

The consequences of electrolyte engineering in electrochemical nitrogen
reduction to ammonia

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Abstract

Anthropogenic nitrogen fixation and ammonia-derived fertiliser have fed the growth of society. However, the nature and economies of scale of the Haber-Bosch process made it a major source of energy consumption and greenhouse gas emissions, while benefiting only a portion of the global population. Electrochemical ammonia production holds potential for decarbonisation and decentralisation.

Aqueous electrolyzers are likely impractical due to the intense competition between nitrogen reduction, and proton reduction to hydrogen. Non-aqueous systems circumvent this problem, with a lithium-mediated approach having been rigorously validated to reduce nitrogen at viable rates. In this system, in situ reduced metallic lithium reacts with nitrogen and protons to produce ammonia. Alike battery anodes, lithium reacts with its electrolyte, forming a passivation layer (the solid electrolyte interphase or SEI), which is thought to prompt the selectivity of this reaction.

This thesis examines and addresses the significant energy burden required to maintain the active lithium metal surface through the lens of electrolyte engineering. A true reference electrode was developed to measure this energy burden and elucidate the role of the electrolyte in mitigating it. Electrolytes were formulated based on this understanding, and the interplay between electrolyte properties, SEI chemistry and selectivity was illustrated with overlapping non-linear relations. Such relations can be translated into a linear correlation between the selectivity of nitrogen reduction to ammonia and the activity of Li-ions and protons. While providing descriptors for identifying higher-performing electrolytes, it highlighted that significant energy efficiency gains can only be achieved by breaking free from lithium. Guided by simulations, new electrolytes based on promising alkali metals such as Ca and Mg were investigated to achieve nitrogen fixation beyond lithium. The fundamental insights gained from these studies are expected to enhance the alkali metal chemistries and help overcome their energy bottleneck, toward sustainable and affordable ammonia production.

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Last but not the least, I want to thank my long partner Margaux, for being the strongest shoulder I could lean on in this journey. You supported me every day two hundred percent no matter how niche and far from reality my work may seem, trusting me with no questions asked. Thank you for getting me to act fast on things when I would be naturally drawn to take my time, for making a big move to London to live with me, for your contagious positivity and enthusiasm for life, for the amazing travels we shared all around the world (but that you essentially planned from start to finish), for the supermarket recipes books fine selection sessions, our weekend day trips by the south coast, our cooking nights with a glass of wine and nibbles always ending in you being full before actual dinner is ready, and the many coffee breaks and 'partos' that punctuated this manuscript writing all along.

This work is a contribution of all your efforts so thank you all.

Academic Contributions

Peer-Reviewed Publications

Nonaqueous Li-Mediated Nitrogen Reduction: Taking Control of Potentials

R. Tort, O. Westhead, M. Spry, B. J. V. Davies, M. P. Ryan, M. M. Titirici, I. E. L. Stephens
ACS Energy Letters **2023**, 8, 2, 1003–1009 – <https://doi.org/10.1021/acsenergylett.2c02697>

The role of Ion Solvation in Lithium Mediated Nitrogen Reduction

O. Westhead, M. Spry, A. Bagger, Z. Shen, H. Yadegari, S. Favero, R. Tort, M. Titirici, M. P. Ryan, R. Jervis, Y. Katayama, A. Aguadero, A. Regoutz, A. Grimaud, I. E. L. Stephens
Journal of Materials Chemistry A **2023**, 11 (24), 12746–12758 – <https://doi.org/10.1039/D2TA07686A>

Water increases the Faradaic Selectivity of Li-Mediated Nitrogen Reduction

M. Spry, O. Westhead, R. Tort, B. Moss, Y. Katayama, M. Titirici, I. E. L. Stephens, A. Bagger
ACS Energy Letters **2023**, 8 (2), 1230–1235 – <https://doi.org/10.1021/acsenergylett.2c02792>

The Origin of Overpotential in Lithium-Mediated Nitrogen Reduction

O. Westhead, R. Tort, M. Spry, J. Rietbrock, R. Jervis, A. Grimaud, A. Bagger, I. E. L. Stephens
Faraday Discussions **2023**, 243, 321–338 – <https://doi.org/10.1039/D2FD00156J>

Searching for the Rules of Electrochemical Nitrogen Fixation

R. Tort, A. Bagger, O. Westhead, Y. Kondo, A. Khobnya, A. Winiwarter, B. J. V. Davies, A. Walsh, Y. Katayama, Y. Yamada, M. P. Ryan, M. M. Titirici, I. E. L. Stephens
ACS Catalysis **2023**, 13, 22, 14513–14522 – <https://doi.org/10.1021/acscatal.3c03951>

Electrochemical Nitrogen Reduction: The Energetic Distance to Lithium

A. Bagger, R. Tort, M. Titirici, A. Walsh, I. Stephens
ACS Energy Lett. **2024**, 9, XXX, 4947–4952 – <https://doi.org/10.1021/acsenergylett.4c01638>

In Preparation

Electrolyte Species Activities Drive Ammonia Synthesis Selectivity – Based on Chapter 4 of this thesis.

Conference Presentations

Poster: Li-mediated N₂ Reduction: Taking Control Over Potential

R. Tort, O. Westhead, M. Spry, D. B. Thornton, B. J. V. Davies, M. P. Ryan, M. Titirici, I.E.L. Stephens
Surfcats Summer School 2022 – Technical University of Denmark. Gilleleje, Denmark, 2022

Poster: A True Reference Electrode for Non-Aqueous Li-mediated N₂ Reduction

R. Tort, O. Westhead, M. Spry, D. B. Thornton, B. J. V. Davies, M. P. Ryan, M. Titirici, I.E.L. Stephens
Imperial College London Electrochemistry Network Industry Day. London, UK, 2022

Talk: Upgrading Li-Mediated Ammonia Synthesis Electrochemical Characterisation – A Battery-Inspired Cell Design

R. Tort, O. Westhead, M. Spry, D. B. Thornton, B. J. V. Davies, M. P. Ryan, M. M. Titirici, I. E. L. Stephens
Proceedings of Materials for Sustainable Development Conference (MATSUS-NFM22). Barcelona, Spain, 2022

Poster: Nonaqueous LiFePO₄ Reference Electrode: Tracking Potentials and Li-ion Activity

R. Tort, O. Westhead, M. Spry, D. B. Thornton, B. J. V. Davies, M. P. Ryan, M. M. Titirici, I. E. L. Stephens
Faraday Discussions – Sustainable Nitrogen Activation. London UK, 2023

Talk: Ambient Nitrogen Reduction to Ammonia: What Makes Lithium so Unique?

R. Tort, A. Bagger, Y. Kondo, O. Westhead, A. Khobnya, M. P. Ryan, M. M. Titirici, I. E. L. Stephens
74th Annual Meeting of the International Society of Electrochemistry. Lyon, France, 2023

Talk: Nitrogen Reduction to Ammonia: Roads Beyond Lithium

R. Tort, A. Bagger, Y. Kondo, O. Westhead, A. Khobnya, M. P. Ryan, M. M. Titirici, I. E. L. Stephens
Proceedings of MATSUS Fall 2023 Conference (MATSUSFall23), #N2X - Recent advances on nitrogen activation and conversion. Torremolinos, Spain, 2023

Poster: Searching for the Rules of Electrochemical Nitrogen Fixation – Poster Prize Award

R. Tort, A. Bagger, O. Westhead, Y. Kondo, A. Khobnya, A. Winiwarter, B. J. V. Davies, A. Walsh, Y. Katayama, Y. Yamada, M. P. Ryan, M. M. Titirici, I. E. L. Stephens
Solar Chemicals Network Symposium. Liverpool, UK, 2024

Talk: Nitrogen Reduction to Ammonia: Drawing a Path Toward Energy Efficiency

R. Tort, A. Bagger, O. Westhead, Y. Kondo, A. Khobnya, A. Winiwarter, B. J. V. Davies, A. Walsh, Y. Katayama, Y. Yamada, M. P. Ryan, M. M. Titirici, I. E. L. Stephens
245th Meeting of the Electrochemical Society. San Francisco, USA, 2024

Talk: Nitrogen Reduction to Ammonia: Breaching the Lithium Monopoly?

R. Tort, A. Bagger, O. Westhead, Y. Kondo, A. Khobnya, A. Winiwarter, B. J. V. Davies, A. Walsh, Y. Katayama, Y. Yamada, M. P. Ryan, M. M. Titirici, I. E. L. Stephens

RSC Electrochem2024. Manchester, UK, 2024

Talk: Nitrogen Reduction to Ammonia : Discovering New Interphases by Learning from Lithium – ChemElectroChem best contributed talk award for the #EEInt symposium.

R. Tort, A. Bagger, O. Westhead, Y. Kondo, A. Khobnya, A. Winiwarter, B. J. V. Davies, A. Walsh, Y. Katayama, Y. Yamada, M. P. Ryan, M. M. Titirici, I. E. L. Stephens

MATSUS Fall 2024 #EEInt. Lausanne, Switzerland, 2024

Prizes and Grants Awarded

Prizes:

- Imperial College President Team Award for Community Engagement – Grantham Climate Friendly Pop-Up Kitchen on Sustainable Eating – Great Exhibition Road Festival 2023
- Solar Chemicals Network Symposium 2023 – Poster Prize
- MATSUS Fall24 – NanoGe Conference #EEInt Symposium – ChemElectroChem best contributed oral talk award

Grants:

- Solar Fuels Network Travel Fund 2022 (£700)
- Royal Society of Chemistry Researchers' Development Grant 2022 and 2023 (£500 x2)
- Armourers and Brasiers' Company Travel Fund, 2022 and 2023 (£250 x2)
- ECS Europe Division Travel Award – 245th ECS Conference San Francisco, May 2024 (£220)
- Solar Chemicals Network Travel Grant – 245th ECS Conference San Francisco, May 2024 (£700)

Outreach Activities

Great Exhibition Road Festival 2022 – Electrochemistry Engagement

Participated in animating a stall at a science outreach festival, walking 6–10-year-old kids and their parents through an educational game explaining the role of electrochemistry in a sustainable future energy nexus.

Great Exhibition Road Festival 2022 – Grantham Climate Friendly Pop-Up Kitchen

Participated in animating a stall at a science outreach festival, offering freshly cooked plant-based food samples to the public and animating a food quiz to raise awareness at the environmental footprint of one's diet and promoting easy fixes to lower it.

Great Exhibition Road Festival 2023 – Grantham Climate Friendly Pop-Up Kitchen

Led the organisation and development of the above-mentioned stall for another round, alongside Clara Gimeno Jesús and Arianna Olivelli. Arranged for the participation of local chefs ([Made in Hackney](#)) in cooking and serving plant-based meals while promoting climate friendly diets and local community engagement. Developed games to raise awareness on the environmental impact of our food chain and highlight how a climate friendly diet benefits one's health while being more affordable.

Imperial Lates 2023 – Grantham Climate Friendly Pop-Up Kitchen

Reframed and repeated the above activity in a setting aimed at a mostly adult audience.

The Invention Rooms 2024 – The Making of a Battery

Participated in an outreach day, animating a workshop developed and led by Dr Anna Winiwarter. The workshop was aimed at teaching children the why and how a battery works, challenging them into making a battery themselves using materials they could find in their own homes.

Nomenclature

ATP – Adenosine Triphosphate

Ca(B(hfip)₄)₂ – Calcium bis(1,1,1,3,3,3-hexafluoroisopropoxy)borate)

CE – Counter Electrode

CP – Chronopotentiometry

CV – Cyclic Voltammetry

d_i – Density of a species *i* (g.ml⁻¹)

DFT – Density Functional Theory

DME – 1,2-Dimethoxyethane (Glyme)

DMM – Dimethoxymethane

DNA – Deoxyribonucleic Acid

ECMS – Electrochemistry - Mass Spectrometry

E_a – Activation Energy

E_i – Biological N₂ reduction intermediate

EIS – Electrochemical Impedance Spectroscopy

EtOH – Ethanol

Fc⁺/Fc – Ferrocenium/Ferrocene Redox

FE – Faradaic Efficiency

FSI – Bis(fluorosulfonyl)imide

G1 – 1,2-Dimethoxyethane (Glyme, DME)

G2 – Diethylene Glycol Dimethylether (Diglyme)

GC – Gas Chromatography

GEIS – Galvanostatic Electrochemical Impedance Spectroscopy

HFE – Hydrofluoroether

IPCC – International Panel for Climate Change

ⁱX-NMR – NMR for the nucleus X of atomic mass *i*

LHCE – Localised Highly Concentrated Electrolyte

LICGCTM – Lithium Ion Conducting Glass Ceramic

LUMO – Lowest Unoccupied Molecular Orbital

LSV – Linear Sweep Voltammetry

Mg(Al(hfip)₄)₂ – Magnesium bis(1,1,1,3,3,3-hexafluoroisopropoxy)aluminate)

M – Metal

MEA – Membrane Electrode Assembly

M_xC_y – Metal Carbide

M_x(CO₃)_y – Metal Carbonate

M_x(CO₂R)_y – Metal Semicarbonate (R = organic group)

M_xF_y – Metal Fluoride

M_xH_y – Metal Hydride

Mⁿ⁺ – Metal-ion (of charge *n*)

M_xN_yH_z – Metal Nitride / Imide / Amide

M_xO_y – Metal Oxide

M_x(OH)_y – Metal Hydroxide

M_xO_yH_z – Metal Oxyhydroxide

n_i – Quantity of Matter of *i* (mol)

NPT – National Pipe Taper

NMR – Nuclear Magnetic Resonance

OCV – Open Circuit Voltage

P_{6,6,6,14} – Trihexyl(tetradecyl)phosphonium

PEEK – Polyetheretherketone

PEIS – Potentiostatic Electrochemical Impedance Spectroscopy

PTFE – Polytetrafluoroethylene

ppm – Parts Per Million

R – Perfect Gas Constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)

RHE – Reversible Hydrogen Electrode

SCE – Standard Calomel Electrode

SEI – Solid Electrolyte Interphase

SHE – Standard Hydrogen Electrode

TEM – Transmission Electron Microscopy

TFSI – Bis(trifluoromethanesulfonyl)imide)

THF – Tetrahydrofuran

TOF – Turnover Frequency (s^{-1})

ToF-SIMS – Time-of-Flight Secondary Ion Mass Spectrometry

$U_{Ox/Red}^0$ – Standard Electrochemical Potential of a Redox Couple Ox/Red

U_{ce} – Counter Electrode Electrochemical Potential

U_L – Limiting Potential for a Transformation to Occur (V vs. SHE)

$U_{Ox/Red}$ – Electrochemical Potential of a Redox Couple Ox/Red

U_{RHE} – Reversible Hydrogen Electrode Electrochemical Potential

U_{we} – Working Electrode Electrochemical Potential

V_i – Volume of i (μl , ml, l or m^3)

v/v – Parts Volume by Volume

$\bar{x}$ – Mean Value for x

XPS – X-ray Photoelectron Spectroscopy

ΔG_i – Variation in Free Energy of Species i (eV)

Chapter 1. Introduction

This thesis is one of many stories of how to –or on many occasions how not to– fixate nitrogen from the air, in a sustainable and accessible fashion. Nitrogen is part of a chemical cycle that includes inert molecular N_2 and more reactive ‘fixated’ species such as NH_3 or NO_x (see Figure 1). I will aim to convince the reader that mastering this ‘nitrogen cycle’ is a challenging but essential task for humanity. Indeed, all of us have a huge reservoir of nitrogen above our heads. However, a reason we have so much nitrogen is that it sits comfortably in the form of a highly stable molecule of N_2 . Breaking down N_2 central triple bond is the key to making it practically useful, but a longstanding challenge. We will first see how intertwined life on earth and the nitrogen cycle are, how civilisation wanted (and managed) to do it faster and bigger in the past century and what heights it took us as a society (section 1.1). Despite the clear benefit artificial nitrogen fixation has brought us, it played a large part in the age we call Anthropocene: the geologic era where humanity altered the climate by our development and activities, releasing greenhouse gases in amounts significant enough to make our environment more hostile to ourselves (section 1.2). This last item is the reason to be of the research presented here. Multiple strategies are expected to target this issue and fixate N_2 more sustainably (section 1.2.2). In this thesis, I will explore one of them, a direct electrochemical route for N_2 reduction to ammonia. I will discuss the fundamental challenges of this reaction (section 1.3), recent progress made in the field to understand/improve it and highlight the remaining challenges ahead (section 1.4). I will finally dive into the research avenues I took to address these, and finish with prospects for electrochemical nitrogen reduction and global nitrogen fixation in a circular society (Chapter 6).

1.1. The Permanent Challenge of N_2 Activation

1.1.1. The Pivotal Role of Nitrogen in Nature

Nitrogen is –alongside oxygen, carbon, phosphorus and sulphur– a building block of life. It is the most abundant element of the five ($\sim 4 \cdot 10^{21}$ g),¹ and is found in all essential drivers of life, such as ATP (Adenosine Triphosphate, universal biological energy carrier), chlorophyll (pigments for photosynthesis), and all amino acids (building blocks of the DNA). However, it is mainly present in our atmosphere in the form of inert N_2 gas. Its fixation into more reactive nitrogen species is needed for life to thrive on earth.² The prevalence of N_2 in air (~ 78 %) is a hint to its inertness, and its activation

is challenging (triple bond dissociation energy of 945 kJ.mol^{-1} at 298K).³ Nevertheless, nature has found ways to do so, harnessing the power of electric arcs from lightning to convert it to reactive NO_x ,⁴ or designing nitrogenase enzymes capable of producing ammonia from N_2 (section 1.3.3).^{5,6} These transformations are part of a global scale cycle, where biological nitrogen fixation, on land and at sea, atmospheric chemistries, and denitrification (process of converting reactive nitrogen back to N_2 or N_2O) all take part in cycling nitrogen across the globe and all living systems at different magnitudes and time scales (Figure 1). We shall get back to this very cycle in more detail at the end of the manuscript (section 6.3).

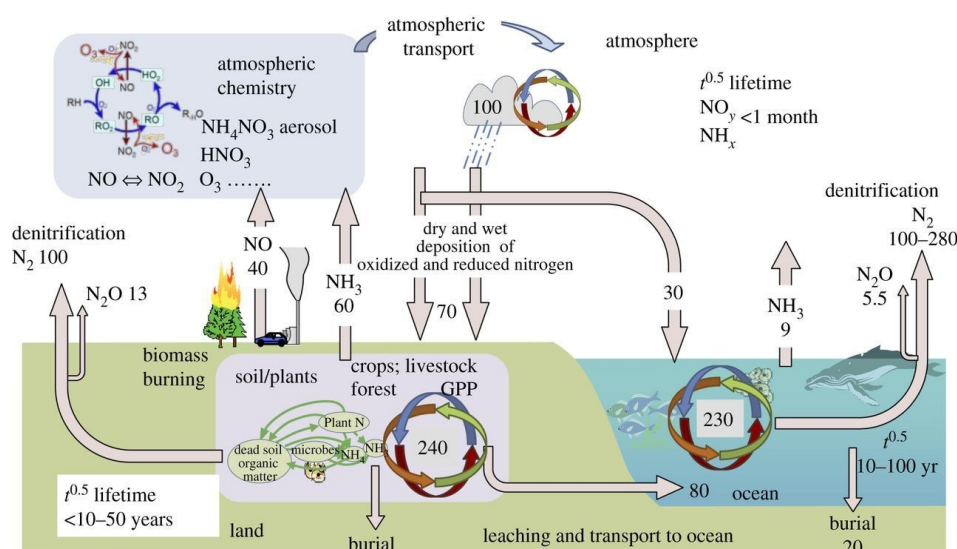


Figure 1. Global overview of the nitrogen cycle, with reactive nitrogen species fluxes identified by their nature (N_2 , NO_x , NH_3 , N_2O , ...) magnitude ($\text{Tg}_\text{N}.\text{y}^{-1}$) and lifetime ($t^{0.5}$ in years) – reproduced with permission from Fowler et al.⁷, © 2013 The Author(s) Published by the Royal Society. All rights reserved.

Human life needs nitrogen too and does not circumvent this principle. We need reactive nitrogen to grow crops and sustain our society. In fact, providing enough food for one's country was the greatest challenge of the 19th-20th century as a food crisis was being projected.⁸ Developed nations started exploring the world for reservoirs of fertiliser they could harvest and use to feed their populations. South American and European nations started competing over the coasts of Peru and Chile for sinks of biologically fixed nitrogen, whether it was *caliche* or *salitre* (sodium nitrate) harvested in the deserts of Atacama and Tarapacá, or *guano* (bird manure) on the Chinchas Islands.⁹ However, only the wealthiest nations at the time could access and fight over such resource, and even then, it was not enough. Countries that did not have a powerful enough marine fleet had to resolve to their own strengths. Germany, for instance, found solace in its strong scientific community.

1.1.2. Haber Bosch – Feeding the World

In the 1800s, Germany was no colonial empire with a strong marine fleet like the United Kingdom or France were at the time. However, what Germany had was great scientists. When in 1898, Sir William Crookes gave his speech on a possible food crisis by the next century, he called for scientist to solve it saying that *“it is the chemist who must come to the rescue of the threatened communities. It is through the laboratory that starvation may ultimately be turned into plenty.”*⁸ German scientists such as Walther Nernst or Wilhelm Ostwald understood the assignment and tried to fixate and make use of this huge reservoir of N₂ we have, but it is Fritz Haber who developed a laboratory process capable of producing ammonia from its constituting elements. Fuelled by politics of economic independence and territorial expansion, and with the help of the growing chemical industry in Germany, Fritz Haber and Carl Bosch took this process to a scale never seen before in the industry. The writings of Thomas Hager convey this scientific, political and human story way better than I would, and I strongly recommend reading it for more details on the subject.⁹

These are the origins of the Haber-Bosch process as we know it. This process converts N₂ and H₂ (H₂ being produced by steam-methane reforming and water gas shift) into NH₃ at high temperatures (>300°C) and pressures (>200 bar) (Figure 2a), in the range of 150-180 Mt.y⁻¹,¹⁰⁻¹² of which 80 % go to fertiliser production,^{13,14} and the rest to produce all sorts of synthetic N-containing molecules (explosives, polymers, pharmaceuticals, ...).^{14,15}

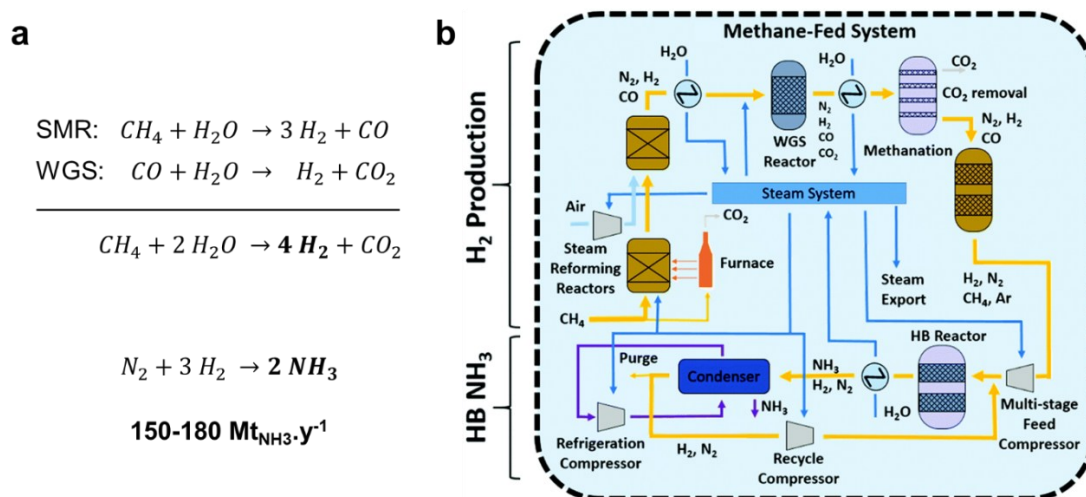


Figure 2. Process for Ammonia Synthesis by Steam-Methane Reforming, Water Gas Shift and Haber Bosch Nitrogen Reduction. (a) Reaction equations for the generation of hydrogen by steam-methane reforming (SMR), water gas shift (WGS) and subsequent production of ammonia via the Haber-Bosch

process. (b) Typical ammonia synthesis plant diagram, displaying heat integration between SMR-WGS and Haber Bosch nitrogen fixation. Yellow arrows represent process gases flows, blue arrows represent water and steam ($\sim$ energy fluxes), purple arrows are for ammonia – Reproduced with permission from Smith et al.¹⁰, © The Royal Society of Chemistry 2020.

Nitrogen reduction to ammonia operates here in a highly integrated process. With heat and mass management perfected over about a hundred years (Figure 2b), decreasing energy use from $60 \text{ GJ.t}_{\text{NH}_3}^{-1}$ in the 1950s to now $27.4\text{--}31.8 \text{ GJ.t}_{\text{NH}_3}^{-1}$, or 62–65 % energy efficiencies, close to the thermodynamic limit ($28.0\text{--}32.6 \text{ GJ.t}_{\text{NH}_3}^{-1}$) hydrogen generation included.¹⁰ Despite the process development spanning over two world wars where it had a significant role, it is the reason half the global population is standing today (Figure 3), and people *who can access ammonia* do not starve anymore.¹⁶

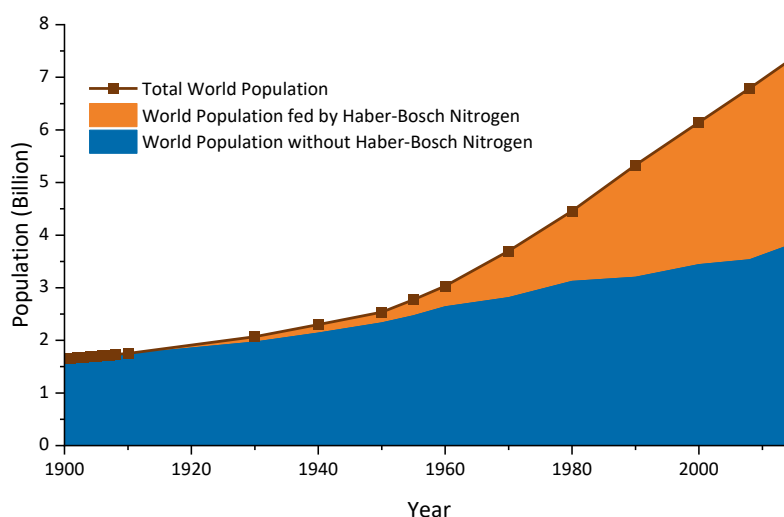


Figure 3. Evolution of the global population over time, and comparison with the expected population capable of living without the Haber-Bosch process – Adapted with permission from Erisman et al.¹⁶, © 2008 Springer Nature Limited.

It is almost good timing to emphasise on the fact that not everyone has access to ammonia derived fertiliser despite the scale of this process, and I will expand on this issue shortly (section 1.2.2). However, another not so well-hidden issue with the Haber Bosch process as it is today lies in the reaction equation written in Figure 2a. There is a side product to all molecules of ammonia produced: CO_2 , and it matters.

1.2. The Way We Fixate Nitrogen Matters

1.2.1. Pushing for Climate Change

I imagine that the reader is already familiar with the carbon cycle, and how human activity disturbed it quite significantly. We release huge amounts of greenhouse gases (e.g. CO_2 , CH_4 , ...) in our atmosphere, every year more than the last, now reaching ~50 billion tons of CO_2 equivalents a year.¹⁷ So much that we are now the main driver for climate change, having increased global mean temperature by 1.1°C since pre-industrial levels, and still going on a path to $+1.5^\circ\text{C}$ by 2030-2050,¹⁸ and up to $+3^\circ\text{C}$ by 2100,¹⁹ which is alarmingly far beyond the target to be reached (Figure 4a).²⁰

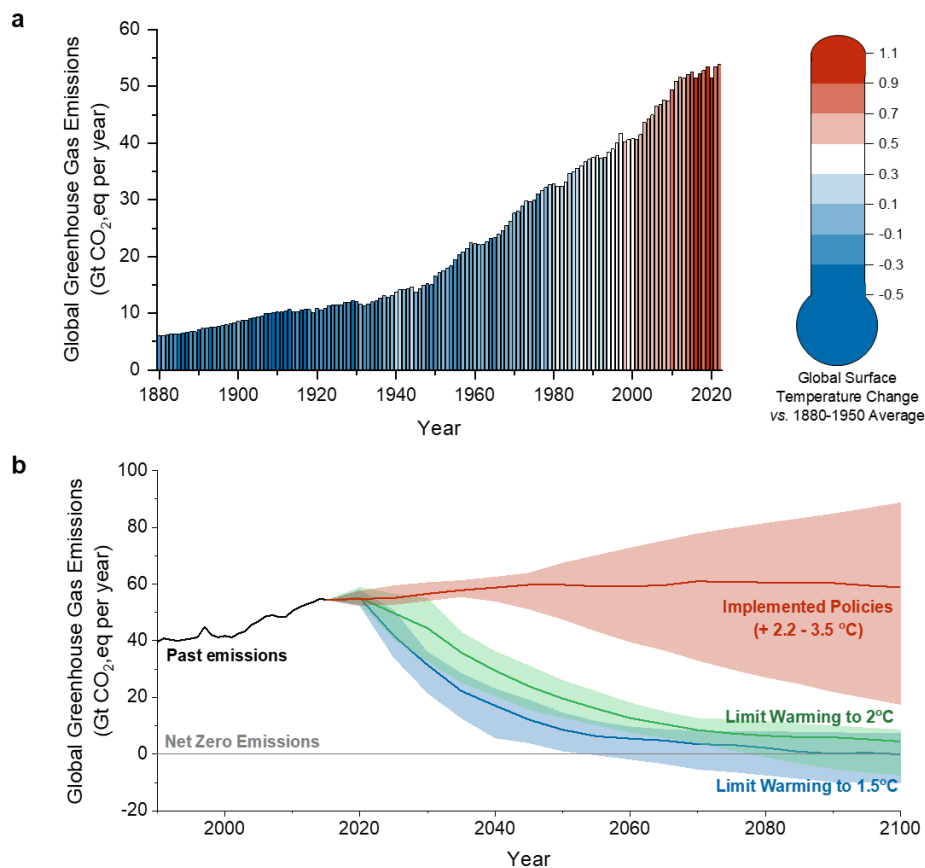


Figure 4. Greenhouse gas emissions over time and their impact on global rising temperatures. **(a)** Global emissions increasing in direct correlation with a global surface temperature increase (colour scale from lower to higher temperatures in blue to red, respectively), with a steep increase to up to $+1.1^\circ\text{C}$ vs. a 1880-1950 average in the past 20 years. **(b)** Past and projected global greenhouse gas emissions with different scenarios depending on implemented policies. Currently implemented policies

may lead to an increase in temperature between 2.2 and 3.5 °C (red line, error range in clear red). Projected paths of greenhouse gas emissions reduction needed to reach a target of +2 °C (green) or +1.5 °C (blue). – Reproduced with permission from the IPCC 6th annual report²¹, © The Intergovernmental Panel on Climate Change.

The International Panel for Climate Change (IPCC) 6th annual report urges the world to limit such increase in temperature to less than +1.5 °C to mitigate the effects of a changing climate on our planet; that means cutting emissions drastically, and fast (Figure 4b). A local increase in temperature of 1 °C may not sound like much, but at the scale of the planet, it is colossal. The IPCC 6th annual report insists on how the future emission rates will affect the extent to which our climate will degrade. Any increase in greenhouse gases in the atmosphere will increase global surface temperature, and that will have dramatic consequence on many levels. Figure 5 summarises some of the most striking effects expected from a global increase in temperatures, including more frequent and intense heatwaves, risk of large biodiversity loss, significant losses in crop yield, more areas becoming uninhabitable to humans and most animals, disruption in soils humidity and so on. I used the future tense until now, but this is already happening, here are a few examples. In the past 20 years, the water cycle has been disturbed so much that droughts and heavy rains have increased in frequency, length and intensity in all regions of the planet.²² Wildlife (represented by 32,000 populations of 5,230 animal species across the globe) is estimated to have declined by 69 % between 1970 and 2018.²³ Hurricanes have increased in intensity due to sea surface temperature increasing.²⁴

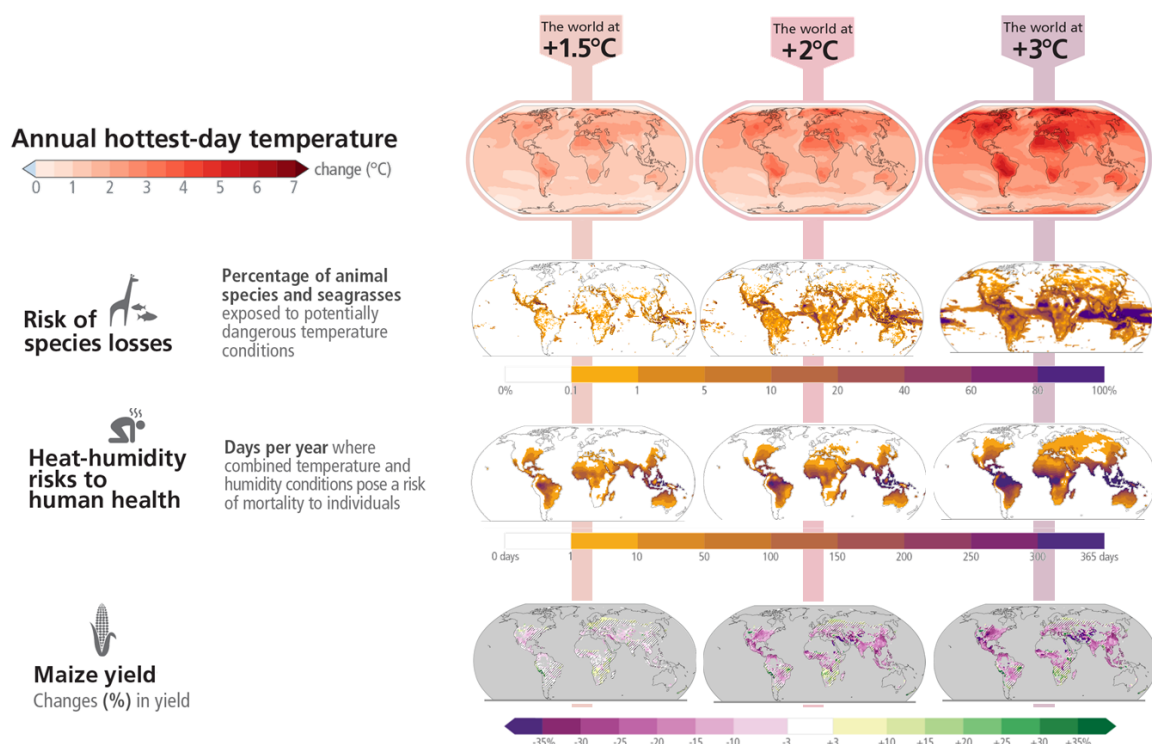


Figure 5. Projected environmental impacts of an increase in global surface average temperature of +1.5 °C, +2 °C and +3 °C. Every step in temperature may result in, from top to bottom: higher annual hottest day temperatures, up to +7 °C compared to a 1880-1950 average ; increase in species confronted to a risk of extinction, up to 90 % in tropical regions ; increase in days in the year where heat and humidity will jeopardise human life, up to having regions uninhabitable all year long ; decrease in maize crop yields, down to –35 %. – Reproduced with permission from the IPCC 6th annual report²¹, © 2024 The Intergovernmental Panel on Climate Change.

Tackling the source of our emissions is therefore an imperative. Going back to our favourite molecule, this is where current ammonia production falls short. Ammonia production units are the largest producers of greenhouse gases among commodity chemicals because of their nature and scale (Figure 6a). They consume 2 % of the global energy supply and are responsible for ~1 % of the global emissions.^{15,25} This is equivalent to 500 Mt CO₂ being released in the atmosphere every year, potentially increasing to 1300 Mt a year by 2050 if the production streamline is not changed.¹⁵ These emissions are largely due to H₂ production from steam-methane reforming and water gas shift,^{10,26} where 75 % of the total energy needed to produce ammonia is used,¹⁵ but the Haber Bosch process, operating in energy-intense centralized units at > 150bar and > 400°C, is a significant contributor as well (contributes to ~20 % of the whole process emissions, Figure 6b).^{10,25} So how are we going to fixate nitrogen tomorrow?

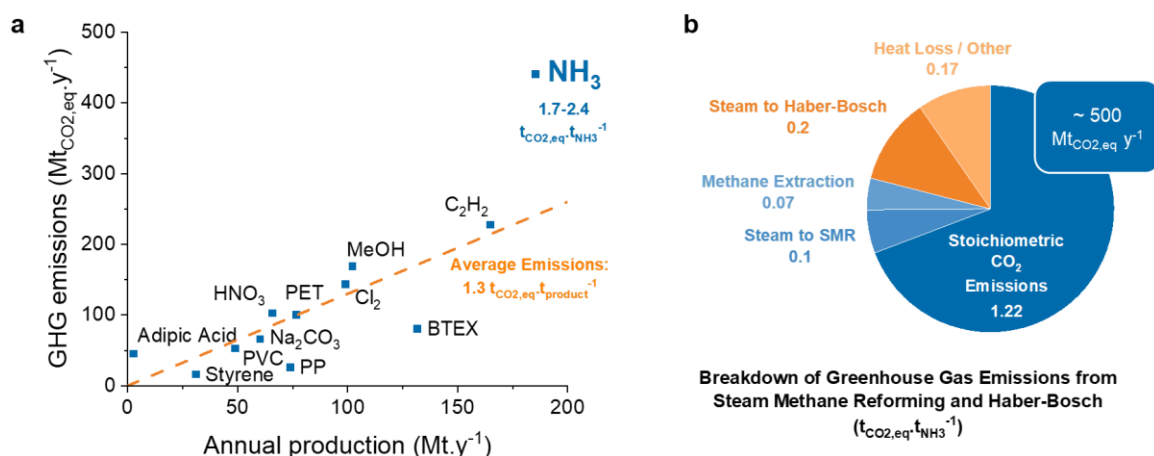


Figure 6. Greenhouse gas (GHG) emissions from commodity chemicals production. **(a)** Emissions of main commodity chemicals, plotted against their rate of production, highlighting ammonia as the largest source of greenhouse gas in the chemical industry.¹² **(b)** Breakdown of emissions from ammonia synthesis by step of the process. Emissions related to Steam Methane Reforming – Water Gas Shift (blue) account for most of the footprint, but ~20 % of the emissions are caused by the Haber Bosch process itself (orange). – Reproduced with permission from Smith et al.¹⁰, © The Royal Society of Chemistry 2020.

1.2.2. Making Ammonia Tomorrow

1.2.2.1. Green Hydrogen Coupled to Haber Bosch – Patching the Carbon Cycle

The energy industry's electrification is a key leverage for the implementation of renewables in our society. Electrochemical H₂ production from water holds great promises in this regard.²⁷ On top of offering a sustainable alternative to methane derived H₂, electrochemically synthesized H₂ can be used as an energy carrier, capable of balancing the electricity grid which is impaired by a fluctuating renewable energy supply. Most occidental political strategies now largely rely on this aspect for decarbonizing the energy and transport sectors.^{28–30} For this reason, operating the Haber-Bosch process with “green” H₂ will probably provide a low-carbon pathway for ammonia production in the nearer future, and play a key role in achieving net-zero emissions by 2050.³¹

However, the Haber-Bosch is a highly integrated process operating at steady state, high temperatures and pressures. This creates three issues. First, it will be difficult to balance it with the dynamic nature of renewable power without a supporting energy storage device. Where electrochemical H₂

production can be turned on and off relatively rapidly (at least in some specific technologies), ramping up and down the temperature and pressure of the Haber-Bosch system isn't as flexible.¹⁰ The strong process integration between steam-methane reforming – water gas shift and Haber-Bosch make it hard to have the latter work without the other, taking steam-methane reforming – water gas shift off the equation and replacing it with water electrolysis means rethinking the process at the whole plant level.^{10,15} The second and third issues lie in the economies of scale associated with this process. Only in the places that can afford to build massive production units can this process be run economically, resulting in highly uneven distribution of ammonia production across the planet (Figure 7a)³². This means that places for which fertiliser transport from the production units is too expensive cannot grow enough food to feed their population, as illustrated by the Global Hunger Index (Figure 7b).³³ It also means that it is fairly easy to overuse nitrogen fertiliser in the areas where it is produced at low cost (Figure 7c). This in turn has devastating effects on our soils and atmosphere, which will be discussed in more depth in section 6.3.

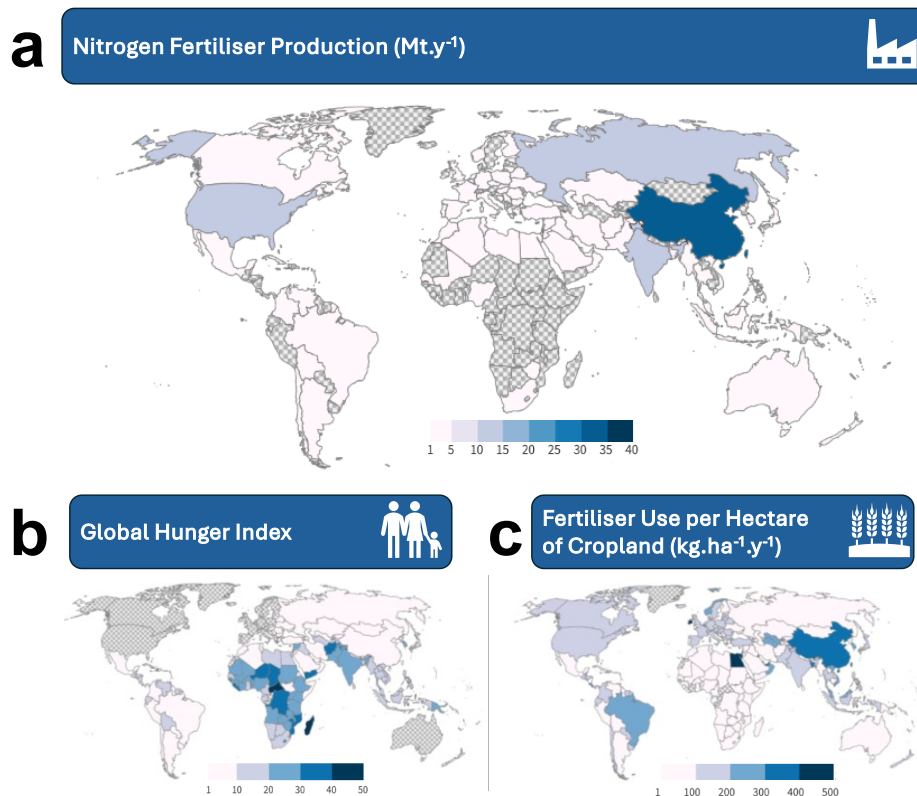


Figure 7. Maps of Nitrogen fertiliser production and utilisation across the world. Correlations between (a) the annual production of nitrogen fertiliser³² (b) the global hunger index,³³ where the places that cannot afford to produce nitrogen fertiliser suffer from low nutrition to starvation, and (c) the use of nitrogen fertiliser per hectare of cropland where oversupply of nitrogen pollute soils.³²

For the three above reasons, downsizing and decentralisation is key in feeding *all* the world (and not only the world that can afford it), in a sustainable fashion.

1.2.2.2. *Direct Decentralised N_2 electrolysis – Fixed Nitrogen, Everywhere*

Decentralised production cannot be achieved through water electrolysis and Haber-Bosch at its current state of the art, and the greenhouse gas emissions directly related to Haber-Bosch will remain. In addition, there is one more incentive to the delocalisation of the production: safety. Many products derived from ammonia are flammable or explosive (hydrazine, ammonium nitrate, ...), and can cause devastating incidents when stored in large quantities, as experienced in France (Brest, 1947) or Lebanon (Beirut, 2020),³⁴ raising concerns just as I write these words as a damaged cargo is docking in a British dock with seven times the amount that exploded in Beirut.³⁵ Co-reduction of protons and nitrogen to ammonia in a single electrochemical cell (Figure 8), is an attractive alternative for production at point of use, effectively decentralising the production of ammonia and offering safe and cost-effective access to carbon-neutral fertiliser for all.

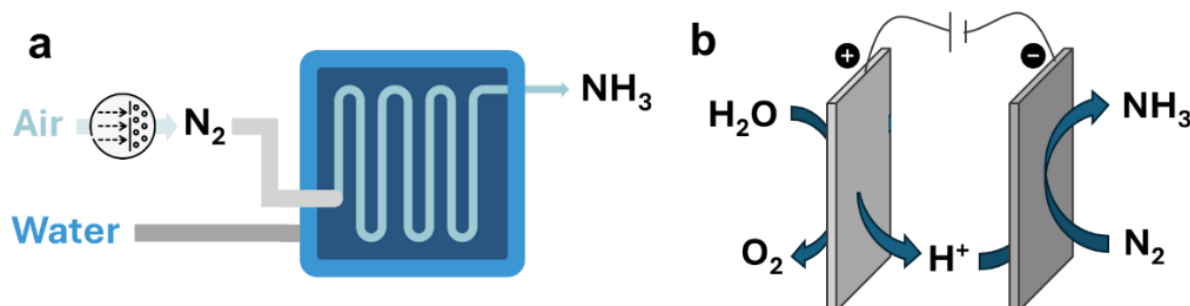
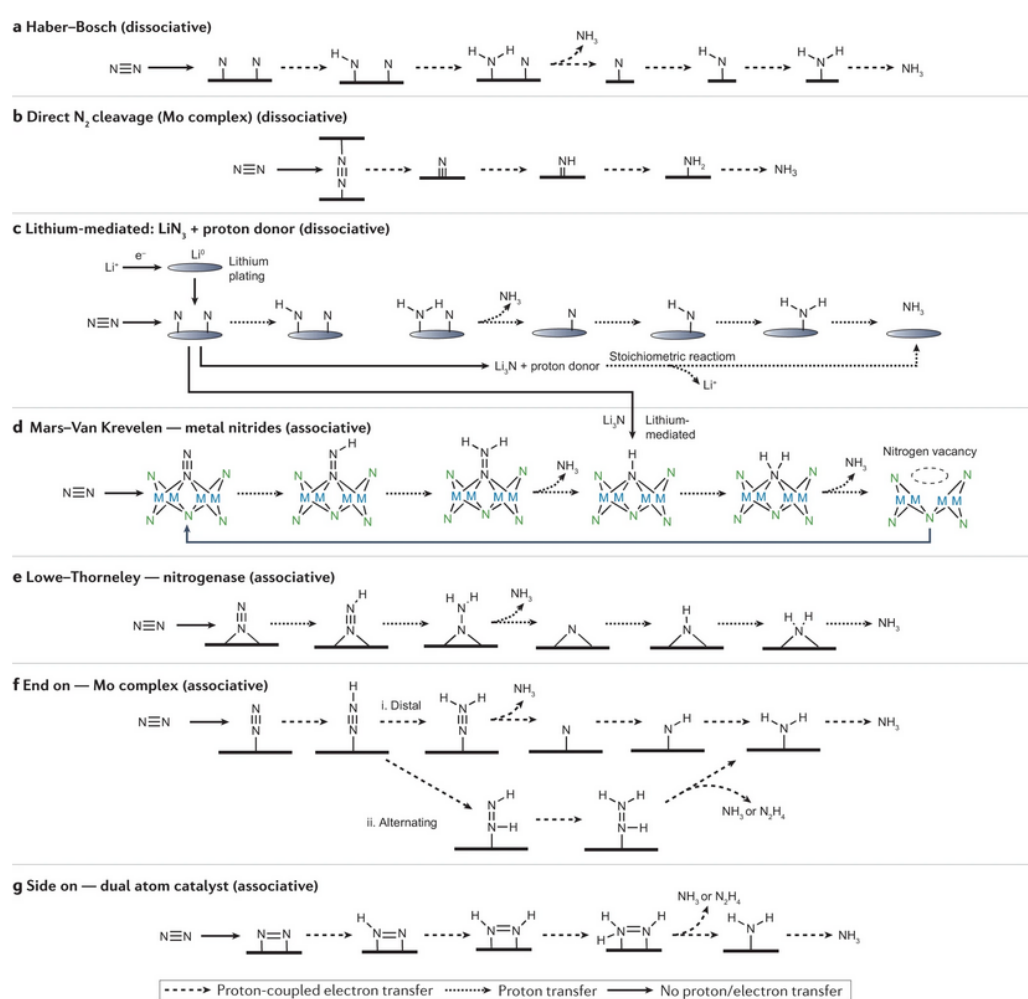


Figure 8. Electrochemical nitrogen reduction to ammonia concept. (a) Schematic process to produce ammonia and nitrogen fertiliser from N_2 (air) and H^+ (water) in an electrochemical cell. (b) Diagram of an electrochemical cell through which electric current is passed, oxidising water to oxygen on the positive electrode, releasing protons that may be transferred to the negative electrode and combined to nitrogen by reduction to ammonia.

