wang et al. argued that given the proofs that trace amount of metal, such as transition metal impurities, could dramatically change the electrocatalytic performance within sp^2 carbon nanomaterials, it is strongly recommended to have a concise elemental analysis before the metal-free claim.¹⁰⁶ Masa et al. also expressed concerns over such claim especially for those developed using metal precursors to aid in the formation of NC structures: since it is necessary to eliminate the metal residues afterwards by leaching with mineral acids, it may not be feasible to completely eliminate the residual metal particles.¹⁰⁷ Despite the controversy, progress has been made by applying sensitive characterisation techniques such as Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES) to detect trace metal.

6.1.2 Heteroatom doping

Later, heteroatom doping with other elements such as boron, phosphorus, and sulfur were attempted to boost the electrocatalytic activity. It turned out that mostly carbon materials doped solely with nitrogen show better performance compared to other mono-doping ones prepared by similar methods.^{108,109} And for co-doped scenario, nitrogen is indispensable for high activity. Economically, nitrogen doping is more cost-effective compared to other heteroatoms. In addition, NC materials are generally more chemically stable than those doped with other heteroatoms as nitrogen has a stronger bond with carbon. Therefore, nitrogen doping is the most widely investigated element for metal-free electrocatalysts based on carbon materials.¹¹⁰

6.1.3 Active site for nitrogen doped carbon

Graphitic materials have been eliminated as candidates for efficient oxygen reduction reaction (ORR) due to their limited ability to only reduce O_2 to H_2O_2 with a high overpotential.¹¹¹ Hence, atomic configurations of NC are crucial in determining the catalytic performance. However, the discussion at the mechanistic level seems to be more perplexing, as it is difficult to determine the precise active sites. Experimental studies trying to differentiate the structures are shown in **Figure 6.1**.

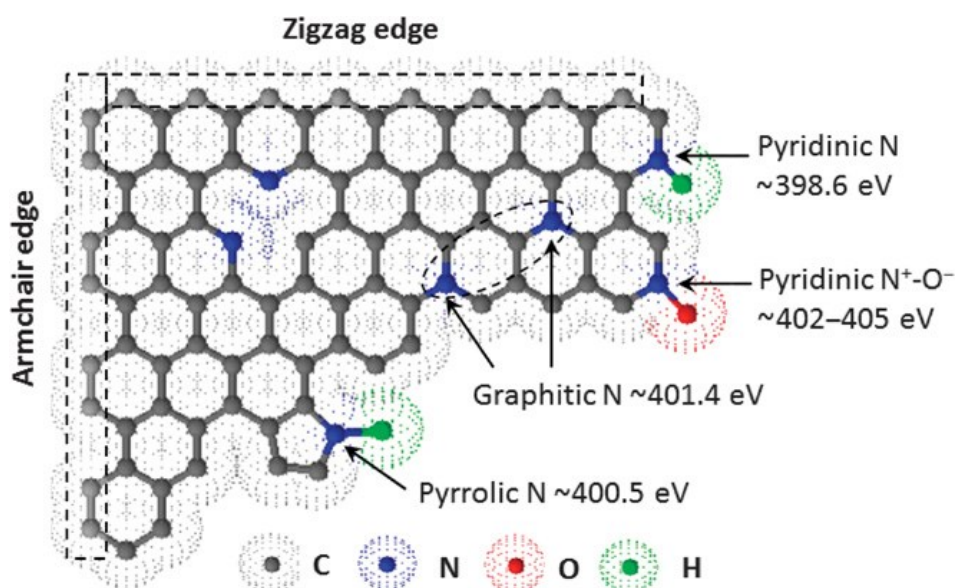


Figure 6.1 Scheme illustration of nitrogen species in nitrogen-containing graphitic carbons. The commonly doped nitrogen species in graphitic carbons with the corresponding reported XPS binding energies.²²

There are characteristic XPS binding energy differences among pyridinic, pyrrolic and graphitic nitrogen. Nevertheless, due to the complexity of the atomic structures, where the edges can have different shapes such as armchair or zigzag, and the presence of various forms of defects and co-existing nitrogen species, a rigorous understanding of the role for each component in the catalytic process is challenging. The main point of the dispute is whether the active sites are pyridinic-N (pyri-N) or graphitic-N (quaternary-N, Q-N) after a series of studies.^{112–118} Since pyrrolic nitrogen (pyrr-N) group is considered inactive due to its low thermal stability.^{113,119,120} Using the highly oriented pyrolytic graphite (HOPG), a highly ordered form of graphite with a well-defined crystalline structure and high conductivity, Guo et. al synthesised the model catalysts and showed that pyri-N creates the active sites for ORR (**Figure 6.2**), where the active sites consist of carbon atoms adjacent to the pyri-N.²³

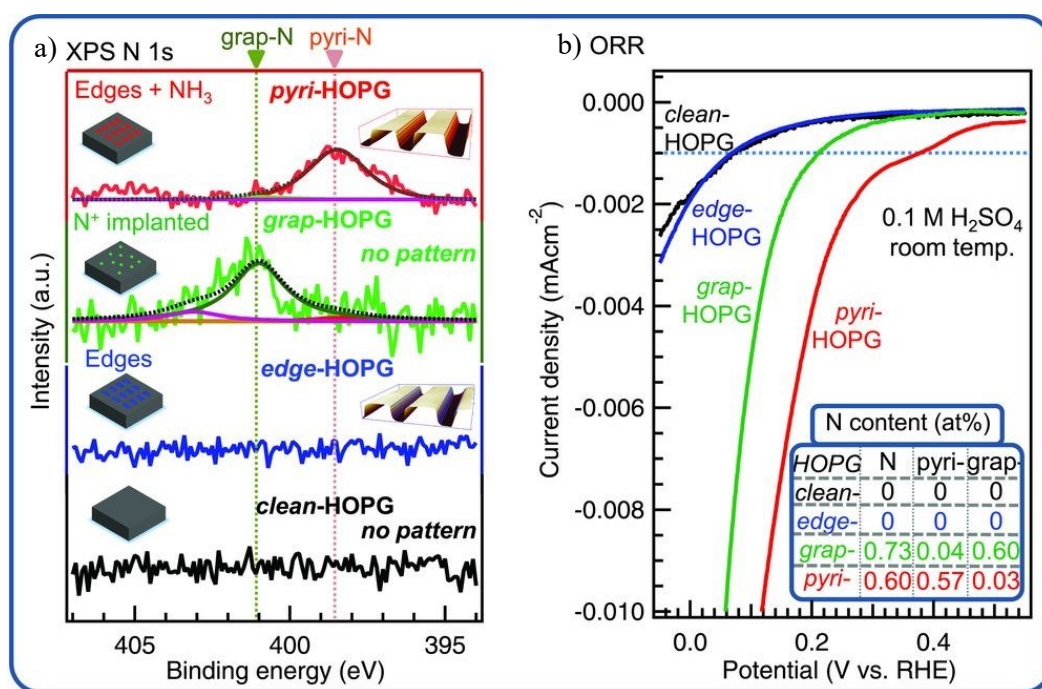


Figure 6.2 a) N 1s XPS spectra of model catalysts. b) ORR results for model catalysts with respect to a). Nitrogen contents of the model catalysts are shown as the inset in b).²³

This is also supported by the DFT studies which confirm the positive charge density of the carbon next to the nitrogen is beneficial for the adsorption of O₂.^{23,121,122} Since then, the HOPG has become the standard substrate for the fundamental research over the issue. But as mentioned earlier, the specific mechanism of ORR for NC remains to be explored.

6.2 Experiment result

Thanks Yue Xu, my collaborator who conducted all the experiments.

6.2.1 Introduction

To elucidate the individual contributions of various nitrogen types in the oxygen reduction reaction (ORR), carbon nanomaterials were fabricated through covalent functionalisation to introduce specific nitrogen structures. The primary goal was to selectively incorporate nitrogen sites in each sample. The study will thoroughly investigate the diverse nitrogen configurations, defects, and electronic structures of these materials, and ORR electrocatalytic properties.

6.2.2 Synthesis

Two distinct types of precursors, namely N-heterocyclic amines and N-heteroaryne precursors, were used to facilitate functionalisation through either the aryl diazonium or aryne cycloaddition reaction. **Figure 6.3** demonstrates the mechanisms involved, using 3,4-pyridyne and 4-aminopyridine as specific examples. In the aryl diazonium reaction with HOPG, utilising 4-aminopyridine as the precursor, 4-aminopyridine underwent diazotisation in the presence of isoamyl nitride. Subsequently, the diazo group was cleaved under heat, resulting in the creation of a reactive aryl radical. Simultaneously, nitrogen gas was released, and a new single C-C sp³ bond (highlighted in red) was formed between the molecule and the HOPG surface. In the cycloaddition reaction between 3,4-pyridyne and HOPG, the

reaction was initiated by adding an organic soluble fluoride reagent, tetrabutylammonium difluorotriphenylsilicate (TBAT), to generate the heteroaryne intermediate in situ. This intermediate rapidly reacted with HOPG, leading to the formation of two new C-C sp^3 bonds (highlighted in red) between HOPG and the molecule, occurring via either a [2+2] or [4+2] reaction pathway. The functionalisation processes were conducted in a specially designed microwave vial, which included a circular baffle that acted as a barrier between the stir bar and the HOPG. This setup was implemented to prevent any potential harm to the HOPG surface caused by vigorous stirring throughout the reaction. Once the reaction was finished, the HOPG sample underwent a washing procedure involving sonicating in DMF and methanol for two minutes each, with multiple repetitions. Subsequently, the sample was dried under vacuum to yield the functionalised HOPG.

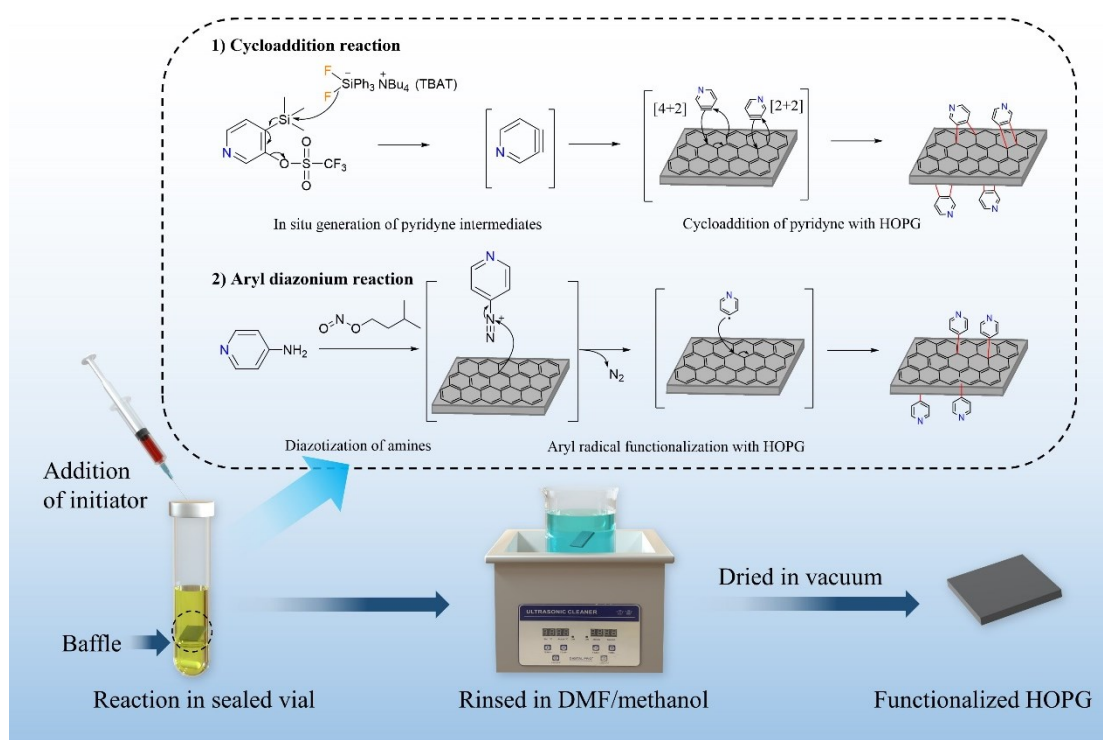


Figure 6.3 Illustration of N-heterocycles functionalisation with HOPG substrate via cycloaddition and aryl diazonium reaction with corresponding reaction mechanisms.

6.2.3 ORR electrochemistry

The ORR performance was evaluated as shown in the **Figure 6.4**. The materials can be roughly categorised into four groups regarding the performance. The first group is 5-quino-HOPG itself, which exhibits significantly higher onsite potential and current density at 0.1 V vs RHE. The second group contains pyridinic 9-acri-HOPG and 6-quino-HOPG with similar trend compared to the first one but half of the current density at 0.1 V vs RHE, which could be due to the saturation of the active site. The third group includes the rest of the pyridinic species that present same current density at 0.1 V vs RHE with the first group. The last group includes pristine HOPG and HOPG functionalised with pyrrolic N, which show negligible ORR activity that is related to sluggish $2e^-$ H_2O_2 process.

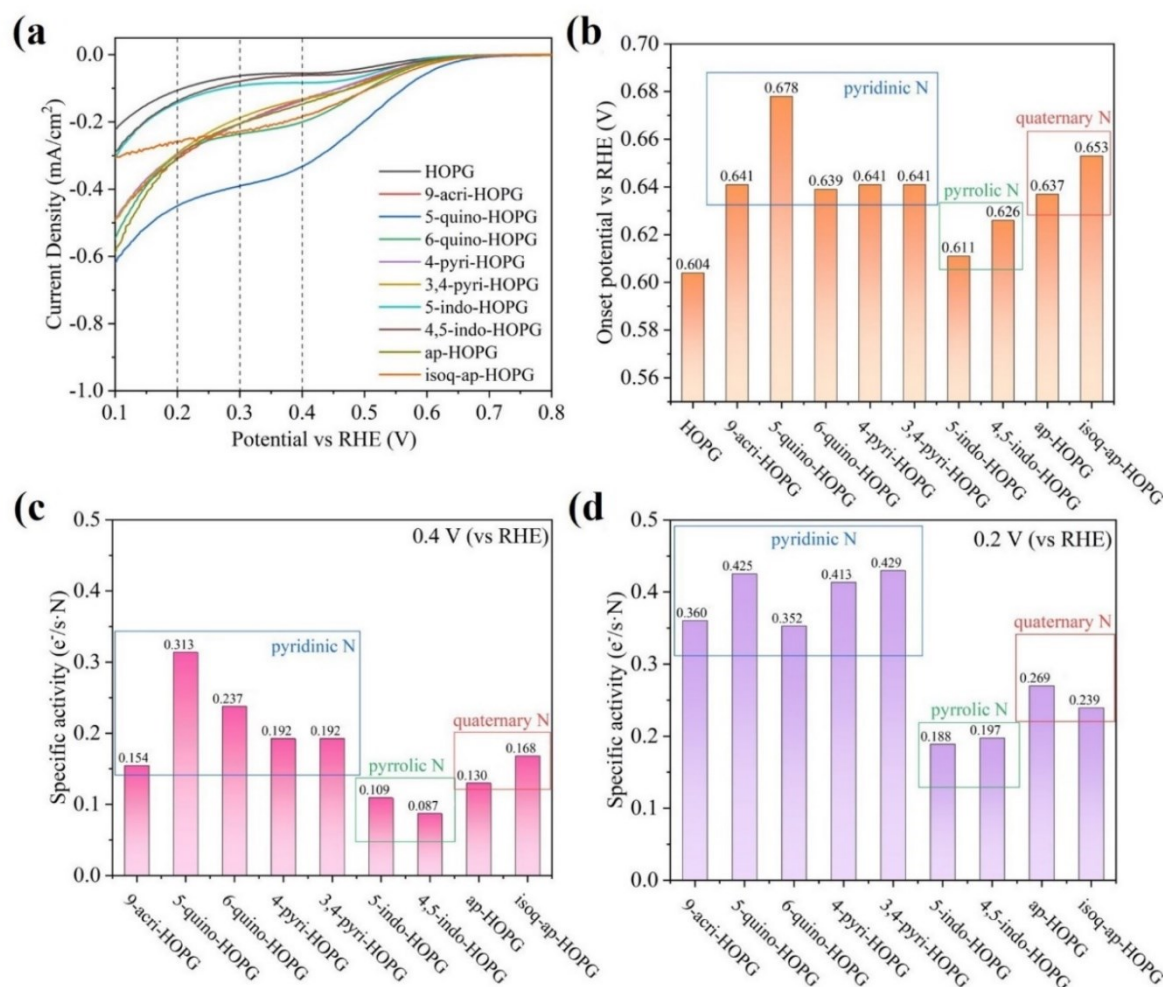


Figure 6.4 a) Liner Sweep Voltammetry (LSV) in O_2 saturated 0.1 M KOH at rotation speed of 1600 rpm with scan rate of 10 mV/s; the background current in N_2 saturated electrolyte was subtracted and iR drop was compensated. b) Onset potential of

prepared catalysts defined at the current density of 0.01 mA/cm²; c) LSV derived specific activity per active N site at 0.4 V (vs RHE); d) LSV derived specific activity per active N site at 0.2 V (vs RHE).