1.3. A New Challenge of Nitrogen Fixation

1.3.1. The Many Mechanisms of Nitrogen Reduction to Ammonia

Nitrogen can undergo reduction to ammonia via many pathways. Single steps can describe these mechanisms, such as nitrogen adsorption, N-N bond cleavage, proton-coupled-electron-transfer steps (where one proton is transferred alongside an electron), and products desorption. However, the order and recurrence of these steps defines the sequence of intermediates being formed and consumed, and therefore the overall mechanism (Scheme 1).



Scheme 1. The various mechanisms of electrochemical nitrogen reduction, including a dissociative mechanism (a Haber-Bosch type, b Molecular Mo complexes, c Li-mediated) or associative (d Mars-von-Krevelen, e Lowe Thorneley, f End on, g Side on). Reproduced with permission from Westhead et al.³⁶ © 2023 Springer Nature Limited.

The mechanism is said to be dissociative if the N_2 triple bond fully breaks before hydrogenation (Scheme 1a,b,c)^{37–39}, and associative if the first proton coupled electron transfer occurs before N_2 cleavage (Scheme 1d,e,f,g). In the latter, the geometry of nitrogen binding to the catalyst can vary as well. It can experience a Lowe-Thorneley mechanism typically speculated in nitrogenase catalysis where a single N atom bridges two active centers (Scheme 1e).⁶ An end-on binding where only one nitrogen atom binds to the metal catalyst (Scheme 1f) is often observed on molecular metal complexes or nitrogenase where hydrogenation can happen one nitrogen at a time (distal)^{40–42}, or sequentially on both N atoms (alternating)^{5,43}. It can finally be a side-on binding where each N atom is bound to a metal centre (Scheme 1g).^{44,45} Alternatively, more exotic mechanisms involving metal nitrides add up to the list. These catalysts are suggested to follow the Mars-von-Krevelen mechanism, where N_2 is a ligand to the catalyst, which upon reduction to ammonia results in a metal with a nitrogen vacancy ready to accept a new substrate.⁴⁶ The lithium mediated nitrogen reduction, which will be the subject of this thesis, is an interesting case where the mechanism is not known yet, but is hypothesised to follow either that same associative Mars von Krevelen mechanism, a dissociative one or a competition of the two.^{39,47,48}

The take-home message from this mechanistic promenade is that it is vital to understand which mechanism is involved in the system under study to improve it. Because it is a multi-step process, the reasons for the sluggish kinetics of N_2 reduction can be multiple, and it is still a challenging question. Is it limited by reagents and products adsorption/desorption or diffusion, N_2 bond splitting or even by the competition between charge transfer and proton activity?

1.3.2. A Selectivity Challenge

1.3.2.1. *False Positives*

Electrochemical N_2 reduction is a fast-expanding field. However, it is plagued by false positives.^{49–51} Indeed, most studies disclose detected ammonia at ppb levels, below likely ammonia contamination levels. Such contamination can occur in two ways:

Direct Contamination: This happens when ammonia is already present in the system before electrolysis, such as in the electrolyte components, materials used, feed gas, lab atmosphere, or even human breath. Ammonia is present in the atmosphere in varying quantities (1-250 ppm),⁵² and its absorption can alter quantification. This contamination can be reduced by working under a controlled

atmosphere, purifying the feed N_2 gas, and measuring ammonia concentration in non-electrolysed samples.

Indirect Contamination: This is more challenging as it occurs when nitrogen-containing species (NO_x , N_2H_4 , nitrides ...) present in the catalyst, cell materials, electrolyte component, or gas feed are reduced to ammonia during electrolysis. These sources of nitrogen can be reduced to ammonia more easily than N_2 , falsely increasing efficiency as more ammonia is detected after electrolysis.⁵¹ Researchers may not always be aware of these contamination sources, leading to inaccurate results.

Proving unequivocal reduction of N_2 to NH_3 is therefore a challenging task. Using rigorous protocols based on isotopically labelled $^{15}N_2$ reduction experiments, several laboratories have disclosed such false positives,^{49–51} and only a handful of systems were proven to work; the lithium-mediated ammonia synthesis which dominated the field and will be the topic of Chapter 3 and Chapter 4,^{49,53} and much more recently calcium-mediated^{54,55} and magnesium-mediated^{55,56} alternatives, which will be the topic of Chapter 5.

1.3.2.2. *The Hare and the Tortoise, the Remake – When H^+ and N_2 Compete*

Consider the negatively charged electrode at which one would want nitrogen reduction to occur. Like other surface-catalysed reactions, the maximum activity of a catalytic reaction is limited by the relative rates of adsorption and desorption of reagents, intermediates, and products, resulting in volcano-like plots (Figure 9b)⁵⁷. This is Sabatier's principle in action: a surface that binds too weakly won't allow reagents to coordinate (Figure 9b right slope, Figure 9a example of Cu)⁵⁷, and a surface that binds too strongly will be poisoned by immobile reaction products (Figure 9b left slope, Figure 9a example of W)⁵⁷. Some of these intermediates binding energies end up being correlated, sometimes in a way that prevents access to maximum catalytic activity⁴². These so-called linear scaling relations can be observed for instance by plotting the binding energies of late reaction intermediates against early ones (Figure 9c, theoretical maximum in red region)⁴². This illustrates the balance needed for optimal activity, but also the need to break free from such scaling relations to get closer to the theoretical maxima.

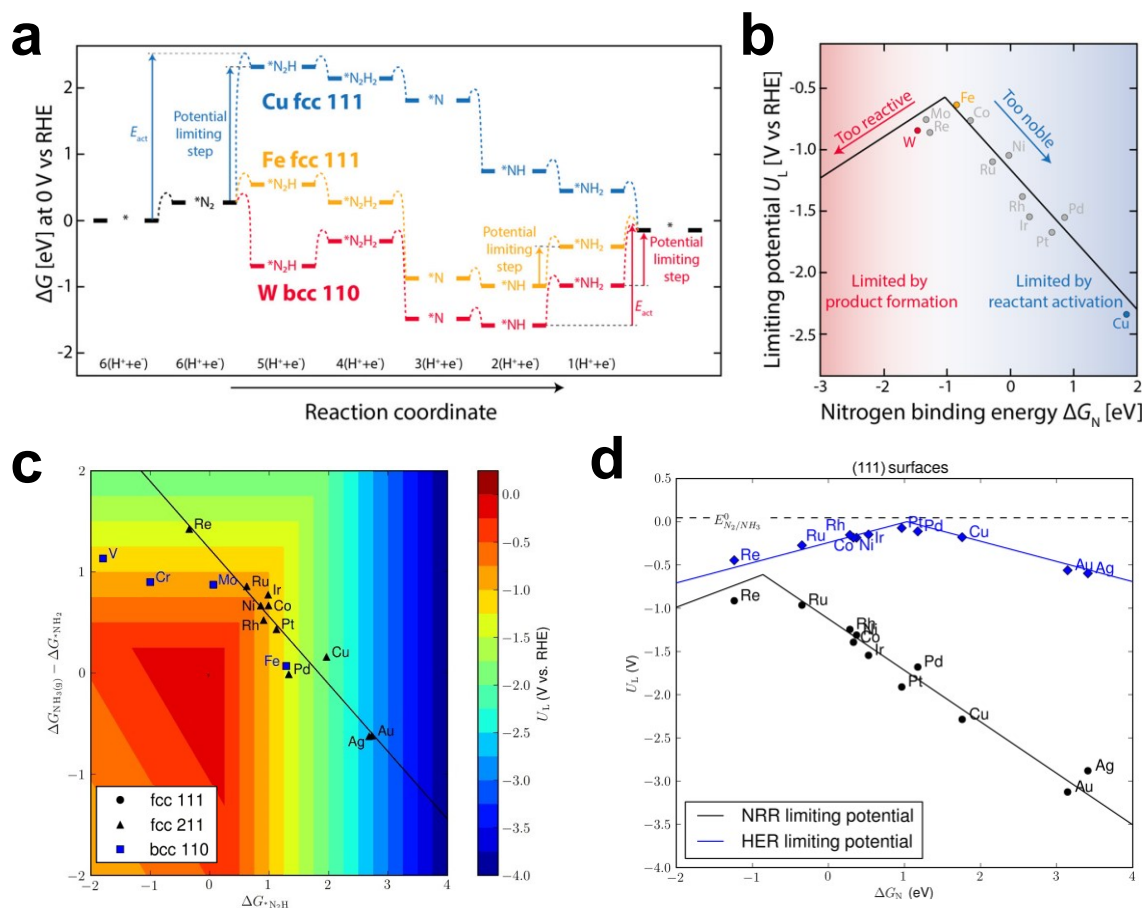


Figure 9. Linear scaling relations in nitrogen reduction. **(a)** Examples of free energy diagrams for electrochemical ammonia synthesis, illustrating cases limited by too strong (W, red) or too weak (Cu, blue) nitrogen binding energy, or in an ideal balanced case (Fe, yellow). **(b)** Volcano plot of the nitrogen reduction reactions limiting potential vs. RHE, plotted against nitrogen binding energy, illustrating the Sabatier principle limiting nitrogen reduction rates through a balance in binding energy strength. **(a)** and **(b)** reproduced with permission from Kibsgaard et al.⁵⁷ © 2019 American Chemical Society **(c)** Scaling relation between the change in binding energy from $*NH_2$ to $NH_{3(g)}$, and $*N_2H$ binding energy, locked away from a theoretical maximum (red zone). **(d)** Volcano plots of the nitrogen reduction (NRR, black) and hydrogen evolution (HER, blue) reactions limiting potential vs. $*N$ binding energy; showing hydrogen binding will always be favoured (vs. nitrogen binding) on a metal surface. – **(c)** and **(d)** Reproduced with permission from Montoya et al.⁴² © 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

So why is it that, among all the reported catalytic systems, most did not work? This is again a problem of competitive binding. As calculated by Montoya et al. in Figure 9d, $*H$ always adsorbs more easily than $*N$ does.⁴² The surface gets poisoned with $*H$ and all the catalyst ends up doing is reducing $*H$ to

hydrogen rather than making ammonia. Most electrochemical ammonia synthesis reports previously disclosed must have encountered that issue, where an aqueous electrolyte with high proton activity must have overloaded the electrodes and poisoned them, preventing nitrogen activation. How can we overcome this challenge?

Here is a poem every single pupil in French (and British so was I told) schools learns once, “The Hare and the Tortoise” by Aesop (later transcribed by Jean de la Fontaine who I thought was the original author!). A hare encounters a tortoise and mocks it for its slowness. The tortoise, flustered, challenges the hare on a race. Challenge accepted. Confident that it would catch up, the hare takes breaks, naps, chats with locals, etc. And before the hare realises, the tortoise got to the finish line first – “There’s no point in running, it’s about making it on time”.

What does it have to do with us? Well, the hare is your protons, and the tortoise is N_2 . To make ammonia, you need to slow down the protons on their way to your catalyst active site, leaving time for nitrogen to reach the finish line first.⁵⁸ This is what nature understood a long time ago and what the lithium-mediated ammonia synthesis is hypothesized to be about. We will now introduce briefly the ways of nitrogenase to favour ammonia synthesis, then dive in the concept of lithium mediated ammonia synthesis and the progress made until now.

1.3.3. How Nature Bypasses Scaling Relations

Enzymes called nitrogenases produce ammonia from nitrogen in living systems.⁵⁹ Although with non-unity Faradaic efficiency, they have a unique method to bypass the scaling relations that hinder this reaction. While this work doesn’t aim to detail the biological mechanism for nitrogen activation, it is crucial to comprehend and derive inspiration from nitrogenase due to its capability to promote NH_3 synthesis over H_2 . It was demonstrated that an isolated sample of the FeMo-cofactor (the active centre of nitrogenase) would favour H_2 evolution over N_2 reduction in the presence of protons with unrestricted access.⁶⁰ Nature’s catalyst therefore abides by the same scaling relations. However, nitrogenase isn’t just an isolated active site, but rather a metallic centre wrapped into an enormous bundle of proteins (Figure 10a), and the latter is key in regulating proton activity and steering selectivity toward NH_3 .

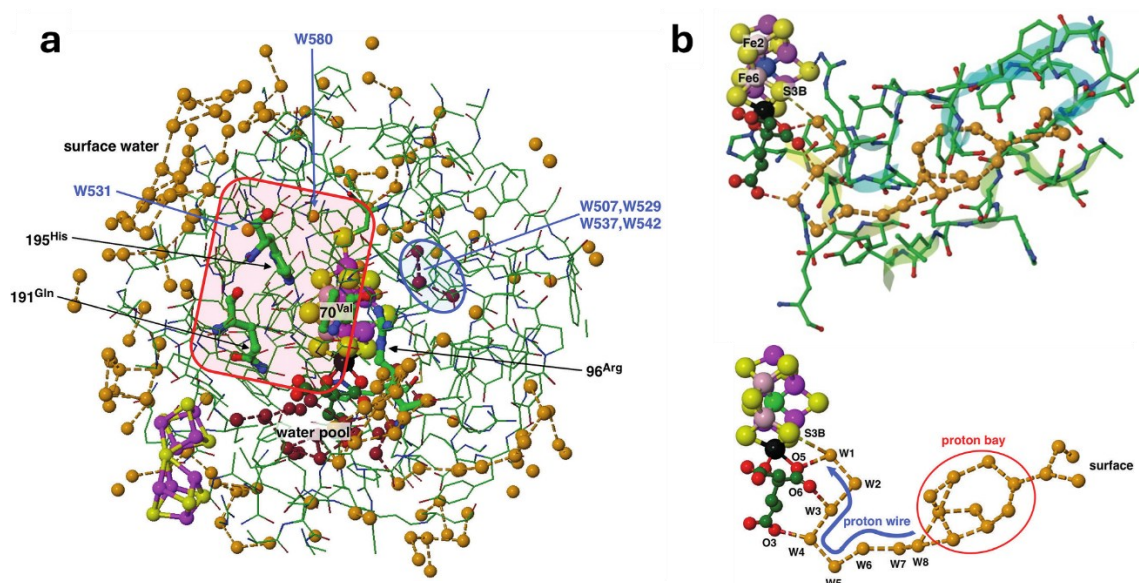


Figure 10. The nitrogenase enzyme. Structure of the FeMo-cofactor and its vicinity in *azotobacter vinelandii* nitrogenase as elucidated by X-ray diffraction of a crystallised protein. (a) FeMo-co domain surrounded by the hydrophobic peptide chain of the protein. All water molecules (orange) are kept away from the FeMo-co, apart from an aggregate in the centre: the proton wire. (b) Side-view of the proton wire connected to the FeMo-co, decorated with its peptide channel (top panel), or deprived from it for clarity (bottom panel). Color coding for atoms: purple, yellow, black, red, orange and green for Fe, S, Mo, O, water molecules and peptide chains, respectively. – Reproduced with permission from Dance⁶¹, © The Royal Society of Chemistry 2012.

The FeMo-cofactor active centre is buried within a hydrophobic matrix, strongly hindering water from accessing the catalytic center.⁶¹ According to this observation, it appears that no single water molecule can reach the catalyst, which is problematic since one also needs protons to fully convert N_2 to NH_3 . However, multiple studies have managed to crystallize nitrogenase proteins and decipher their structure by high resolution X-ray crystallography.^{60–65} By combining this data and studying the proteins structures, Dance reported the shared presence of a channel within the protein that accommodates for what he calls a proton wire (Figure 10b,c).⁶¹ He noted that mutation of the peptide chain in the vicinity of this proton wire leads to decreased performance, confirming its role in the efficiency and selectivity reached by nitrogenases. First suggested by Durrant,⁶⁰ this chain is a sequence of about 20 water molecules that progress through the hydrophobic mantle of the protein, directly connecting the FeMo-co to the protein surface. Going from the S3B position (one of the sulfur atoms close to the active centre), a chain of 8 water molecules goes towards the surface and meets a

larger interstice at the position W8 (Figure 10c), filled with interconnected water molecules creating a bay that further reaches the surface. The mechanism by which this proton wire feeds the FeMo-co with new water molecules, however, is quite original. It is at the S3B centre of the FeMo-co that a proton-pump system is triggered. By accepting an electron, the FeMo-co centre becomes more negatively charged and the S3B becomes more basic. This basic centre attracts a proton at the start of the wire, that migrates to the charged Fe centre, leaving a vacancy at its initial position. At this stage starts a chain reaction where protons further away get attracted one by one to fill the empty space left by the preceding through a Grotthuss mechanism. Consumption of a hydrogen atom to yield ammonia closes the cycle and leaves room for more protons to be drawn towards the active site.⁶¹ One key message for us, conveyed by ages of evolution leading to the structure of nitrogenase: the access of protons must be regulated to drive selectivity towards ammonia (here the hydrophobic shell and its proton wire).

1.4. Electrochemical Ammonia Synthesis Mediated by Lithium

1.4.1. Activating Nitrogen

Until 2019, the only verified systems able to reduce nitrogen to ammonia were nature's nitrogenase (in its natural environment)^{60,66} and some molecular complexes.^{38,40} However, on a solid electrode only the works initially disclosed by Fichter *et al.* in 1930,⁶⁷ and later developed by Tsuneto *et al.*^{53,68} were then validated by multiple groups using a rigorous ¹⁵N₂ isotope labelled protocol, using a lithium-mediated approach (Figure 11a).^{48,49,69}

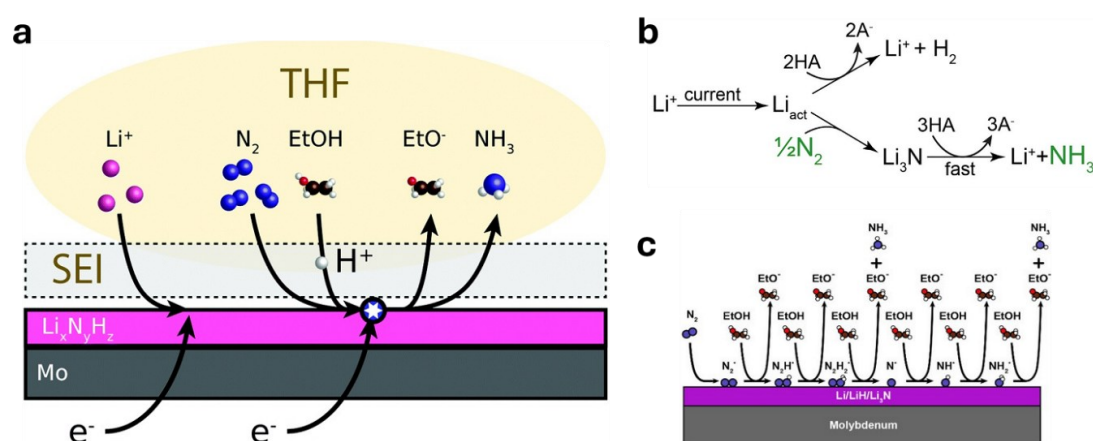


Figure 11. Seminal mechanistic studies of the lithium mediated N₂ reduction. (a) Concept of the lithium mediated ammonia synthesis at the reactive interface and solid-electrolyte interphase (SEI). (b)

Proposed dissociative reaction mechanism for selective ammonia synthesis over lithium involving lithium nitride. (c) Proposed associative reaction mechanism involving a mixed lithium hydride, nitride, imide and amide species – Reproduced from Lazouski et al.⁴⁸, and Schwalbe, Andersen and co-workers^{39,47} – Reproduced with permission from © The Royal Society of Chemistry 2020, © 2019 Elsevier Inc. and © 2020 Wiley-VCH Verlag GmbH.

This electrocatalytic system is special in the sense that the catalytic mediating surface for this reaction is made *in situ*. A lithium salt is dissolved in an aprotic solvent, to which is added a small amount of ethanol to provide protons for ammonia generation. The dissolved lithium salt is reduced to Li^0 upon application of a negative enough potential, creating the active surface for nitrogen to be reduced. Lithium metal is then able to react with nitrogen and protons in different possible orders and release ammonia. Different mechanisms could be at competition as discussed in section 1.3.1 (dissociative, associative, Mars von Krevelen). Several are proposed in the literature (Figure 11b and c), but a recurring observation is the presence of lithium nitride on the electrode, as measured by ex situ X-Ray Photoelectron Spectroscopy (XPS),⁷⁰ in situ X-Ray Diffraction (XRD)⁷¹ and *operando* X-Ray scattering.⁷² What happened to the fact that all catalytic surfaces will be poisoned with $^*\text{H}$ in an unrestricted environment? Should this not apply to lithium too? Let us go back to chemistry undergraduate classes. What happens if you drop a lithium metal chip in water? You will surely end up making lots of hydrogen (let aside risking burning the room if you put enough effort into it), but no ammonia. The reason why Fichter and Tsuneto managed to make ammonia on lithium is expected to be the same reason why (most) lithium batteries in your phone do not burn in your hands: the *solid-electrolyte interphase* (SEI).

1.4.2. The Solid Electrolyte Interphase - Keeping Protons at Bay

In some ways, the lithium-mediated ammonia synthesis is analogous to a lithium metal battery during its charging state. When the battery is being charged, lithium ions in a non-aqueous electrolyte are reduced to a metal on the negative electrode. This metal is highly reactive and will readily react with protons in water. In a battery containing a non-aqueous electrolyte, things are different: it will only partially decompose the electrolyte (solvent, anions, additives) to form a passivation layer, the so-called Solid Electrolyte Interphase or SEI.^{73–75} The SEI is a complex nm to μm scale layer at the interface between the electrode and electrolyte, which governs battery performance.⁷⁴ Different models are proposed to describe it (Figure 12),^{73,76,77} but it comes in all compositions and shapes.

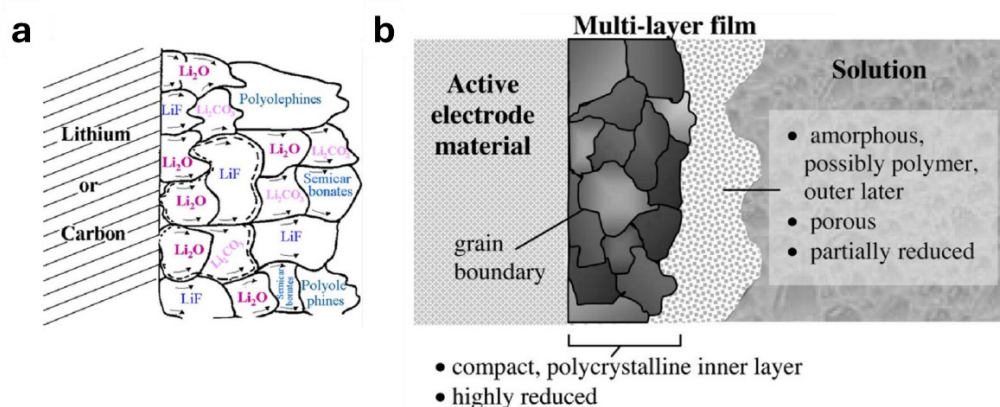


Figure 12. The solid electrolyte interphase coined structure. (a) mosaic and (b) double layer models for SEI composition – Reproduced with permission from Peled, Christensen et al.^{73,77} ((a) © The Author(s) 2017, published by ECS, and (b) © 2004 The Electrochemical Society.)

Made of different layers of compact inorganics (LiF , Li_2O , Li_2CO_3 , ...) and more flexible organics (alkoxides, oligomers, polymers, ...), the SEI offer a range of properties that stabilise reactive Li metal, prevent continuous electrolyte degradation and eventual cell death.^{73,77–79}

- **Electronic insulation** – Electron transfer to the electrolyte leads to uncontrolled degradation, SEI thickening, up to a complete blockage of ion migration to and away from the electrodes.
- **Uniform and fast Li-ion transport** – Ions must be well distributed at the surface of the charged electrode, to plate Li evenly and avoid charge build-up or Li dendrites formation.
- **Electrochemical stability** – SEI formation consumes charge and must be stabilised.
- **Mechanical stability** – Volume changes during battery cycling can lead to cracking.

Coming back to ammonia, this interphase is expected to modulate the access of reactants to –and products away from– the active lithium surface (Figure 13a).

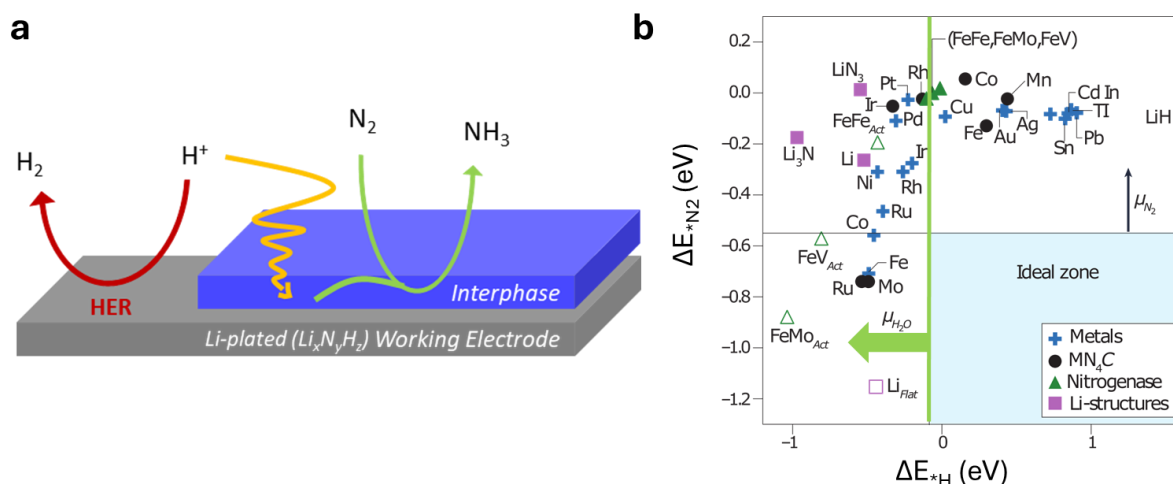


Figure 13. A solution to the selectivity issue in nitrogen reduction to ammonia. (a) Li-mediated nitrogen reduction to ammonia, where the solid electrolyte interphase (in blue) is hypothesised to mitigate the access of reactants and products to and from the active surface to make ammonia selectively, slowing down protons on their way to the active surface, lowering their local chemical potential. (b) $^*\text{N}_2$ binding and $^*\text{H}$ binding energies plotted against each other, showing that no single metal can bind $^*\text{N}_2$ better than it binds $^*\text{H}$, and only when a barrier to $^*\text{H}$ binding is included (reducing the chemical potential of $^*\text{H}$ at the electrochemical interface, green arrow) can a catalyst operate in conditions favourable to selective nitrogen reduction to ammonia. – Reproduced with permission from Westhead et al.³⁶ © 2023 Springer Nature Limited.

It is under hot debate whether the criteria for a SEI yielding selective ammonia synthesis are the same as the ones coined for a SEI providing good battery operation.^{70,80–84} Nonetheless, the point is this SEI is also a key player in tailoring reactivity of nitrogen reduction to ammonia. While it is still easier to bind $^*\text{H}$ than it is to bind $^*\text{N}$, this regulating SEI combined with the low proton activity in these non-aqueous electrolytes lowers the chemical potential of protons (Figure 13b, green arrow) so much that it provides a working environment for lithium to make ammonia from its constituent elements.

1.4.3. What is a Good Interphase for Ammonia Synthesis?

The SEI composition is largely derived from the nature of the electrolyte used, and huge progress has been made in tailoring such electrolytes to reach high coulombic efficiencies, defined by the ratio of charge capacity during discharge to the charge capacity of a battery during a single cycle (Figure 14).⁷⁴

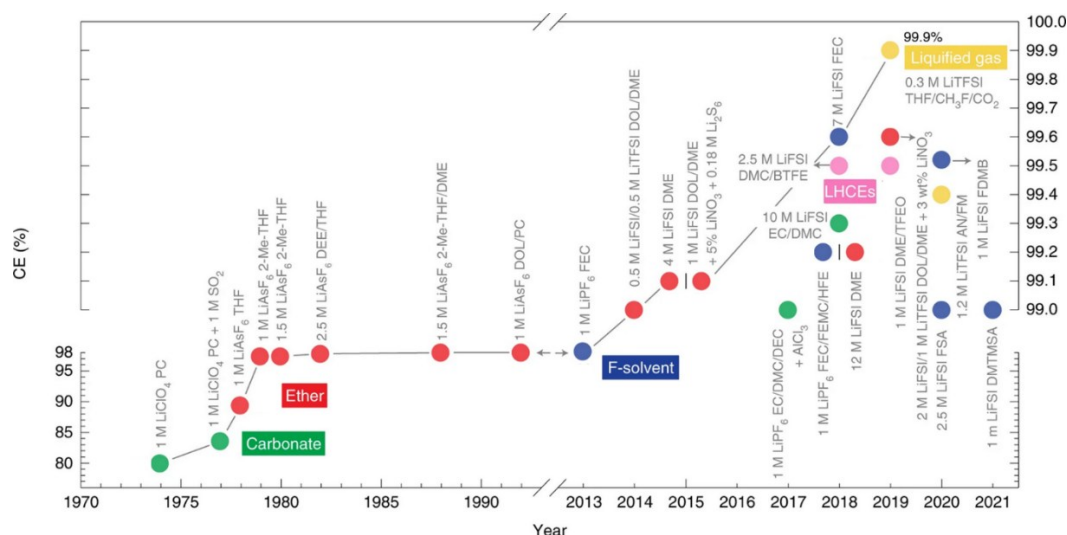


Figure 14. Timeline of electrolyte development for anode-less Li-metal batteries, with coulombic efficiency (CE) plotted against year of publication. Reproduced with permission from Hobold *et al.*⁷⁴, © 2021, Springer Nature Limited.

The question of a good interphase is therefore majorly a question of good electrolyte, even though other factors matter such as current collector nature^{85,86} or electrochemical operation conditions.^{87,88} Despite the massive progress made, with a history of more than 40 years, no electrolyte ‘genome’ was derived from the thousands of experimental outputs from the community to predict the composition and performance of battery SEIs from an electrolyte. What about a 5-year-old system such as the lithium-mediated ammonia synthesis then?

Inspired from battery research, the ammonia synthesis electrolyte and the SEI that results from its use has been the centre of attention since its discovery. We will touch on the role of the electrolyte in creating a stable inorganic-rich SEI, the interference of traces protic species (water, alcohols, ...), and how dynamic the interphase is expected to be, and see how they translated so far from battery research to the ammonia synthesis community.

1.4.3.1. The role of Inorganics/Organics

In lithium metal batteries, inorganic phases such as LiF or Li₂O often form from the degradation of inorganic components in the electrolyte (salt anion, additives, ...). Notably, the fluorination of electrolytes and the resulting incorporation of LiF has been a major factor in making stable SEIs and efficient batteries (Figure 14). Increasing the amount of LiF in the SEI soon became a go to.^{73,75,89} However, amongst better performing anode less batteries, recent works from Hobold *et al.* suggest that lithium oxide (Li₂O) correlates even better with coulombic efficiency.⁹⁰ These inorganic materials,

when covering a Li metal electrode are suggested to drastically reduce electronic conductivity while maintaining decent Li-ion conductivity, providing a stable layer that prevents further electrolyte degradation (Figure 15a,b).^{91,92} While LiF and Li₂O are both coined to balance this ionic/electronic conductivity, Li₂O is suggested to work even better in this regard, as suggested by ionic conductivity measurements performed on *ex situ* prepared pure Li|Li₂O and Li|LiF interphases (Figure 15c).⁹²

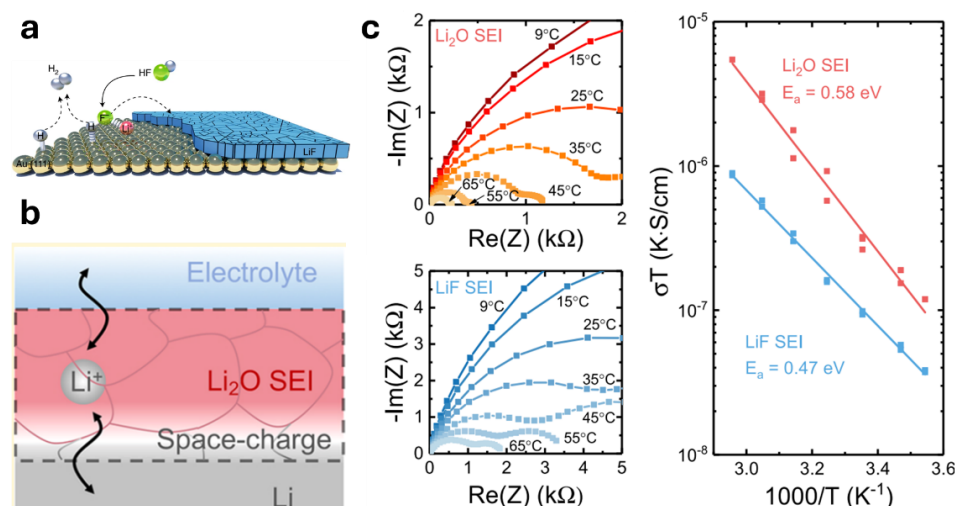


Figure 15. The role of inorganics in battery SEIs. Stabilising Li electrodes with an electron insulating layer (a,b) that maintains ionic conductivity (c). – (a) Reproduced with permission from Strmcnik *et al.*⁹¹, © 2018 Macmillan Publishers Limited, and (b,c) from Guo *et al.*⁹², © 2020 American Chemical Society.

Li-mediated ammonia synthesis behaves similarly in that regard. The original report by Tsuneto *et al.* uses an electrolyte made of 0.2 M LiClO₄ in THF:EtOH 99:1 v/v. In our group, we found that, by increasing the LiClO₄ salt concentration in the electrolyte, the ratio of inorganics to organics in the SEI increased (Figure 16b): delivering a more stable interphase through the prevention of continuous electrolyte reduction and organic SEI build-up (Figure 16a).⁸⁰ Alternatively, the addition of small amounts of oxygen has been efficient in improving SEI passivation properties and stabilising ammonia synthesis (Figure 16c).^{70,93} Li *et al.* even achieved a drastic increase in Faradaic efficiency toward ammonia by such means (Figure 16d),⁷⁰ although a clear relation with SEI chemical composition was not established. In our group, we looked at the addition of controlled amounts of water in the electrolyte, and similarly, this took part in stabilising the electrode potential (through SEI stabilisation) and increasing Faradaic efficiency to ammonia (Figure 16f).⁸¹ A *post mortem* XPS investigation of the SEI layer suggests a correlation between the presence of Li₂O/LiOH and selectivity to ammonia (Figure

16e), again highlighting the importance of inorganics in the SEI like in batteries. The role of oxygen and water were hypothesised to be equivalent.

While the discussion above concerns engineering the original 'Tsuneto electrolyte',^{53,68} there is no fluorine involved yet. Several research groups brought it in, either using $\text{LiOSO}_2\text{CF}_3$ (triflate, LiOTf), $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ (bis(trifluoromethanesulfonyl)imide, LiNTf₂) or LiBF_4 (tetrafluoroborate) to replace the LiClO_4 salt.^{82,84,94} Both strategies led to a strong increase in selectivity toward ammonia, close to 100 % selectivity in the former (Figure 16h), demonstrating days of stable operation.⁸⁴ Both reports correlate this increase in performance with the presence of LiF in the formed SEI. Li *et al.* suggest that an LiF-enriched SEI reduces through-plane diffusion while increasing in-plane diffusion (Figure 16g), resulting in uniform Li plating across the electrode surface, a similar effect in electrode stabilisation and more efficient ammonia synthesis.⁸² Interestingly, Lim et al have shown a similar effect with the incorporation of sulfur in the SEI. By adding small amounts of dimethylsulfide to the electrolyte, decomposition to species such as Li_2S or Li_2SO_4 seem to increase SEI ion conductivity and yield uniform Li deposition, stabilising the electrode potential and favouring ammonia synthesis equally.⁹⁵

The role of inorganics seems therefore transferable from battery chemistries to ammonia synthesis, although not universal. Comparative studies of Li-salts show that fluorination is not always the answer, and their functionality matters.^{82,84,96} There are multiple reasons for this. First, some salts may react with lithium to produce undesired byproducts. One example reported in batteries is the degradation of LiPF_6 to HF in the presence of trace water.^{97,98} While this HF can be converted to LiF and provide a good SEI,⁹¹ it also is a very strong acid that may be detrimental to selective ammonia synthesis. The same argument brings about a more mixed role for water in fluorinated electrolytes (as opposed to previously discussed works in LiClO_4 electrolytes). Studies of ammonia synthesis in LiOTf based electrolytes ($\text{LiOSO}_2\text{CF}_3$) suggest that minimising the amount of water present will improve performance,⁹⁴ while studies in LiBF_4 based ones suggest that trace water can be accommodated without significant decrease in performance.⁹⁹ Other examples include byproducts that trigger solvent degradation, or salts that are much more easily reduced than N_2 (e.g. carbonyl-containing salts).⁹⁶ Second is a point that we have not touched on yet: the counter electrode reaction. A typical counter electrode reaction investigated for ammonia synthesis is H_2 oxidation (Figure 20).^{100,101} While I will not discuss it to great extent in this work, it is worth noting that some salts and their degradation byproducts may affect this reaction too. LiNTf₂, which was previously highlighted as a high performing one, can also break down to LiS_x soluble species that were found to poison the Pt-based catalysts for hydrogen oxidation, substantially decreasing overall performance.^{96,101}

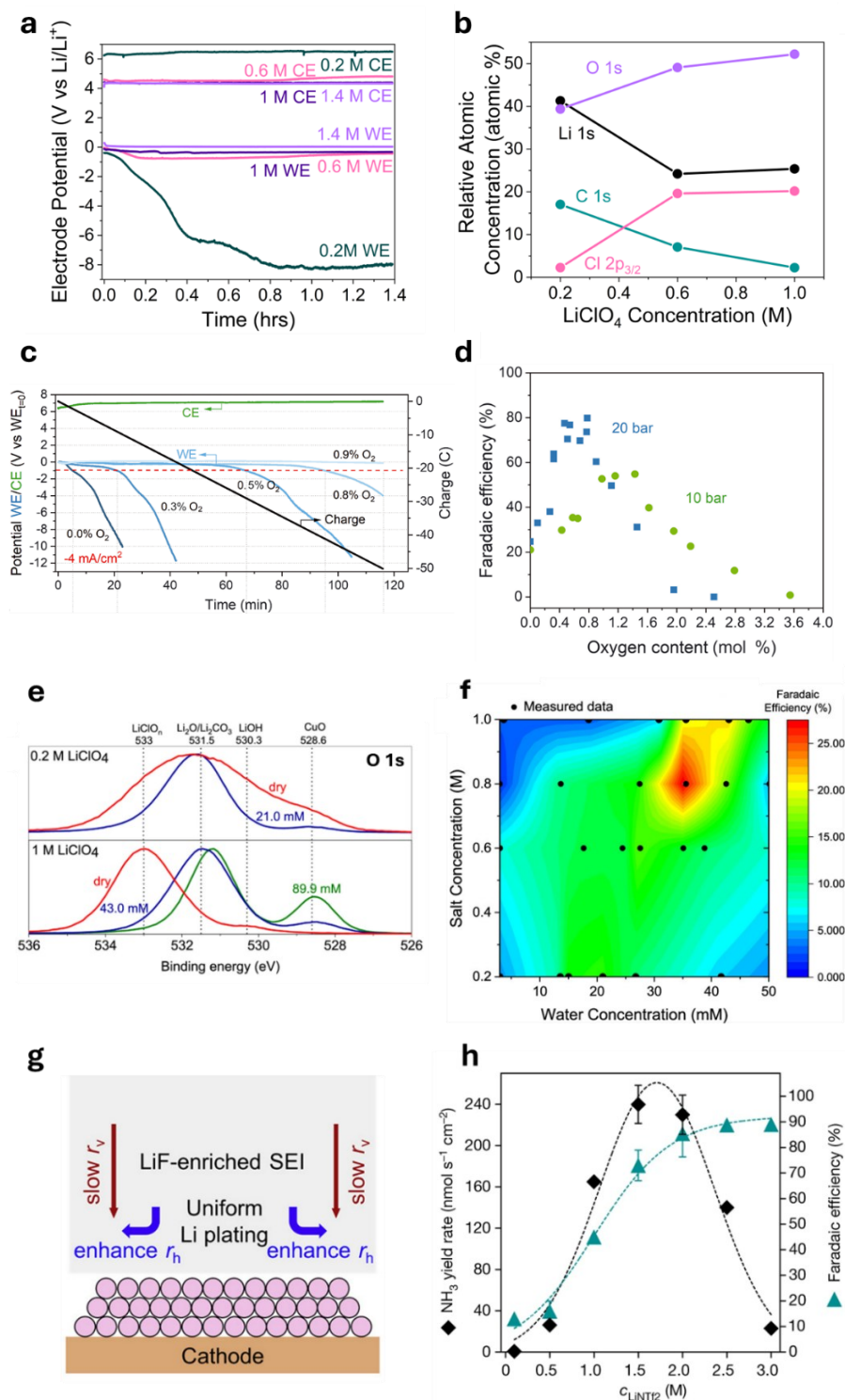


Figure 16. The role of inorganics in stabilising the Li-mediated N_2 reduction SEI and improving selectivity toward ammonia. (a,b) Increasing salt concentration increases the inorganic content of the SEI (a) and improves electrode stability (b) – Reproduced from Westhead et al.⁸⁰ with permission from the Royal Society of Chemistry. (c,d) Addition of molecular oxygen increases electrode stability (c) and improves

selectivity toward ammonia (**d**) – Reproduced with permission from Li et al.⁷⁰ © 2021 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. (**e,f**) Addition of trace water increases the amount of Li₂O/LiOH in the SEI, steering selectivity toward ammonia – Reproduced from Spry et al.⁸¹ with permission from © 2023 The Authors. Published by American Chemical Society. (**g,h**) Fluorination of the electrolyte results in a LiF-rich SEI that favours Li in plane diffusion over through plane (**g**), and higher selectivity toward ammonia (**h**) – Reproduced with permission from Li et al.⁸² © 2022 The Author(s). (Published by Elsevier Inc.) and from Du et al.⁸⁴ © 2022, The Author(s), under exclusive licence to Springer Nature Limited.

1.4.3.2. The Impact of Protic Species

Protons are a prerequisite to produce ammonia from nitrogen, and the choice of proton carrier matters. Ethanol was selected in the first demonstration of ammonia synthesis,⁵³ but alternatives are plentiful. Several research groups have screened other alcohols or stronger acids.^{102–104} A high variability in performance was observed based on the choice and concentration of proton source, suggesting butanol¹⁰² or phenol¹⁰⁴ as potentially better proton carriers although disagreement are found between such reports.^{102,104} While one could expect the acidity of such protons to be a major component in steering selectivity toward ammonia, no straight correlation with pKa was observed.¹⁰² More refined descriptors were proposed, including Kamlet-Taft parameters based on hydrogen bond donation/acceptance ability (Figure 17a),¹⁰² or an acidity/diffusivity mapping (Figure 17b).¹⁰⁴ However, none of these parameters capture the interfacial aspects of the changes in chemistry and high variabilities on these parameters scales are not yet explained.

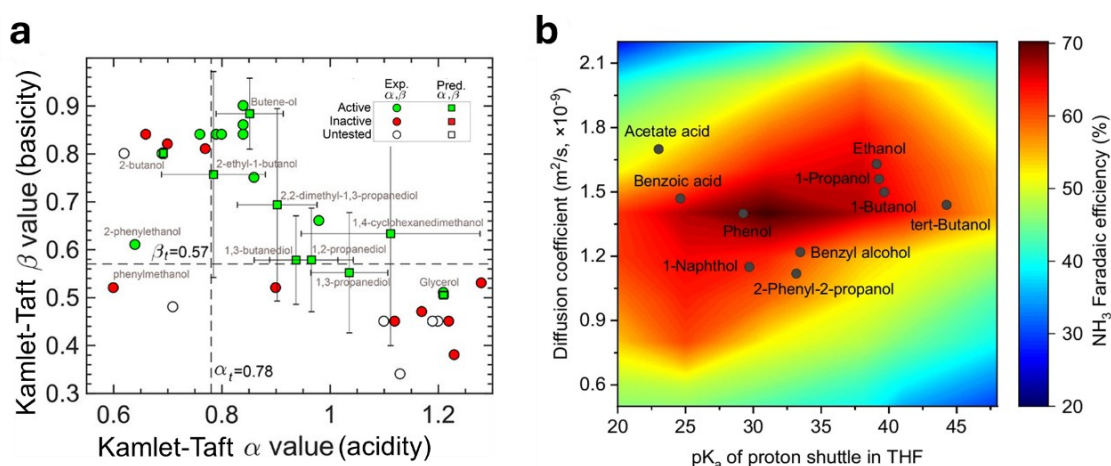


Figure 17. Proposed descriptors for the evaluation of proton carriers in driving selective Li-mediated ammonia synthesis. (**a**) Experimentally determined or theoretically predicted α - β Kamlet-Taft

parameters values describing the hydrogen bond donating (α , acidity) and accepting (β , basicity) ability, suggesting an optimal trade-off to achieve selective ammonia synthesis (green points) – Reproduced with permission from Krishnamurthy et al.¹⁰² © 2021 The Authors. Published by American Chemical Society. (b) Mixed activity-diffusion model suggesting a trade-off between acidity and proton carrier diffusivity to achieve optimal H^+ flux to the active electrode – Reproduced with permission from Fu et al.¹⁰⁴, © The Authors 2024. Published by Springer Nature Limited.

The bulk properties do matter in the selection of protic species for ammonia synthesis. However, they are not simple bystanders in the interface chemistry and SEI formation. Different alcohols were reported to take part in the electrolyte degradation chemistry during Li-mediated ammonia synthesis.¹⁰³ It would be no surprise to observe an interaction with electrolyte breakdown to SEI components. Alcohols such as the ones used in Li-mediated ammonia synthesis are uncommon in battery chemistry, but a more structurally simple proton source has been heavily investigated, water. The presence of trace water can affect both battery chemistries and ammonia synthesis (Figure 15 and Figure 16), notably through the formation of different SEI components and/or the formation of HF.^{81,91,97,98} But water participates in SEI formation in more indirect ways. Water reduction and interfacial behaviour are largely dictated by its solvation environment,¹⁰⁵ and studies in aqueous and/or water-in-salt electrolytes (i.e. aqueous electrolytes with salt concentrations so high that most water exists in a salt-coordinated state, as opposed to standard aqueous electrolyte where water exists in a network of coordinated water molecules) show that water reduction and hydrogen evolution can lead to reactive HO^- species that participate not only in $Li_2O/LiOH$ formation but also chemical decomposition of salts to SEI products (Figure 18a).¹⁰⁶

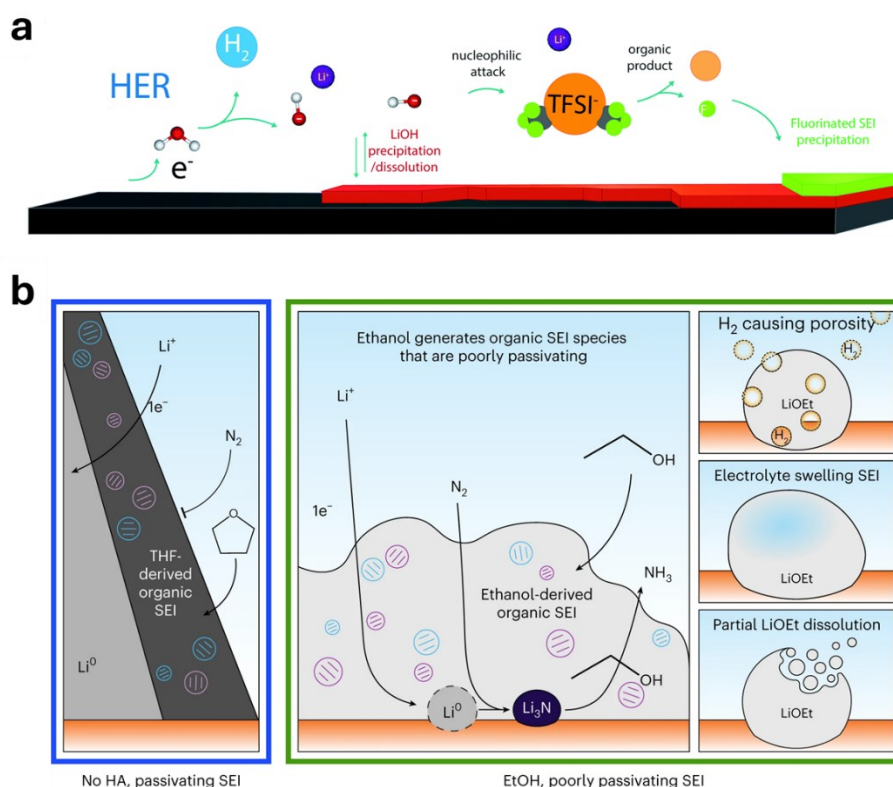


Figure 18. Effect of protic species on SEI morphology and composition in (a) battery water-in-salt electrolytes and (b) Li-mediated ammonia synthesis. (a) Water participates in catalysing salt reduction to SEI products in water-in salt electrolytes – Reproduced with permission from Dubouis *et al.*¹⁰⁶, © The Royal Society of Chemistry 2018. (b) Schematic representation of cryo-TEM imaging of the N_2 reduction SEI: Ethanol participates in creating a permeable SEI that allows access of reactants and products to and from the active surface. – Reproduced with permission from Steinberg *et al.*⁸³, © 2022, The Authors, under exclusive licence to Springer Nature Limited.

During ammonia synthesis, the contributing effects of ethanol have also been investigated. Steinberg *et al.* showed that, in agreement with previous studies, when no ethanol was present, no ammonia could be generated.^{68,83} While the generally accepted explanation was that one needs protons from ethanol to produce ammonia, Steinberg *et al.* imaged the SEI by cryo-TEM (Transmission Electron Microscopy) and showed that ethanol is a key SEI former (Figure 18b),⁸³ as corroborated by *operando* X-ray studies from Deissler *et al.*⁷² Just like in battery fluorinated electrolytes (Figure 15a) or water-in-salt electrolytes (Figure 18a), ethanol reduction alters the SEI structure. Bubble formation from hydrogen evolution, ethanol breakdown to poorly passivating species or SEI swelling/dissolution, all seem to contribute toward making an interphase that remains permeable to reactants and lets Li react with N_2 to form ammonia. In fact, Mygind *et al.* showed that once such SEI is formed, ethanol can even

be removed from the electrolyte and ammonia still be produced, albeit at highly variable rates.¹⁰⁷ Indeed, protons generated at the counter electrode by solvent oxidation and/or hydrogen evolution may be sufficient to sustain H⁺ delivery and ammonia synthesis.¹⁰⁸ However, not all protic sources behave equally in making such a permeable SEI, and even slight changes in the proton source concentration and chemical structure can alter its ability to generate a permeable enough SEI for selective ammonia synthesis.¹⁰⁹ More work needs to be done to understand the high sensitivity of the interface to small electrolyte variations such as the ones described in this introduction (ethanol, water or O₂ concentrations).

1.4.3.3. *Is the SEI a Dynamic or Steady Layer?*

The SEI formation is influenced by a multitude of factors, and more are to be discovered. But does it ever stop forming? Does it decompose? It would be ideal to fully stabilise this interphase: not only to stop losing charge toward formation, but also so that one can learn from that interphase and translate it to other systems free of Li (see Chapter 5). However, there is no clear evidence of such stability. In fact, this has been a subject of interest in battery SEIs as well. While Li-metal batteries now reach coulombic efficiencies >99.9 % (Figure 14), suggesting that little charge is lost to SEI reconstruction, there is experimental evidence that such reconstruction is occurring. LiF, the battery researcher's favourite adduct, was synthesised *ex situ* as an artificial layer over Li by multiple groups.^{89,110} However, when used in a battery where Li metal is being plated, such layer does not perform as well as *in situ* generated LiF SEIs. When exposed to an electrolyte and subjected to metal plating, the coating is quickly mechanically breached, creating Li-exposed regions affecting stability (Figure 19a).¹¹⁰ It is through permanent reconstruction in F-containing electrolytes that *in situ* produced SEIs seem to recover from their damage.

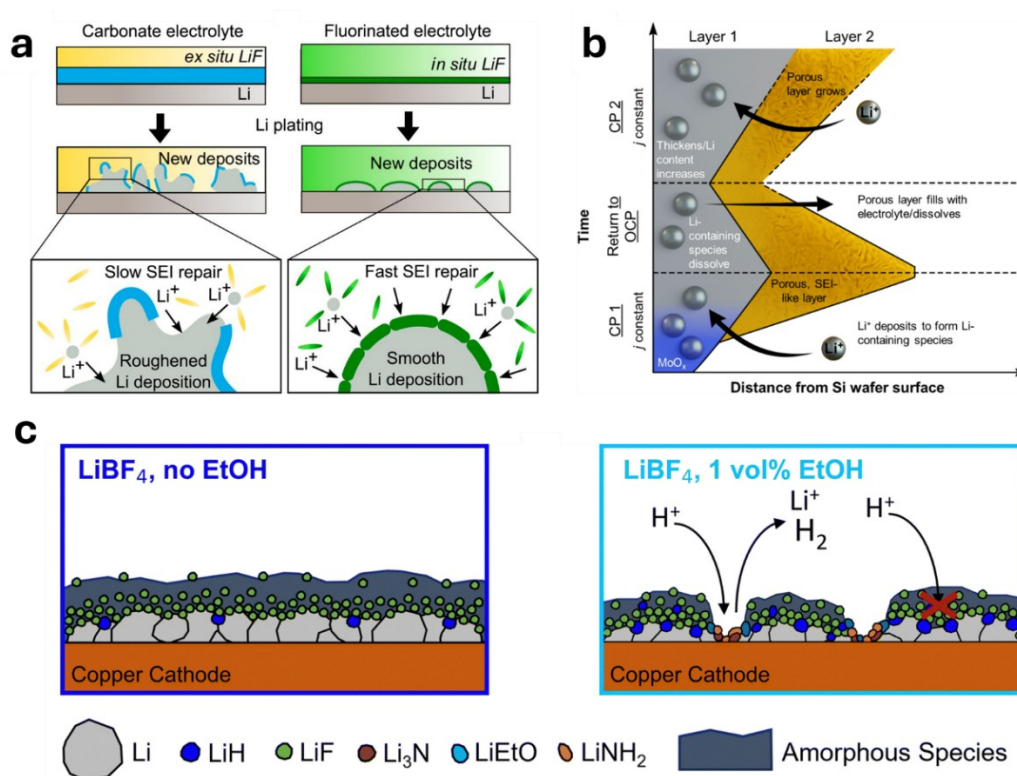


Figure 19. The dynamic aspects of the SEI. (a) Schematic of mechanical damage of in situ or ex situ grown LiF SEI layers, where SEI fast repair in native fluorinated electrolytes is suggested to maintain the protected Li metal surface. – Reproduced with permission from He et al.¹¹⁰ © 2020 PNAS license. (b) Schematic representation of the dynamic SEI growth and dissolution during chronopotentiometric (CP) N_2 reduction and standby at open circuit (OCP), respectively, as observed by in situ neutron reflectometry and X-ray diffraction. – Reproduced with permission from Blair et al.⁷¹, © The Royal Society of Chemistry 2023. (c) Schematic representation of the crack formation in ethanol-containing systems allowing access of ammonia-forming reagents to the active Li surface, as observed by operando X-ray scattering – Reproduced with permission from Deissler et al.⁷², © The Royal Society of Chemistry 2024.

In the case of ammonia synthesis, a report from Mygind et al. shows that one can form an SEI in an EtOH-containing electrolyte, switch the electrolyte to an EtOH-free one and still produce ammonia like in the presence of EtOH, suggesting that a stable layer may be produced, but the Faradaic efficiencies are so variable that either ethanol was not fully flushed, or that it may not be as stable as concluded. In fact, multiple reports suggest that the SEI evolves over time of N_2 electrolysis. McShane et al. have shown that SEI thickness increases with charge passed,¹¹¹ and operando studies by neutron reflectometry and X-ray diffraction/scattering have shown that after continuous growth of a SEI layer

during electrolysis, when left at open circuit, the SEI slowly dissolves and disappears (Figure 19b).⁷¹ During operation, cracks are even suspected to form in the SEI (likely/partly caused by the proton source), potentially providing access channels for reagents to reach the active surface and ammonia synthesis to occur successfully (Figure 19c), as observed by *operando* X-ray scattering experiments.⁷² All these observations are hints that the interphase is highly dynamic; this dynamism might play a role in the transport of reagents and products to and away from the active lithium metal. However, the mechanistics of it are yet to be elucidated.

Just like in batteries, the role of inorganics is crucial in providing stability, proton sources interfere in many ways with SEI formation, and a lot of dynamics may be present in the interphase formation processes occurring during electrolysis. To summarise this section (1.4.3) in a sentence: battery knowledge is transferable to ammonia synthesis, always with a pinch of salt and an extra dash of complexity. Let us keep this sentence in mind as it will be a recurring theme in the presented work.

1.4.4. The Burden of Lithium

The above learnings were fruitful in improving the performance of ammonia synthesis, and a fast-paced progress was made in 5 years (Figure 20a). Starting with Faradaic efficiencies below 10 % at ambient pressures, stable operation of about an hour at 2 mA currents, and sacrificial electrolyte oxidation as a counter electrode reaction,^{49,53} state of the art technologies now embed hydrogen oxidation as a sustained counter electrode reaction providing protons to yield ammonia in liquid flow cell or membrane electrode assemblies,^{100,112} operating for up to 12 days at currents of 150 mA ($6\text{mA}\cdot\text{cm}^{-2}$), and Faradaic efficiencies of $64 \pm 1\%$ toward ammonia, nearly all collected in the gas phase (Figure 20b,c).⁹⁹ Isolated performance records also include Faradaic efficiencies above 95 %, ⁸⁴ and current densities of up to $1\text{A}\cdot\text{cm}^{-2}$.¹¹³

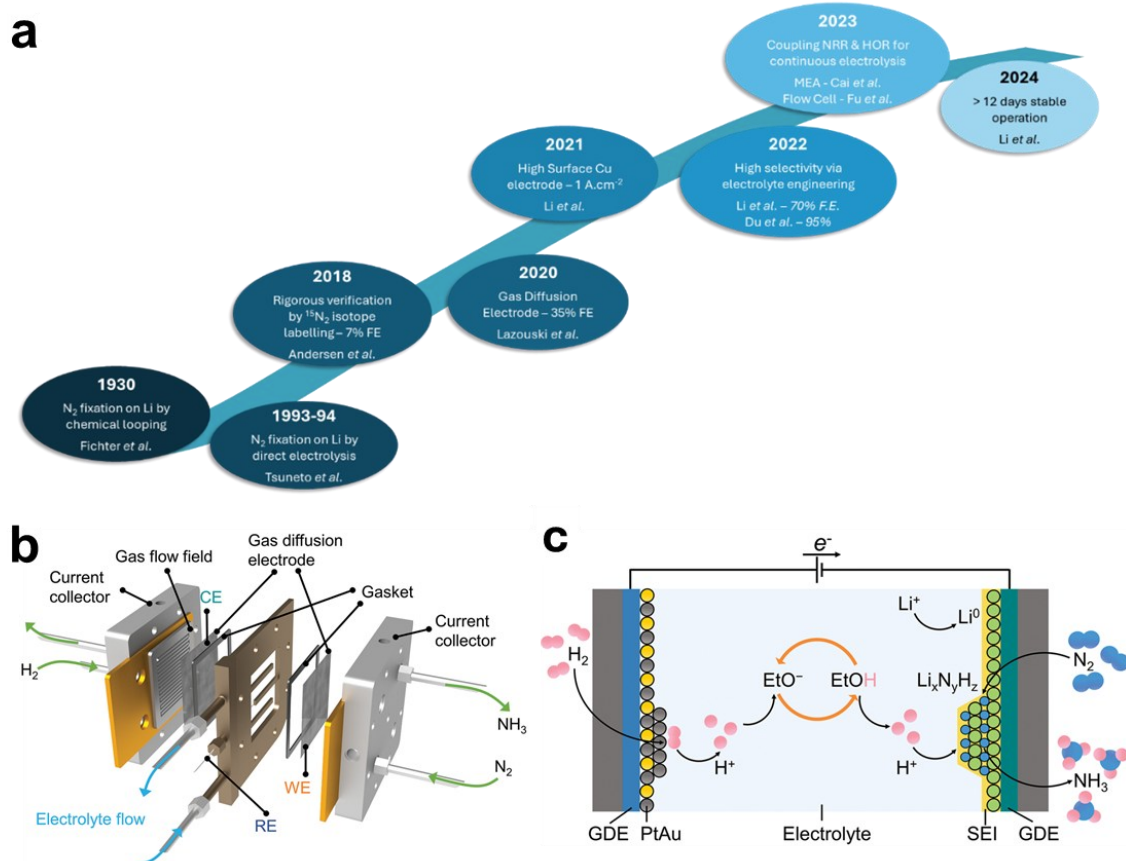


Figure 20. State of the art in Li-mediated nitrogen reduction. **(a)** Timeline of technological breakthrough made in the field of Li-mediated ammonia synthesis. **(b,c)** state of the art flow cell device for paired N₂ reduction and H₂ oxidation for continuous ammonia synthesis: **(b)** Flow cell parts schematics and **(c)** underlying chemistry. Reproduced with permission from Fu *et al.*¹⁰⁰ © 2023 The Authors, AAAS.

However, some metrics still suffer in this system, and one inherent limit to it is lithium. Indeed, one must continuously operate at Li plating potential (-3.04 V vs. SHE) to sustain the active surface that mediates N₂ reduction. This implies a massive overpotential since the equilibrium potential for ammonia synthesis is > 3 V above that threshold.¹¹⁴ Haber-Bosch plants can produce ammonia at costs as low as \$160 for a ton of ammonia, with market price averaging \$600 a ton when considering costs of storage and transports.¹¹⁵ At its current state, electrochemical Li-mediated N₂ reduction is far from economic parity with Haber-Bosch. The cost of electricity associated with the generation of H₂ by water electrolysis and the operation at Li plating potential for N₂ activation severely hamper the cost of ammonia production through this means.^{115,116} A techno-economic analysis from Lazouski *et al.*

suggests that reaching market price ($< 0.6 \text{ \$}/\text{kg}_{\text{NH}_3}$) in this setup will require drastic improvement in operating cell voltages and current densities (Figure 21).¹¹⁶

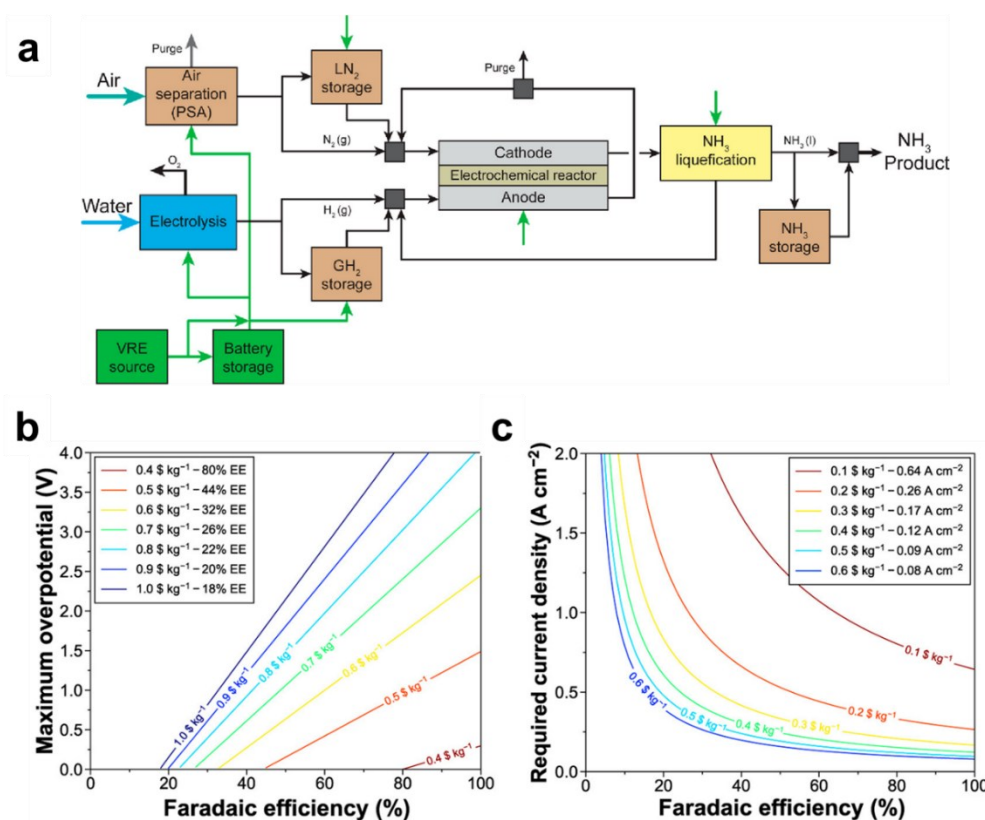


Figure 21. Techno-economic analysis of the electrochemical nitrogen reduction to ammonia. (a) Scope of the cost analysis, embedding variable renewable energy (VRE) generation and storage, H_2 production by water electrolysis, ammonia synthesis by N_2 reduction and H_2 oxidation, and ammonia liquefaction and storage. (b) Maximum overpotential tolerable to reach threshold costs of ammonia production at set Faradaic efficiency to ammonia. (c) Required current density to achieve ammonia production at a threshold cost depending on Faradaic efficiency to ammonia. – Reproduced with permission from Lazouski et al.¹¹⁶ © 2022, American Chemical Society.

Assuming a 70 % faradaic efficiency to ammonia, which is the operating selectivity for the most stable system designed so far (12 days operation),⁹⁹ reaching market price would mean operating at overpotentials below 1.3 V and current densities above 100 mA.cm^{-2} . In a configuration where faradaic efficiency reaches close to unity, which has been achieved for 4 days of operation,⁸⁴ that would shift metrics to $< 2.5 \text{ V}$ overpotential and $> 80 \text{ mA.cm}^{-2}$ current densities. In both cases, none of these metrics are in reach, typically operating at current densities of $< 10 \text{ mA.cm}^{-2}$ and overpotentials $> 3 \text{ V}$.^{48,81,84,99,100} However in reality, the above stated cut-off market price is modulated by high volatility of fertiliser costs due to geopolitical supply chain disruptions and gas price variations.¹¹⁷

Electrochemical ammonia synthesis mediated by Li, with further improvements, could still represent an economic case in situations of high production input prices or in remote locations where Haber-Bosch derived ammonia is too expensive to produce or ship.^{116,118} However, decarbonising all ammonia production through this pathway –and complying with the net zero emission targets set by the United Nations¹¹⁹– will only happen by alleviating the burden of lithium.¹¹⁷

The work presented in this thesis aims at addressing this problem in three steps: (i) measuring the energy penalty associated with N₂ reduction on Li (Chapter 3), (ii) alleviating that burden by modulating Li plating potential through electrolyte engineering (Chapter 4), (iii) bypassing Li and investigating new chemistries (Chapter 5). We will finally conclude on the perspectives of electrochemical nitrogen fixation for fertiliser and carbon-neutral fuels production and ponder the meaning of ‘green’ ammonia in the framework of a circular society (Chapter 6).

Chapter 2. Experimental Methods

2.1. Materials

Mo foil ($\geq 99.9\%$, 125 μm thick), Cu foil ($\geq 99.9\%$, 0.5 mm thick), Pt foil ($\geq 99.95\%$, 25 μm thick) and Pt mesh ($\geq 99.9\%$, 60 μm thick) were purchased from Goodfellow Cambridge. LiFePO_4 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ 18 mm diameter discs were cut out of pre-coated commercial sheets: LiFePO_4 coated on Al sheets (BR0188, 135 mA.h.g^{-1} capacity, 28 mg.cm^{-2} loading) purchased from MSE supplies, and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coated on Cu sheets (Nanomyte® BE-10E, 90 % active material, 5 % PVDF, 5 % Super P 170 mA.h.g^{-1} capacity, 7.3 mg.cm^{-2} loading), purchased from NEI Corp. 15 mm diameter lithium discs, coin cell cases, spacers and wave-springs were purchased from Pi-Kem. Bis(trifluoromethanesulfonyl)imide (NTf_2) salts were purchased from Solvionic Inc. (Li: $\geq 99.9\%$, < 20 ppm water; Ca: $\geq 99.5\%$, < 250 ppm water; Mg: $\geq 99.5\%$, < 250 ppm water; Na: $\geq 99.5\%$, < 20 ppm water). Lithium Perchlorate (LiClO_4 , 99.99 %, battery grade) Tetrahydrofuran (THF) (anhydrous, $\geq 99.9\%$, inhibitor-free), 1,2-Dimethoxyethane (DME) (anhydrous, $\geq 99.5\%$, inhibitor-free), Triethylphosphate (ReagentPlus®, $\geq 99.8\%$), HCl (30 %, Suprapur®), H_2SO_4 (96 %, Suprapur®), HCl (solution 4.0 M in 1,4-dioxane), (Ammonium Chloride (ReagentPlus®, $\geq 99.5\%$), Ammonium- ^{15}N chloride (≥ 98 atom % ^{15}N , $\geq 99\%$), Lithium Nitride (-60 mesh, $\geq 99.5\%$), Calcium Nitride (powder, -200 mesh, 99 % trace metals basis), Magnesium Nitride (cubic phase, -325 mesh, $\geq 99.5\%$ trace metals basis), Aluminium Nitride (powder, -200 mesh, 99.8 % trace metals basis), Sodium Salicylate ($\text{C}_6\text{H}_4(\text{COONa})(\text{OH})$, ReagentPlus®, $\geq 99.5\%$), D_2O (99.9 % D, MagniSolv™ for NMR spectroscopy), Methanol (suitable for HPLC, $\geq 99.9\%$), Methanol-OD (reagent grade, ≥ 99 atom % D), Ferrocene (98 %), Nitrogen- $^{15}\text{N}_2$ gas (364584-115L-EU, 98 atom % ^{15}N , $\geq 99\%$) Potassium Nitrate (ACS Reagent, $\geq 99.0\%$), Potassium Hydroxide Solution (45 wt. % in H_2O), Nitrite Test kit (photometric, 0.002-1.00 mg.l^{-1} ($\text{NO}_2^- \text{N}$), 0.007-3.28 mg.l^{-1} (NO_2^-), Spectroquant®) and coin cell separators (Whatman® glass microfiber filters, Grade GF/A, dried overnight under dynamic vacuum before use) were purchased from Merck KGaA Darmstadt (Sigma Aldrich). Ethanol ($\geq 99.5\%$, Extra Dry, absolute, AcroSeal™), Potassium Nitrite ($\geq 97\%$, Thermo Scientific Chemicals), Toluene (anhydrous, 99.8 %, packaged under Argon in resealable ChemSeal™ bottles), Diethylether (Et_2O , 99+ %, ACS reagent, anhydrous, stabilized with BHT) were bought from Thermofischer Scientific™. Sodium Pentacyanonitrosylferrate(III) dihydrate (ACS, 99 – 102 %) was purchased from Alfa Aesar, Sodium Hypochlorite (14 % Cl_2 in aqueous solution, GPR RECTAPUR®), Sodium Hydroxide (pellets, AnalaR NORMAPUR), Tetrahydrofuran- $[\text{D}_8]$ ($> 99.50\%$ D, Screw top bottle), Acetone ($\geq 99\%$, Technical),

Molecular sieves (4 Å, GPR RECTAPUR®, sonicated in acetone for 10 min, then dried at 100 °C under dynamic vacuum overnight before use) and 1,1,2,2-tetrafluoroethylene 2,2,3,3-tetrafluoropropyl ether (TTE, 99 %, contain < 200 ppm water, further dried on molecular sieves to < 20 ppm) were purchased from VWR UK. Single compartment glass cell and gas traps were custom made by Terri Adams, Artistic and Scientific Glassware, Oxford. The single compartment PEEK cell was made in house at the Chemical Engineering workshop, using Swagelok 1/8 in. tube fittings to connect gas lines. Purifiers for the Ar and N₂ gas lines providing purity levels of H₂O, H₂, CO₂, O₂, CO, nonmethane hydrocarbon (NMHC), CH₄, NH₃, NO_x to < 0.5 ppb were purchased from NuPure. N6 Ar and N6 ¹⁴N₂ gas were purchased from BOC. Magnesium 1,1,1,3,3,3-hexafluoroisopropoxy aluminate salt (Mg[Al(hfip)₄]₂) was prepared by Andrijana Marojević and Dr Jan Bitenc from the National Institute of Chemistry in Slovenia, according to a procedure developed in their group (section 2.2.2),¹²⁰ and sent to us under dry Argon in a sealed pouch. Electrochemistry and electrolyte preparation was carried out in an Ar atmosphere glovebox (MBraun, H₂O < 0.3 ppm, O₂ < 0.3 ppm).

2.2. Synthesis of Metallic Salts

2.2.1. Calcium bis((1,1,1,3,3,3-hexafluoroisopropoxy)borate)

A procedure was adapted from previous works for the synthesis of Calcium bis((1,1,1,3,3,3-hexafluoroisopropoxy)borate) (Ca[B(hfip)₄]₂).⁵⁴ All liquid reagents were first dried over activated molecular sieves for 3 days (aiming for < 5 ppm water). In an Argon glovebox, Ca(BH₄)₂·2THF (3 mmol, 642 mg) was dissolved in tetrahydrofuran (THF) (9.4 ml), into a round bottom flask. Separately, hexafluoroisopropanol (hfip-H, 8.125 equivalents, 2.56 ml) was diluted with THF (4 ml) and left to cool down. This latter solution was then slowly added dropwise to the former, continuously stirring, and left to stir (reaction releasing H₂ and heat immediately). After H₂ generation was completed and solution reached room temperature, the reaction mixture was stirred at room temperature for 24 h. Then, the solvent and excess hfip-H were evaporated by sparging purified Argon through the liquid at a rate of 50 ml.min⁻¹ for several hours, then transferred to a vacuum oven to be dried at 45°C for 24h. The product was then characterised by ¹H-, ¹⁹F and ¹¹B-NMR (in *d*8-THF, Figure 22) and stored in Argon.

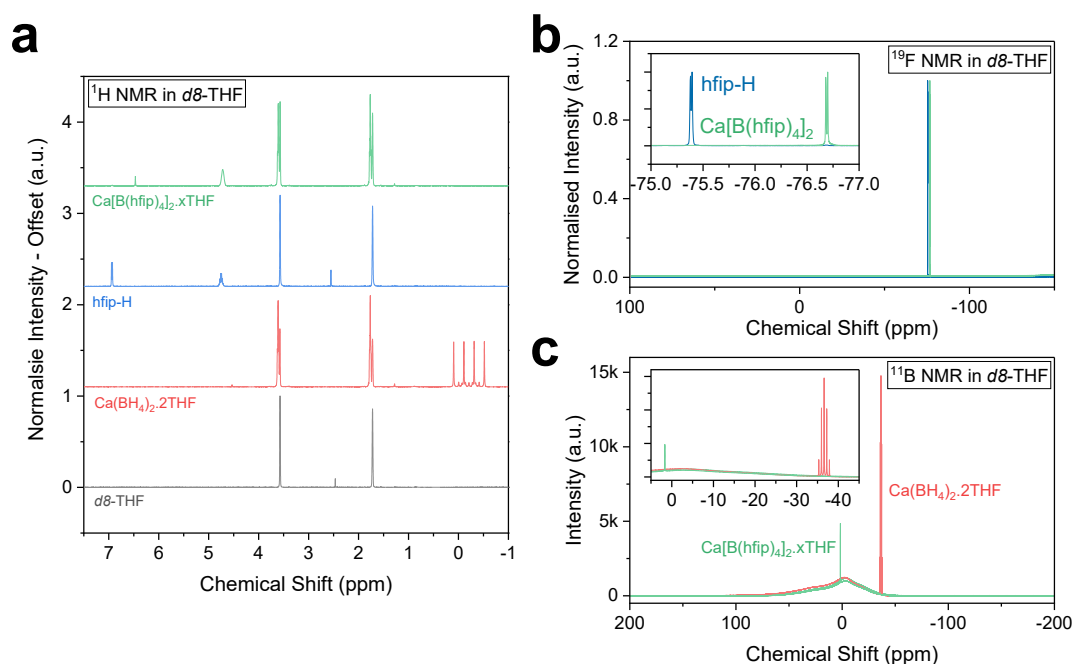


Figure 22. NMR analysis of as synthesised calcium bis((1,1,1,3,3,3-hexafluoroisopropoxy)borate). **(a)** ^1H NMR, **(b)** ^{19}F NMR, **(c)** ^{11}B NMR.

2.2.2. Magnesium bis((1,1,1,3,3,3-hexafluoroisopropoxy)aluminate)

The synthesis of this salt was performed by our collaborator Andrijana Marojević, under the supervision of Dr Jan Bitenc (National Institute of Chemistry in Slovenia), according to a procedure developed in their research group by Dr Tjaša Pavčnik *et al.*^{120,121}

“1,2-dimethoxyethane (DME) and diglyme underwent a three-step drying procedure, including drying with 4 Å molecular sieves for 3 days, one day under reflux with Na/K alloy (1/3 wt%), and fractional distillation. The final water content of the as-dried solvents, determined by Karl Fischer titration, was below 1 ppm, which is the detection limit of the instrument at a specific sample volume of 5–10 ml. 1,1,1,3,3,3-hexafluoroisopropanol (hfip-H, 2.5 eq. versus Mg, 18.8 mmol, 2.0 ml) was added dropwise to a solution of $n\text{-Bu}_2\text{Mg}$ 1 M in heptane (7.5 mmol, 7.5 ml). The solvent and remaining hfip-H were removed under vacuum, resulting in the formation of a white powder, $\text{Mg}(\text{hfip})_2$. $\text{Mg}(\text{hfip})_2$ was dissolved in 30 mL of DME, and a solution of $\text{Al}(\text{CH}_3)_3$ in toluene (2.02 eq. versus Mg, 15.1 mmol, 7.6 ml) was added. Afterwards, hfip-H (3.5 eq. versus Al, 52.6 mmol, 5.6 ml) was added gradually over a period of 1 hour. After stirring at room temperature for 24 h, the solution was concentrated under

reduced pressure and added to hexane to precipitate the $Mg[Al(hfip)_4]_2$ salt. The salt was filtered and dried under a vacuum at 50 °C for 48 hours.”

2.3. Electrolytes Preparation and Characterisation

2.3.1. Electrolytes Formulation

Purchased salts were dissolved in anhydrous THF or DME and tested for water content by Karl Fisher titration. If they contained < 50 ppm water, they were used as purchased. If they contained more water, they were dried under dynamic vacuum at 100 °C for at least 3 days before use. Appropriate amounts of salts were weighed within an Ar glovebox, the dissolved in a few ml of appropriate solvent, left to stir if needed. Appropriate amounts of EtOH were added, and the solutions was transferred to a volumetric flask, completed with solvent to reach the desired volume. Water content of such electrolyte was monitored before use by Karl Fisher titration. All electrolytes made reported water content below 50 ppm.

2.3.2. Electrolyte Solvation Structure Spectroscopic Characterisation

Raman spectra of as prepared electrolyte were recorded by the following method. A glass capillary was sealed at one end using a blowtorch, then filled with electrolyte samples using a syringe and needle inside the glovebox, then sealed with tape and parafilm. The sample was then transferred to the Raman spectrometer. Raman spectra were collected using a Renishaw confocal Raman microscope operated with an incident 532 nm laser beam, focused through a 50x objective. The laser intensity was set to 100mW (5% of its power) and Raman spectra were collected between 500-1400 cm^{-1} wavenumber with an exposure time of 5 s and 5 repetitions each.

2.3.3. Nitrogen Gas Solubility and Diffusivity Determination

A porosity analyser 3Flex from Micromeritics was used to measure N_2 solubility and diffusivity in as prepared electrolytes, using the Brunner-Emmett-Teller Theory and following a method reproduced from our previous works,⁸⁰ similar to that used by Zubeir *et al.*¹²² I thank Dr Silvia Favero for performing the measurements and processing the data.

Freeze-thaw: To remove any dissolved gas in the solvent, we performed 3 freeze-thaw cycles *in situ*. 3 ml was used for each measurement. After loading the sample, the tube was secured on the porosity analyser. The sample was then frozen by immersion in a liquid nitrogen bath. The manifold line was put under vacuum and the sample valves were opened, to degas the solidified samples. Vacuum was applied for 10 minutes, at the end of which, the sample valves were closed again and the nitrogen bath removed. The samples were then left to thaw under vacuum, during this step gas bubbles were visible. The process was repeated until no more bubbles were observed upon thawing.

Free volume determination: The free volume is an essential parameter to calculate gas solubility from the pressure vs. time data. In normal porosity analysis with solid samples, the free volume is determined by degassing, followed by dosing a non-adsorptive gas (usually Helium) to around 0.3 bar. This approach cannot be used for the case of low vapour pressure solvents. Therefore, the free volume was initially determined in absence of the sample and then the sample volume (3 ml) was subtracted.

Solubility data points: After the freeze-thawing cycles, the sample was once again frozen with a liquid nitrogen bath. Nitrogen was fed into the system to reach a pressure of 0.2 bar. The sample valves were again closed, the nitrogen bath removed, and the pressure left to equilibrate, using an equilibration interval of 1 hour. The initial pressure (0.2 bar) was selected because around half of the sample tube is surrounded by liquid nitrogen, so upon removal of the nitrogen bath the pressure approximately doubles, obtaining a pressure above the saturation pressure of THF at 25 °C (0.24 bar). A known amount of nitrogen is dosed, and the pressure recorded in steps of 0.2 bar up to 1 bar, which is the limit of the machine. The equilibration time for these measurements was 15 minutes and each data point took 2 to 5 hours to equilibrate. The pressure was then reduced to 0.4 bar again and the process repeated 3 times. The reported data represents the average of 3 runs (with the same sample). To extrapolate nitrogen solubility, the mixture was assumed to follow Raoult's law.

Calculating N₂ solubility:

Short Name	Description (unit)
V_{free}	Free volume or volume of the sample holder minus that of the sample (cm ³)
V_{dosed}	Total gas volume dosed (cumulative, cm ³ stp)
T_{sample}	Temperature of the sample bath (K)
T_{stp}	Temperature at standard T and P (298 K)
P_{meas}	Measured pressure in the tube (mmHg)

P_{stp}	Pressure at standard T and P (750 mmHg)
$V_{\text{ads,stp}}$	Adsorbed volume at standard T and P (cm^3 stp)
n_{ads}	Moles of adsorbed gas (mol)
P_{theor}	Theoretical pressure: pressure expected in the tube if no gas was absorbed (mmHg)

Let us have $n_{\text{dosed}} = \frac{P_{\text{stp}} V_{\text{dosed}}}{R T_{\text{stp}}}$, $P_{\text{theor}} = \frac{n_{\text{dosed}} R T_{\text{sample}}}{V_{\text{free}}}$ and $\Delta P = P_{\text{meas}} - P_{\text{theor}}$

So $n_{\text{ads}} = \frac{\Delta P V_{\text{free}}}{R T_{\text{sample}}} = \dots = \frac{P_{\text{meas}} V_{\text{free}}}{R T_{\text{sample}}} - \frac{P_{\text{stp}} V_{\text{dosed}}}{R T_{\text{stp}}}$ and $V_{\text{ads,stp}} = \frac{P_{\text{meas}} T_{\text{stp}} V_{\text{free}}}{P_{\text{stp}} T_{\text{sample}}} - V_{\text{dosed}}$

Calculating N_2 diffusivity:

The diffusion coefficient is calculated by fitting the solution of the 1d Fick's equation $\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2}$,

Which solution is: $\bar{C} = C_s \left(1 - 2 \left(1 - \frac{C_0}{C_s} \right) \sum_{\lambda=0}^{\infty} \frac{1}{\lambda_n} e^{-\frac{\lambda_n^2 D t}{L^2}} \right)$ where $\lambda_n = \left(n + \frac{1}{2} \right)^2 \pi^2$

By fitting the equation (Figure 23), we can calculate the steady state N_2 concentration and the diffusion coefficient. Note that the solution is an infinite sum but has been approximated to the first 10 digits.

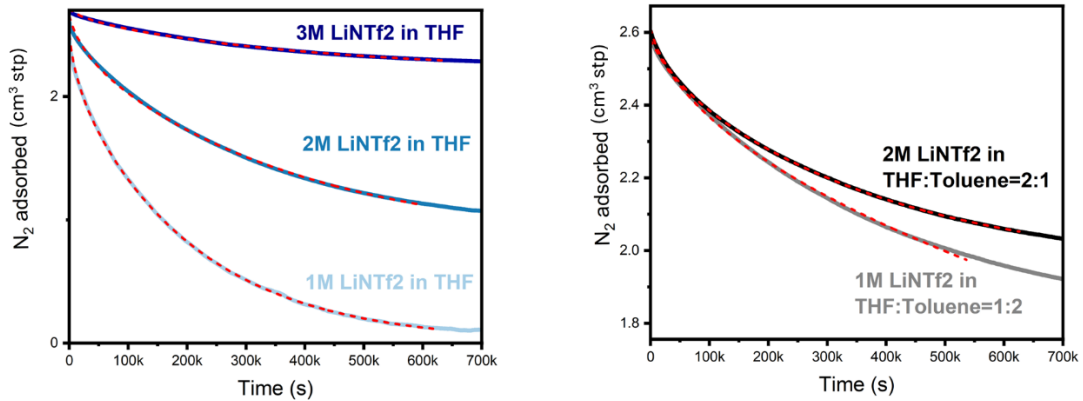


Figure 23. Nitrogen gas adsorption measurements for LiNTf_2 electrolytes dissolved in THF or mixtures of THF and toluene. Volume of adsorbed N_2 versus time. Dashed red lines are fittings for determination of diffusion coefficients from the solution to Fick's second law. Measurements and data processing by Dr Silvia Favero.

2.4. LiFePO_4 or $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Reference Electrode Preparation

2.4.1. Coin Cell Assembly

Within an Ar-filled glovebox, a Li disc was mounted on stainless steel spacer and spring, placed in the negative case of a coin cell (all previously cleaned by sonication in EtOH for 10min and drying in air). A 18 mm diameter disc was cut out of the active materials sheets (LiFePO_4 or $\text{Li}_4\text{Ti}_5\text{O}_{12}$), then placed in the opposite positive case and covered with a glass fiber separator, which was wetted with 70-100 μL electrolyte (1 M Li salt in appropriate solvent, e.g. THF). (Figure 24a) Cell was closed with a press and left to rest for at least 1 day.

2.4.2. Lithiation/Delithiation Procedures

Partial lithiation (for $\text{Li}_4\text{Ti}_5\text{O}_{12}$) or delithiation (for LiFePO_4) methods were reproduced and adapted from La Mantia *et al.* and Costard *et al.* $\text{LiFePO}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ materials assembled cells were discharged (1.56 $\text{mA.g}^{-1}\text{LiFePO}_4$, 0.01 C rate) / charged (10 $\text{mA.g}^{-1}\text{Li}_4\text{Ti}_5\text{O}_{12}$, 0.06 C rate) respectively, until a cut-off voltage of 4.0 or 1.3 V vs. Li^+/Li , respectively.^{123,124} The cell was left to relax to a potential plateau (+3.428 $\pm$ 0.003 V vs. Li for LiFePO_4 , +1.564 $\pm$ 0.002 V vs. Li^+/Li for $\text{Li}_4\text{Ti}_5\text{O}_{12}$), stable for days in coin cell. (Figure 24b,c).

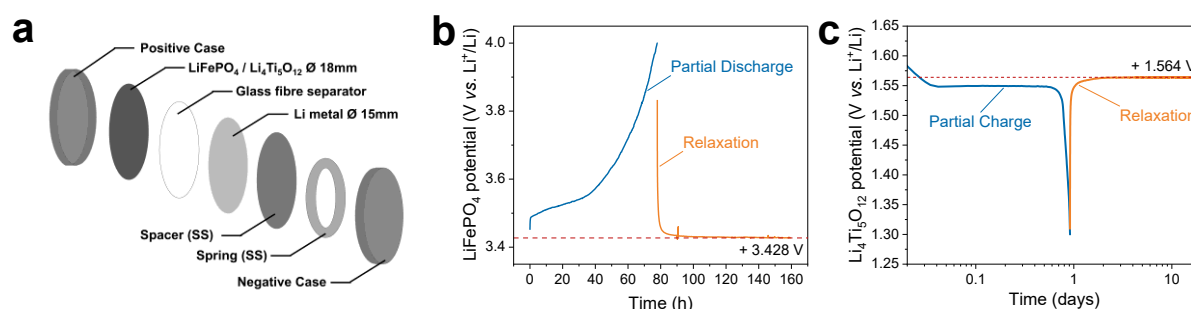


Figure 24. LiFePO_4 or $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Reference Electrode Preparation. (a) Coin cell assembly method for LiFePO_4 or $\text{Li}_4\text{Ti}_5\text{O}_{12}$ conditioning, wetting the separator with 70 μL LiNTf_2 1 M in THF, at 20 $^\circ\text{C}$. (b,c) Typical chronovoltammograms for galvanostatic (b) LiFePO_4 partial delithiation and (c) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ partial lithiation at 10 mA.g^{-1} active material, showing the obtention of a stable potential of + 3.428 $\pm$ 0.003 V vs. Li and + 1.564 $\pm$ 0.001 V vs. Li^+/Li , respectively. – Reproduced from my work.¹²⁵ with permission from © 2023 The Authors. Published by American Chemical Society.

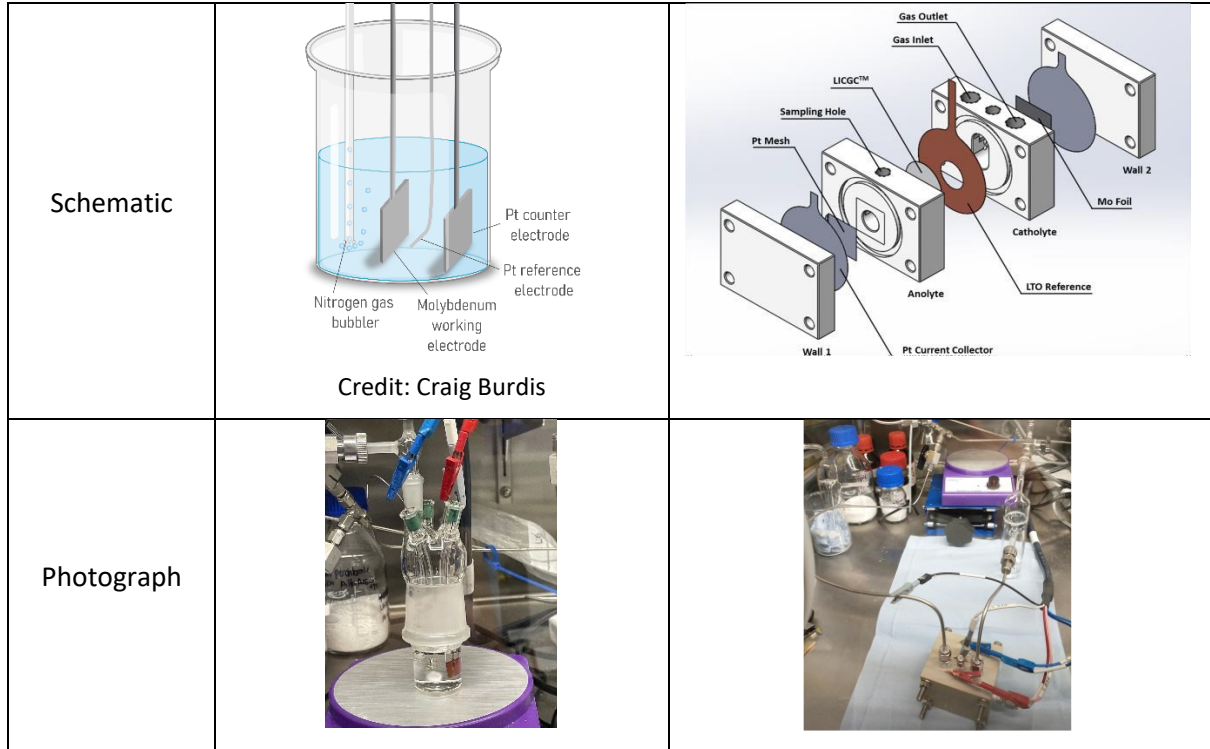
2.5. Electrochemistry Experiments

2.5.1. Electrochemical Cells Assembly

Two kinds of one compartment electrochemical cells were used for ammonia synthesis or other electrochemical testings (Table 1). However, the assembly procedure is analogous and as follows. A 1 cm² Mo foil working electrode, polished with 400, 1500 and 2500 grit silicon carbide paper (and wetting with ethanol) to a mirror finish, mounted on a Cu current collector and dipped in 4 M HCl and sonicated in ethanol for 10 min. Pt reference and counter electrodes were annealed under a flame. LiFePO₄ and Li₄Ti₅O₁₂ references were prepared as described in section 2.4. Within an Ar-filled glovebox, the cell was assembled (see geometry in Table 1). Cell compartments were filled with electrolyte, sealed gas tight and connected to gas feed and exhaust. A glass pre-bubbler containing the solvent was mounted ahead of the cell to saturate the inlet gas with solvent vapour (Table 1 picture). When mentioned, an acid trap made of HCl 0.5 M in 1,4-dioxane/THF was set up downstream from the cell to trap any ammonia ending in the gas phase. The setup was leak tested by flowing Argon at 10 ml.min⁻¹. The cell was then saturated with solvent-pre-saturated gas of interest (typically N₆ N₂), bubbling for 40 min at a flow rate of 10 ml.min⁻¹, then down to 2 ml.min⁻¹ for electrochemical testing.

Table 1. Electrochemical cell designs used for the research presented.