Such classification is consistent with their onsite potential shown in **Figure 6.4b**. The curvature of the LSV for these materials are shifting with the potential which indicates more complex mechanisms. To understand the complications, specific activities per N site at 0.4 V and 0.2 V vs RHE were calculated in **Figure 6.4c, d**. The specific activity trend at 0.4 V vs RHE is almost the same as onsite potential as expected. Nonetheless, at 0.2 V vs RHE 5-quino-HOPG shows no advantage anymore, which may suggest that it is only as good as the whole pyridinic group, and the early onsite potential may not be correlated to the pyridinic N. Therefore, by their nitrogen characteristics the groups should be three, with the 5-quino-HOPG as outlier.

6.3 DFT study on model catalyst for ORR

6.3.1 Introduction

As illustrated by the synthesis process, the binding configurations between the molecule and the HOPG can vary. Since most of the molecules are expected to bind with HOPG covalently with a single C-C bond, connection via a single carbon atom is proposed as the model to study the ORR (**Figure 6.5**).

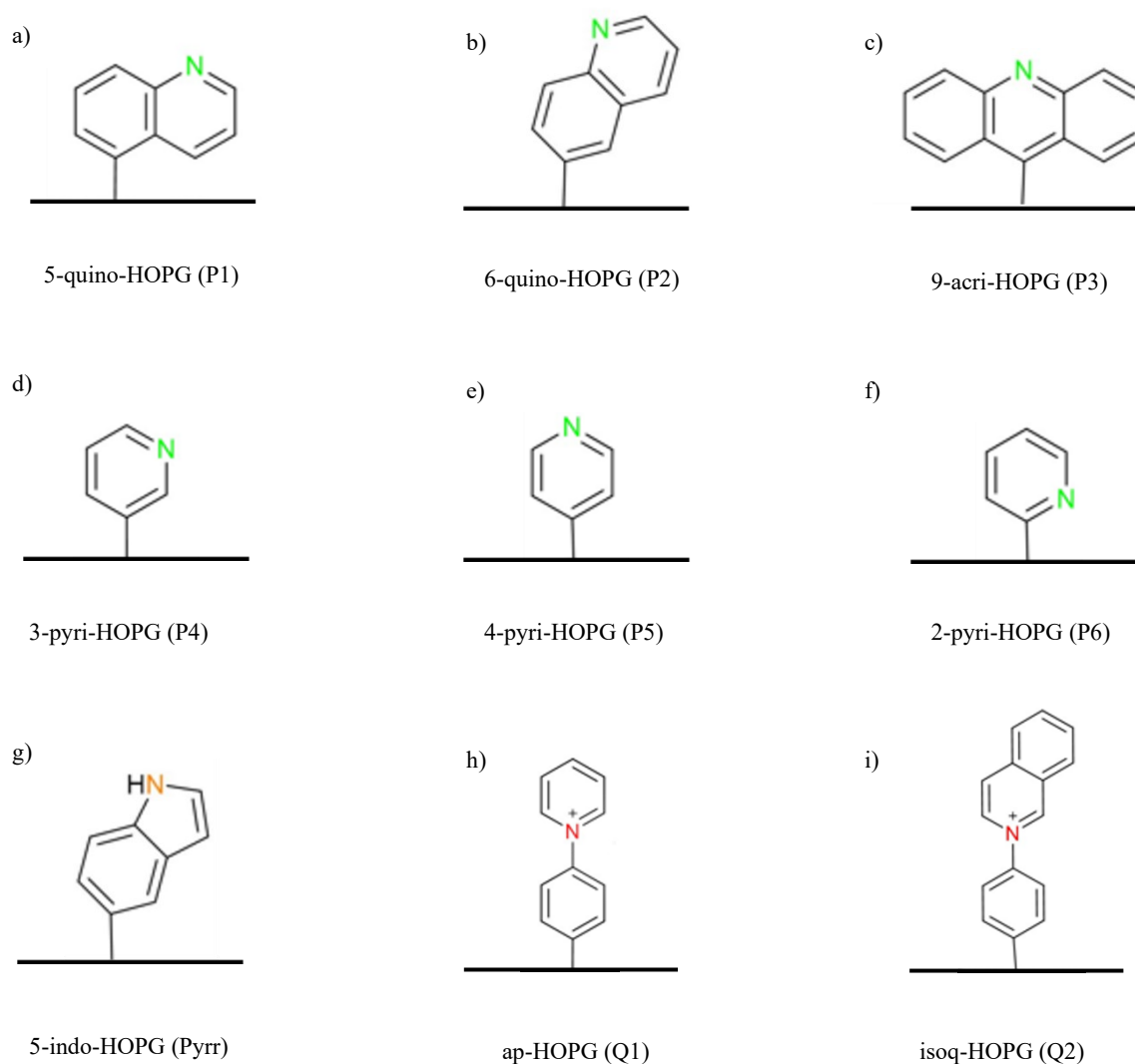


Figure 6.5. Proposed models in accordance with the experiment, where a-f), P1-P6 are pyridinic N, g) Pyrr is pyrrolic N and h-i) Q1-Q2 are quaternary N, the black line stands for the substrate.

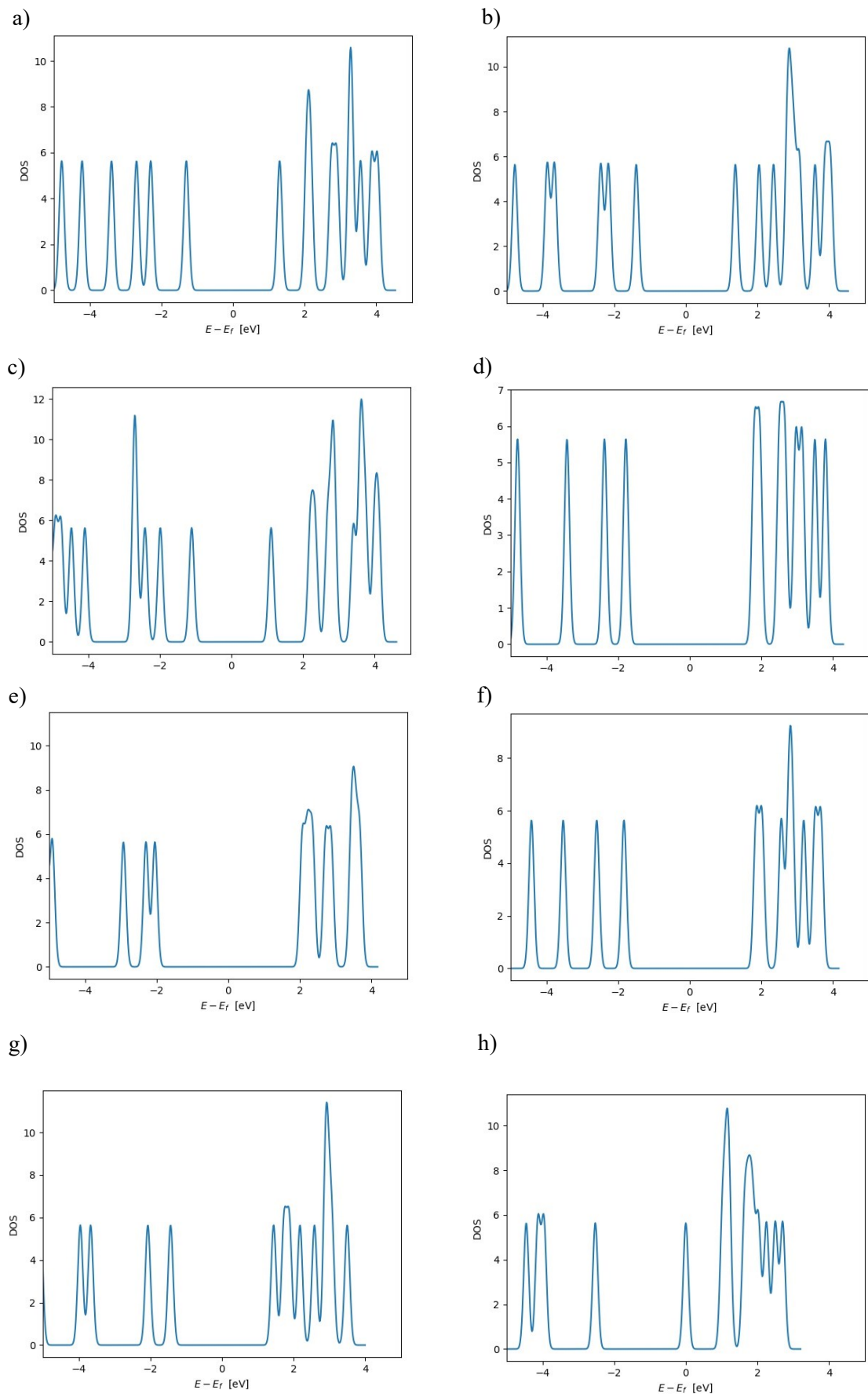
6.3.2 Intrinsic activity

To deconvolute the complexity from the combination of graphene and synthesised molecules, the molecules intrinsic activity on nitrogen needs to be clarified in the first place. The table provided calculates the free energy of *OH when it is on nitrogen, taking into account the thermal correction discussed in chapter 4.3.2.

Name	Energy (eV)	G(*OH) (N)
	P1	2.63
	P2	2.67
	P3	2.59
	P4	2.72
	P5	2.45
	P6	2.77
	Pyrr	2.41
	Q1	0.19
	Q2	0.11

Table 6.1 DFT energies of the molecules and OH on nitrogen of the molecules marked with * and *OH (N) respectively. G(*OH) (N) are the free energies of OH on nitrogen.

It can be concluded that for plain molecules the nitrogen is not the active site for ORR. This is because the thermal corrected binding energy is either too strong, for example Q1 and Q2, or too weak for the rest of the species (>2 eV). However, as the energy values are hardly close to reasonable values for a volcano plot, it is possible that the entire computational hydrogen electrode (CHE) model is not suitable for this situation. As an important premise for CHE is that the proton electron pair are in equilibrium with hydrogen, which indicates that the supply of the electrons cannot be the bottleneck, or in other words the molecules must be conductive. To understand the conductivity of these molecules, their density of states (DOS) are given:



i)

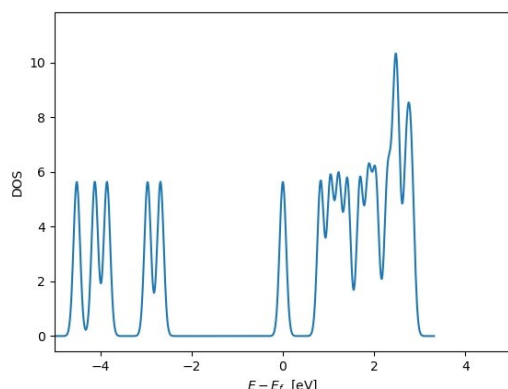


Figure 6.6 DOS plots truncated from -5 to 5 eV. The symbol from a) to i) corresponds to the molecule P1, P2, P3, P4, P5, P6, Pyr, Q1 and Q2. The results are aligned with the Fermi level E_f .

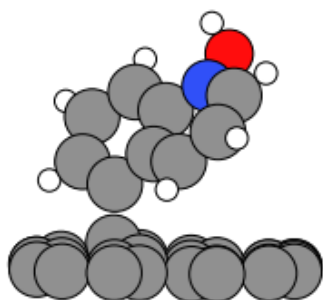
Except Q1 and Q2 as shown in **Figure 6.6h** and **i**, the rest molecules present no states near the Fermi level with an energy gap of at least 2 eV, suggesting they are semiconducting. Although Q1 and Q2 do have the spikes at the Fermi level, the sparse states near the region indicate they are only slightly more conductive than the rest. Even so, at the nitrogen site, Q1 and Q2 are not active for ORR because they have an excessively strong binding of OH. The rest of the molecules are beyond the framework of CHE as they are semiconducting. However, an electrocatalyst must possess conductivity to function, and therefore these semiconducting molecules are not active for ORR.

6.3.3 Molecules on graphene

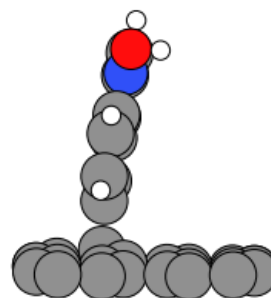
To simulate the synthesised molecules on HOPG, the defect free graphene is incorporated into the calculations. Inspired by the study of the intrinsic activity, conductivity is possible to act as an independent variable that is worth considering. Therefore, two kinds of graphene are investigated: semiconducting zigzag (4, 4) graphene and conducting zigzag (9, 3) graphene. In addition, the comparison group with gold substrate that solely provides the conductivity will be discussed in chapter 6.3.4. For semiconducting zigzag (4, 4) graphene, the calculated results, including the optimised

geometry structures, binding energies, density of states (DOS) plots and partial density of states (PDOS) plots are shown below:

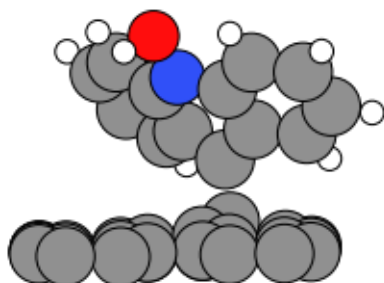
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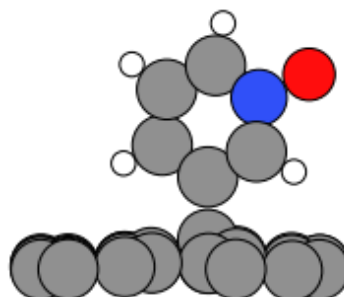
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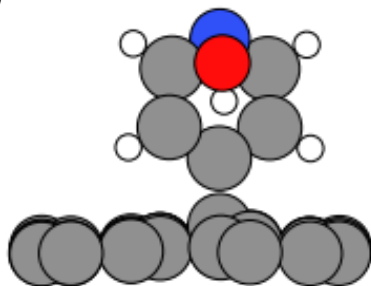
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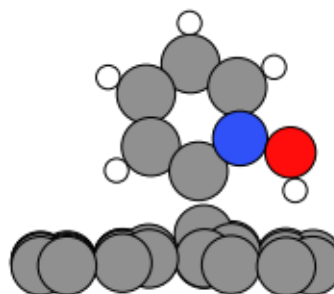
4)



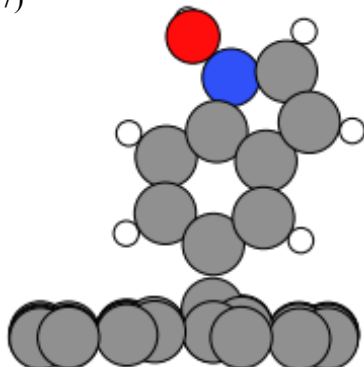
5)