Cell	A – Glass Cell	B – Sandwich Cell
Material	Glass	PEEK
V _{electrolyte} (ml)	10 to 15	5
Working electrode	1cm ² square Mo foil mounted on Cu wire, double sided	1cm ² Mo foil disc mounted on Cu foil, single sided
Reference electrode	Pt wire, or LiFePO ₄ / Li ₄ Ti ₅ O ₁₂ foil mounted on Cu wire	Pt mesh (or foil), LiFePO ₄ or Li ₄ Ti ₅ O ₁₂ mounted on Cu foil
Counter electrode	1cm ² _{geo} square Pt mesh mounted on a Pt wire	1cm ² _{geo} Pt mesh disc mounted on a Pt foil
3-electrode geometry	Working and counter electrodes roughly parallel facing each other, 8 ± 2 mm apart, reference electrode midway through.	Working and counter electrodes exactly parallel facing each other, 34 ± 0.1 mm apart, reference electrode midway through.
Stirring?	Yes	No



2.5.2. Ohmic Drop Correction

The uncompensated resistance between the working (or counter) and reference electrode R_{ele} was assessed by electrochemical impedance spectroscopy before N_2 reduction (PEIS at open circuit, 20 mV oscillation, 100 kHz to 500 mHz frequency range).^{126,127} R_{ele} is obtained here through fitting of the experimental data to a suitable equivalent circuit and its impedance equation (Figure 25):

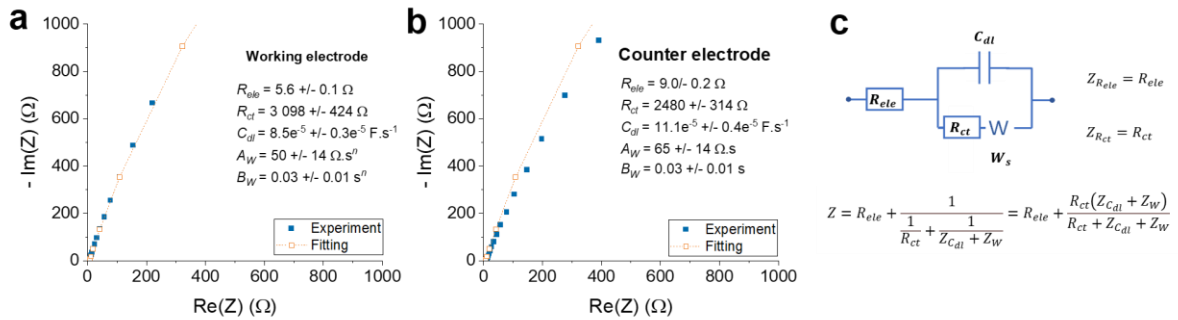


Figure 25. Impedance spectroscopy measurement method. **(a,b)** Examples of impedance spectra of the **(a)** working and **(b)** counter electrodes for the cell assemblies described above. Recorded by potentiodynamic electrochemical impedance spectroscopy (PEIS) at open circuit voltage, with an oscillation amplitude of 20 mV at frequencies ranging from 200 kHz to 500 mHz. The ohmic drop

correction was performed manually post experiments by correcting potentials with the formula $U_{eff} = U_{recorded} - R_{ele}i$ where U_{eff} is the corrected electrode potential, $U_{recorded}$ is the raw potential measured during experiments and i is the current passed during experiments. R_{ele} is the uncompensated resistance between the working (or counter) and reference electrode, collected from the PEIS measurements. R_{ele} is obtained here through fitting of the experimental data to a suitable equivalent circuit. (c) Equivalent circuit used to fit the impedance spectra and extract R_{ele} as well as other impedance contributions. – Reproduced from my work.¹²⁵ with permission from © 2023 The Authors. Published by American Chemical Society.

With R_{ct} the charge transfer resistance, $Z_{C_{dl}} = \frac{1}{j\omega C_{dl}}$ and C_{dl} the double-layer capacitance, $Z_W = \frac{A_W}{\sqrt{j\omega}} \tanh(B_W \sqrt{j\omega})$ the Warburg impedance (with its two parameters A_W and B_W) describing diffusion processes, ω the frequency, j the imaginary number representing the square root of -1. The ohmic drop correction was performed manually after the experiments by correcting potentials with the formula $U_{eff} = U_{recorded} - R_{ele}i$ where U_{eff} is the corrected electrode potential, $U_{recorded}$ is the raw potential measured during experiments and i is the current passed during experiments. Despite being the most appropriate way for us to estimate ohmic drop, we acknowledge that in some instances, it might be overestimated and therefore overcompensated in some measurements. Changes in electrolyte resistance were assessed by GEIS (Galvanostatic Electrochemical Impedance Spectroscopy, see section 2.5.3)

2.5.3. Nitrogen Reduction Experiments

The following electrochemical procedure was performed in the Argon glovebox at room temperature, using a Biologic SP-150 potentiostat. In a typical experiment (subject to variations which are disclosed appropriately), electrolyte resistance was assessed using impedance spectroscopy (PEIS at open circuit, 20 mV oscillation, 100 kHz to 500 mHz frequency range, see fitting method in section 2.5.2). Then, the working electrode potential was swept from open circuit voltage down to a voltage with a cut-off current density of -2 mA.cm^{-2} . After that, it was set at -2 mA.cm^{-2} , passing a total of 10 C charge (1 h 23 min 20 s). Electrolyte resistance change was assessed post electrolysis by impedance spectroscopy (GEIS at -2 mA.cm^{-2} , 0.5 mA.cm^{-2} modulation, 100 kHz to 500 mHz frequency range, see fitting method in Figure 55c,d), and the setup was purged with N6 Argon for 15 min at a flow rate of 10 ml.min^{-1} . Electrochemical measurements were corrected for ohmic drop after the experiment was finished. After experiments, the cell was rinsed with EtOH out of the glovebox and boiled in ultrapure

water (>18.2 MΩ, Sartorius), then dried in a vacuum oven at 70 °C. The electrolyte and the downstream trap (if relevant) were both sampled for ammonia quantification.

2.5.4. Recording the Half-Peak Potential of the Ferrocene Redox

The ferrocene-ferrocenium couple was approved as an internal reference redox couple with a defined 1 electron redox equilibrium, which half-peak potential is assumed to be independent of its chemical environment and therefore comparable across electrolytes.^{128–130} Recording the couple's half-peak potential against different electrodes in different electrolytes was deemed useful in different parts of this thesis' work. To estimate it, a voltammogram of an electrolyte of interest containing 10 mM ferrocene was recorded by sweeping a Mo foil working electrode potential at a 50 mV.s⁻¹ rate vs. an electrode of interest (e.g. a Pt, LiFePO₄ or Li₄Ti₅O₁₂ reference electrode, or Li metal; see section 2.4.) for preparation). $U_{Fc^+/Fc}$, the average between the potentials at which peak cathodic and anodic currents are reached, is an estimate of its half-peak potential.^{130,131}

2.5.5. Determination of the Potential Drift of Reference Electrodes

To estimate a drift in the potential of a (*pseudo*) reference electrode of interest (e.g. Pt, LiFePO₄ or Li₄Ti₅O₁₂) in different electrolytes and in the presence of different gases, $U_{Fc^+/Fc}$ was periodically recorded, as described in section 2.5.4. Following the evolution of the opposite of this potential in time allows one to estimate the reference electrode drift (Figure 26). An important sidenote with respect to the estimation of potential drift over the course of a Li-mediated ammonia synthesis experiment: during electrolysis, an unavoidable passivation layer (the SEI) forms at the working electrode. To avoid contribution of this layer to the reactivity of ferrocene, post-electrolysis measurements were done after replacing the working electrode with a fresh one, while keeping the same electrolyte.

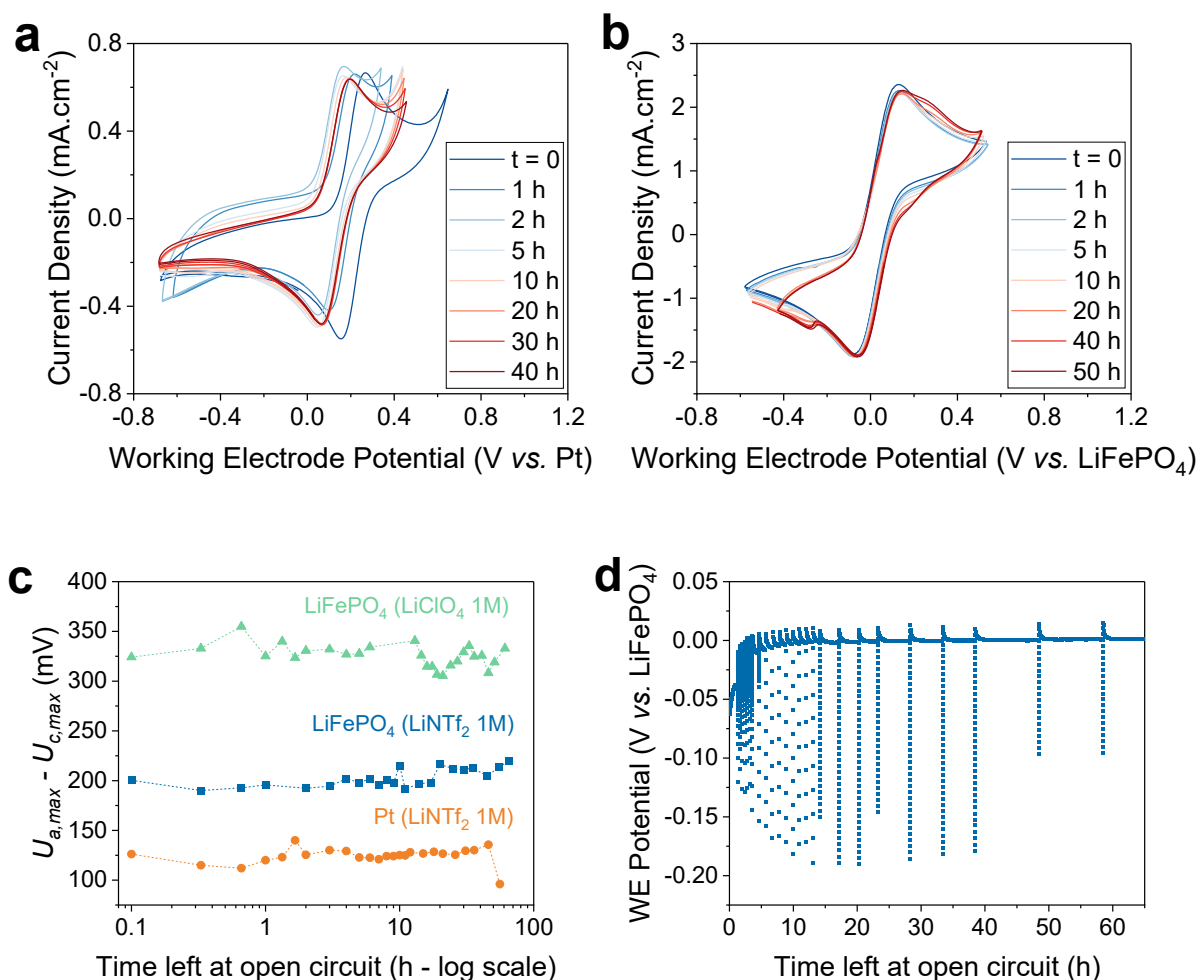


Figure 26. Cyclic voltammetry (CV) analysis of ferrocene containing electrolytes. **(a,b)** CVs of 10 mM ferrocene in 1 M LiTf₂ in THF/EtOH 99:1 v/v at different times of aging at open circuit, using **(a)** Pt and **(b)** LiFePO₄ as reference electrodes. **(c)** Peak potentials difference ($U_{a,max} - U_{c,max}$) vs. time at open circuit used to calculate U_{Fc/Fc^+} . **(d)** Working electrode potential recorded between ferrocene cycling steps, showing partial to full relaxation to OCP between each experiment. – Reproduced from my work.¹²⁵ with permission from © 2023 The Authors. Published by American Chemical Society.

2.5.6. Determination of the Equilibrium Potential of the Li⁺/Li Redox

Literature precedents show that the equilibrium potential of the Li⁺/Li redox couple ($U_{Li^+/Li}$) is strongly affected by the electrolyte composition and more precisely the activity of Li ions in solution.^{132,133} $U_{Li^+/Li}$ was estimated following a reported procedure.¹³⁴ Within an Ar-filled glovebox, a coin cell was assembled with a Li disc mounted on stainless steel spacer and spring, placed in the negative case of a coin cell (all previously cleaned by sonication in EtOH for 10 min and drying in air).

A Mo 18 mm diameter disc was placed in the opposite positive case and covered with a glass fibre separator, which was wetted with 70-100 μ l electrolyte. (2.4.1) The cell was closed with a press and left to rest for 1 day. Then, $U_{Fc^+/Fc}$ was recorded as described in section 2.5.4. The opposite of this value is $U_{Li^+/Li}$ vs. Fc^+/Fc and is compared across electrolytes.

2.5.7. Determination of the RHE Potential in Non-Aqueous Electrolytes

A method for the determination of the RHE potential in non-aqueous electrolytes was adapted from previous works in the group.¹¹⁴ A 1 cm² Pt foil attached to a Pt wire was used as the working electrode. A Pt mesh attached to a Pt wire of surface area larger than 1 cm² was used as the counter electrode. A LiFePO₄ electrode hooked on a Cu wire (prepared as in section 2.4) was used as reference. All Pt electrodes were electropolished in 70% nitric acid at least +1 V vs. a Pt mesh for 2 min and rinsed in ultrapure water and flame annealed. A cell was assembled with such electrodes in the same way as it is assembled in section 2.5.1. for nitrogen reduction experiments (configuration A, glass cell). The cell was purged with H₂ gas at 10 ml.min⁻¹ for 10 min while recording the open circuit voltage, stirring. After 10 min or when the working and counter electrode potentials experienced a clearly visible drift of their open circuit potentials due to Pt saturation with hydrogen, the gas flow was changed to 1 ml.min⁻¹ and stirring stopped to avoid too much electrolyte evaporation and settle the liquid down. Once open circuit potentials had stabilised, an impedance spectrum (PEIS at open circuit, 20 mV oscillation, 100 kHz to 500 mHz frequency range) to estimate ohmic losses. 10 Cyclic Voltammograms (CVs) were then recorded from -0.1 to +0.1 V vs. OCV (20 mV.s⁻¹ scan rate) to estimate the RHE potential before N₂ reduction ($U_{RHE,i}$). The impedance spectrum was recorded again in the same way to check for any change in ohmic drop, and the cell was purged with Argon at 20 ml.min⁻¹ for 30 min.

Following this, the cell was disassembled within the glovebox and the working electrode was switched with a Mo foil mounted on a Cu wire and conditioned as described in section 2.5.1, and a nitrogen reduction experiment was performed (see section 2.5.3). Following that, the cell was disassembled again, the working electrode was swapped back to the Pt foil, and the procedure for RHE potential measurement was repeated in the electrolyte that experienced a nitrogen reduction experiment to estimate the RHE potential after N₂ reduction ($U_{RHE,f}$).

The RHE potential was calculated by measuring the average over 10 cycles of cyclic voltammetry of the difference between the two potential points around OCV at which the current is zero (Figure 42).

2.6. Isotopically labelled $^{15}\text{N}_2$ Reduction Experiments

2.6.1. Gas Recycling Setup

A gas recycling setup was constructed to perform electrolysis of a fixed volume (closed loop) of $^{15}\text{N}_2$, based on previously published works from Nielander *et al.* (Figure 27).¹³⁵ The setup consists of a glass one-way dual action gas flow tube connected to a set of $\frac{1}{4}$ " stainless steel gas lines, which are also connected to an electrochemical cell. In the glass part, two 316 stainless steel springs circle a magnetic piston (a magnet embedded in a PEEK cylinder), which drives gas flow by back-and-forth movement. The piston's movement power and frequency are controlled using a set of copper wire coils wrapped around a plastic support that fits around the glass tube. The coils' magnetic fields were alternated by sequentially inverting the electrical current going through them, moving the piston back and forth by induction. The gas lines have two working positions. The first "open" one lets an inlet gas go through the glass tube, the gas lines, and the electrochemical cell down to an exhaust to saturate the gas phase with a desired gas. The second "closed" position lets the gas present in the glass part and the electrochemical cell circulate through a closed loop of gas lines, to saturate the cell's electrolyte with present gas. One can switch between working positions using a four-way valve. Switching between Ar, $^{14}\text{N}_2$ and $^{15}\text{N}_2$ can be done using a set of two-way and three-way valves ahead of the gas recycling setup. Ar and $^{14}\text{N}_2$ feeds are the same as described in previous paragraphs. A $^{15}\text{N}_2$ feed (364584-115L-EU, 98 atom % ^{15}N) cylinder that is sequentially connected to a gas regulator, a gas purifier (identical to the one used for $^{14}\text{N}_2$ and Ar), and the recycling setup.

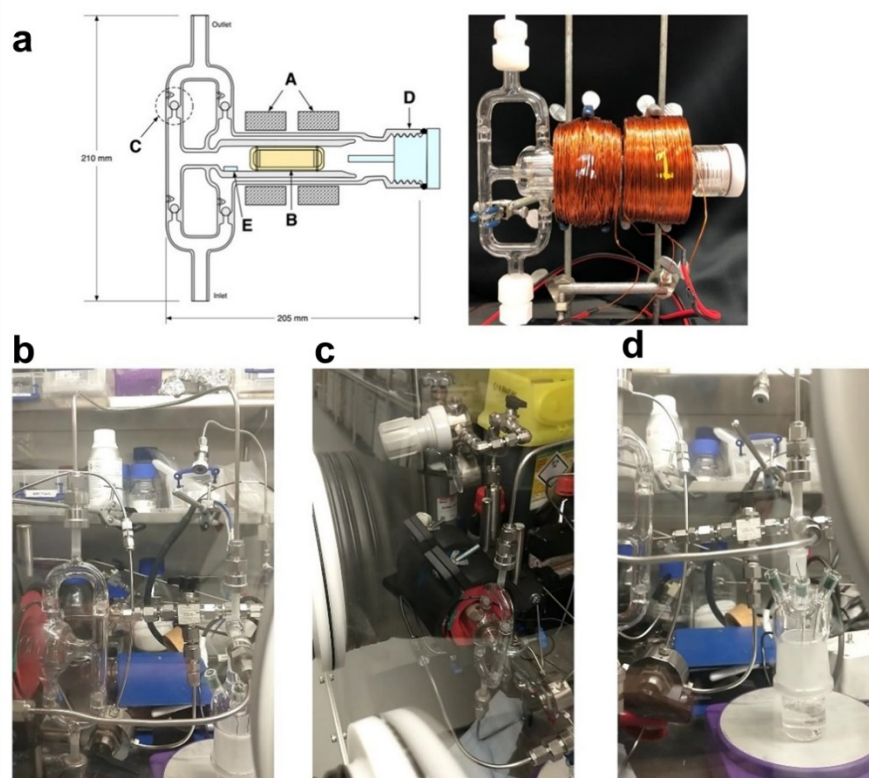


Figure 27. Gas recycling setup with electrochemical cell for isotopically labelled nitrogen reduction experiments, using $^{15}\text{N}_2$, $^{14}\text{N}_2$ or Ar. Setup designed by Dr Olivia Westhead – (a) reproduced with permission from Nielander et al.¹³⁵ © 2020 American Chemical Society.

2.6.2. Cell Setup and Gas Flow Procedure for Electrolysis

The single compartment glass cell with a working volume of 12 ml was used for electrolysis and connected to the gas recycling setup, in its “open” position. N6 grade Ar gas (purified as described earlier) was passed through the setup for 20 min at a rate of $20 \text{ ml} \cdot \text{min}^{-1}$ to remove impurities from the glovebox atmosphere. Then, the gas inlet was switched to either $^{14}\text{N}_2$ or $^{15}\text{N}_2$, flowing at a rate of $10 \text{ ml} \cdot \text{min}^{-1}$ (approximate rate for $^{15}\text{N}_2$ since no mass flow controller was mounted on this inlet) for 15 min to replace Ar. After that, the recycling setup was switched to its “closed” position, and the magnetic piston was activated to flow gas for 30 min. Electrolysis was then performed as described in section 2.5.3. Finally, the setup was switched back to its open position, flowing Ar through the setup for 20 min at a rate of $20 \text{ ml} \cdot \text{min}^{-1}$ and the cell was disassembled before ammonia quantification.

2.7. Nitride Protonolysis Model Experiments

Appropriate amounts of commercial (or synthesized) nitrides were suspended in either 15 equiv. EtOH 1 % v/v in THF or DME (in the glovebox), or simply water (out of the glovebox). They were then left to stir at room temperature over 3 days. After this time, suspensions were left to decant for at least 5 h, and the supernatant was sampled for ammonia quantification using the salicylate colorimetric UV-vis detection method or Ion Chromatography (section 2.8.3).

2.8. Ammonia Quantification in Non-Aqueous Electrolytes

2.8.1. By Colorimetric Quantification (UV-vis)

2.8.1.1. Sample Preparation

Electrolyte or acid trap post electrolysis were collected, with its total volume measured. 3 x 400 μ l were collected alongside 400 μ l of previously saved pristine electrolyte blank in separate vials. 30 μ l of 4 M aqueous HCl was added to each one of the four vials to trap NH_3 as NH_4Cl , which were then placed in a heated water bath (between 70 °C and 90 °C depending on sample viscosity and solvents boiling point) for 1 to 2 h to evaporate solvents. Each concentrate was then redissolved to 2 ml with ultrapure water for colorimetric quantification (section 2.8.1.3) and/or ^1H NMR quantification (section 2.8.2).

2.8.1.2. Salicylate Reagents Preparation

A sodium hypochlorite alkaline solution was prepared by mixing sodium hypochlorite 14 % w/w and sodium hydroxide 0.4 M in a 1:9 v/v ratio. This solution must be done shortly before every quantification experiment as the stock solution stability is limited in time. A “salicylate – catalyst” solution was prepared by dissolving 40 g sodium salicylate powder in 50 ml ultrapure water, to which 1 ml of a 50 mM aqueous sodium nitroprusside ($\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$) solution was added. Volume was completed to 100 ml in a volumetric flask, to yield a solution containing 2.5 M sodium salicylate and 0.5 mM sodium nitroprusside catalyst. The solution was stored at 5 °C in the dark for several months. Sometimes, the sodium salicylate powder was contaminated with ammonia salts impurities. To purify it from these interferents, 40 g sodium salicylate was dissolved in 300 ml DI water, to which 50 ml of 6 M aqueous HCl was added dropwise under constant stirring. The salicylic acid precipitate

was filtered and washed with three times 200 ml ultrapure water, then dried under vacuum at 40 °C. For 20 g of obtained salicylic acid, the solid was dissolved in 35 ml sodium hydroxide 4 M, to which were added 580 μl of sodium nitroprusside 50 mM solution, then completed with ultrapure water to 58 ml.

2.8.1.3. Salicylate Method and Standard Addition

We follow a colorimetric detection method based on the complexation of ammonia with sodium salicylate to create a blue dye.¹³⁶ For this method, a 1 ml sample was diluted to a volume of 2 ml with ultrapure water. Then, 280 μl of the “salicylate – catalyst” solution was added, followed with 280 μl of the sodium hypochlorite alkaline solution. Samples were left to age in the dark for 45 min (up to 2 h), then characterised by UV-vis absorption spectroscopy, measuring absorbance of light between 500 and 900 nm wavelengths, and measuring the difference in absorbance between the maximum (650 nm) and baseline (900 nm). In this work, we couple this quantification experiment to the quantification method of standard addition (Figure 28),^{137,138} spiking sequential amounts of a NH_4Cl standard solution (500 ppm, 9.35 mM) to the as prepared 2 ml samples and performing the salicylate quantification method to each one of these samples.

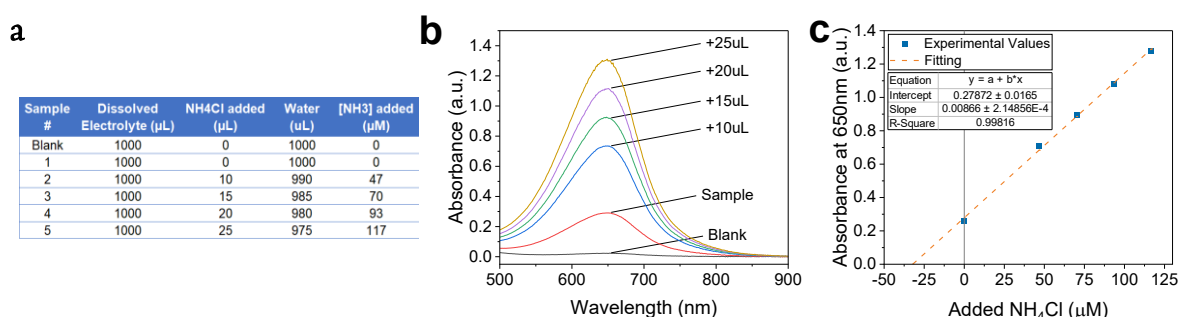


Figure 28. Ammonia quantification via salicylate standard addition – data analysis. (a) samples preparation volumes, (b) resulting UV-vis spectra, (c) reported maxima vs. added NH_4Cl . Reproduced with permission from my work,¹²⁵ © 2023 The Authors. Published by American Chemical Society.

By doing a linear regression on the obtained measurements, one can trace back to the ammonia present in the electrolyte, corresponding to negative of the intercept between the linear plot and the x axis (or the ratio between the slope m of the linear regression and its intercept b) (see equations (1,2,3)). $[\text{NH}_3]$ is the ammonia concentration in the electrolyte, V_{ele} is the electrolyte volume, F is the Faraday constant, Q is the total charge passed during the experiment, FE is the Faradaic Efficiency to ammonia, S is the working electrode geometric surface area.

$$(1) [NH_3] = \frac{b}{m}$$

$$(2) FE = \frac{3[NH_3]V_{ele}F}{Q}$$

$$(3) Yield Rate = \frac{[NH_3]V_{ele}}{S.exp\ time}$$

Variances (σ_k^2) and standard errors (s_k) in measurements are estimated using the below statistical equations (4,5,6). A_i is the absorbance of sample with concentration c_i , $\bar{A}$ and $\bar{c}$ are the mean absorbance and concentration, respectively. m and b are the slope and intercept of the fitted linear regression. N is the overall number of measurements.

$$(4) \sigma_A^2 = \sum_i (A_i - \bar{A})^2 - m^2 \sum_i (c_i - \bar{c})^2$$

$$(5) \sigma_m^2 = \frac{\sigma_A^2}{\sum_i (c_i - \bar{c})^2}$$

$$(6) \sigma_b^2 = \sigma_A^2 \frac{\sum_i c_i^2}{\sum_i (c_i - \bar{c})^2}$$

$$(7) s_k = \sqrt{\frac{\sigma_k^2}{N-1}} \quad (k = A, m, b)$$

$$(8) s_{[NH_3]} = \sqrt{\frac{\sigma_{[NH_3]}^2}{N-1}} = [NH_3] \sqrt{\left(\frac{s_b}{b}\right)^2 + \left(\frac{s_m}{m}\right)^2}$$

2.8.2. By ^1H NMR Quantification

2.8.2.1. Sample Preparation

Samples for ^1H NMR quantification can include non-aqueous electrolytes where solvent was evaporated and remaining deposit redissolved in water (section 2.8.2.1), or aqueous solutions resulting from the protonolysis of an electrode material of interest (section 2.9.6). 400 μ l of such aqueous sample containing ammonia were added 100 μ l of a solution containing 1 mM MeOH, 5 % v/v HCl and 10 % v/v D_2O in ultrapure water, to be used for ^1H NMR quantification (200 μ M MeOH, 5 % v/v HCl, 2 % v/v D_2O). This sample was then subjected to the following ^1H NMR procedure.

2.8.2.2. ^1H NMR Experiment

The experiments were measured on a Bruker Avance III HD 500 MHz spectrometer running TopSpin3.6.5 and equipped with a z-gradient Prodigy/5mm tuneable probe and a BSMS GAB 10amp gradient amplifier providing a maximum gradient output of 53.5 G/cm (5.35 G/cmA). Water suppression was achieved using a standard Bruker pulse program zgpgw5 which employs a Watergate W5 sequence. The gradient ratios for this double echo experiment were 34:22. The spectra were collected at a frequency of 500.13 MHz with a spectral width of 9014 Hz (centred on the water signal at ~ 4.7 ppm) and 65536 data points giving an acquisition time of 3.64 s. A relaxation delay of 1 s was employed along with a binomial water suppression delay of 111 μ s. Smoothed-square shaped (SMSQ10.100) gradient pulses were 1 ms in length with a recovery delay of 200 μ s. Number of scans

was 512 with 4 dummy scans which were not taken as output data. The data was processed with one order of zero-filling and using an exponential function with a line broadening of 0.3 Hz.

Gathered data was compared against a calibration curve to calculate the amount of ammonia present (Figure 29). Such calibration curve was made by subjecting to the same NMR experiment different solutions of $^{14}\text{NH}_4\text{Cl}$ or $^{15}\text{NH}_4\text{Cl}$ (in 200 mM MeOH, 5% v/v HCl and 2% v/v D_2O in water).

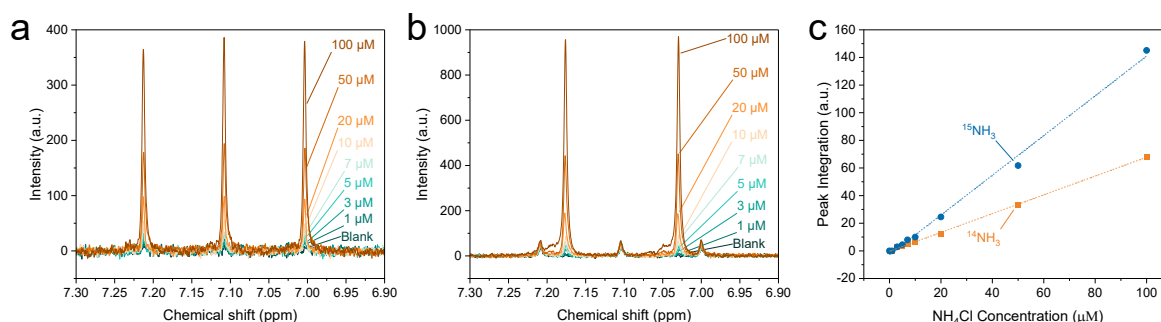


Figure 29. ^1H NMR quantification of $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$. NMR signals obtained from the preparation of samples with known concentrations of (a) $^{14}\text{NH}_4\text{Cl}$ and (b) $^{15}\text{NH}_4\text{Cl}$. (c) Resulting calibration curves for $^{14}\text{NH}_4\text{Cl}$ and $^{15}\text{NH}_4\text{Cl}$. NMR measurements performed by the NMR facility manager Peter Haycock.

2.8.3. By Ion Chromatography

A solution of interest containing ammonia was diluted by a factor of 10 in ultrapure water and subjected to the following ion chromatography method. Each sample was eluted using a Metrohm 930 Compact IC Flex instrument, on a Metrosep C Supp 2 column, using 5.0 mM nitric acid and 50 ppm rubidium nitrate aqueous eluent, flowing at $1.0 \text{ ml} \cdot \text{min}^{-1}$ at a pressure of 13–14 MPa, and separated cations were detected on a conductivity detector (baseline conductivity, $\sim 0.2 \mu\text{S} \cdot \text{cm}^{-1}$). The column was then regenerated by purging with a regenerant solution of 70 mM Na_2CO_3 and 70 mM NaHCO_3 in DI water. Areas of peaks detected (including Li^+ , Na^+ , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+}) were compared against a calibration curve, to yield in this case the amount of ammonia produced. Calibration curves were made periodically by preparing known amounts of NH_4OH in water and subjecting to the same calibration curve to ensure accurate quantification.

2.9. Interphase Species Titration

Interphase species of different alkali metal chemistries (Metal, Metal-ions, M_xH_y , $M_x(CO_3)_y$, $M_xN_yH_z$, M_xF_y , M_xO_y , $M_x(OH)_y$, ...) were quantified (not always all of them) through the following workflow (Figure 30), using different analytical techniques to monitor each analyte resulting from the protonolysis of the electrode material with a titrant solution.

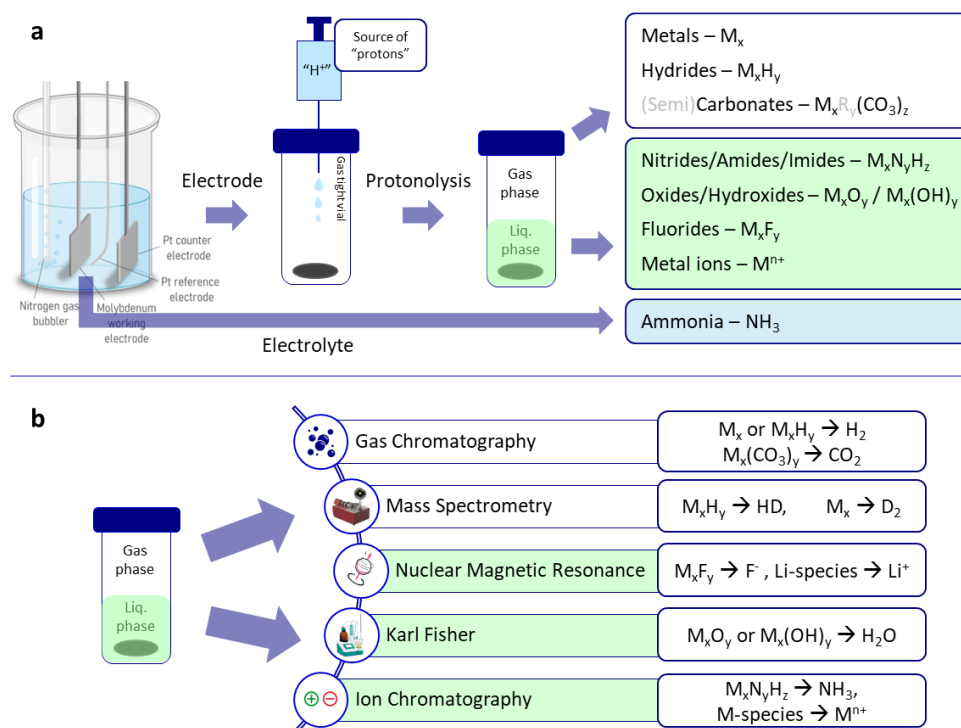


Figure 30. Workflow for the titration of electrode interphase species. A material of interest is placed in a sealed vial, to which is added a "titrant", a protic species that protonolyses the material's components, to yield analytes in the gas phase or liquid phase that can be quantified. – Cell drawing courtesy of Craig Burdis. Analytical techniques developed with the help of Dr Bethan Davies, Dr Anna Winiwarter, Yuxiang Zhou and Aishah Faisal.

2.9.1. Sample Preparation and Protonolysis

Protonolysis of an electrode sample consists in reacting the electrode material with a protic molecule to yield an analyte that is quantifiable. Different electrode materials require different titrants to be able to quantitatively estimate their amount (Table 2). In our case, five nitrogen reduction experiments were performed for each electrolyte composition. Three of the as produced electrode

deposit them were dipped in THF to wash off residual electrolyte, and titrated with MeOD, allowing the quantification of Li^0 , LiH, $\text{Li}_x\text{N}_y\text{H}_z$, $\text{Li}_2\text{O}/\text{LiOH}$ and total amount of Li species in the SEI. The two remaining electrode deposits were not washed with solvent this time, and titrated with D_2O , enabling titration of LiF but also Li^0 , LiH and $\text{Li}_x\text{N}_y\text{H}_z$ like previously. Unfortunately, this means that titration of Li_2CO_3 will not be possible (only converted to GO_2 gas quantitatively with acidic aqueous titrants, see section 2.9.3). However, Li_2CO_3 is suggested to be a metastable species in lithium metal battery SEIs and suggested to convert relatively fast to LiF and CO_2 in fluorinated electrolytes,¹³⁹ and we will therefore assume a neglectable amount of Li_2CO_3 to be present in such SEIs. The orthogonality between LiF and $\text{Li}_2\text{O}/\text{LiOH}$ titration originates from the fact that LiF is only soluble in water (section 2.9.5), and $\text{Li}_2\text{O}/\text{LiOH}$ can only be titrated in non-aqueous media (section 2.9.4).

Table 2. Interphase species of interest, compatible titrants, reactions they undergo with such titrant, and which species one cannot co-titrate with.

Species of Interest	Titrants	Reaction (analyte in bold)	Analytical Technique	Incompatible
M (metal)	H_2O , D_2O , Acid, MeOH, MeOD	$M + n \text{H}^+ \rightarrow n/2 \text{H}_2 + M^{n+}$ or $M + n \text{D}^+ \rightarrow n/2 \text{D}_2 + M^{n+}$	Gas Chromatography	-
M_xH_y (hydride)	D_2O , DCl in D_2O , MeOD	$\text{M}_x\text{H}_y + y \text{D}^+ \rightarrow y \text{HD} + x \text{M}^{y/x+}$	Mass Spectrometry	-
$\text{M}_x(\text{CO}_3)_y$ (carbonate)	Aqueous Acid	$\text{M}_x(\text{CO}_3)_y + 2y \text{H}^+ \rightarrow y \text{CO}_2 + y \text{H}_2\text{O} + x \text{M}^{2y/x+}$	Gas Chromatography	M_xO_y , M_xF_y
M_xO_y / $\text{M}_x(\text{OH})_y$ (oxide/hydroxide)	MeOH, MeOD	$\text{M}_x\text{O}_y + 2y \text{MeOH} \rightarrow y \text{H}_2\text{O} + x \text{M}(\text{OMe})_{2y/x}$	Karl Fisher	M_xF_y , $\text{M}_x(\text{CO}_3)_y$
M_xF_y (fluoride)	H_2O , D_2O	$\text{M}_x\text{F}_y + \text{H}_2\text{O} \rightarrow y \text{F}^-_{\text{aq.}} + x \text{M}^{y+}_{\text{aq.}}$	^{19}F NMR	M_xO_y , $\text{M}_x(\text{CO}_3)_y$
M_xN_y / $\text{M}_x\text{N}_y\text{H}_z$ (nitrides/amides)	H_2O , D_2O , Acid, MeOH, MeOD	$\text{M}_x\text{N}_y\text{H}_z + (3y - z)\text{H}^+ \rightarrow y \text{NH}_3 + x \text{M}^{y+}$	UV-Vis / Ion Chromatography	-
Alkali metal-ions in interphase	H_2O , D_2O , Acid, MeOH, MeOD	Rough eqn : $\text{M}_x\text{R} + xn \text{H}^+ \rightarrow x \text{M}^{n+} + xn \text{RH}$	^7Li NMR / Ion Chromatography	-

Within a glovebox, an electrode of interest was isolated, and dipped in an aprotic solvent to wash off excess electrolyte (if mentioned). The layer of solvent on the electrode was left to evaporate in the glovebox (or under vacuum in the glovebox antechamber), and then transferred to a sealed septum vial with a volume capacity of 42 ml:

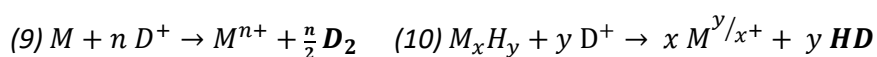
- For aqueous titrants: The sample was taken out of the glovebox, and 2 ml of titrant was added using a syringe (septum cap closed).

- For non-aqueous titrants: The titrant was stored in the glovebox, dried over activated molecular sieves (1/3 vol.) for 3 days to yield a solution with < 20 ppm water. 2 ml of this titrant was added to the sample using a syringe, and the sample was taken out of the glovebox.

Gas evolution was monitored visually (bubbles formation), taking seconds for flat Li metal samples, up to several minutes or hours for less reactive –or porous– materials. The sample was then taken to gas phase analysis techniques (Gas Chromatography, Mass Spectrometry). The sample was then stored for >10 h (inside glovebox for non-aqueous titrants), and only then the liquid phase was analysed (Karl Fisher, NMR, Ion Chromatography, ...).

2.9.2. Metal (M) and Hydride (M_xH_y) Titration – GC + MS

A method developed by Meng and co-workers^{140,141} for the titration of Li metal was adapted to the quantification of alkali metals on the electrodes used in electrolytic ammonia synthesis experiments to estimate the amount of excess metal plated and metal hydride formed. By adding a deuterated proton source to a certain amount of metal (or metal hydride), D₂ (or HD, respectively) is generated following the reactions in equations (9,10). The amount of D₂ and HD altogether can be quantified by gas chromatography (section 2.9.2.2), and the ratio between the two can be measured by mass spectrometry (section 2.9.2.3), to trace back to the amount of metal and metal hydride present.



2.9.2.1. Gas Chromatography Calibration for Hydrogen (H₂, D₂, HD) Signal

All Gas Chromatography experiments were performed using a 8610C Multiple Gas Analyzer #5 GC (TCD-FID-METH) from SRI Instruments. A calibration curve was built by hooking a stock gas cylinder containing 1000 ppm (molar) H₂ in CO₂ to the GC in line analysis mode, sampling several dilutions, and running them through the in-line gas chromatography mode. Since we operate in headspace mode for electrodes titration (section 2.9.2.2), the calibration curve was proofed in different ways. First, it was extended to higher H₂ contents by hydrolysing known amounts of LiAlH₄ with water (samples made by making several dilutions of 1 M LiAlH₄ in THF), which resulted in a calibration curve with a similar slope (Figure 31, green dots). Second, one of the points from the in line H₂ gas calibration was repeated using the headspace mode as follows. An open 42 ml septum vial was sunk in a container of ultrapure water, filled with that water and tilted upside down. A gas line

was then brought into the vial, flowing and filling it with a mixture of H_2 1000 ppm (molar) in CO_2 (same gas used for the calibration curve). Once full and saturated, the vial was closed with the septum cap while still in the water. The vial was then transferred to the headspace GC for quantification of H_2 as described below here (section 2.9.2.2). The results between flow mode and headspace mode concur nicely (Figure 31, red dot). Thirdly, the calibration was also proofed by running the titration of known amounts of lithium. For this, a standard coin cell was assembled using an analogous procedure to the one described in section 2.4.1 with a 18 mm Cu current collector facing a Li metal counter electrode, separated by a Whatman glass fiber disc and a Celgard separator closer to the Cu current collector (to avoid losing too much Li metal stuck to the glass fiber), all wetted with 100 μL of LP57 electrolyte (1 M LiPF_6 in EC/DMC). The coin cell was run by passing enough charge to plate 100 μg of Li metal at $-250 \mu\text{A}$. An identical cell was run in the same conditions, then Li metal was stripped at constant current ($-250 \mu\text{A}$) to estimate how much Li metal had been plated (coulombic efficiency of $18 \pm 2 \%$ observed, $2.65 \pm 0.02 \mu\text{mol Li}^0$ expected). The Cu current collector of the first cell was then isolated and stored in a GC vial for titration. The amount of H_2 detected from this sample is roughly where it is expected (Figure 31, blue dot). A slight underestimation is expected as some of the Li metal may have been lost to the current collector when isolating the electrode of interest, or further reacted with electrolyte before isolating the electrode from the coin cell. Some of the generated H_2 might also have been lost through leaks in the GC vial during titration. The results seemed promising enough and the calibration was therefore used as is moving on.

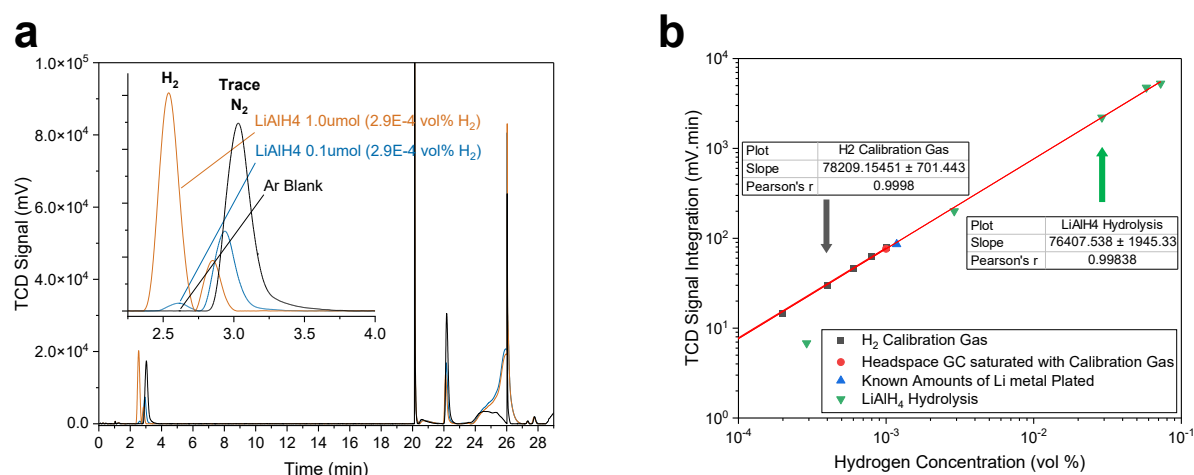


Figure 31. Calibration curves for GC quantification of hydrogen gas generated from metals and hydrides. (a) Typical GC chromatograms for hydrogen detection from a titrated sample: showing different amounts of LiAlH_4 hydrolysed with water alongside an Argon blank, measurements

performed by Aishah Faisal and Dr Anna Winiwarter. Insert showing hydrogen peak. **(b)** Calibration curve for the quantification of hydrogen by different methods. In-line hydrogen gas flow calibration (grey points, performed by Yuxiang Zhou) and titration of known amounts of 1 M LiAlH₄ in THF with water (green points, performed by Aishah Faisal and Dr Anna Winiwarter). Calibrations proofed against headspace analysis of a known mixture of hydrogen gas in CO₂ (red point), and titration of known amounts of lithium plated in a coin cell (blue point).

2.9.2.2. Sample Analysis by Gas Chromatography – Quantifying ‘Hydrogen’ (H₂, D₂, HD)

After protonolysis of the electrode sample, it was transferred to the headspace gas chromatography (GC) device, eluting the gas to quantify the amount of hydrogen (H₂, D₂ and HD altogether) and CO₂ generated, operating at 50 °C during analytes elution. Argon was used as a carrier gas, FID (for CO₂) and TCD (for Hydrogen) detector were used, with the first one being fed by H₂ generated by a side H₂ generator. A temperature program was set for the GC to operate at 50 °C for the first 20 min, then ramp up to 120 °C (10 °C.s⁻¹) and hold for 5 min to bake out the column. Using the software PeakSimple, the following sequence was run to sample the vial and elute the gas:

Time (min)	Valve and Action	Description
0	Zero	Start of the analysis
0	Sound	Make a sound to alert the user
0.1	E – ON (Valve3Rotate)	Pressurising headspace vial (+ 8 psi)
0.2	E – OFF (Valve3Rotate)	Stop pressurising
0.3	C – ON	Vents the vial into the sample loop
0.4	C – OFF	Stop venting, sample isolated into sample loop
1.0	B – ON (InjectorVent)	Injecting sample into the GC column
20.0	B – OFF (InjectorVent)	End of injection (Ar only into the column)
20.1	F – ON (Valve2Rotate)	Backflush (removing non-eluted components which may interfere with subsequent runs)
26.0	F – OFF (Valve2Rotate)	Stop Backflush

The area of the H₂ peak at ~2 min was noted and traced back to the amount of hydrogen in the glass vial, using the calibration factor generated from the calibration curve (Figure 31). If Hydrogen in Argon (or CO₂) behaves as an ideal gas, we have (equation (11)):

$$(11) n_{hydrogen,GC} = Dil_P \frac{PV_{hydrogen}}{RT} = Dil_P \frac{PV_{gas}}{RT} vol\%_{hydrogen} = Dil_P \frac{PV_{gas}}{RT} \frac{Area_{hydrogen,GC}}{78209.155}$$

$$\text{Where } Dil_P = \frac{101325+55158}{101325} \text{ (GC vial gas dilution during pressurisation of 8 psi = 55158 Pa)}$$

$$P = 1 \text{ atm} = 101325 \text{ Pa}, \quad V_{\text{gas}} = (42 - V_{\text{titrant}}) * 10^{-6} \text{ (in m}^3\text{)},$$

$$R = 8.314 \text{ J.K}^{-1}.\text{mol}^{-1} \quad \text{and} \quad T = 20^\circ\text{C} = 293.15 \text{ K}$$

2.9.2.3. *D₂-HD ratio by Mass Spectrometry – Metal and Hydride Deconvolution*

The mass spectrometer used for this analysis is a SpectroInlets on-chip mass spectrometer, allowing subsecond detection of gases and volatile species with high sensitivity.^{142–144} This is possible due to a unique membrane chip that can support liquid or gas on its topside and a gas sampling volume below which is connected to a mass spectrometer through a capillary. The membrane and capillary are fabricated using semiconductor fabrication techniques and are contained within a thumb-sized silicon chip, they allow fast equilibration between a top volume and bottom gas sampling volume. A closed cell sits on top of the silicon chip and has a disc-shaped working volume (9 mm diameter, 100 μm thickness). Both top volume and bottom gas sampling volume are pumped down to a vacuum of ~10 mbar before injecting an analyte in the system.

Once the septum vial was sampled for GC analysis, it was taken out of the GC sampler, and 0.5 ml of that same gas phase was sampled from the vial using a gas tight Hamilton syringe and injected into the closed cell built on the mass spectrometer. Masses 2, 3 and 4 (and any other of interest) were recorded before, during and after the injection of the analyte.

The quantification of D₂ (mass 4), HD (mass 3) and H₂ (mass 2) was by integrating such mass signals and deconvoluting them from the signal originating from other species (titrant vapours, other gases ...), using a Python program coded by Dr Anna Winiwarter with the Python package Ixdat (<https://ixdat.readthedocs.io/en/latest/>), where the idea behind this code is described in more details in the PhD Thesis of Dr Søren B. Scott.¹⁴³

2.9.2.4. *Calculation of the Total Amount of Metal and Metal Hydride*

Once the amount of D₂+HD combined (GC), and their ratio is measured (Mass Spectrometry), the amount of metal and metal hydride in a sample can be calculated by equations (12,13):

$$(12) n_{M_xH_y} = \frac{1}{y} \cdot n_{\text{hydrogen,GC}} \cdot \frac{n_{HD}}{n_{HD+D_2}} \quad \text{and} \quad (13) n_{\text{Metal}} = \frac{2}{m} n_{\text{hydrogen,GC}} \cdot \frac{n_{D_2}}{n_{HD+D_2}}, \quad \text{with}$$

m the metal ion charge (Li, Na, K : 1 ; Mg, Ca : 2 ; etc.), and y the Hydride H stoichiometry.

2.9.3. Metal Carbonate ($M_x(CO_3)_y$) Titration – Gas Chromatography

The electrode sample was hydrolysed with either methanol-OD, D₂O or an aqueous acid. Following that, the sample was subjected to GC analysis, as described in section 2.9.2.2 for metal titration. Then, one can calculate the amount of CO₂ in the gas and therefore carbonate on the titrated electrode. Assuming CO₂ in Argon behaves as an ideal gas, we have (equations (14,15)):

$$(14) n_{CO_2,GC} = [CO_2] \cdot V_{gas} = \frac{Area_{CO_2,GC}}{CO_2 \text{ calibration factor}} \cdot V_{gas} \quad \text{and} \quad (15) n_{M_x(CO_3)_y} = \frac{n_{CO_2,GC}}{y}$$

$$n_{CO_2,GC} \text{ in } \mu\text{mol}, [CO_2] \text{ in } \mu\text{mol} \cdot l^{-1}, V_{gas} = (42 - V_{titrant}) * 10^{-3} \text{ in liters}$$

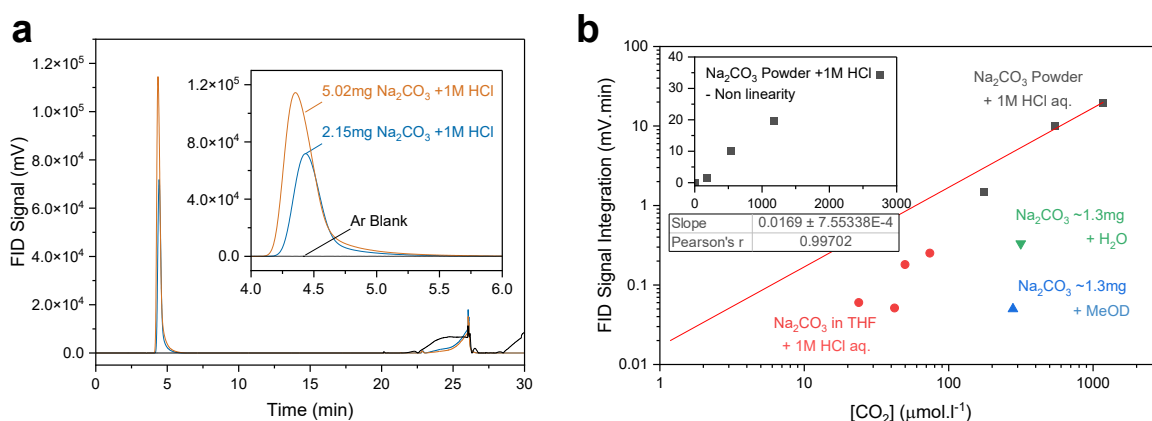


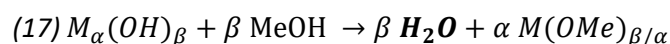
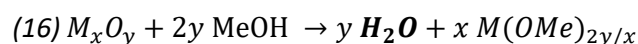
Figure 32. Calibration curves for GC quantification of CO₂ gas generated from carbonates. **(a)** Typical GC chromatograms for CO₂ detection from a titrated sample: showing different amounts of Na₂CO₃ hydrolysed with 1 M HCl aq. alongside an Argon blank. Insert showing CO₂ peaks. **(b)** Calibration curve for the quantification of CO₂ made by reacting different amounts of Na₂CO₃ with aqueous 1 M HCl (measurements done by Aishah Faisal and Dr Anna Winiwarter, grey points). Identical measurements done by reacting a solution of Na₂CO₃ in diglyme with 1 M HCl (red points) or reacting Na₂CO₃ powder with H₂O (green) or MeOD (blue), showing underestimations in all cases.

Unfortunately, using water as a titrant (or worse, a non-aqueous proton source such as MeOD) will result in underestimations for two reasons. First, if the source of protons is not acidic enough, the conversion of carbonate to CO₂ (analyte of interest) will not occur. Second, CO₂ generated is insoluble in acidic media but rather soluble in water, and even more in non-aqueous solvents. Some of it might remain dissolved in the liquid phase and not be detected by GC. This is what we observed by GC analysis of sodium carbonate samples titrated by D₂O and MeOD (Figure 32). In the case of D₂O, it is

likely to be a combination of the two factors. In the case of titrations with methanol-OD, we suggest that carbonates do not even react with such titrant. Indeed, water should be generated from the protonolysis of sodium carbonate, and no significant amounts of water were detected after titration in MeOD (see section 2.9.4), consistent with previous studies.⁹⁰

2.9.4. Metal Oxide/Hydroxide (M_xO_y / $M_x(OH)_y$) Titration – Karl Fisher

An electrode sample inside a sealed GC vial was protonolysed using 2 ml dry (< 20 ppm) methanol (MeOH or MeOD), where methanol reacts according to equations (16,17):



After gas phase analysis (sections 2.9.2-2.9.3), the GC vial was stored for >10 h inside the glovebox for methanol to digest all metal oxide/hydroxide in the absence of adventitious water. 1.5 ml of this sample was then transferred to a 7 ml septum vial, and the content analysed by Karl Fisher titration. 2-3 ml of the clean “dry” methanol was analysed alongside it for background subtraction, and amount of water detected is calculated with equation (18):

$$(18) n_{H_2O, KF} = \frac{C_{H_2O, ppm} \cdot V_{spl} \cdot d_{MeOD/H}}{M_{H_2O}}$$

$$\text{where } d_{MeOH} = 0.792 \text{ g.ml}^{-1}, d_{MeOD} = 0.813 \text{ g.ml}^{-1} \text{ and } M_{H_2O} = 18 \text{ g.mol}^{-1}$$

In theory, the amount of water detected does not directly trace back to the amount of metal oxide or hydroxide detected. As seen in section 2.9.3, the titration of metal carbonates $M_x(CO_3)_y$ should release CO_2 and water in stoichiometric amounts (equation (14,15)). However, we observed no significant amounts of water generated after mixing known amounts of sodium carbonate in MeOD for a day (Figure 33), suggesting that any present carbonate in the system remains unreacted in the time frame of the analysis, consistent with the absence of detected CO_2 by GC in the same samples (Figure 32), and consistent with previous studies.⁹⁰

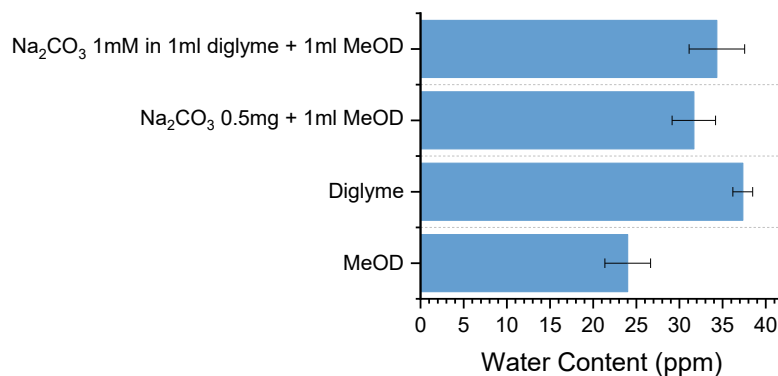


Figure 33. Karl Fisher titration of samples of Na₂CO₃ in mixtures of organic solvents and MeOD.

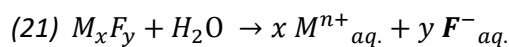
This means that we could not quantify the amount of carbonate in the SEI, but also that all water can be assumed to be derived from the protonolysis of M_xO_y/M_x(OH)_y only. The amount of metal oxide (or hydroxide) in a sample can therefore be calculated with equations (19,20):

$$(19) \ n_{M_xO_y} = \frac{1}{y} n_{H_2O, KF} \quad \text{or} \quad (20) \ n_{M_\alpha(OH)_\beta} = \frac{1}{\beta} n_{H_2O, KF}$$

A limitation of this method is the inability to discriminate metal oxide from hydroxide. Therefore, one must assume whether there is mostly oxide or hydroxide and approximate it to 100 % of that phase. This is not a major issue in battery electrolytes where only trace amounts of protic sources leading to metal hydroxide are present, and it can be approximated to 100 % metal oxide.^{90,145} However, this assumption does not hold for Li-mediated ammonia synthesis electrolytes where protic sources are present and both Li₂O and LiOH were observed.⁸¹ This is not a problem in quantification of monovalent and trivalent ions (e.g. Li₂O/LiOH or Al₂O₃/Al(OH)₃) since oxides and hydroxides release water in identical stoichiometries ($y = \beta$) upon reaction with methanol. However, for divalent cations (Ca, Mg, ...) one molecule of metal oxide (MO, $y = 1$) releases one molecule of water, but a molecule of metal hydroxide (M(OH)₂, $\beta = 2$) releases two molecules of water, leading to over- or under-estimation whether one approximates the total to oxide or hydroxide, respectively.

2.9.5. Metal Fluoride (M_xF_y) Titration – ¹⁹F NMR

An electrode sample inside a sealed GC vial was hydrolysed using 2 ml H₂O or D₂O (equation (21)):



After gas phase analysis (sections 2.9.2-2.9.3), the GC vial was stored for >10 h in a fume cupboard for water to digest all metal fluoride. The liquid was then either diluted by a factor of 1/5 with D₂O (if titrated with H₂O) and transferred to a NMR tube, or directly transferred to a NMR tube if the titrant was D₂O. The as prepared sample was subjected to the following NMR procedure.

The experiments were measured on a *Bruker BioSpin* 400 MHz UltraShield NMR magnet with Avance III HD NanoBay console, running TopSpin3.6.5 and equipped with a z-gradient Prodigy/5mm tuneable probe or similar. The spectra were collected at a frequency of 400 MHz with a spectral width of 10 ppm, and 8196 data points giving an acquisition time of 1.09 s. A relaxation delay of 19 s was employed to make sure the signal fully relaxes, running 16 scans and -122.5 ppm offset.

The peak at roughly -122 ppm chemical shift (varies with chemical environment) was then integrated and compared against a calibration curve made by subjecting samples with different amounts of LiF dissolved in D₂O to the same NMR procedure (Figure 34).

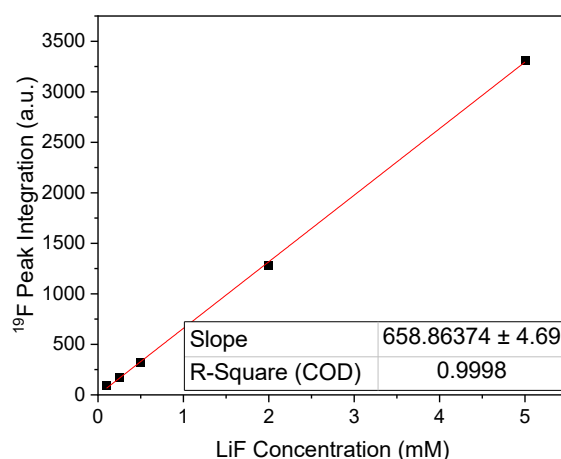
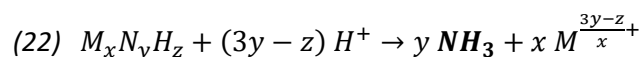


Figure 34. ¹⁹F NMR calibration curve of LiF. Using the signal at ~-122 ppm corresponding to free F-ions, made by dissolving known amounts of LiF in D₂O and subjecting to the quantitative ¹⁹F NMR titration method. NMR experiment developed with the help of Dr Stuart Elliott, NMR facility manager.

2.9.6. Metal Nitride/Amide (M_xN_yH_z) Titration – Ion Chromatography

An electrode sample inside a sealed GC vial was protonolysed using 2 ml titrant (any protic source works), reacting according to equation (22):



After gas phase analysis (sections 2.9.2-2.9.3), the GC vial was stored for >10h inside the glovebox for the titrant to digest all metal nitride/imide/amide and yield ammonia. The amount of ammonia produced can be quantified using the same techniques used for ammonia detection from N₂ reduction experiments (section 2.8) and traced back to the amount of metal nitride/imide/amide (equation (23)).

$$(23) \quad n_{M_x N_y H_z} = \frac{1}{y} n_{NH_3}$$

2.9.7. Metal-ions in Interphase Titration – Ion Chromatography or ⁷Li NMR

An electrode sample inside a sealed GC vial was protonolysed using 2 ml protic titrant (for Li, any protic source works, more acidic sources may be needed for less reactive metals), to dissolve all metallic salts into solvated metal ions. The amount of such ions can be quantified by Ion Chromatography, or by quantitative ⁷Li NMR for lithium electrodes.

2.9.7.1. By Ion Chromatography

The prepared liquid sample containing the metal ion was diluted by a factor of 1/10 in ultrapure water and subjected to the following ion chromatography method. Each sample was eluted using a Metrohm 930 Compact IC Flex instrument, on a Metrosep C Supp 2 column, using 5.0 mM nitric acid and 50 ppm rubidium nitrate aqueous eluent, flowing at 1.0 ml.min⁻¹ at a pressure of 13-14 MPa, and separated cations were detected on a conductivity detector (baseline conductivity, ~0.2 μS.cm⁻¹). The column was then regenerated by purging with a regenerant solution of 70 mM Na₂CO₃ and 70 mM NaHCO₃ in DI water. Areas of peaks detected (including Li⁺, Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺) were compared against a calibration curve, to yield in this case the amount of ammonia produced. Calibration curves were made periodically by preparing known amounts of NH₄OH in water and subjecting to the same calibration curve to ensure accurate quantification. The metal-ion calibration curves were made by subjecting a range of solutions of metal nitrate in ultrapure water to the same ion chromatography method.

2.9.7.2. By ^7Li NMR

The prepared liquid sample containing the metal ion was diluted by a factor of 1/5 in D_2O (if titrated with H_2O) and transferred to an NMR tube, or directly transferred to an NMR tube if the titrant was D_2O . It was then subjected to the following NMR procedure.

The experiments were measured on a *Bruker BioSpin* 400 MHz UltraShield NMR magnet with Avance III HD NanoBay console, running TopSpin3.6.5 and equipped with a z-gradient Prodigy/5mm tuneable probe or similar. The spectra were collected at a frequency of 400 MHz with a spectral width of 50 ppm, and 32768 data points giving an acquisition time of 2.11 s. A relaxation delay of 156.65 s was employed to make sure the signal fully relaxes, running 1 scan and 0 ppm offset.

The peak at roughly 0 ppm chemical shift (varies slightly with chemical environment) was then integrated and compared against a calibration curve made by subjecting samples with different amounts of LiCl dissolved in D_2O to the same NMR procedure (Figure 35).

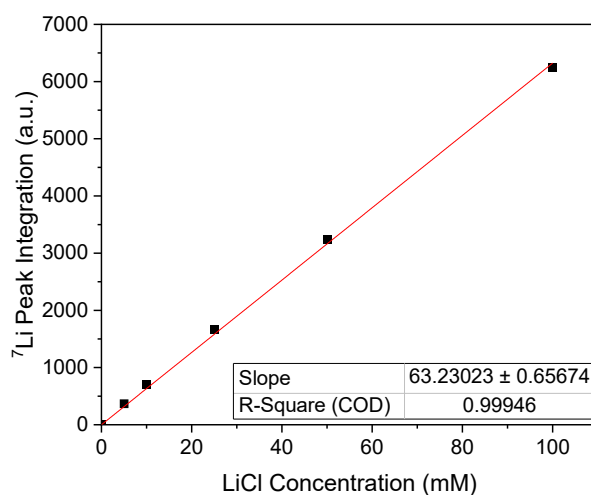


Figure 35. ^7Li NMR calibration curve for Li^+ . Using the signal at ~ 0 ppm corresponding to Li-ions, made by dissolving known amounts of LiCl in D_2O and subjecting to the quantitative ^7Li NMR titration method. NMR experiment developed with the help of Dr Stuart Elliott, NMR facility manager.

2.10. ToF-SIMS Analysis of Electrodes Surface

ToF-SIMS analysis of electrodes was all done by my colleague Olivia Westhead. After electrolysis, the electrochemical cell was dismantled into the glovebox, and the working Mo electrode was put in a vial, heat sealed in moisture barrier bags (RS Components, United Kingdom) and transported to a different Ar-glovebox ($\text{H}_2\text{O} < 0.1$ ppm, $\text{O}_2 < 0.1$ ppm) where they were mounted on a back-mount sample holder and loaded into an inert atmosphere transfer suitcase. The samples were then transferred to the ToF-SIMS machine (TOF.SIMS5 IONTOF GmbH, Münster, Germany) in an Ar atmosphere. The transfer suitcase was only opened when the pressure of the loadlock chamber was lower than 3×10^{-5} mbar. The analysis was performed with a 25keV Bi^+ primary ion beam with the current of 1.2 pA and the high current bunched mode was applied to achieve high mass resolution. Samples were sputtered using GCIB (Gas Cluster Ion Beam) Ar_n^+ (n between 1100 and 1200) at 10 nA, which is very gentle and minimises sample damage.¹⁴⁶ Analysis area was $200 \mu\text{m} \times 200 \mu\text{m}$. Sputter area was $500 \mu\text{m} \times 500 \mu\text{m}$. Some samples had a very uneven topography, which made it difficult to analyse the data due to difference in time-of-flight of the same fragments from different parts of the analysis area. To mitigate this problem, smaller regions of interest were analysed which were all at the same height.

2.11. Electrochemistry-Mass Spectrometry Experiments

Electrochemistry-Mass Spectrometry experiments are carried out by my colleague Artem Khobnya, using the Spectro Inlets Electrochemistry-Mass Spectrometry System which is housed inside an N5 Argon glovebox. Electrochemistry-Mass Spectrometry allows sub second, real-time detection of gases and volatile species in electrochemical processes.^{142–144} This is possible due to a unique membrane chip that can support liquid on its topside and a gas sampling volume below which is connected to a mass spectrometer through a capillary. The membrane allows fast equilibration between the liquid and gas sampling volume. Furthermore, gases can be introduced into the sampling volume and quickly saturate the liquid. All experiments were carried out introducing N6 Nitrogen through the sampling volume of the membrane chip. The membrane and capillary are fabricated using semiconductor fabrication techniques and are contained within a thumb-sized silicon chip. The electrochemical cell sits on top of the silicon chip and has a disc-shaped working volume in which the electrodes and separators are housed. The working space has a diameter of 9 mm and a $100 \mu\text{m}$ thickness (Figure 36).

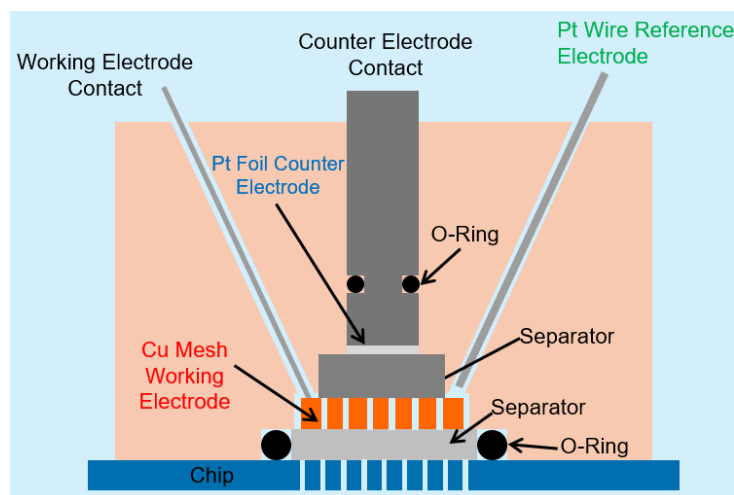


Figure 36. Schematic of the Electrochemistry – Mass Spectrometry cell for in line gas evolution analysis. Reproduced with permission from my work, courtesy of Artem Khobnya.¹⁴⁷ © 2023 The Authors. Published by American Chemical Society.

The layers inside the cell are assembled in ascending order: 8 mm diameter 25 μm Celgard® 2500 separator, 5 mm diameter 40 μm thick copper mesh (EL-Cell GmbH) 6 mm diameter 260 μm Whatman® glass microfiber filter GF/A grade. The counter electrode is a 5 mm diameter 25 μm thick Pt foil from MaTeck. A 5 mm diameter stainless steel plunger is used to contact the counter electrode and apply pressure to the cell for good electrical contact. The cell has 3 x 0.8 mm diameter ports, a 0.5 mm Pt wire (acting as the reference electrode) is inserted into one and a 0.5 mm copper wire is inserted into the other, the latter contacting the copper mesh working electrode. Once assembled, the electrolyte is injected into the cell using a 3 ml syringe connected using a Luer adapter.

Further to this, the cell was left to equilibrate at open circuit for 20 min before electrochemical testing. Electrolyte resistance was assessed by impedance spectroscopy (PEIS at open circuit, 20 mV oscillation, 100 kHz to 1 Hz frequency range, see section 2.5.2). The working electrode potential was swept from open circuit voltage down to a potential with a cut-off current density of $-2 \text{ mA}\cdot\text{cm}^{-2}$. Once this current was reached, it was held at this level to pass enough charge for the said experiment.

2.12. Density Functional Theory Simulations

All simulations were carried out by Alexander Bagger. He did two sets of simulations for nitride formation energies and *N binding energies with accessible databases and analysis scripts on https://github.com/AlexanderBagger/Beyond_Li_N2_reduction.

For the Nitride formation energy and hydride formation energy the most stable structure and metal structure was selected from the materials project.¹⁴⁸ Such structures were initiated with spin and optimized to a force below 0.05 eV.Å⁻¹ using the RPBE functional,¹⁴⁹ a 800 eV planewave cutoff and an automated k-point density set to 25/cell sizes using ASE¹⁵⁰ GPAW.^{151,152} As each nitride and hydride structure has different stoichiometry, formation energies are calculated as in equations (24) and (25):

$$(24) \text{ Nitride formation energy} = E_{M_xN_y-M_x} * E_{M-N_y} * \frac{1}{2}E_{N_2}$$

$$(25) \text{ Hydride formation energy} = E_{M_xH_y-M_x} * E_{M-H_y} * \frac{1}{2}E_{H_2}$$

where $E_{M_xN_y}$, $E_{M_xH_y}$ and E_M are the simulated DFT bulk energies and E_{N_2} and E_{H_2} are the molecular energies.

For the N* binding energy, bulk hpc, fcc and bcc structures were optimized, following build 2x2x4 structures with the three lower layers fixed. The system is then relaxed with a 500 cutoff plane wave basis set and RPBE functional using ASE/GPAW. The binding energies are calculated by equation (26):

$$(26) \text{ N}^* \text{ binding energy} = E_{N^*} - E^* - \frac{1}{2}E_{N_2}$$

where E_{N^*} is the relaxed slab structure with N adsorbed, E^* is the bare slab and E_{N_2} is the nitrogen molecule.

Chapter 3. Measuring the Energy Penalty of Li-Mediated Ammonia Synthesis

3.1. Electrochemical Potentials in Non-Aqueous Systems

If we were to measure an energy penalty for N_2 reduction on Li, we would need a scale or point of reference to compare measurements against. In that case, measuring an energy penalty comes with measuring a voltage and how much of that voltage exceeds the theoretical voltage required to activate N_2 . However, we do not have a base to measure that excess against. Typical N_2 reduction studies have been employing 3-electrode setups, using Pt or Ag wires as *pseudo* references in conventional 3-electrode systems.^{69,70,84,109} However, these metals are not in redox equilibrium with a more oxidised species. The equilibrium defining their electrochemical potential is therefore unknown,¹⁵³ and independent control over the electrochemical potential of each electrode –as opposed to total cell voltage– is out of reach. Slight variations in electrochemical potential can have significant effects on the electrochemical processes associated with N_2 reduction, like observed in the selectivity of organic electrosynthetic reactions or CO_2 reduction, for instance.^{154,155} Not having control over such potentials also makes it difficult to establish where losses in energy efficiency are and hence limits improvements in that regard.¹⁵⁶ Like other electrochemical reactions,^{153,157,158} N_2 reduction studies would improve in quality if there was such a reference electrode, allowing control over an applied potential, and deconvoluting cathodic and anodic processes precisely. Section Chapter 3 is an extended discussion of our previously published work.¹²⁵

A *true* reference electrode meets the following criteria: (i) a defined, fast, exclusive, and reversible redox equilibrium,¹⁵⁸ (ii) electrochemical potential reproducibility,¹⁵⁹ (iii) low polarisability,¹⁵⁹ and this (iv) in different electrolytes.^{160,161} Several types of reference electrodes have been developed to satisfy these criteria in non-aqueous electrochemistry studies, including Ag^+/Ag redox couples,^{153,162} $AgCl/Ag$,¹⁶³ Ag_2S/Ag ,¹⁶⁴ the ferrocenium/ferrocene redox couple,^{129,130,165} Li metal and its alloys,^{153,158,159,166} or Li intercalation materials such as $LiFePO_4$ or $Li_4Ti_5O_{12}$ (Figure 37).^{123,124,153,158}

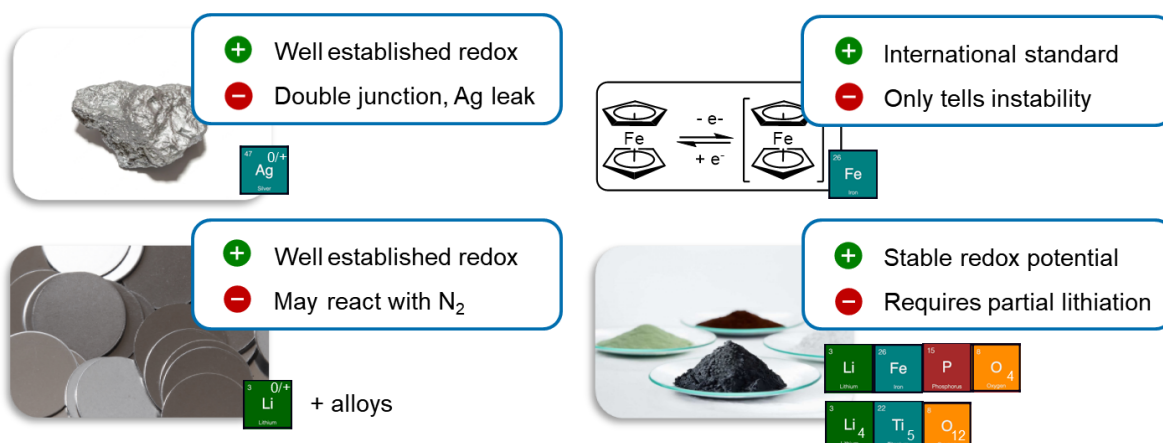


Figure 37. Main advantages and drawbacks of non-aqueous reference electrodes.
123,124,165,166,129,130,153,158,159,162–164

Redox couples of Ag are the most common systems in fundamental electrochemistry for their supposed stability, versatility and ease of use,^{153,162–164} and reference electrodes containing an Ag wire in a solution of Ag⁺ ions have been used in the scope of N₂ reduction studies.^{47,167} However, these Ag-based electrodes have drawbacks: (i) Ag/Ag⁺ references require the Ag⁺ supporting electrolyte to be enclosed within a fritted tube, creating a junction potential at the frit interfaces which can be *unstable, non-reproducible, and variable between electrolytes*^{129,168}; (ii) Ag⁺ ions can leak through that same frit into the bulk electrolyte and can affect electrochemistry by co-plating with lithium for instance,^{168–171} (note that Ag co-deposition can affect ammonia synthesis significantly)¹⁷²; (iii) Ag/Ag⁺ references need to be freshly prepared for every experiment since the Ag salts used to make their electrolyte are light-sensitive and may degrade¹⁶⁷; (iv) the hygroscopicity of Ag-salts may strongly affect N₂ reduction experiments because of their sensitivity to water content in the electrolyte.^{94,173}

The ferrocenium/ferrocene redox couple is a possible alternative, acting as an external reference redox system approved by the IUPAC (International Union of Pure and Applied Chemistry) with a defined one electron redox equilibrium, which electrochemical potential is independent of its chemical environment.¹³⁰ However, it is not a reference electrode *per se* but rather a point of comparison to scale reference electrodes against *pre/post* experiments; plus, the incorporation of Fe-ions in the electrolyte may have undesired side effects just like the contamination with Ag-ions does, making it unsuitable for the active control of electrochemical potentials during N₂ electrolysis.¹⁷²

Li metal and its alloy have been used as reference electrodes in batteries and could be a stable alternative, especially as the electrolyte used for N₂ reduction contains Li⁺ which can yield a stable

Li^+/Li redox equilibrium. However, Li metal (and potentially some of its alloys) will likely react with nitrogen and protons in the electrolyte and therefore cannot be translated to N_2 reduction electrochemical cells.^{174,175}

As a final alternative, battery intercalation materials such as lithium iron phosphate (LiFePO_4) and lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) stand out. Once partially (de)lithiated, these materials possess a range of phases that are in a fast and reversible equilibrium of (de)intercalation of Li-ions (Figure 38b,c). In addition, they do not polarise strongly (Figure 38a), and their electrochemical equilibrium potential tends to be stable against Li metal.^{153,158} Such reference electrodes have been successfully implemented in 3-electrode batteries,^{123,124,166,176} but not in an electrolytic cell.

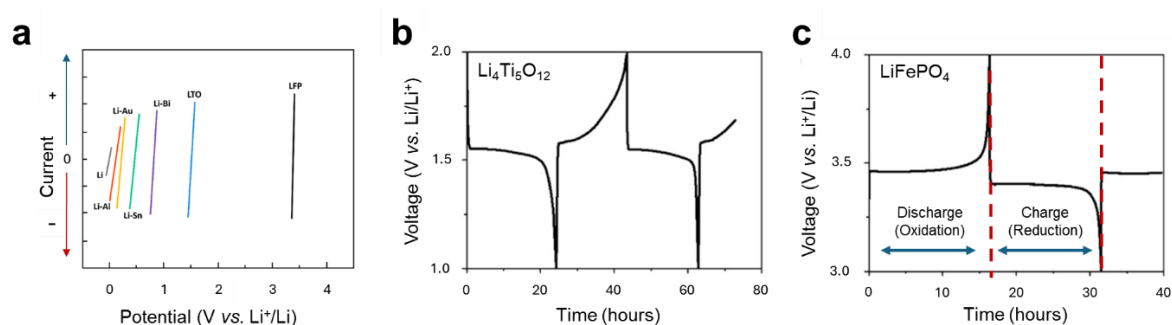


Figure 38. Comparing non-aqueous reference electrodes. (a) Polarisation curves of selected materials for Li battery reference electrodes – reproduced with permission from Raccichini et al.¹⁵⁹ (b,c): Charge and discharge profiles for the (de)intercalation of (b) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and (c) LiFePO_4 reference electrodes, showing a stable potential plateau over a range of Li-intercalation content – Reproduced with permission from La Mantia et al.¹²³ © 2013 Elsevier B.V.

3.2. A Stable and Reproducible LiFePO_4 Reference Electrode

Intercalation materials such as LiFePO_4 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ require an initial conditioning step where their structure is being partially (de)lithiated to a range of phases with stable electrochemical potential (Figure 38b,c). They are typically (de)lithiated by assembling a battery coin cell where the material of interest is faced against Li metal in a Li^+ containing electrolyte and applying a constant current to partly (de)intercalate Li-ions (e.g. LiPF_6 in alkyl carbonate).^{123,124} Such method was adapted to our system and electrolytes of interest (see experimental section 2.4), and electrodes of LiFePO_4 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were both successfully prepared, reproducibly equilibrating to a respective potential of $+3.428 \pm 0.003$

V vs. Li^+/Li and $+ 1.564 \pm 0.004$ V vs. Li^+/Li (10 repeats) after relaxation, which remained stable for days in this configuration (Figure 24). As prepared reference electrodes were then tested for electrochemical potential reproducibility and stability in the conditions of ammonia synthesis.¹⁷⁷ All the following steps were undertaken in an argon glovebox, described in more details in experimental section 2.5. The as prepared LiFePO_4 or $\text{Li}_4\text{Ti}_5\text{O}_{12}$ disc was isolated from its preparation medium, punched through to make a ring electrode and assembled in a 3-electrode sandwich cell (Table 1, cell configuration B) midway between a Mo foil working electrode and a Pt mesh counter electrode. The cell was sequentially filled with test electrolytes and saturated with a gas (Ar , N_2 , H_2). Unless stated otherwise, 1 M LiNTf_2 in THF:EtOH 99:1 v/v with 10 mM ferrocene was chosen as a model electrolyte for the salt's high conductivity and the stable working electrode potential observed during N_2 electrolysis.^{80,84}

Figure 39a displays a typical cyclic voltammogram of the Fc^+/Fc redox couple, recorded at a rate of 50 mV.s^{-1} . The electrochemical potential of the ferrocenium-ferrocene couple can be described by the $U_{\text{Fc}^+/\text{Fc}}$ value, defined by the average between the potentials at which peak cathodic ($U_{\text{c,max}}$) and anodic ($U_{\text{a,max}}$) currents are reached (Figure 39a), which is an estimate of its half-peak electrochemical potential.¹⁷⁸ This record of $U_{\text{Fc}^+/\text{Fc}}$ is the basis for all the measurement plotted in Figure 39.

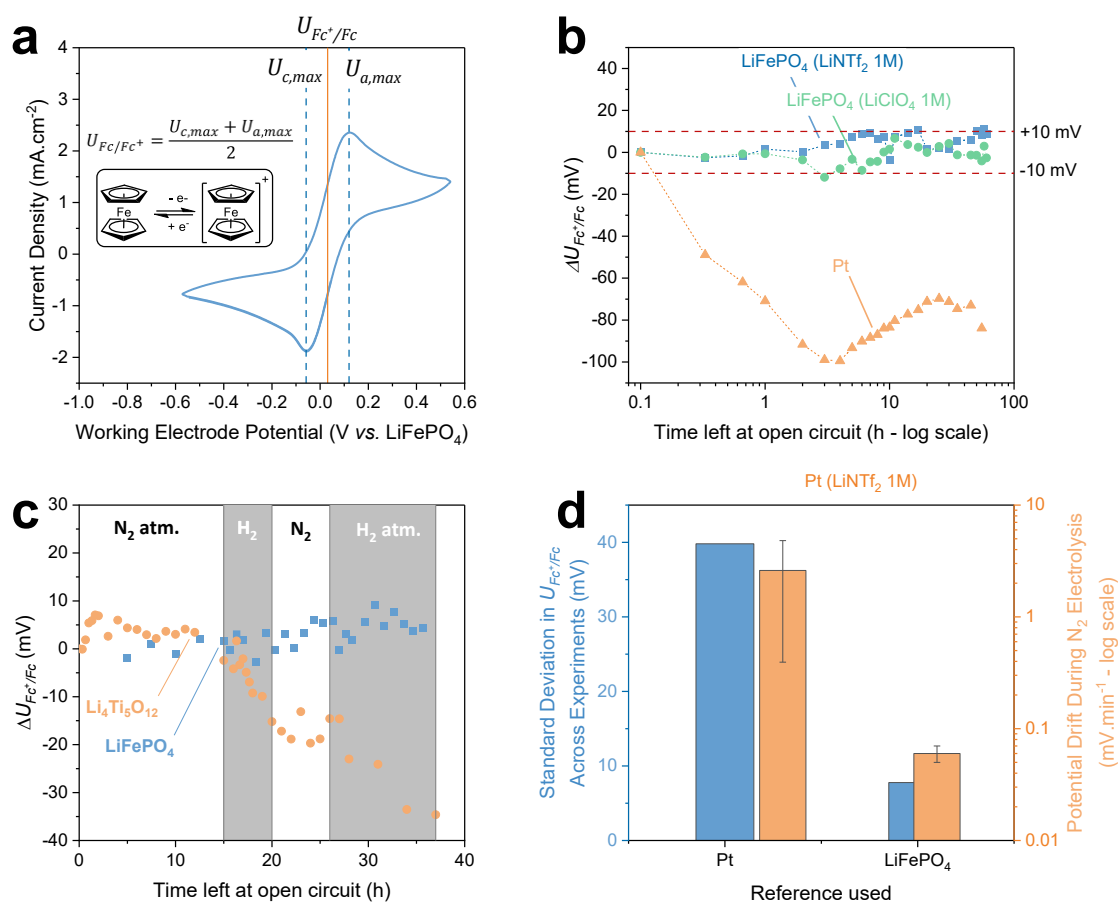


Figure 39. Stability analysis of the LiFePO_4 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ reference electrodes. **(a)** Typical cyclic voltammogram of 10 mM ferrocene with 1 M LiNTf_2 in THF/EtOH 99:1 v/v – used to monitor changes in reference electrode potentials. Insert: scheme for the ferrocene-ferrocenium equilibrium. **(b,c)** Comparison of LiFePO_4 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Pt electrodes stability at open circuit in 1 M LiNTf_2 (blue squares and orange triangles, respectively) or 1 M LiClO_4 (green circles), in THF/EtOH 99:1 v/v, saturated with **(b,c)** N_2 or **(c)** H_2 gas. **(d)** Reproducibility (blue) and stability (orange) comparison over the course of an electrolysis passing 10 C of charge at a constant current of $-2 \text{ mA} \cdot \text{cm}_{\text{geo}}^{-2}$ for 1 h 23 min 20 s, in 1 M LiNTf_2 in THF/EtOH 99:1 v/v. – Reproduced from my work,¹²⁵ with permission from © 2023 The Authors. Published by American Chemical Society.

Figure 39b shows periodic measurements of $U_{\text{Fc}^+/ \text{Fc}}$ versus different reference electrodes in the above-mentioned configuration (see cyclic voltammograms in Figure 26), left at open circuit for multiple days. LiFePO_4 displays a stable electrochemical potential in different electrolytes, where variability (± 10 mV) can be caused by oscillation of the LiFePO_4 electrochemical potential and

instrumental error. However, such variability is neglectable when compared to the large potential drift observed with a Pt *pseudo* reference, drifting unsteadily by up to 100 mV in less than 4 hours. Assuming the largest possible drift of 10 mV for LiFePO₄ (i.e. the ± 10 mV oscillation observed in these measurements) over the course of the 60 h experiment depicted in Figure 39b, this counts as a drift of 0.17 mV.h⁻¹, similar to drifts of 0.2 mV.h⁻¹ reported for Ag/Ag⁺ non-aqueous reference electrodes.^{168,177} LiFePO₄ is also stable in the presence of saturated H₂ in the electrolyte, while alternative references such as Li₄Ti₅O₁₂ or Pt are not in such non-aqueous electrolytes, the former being too reactive (Figure 39b,c), the latter being easily poisoned.¹⁷⁹ This is a major feature of this reference considering the high reactivity of hydrogen and the fact that hydrogen oxidation would be the counter electrode's reaction in a practical device.^{100,115,180} A concomitant study developing such LiFePO₄ reference electrode suggests that it is also stable to a range of gases including O₂, CH₄ and CO₂ all 5 % in Ar, and that such electrodes do not lose significant material by dissolution into non-aqueous electrolytes typically used for ammonia synthesis.¹⁷¹ We noticed that Li₄Ti₅O₁₂ was interfering with ammonia synthesis, a consistent decrease in performance was observed in its presence (Table 4).

LiFePO₄ displays great electrochemical potential reproducibility, varying by ± 8 mV across experiments ($U_{\text{Fc}^+/\text{Fc}} = 0.042 \pm 0.008$ V vs. LiFePO₄, consistent with literature precedents),^{123,161} while Pt varies by ± 40 mV ($U_{\text{Fc}^+/\text{Fc}} = 0.17 \pm 0.04$ V vs. Pt, see Figure 39d blue bars). However, during electrolysis, the electrochemical environment is evolving, and such changes, like electric field or electrolyte content, can affect the electrochemical potential of a reference electrode.^{160,181} The LiFePO₄ reference stays robust in these conditions (Figure 39d, orange bars), with a stable electrochemical potential over the course of a galvanostatic electrolysis (drift of 0.06 ± 0.01 mV.min⁻¹, ~ 5 mV variation over the course of electrolysis, within measurement error range).

3.3. Measuring the Burden of Lithium

Now that we have a stable reference to measure electrochemical potentials against, we can investigate the overpotential associated with ammonia synthesis. To do this, we performed separate N₂ electrolysis experiments at constant currents of different values (from 0.1 to 10 mA.cm⁻¹) and recorded the operating potential at each one of these current densities *versus* LiFePO₄ (Figure 40), where ammonia is being produced at the negative electrode while solvent/ethanol is being oxidised at the counter electrode.

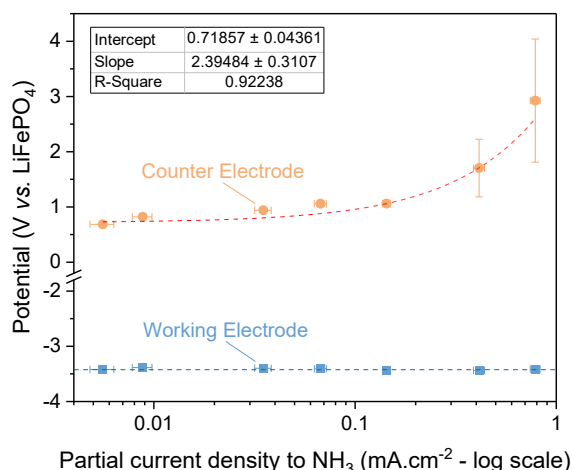


Figure 40. Average electrode potentials recorded after constant current electrolysis of 1 M LiNTf_2 in THF:EtOH 99:1 v/v, at 0.1 to 10 $\text{mA.cm}_{\text{geo}}^{-2}$ (3 repeats each), passing 10 Coulomb of charge through a 1 cm^2 Mo working electrode and Pt mesh counter electrode parallel to each other, spaced by 3.6 cm with the LiFePO_4 reference electrode midway through. Produced ammonia was quantified to calculate partial current densities. The polarisation analysis displays a constant working electrode potential of $-3.423 \pm 0.019 \text{ V vs. LiFePO}_4$, and a linear increase in counter electrode potential – Reproduced from my work,¹²⁵ with permission from © 2023 The Authors. Published by American Chemical Society.

Figure 40 (blue squares) shows that the operating potential at the negative electrode is independent of the partial current density to ammonia (product of current density and Faradaic efficiency to NH_3) and remains constant over the tested operation range. In a more concise way, this means a ‘flat Tafel slope’. This current-independent potential suggests that, after Li deposition and SEI formation, no further electrochemical processes are limiting ammonia synthesis, but rather physical processes such as reagents and products diffusion. The counter electrode potential behaves differently, rising linearly with partial current density to ammonia (Figure 40, orange circles), suggesting increasing poisoning by organic species (under non-poisoning conditions, an exponential relationship should be observed).

Overall, a reference electrode based on LiFePO_4 was developed to measure electrode potentials independently. This electrode possesses a stable and reproducible potential in electrolytes relevant to N_2 reduction to ammonia, which is unaffected by the presence of saturated Ar, N_2 or H_2 gas. Decoupling the processes occurring at the working and counter electrodes enabled the estimation of the voltage cost associated with lithium plating and beyond it. Tafel analysis of the reaction in a single electrolyte suggest that only limiting the energy input for Li deposition (section Chapter 4) or moving away from Li at all (section Chapter 5) will improve energy efficiency significantly on the cathode side.

Chapter 4. Alleviating the Burden – Upshifting Li Electrochemical Potential

4.1. Can we Lower Cell Voltage by Engineering the Electrolyte?

The state-of-the-art nitrogen electrolyser produces ammonia by coupling N_2 reduction with H_2 oxidation to produce protons and balance charge,^{99,100} although on the longer term it would be more ideal to oxidise water to O_2 to produce such protons (bypassing H_2 production).¹¹⁵ The most straightforward way to increase energy efficiency is to decrease cell voltage, and that can be done by either decreasing the positive electrode potential, reducing ohmic resistance of the electrolyte and SEI, or shifting the negative electrode potential up (Figure 41). Since the active surface for ammonia synthesis is made *in situ*, we will study each case from the perspective of electrolyte engineering.

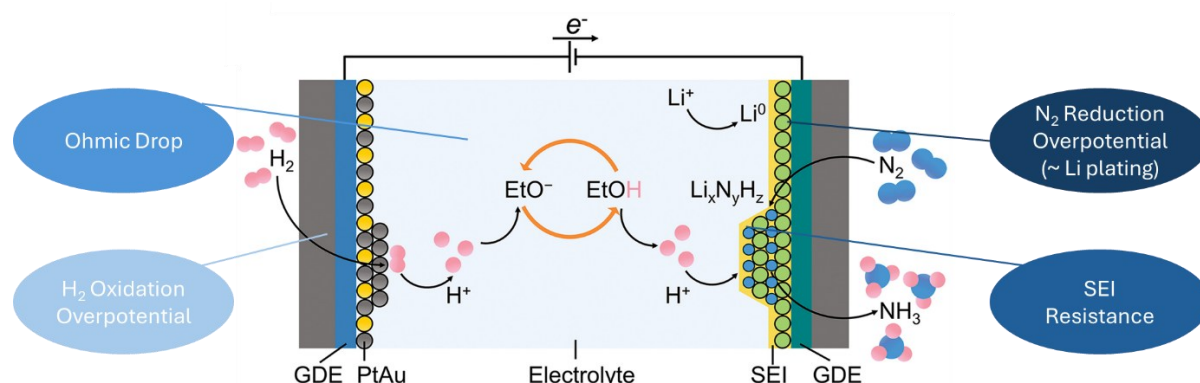
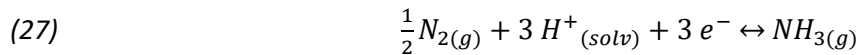


Figure 41. Model of a N_2 and H_2 fed nitrogen electrolyser for the synthesis of ammonia, and four major sources of energy losses. – Central drawing reproduced with permission from Fu and Pedersen et al¹⁰⁰, © 2023 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science.

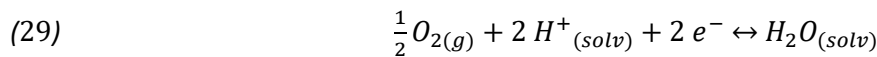
4.1.1. Decreasing the Positive Electrode Potential?