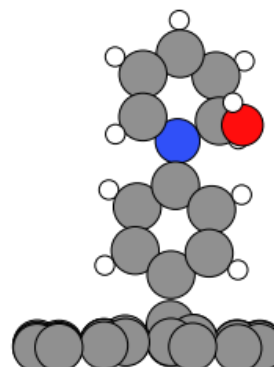
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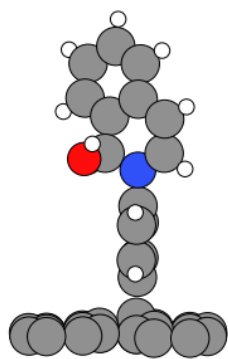
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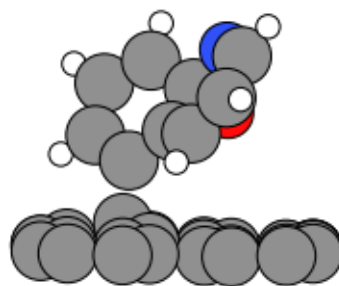
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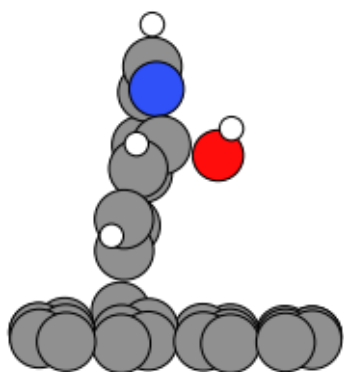
9)



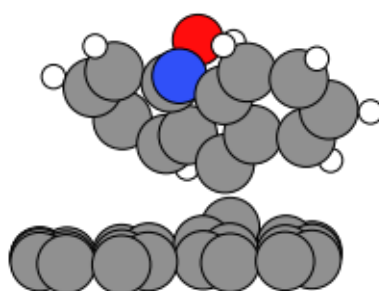
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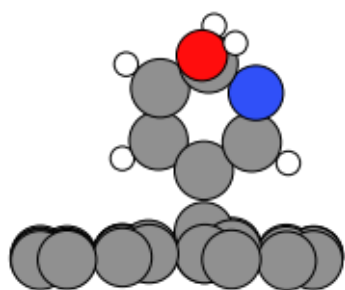
11)



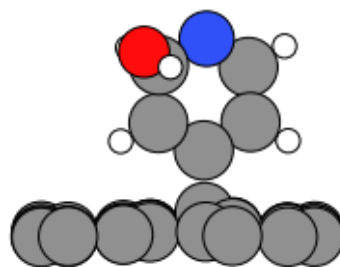
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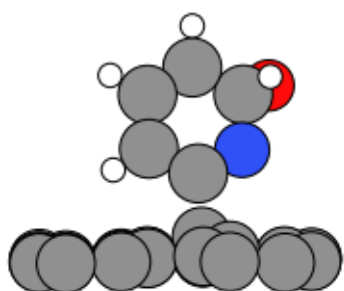
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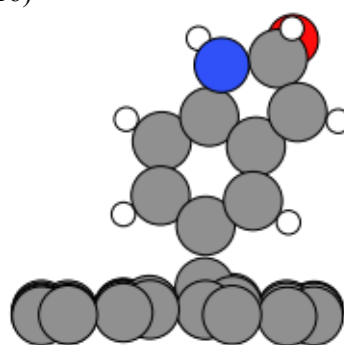
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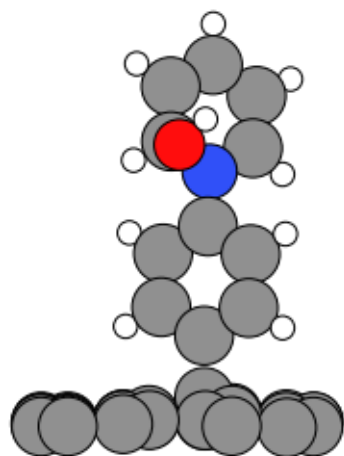
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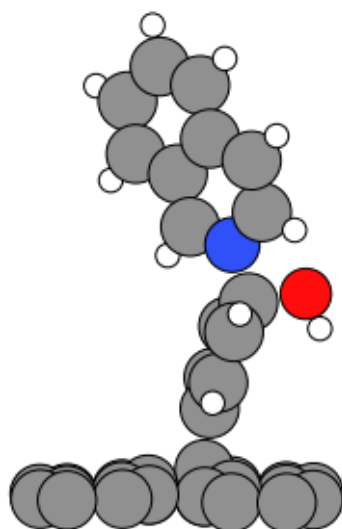
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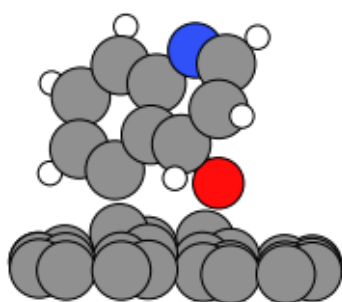
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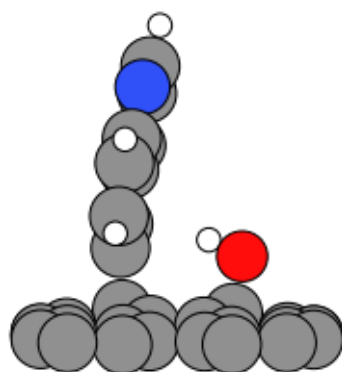
18)



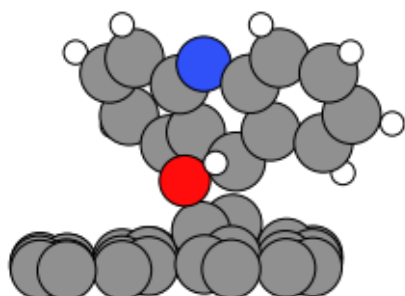
19)



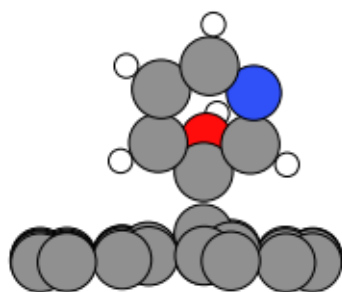
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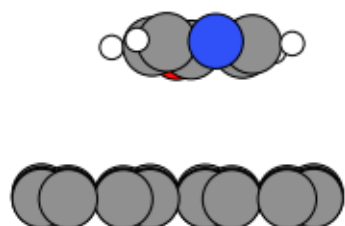
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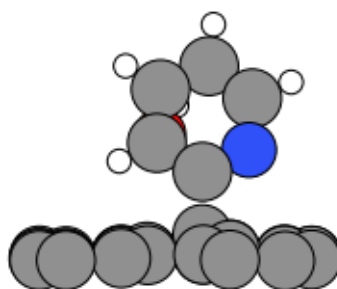
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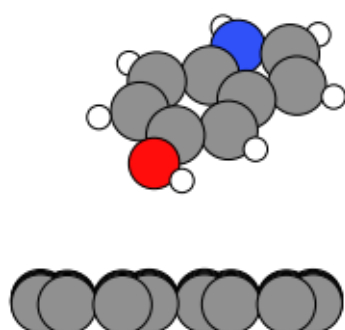
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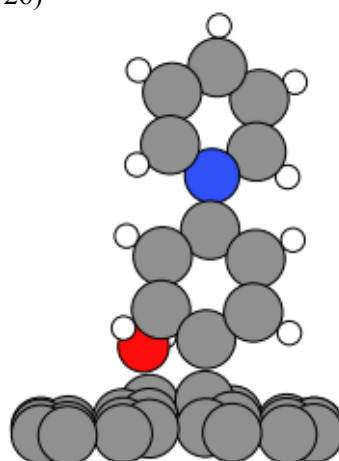
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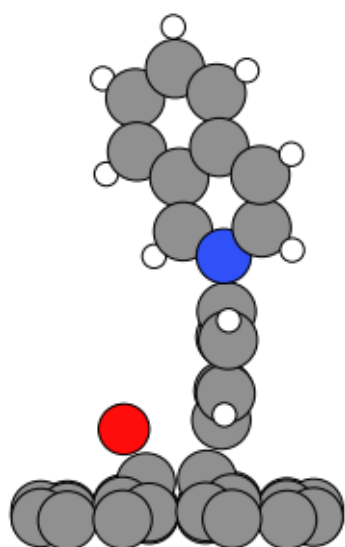


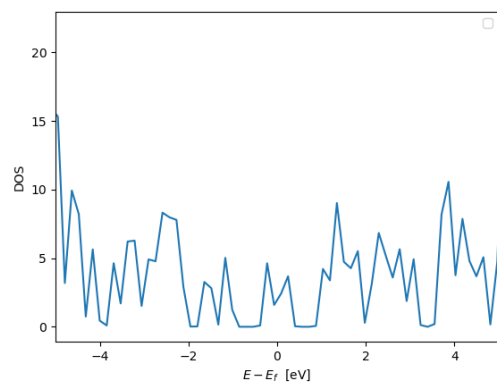
Figure 6.7 Optimised geometries of molecules on zigzag (4, 4) graphene. 1) to 9) represents optimised molecules in sequential order of **Table 6.1**. with OH on N as initial structure. 10) to 18) OH on carbon near the nitrogen and 19) to 27) OH on random sampling of carbon on graphene plane. Periodic boundary conditions are set to be true within graphene plane.

For OH binding on N (**Figure 6.7 1-9**) some of the optimised structures (Q1, Q2) deviates from the original conformations, while for C2 some of the molecules end up in completely different conformations, suggesting the complexity of the electronic structures. Nevertheless, all the C1 show the binding on the carbon site.

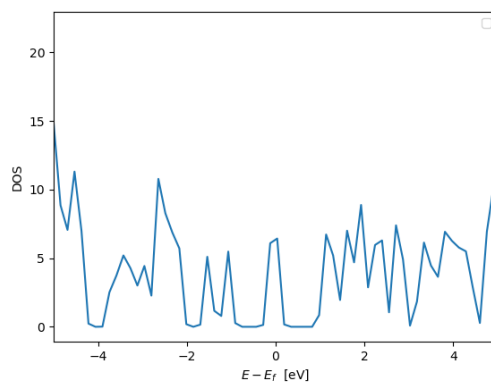
Energy(eV) Name	G(*OH) (N)	G(*OH) (C1)	G(*OH) (C2)
P1	2.66	2.66	2.68
P2	2.77	2.77	1.49
P3	2.12	2.93	1.79
P4	2.89	2.22	2.60
P5	2.70	2.28	2.59
P6	2.98	2.23	2.50
Pyrr	2.70	1.74	1.55
Q1	0.36	0.41	1.72
Q2	0.26	0.93	2.56

Table 6.2 On zigzag (4, 4) graphene, DFT energies of the molecules and OH on nitrogen of the molecules marked with * and *OH (N) respectively. C1 means OH bind on the closest non-quaternary carbon near the nitrogen, and C2 are carbon atoms sampled on the graphene plane. Columns starts with G are the free energies of the corresponding configurations.

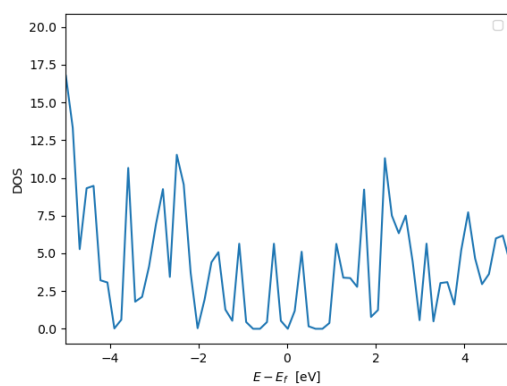
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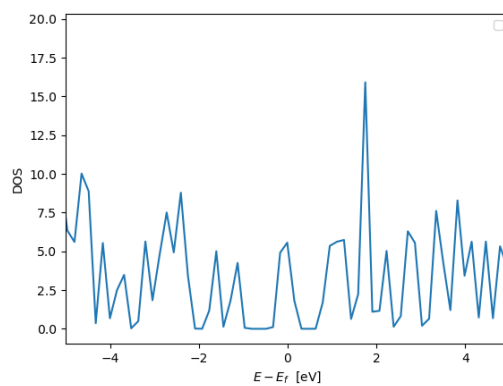
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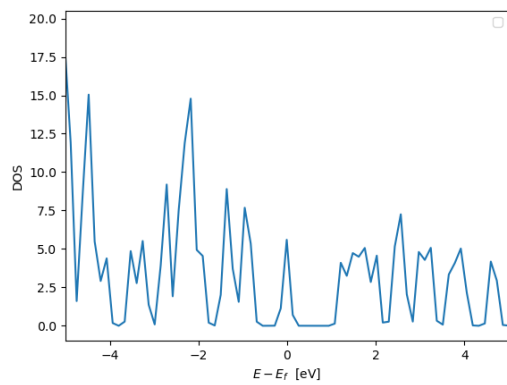
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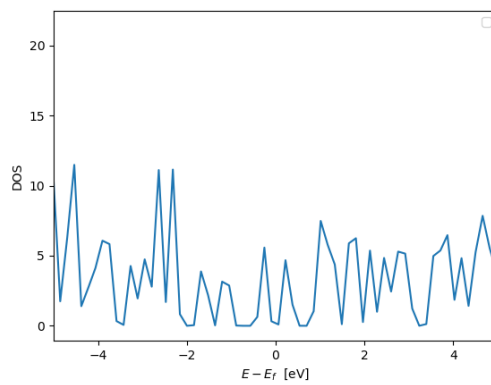
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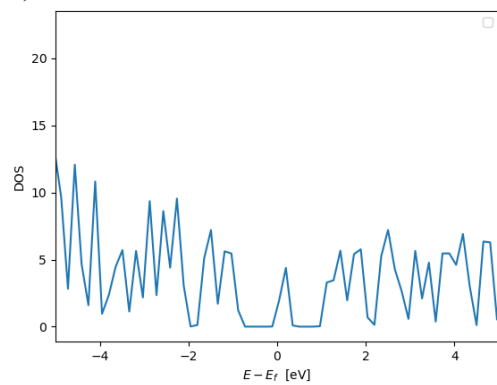
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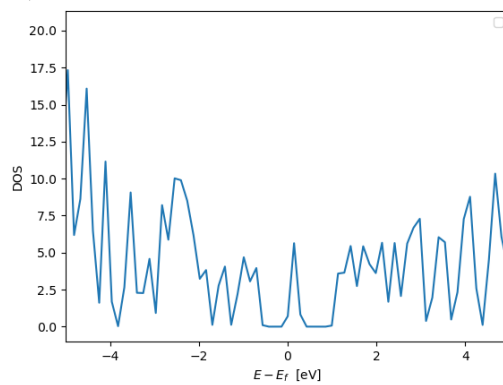
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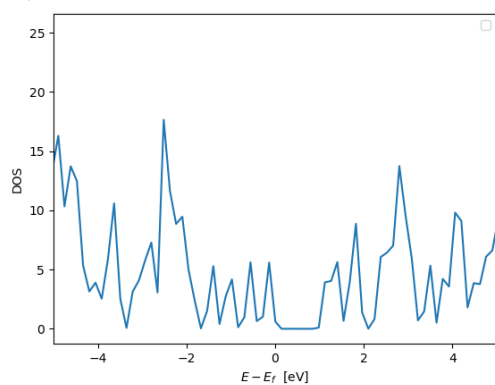
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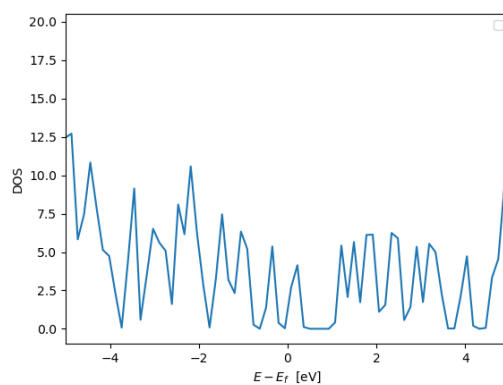
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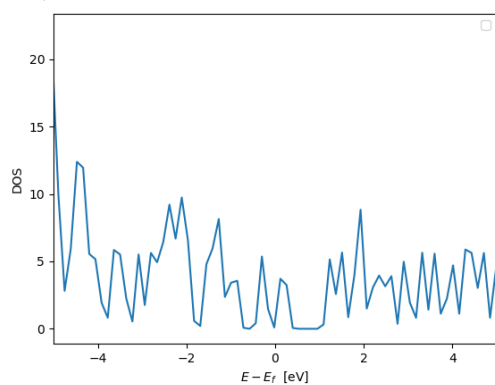
9)