Like in water electrolyzers and hydrogen fuel cells, a lot of emphasis is put on reducing the voltage losses associated with oxygen evolution or hydrogen oxidation, respectively. A lot of effort is being made on designing more active electrocatalysts to lower the overpotentials associated with such reactions.^{182–184} In a hydrogen-fed (hydrogen oxidation at the positive electrode) or water-fed (oxygen

evolution at the positive electrode) nitrogen electrolyser, similar considerations can be done. In our case, since the electrolyte plays such a major role in guiding efficient ammonia synthesis, it would be interesting to investigate this question from the point of view of the electrolyte. Can we engineer the electrolyte to lower the operating potential required for hydrogen oxidation or oxygen evolution? Equations (27), (29) and (31) display the N_2 reduction, H_2 oxidation and O_2 evolution reaction equations and the respective Nernst equations describing them (equations (28), (30) and (32), respectively). Note that gas phase ammonia may not be the best reference state to study this reaction.



$$(28) \quad U_{N_2/NH_3} = U_{N_2/NH_3}^0 - \frac{RT}{3F} \ln \left(\frac{a_{NH_3(g)}}{\sqrt{a_{N_2(g)}} a_{H^+_{(solv)}}^3} \right) = U_{N_2/NH_3}^0 - \frac{RT}{3F} \ln \left(\frac{a_{NH_3(g)}}{\sqrt{a_{N_2(g)}}} \right) + \frac{RT}{F} \ln a_{H^+_{(solv)}}$$



$$(30) \quad U_{O_2/H_2O} = U_{O_2/H_2O}^0 - \frac{RT}{2F} \ln \left(\frac{a_{H_2O(solv)}}{\sqrt{a_{O_2(g)}} a_{H^+_{(solv)}}^2} \right) = U_{O_2/H_2O}^0 - \frac{RT}{2F} \ln \left(\frac{a_{H_2O(solv)}}{\sqrt{a_{O_2(g)}}} \right) + \frac{RT}{F} \ln a_{H^+_{(solv)}}$$



$$(32) \quad U_{H^+/H_2} = U_{H^+/H_2}^0 - \frac{RT}{2F} \ln \left(\frac{a_{H_2(g)}}{a_{H^+_{(solv)}}^2} \right) = U_{H^+/H_2}^0 - \frac{RT}{2F} \ln a_{H_2(g)} + \frac{RT}{F} \ln a_{H^+_{(solv)}}$$

Where R ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) is the ideal gas constant, T is the temperature (K), F is the Faraday constant ($96485 \text{ C} \cdot \text{mol}^{-1}$), $U_{i/j}^0$ is the standard electrochemical potential for the redox couple i/j , and a_i is the activity of species i .

Once developed, these equations display a common parameter: a direct correlation with the activity of protons (in bold). These protons, present initially in the formulated electrolyte, could have their activity altered by engineering the electrolyte.^{106,185} However, any change in proton activity results in an identical shift in electrochemical potential for all three reactions presented. A decrease in the positive electrode electrochemical potential through this means will eventually translate in the decrease of the nitrogen reduction electrochemical potential. While this downshift would close the

gap between Li plating potential and $\text{H}_2/\text{H}_2\text{O}$ oxidation, the theoretically achievable cell voltage will remain the same in chemistries where nitrogen reduction is not limited by a strongly reducing reaction such as lithium plating. In addition, in the current state of the technology, proton activity increases over time as hydrogen/electrolyte oxidation occurs, progressively acidifying the electrolyte, as pointed out by Krempel *et al.*,¹⁰⁸ making proton activity a parameter that is difficult to control until this acidification problem is solved (see section 4.1.3, Figure 42a,b). One could venture into altering the activity of ammonia (equation (28)), water/oxygen (equation (30)), or hydrogen (equation (32)) in such electrolytes, but their absence (or uncontrolled presence) in the initial stages of electrolyte formulation make them more difficult to investigate. It is therefore challenging to gain significant and long-lasting improvements in energy efficiency on the positive electrode side through electrolyte engineering.

4.1.2. Lowering Ohmic Resistance

Non-aqueous electrolytes are typically more resistive than aqueous ones, and lowering ohmic drop is surely an important source of improvement, especially when the technology reaches high operating current densities. That may be done for instance by decreasing the gap between the positive and negative electrodes, or by increasing the ion mobility in the electrolyte or improving the charge transfer rates at the electrode-electrolyte interface.^{186,187} However, our group looked at the origin of overpotential in Li-mediated ammonia synthesis, and at the operating currents attainable in the state of the art technology ($1\text{-}10\text{ mA}\cdot\text{cm}^{-2}$), the largest source of voltage loss comes from the intrinsically low electrochemical potential required for metallic lithium to be stable and catalyse N_2 reduction (Figure 42d),¹¹⁴ although electrolyte resistance will surely become an increasingly important source of energy losses as the field progresses toward higher currents. When it comes to managing SEI resistance, it is still unclear what parameters are important for such SEI to yield ammonia selectively (see section 1.4.3), reducing ohmic losses from that angle may be considered at later stages of development. It therefore makes sense to target losses from the negative electrode first. We also found that once Li plating potential is reached, there is neglectable overpotential associated with an increase in current density (Figure 40).¹²⁵ So, how does one alter that operating potential when the necessary Li electrode is being made *in situ*?

4.1.3. Increasing the Negative Electrode Potential

Section 3.3 concluded on the fact that the negative electrode potential is mostly dictated by the electrochemical potential at which Li plating occurs. Is it the case in all electrolytes? In our group, we investigated the origin of overpotential in this reaction when varying the amount of ethanol in the electrolyte. The project was led by Dr Olivia Westhead who developed a method to measure the reversible hydrogen electrode potential in different electrolytes, defined by the equilibrium electrochemical potential for the reaction of hydrogen evolution depicted in equations (31) and (32).¹¹⁴ We measured the RHE potential in H_2 saturated electrolytes of 0.6 M $LiClO_4$ in THF with added EtOH, then recorded N_2 reduction potentials against this scale in N_2 saturated electrolytes (Figure 42).

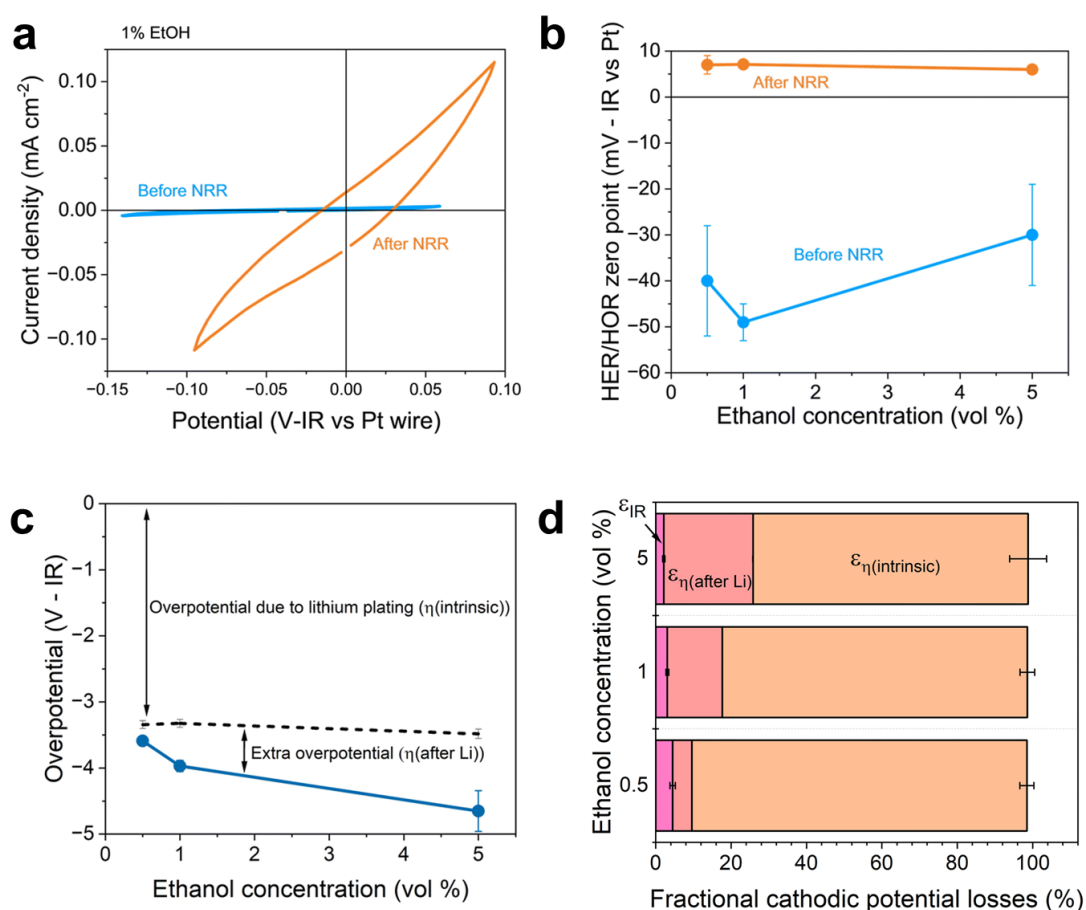


Figure 42. Measuring the overpotential for N_2 reduction using the RHE potential as a reference scale. (a) Typical cyclic voltammogram of an electrolyte made of 0.6 M $LiClO_4$ in THF:EtOH 99:1 v/v, saturated with H_2 gas, cycling at open circuit ± 100 mV at a rate of 20 mV.s^{-1} , showing an increased activity in hydrogen oxidation/evolution after N_2 electrolysis. (b) RHE potential defined by the zero point for hydrogen evolution/oxidation, across a range of concentrations of ethanol in 0.6 M $LiClO_4$ in THF

saturated with H_2 showing the same effect of increased H^+ activity after N_2 electrolysis. (c) Calculated overpotential for nitrogen reduction, excluding ohmic drop, based on the electrochemical equilibrium potential for nitrogen reduction of +0.057 V vs. RHE. Overpotential is separated by losses due to Li plating (dashed line, $\eta(\text{intrinsic})$), and extra overpotential (blue, $\eta(\text{after Li})$). (d) Fractional voltage losses depending on ethanol concentration: Li plating ($\mathcal{E}_{\eta(\text{intrinsic})}$), Ohmic drop ($\mathcal{E}_{IR}$), and other losses ($\mathcal{E}_{\eta(\text{after Li})}$), displaying losses dominated by Li deposition. – Reproduced with permission from Westhead *et al.*¹¹⁴, © The Royal Society of Chemistry 2023.

The above experiments were done before a true reference electrode had been developed and would ideally be repeated with a true LiFePO_4 reference.^{125,171} Absolute RHE potential measurements must therefore be taken with a pinch of salt for the reasons stated in section 3.1. However, Figure 42 makes three points. First, that the amount of ethanol present affects the overpotential associated with N_2 reduction (Figure 42c), feeding in the debate for the role of ethanol beyond just a proton carrier,^{83,103,107} but also meaning that electrolyte engineering in that way can play a significant role in improving energy efficiency (Figure 42d). The reason for the increase in voltage losses with ethanol concentration was attributed to an increase in SEI resistance.¹¹⁴ Second, that the electrolyte acidifies over the course of an electrolysis experiment (Figure 42a,b), as demonstrated by Krempel *et al.*,¹⁰⁸ making the activity of protons a difficult parameter to control and use as a descriptor for electrolyte modifications. Finally, Li plating is indeed the main source of energy losses, and that in different electrolyte compositions (Figure 42c,d) and operating conditions (Figure 40). If one wants to reduce energy losses considerably, it must be done by targeting Li plating. Interestingly, we noticed that when measured against LiFePO_4 , the potential at which ferrocene oxidises and reduces ($U_{Fc^+/Fc}$) changed based on electrolyte composition (here LiNTf_2 salt concentration, Figure 43a).¹²⁵

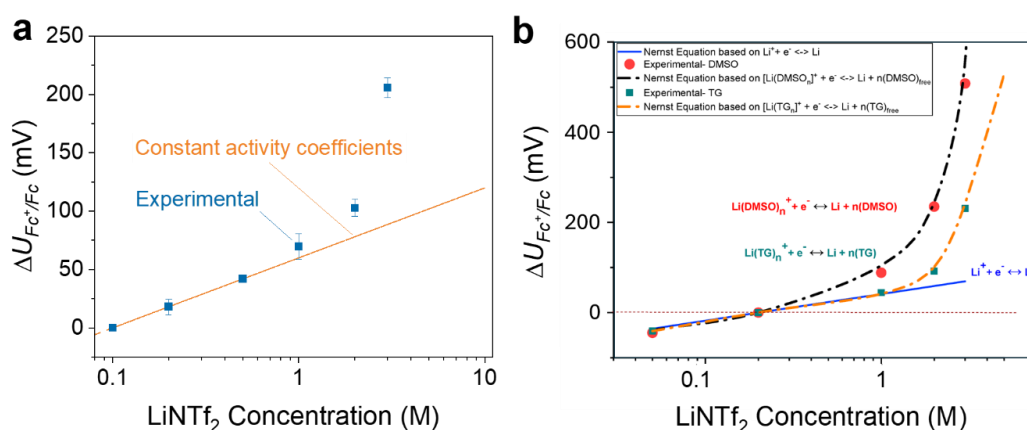
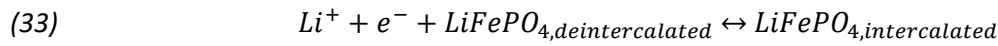


Figure 43. Effect of a change in electrolyte composition on electrochemical potentials. (a) $\text{Li}^+/\text{LiFePO}_4$ against LiNTf_2 in $\text{THF}:\text{EtOH}$ 99:1 v/v, and (b) Li^+/Li against LiNTf_2 in DMSO or tetraglyme, both

illustrated by the difference in the measured electrochemical potential of ferrocene $U_{Fc^+/Fc}$ between two electrolyte concentrations. – (a) Reproduced with permission from my work,¹²⁵ © 2023 The Authors. Published by American Chemical Society, and (b) Reproduced with permission from Kottam et al,¹³³ © The Author(s) 2019. Published by ECS.

However, $U_{Fc^+/Fc}$ should be independent of its chemical environment.^{130,165} It must therefore be the electrochemical potential of the reference that is changing with Li salt concentration. The Nernst equation describing the redox equilibrium of the intercalation of Li-ions in $LiFePO_4$ (equation (33)) can explain this change. The difference in such reaction's electrochemical equilibrium potential $U_{Li^+/LiFePO_4}$ between an electrolyte a or b will be affected by the activity (*i.e.* the product of activity coefficient and concentration) of Li-ions in both electrolytes (equations (34), (35)).



$$(34) \quad U_{Li^+/LiFePO_4} = U_{Li^+/LiFePO_4}^0 - \frac{RT}{F} \ln \left(\frac{a_{LiFePO_{4,intercalated}}}{a_{LiFePO_{4,deintercalated}} a_{Li^+}} \right) \approx U_{Li^+/LiFePO_4}^0 + \frac{RT}{F} \ln a_{Li^+}$$

$$(35) \quad \Delta U_{(Li^+/LiFePO_4)_{a,b}} = U_{(Li^+/LiFePO_4)_b} - U_{(Li^+/LiFePO_4)_a} = \frac{RT}{F} \ln \frac{a_{Li^+_b}}{a_{Li^+_a}} = \frac{RT}{F} \ln \left(\frac{\gamma_{Li^+_b} [Li^+]_b}{\gamma_{Li^+_a} [Li^+]_a} \right)$$

Where R (8.314 J.mol⁻¹.K⁻¹) is the ideal gas constant, T is the temperature (K), F is the Faraday constant (96 485 C.mol⁻¹), $U_{i/j}^0$ is the standard electrochemical potential for the redox couple i/j , a_i is the activity of species i , γ_i is the activity coefficient of species i , and $[Li^+]_k$ is the concentration of Li-ions in electrolyte k .

In fact, this explanation has been formulated before to describe a similar phenomenon observed on Li metal, where the electrochemical potential of the Li^+/Li redox equilibrium followed an almost identical trend (Figure 43b), increasing exponentially with Li salt concentration. An analogous Nernst equation (equation (36)) for the redox equation of Li plating explains that trend too, where electrochemical potential does indeed scale exponentially with the activity of Li-ions.

$$(36) \quad U_{Li^+/Li} = U_{Li^+/Li}^0 - \frac{RT}{F} \ln \left(\frac{a_{Li}}{a_{Li^+}} \right) \approx U_{Li^+/Li}^0 + \frac{RT}{F} \ln a_{Li^+} = \frac{RT}{F} \ln (\gamma_{Li^+} [Li^+])$$

A note for later (see sections 4.2 and 4.1): Figure 43a and b both show an exponential relation between measured electrochemical potential difference and salt *concentration*, until a point where the potential difference deviates from that exponential relation (orange and blue lines in Figure 43a and

b, respectively). This was suggested to be caused by change in the activity coefficients (γ_i) of Li-ions in solution as their solvation sheath reorganises.^{132,133,160,185} Until a set concentration, γ_i remains relatively constant, and activity coefficients terms cancel out in equation (35). At high enough concentrations, activity coefficients become transient, and their evolution overlap with concentration change, making the measured potential difference shoot up. Back to our first interest, tailoring the overall activity of Li-ions in the right way may shift $U_{Li^+/Li}$ to more positive values according to Figure 43, potentially increasing the potential at which N_2 reduction occurs. To what extent can we use this dial? Fu and Pedersen *et al.* calculated the energy efficiency for electrochemical ammonia synthesis by coupling water electrolysis for H_2 production with N_2 reduction in a H_2 -fed electrolyser, per the following equation (37).¹⁰⁰

$$(37) \quad e.e. = \frac{E_{out}}{\sum E_{in}} = \frac{V_{NH_3\ syn}^0 + V_{H_2\ syn}^0}{\frac{V_{H_2\ syn}^0 + \eta_{H_2\ syn}}{FE_{H_2}} + V_{NH_3\ syn}^0 + \eta_{Li} + \eta_{NH_3\ syn}} \cdot FE_{NH_3}$$

with the energy output: $E_{out} = n_{NH_3} \Delta G_{R, NH_3 \rightarrow H_2O}^0 = 3Fn_{NH_3} V_{R, NH_3\ to\ H_2O}^0 = 3Fn_{NH_3} (V_{NH_3\ syn}^0 + V_{H_2\ syn}^0)$

and the energy input: $\sum E_{in} = E_{H_2\ syn} + E_{NH_3\ syn} = \frac{3Fn_{NH_3}}{FE_{NH_3}} \left(\frac{V_{H_2\ syn}^0 + \eta_{H_2\ syn}}{FE_{H_2}} + V_{NH_3\ syn}^0 + \eta_{Li} + \eta_{NH_3\ syn} \right)$

with $\Delta G_{R,i}^0$ the standard Gibbs free energy of reaction i , V_i^0 the reversible electrochemical potential of reaction i ($V_{NH_3\ syn}^0 = -0.06V$, $V_{H_2\ syn}^0 = 1.23V$), $\eta_{j\ syn}$ the overpotential associated with the synthesis of j , η_{Li} the overpotential associated with the need to plate Li metal, and FE_j the Faradaic efficiency toward production of species j .

In an (over)idealised case where water splitting occurs at neglectable overpotentials and unity Faradaic efficiency to H_2 & O_2 ($\eta_{H_2\ syn} \approx 0$, for lack of better figure of merit), and assuming that the overpotential for ammonia synthesis beyond Li plating (-3.04 V vs. SHE) is neglectable ($\eta_{NH_3\ syn} \approx 0$, partly untrue according to Figure 42d), maximum energy efficiency is given by equation (38).¹⁰⁰

$$(38) \quad e.e. \approx \frac{V_{NH_3\ syn}^0 + V_{H_2\ syn}^0}{V_{H_2\ syn}^0 + V_{NH_3\ syn}^0 + \eta_{Li}} = \frac{1.23 - 0.06}{1.23 - 0.06 + 3.04} = 27.8\%$$

If η_{Li} becomes a variable we can shift up, in the same assumptions, then $e.e. = \frac{1.17}{1.17 + \eta_{Li}}$ (Figure 44).

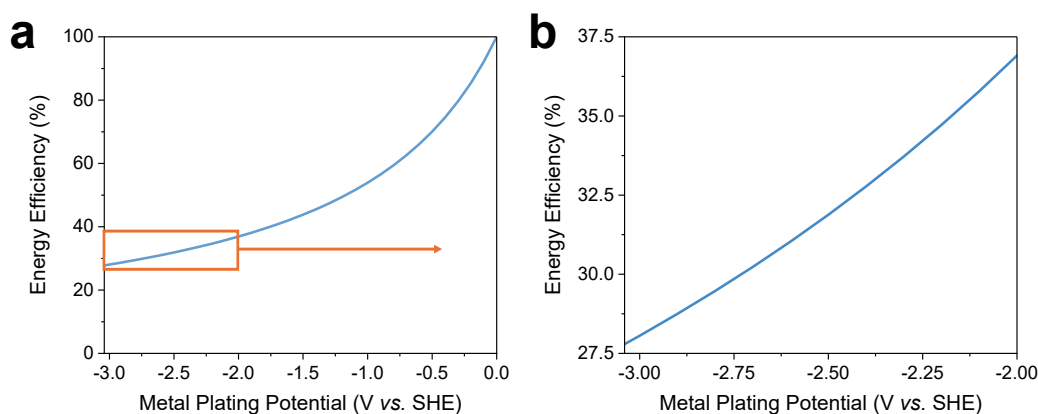


Figure 44. Energy efficiency for electrochemical ammonia synthesis against metal plating electrochemical potential, as calculated by equation (38),¹⁰⁰ (a) Full scale, (b) orange insert zoom.

While it is unrealistic to achieve Li plating at potentials as high as the ones depicted in Figure 44, it is still worth asking ourselves how much we can upshift that Li plating potential. But what effect will this have on Li plating morphology, SEI formation and ammonia synthesis selectivity? It turns out battery scientists have asked themselves some of these questions and looked at the effect of shifting this electrochemical potential on the cyclability of Li-metal anodes.

4.2. Modulating the Li^+/Li Electrochemical Potential

4.2.1. The Effect of a Potential Upshift on Li Metal Plating

Equation (36) suggests that changes in electrolyte composition and Li-ion activity will indeed modulate the electrochemical potential for Li plating $U_{\text{Li}^+/\text{Li}}$. Multiple studies have verified that phenomenon through a combination of spectroscopic and electrochemical measurements and shown that changing the concentration of a lithium salt and the nature of the solvent can yield shifts of up to +600 mV in $U_{\text{Li}^+/\text{Li}}$ (Figure 43).^{125,132–134,188} For reference, this means a possible increase in energy efficiency for ammonia synthesis of ~5 % according to equation (38).

How can we rationalise this change in $U_{\text{Li}^+/\text{Li}}$ and change in Li-ion activity? Ko *et al.* measured $U_{\text{Li}^+/\text{Li}}$ in a range of electrolytes of lithium bis(fluorosulfonyl)imide (*i.e.* $\text{LiN}(\text{SO}_2\text{F})_2$ also known as LiFSI) dissolved in different concentrations and different solvents, using a technique analogous to the one described in Figure 39a, against Li metal.¹³⁴ By recording the Raman spectrum of such bulk electrolytes, they correlated the change in $U_{\text{Li}^+/\text{Li}}$ with a change in the solvation environment of Li-ions (Figure

45a,b). A typical vibration peak for the $(\text{SO}_2\text{F})_2\text{N}^-$ anion (here the symmetric stretching of the S-N-S bond) shifts depending on electrolyte composition (Figure 45a), consistent with previous reports.^{189–}

¹⁹¹ A shift in an anion's Raman peak is attributed to a change in the coordination environment of this anion, whether it is strongly or loosely bound to Li^+ , solvent or other anions. Indeed, Li-ions are always solvated in a sheath of solvents and/or ions once dissolved. Depending on the concentration of Li^+ , and the relative extent to which solvents and anions are ready to coordinate to Li^+ will yield different solvation environments (Figure 45f,g,h).^{189–192} At low concentrations or solvent high solvating ability, most Li-ions and anions come as a *solvent-separated ion pair* (Figure 45f), where Li^+ is fully coordinated to solvent molecules only. When concentration increases (Figure 45c) or solvating ability decreases (Figure 45d,e), anions enter the Li^+ solvation sheath to create *contact ion pairs* (Figure 45g or h, respectively) where one Li^+ is coordinated to one anion (*n.b.* the anion environment changes and therefore its Raman vibration shifts). Keep increasing concentration or decreasing solvating ability and more anions will coordinate to Li^+ , to a point where *aggregates* of multiple Li^+ and anions coalesce into larger and larger ionic pockets surrounded by solvents in the outer spheres (Figure 45g,h).

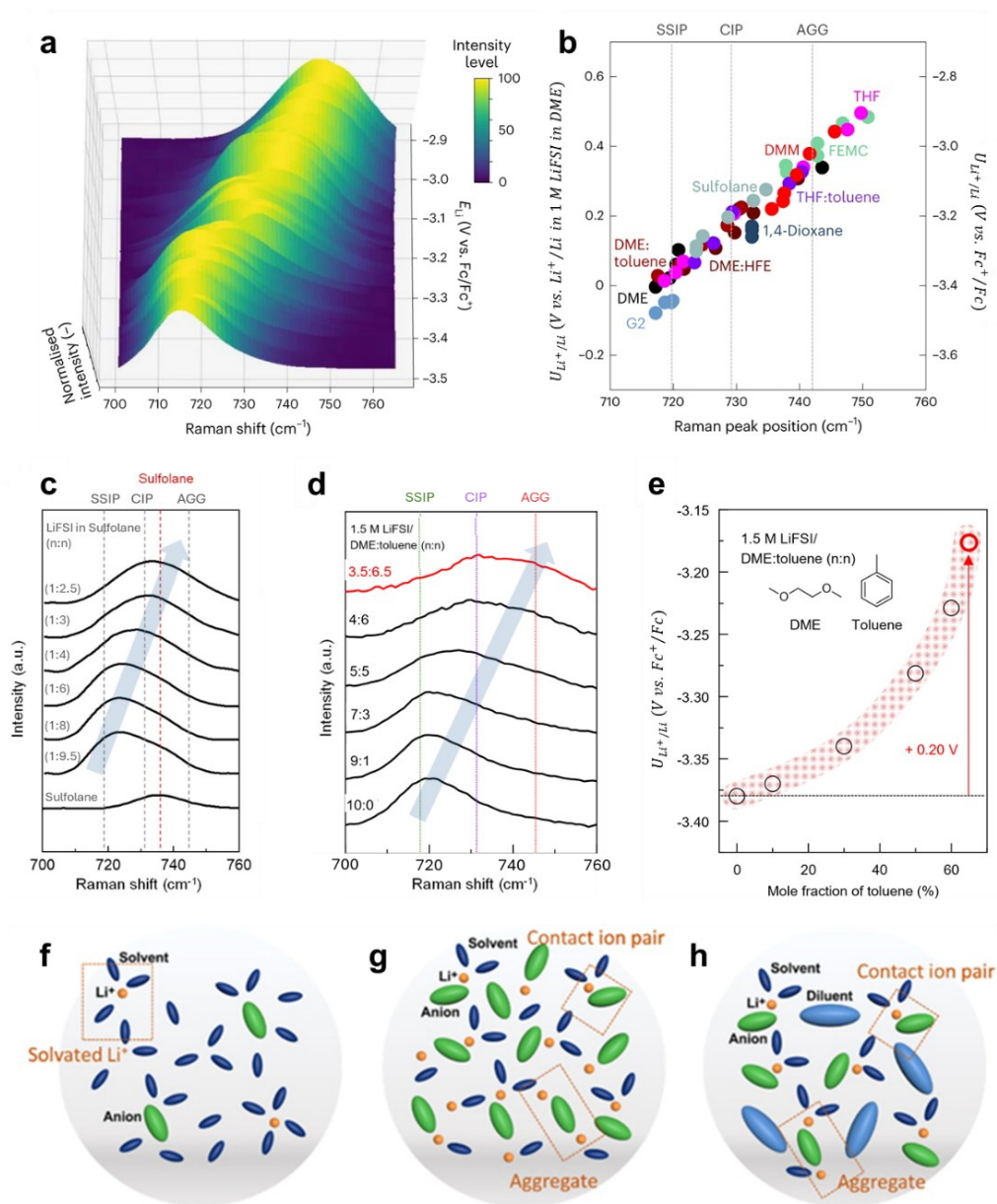


Figure 45. Li-ion environment change and its effect on Li^+ solvation, Li-ion activity and $U_{Li^+/Li}$. **(a,b)** Correlation between the Raman shift of the $(SO_2F)_2N^-$ anion (S-N-S symmetric vibration) and $U_{Li^+/Li}$ with plotted **(a)** Raman spectra, and **(b)** peak maxima labeled by solvent. **(c)** Raman spectra of $LiN(SO_2F)_2$ /Sulfolane electrolytes of increasing concentrations, where the Raman signals of the anion overlap with a signal from sulfolane (symmetric stretching of C-S-C), showing an increase in Raman shift with concentration, from solvent-separated ion pair (SSIP) to contact ion pairs (CIP) and aggregates (AGG). **(d)** Raman spectra of 1.5 M $LiN(SO_2F)_2$ in DME:toluene mixtures, where the Raman shift for the anion signal increases as the solvating ability of the solvent mixture decreases (toluene content increases). **(e)** Corresponding effect of a decrease in solvation ability of the solvent mixture in

increasing $U_{\text{Li}^+/\text{Li}}$. **(f-h)** Schematic representation of electrolyte architectures in **(f)** a low concentration / highly solvating electrolyte where Li-ions remain fully solvated (solvent-separated ion pairs), **(g)** a more concentrated electrolyte where contact ion pairs and aggregates form, and **(h)** an electrolyte where solvent is diluted with a less solvating molecule to yield similar ionic aggregation. – (a-e) reproduced with permission from Ko *et al.*,¹³⁴ © 2024 Springer Nature Limited. (f-h) with permission from Cao *et al.*,¹⁹² © 2021 The Authors. Published by IOP Publishing Limited.

Li^+ solvation in the electrolytes affects its activity and $U_{\text{Li}^+/\text{Li}}$, but what does it mean for Li plating and battery anode cycling? Ko *et al.* tested the above investigated electrolytes in a Li-metal battery 2-electrode half-cell (Cu working electrode | Li^0 counter electrode) and noted a strong correlation between Li plating/stripping coulombic efficiency and $U_{\text{Li}^+/\text{Li}}$: the higher the $U_{\text{Li}^+/\text{Li}}$, the better the cell cycled (Figure 46a).

There are two possible explanations that corroborate this observation. The first –and historical– one is a kinetic one. What species electrochemically degrade at the electrode interface is largely influenced by what species do reach the interface first. The change in Li^+ solvation toward more ion pairs and aggregates means that more ionic species are being dragged along with Li^+ when a negative potential is applied to the electrode of interest. This in turn means that more ionic species will reach the electrode interface, possibly reacting with Li metal (or the negatively charged current collector directly), to yield inorganic SEI components, which we know to be favourable SEI components for stable Li cycling in metal batteries (section 1.4.3). Making a stable SEI (from an anion-solvated Li^+ electrolyte) in the first place allows the kinetic stabilisation of the interface and prevents further coulombic losses to electrolyte degradation, going along the relationship between high $U_{\text{Li}^+/\text{Li}}$ and high coulombic efficiencies.

However, Ko *et al.* suggest a rather thermodynamic explanation. While the large contribution of an SEI to stable cycling in batteries is extensively verified in the field, they observe that some electrolytes yielding equivalent SEIs have different $U_{\text{Li}^+/\text{Li}}$ and different coulombic efficiencies that follow the above-mentioned trend. And in fact, the observed trend in Figure 46a does not hold in the first cycles of Li plating/stripping, where most of the SEI is being formed (Figure 46b), suggesting that the efficiency with which the SEI forms is not well correlated with $U_{\text{Li}^+/\text{Li}}$ and Li-ion solvation in these conditions. They rather propose the electrochemical potential of Li metal as the main driver for its reactivity toward the electrolyte.

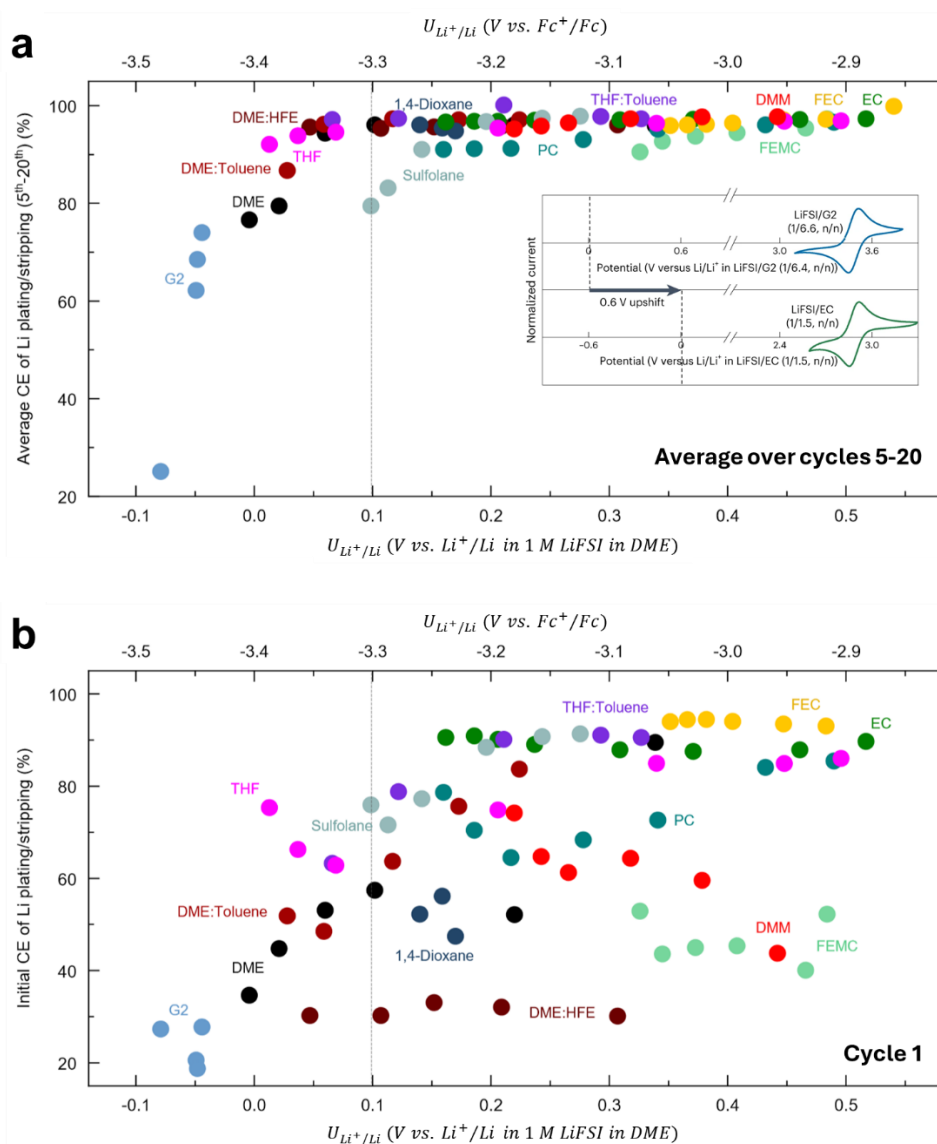


Figure 46. Correlation between $U_{Li^+/Li}$ and coulombic efficiency of Li metal anodes plating/stripping in different electrolytes, labelled by solvent used. **(a)** Average coulombic efficiency over the 5th to 20th plating/stripping cycles showing a correlation. **(b)** Absence of correlation in the coulombic efficiency of the first cycle, attributed to a strong contribution of charge lost to SEI formation in the first cycle of plating/stripping. – Reproduced with permission from Ko et al.,¹³⁴ © 2024 Springer Nature Limited.

We know from work in our group that Li^+ solvation does matter in making an inorganic-rich SEI that allows steady ammonia production,⁸⁰ and that inorganics such as Li_2O or LiF are important in doing it at higher selectivity (Figure 16).^{70,81,82,93} However, high variability across slight electrolyte modifications (e.g. sensitivity to $EtOH$,^{48,68} H_2O ^{81,94} or O_2 content^{70,93}), difficulties in comparing observations made in fluorinated and non-fluorinated electrolytes (e.g. the controverted role of

water),^{81,94} and discrepancies between studies (ideal proton carrier^{102,104}, solvent stability^{99,193}) exist in the field, making electrolyte development a challenging task. Would $U_{\text{Li}^+/\text{Li}}$ explain better some of the observed trends and be a better descriptor for electrolyte screening, like it did for batteries?

A recent application of this concept to the field of Li metal batteries is done through the design of (*localised*) *high concentration electrolytes*.^{192,194–197} Take a Li salt dissolved at low concentration in a solvating ether such as glyme, diglyme or THF ; most Li-ions in such electrolytes will be coordinated to solvent molecules (Figure 45f), have a low $U_{\text{Li}^+/\text{Li}}$ and poor cycling efficiency. Increase the concentration of that salt and contact ion pairs or aggregates start forming, in turn increasing $U_{\text{Li}^+/\text{Li}}$: this is a '*high concentration electrolyte*' (Figure 45g), which is better at cycling Li. Now, take this highly concentrated salt and dilute it with a non-coordinating molecule (*e.g.* toluene, hydrofluoroethers): the ionic aggregates of the high concentration electrolyte are preserved while effective Li^+ concentration is decreased, maintaining high $U_{\text{Li}^+/\text{Li}}$ and cycling coulombic efficiency. This is a '*localised high concentration electrolyte*' (Figure 45h). The role of such diluents in the bulk electrolyte structure and at the electrochemical interfaces is still under debate, as more complex structures are being elucidated such as micelle-like ionic pockets,¹⁹⁶ ion transport may be largely altered,^{194,198} and some diluents may not be innocent to the development of negative and positive electrode interphases.^{194,199,200} Nevertheless, the relationship between a change in $U_{\text{Li}^+/\text{Li}}$ and improvements in Li anode plating/stripping efficiency applies to these structural changes, where (*localised*) high concentration electrolytes (high $U_{\text{Li}^+/\text{Li}}$) perform better than low concentration (low $U_{\text{Li}^+/\text{Li}}$) ones in that regard. We will use this concept to deconvolute Li^+ concentration from Li^+ activity and $U_{\text{Li}^+/\text{Li}}$ in the investigation of ammonia synthesis electrolytes, which we know to be sensitive to the former.^{80,84}

4.2.2. Not as Straightforward in Li-mediated Ammonia Synthesis?

In this section, we investigated the above concept of Li metal electrochemical potential in low, high and *localised high concentration* electrolytes to the description of ammonia synthesis, with the goal of upshifting the operating potential for ammonia synthesis. Electrolytes made of LiNTf_2 and EtOH in mixtures of THF and toluene or TTE (1,1,2,2-tetrafluoroethylene 2,2,3,3-tetrafluoropropyl ether) were selected for the following reasons. LiNTf_2 is a Li salt which displays high conductivity,⁸⁴ high solubility,²⁰¹ records of high coulombic efficiencies in Li metal batteries⁷⁴ and high Faradaic efficiency to ammonia.⁸⁴ The solvent THF was selected for its historical use in Li-mediated ammonia synthesis as best in class at the time of the study^{49,53} and its high solvation ability.¹³⁴ Finally, toluene and TTE were

tested as (supposedly) non-coordinating diluents for their reported use in ether-based electrolytes.^{134,197,202} Inspired by work from Ko *et al.*,¹³⁴ we measured $U_{\text{Li}^+/\text{Li}}$ (Figure 47a, see section 2.5.6) in these electrolytes and recorded their Raman spectra (Figure 47b, see section 2.3.2).

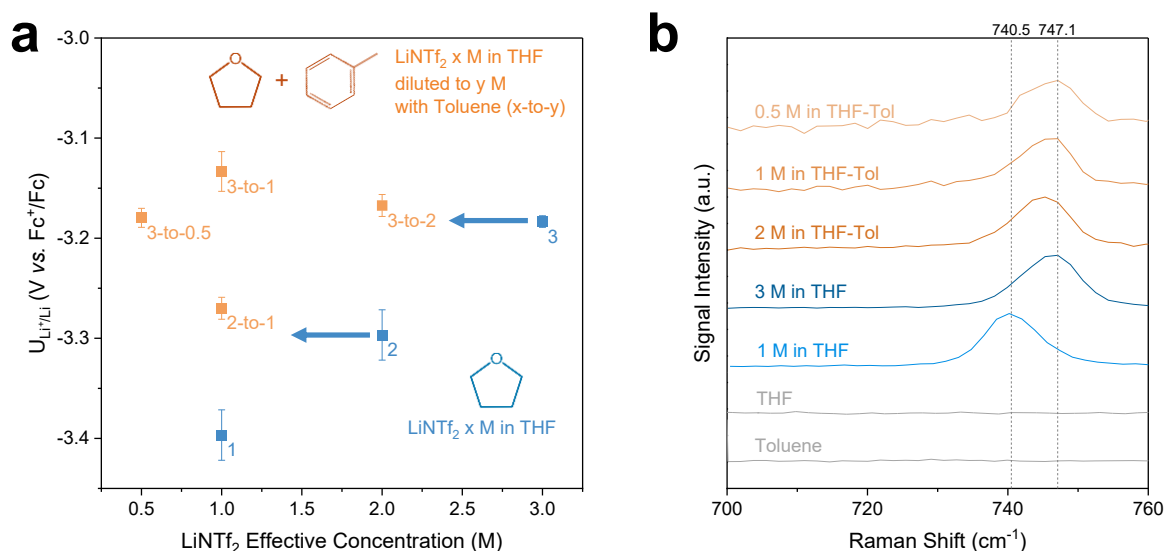


Figure 47. Electrochemical and spectroscopic characterisation of N_2 reduction electrolytes. **(a)** $U_{\text{Li}^+/\text{Li}}$ measured against the ferrocenium-ferrocene redox in THF-based electrolytes (blue), and high concentration THF electrolytes diluted with toluene (orange). **(b)** Raman spectra of the same electrolytes without (blue) and with (orange) toluene, zoomed in the region of the anion vibration.

The selected electrolytes display a trend reproducible to the same effect as the one reported in Figure 45b, where the anion vibration peak shifts up when $U_{\text{Li}^+/\text{Li}}$ increases. When increasing Li-ion concentration in THF, $U_{\text{Li}^+/\text{Li}}$ increases (by ~ 200 mV from 1 to 3 M, Figure 47a), and the Raman shift associated with the anion vibration increases from 740 cm^{-1} to 747.1 cm^{-1} when going from 1 M to 3 M in THF (Figure 47b). When diluting this highly concentrated 3 M electrolyte with toluene, $U_{\text{Li}^+/\text{Li}}$ remains upshifted even when effective concentration is brought back down to 0.5 M in THF-Toluene, and that translates to a Raman shift maintained at roughly 747 cm^{-1} in these conditions. However, when using TTE as the diluent (electrochemical and Raman measurements of TTE-containing electrolytes done by Guanglei Chen during his master's project I was co-supervising, Figure 68a,b), the upshifted $U_{\text{Li}^+/\text{Li}}$ is not fully retained. Whether TTE is used to dilute a 3 M or 4 M electrolyte of LiNTf_2 in THF, $U_{\text{Li}^+/\text{Li}}$ progressively goes back down as effective Li^+ concentration decreases. This observation translates to a decay in the average Raman shift of the anion vibration as well, where a bump at lower Raman shifts starts forming as a highly concentrated electrolyte of LiNTf_2 in THF is being diluted with

TTE. TTE was therefore deemed unideal for the below study, and further experiments were carried using toluene as a diluent. We also verified the effect of changing the solvent to one that has better or worse ion solvation than THF by measuring $U_{\text{Li}^+/\text{Li}}$ in 1 M LiNTf₂ in diglyme and 1,1-dimethoxymethane. As expected, $U_{\text{Li}^+/\text{Li}}$ increases in the order of diglyme < THF < 1,1-dimethoxymethane (Figure 68c). N₂ electrolysis experiments were performed using THF and THF-toluene based electrolytes, with 0.2 % v/v of EtOH as the proton carrier, and Faradaic efficiency to ammonia was reported against measured $U_{\text{Li}^+/\text{Li}}$ (Figure 48a).

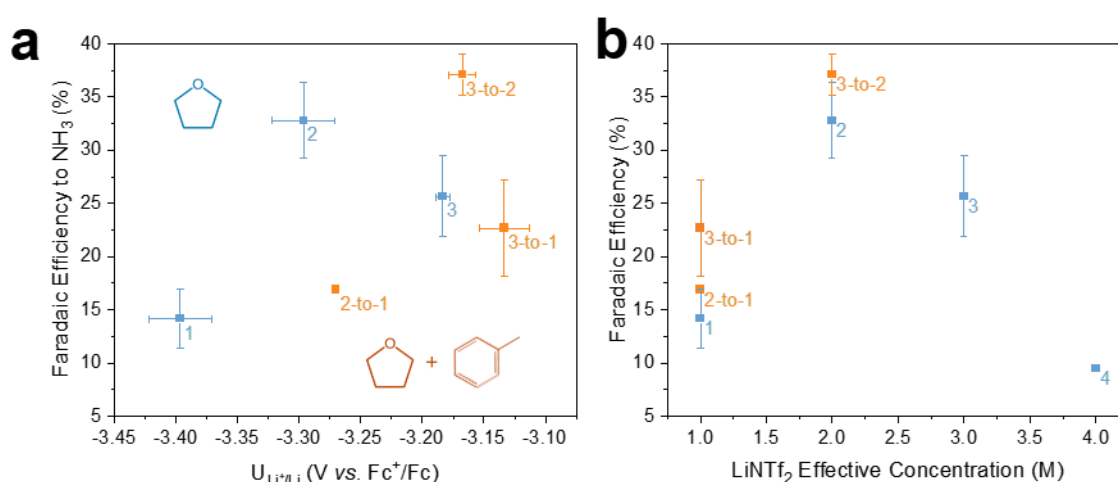


Figure 48. Faradaic efficiency to ammonia and Li metal potential, measured from the reduction of N₂ in LiNTf₂ + 0.2 % v/v EtOH in THF (blue) or in a THF-toluene mix (orange). Plotted against (a) $U_{\text{Li}^+/\text{Li}}$ and (b) Li⁺ concentration. Labels on data points correspond to concentration of LiNTf₂ in THF (blue) and THF-toluene mixtures (orange, 'x-to-y' is a 'x' M electrolyte in THF diluted to 'y' M with toluene).

Figure 48a does not display a clear correlation between Faradaic efficiency to ammonia and $U_{\text{Li}^+/\text{Li}}$, in opposition to a recent report which focus was on changing the salt nature and concentration while using the same solvent.²⁰³ Surprisingly, the trend associated with Li-ion concentration and solvation (suggested by previous works using LiClO₄⁸⁰ or LiNTf₂⁸⁴) does not hold either in this larger scope, and electrolytes of identical concentrations yield different amounts of ammonia (Figure 48b). Same goes for solvation, electrolytes with expectedly identical solvation environments (e.g. 3 M, 3-to-2 M and 3-to-1 M) behave differently. Rather, a combination of the two factors seems to be at play. Indeed, for a set concentration of Li⁺, increasing $U_{\text{Li}^+/\text{Li}}$ improves selectivity (e.g. 1 < 2-to-1 < 3-to-1 M, and 2 < 3-to-2 M), although it is difficult to tell whether it is a coincidence. In conclusion, neither $U_{\text{Li}^+/\text{Li}}$ and Li⁺

solvation/concentration alone are able capture SEI formation, Li plating and the reactivity of N₂ on Li. Another factor linked to concentration seems to take part in steering selectivity.

4.1. Mapping Electrolyte Design: Ion Activities or SEI Chemistry?

4.1.1. Selectivity against Li⁺ Activity, H⁺ Activity, and N₂ Mass Transfer

Unlike batteries, it is not just one species that is involved in the chemical transformation of interest but three: Li⁺, H⁺ and N₂. Changing the electrolyte composition may alter the behaviour of species other than Li⁺ equally. Consequently, we looked at measuring activities of nitrogen and protons too, or rather proxies for it. We measured N₂ gas solubility and diffusivity through a method developed in our group (Figure 49a, measurements kindly done by Dr Silvia Favero, experimental section 2.3.3). Inspired by the use of $U_{\text{Li}^+/\text{Li}}$ as a proxy for the activity of Li-ions and by our experience in measuring the reversible hydrogen electrode (RHE) potential in non-aqueous media (method developed by Dr Olivia Westhead),¹¹⁴ we also took the RHE potential as a scale to compare proton activity (Figure 49b, experimental section 2.5.7), since the two are linked by the Nernst equation for H₂ evolution (equation (32)). Each metrics evolve significantly over the range of electrolytes tested.