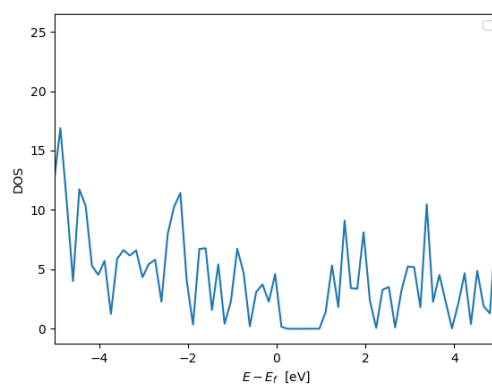
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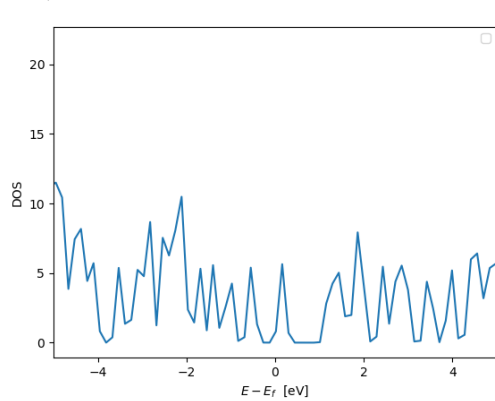
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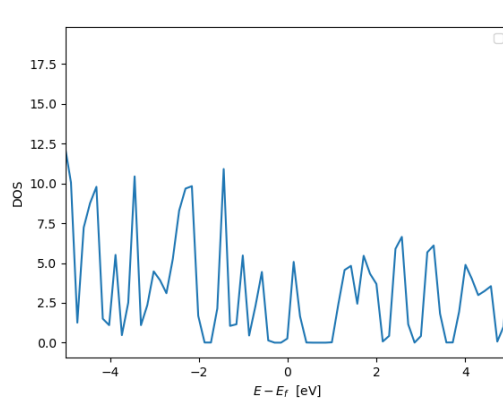
12)



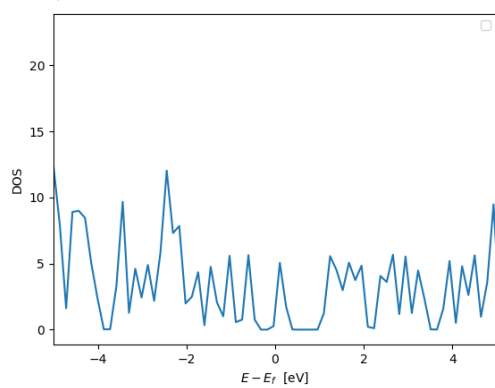
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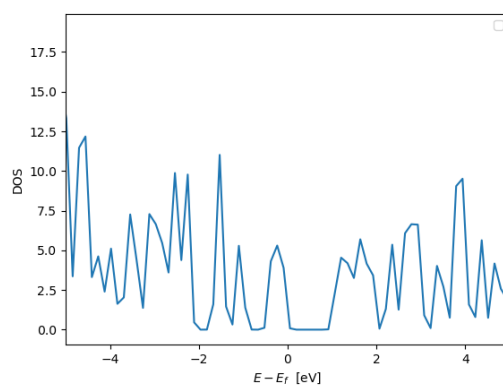
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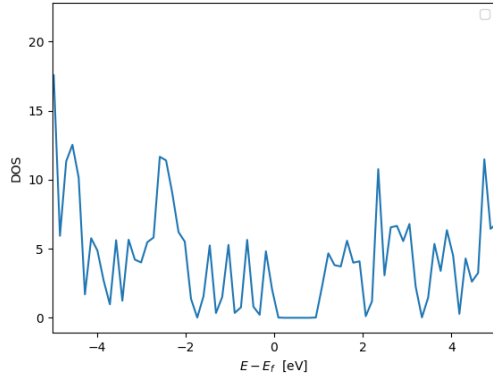
15)



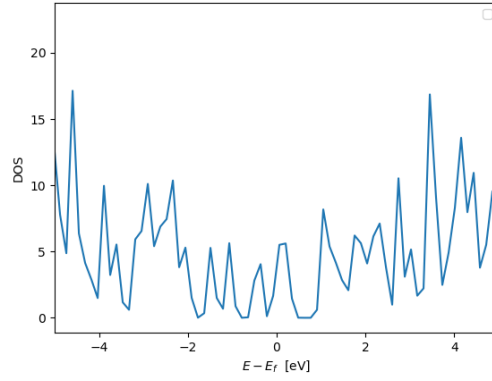
16)



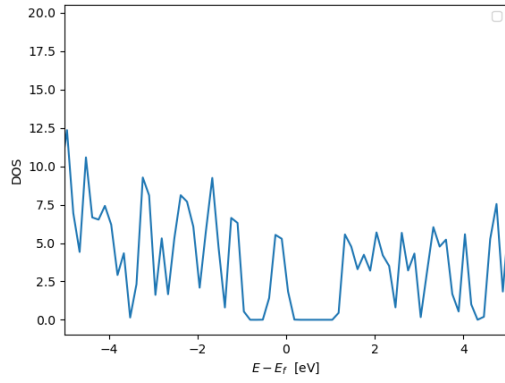
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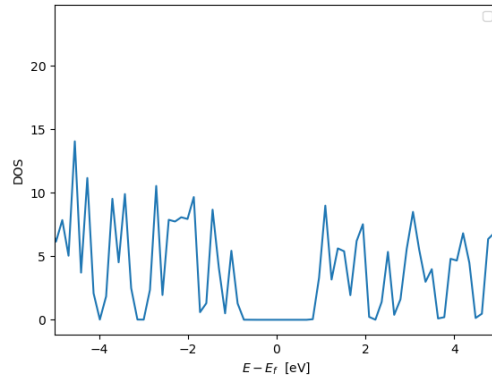
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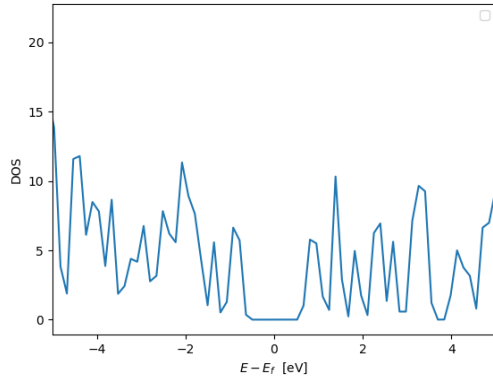
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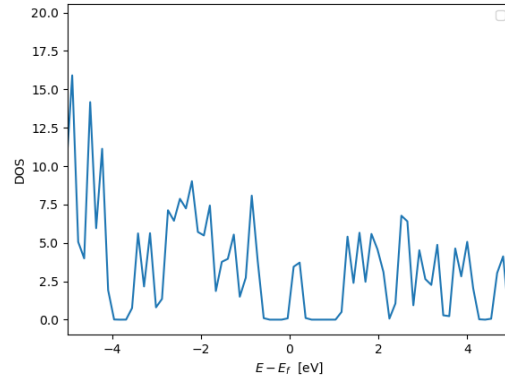
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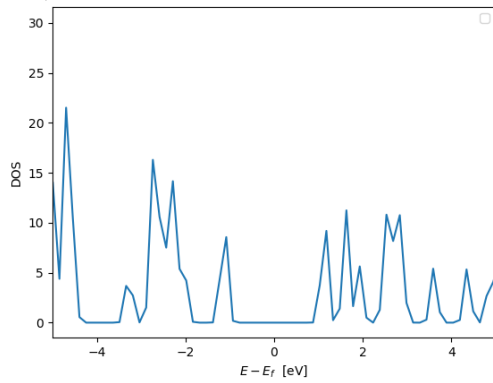
21)



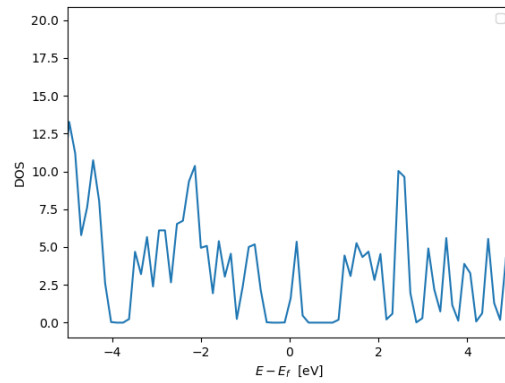
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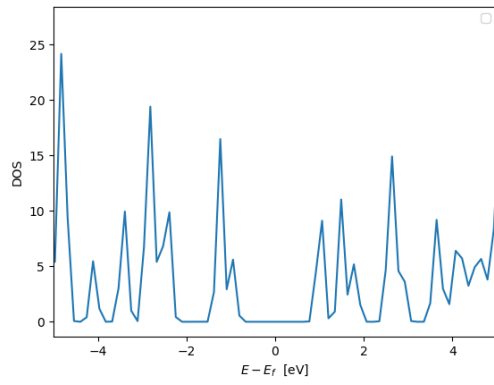
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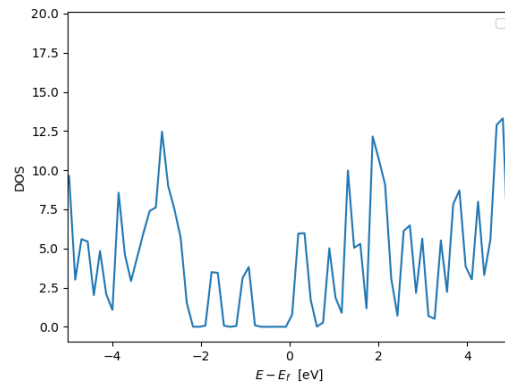
24)



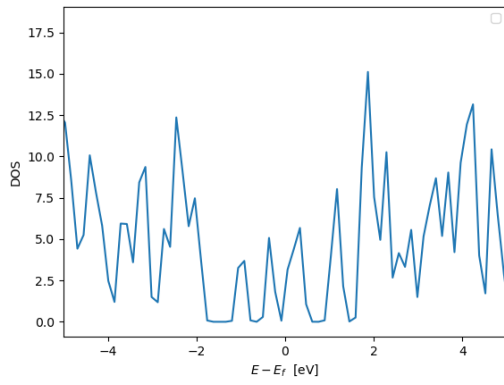
25)



26)



27)



28)

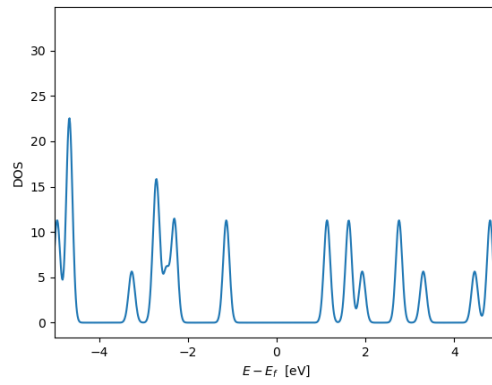
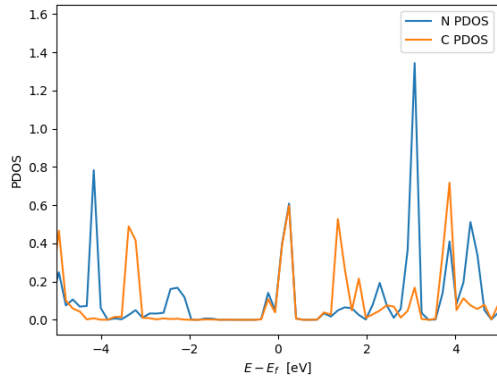
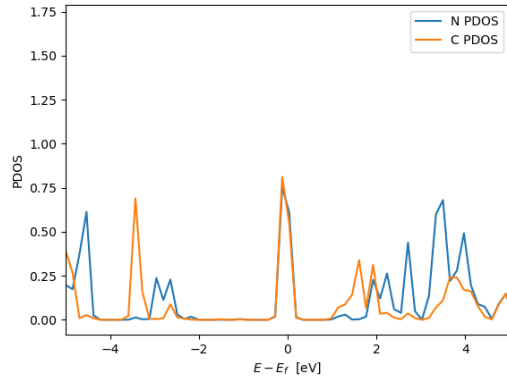


Figure 6.8 DOS plots aligned with the Fermi level (E_f), truncated between -5 and 5 eV. The labelled numbers are aligned with **Figure 6.7** and **Table 6.2** except for 28), which is the DOS of zigzag (4, 4) graphene.

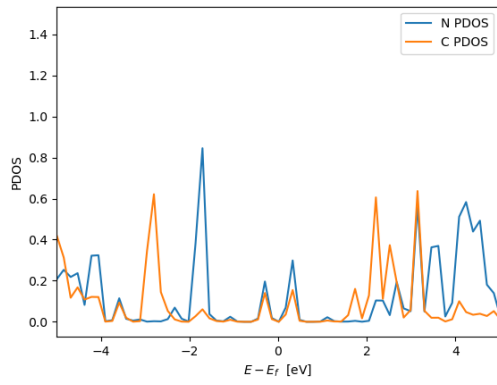
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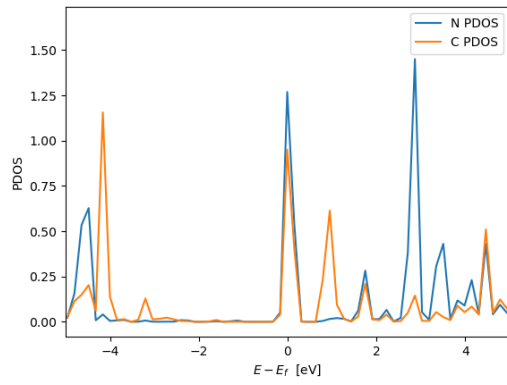
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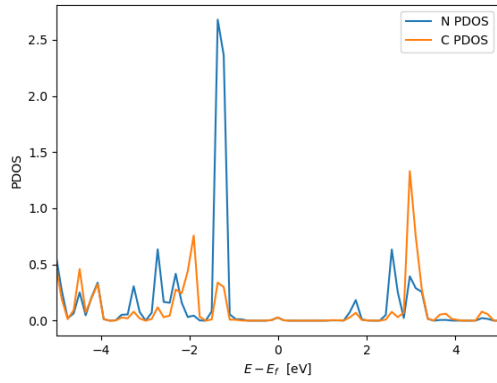
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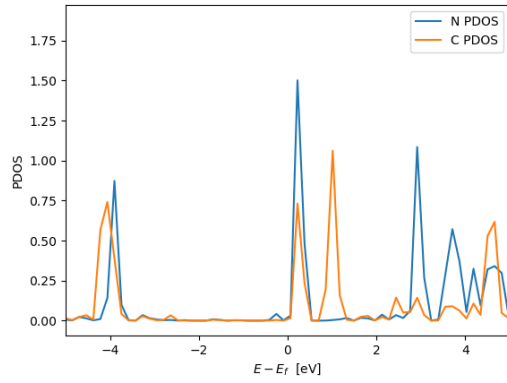
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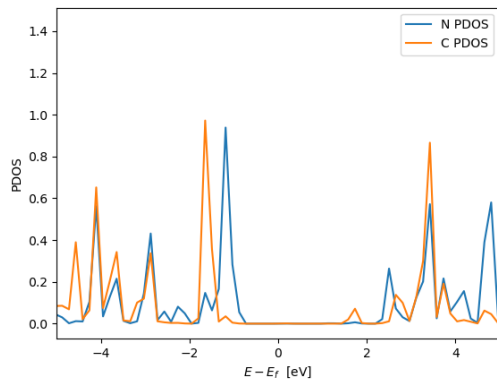
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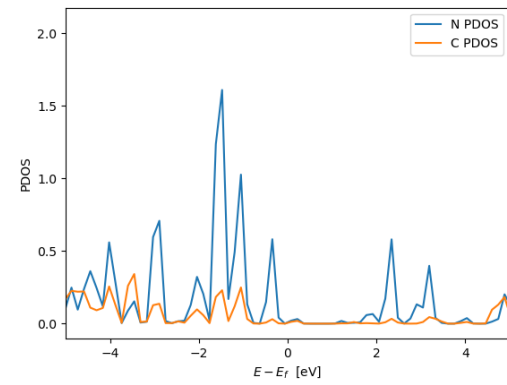
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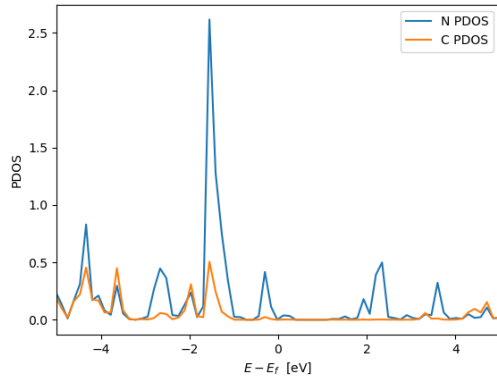
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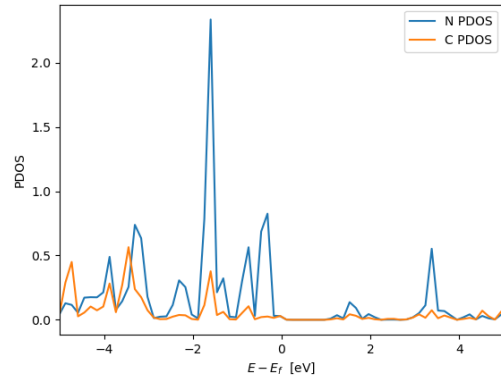
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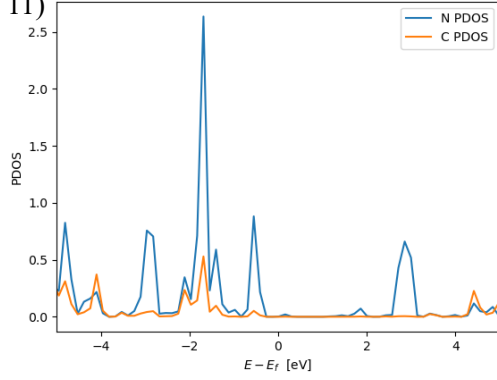
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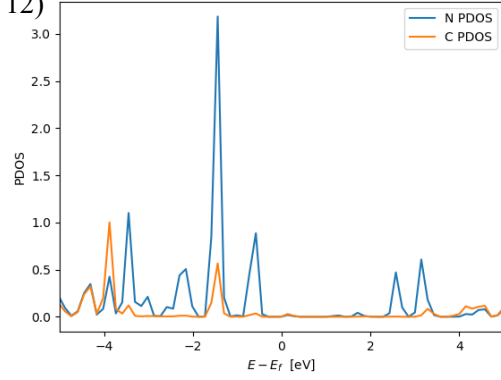
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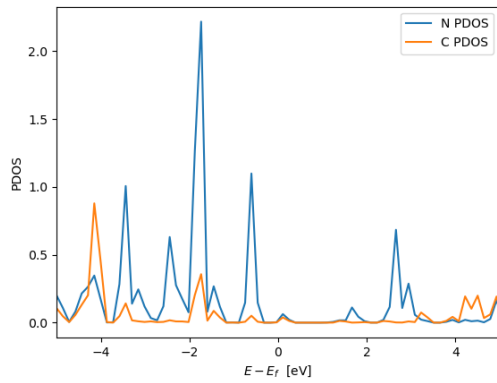
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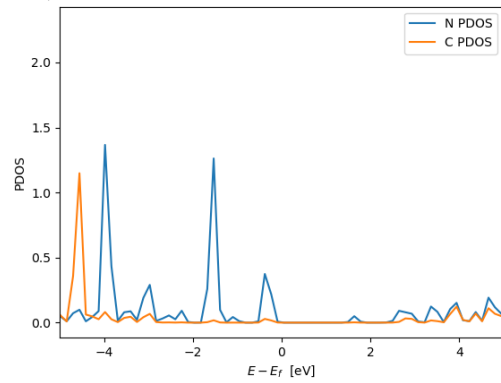
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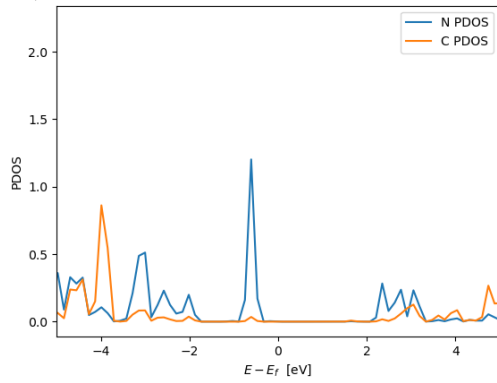
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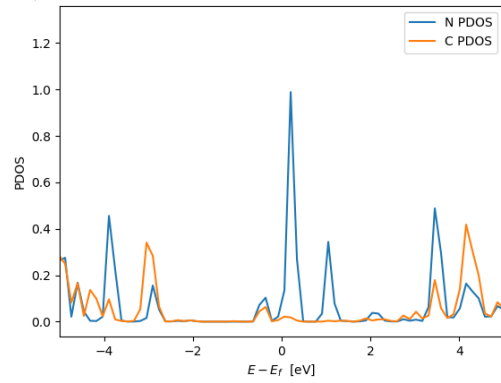
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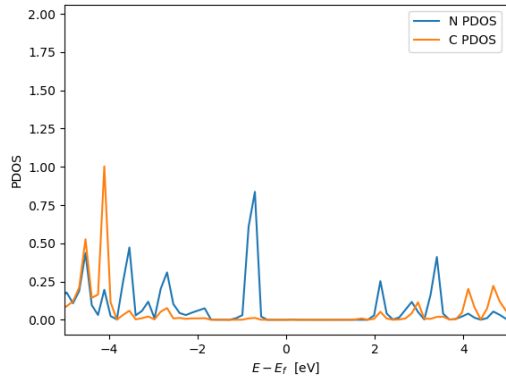
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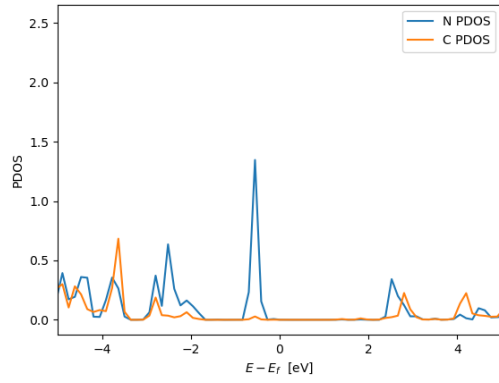
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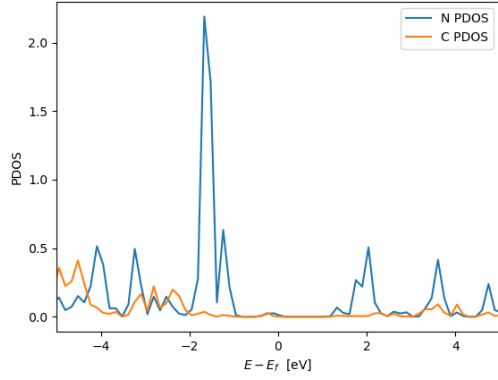
17)



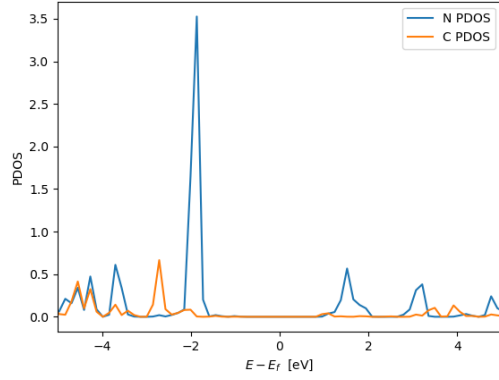
18)



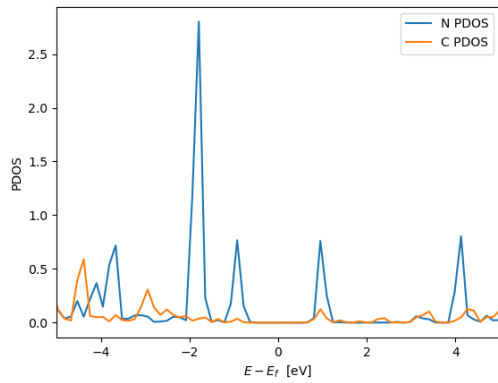
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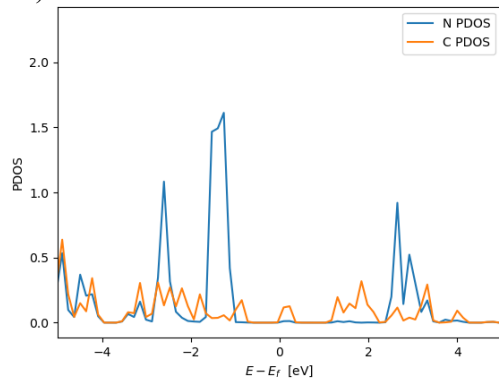
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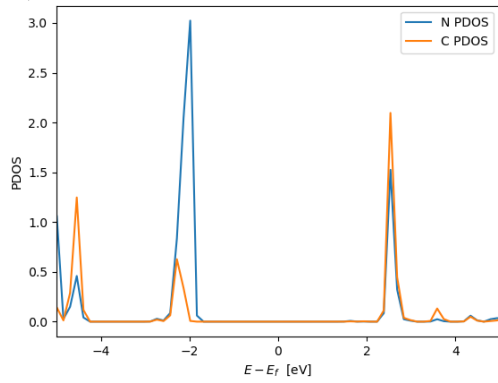
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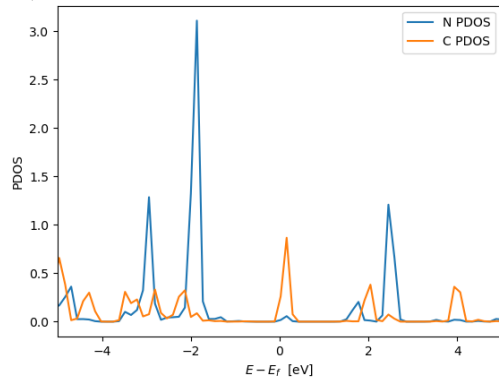
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23)



24)



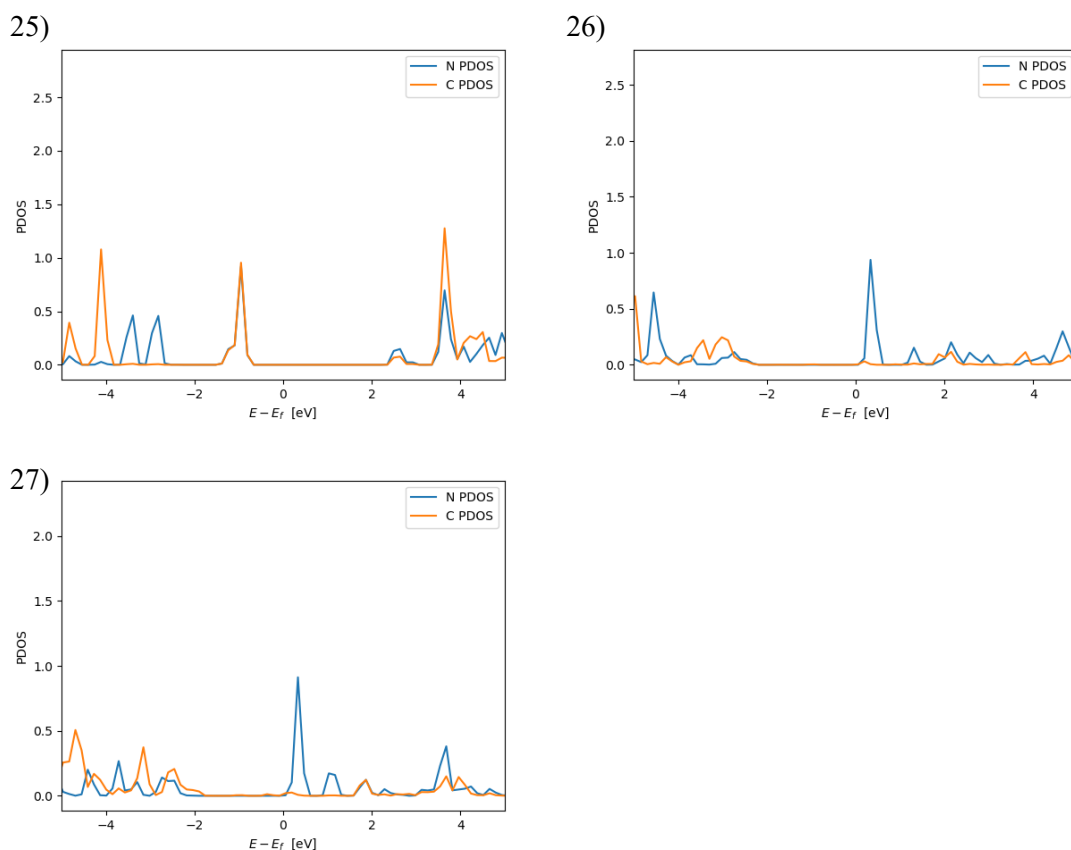


Figure 6.9 PDOS plots aligned with the Fermi level (E_f), truncated between -5 and 5 eV. The N stands for the nitrogen atom and C is the closest carbon connected with N and OH group for C1 in **Table 6.2**. The labelled numbers are aligned with **Figure 6.7** and **Table 6.2**.

Figure 6.8 confirms that zigzag (4, 4) graphene and its combinations except Q1 and Q2 (**Figure 6.8 – 17, 18**) are semiconductors. Q1 and Q2 with the zigzag (4, 4) graphene exhibits many more states near the Fermi level compared to their plain form. Their *OH (N) bindings are slightly higher compared to the pristine molecule, though the nitrogen is not expected to be the active site. On the other hand, the C1 is deemed as the active site as reviewed but only Q1 and Q2 fit into this scheme. And their catalytic performances are related to the DOS or conductivity as Q1 has a small gap above the Fermi level. It suggests that previous concern over the conductivity seems to be rational. Additional samplings on graphene plane also failed to explain the activity. The spikes in PDOS of the nitrogen and carbon near the nitrogen around the Fermi level make up less than about 25% of the total DOS counts for Q1 and