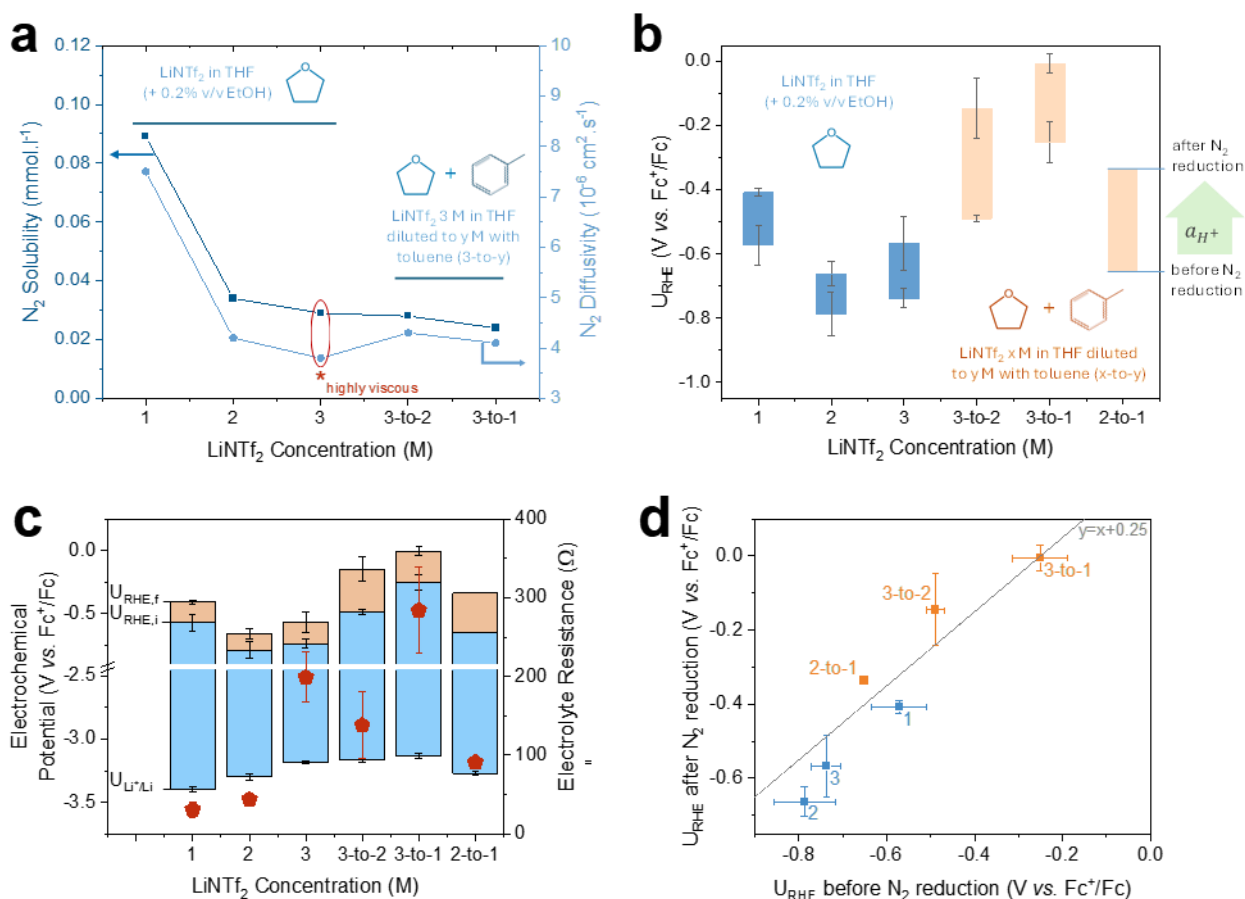


Figure 49. Measurements of proxies for the bulk activity of nitrogen and protons in electrolytes of LiNTf₂ and EtOH, dissolved in mixtures of THF and toluene. **(a)** N_2 gas solubility and diffusivity measured by Brunauer-Emmett-Teller gas sorption. Particularly high viscosity of the 3 M electrolyte marked by a red star. Measurements performed by Dr Silvia Favero. **(b)** RHE potential recorded on a Pt electrode vs. LiFePO₄, reported against the electrochemical potential of ferrocene redox, observing an increase in RHE potential and proton activity before (bar bottom) and after (bar top) N_2 electrolysis. **(c)** Theoretical minimum cell voltage achievable in different electrolytes, measured by the difference between U_{RHE} and $U_{\text{Li}^+/\text{Li}}$ before and after N_2 electrolysis; with resistance of the electrolyte between the counter and working electrodes in the experimental setup used for N_2 electrolysis (red spots). **(d)** Comparison of RHE potential measured before and after electrolysis, showing relatively similar acidification rates (following a $y = x + 0.25$ slope).

Nitrogen solubility and diffusivity follow an identical pattern where an increase in LiNTf₂ concentration brings about a decrease in both solubility and diffusivity. An increase in ionicity of the mixture was expected to be the cause for that decrease in N_2 mass transfer. However, diluting a highly

concentrated electrolyte with toluene –and therefore lowering ionicity of the electrolyte– did not solve that issue. In fact, it was surprising to observe that N_2 mass transfer properties remain roughly the same as at high concentrations. In addition, visual observation suggests that the 3 M electrolyte (Figure 49a, star mark) is markedly more viscous than the rest of the electrolyte set, it would be interesting to compare viscosity quantitatively. Consequently, at equal diffusion rates, mass transfer may be lowered by convection limitations in this highly concentrated electrolyte, limiting access of reagents to the electrode surface. The effect on nitrogen reduction selectivity will be discussed later in this chapter. The RHE potential (and therefore electrolyte acidity according to equation (32)) evolves across the range of electrolytes tested, being notably affected by Li^+ concentration (Figure 49b), where initial acidity may be lowered at higher salt concentrations. Like reported before, acidity increases over the course of electrolysis¹⁰⁸, with no significant difference in its extent across electrolytes (Figure 49d). Considering the necessity to balance Li , H^+ and N_2 at the reactive interface, we deemed RHE potential and N_2 mass transfer to be interesting parameters to explore as descriptors for selective ammonia synthesis. We first plotted the Faradaic efficiency to NH_3 against RHE potential (U_{RHE}) and Li potential $U_{Li^+/Li}$ (Figure 50a).

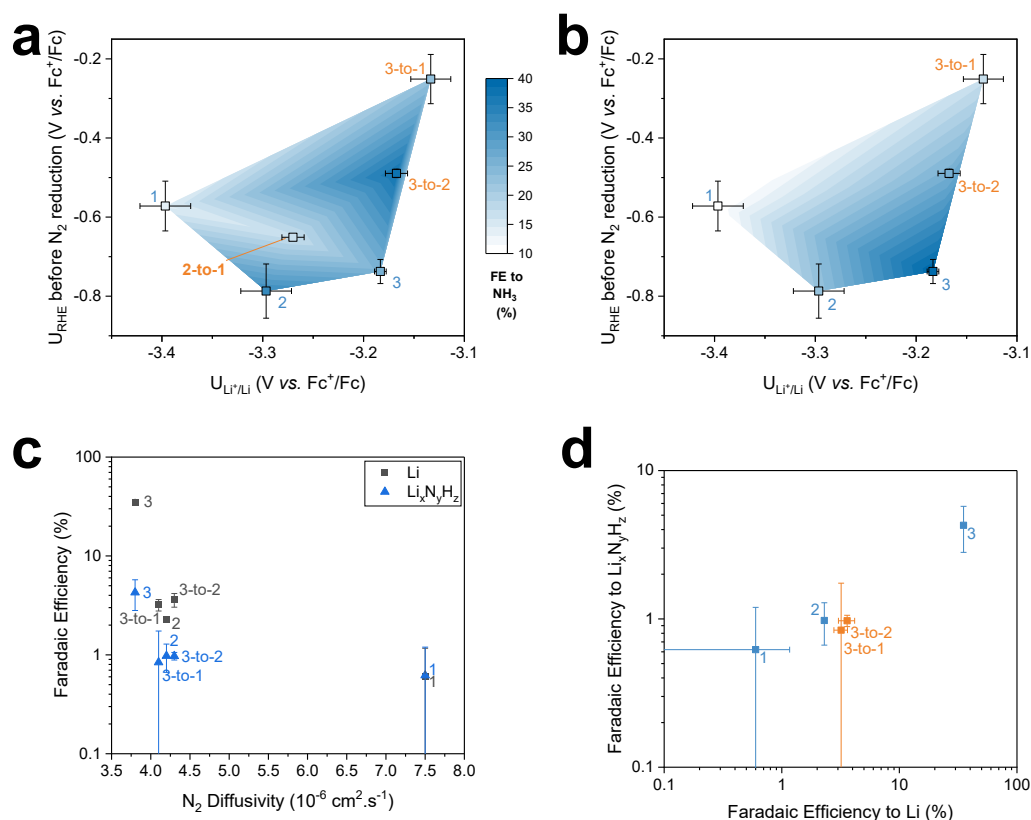


Figure 50. Incorporation of RHE potential and N_2 mass transfer in assessing the selectivity of Li -mediated ammonia synthesis. (a,b) U_{RHE} before electrolysis plotted against $U_{Li^+/Li}$, coloured by

Faradaic efficiency to **(a)** NH_3 or **(b)** $\text{NH}_3 + \text{Li}_x\text{N}_y\text{H}_z + \text{Li}$, with a backing contour plot. **(c)** Faradaic efficiency to Li and $\text{Li}_x\text{N}_y\text{H}_z$ after N_2 electrolysis, plotted against N_2 diffusivity. **(d)** Correlation between Faradaic efficiency to Li and $\text{Li}_x\text{N}_y\text{H}_z$.

Figure 50a displays a weak trend suggesting that low U_{RHE} (low acidity) and high $U_{\text{Li}^+/\text{Li}}$ (low Li metal reactivity) may provide a better environment for selective ammonia synthesis. The exception to this trend is the 3 M LiNTf_2 in THF electrolyte. We hypothesise that the viscosity of such electrolyte impairs mass transfer of N_2 and proton carriers by convection (when stirring the electrolyte like it was done in these experiments), which could explain an underestimation of ammonia synthesis selectivity in a 3 M electrolyte. Work from Du *et al.* claiming that a 3 M LiNTf_2 performs similarly to at 2 M when run at higher N_2 pressures corroborate this hypothesis.⁸⁴ To test this hypothesis further, the amounts of unreacted Li and $\text{Li}_x\text{N}_y\text{H}_z$ present in the electrode deposits were quantified by titration, as a proxy for what could have become ammonia at high N_2 and proton coverage (experimental section 2.9).^{140,141} By reacting an electrode deposit with D_2O within a sealed vial, Li is converted to D_2 . D_2 can be quantified by a combination of gas chromatography and mass spectrometry,^{140,141} and used to back calculate the amount of Li present on the tested electrodes (section 2.9.2). Quantification of ammonia in the resulting liquid gives the amount of $\text{Li}_x\text{N}_y\text{H}_z$ present on the electrode deposits (section 2.9.6). The larger accumulation of Li and $\text{Li}_x\text{N}_y\text{H}_z$ in a 3 M electrolyte compared to electrolytes of similar N_2 diffusivity (Figure 50c) could go along the hypothesis of poor convective mass transport, and Li remaining out of reach of N_2 (and H^+), although we cannot exclude at this juncture the possibility that this is the result of a more passivated SEI.⁸³ When adding up the amount of such compounds to the amount of ammonia produced, the trend in reactivity scaled by both U_{RHE} and $U_{\text{Li}^+/\text{Li}}$ is clearer (Figure 50b). It would be interesting to test these electrolytes in a gas diffusion electrode setup (high N_2 availability at the electrode surface) to circumvent this possible convection artifact and confirm the above hypotheses. In a regime that is not limited by mass transfer to the electrolyte, U_{RHE} and $U_{\text{Li}^+/\text{Li}}$ may be two reliable and experimentally measurable parameters to screen a larger library of electrolytes without performing N_2 reduction. These parameters should be explored in a broader range of chemistries, including other solvents (e.g. diglyme, dimethoxymethane, etc., see Figure 68), other salts (LiClO_4 , LiBF_4) or different amounts of proton carriers to estimate the validity of such parameters on a broader scale.

From the above results and literature, we identify two pitfalls that may skew the interpretation of the above measurements, respectively related to possible toluene oxidation and reduction. First, there is

a marked difference in the extent to which electrolytes containing (or not containing) toluene acidify over the course of N₂ electrolysis. Toluene containing electrolytes experience a larger increase in their RHE potential (Figure 49b, size of floating bars). The reason is unknown, however could be due to oxidation of toluene at the counter electrode, producing acidic compounds such as benzyl alcohol, methyl-phenols, benzaldehyde or even benzoic acid.^{204–207} In the presence of toluene only, we observe a strong colour change to a bright yellow, which goes along the hypothesis of toluene oxidation (such oxidation products can be chromophores). As produced acidic byproducts might impair selective ammonia synthesis down the line. For the above reasons, it would be interesting to test these electrolytes in a setup where H₂ oxidation is performed rather than purely solvent oxidation (preventing or limiting the extent of possible toluene oxidation). Another possible issue with the use of toluene is its reduction on Li. Indeed, Birch reduction of arenes to 1,4-dienes using stoichiometric amounts of Li metal is a well-known synthetic reaction to access complex organic structures.^{208,209} Peters *et al.* demonstrated an electrochemical Li-mediated pathway for this reduction, which operates similarly to the one under study here.¹⁵⁴ They demonstrated the method applicability to a broad range of arenes, including structures analogous to toluene, although not toluene itself. This reaction could result in selectivity losses in our system. However, for this reaction to be selective, specific electrolyte additives as well as low temperatures are required, making it less likely to happen in our case. Toluene was also reported to be stable against Li in the typical metal battery operations we base our work on.^{134,202} Aliquots of electrolyte were analysed by ¹H and ¹³C NMR showing no obvious degradation of toluene, but rather possible oxidation of THF which has been reported before (Figure 76).¹⁹³

The reader may have noted that in this section, the role of the SEI has been mostly occulted from the discussion. The purpose for this omission was to raise questions that we alluded to in the introduction. Is the SEI a defined and stable structure which chemistry discriminates diffusion of different reagents and products to and away from the electrode active surface? Or is it rather a layer that kinetically controls Li reactivity with the electrolyte and reagents, allowing the rates of lithium plating to match the rates at which reactants are converted to ammonia? Another way to phrase it would be: can we predict ammonia synthesis selectivity by the bulk and interfacial properties of the electrolyte rather than the SEI itself? Do we ‘just’ need to control the growth of such SEI to cover the reservoir of lithium we continually produce? In the next section, we will probe electrode deposits post electrolysis through a portfolio of titration methods, evaluating possible trends across the SEI chemical composition. While this is solely a chemical analysis (as opposed to a morphological one), we hope that this will answer some of the above questions.

4.1.2. Does the SEI Chemistry Correlate with Selectivity to Ammonia?

Many works to date have related ammonia synthesis selectivity to the chemical composition and morphology of the SEI, through qualitative *in/ex situ* X-ray photoelectron spectroscopy (XPS),^{70,80–82,95,172,210} Time-of-flight secondary ion mass spectrometry (ToF-SIMS),^{80,147,172,210} X-ray diffraction (XRD),⁷⁰ cryo-electron microscopy⁸³ or scanning electron microscopy (SEM)^{95,210}. A first issue with these analytical techniques is their surface sensitivity, only relating to the surface chemistry of the SEI and not its bulk. Depth profiling can be done to address this issue in XPS or ToF-SIMS measurements, but it should be done with great care since electrons/ions sputtered at the sample can damage it (e.g. reduction by electrons) and skew the interpretation; cluster-ion sputtering is preferred.⁸⁵ The second issue comes with the *ex situ* nature of these measurements, where the probed interface may be different to the one under operation, either due to a change in environment or degradation during sample transfer to the analytical equipment. *Operando* techniques have been developed to study SEI formation and behaviour during the process of ammonia synthesis and have proven useful in understanding the formation steps of the SEI.^{71,72,211} However, these usually need specialised equipment and expertise, and can be difficult to interpret. Here, we propose a method for *ex situ* quantitative analysis of the SEI chemical content (Li^0 , LiH , $\text{Li}_x\text{N}_y\text{H}_z$, $\text{Li}_2\text{O/LiOH}$, Li_2CO_3 , LiF) through a portfolio of chemical titration methods inspired from the field of Li metal battery research (Figure 51).^{90,140,141,145} This method requires more commonly available equipment (gas chromatography, mass spectrometry, Karl Fisher, NMR, ion chromatography), and was developed with enormous support from my colleagues Dr Bethan Davies, Dr Anna Winiwarter, Yuxiang Zhou and Aishah Faisal. The workflow and techniques employed have their own flaws (*ex situ* techniques, no morphological information, methods incompatibilities), which will be pointed out when appropriate, but this method has the advantage of accessibility, ease of interpretation, and a bulk evaluation of the SEI (as opposed to a surface selective and short scale analysis).

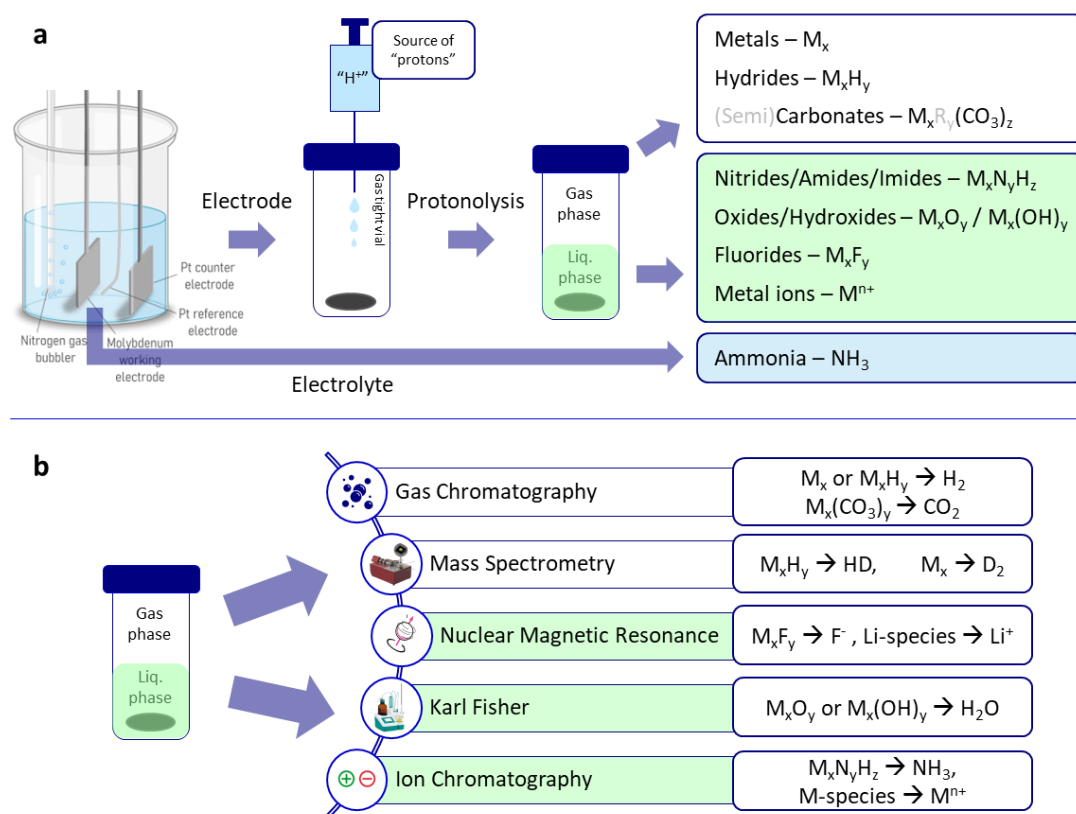


Figure 51. Workflow for the titration of electrode interphase species: a material of interest is placed in a sealed vial, to which is added a protic “titrant” that protonolyses the material’s components, to yield analytes in the gas phase or liquid phase that can be quantified. – Cell drawing courtesy of Craig Burdis. Analytical techniques developed with the help of Dr Bethan Davies, Dr Anna Winiwarter, Yuxiang Zhou and Aishah Faisal.

The chemical titration of the electrode deposits (detailed in section 2.9) goes as follows. An ammonia synthesis electrode was extracted from its surrounding electrolyte while a reductive potential is still being applied, then it was disconnected from the potentiostat. After being dipped (or not, see experimental methods and end of this paragraph) in THF to wash electrolyte off, the electrode deposit was isolated in a sealed vial and reacted with a source of deuterated protons. SEI components like Li^0 , LiH , Li_2CO_3 , $Li_xN_yH_z$, $Li_2O/LiOH$, LiF are respectively converted to D_2 , HD , CO_2 , ammonia, water and dissolved F^- . Such analytes can be quantified by gas chromatography (hydrogen, CO_2), mass spectrometry (D_2 vs. HD), UV-vis colorimetric assay or ion chromatography (ammonia), Karl Fisher (water), quantitative ^7Li NMR (Li^+) and quantitative ^{19}F NMR (F^-). This method was applied to analyse the chemical composition of the SEIs generated in the electrolytes devised in section 4.2.2. Multiple sources of protons can be used to react the electrode deposit and quantify the resulting analytes

(aqueous acids, water, alcohols, *etc.*). However, to measure all the above listed SEI components, a few conditions must be met. First, Li metal and LiH will both react with the source of protons to yield hydrogen. Only a deuterated source of protons will discriminate the two, yielding D₂ for the former and HD for the latter, which ratio can be determined by mass spectrometry. Second, the detection of Li₂O/LiOH relies on the quantification of water by Karl Fisher titration. An aqueous titrant will therefore prevent the quantification of trace water. Third, LiF is only soluble in water (or D₂O) and will not be detected by titration with acidic or non-aqueous titrants.¹⁴⁵ Finally, Li₂CO₃ titration was not possible, neither with MeOD nor D₂O. CO₂ is too soluble in D₂O to be detected in the gas phase quantitatively. MeOD may not be acidic enough to convert Li₂CO₃ to CO₂, and/or CO₂ may be too soluble in MeOD to be detected in the gas phase by gas chromatography. The titration of Li₂CO₃ should release water as byproduct (and interfere with Li₂O/LiOH titration), but our experiments (Figure 33) and a recent report show that the dissolution of sodium carbonate in alcohols do not release CO₂ nor does it release significant amounts of water, suggesting only dissolution but no conversion of carbonate to CO₂ and water.⁹⁰ These prerequisites mean that there are no single titrants that can measure all SEI components at once, and separate ammonia synthesis experiments are required to quantify all species of interest. Table 3 summarises selected experimental parameters for titration.

Table 3. Interphase species of interest, titrant used, reactions they undergo with it, issues we encountered in quantifying such species, and which species one cannot co-titrate on a single sample.

SEI Species	Titrant	Reaction (analyte in bold)	Analytical Technique	Issue encountered	Not compatible
Li	MeOD and D ₂ O	$Li + D^+ \rightarrow \frac{1}{2} \mathbf{D_2} + Li^+$	Gas Chromatography	-	Li ₂ CO ₃
LiH	MeOD and D ₂ O	$LiH + D^+ \rightarrow \mathbf{HD} + Li^+$	Mass Spectrometry	MeOD interferes with m/z = 3 signal (LiH)	Li ₂ CO ₃
Li ₂ CO ₃	Not Titrated	$Li_2CO_3 + 2 D^+ \rightarrow \mathbf{CO_2} + D_2O + 2 Li^+$	Gas Chromatography	Li ₂ CO ₃ only converts to CO _{2,g} in aqueous acids	Li ₂ O/LiOH, LiF
Li ₂ O / LiOH	MeOD	$Li_2O + 2 MeOD \rightarrow \mathbf{D_2O} + 2 LiOMe$	Karl Fisher	-	LiF, Li ₂ CO ₃
LiF	D ₂ O	$LiF + D_2O \rightarrow \mathbf{F^-}_{aq.} + Li^+_{aq.}$	¹⁹ F NMR	LiF only soluble in water/D ₂ O	Li ₂ O/LiOH, Li ₂ CO ₃
Li _x N _y H _z	MeOD and D ₂ O	$Li_xN_yH_z + (3y - z)D^+ \rightarrow y \mathbf{ND_{3-z}H_z} + x Li^+$	Ion Chromatography	-	Li ₂ CO ₃
Li-ions in SEI	MeOD	$Li_xR + x D^+ \rightarrow x \mathbf{Li^+} + x \mathbf{RD}$	⁷ Li NMR	-	Li ₂ CO ₃

N₂ reduction experiments were repeated five times for each electrolyte composition. Three of the as produced electrode deposit them were dipped in THF to wash off residual electrolyte, and titrated with MeOD, allowing the quantification of Li⁰, LiH, Li_xN_yH_z, Li₂O/LiOH and total amount of Li species in the SEI. The two remaining electrode deposits were not washed with solvent this time, and titrated with D₂O, enabling titration of LiF but also Li⁰, LiH and Li_xN_yH_z like previously. Unfortunately, this means

that titration of Li_2CO_3 will not be possible. However, Li_2CO_3 is suggested to be a metastable species in lithium metal battery SEIs, converting relatively fast to LiF and CO_2 in fluorinated electrolytes,¹³⁹ and we will therefore assume a neglectable amount of Li_2CO_3 to be present in such SEIs. LiF and Li_2O are both coined as key components of the SEIs studied so far in Li-mediated ammonia synthesis SEIs and will be probed here.^{70,81–84,90} Li , LiH and $\text{Li}_x\text{N}_y\text{H}_z$ are hypothesised to take part in the N_2 reduction reaction^{47,71,72} (or participate in ‘dead’ Li growth in battery SEIs in the case of LiH).²¹² and are therefore interesting species to probe alongside ammonia formation. A species that was not probed through this method is lithium ethoxide (LiOEt). LiOEt has been proposed as a major organic SEI component during ammonia synthesis.^{72,111} However, attempts at detecting it by ^1H NMR failed due to the low sensitivity of the technique and difficult deconvolution from ethanol coming from residual electrolyte. LiOEt was therefore omitted from the list of SEI components titrated. Note that using MeOD as a titrant for such quantification came with an issue we did not anticipate. The mass spectrum for MeOD overlaps with mass to charge ratios (m/z) 2 and 3, corresponding to H_2 and HD . This makes the titration of LiH by mass spectrometry difficult, but could be overcome with more work on masses deconvolutions.¹⁴³ However, little variation in calculated Li/LiH ratios was observed across MeOD - and D_2O -titrated samples. A summary of such titration’s is below (Figure 52).

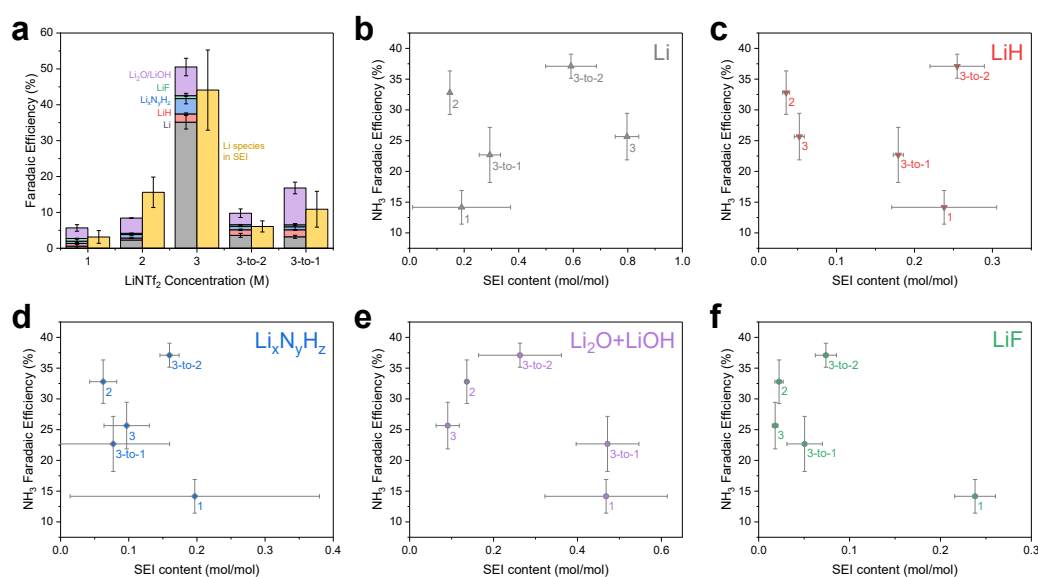


Figure 52. Summary of electrode deposits titration across electrolytes tested for ammonia synthesis (5 repeats including 2 for LiF , 3 for $\text{Li}_2\text{O}/\text{LiOH}$ and SEI Li species and 5 for NH_3 , Li , LiH and $\text{Li}_x\text{N}_y\text{H}_z$). **(a)** Bar graph of the Faradaic efficiency toward the formation of titrated SEI components. The “SEI Li ” (right bar) accounts for all forms of Li species and should be equal to or larger than the sum of the specific species titrated in this work (left bar). **(b-f)** Faradaic efficiency toward ammonia plotted against the SEI content (mol vs. mol of “SEI Li ”) of **(b)** Li , **(c)** LiH , **(d)** $\text{Li}_x\text{N}_y\text{H}_z$, **(e)** $\text{Li}_2\text{O}/\text{LiOH}$ and **(f)** LiF .

The combined Faradaic efficiency to the formation of Li^0 , LiH , $\text{Li}_x\text{N}_y\text{H}_z$, LiF and $\text{Li}_2\text{O}/\text{LiOH}$ approaches the Faradaic efficiency to all Li-containing species (calculated by the sum of Li^+ detected by quantitative ^7Li NMR after MeOD titration and LiF detected by ^{19}F NMR after D_2O titration) for all electrolytes tested (Figure 52a). This suggests that the errors associated with the titration methods employed are not too significant, and that the majority of the SEI is being probed by this mean. There is no apparent monotonic correlation between electrode deposit contents and Faradaic efficiency to ammonia (same against Faradaic efficiency to each of these compounds, Figure 75). However, a peak-shaped relation emerges between $\text{Li}_2\text{O}/\text{LiOH}$ content in the electrode deposits and Faradaic efficiency to ammonia (Figure 52e). This effect was previously reported in LiClO_4 based electrolytes,^{70,81} and it is interesting to notice its dominance in fluorinated electrolytes too. Alike Li metal battery performance and electrode deposit content, the trend is clearest with $\text{Li}_2\text{O}/\text{LiOH}$ content, although not as straightforward as in batteries.⁹⁰ Previous works studying the role of $\text{Li}_2\text{O}/\text{LiOH}$ in the SEI advocate for an optimal amount in the SEI for maximum selectivity, consistent with Figure 52e.^{70,81} This optimum is hypothesised to result from a kinetic trade-off between having enough $\text{Li}_2\text{O}/\text{LiOH}$ to cover and protect lithium from reacting too violently with the electrolyte, and growing too much $\text{Li}_2\text{O}/\text{LiOH}$ so that it prevents Li from reacting at all with N_2 and H^+ to yield ammonia. This trade-off can help rationalise the results observed in the electrolytes tested here, illustrated in Figure 53.

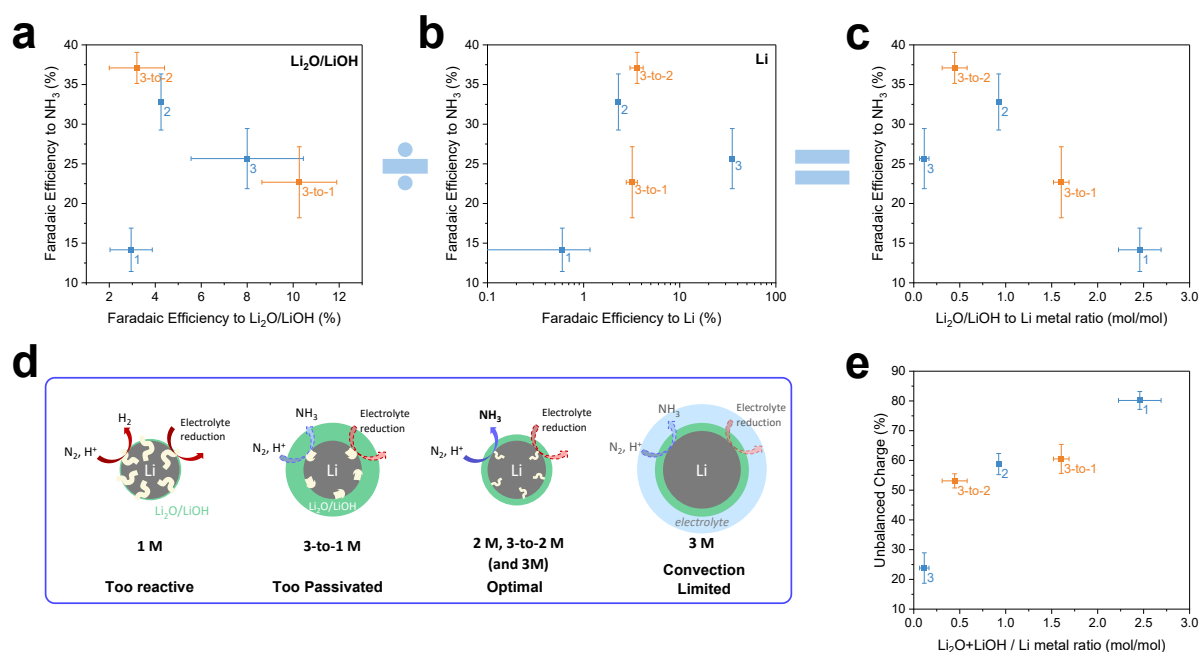


Figure 53. The effect of $\text{Li}_2\text{O}/\text{LiOH}$ and Li metal relative contents on nitrogen reduction performance. (a-c) A minimised ratio between $\text{Li}_2\text{O}/\text{LiOH}$ and Li metal, calculated by dividing Faradaic efficiency to (a) $\text{Li}_2\text{O}/\text{LiOH}$ and (b) Li, relates to (c) a maximised Faradaic efficiency to ammonia. (d) Hypothesised

mechanistic explanation of the relation between $\text{Li}_2\text{O}/\text{LiOH}$ to Li metal ratio and reactivity towards N_2 , H^+ and the electrolyte. (e) Unbalanced charge, supposedly toward electrolyte degradation and H_2 evolution, against $\text{Li}_2\text{O}/\text{LiOH}$ to Li metal ratio.

At too low $\text{Li}_2\text{O}/\text{LiOH}$ coverage (e.g. 1 M electrolyte), lithium is too exposed to the electrolyte, resulting in very low Faradaic efficiency to ammonia, severe parasitic electrolyte reduction (expectedly to H_2 evolution and electrolyte degradation, Figure 53e) and low amounts of Li remaining in the electrode deposits (i.e. high $\text{Li}_2\text{O}/\text{LiOH}$ to Li ratio). At too high $\text{Li}_2\text{O}/\text{LiOH}$ coverage (e.g. 3-to-1 M electrolyte), the deposited lithium is too well protected from the electrolyte, resulting in low Faradaic efficiency to ammonia but also little parasitic reduction, and more unreacted Li remaining on the electrode (i.e. intermediate $\text{Li}_2\text{O}/\text{LiOH}$ to Li ratio). At optimal $\text{Li}_2\text{O}/\text{LiOH}$ coverage (e.g. 2, 3 and 3-to-2 M electrolyte), lithium is protected enough without being too passivated, resulting in selective ammonia synthesis, mitigated parasitic reduction reactions, and intermediate amounts of leftover unreacted Li (i.e. low $\text{Li}_2\text{O}/\text{LiOH}$ to Li ratio). As a result, a clear negative correlation is observed between Faradaic efficiency to ammonia, and the ratio between $\text{Li}_2\text{O}/\text{LiOH}$ and Li metal remaining in the electrode deposit (Figure 53c). Deviation of the 3 M electrolyte from this correlation may be explained by the slower convective transport in this electrolyte, offering an additional layer of protection to Li (as seen by the lowest unbalanced charge in this dataset). This in turn contributes to overrepresented unreacted Li which could have been converted to NH_3 or other byproducts when in contact with N_2 and H^+ . The opposite deviation observed when adding up Faradaic efficiency to $\text{NH}_3 + \text{Li} + \text{Li}_x\text{N}_y\text{H}_z$ in Figure 73 supports this hypothesis (too much unreacted Li).

Then, are we better off describing selective nitrogen reduction to ammonia through bulk activity of reagents, or through SEI composition? Probably both, but the former may explain the latter. Previous works have verified experimentally that the solubility of SEI-like components is proportional to the ratio of lithium salt concentration to Li^+ activity coefficient in solution, as the dissolution reaction equilibrium equation suggests.²¹³ We verify the presence of this relation, as illustrated by the content of $\text{Li}_2\text{O}/\text{LiOH}$ in the electrode deposit (i.e. what is not being dissolved) and corresponding $U_{\text{Li}^+/\text{Li}}$ qualitatively following the said proportionality relation (Figure 54a). Adjacentlly, at roughly constant $U_{\text{Li}^+/\text{Li}}$, $\text{Li}_2\text{O}/\text{LiOH}$ content increases with U_{RHE} (Figure 54b). This observation is consistent with $\text{Li}_2\text{O}/\text{LiOH}$ content increasing with the addition of water (or oxygen) to LiClO_4 electrolytes,^{70,81} or the addition of ethanol in LiNTf_2 based electrolytes (manuscript in preparation with Dr Olivia Westhead) which are all expected to increase U_{RHE} . A combination of these two parameters results in a linear

correlation between $\text{Li}_2\text{O}/\text{LiOH}$ content in the electrode deposits and $U_{\text{Li}^+/\text{Li}} - U_{\text{RHE},i}$ (Figure 54c), suggesting that $U_{\text{Li}^+/\text{Li}} - U_{\text{RHE},i}$ can describe the control of $\text{Li}_2\text{O}/\text{LiOH}$ growth and Li metal reactivity. This stabilisation is also illustrated by a decrease in unbalanced charge with: (i) increasing $U_{\text{Li}^+/\text{Li}}$ at constant U_{RHE} (Figure 54d), and (ii) decreasing U_{RHE} at constant $U_{\text{Li}^+/\text{Li}}$ (Figure 54e). Again, the overlap of these two factors results in a negative correlation between unbalanced charge and $U_{\text{Li}^+/\text{Li}} - U_{\text{RHE},i}$ (Figure 54f). Is the stabilisation only kinetic though? A second explanation could be thermodynamic. An increase in $U_{\text{Li}^+/\text{Li}}$ should theoretically translates to a less reducing Li metal surface that could explain the lower unbalanced charge observed at increased $U_{\text{Li}^+/\text{Li}}$ and constant U_{RHE} (Figure 54d). Conversely, at roughly constant $U_{\text{Li}^+/\text{Li}}$, an increase in U_{RHE} results in higher unbalanced charge (Figure 54e), which could also be related to a more acidic electrolyte and therefore more reactive to the reducing Li surface.

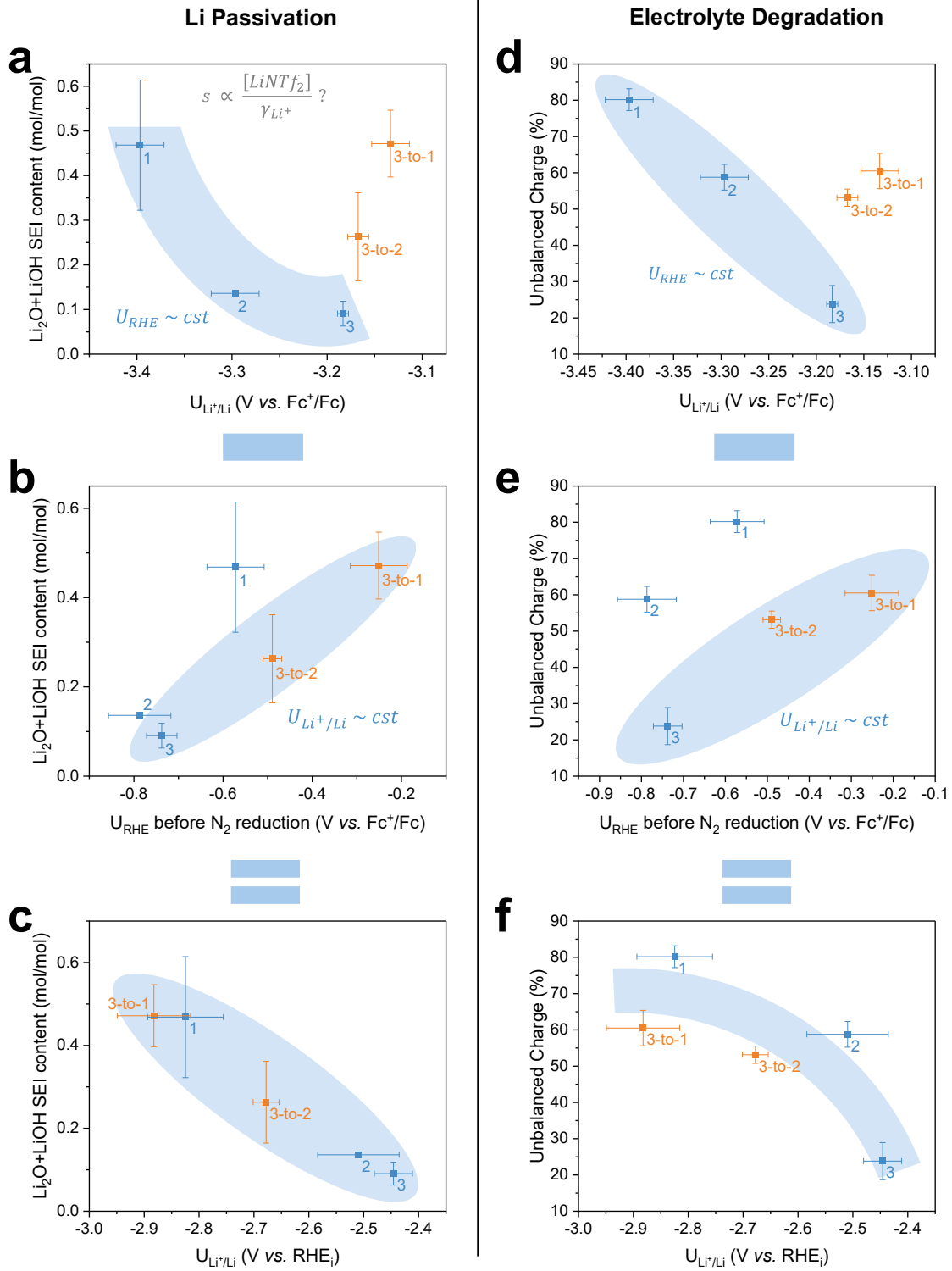


Figure 54. The relation between electrode deposits content, unbalanced charge, $U_{Li^+/Li}$ and $U_{RHE,i}$. (a-c) Linear relation between $Li_2O/LiOH$ to Li ratio and $U_{Li^+/Li} - U_{RHE,i}$ as a potential consequence of (a) a dependence of $Li_2O/LiOH$ content in the electrode deposits, and the concentration/activity

coefficient of Li^+ in solution, and **(b)** an increase in electrolyte acidity at constant $U_{\text{Li}^+/\text{Li}}$. **(d-f)** Negative correlation between charge to electrolyte reduction and $U_{\text{Li}^+/\text{Li}} - U_{\text{RHE},i}$ as a potential consequence of **(d)** the lower reducing capability of Li at higher $U_{\text{Li}^+/\text{Li}}$ and constant U_{RHE} , and **(b)** the milder reactivity of electrolyte with lower acidity, at constant $U_{\text{Li}^+/\text{Li}}$. Blue ellipses in **(a,b,d,e)** are guide for the eye of observed trends at relatively constant $U_{\text{Li}^+/\text{Li}}$ and U_{RHE} (as labelled). Blue ellipses in **(c)** and **(f)** highlight the trends resulting from the subtraction of $U_{\text{Li}^+/\text{Li}}$ and U_{RHE} .

Overall, we proposed a method to alleviate the voltage burden associated with lithium plating through the modulation of the lithium plating potential ($U_{\text{Li}^+/\text{Li}}$). Through a series of electrolyte bulk and interfacial characterisations, we unveiled how changes in this potential (and Li^+ activity), in the RHE potential (U_{RHE} , proton activity) and in N_2 mass transfer may predict accurately electrolyte formulations toward high ammonia synthesis selectivity. We suggest that, under comparable convective mass transfer, electrolytes with high lithium plating potential and low RHE potential (*i.e.* high Li^+ activity and low proton activity) may provide a more adequate environment for nitrogen to convert to ammonia. Closing the gap between $U_{\text{Li}^+/\text{Li}}$ and U_{RHE} may mitigate the growth of passivating $\text{Li}_2\text{O}/\text{LiOH}$ while lowering both the reactivity of Li and the acidity of the electrolyte, resulting in a low $\text{Li}_2\text{O}/\text{LiOH}$ to Li ratio and diminished parasitic electrolyte reduction. The kinetic or thermodynamic dominance of this stabilisation remains a question at this stage, as similarly performing electrolytes result from similar $U_{\text{Li}^+/\text{Li}}$, U_{RHE} and absolute amounts of the SEI species probed in this work (Figure 75). Deconvoluting these two aspects would require the investigation of SEI species and deposits morphology on a broader electrolyte library.¹³⁴ In addition, $U_{\text{Li}^+/\text{Li}}$ and U_{RHE} may be involved in other aspects of the process. For instance, SEI morphology (thickness, porosity, dynamics, *etc.*) is expected to play a large role in taking reagents and products to and away from the active sites of N_2 reduction. Lithium metal battery charge/discharge rates have shown effects on Li metal plating morphology and battery performance.⁸⁷ How a change in $U_{\text{Li}^+/\text{Li}}$ and U_{RHE} affect Li metal morphology in this system and how that affects ammonia selectivity is yet to be determined. Cryo-electron microscopy images and operando X-ray scattering experiments suggest that ethanol in the electrolyte may affect SEI thickness and porosity through bubble templating by hydrogen evolution, swelling or ‘corrosion’ to name a few.^{72,83} The RHE potential (U_{RHE}) measured in this work and its relation with proton activity could potentially encompass some of those aspects. Finally, an open question in the field of Li-mediated ammonia synthesis is on the dynamic or static aspect of the SEI generated in this system. In this study, acidity is always observed to increase over the course of an

experiment (Figure 49d). However, using the initial RHE potential ($U_{\text{RHE},i}$) to describe ammonia synthesis typically generates better trends than the RHE potential after N_2 electrolysis ($U_{\text{RHE},f}$) (Figure 74). If the SEI does take part in steering that selectivity, it would mean that interfacial proton activity stabilises closer to $U_{\text{RHE},i}$ due to local proton depletion, and/or that the SEI structure may have reached a steady state early on. Further investigation is required in that regard. Nevertheless, these results bridge ammonia synthesis selectivity, SEI chemistry and bulk electrolyte properties, to yield more accessible and universal descriptors for the fast screening of larger electrolyte libraries toward stable and selective nitrogen reduction. In practice, the gains in voltage demonstrated in this work are counteracted in two ways. First, most electrolyte engineering strategies employed here come with a decrease in electrolyte conductivity (Figure 49c, red dots). As the operating current for N_2 electrolysis increases, ohmic drop will overcome the benefits from a reduced gap between U_{RHE} and $U_{\text{Li}^+/\text{Li}}$. Second, an overpotential additional to ohmic drop is observed past lithium metal potential, as recorded by the difference in potential between the potential measured during constant current N_2 reduction at $-2 \text{ mA}\cdot\text{cm}^{-2}$ and $U_{\text{Li}^+/\text{Li}}$ (Figure 55a). Galvanostatic electrochemical impedance spectroscopy measurements suggest that charge transfer and SEI resistance are both increasing with $U_{\text{Li}^+/\text{Li}}$ (Figure 55c,d), which could explain the positive correlation between overpotential and $U_{\text{Li}^+/\text{Li}}$.