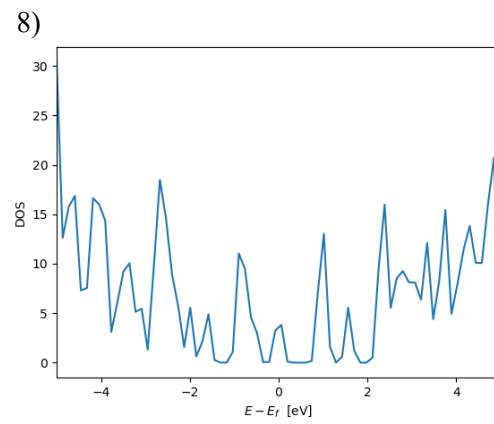
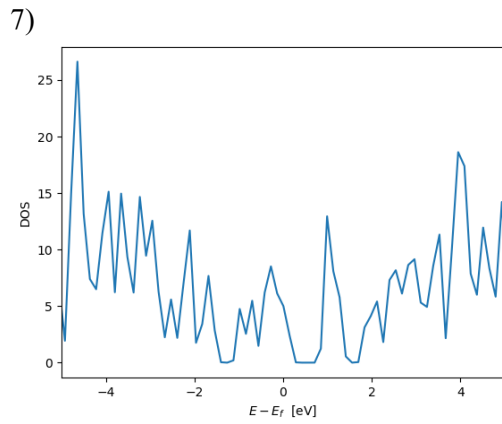
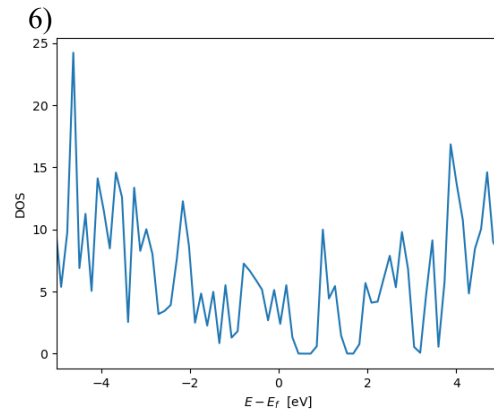
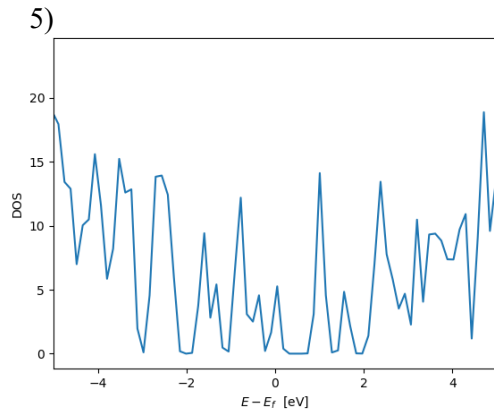
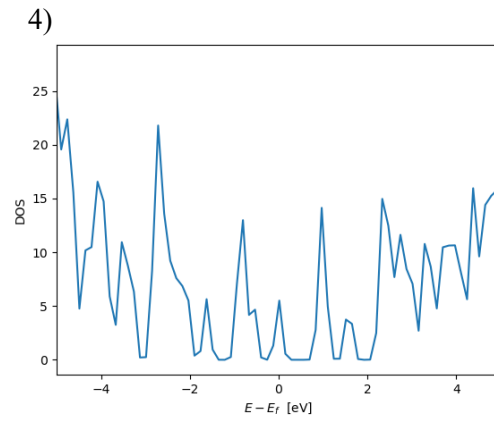
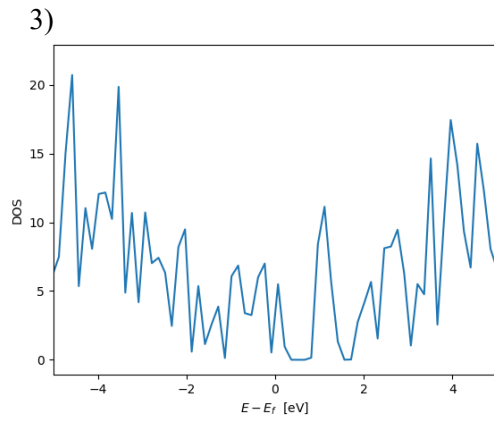
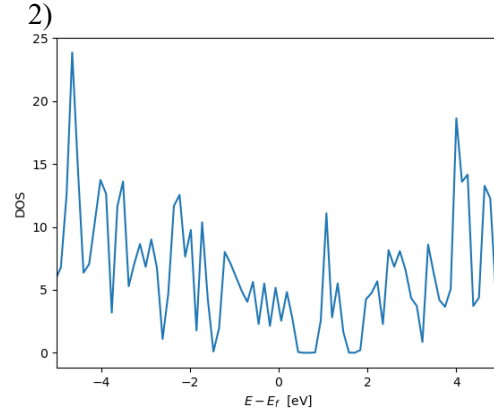
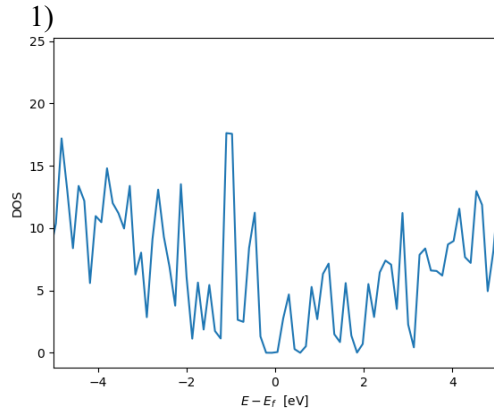
Q2, and other semiconducting molecules also show proportional spikes, which suggest that the electrocatalytic activity cannot be attributed solely to either the N or C atom.

As the classification of the nitrogen kinds dominates their binding energy, which is seen from **Table 6.1** and **Table 6.2**, a subsampling of the pyridinic, pyrrolic and quaternary nitrogen are perceived as representative for the conclusion, reducing the computation overload. Thus, P1, P5, pyrr, and Q1 are selected from their respectively group for the following discussion.

For conducting zigzag (9, 3) graphene, the results are shown below:

Energy(eV)	G(*OH) (N)	G(*OH) (C)
Name		
P1	2.85	2.15
P5	2.63	2.19
Pyrr	2.62	1.63
Q1	0.49	0.39

Table 6.3 On zigzag (9, 3) graphene, DFT energies of the molecules and OH on nitrogen of the molecules marked with * and *OH (N) respectively. C means OH bind on the closest non-quaternary carbon near the nitrogen. Columns starts with G are the free energies of the corresponding configurations.



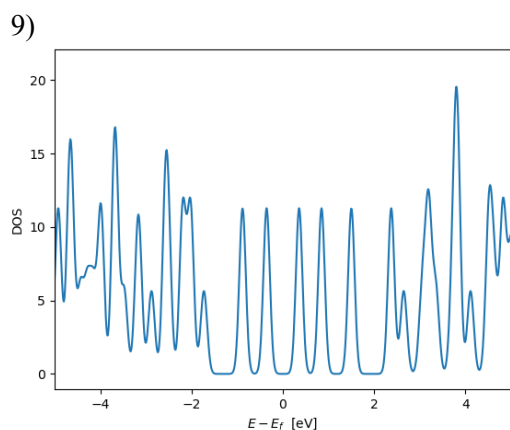


Figure 6.10 DOS plots truncated from -5 to 5 eV. The symbol from 1) to 4) correspond to G(*OH) (N) columns in **Table 6.3** while 5) to 8) are G(*OH) (C) columns. 9) is the DOS of zigzag (9, 3) graphene. The results are aligned with the Fermi level E_f .

The DOS plots in **Figure 6.10** confirm that the conductivity is no longer the constraint. Nevertheless, from **Table 6.3** the binding energies are still similar to those that have been obtained in the semiconducting scenario. The failures to explain the origin of the activity leads to two more hypotheses: the molecules are not bonded with the graphene, whereas they are parallel to the graphene plane. Or the carbon matrix may provide more interactions other than conductivity, and it is not the optimal independent investigator. For the first one, simulations placing the molecules parallel to the graphene plane were executed. Although the Van der Waals interaction is not thoroughly considered due to the limitation of semi-local RPBE functional, the main point is to have an insight of the binding energies. And the second one will be presented in chapter 6.3.4.

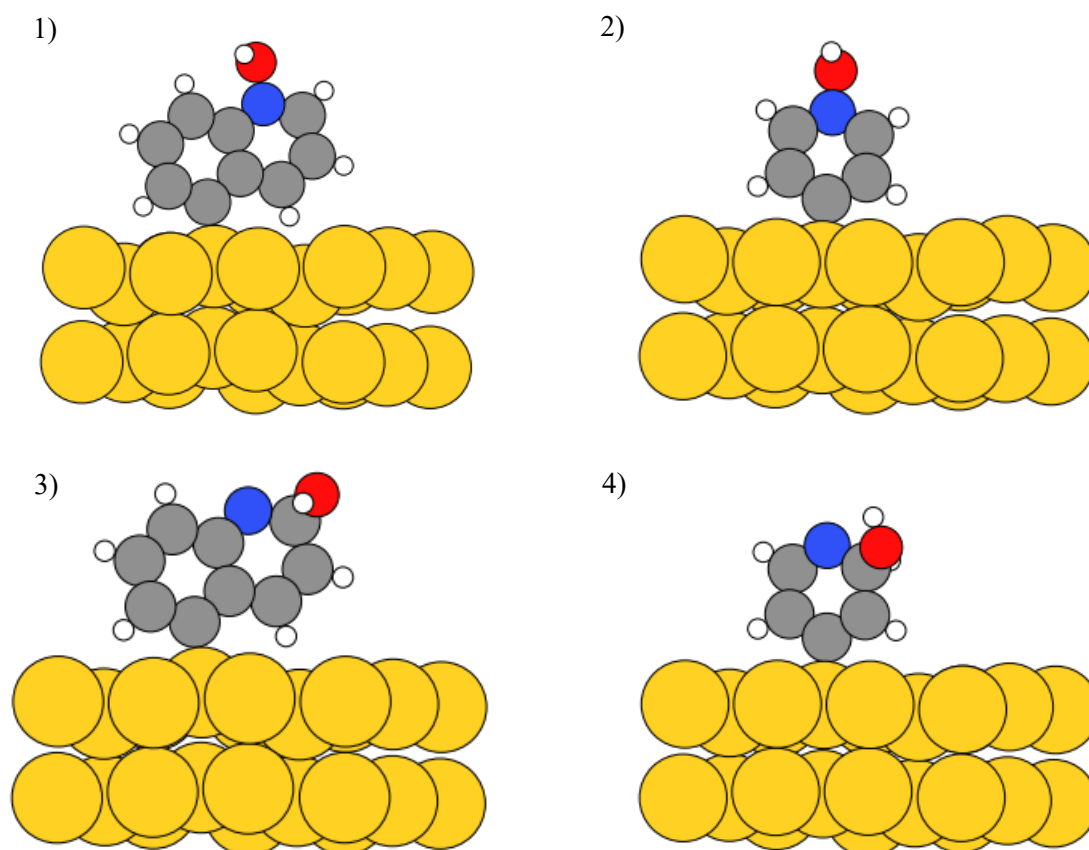
Energy(eV)	G(*OH) (N)	G(*OH) (C)
Name		
P1	2.81	1.98
P5	2.65	2.06
Pyrr	2.44	1.55
Q1	0.25	0.19

Table 6.4 Parallel to zigzag (4, 4) graphene, DFT energies of the molecules and OH on nitrogen of the molecules marked with * and *OH (N) respectively. C means OH bind on the closest non-quaternary carbon near the nitrogen. Columns starts with G are the free energies of the corresponding configurations.

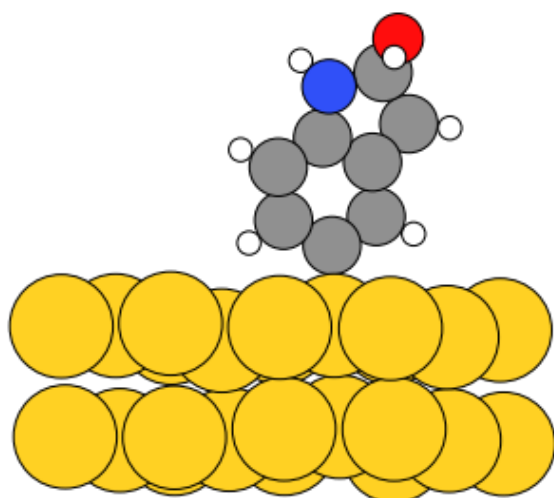
It seems that that binding configurations are not the cause of the activity. And up to now the only species that can barely account for the activity is quaternary nitrogen, although there is still a significant margin of error. It is noted that the values in **Table 6.4** should be interpreted qualitatively rather than quantitatively due to the functional error.

6.3.4 Molecules on gold

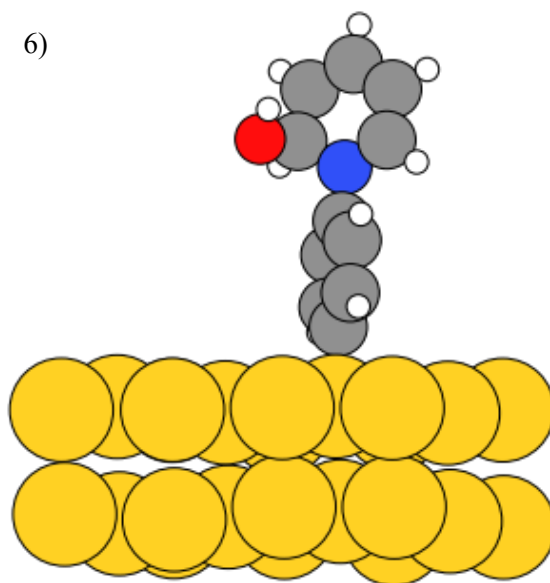
To provide the conductivity and decouple the interactions between the molecules and graphene, gold substrates are used in simulations. The conformations are in **Figure 6.11**. The calculated free energies are shown in **Table 6.5**. And their DOS/PDOS are presented in **Figure 6.12**, **Figure 6.13** respectively.



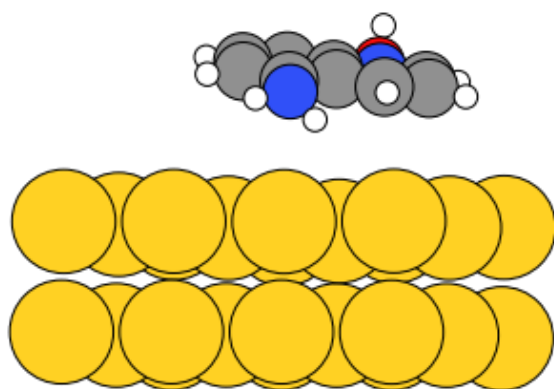
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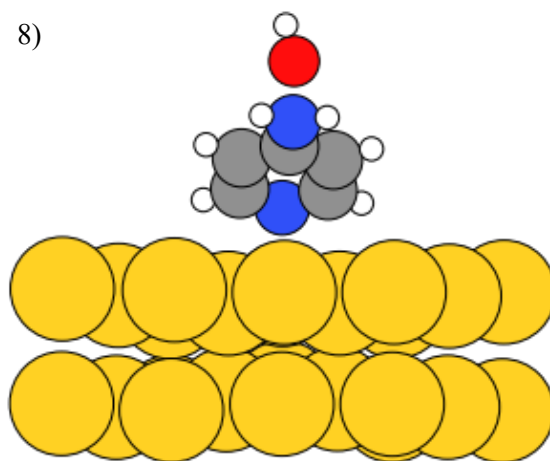
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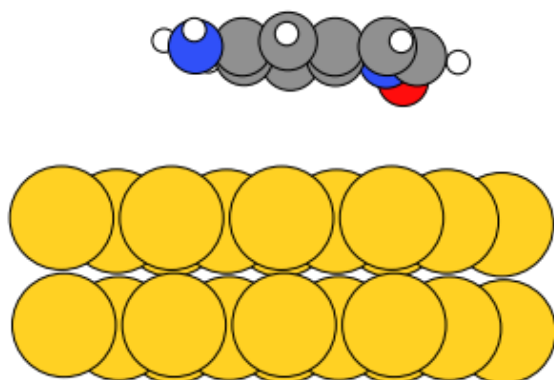
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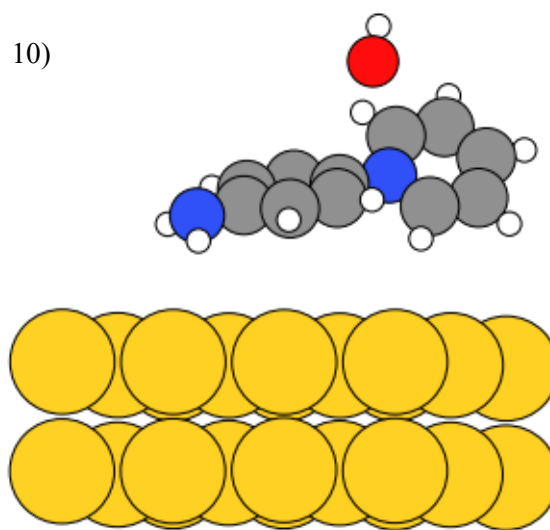
8)



9)



10)



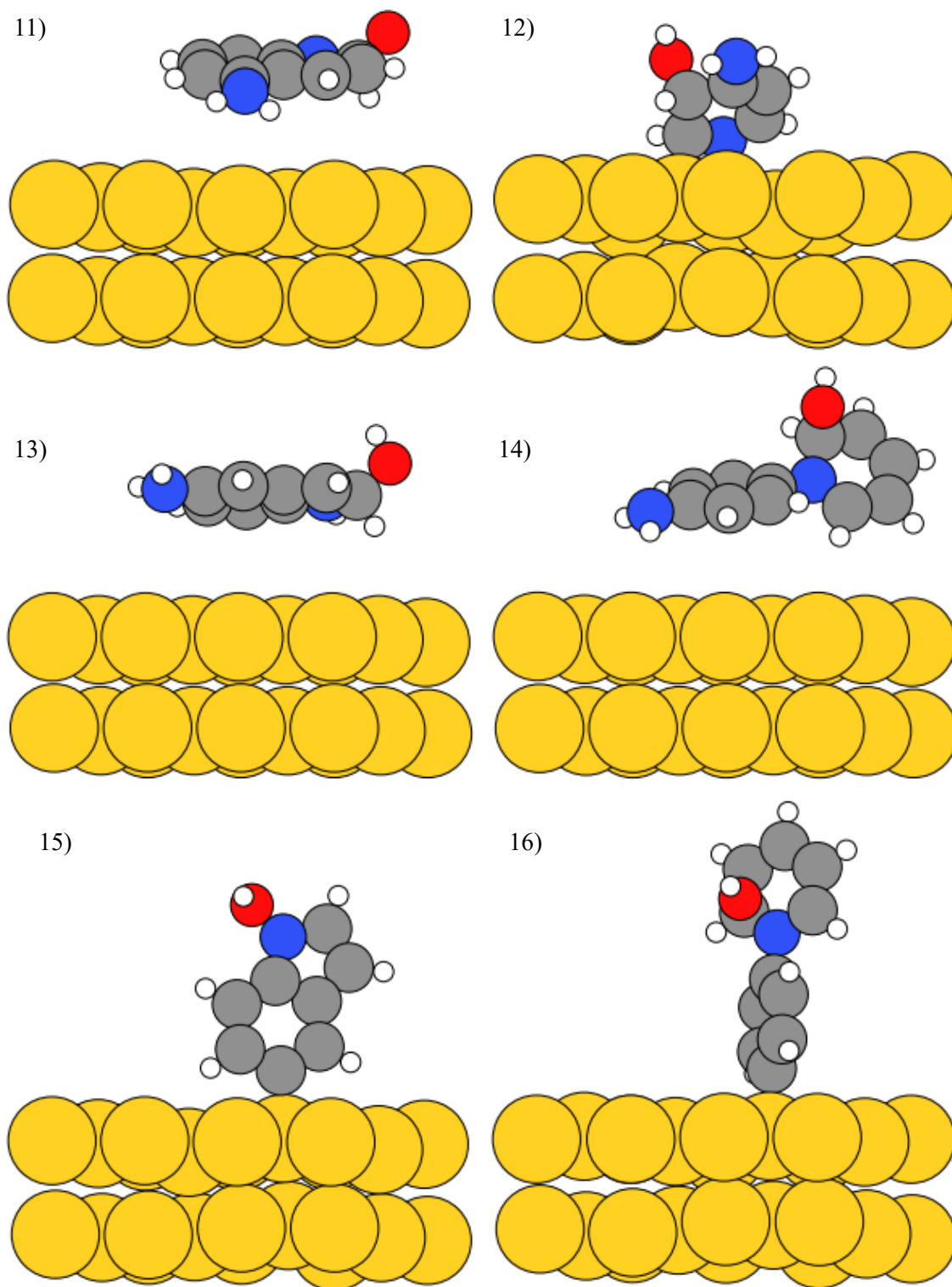
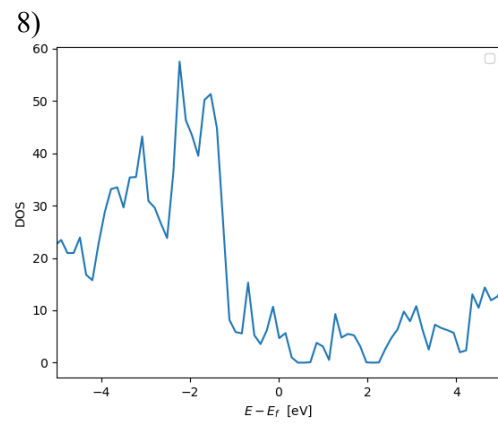
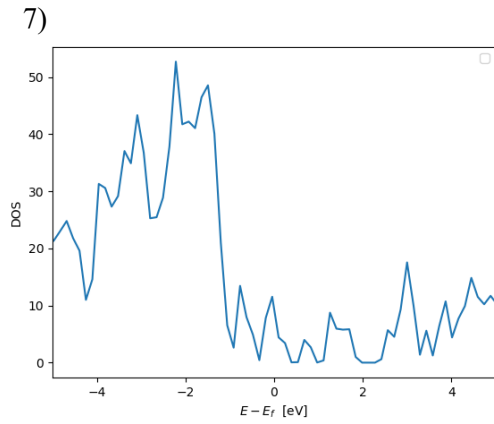
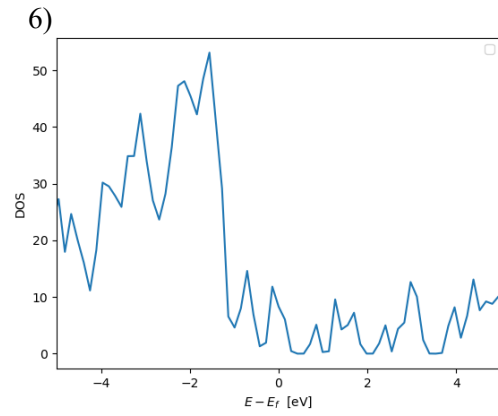
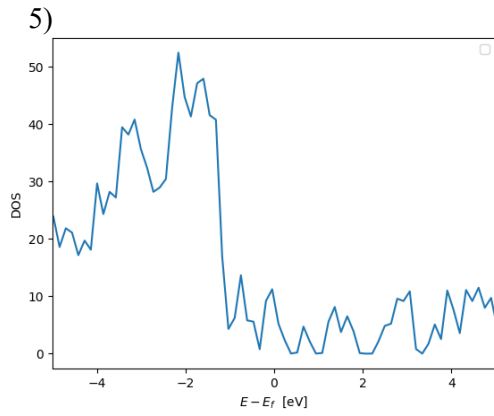
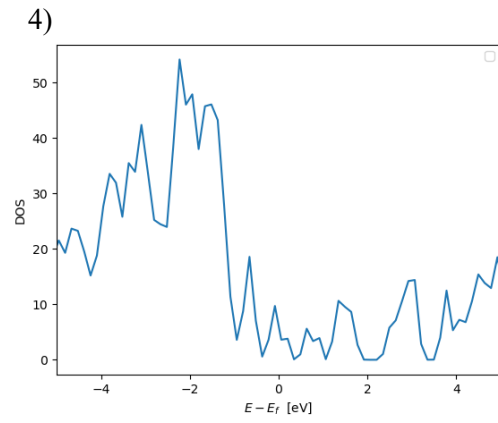
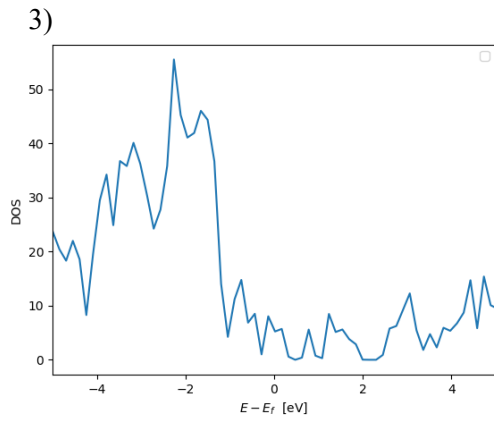
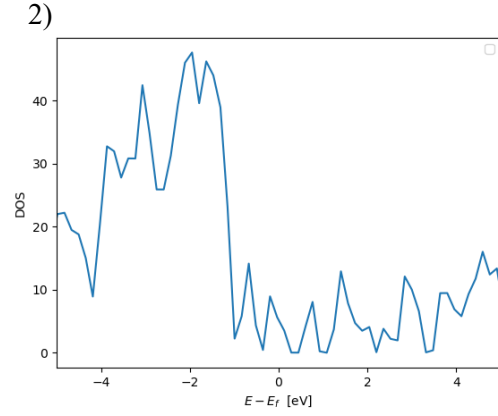
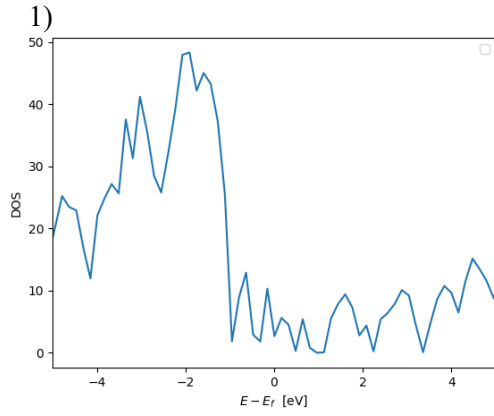


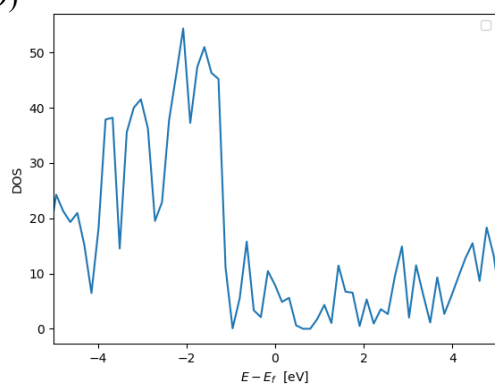
Figure 6.11 Conformations of molecules on gold. The alphabetical order represents the traversal from carbon atoms directly bonded in C-OH or N-OH configurations to those parallel to the gold planes. In the latter case, the original ammonia group is restored.

Energy(eV)	G(*OH) (N)	G(*OH) (C)
Name		
Bonded		
P1	1.99	2.01
P5	1.85	1.98
Pyrr	2.52	1.36
Q1	1.93	0.77
Parallel		
P1	2.04	1.93
P5	2.64	1.73
Pyrr	2.60	1.22
Q1	2.02	1.07

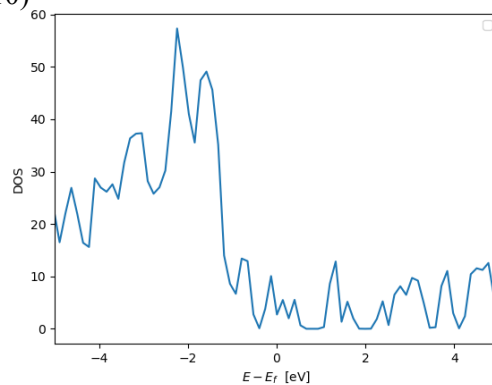
Table 6.5 DFT energies of the molecules and OH on nitrogen of the molecules marked with * and *OH (N) respectively. C means OH bind on the closest non-quaternary carbon near the nitrogen. Columns starts with G are the free energies of the corresponding configurations. Molecules are either bonded through a carbon atom with gold (Bonded) or parallel to the gold plane (Parallel).



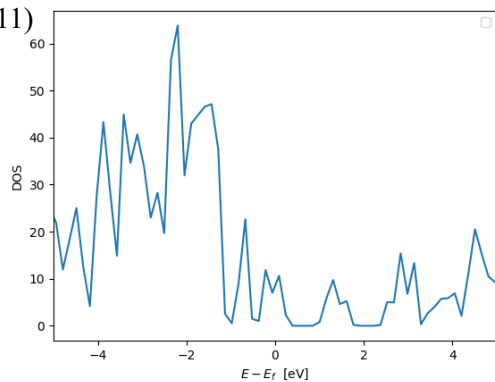
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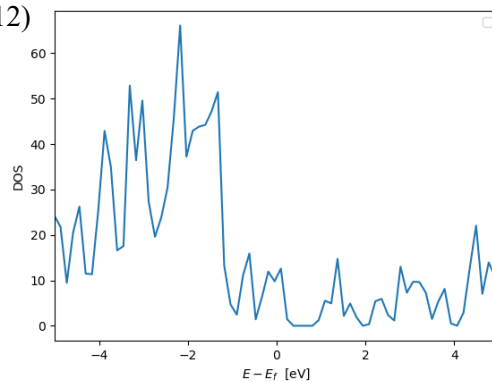
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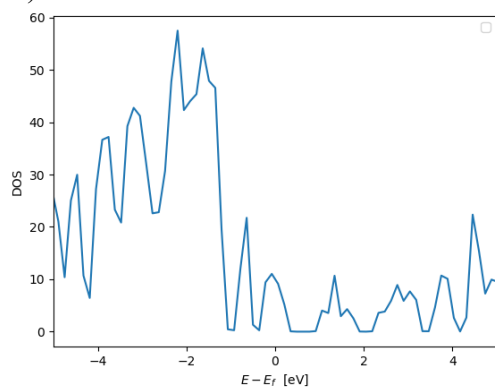
11)



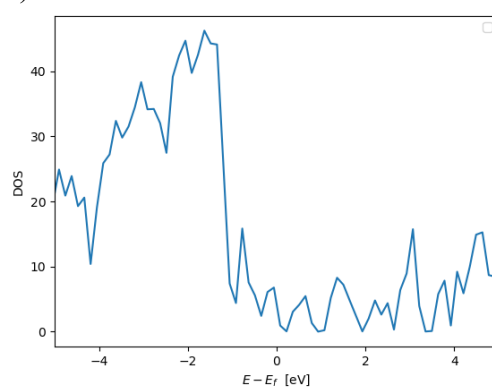
12)



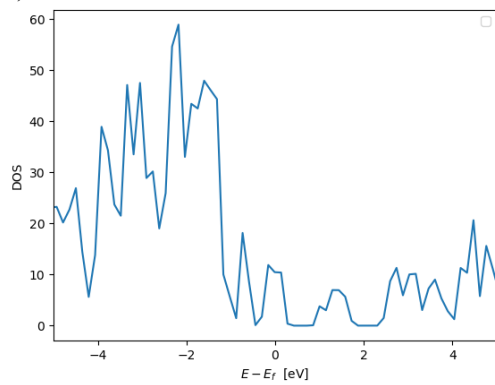
13)



14)



15)



16)

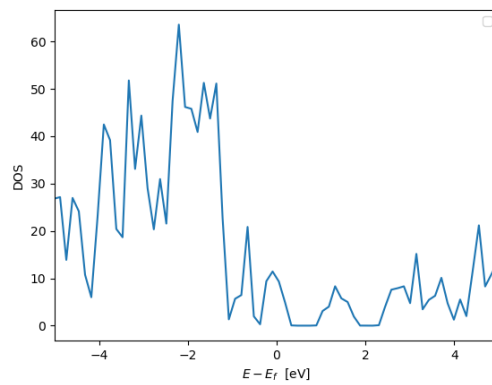
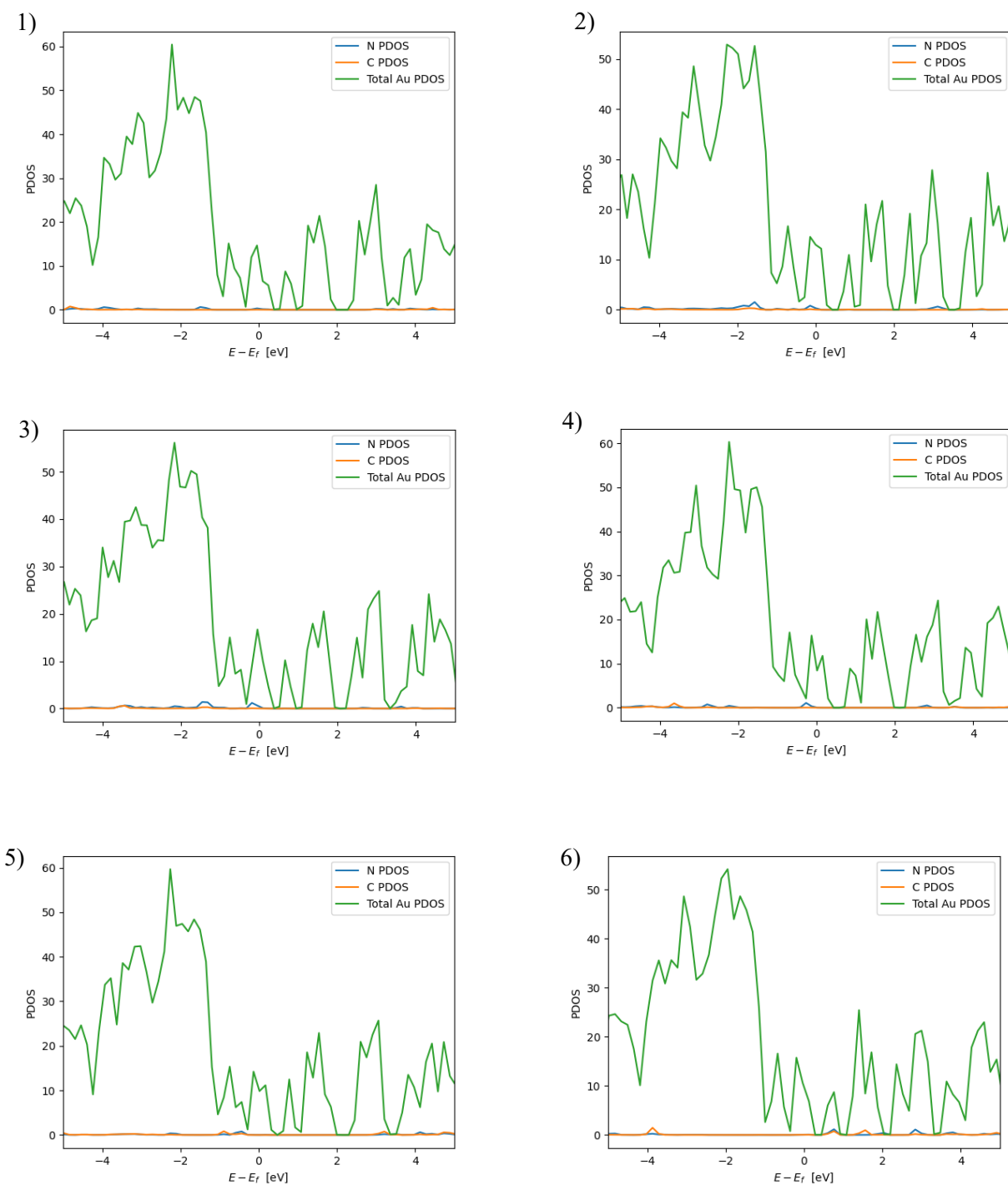
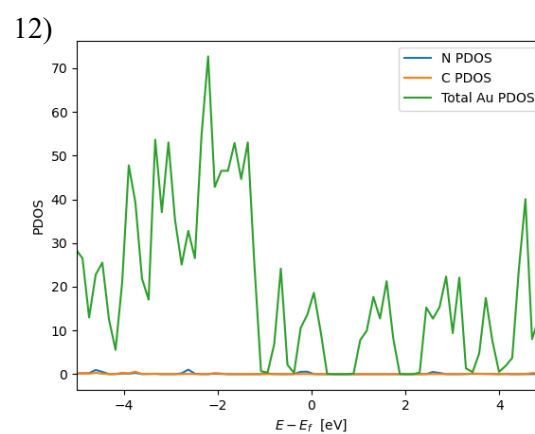
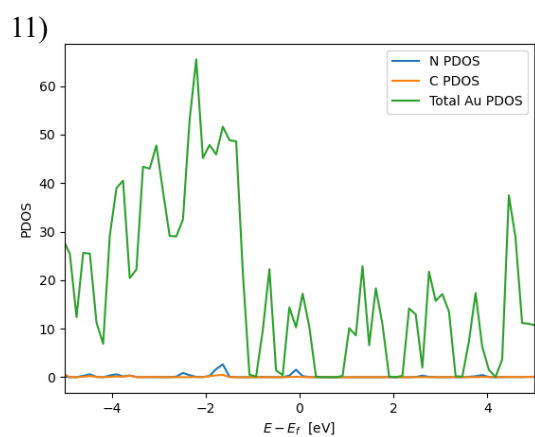
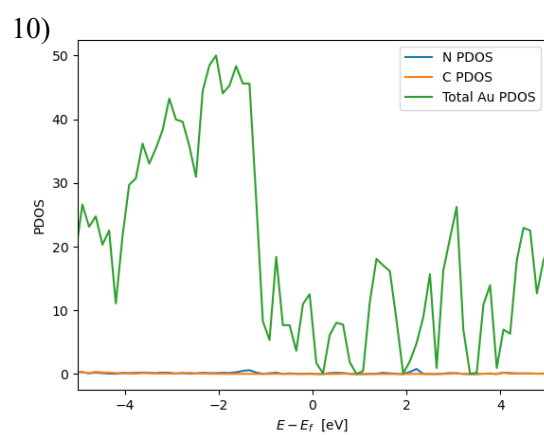
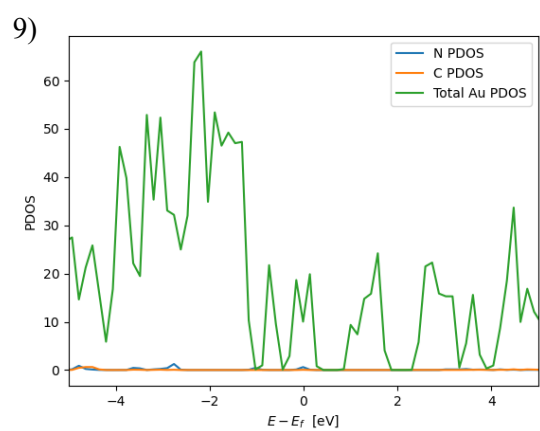
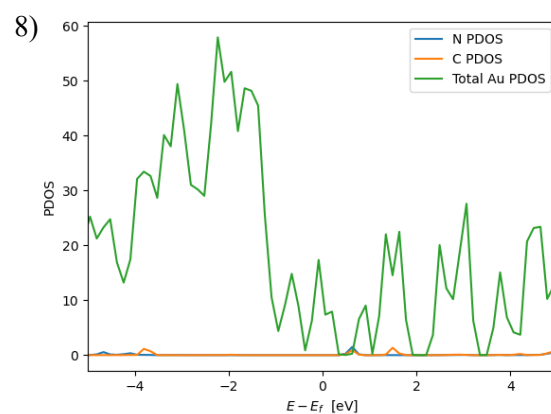
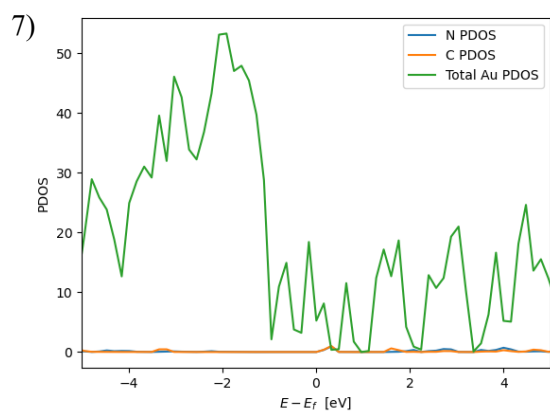


Figure 6.12 DOS plots truncated from -5 to 5 eV. 1) to 16) correspond to the molecules in **Figure 6.11**. The results are aligned with the Fermi level E_F .





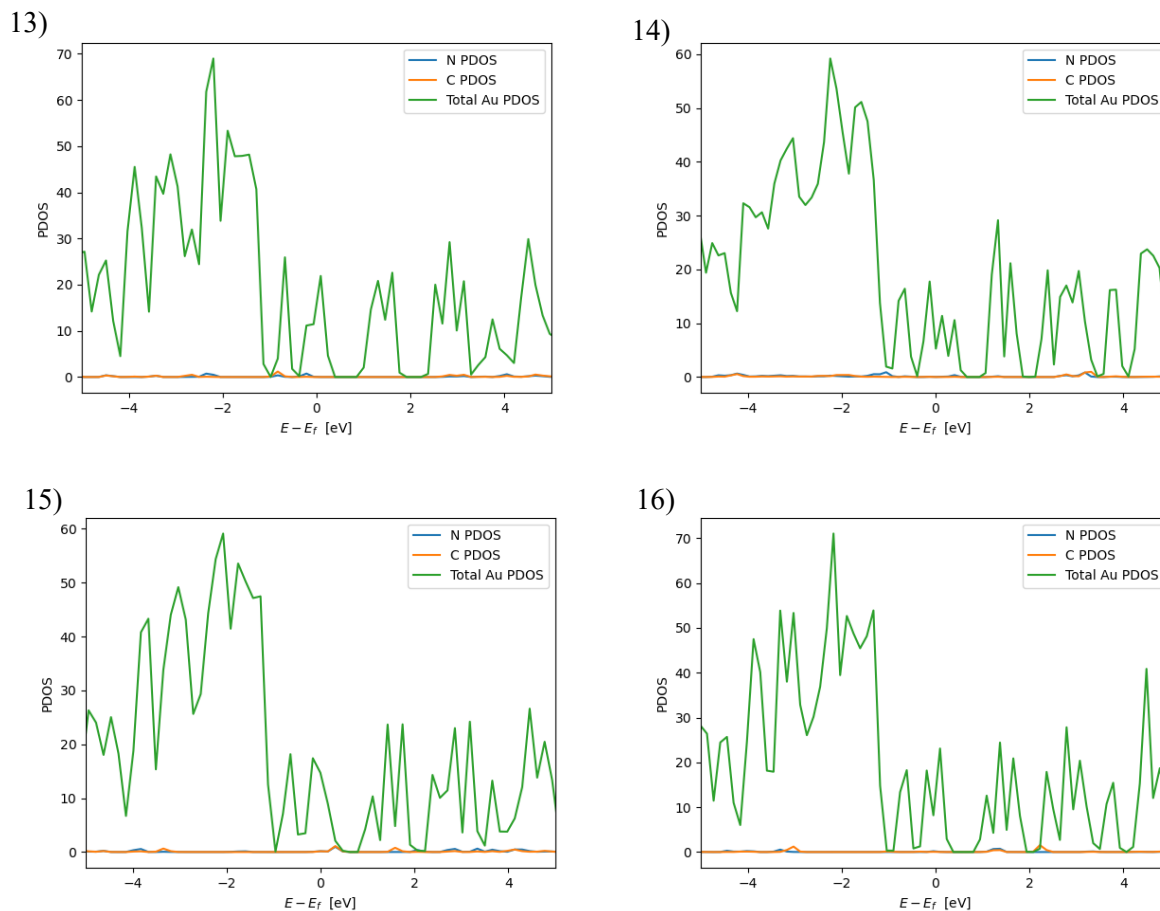


Figure 6.13 PDOS plots truncated from -5 to 5 eV. 1) to 16) correspond to the molecules in **Figure 6.11**. The results are aligned with the Fermi level E_f .

From the DOS and PDOS gold is the only source that provides the conductivity as it almost monopolies the states near the Fermi level. This further validates the observations that the pyridinic and pyrrolic nitrogen type of the molecules are not active for the ORR, as regardless of the conductivity, their binding of OH are too weak. The only nitrogen type that is possible to explain the origin of the ORR activity is quaternary nitrogen. In this case the active site could either be the nitrogen or the non-quaternary carbon near the nitrogen. However, this is also subject to a specific conductive carbon matrix, which is not thoroughly revealed in the zigzag (4, 4) or (9, 3) simulations.

6.4 Conclusion

In this chapter, metal free nitrogen doped carbon as ORR electrocatalyst is briefly introduced. The focus is on the active sites that contribute to the ORR current density. Experimentally, pyridinic, pyrrolic and quaternary nitrogen containing small molecules were synthesised and incorporated into the HOPG. Theoretically, corresponding models with graphene and gold were built to understand the origin of the ORR activity. Nonetheless, the models can only show the activity relate to the quaternary nitrogen, while the rest species are not active for ORR. This could be due to the synthesis might not occur as designed, or the entangled configurations and defects of the materials have a great impact, where a single molecule functionalisation model is underfitting.

Chapter 7

Summary and outlook

The fundamental electrocatalytic mechanisms play a critical role in unlocking the potential of electrochemical approaches to effectively tackle the pressing issues of climate change and the ever-growing demands for energy. Specifically, this research studies the mechanisms of Fe-macrocycles and metal free nitrogen doped carbon for ORR, and transition-metal-macrocycles for CO₂RR.

The primary conclusions and outlooks derived from this thesis are as follows:

- (1) For ORR in the Fe macrocycle system, the scaling relation still holds. *OH desorption is the reason for proton electron transfer detected by the experiment, where the initial valence of Fe can be either ferric or ferrous. The peroxide selectivity can be explained by the destabilisation of the *O intermediate with respect to *OOH. As for the CV peak(s) shown in the experiment, DFT calculations indicated that molecules with two peaks are more active compared to those with a single peak, irrespective of the final oxidation state. This indicates a different mechanism for the latter group. The mechanism for the single peak group is closely associated with the absence of high potential peaks, which should correspond to *OH desorption. Combining the evidence from XAS and analysis from DFT data, proposed explanation was that water might bind to the back side of the molecule, allowing the electron to accommodate the spin during *OH desorption. To further verify the proposal, in-situ high quality XAS experiment data would be beneficial.
- (2) For CO₂RR in the M-N-C (M = Fe, Co, Ni, Cu) macrocycle system, Fe macrocycles were proposed as promising alternatives to replace Cu as the electrocatalyst due to the more thermodynamically favourable binding energies of H*, CO* and COOH* and lower cost. In-depth analysis with variation of charges further screens 4NH₂FePC as the most promising catalyst that could produce more valuable products. CO₂RR Experiment could be set up to test this material in the future.

(3) For ORR in the metal free nitrogen doped carbon system, various hypotheses and models were explored to understand the origin of the electroactivity. Progress was made in the comprehending the roles of different nitrogen types despite the complexity of the topic. It is believed that quaternary nitrogen is responsible for the activity for the ORR, and the nearest non-quaternary carbon atom is the active site. For pyridinic and pyrrolic nitrogen, decoupled models suggested no activity that contrasted with the experimental result. This is potentially due to the entangled interactions from the moieties and the defects as suggested in experimental result. More conductive molecular configurations are needed to better understand this system.

This thesis has shed light on the fundamental understandings of the ORR and CO₂RR and has provided valuable insights into the future paths of research in both theoretical and experimental studies.

Appendix

Molecules	H ₂	CO	CO ₂	H ₂ O
Energy (eV)	-6.70	-14.94	-23.01	14.29

Table 1 DFT energies of small molecules were calculated using the RPBE functional and optimised with a maximum force criterion of 0.001 eV/Å.

ΔG (eV) Name	*OH (m=0, TTF)	*OH (m=0, FFF)	*OH (m=2, TTF)	*OH (m=2, FFF)
4PhFeP	0.22	0.23	0.77	0.76
AABB_8EtFeP	0.31	0.23	0.85	0.82
ABAB_8EtFeP	0.33	0.26	0.88	0.87
FePC	0.44	0.34	0.95	0.92
16ClFePC	0.50	0.38	0.98	0.95
4NH ₂ FePC	0.43	0.32	0.89	0.85
4COOHFePC	0.48	0.38	0.99	0.96

Table 2 Free energies of macrocycles with *OH in different periodic conditions. TTF and FFF stand for True, True, False and False, False, False along x, y, z axis respectively, where FeN₄ plane coincide with xy plane.

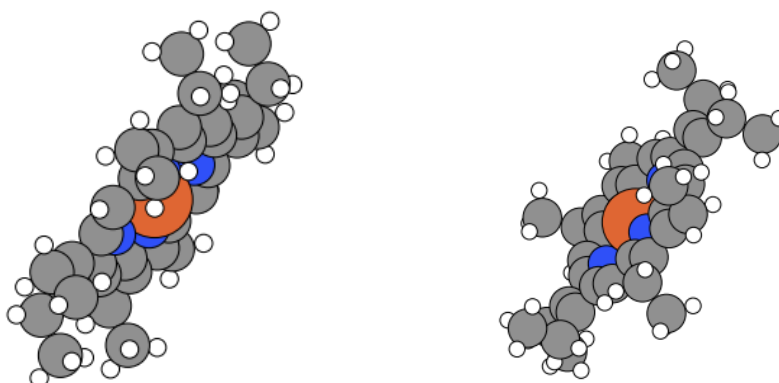


Figure 1 Illustration of AABB_octa and ABAB_octa. AABB indicates half of the amino groups are on the one side while the rest on the other side. ABAB stands for the alternating amino groups in the backbone.

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