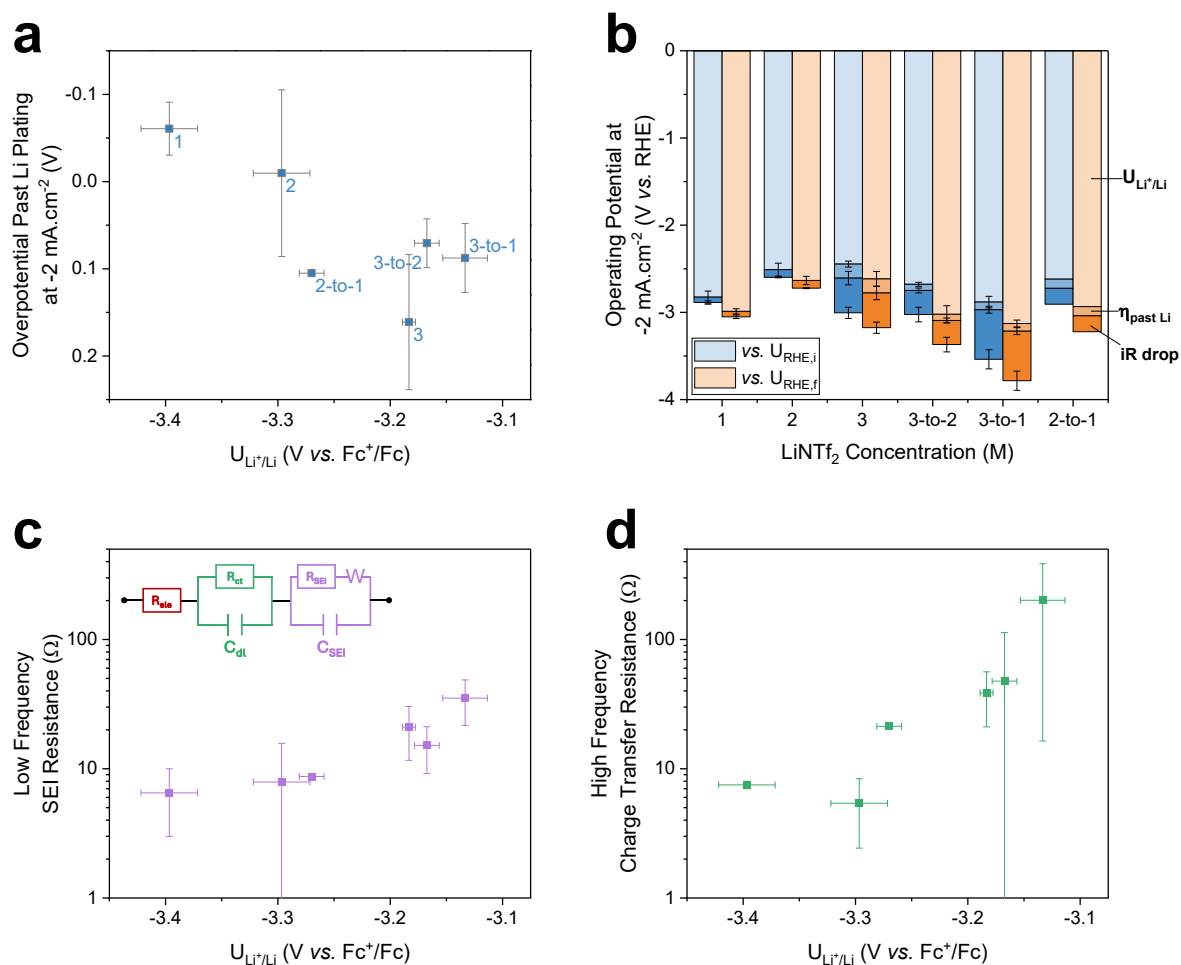


Figure 55. The remaining burdens of lithium. **(a)** Overpotential past lithium plating potential against $U_{\text{Li}^+/\text{Li}}$. The overpotential is defined and calculated by the difference between the average potential measured during nitrogen reduction at -2 mA.cm^{-2} constant current, and $U_{\text{Li}^+/\text{Li}}$. **(b)** Operating potential at -2 mA.cm^{-2} versus RHE potential ($U_{\text{RHE},i}$ in blue, $U_{\text{RHE},f}$ in orange) for the set of tested electrolytes, broken down by potential associated with Li plating ($U_{\text{Li}^+/\text{Li}}$), losses past it ($\eta_{\text{past Li}}$), and iR drop due to electrolyte resistance. **(c,d)** Estimation of the contributions to $\eta_{\text{past Li}}$ due to **(c)** SEI resistance and **(d)** charge transfer resistance as calculated by recording a galvanostatic impedance spectrum at the end of electrolysis, at $-2 \pm 0.5 \text{ mA.cm}^{-2}$ (see methods), and fitting against the equivalent circuit inserted in **(c)**.

A likely root cause to these voltage losses lies in Li-ion solvation. Indeed, increasing $U_{\text{Li}^+/\text{Li}}$ in these electrolytes comes with an anion-rich Li-ion solvation sheath, as evidenced by Raman spectroscopy (Figure 47b). While it has benefits in creating an inorganic rich SEI that stabilises electrode potential during ammonia synthesis,^{80,93} this has several drawbacks. First, SEI resistance is fundamentally linked

to its electronic insulating character,⁹² and some of that passivation is inevitable for selective ammonia synthesis. Second, ion pairs and aggregates in the electrolyte make Li^+ bulk transport slower, decreasing overall electrolyte conductivity.¹⁸⁷ Second, Li^+ desolvation energy from an ionic solvation sheath is higher than it is from a neutral solvent, making overall charge transfer slower as ion solvation gets more ionic,²¹⁴ and therefore as $U_{\text{Li}^+/\text{Li}}$ increases. This inherent issue has to be addressed to achieve voltage gains in the Li-mediated nitrogen reduction. Electrolyte formulations have been proposed to ease Li-ion mobility and increase Li-ion desolvation kinetics in Li metal batteries, while still dragging an inorganic rich environment toward the electrochemical interface, yielding stable Li cycling without compromising on conductivity and charge transfer rates.^{187,214–216} Exploring such avenues while targeting high $U_{\text{Li}^+/\text{Li}}$ and low U_{RHE} may result in more energy efficient, selective and stable Li-mediated nitrogen reduction to ammonia. Nevertheless, even voltage gains by a volt will not be enough to match the Haber-Bosch process, energy-wise.¹¹ Only moving away from lithium will enable a leap in energy efficiency.

Chapter 5. Bypassing the Issue – Beyond Lithium

The overpotential associated with continuous lithium plating can be quantified (section Chapter 3) and partially alleviated by altering Li metal potential ($U_{\text{Li}^+/\text{Li}}$) and RHE potential (U_{RHE}) through electrolyte engineering, even increasing selectivity to ammonia on the way (section Chapter 4). However, such gains are partly masked by other unidentified sources of voltage losses that prevent significant gains in energy efficiency. Figure 56a displays the huge progress made in terms of activity and stability in the production of ammonia. This figure reproduced and amended from previous works,³⁶ requires a few assumptions to be made to scale potentials against RHE, which may not always be accurate. Limitations are discussed in section 0, but the data still reflects the point made below.

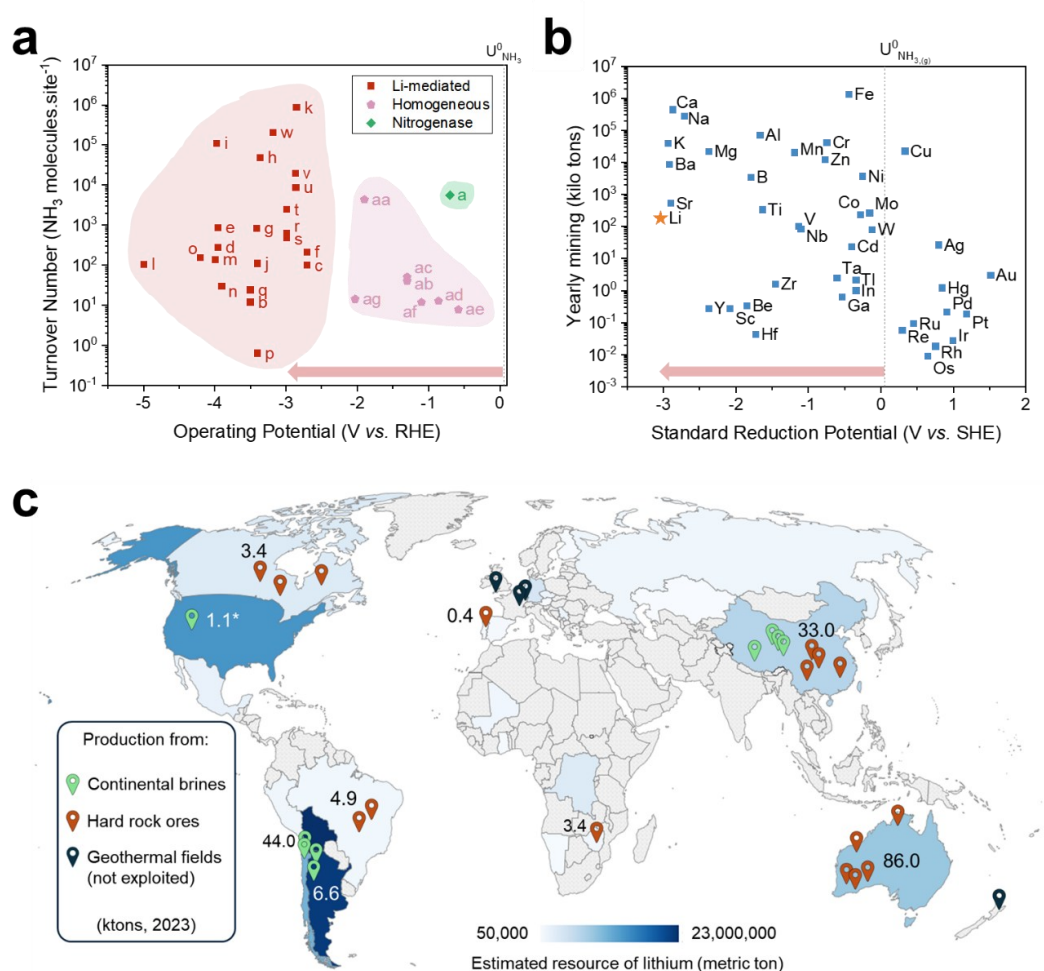


Figure 56. The limits to the use of Li for ammonia synthesis. (a) Turnover Frequency reported for ammonia synthesis using a Li-mediated system, homogeneous catalysts, or nitrogenase. Showing the burden associated with the operation at Li plating potential (red arrow). – Reproduced with permission

from Westhead et al.³⁶ (a²¹⁷, b⁴⁹, c⁴⁸, d,e³⁹, f²¹⁸, g¹¹³, h,i⁶⁹ j⁷⁰, k⁸⁴, l,m⁸², n,o,q⁸⁰ p⁸¹, r,s,t¹⁰⁰, u,v,w⁹⁹, x,y⁵⁴, z⁵⁶, aa⁴¹. ab,ac²¹⁹, ad²²⁰, ae²²¹, af²²², ag²²³), © 2023 The Authors. Published by American Chemical Society. (b) Elements global mining (2023) vs. standard reduction potential.^{224,225} (c) Map of the world resources in lithium (blue colour scale), main mines and amounts produced by country in 2023.^{225–227}

However, even a decrease in the overpotential associated with Li plating by hundreds of mV would maintain it as the main source of energy losses (Figure 42c,d),¹¹⁴ making it far out of reach of an ideal electrode and unable to compete with systems based on molecular electrocatalysts or the nitrogenase enzyme on that perspective. In fact, lithium might be the worst element to pick in the periodic table on the sole prospect of energy efficiency, with a reduction potential standing the furthest away from the equilibrium potential for ammonia synthesis (Figure 56b). In a device combining N₂ reduction on lithium, with H₂ oxidation as a counter reaction, and assuming 100 % Faradaic efficiency and 0 V overpotential to both reactions (-3.04 V vs SHE for the negative electrode), energy cost was calculated to be of 51.8 GJ.t_{NH₃}⁻¹, against 3.9-6.5 GJ.t_{NH₃}⁻¹ required for the sole step of combining N₂ and H₂ via the Haber-Bosch process (irrespective of prior steam methane reforming).¹¹ Such system will only be able to compete with the Haber Bosch process if ammonia shipping costs overtake electricity costs, favouring a decentralised production.^{15,116} Lithium raises more concerns that justify diversification. Figure 56c displays the lithium *resource* by country, defined by the US Geological Survey as “the concentration of Li in or on the Earth’s crust in such form and amount that economic extraction from the concentration is currently or potentially feasible”.²²⁵ We chose this metric to describe lithium availability across the globe instead of a more typically employed lithium *reserve*, which roughly corresponds to the part of that lithium resource that is economically extractable at the time of the estimation, making the former metric more adapted to technological improvements that may expand the future lithium *reserve*. The uneven distribution of lithium ore over the globe^{225,227} and the growing demand for the battery market (increasing from 23 % to 87 % of the lithium production between 2010 and 2023, Figure 77)^{225,228} made it a critical material to secure for most nations.^{224,229} Finally, its production from continental brine evaporation or hard rock mining is deemed to have significant environmental impacts. Extraction from brine comes with the evaporation of 100–800 m³ of brine water for each tonne of lithium, as well as a need for large amounts of freshwater, disturbing the water cycle around the production sites.²²⁷ This has already triggered landscape desertification,²³⁰ losses in biodiversity²³¹ and social conflicts.^{232,233}

For electrochemical nitrogen reduction to bypass the above-mentioned issues, one needs to find new catalytic systems that ideally use readily available materials and operates at much more positive potentials. As a mitigating note, the amount of lithium required to provide an optimistic 10 % of the world's ammonia demand using the lithium-mediated nitrogen reduction would require less than 0.1% of the lithium yearly supply in a system with reasonable performance improvements compared to today's state of the art (see appendix page 207 for hypotheses and calculations). Therefore, the long-term bottleneck of this technology lies in the electricity operating costs associated with continuous lithium plating rather than lithium supply. Nonetheless, it is difficult to find an alternative without guiding rules, and it is difficult to devise rules without multiple alternatives to compare.

5.1. Matching Energetics in the Periodic Table

The mechanism of N_2 reduction on Li is still unknown. However, multiple studies converge toward the observation of lithium nitride as a likely intermediate, via *ex situ* XPS,⁷⁰ *in situ* XRD⁷¹ and *operando* X-ray scattering (Figure 19).⁷² Figure 50c,d displays correlations between nitrogen diffusivity and the amount of ammonia, lithium and $Li_xN_yH_x$ observed on electrodes used for ammonia synthesis, suggesting the participation of each of these species in nitrogen reduction to ammonia. These observations indicate that finding a material capable of producing a stable and dissociated nitride (*i.e.* two N atoms separated) may be a good starting point to find new materials beyond Li.

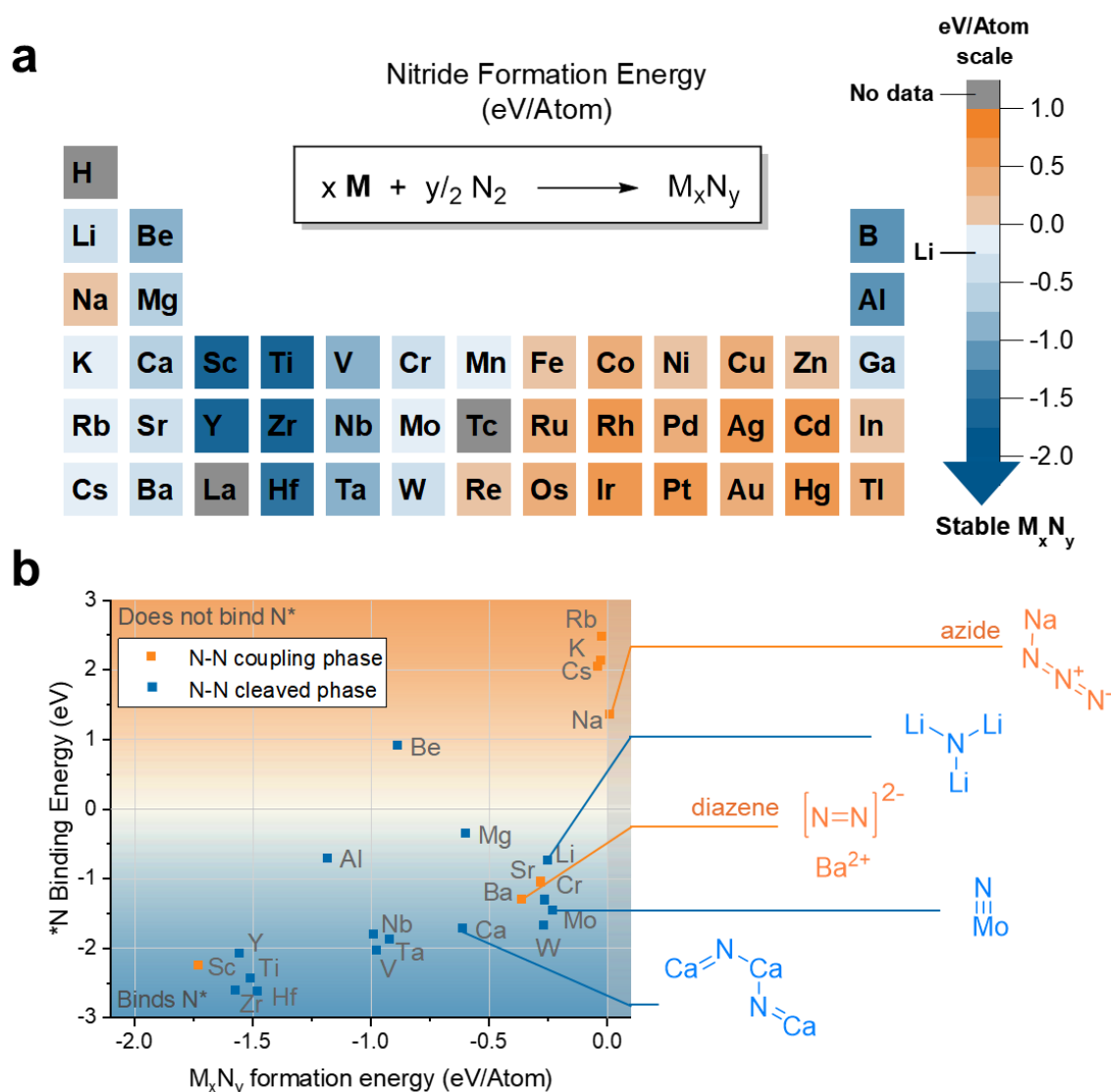


Figure 57. Matching energetics in the periodic table with respects to lithium and nitrogen (**a**) Periodic table (cut) coloured by the energy of formation of a metal nitride from N_2 on a metal surface, calculated by DFT (metal nitride stoichiometries in Table 5, La and Tc omitted due to a missing basis set). (**b**) Calculated $^*\text{N}$ binding energy of elements against their nitride formation energy, with illustrative chemical structures of cleaved metal phases (where N-atoms are dissociated from one another, e.g. Li_3N , Ca_3N_2 , MoN) and coupling phases (N-atoms still covalently bound, e.g. NaN_3 , BaN_2). All calculations were performed by Dr Alexander Bagger. Adapted from my work,¹⁴⁷ with permission from © 2023 The Authors. Published by American Chemical Society.

Figure 57a scales the calculated energy of formation of metal nitrides from N_2 on a range of metals from the periodic table (all DFT calculations were performed by Dr Alexander Bagger, see experimental section 2.12). Roughly half the space explored exhibits elements with a stable metal nitride phase

(Figure 57a, blue elements), all with a more positive reduction potential and some of them being produced at larger scales (*e.g.* Al, Ca, Mo, W, and Mg). However, it is a good time to remind the reader that a prerequisite for ammonia synthesis is also the need to bind nitrogen (not too strongly, not too weakly, Figure 9). We therefore calculated the nitrogen binding energy of the same elements screened here (*N, where * denotes a bond to the surface), which is linked through BEP (Brønsted–Evans–Polanyi) relations to the ability for nitrogen to dissociate at room temperature.²³⁴ Many elements satisfy both criteria of binding *N and converting N₂ to a stable metal nitride (Figure 57b, blue area). However, some of these metal nitrides remain in a coupling phase which does not split N₂ (*e.g.* Sc, Ba, Sr). Lithium is in an interesting location with close to neutral *N binding energy (−0.73 eV), and metal nitride formation energy (−0.25 eV/atom). Mg, Ca, W, Cr and Mo come close. This screening pinpoints 13 elements, interestingly all with a nitride formation energy more negative than –or equivalent to– their hydride formation energy (Table 5). In addition to having such negative nitride formation energies and *N binding energies (except for Na), elements such as Ca, Mg, Na and Al have been studied in the context of electrochemical energy storage alongside Li. They all have working examples of non-aqueous electrolytes producing a solid-electrolyte interphase upon contact between the metal and such electrolyte, sometimes analogous to lithium.^{235–237} The flourishing field of “beyond-Li” batteries is therefore a pertinent space to explore.

5.2. Taking Candidate Elements to the Laboratory

5.2.1. Making Ammonia?

Our theoretical screening suggests Mg and Ca (among others) as potential alternatives to lithium for nitrogen reduction, both having negative metal nitride formation energies and *N binding energies, and reported solid electrolyte interphases being formed in non-aqueous electrolytes. However, like observed in the case of lithium-mediated ammonia synthesis,^{70,80,81,94,102} it is likely that a large number of parameters will affect the performance of beyond-lithium electrolytes making a holistic screening challenging. For comparative purposes, we revisited the Li-based electrolytes with their Na, Ca and Mg equivalents using a model electrolyte: a NTf₂ salt dissolved in an ether solvent (tetrahydrofuran (THF), or 1,2-dimethoxyethane (DME) for Mg(NTf₂)₂) at different concentrations (0.1 to 1 M) and EtOH contents (0.2 to 5 % v/v). While this type of electrolyte has already been successful at plating Na,^{238–240} Mg,^{236,241,242} and Ca metals reversibly,^{236,243–245} aluminium batteries typically operates on a different chemistry based on ionic liquids,²⁴⁶ hence an Al candidate being left out of the beyond-Li inspired

alternatives for now. DME was chosen as a solvent for $\text{Mg}(\text{NTf}_2)_2$ for its ability to dissolve the Mg salt chosen, and for its reported use in both Mg batteries^{236,242} and Li-mediated ammonia synthesis.^{99,193} Based on our theoretical screening, sodium should not be able to activate nitrogen. However, Na and Li electrolytes are relatively analogous in their chemistry (single charge ions, similar reduction potentials, metal-ion conducting SEI, etc). We therefore hypothesised that metal nitride formation energy and *N binding energy were the major difference between Li and Na in this system, and that Na would act as a control experiment to verify it. If a set of electrolytes based on Li produces ammonia by nitrogen reduction, and an identical set of electrolytes based on sodium does not, it is likely that the selected energetic parameters describing the behaviour of the two metals toward nitrogen are a correct parameter to investigate new systems. If Na makes ammonia in these conditions, then the energetic parameters are not the right ones for this exploration. Note that the seminal work of Tsuneto *et al.* compared a Li-based and a Na-based system, producing ammonia on Li but not on Na.⁶⁸ On the other hand, Mg and Ca tick all the boxes so far but had not been tested at the time of this study. Comparing their reactivity against the one of Li will either yield a new electrochemical method for N_2 reduction or help us understand the distinctive features of lithium.

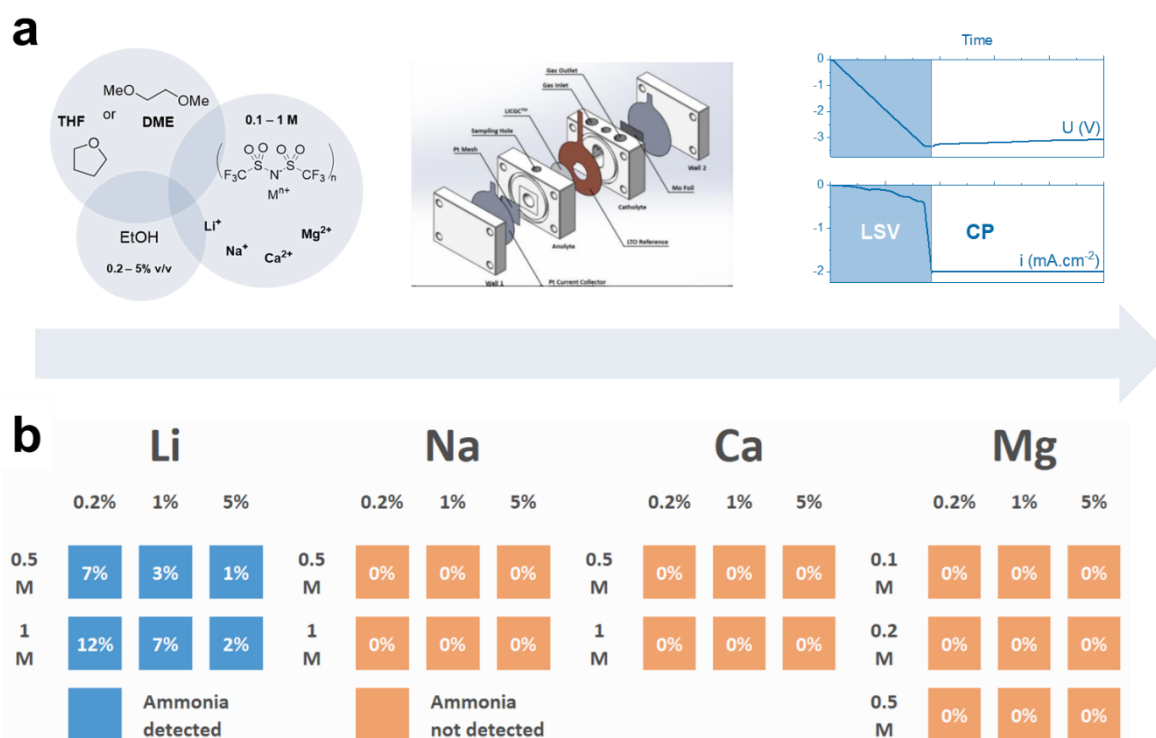
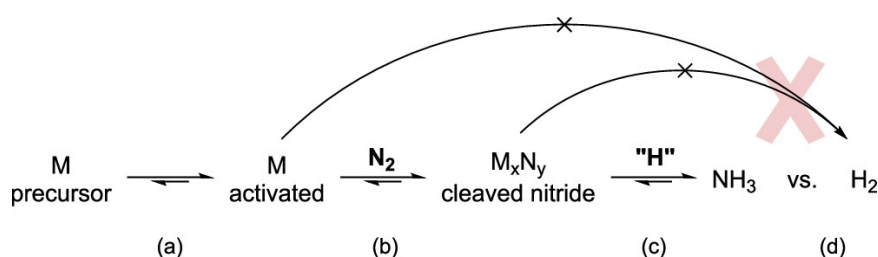


Figure 58. Experimental screening of Li, Na, Ca and Mg electrolytes for N_2 reduction. (a) Electrolyte preparation and testing method illustration. An electrolyte made of a NTf_2^- salt, an ether solvent (DME for Mg electrolytes, THF for the rest) and some EtOH, all in different proportions, is assembled in a

sandwich cell saturated with N_2 (Table 1, configuration B). Electrochemical testing consists of a linear potential sweep down to a cutoff current density of $-2 \text{ mA.cm}^{-2}_{\text{geo}}$ followed with chronopotentiometric electrolysis at that current, passing 10 C of charge. **(b)** Faradaic efficiency to ammonia of different electrolytes tested. Rows: Varying $M(\text{NTf}_2)_n$ salt concentrations, mol.l^{-1} (or M), columns: EtOH content (0.2, 1, and 5 % v/v, or 0.034, 0.171, and 0.857 mol.l^{-1} , respectively). Adapted from my work,¹⁴⁷ with permission from © 2023 The Authors. Published by American Chemical Society.

Selected electrolytes were tested electrochemically (Figure 58a, see section 2.5.3, cell B), and ammonia in the electrolyte was quantified *post* electrochemistry (section 2.8). Expectedly, sodium chemistries did not produce any ammonia in conditions identical to the ones of lithium, suggesting that the above hypotheses are fair (Figure 58b). Unfortunately, in this restricted experimental parameter space, Mg and Ca did not either. Only Li-based electrolytes resulted in the generation of ammonia. In fact, even in the case of lithium, a large variation in selectivity toward ammonia is observed, consistent with previous reports.^{53,80,102} N_2 reduction performance is indeed highly sensitive to Li electrolyte variations ; Mg and Ca electrolytes may very well be as sensitive,^{121,236,247} and a restricted experimental parameter space may contribute to false-negative observations. We deemed essential to understand why Mg and Ca failed to produce ammonia: was the experimental space too narrow, or are these materials just not capable of reducing N_2 ?

5.2.2. Understanding the Limitations of Ca and Mg



Scheme 2. Hypothetic reaction pathway for selective nitrogen reduction to ammonia. (a) Metal electrochemical activation (e.g. reduction), (b) N-dissociated nitride formation (M_xN_y), (c) conversion to NH_3 (d) always selectively over H_2 evolution.

Scheme 2 represents a hypothetic pathway for selective nitrogen reduction to ammonia, based on the hypotheses that tested catalyst candidates should (a) be reduced to their metallic state, (b) convert favourably N_2 to a dissociated (cleaved) metal nitride which (c) is readily converted to ammonia once

in contact with protons, and this (d) in a selective fashion vs. H_2 evolution. Here, we present model experiments with the aim of explaining the failure of Ca and Mg to produce ammonia (Figure 59).

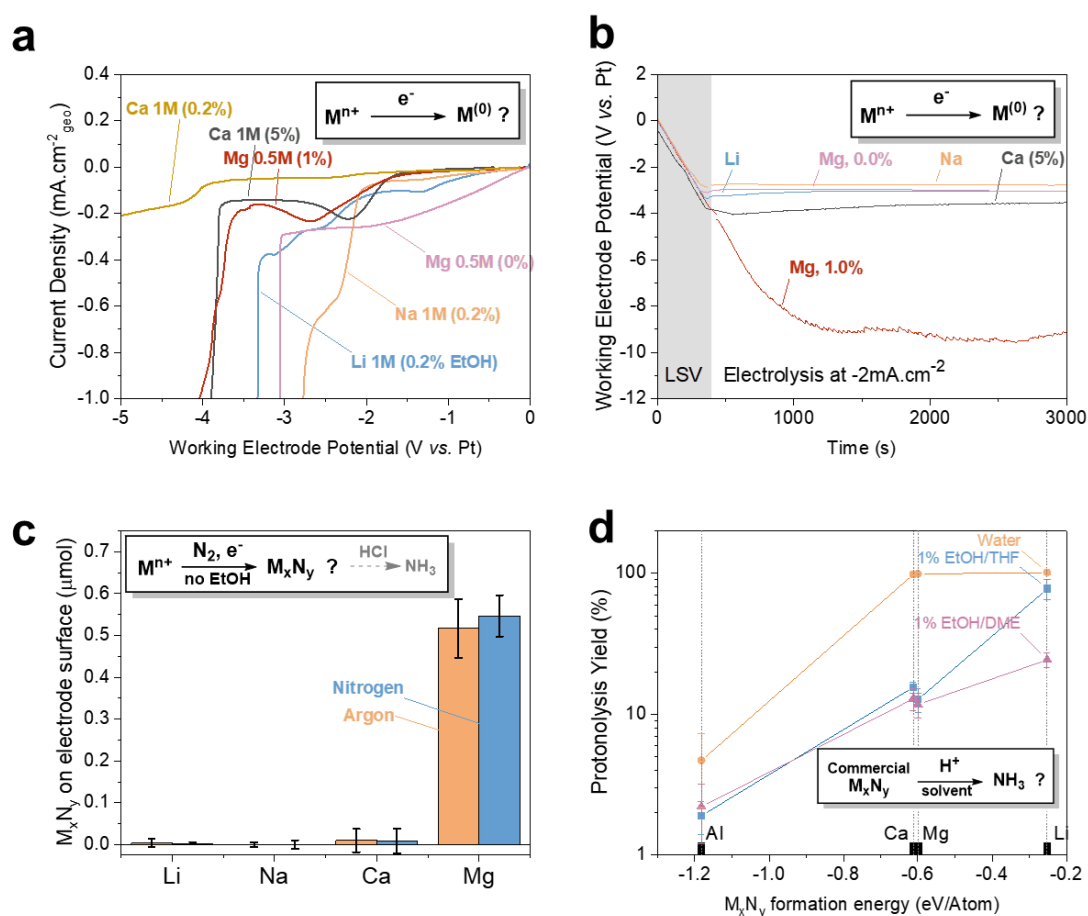


Figure 59. Model experiments for the identification of obstacles to nitrogen reduction on Ca and Mg. (a) Linear sweep voltammograms (LSV) on $1cm^2$ Mo foil showing metal plating for each element in selected electrolytes ($10 mV cm^{-1}$ sweep from open circuit to $-5 V$ vs. Pt or until $-1 mA cm^{-2}$ current density is reached, iR corrected) ; labelled by salt concentration and EtOH content (% v/v) in brackets. Voltammograms for Ca electrolytes show electrode passivation when too little EtOH is present (0.2 % v/v). (b) Recorded potentials for the same electrolytic systems during LSV and following constant current electrolysis, showing electrode passivation in Mg electrolytes containing EtOH. (c) M_xN_y quantified from electrode deposits following the electrolysis of electrolytes (0.5 M salt, 0 % EtOH) saturated with Ar or $^{14}N_2$. Nitrides were quantified by hydrolysis of the electrode in 4 M HCl and colorimetric quantification of as produced ammonia. (d) Yield of protonolysis of commercial nitrides (Li_3N , Ca_3N_2 , Mg_3N_2 , AlN) left in different protic suspensions, scaling with nitride formation energy.

5.2.2.1. Plating Metals

All tested electrolytes underwent a linear voltage sweep (LSV, Figure 59a) followed by constant current electrolysis (Figure 59b). During the LSV, sharp increase in current after a threshold potential suggests successful metal plating and this in at least one electrolyte compositions for each element, which was expected.^{236,240,242} The overpotential sometimes observed during metal plating, particularly in Mg electrolytes, could be attributed to the use of a Mo current collector, which could be suboptimal for metal nucleation and plating.²⁴⁸ Although a more suitable substrate could enhance metal plating, this was beyond the scope of our study and did not hinder the plating process overall. However, plating from Ca or Mg electrolytes often results in the formation of a passivating layer that impedes the conduction of Mg/Ca ions, thereby preventing continuous electrodeposition.^{236,242,243,249,250} This passivation is evidenced by a significant increase in cell voltage in Ca and Mg systems over the course of electrolysis (Figure 59a,b). For Ca, passivation occurs when low concentrations of EtOH are employed (up to 0.2 % v/v) up to a point where continuous plating is impossible. Higher EtOH concentrations prevent this passivation, though it remains unclear whether it is because EtOH disrupts the passivating layer like in the Li system⁸³ or because hydrogen evolution takes over. Improved performance might be achieved with Boron based anion electrolytes such as $\text{Ca}(\text{BF}_4)_2$ or $\text{Ca}(\text{BH}_4)_2$, which typically exhibit less resistive interfaces/interphases.^{243,244} In contrast, Mg can only plate in the absence of EtOH. Mg is highly sensitive to oxygenated protic species which form oxides upon contact with Mg metal, inhibiting Mg-ion conduction.^{236,249,251} This could be a reason why we could not plate Mg in the presence of EtOH. In the scope of this study, the incompatibility of Ca and Mg with EtOH likely poses a challenge for subsequent NH_3 generation.

5.2.2.2. Splitting Nitrogen on Plated Metals

The formation of cleaved nitrides from N_2 is energetically favourable on Li, Ca, and Mg. Extensive literature documents the synthesis of nitrides under specific conditions,^{252–256} but does it happen at all in our system? We conducted identical electrolysis experiments in an aprotic medium so that any plated metal capable of reacting with N_2 would do it in the absence of competition with protons reduction and yield a metal nitride. Post-mortem hydrolysis of the electrode deposits and subsequent ammonia quantification indicate that nitride formation occurs exclusively on a Mg surface (Figure

59c). This finding is corroborated by time-of-flight–secondary ion mass spectrometry (ToF-SIMS) analysis of the electrode *post mortem* (Figure 60a,b,c, analysis kindly done by Dr Olivia Westhead), which reveals Mg_xN_y fragments ($x = 1,2,3$ and $y = 1,2$). However, equivalent amounts of nitride are generated in the absence of N_2 , and similar Mg_xN_y fragments are observed by ToF-SIMS, suggesting they originate from the breakdown of NTf_2^- ions (sole N-containing species other than N_2 in this system). $^{15}\text{N}_2$ isotope-labelled experiments confirm the adventitious nature of the nitride reminding us of the prevalence of false positives in nitrogen fixation studies.^{49,50,257}

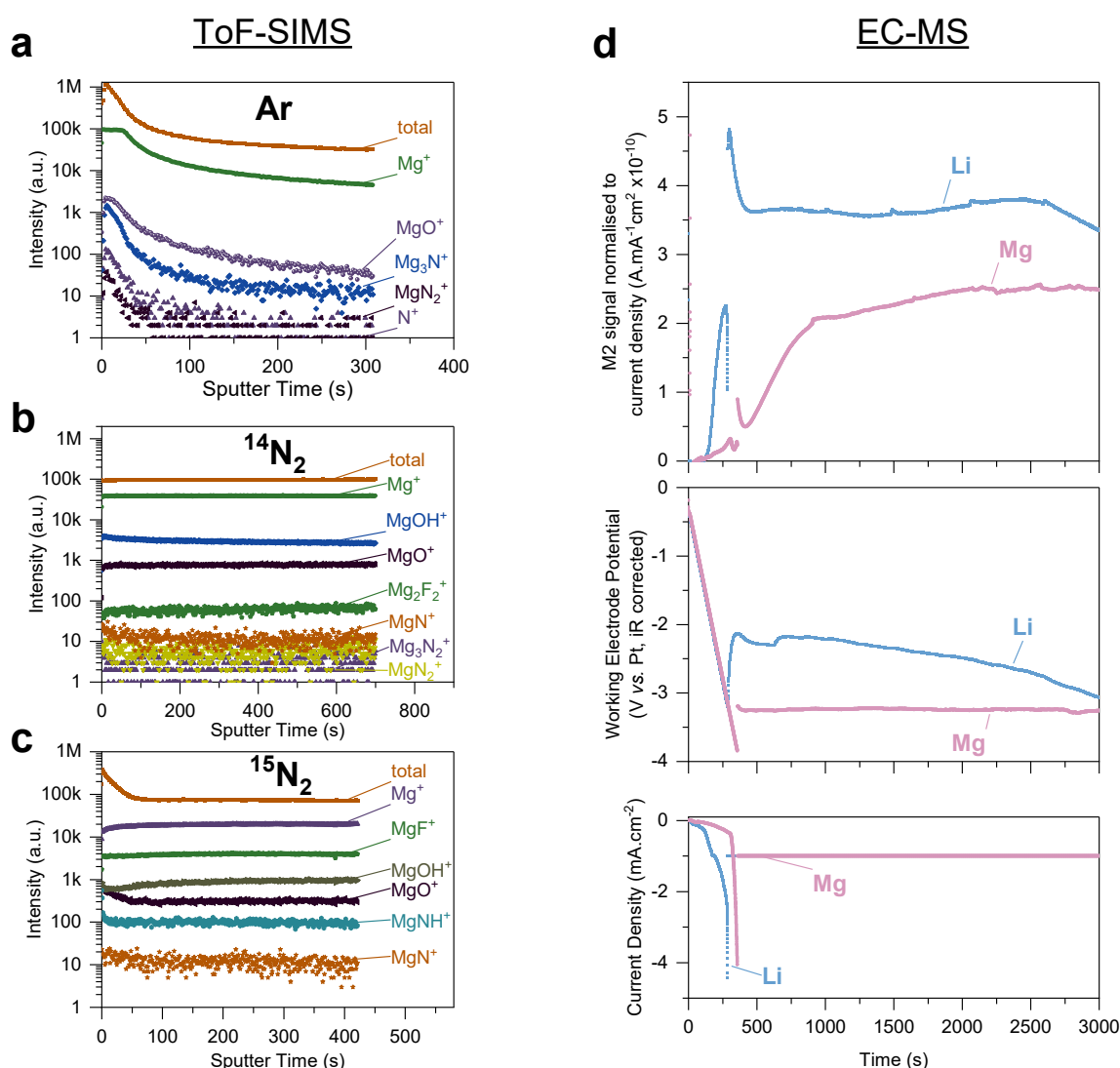


Figure 60. Mg electrode behaviour characterisation using ToF-SIMS (time-of-flight–secondary ion mass spectrometry) and EC-MS (electrochemistry–mass spectrometry). (a–c) ToF-SIMS positive ion sputtering (method in section 2.10) of Mg electrodes after electrolysis in (a) Ar, (b) $^{14}\text{N}_2$, and (c) $^{15}\text{N}_2$, detecting $\text{Mg}_x^{14}\text{N}_y$ fragments in all cases. Measurements performed by Dr Olivia Westhead. (d) Detection of generated H_2 by operando mass spectrometry (EC-MS) during electrolysis of a LiNTf_2 or

Mg(NTf₂)₂ 0.5 M in DME (method in section 2.11), showing a larger signal for $m/z = 2$ during linear sweep voltammetry and initial stages of constant current electrolysis (top plot), but also a largely negative potential for the Mg medium electrolysis (central plot). Measurements performed by Artem Khobnya. Adapted from my work,¹⁴⁷ with permission from © 2023 The Authors. Published by American Chemical Society.

To understand the inability of Mg to reduce N₂ here, we performed the same electrolysis in an *operando* electrochemistry–mass spectrometry setup, which allows sub second detection of volatile species.^{142,144} We compared gas evolution from an electrolyte composed of Mg(NTf₂)₂ or LiNTf₂ 0.5 M in DME. The $m/z = 2$ (M₂) signal attributed to H₂, was plotted against the electrolysis time, emphasising the raw and semiquantitative nature of the data. This signal is less intense in the Mg system compared to Li (Figure 60d), being 6–7 times lower initially ($t = 400\text{--}500$ s). This suggests that the Mg surface is less reactive to both N₂ and hydrogen sources. This difference diminishes over time, likely due to the lower volume and shorter interelectrode distance in this setup compared to the standard electrochemical cell used for electrolyte screening. As electrolysis progresses, H⁺ generated at the counter electrode may accumulate and alter the electrolyte composition,^{108,144} making the initial conditions more representative of the processes in the original electrochemical cell. Our ToF-SIMS analysis of the Mg electrode (Figure 60) shows traces of Mg_xF_y and Mg_xO_y species, which are known to be formed by NTf₂[−] anion and/or water reduction and passivate Mg metal in batteries.^{236,249} The extreme potentials experienced by the working electrode during electrolysis (>1 V over the Mg reduction potential) support this idea, similar to the Li system under unoptimised conditions.⁸⁰ Presumably, this passivation makes electrode more inert than Li, potentially hindering N₂ activation.

5.2.2.3. Converting Metal Nitrides to Ammonia

The conversion of Li, Ca and Mg nitrides to ammonia has previously been reported under specific conditions.^{256,258–260} To determine if these conditions limit ammonia synthesis in our system, we conducted protonolysis of commercial nitrides in various protic media (Figure 59d). The yield of protonolysis correlates with the formation energy of the nitrides and their Gibbs free energies of hydrolysis, as calculated by Gao *et al.*²⁵⁸ This indicates that nitrides that are easier to form will be more challenging to convert to ammonia, making lithium the easiest metal to deal with in that perspective (nitride formation energy closest to 0 eV/atom). Repeating this experiment in water illustrates that point: the proton activity significantly increases so that Ca and Mg nitrides fully hydrolyse, although this was still insufficient to completely convert AlN—the most stable nitride—to NH₃. This was also

verified by Peng *et al.* on a broader range of metal nitrides, where the yield of hydrolysis after being suspended in 0.1M $\text{H}_2\text{SO}_{4,\text{aq}}$ for 24 hours scales relatively well with metal nitride formation energy (Figure 78).²⁶¹ However, we recognise that the transport of reactants through the solid electrolyte interphase (SEI) likely introduces additional complexity to this analysis.^{70,83}

5.2.2.4. *Doing it All at Once in a Selective Fashion*

The electrolyte screening presented in Figure 58 suggests that no metal beside Li can achieve selective N_2 reduction to ammonia through the pathway proposed in Scheme 2. While Mg and Ca can theoretically form stable nitrides (Figure 57a) that decompose readily to ammonia (Figure 59d), only Li was able to generate ammonia in the tested conditions. The consensus within the research community is that control over the structure and composition of the solid electrolyte interphase (SEI) is as crucial for metal plating and stripping as it is for selective ammonia synthesis, and that is largely dictated by the choice of electrolyte composition.^{71,73,80,82,83,90} Despite significant advancements in battery chemistries beyond Li, substituting Li is not straightforward.^{235,239} The Li battery SEI is distinguished by its stability, unlike the more soluble Na SEI,²⁶² and its ability to conduct active ions through inorganics such as LiF or Li_2O , unlike Mg and Ca which do not conduct through metal oxides or metal fluorides for instance.^{236,263} In batteries, the focus is on maximising ion transport through the SEI while preventing electrons from reaching the electrolyte.⁷³ However, the requirements may differ for ammonia synthesis. The electron-insulating role of the SEI remains essential for selective ammonia synthesis, but it should also moderate the transport of Li^+ and H^+ while maximising the diffusion of N_2 and NH_3 .³⁹ Therefore, the ideal interphase composition for ammonia synthesis is likely different from that required for batteries, making the translation of Li and beyond-Li chemistries non-trivial. Then, have we just not found the right electrolyte for Ca and Mg to generate the interphase that will enable ammonia synthesis?

5.3. It is Not Just About Electrode Energetics

5.3.1. When You Find the Right Electrolyte

5.3.1.1. *N_2 Fixation Mediated by Calcium and Magnesium*

Chemistries beyond Li (*e.g.* Ca and Mg) failed at reducing N_2 selectively for various reasons (section 5.2.2), suggesting that despite favourable electrode energetics, such metals could not activate N_2

because of suboptimal interfacial reactivity. As the above study reached to an end, Fu *et al.* disclosed the formulation of a calcium electrolyte that could indeed plate metallic calcium and reduce N_2 to ammonia (Figure 61a).⁵⁴ In fact, this study screened multiple candidate calcium salts. Interestingly, when using $Ca(BF_4)_2$ and $Ca(ClO_4)_2$ as electrolyte salts, no significant calcium plating was observed at these low concentrations of ethanol, consistent with our observations when using a $Ca(NTf_2)_2$ salt (Figure 59a). However, they circumvented this issue using two separate strategies. One is through the use of a $Ca(BH_4)_2$ salt, where the reactive borohydride anion is expected to act as a scavenger for electrolyte species that may yield passivating SEI components (e.g. CaO , $Ca(OH)_2$, $CaCO_3$).²³⁶ Instead, plated Ca metal reacts with the BH_4^- anions in the electrolyte to produce a protecting layer of CaH_2 that conducts Ca ions and allows reversible Ca plating at room temperature.²⁴⁴ However, borohydride anions are incompatible with protic species, reacting stoichiometrically to yield hydrogen gas (Figure 61c insert equation). Such electrolytes are therefore incapable of achieving continuous ammonia synthesis, and nitrogen reduction in these conditions produces a calcium nitride, which is then hydrolysed *ex situ* to yield ammonia (Figure 61b). A second, more fruitful, strategy used an electrolyte formulated with a home-made calcium tetrakis(hexafluoroisopropoxy)borate salt (Figure 61c insert), 0.2 M $Ca[B(hfip)_4]_2$ dissolved in THF with 0.25 % v/v ethanol. This salt has been reported to be more conductive and, upon contact with Ca metal, capable of producing an SEI more conductive to Ca ions than ones derived from $Ca(BF_4)_2$ or $Ca(NTf_2)_2$ electrolytes, with lower amounts of insulating CaF_2 deposits produced.^{264,265} In these conditions, calcium plating was possible, this time in the presence of low amounts of ethanol.

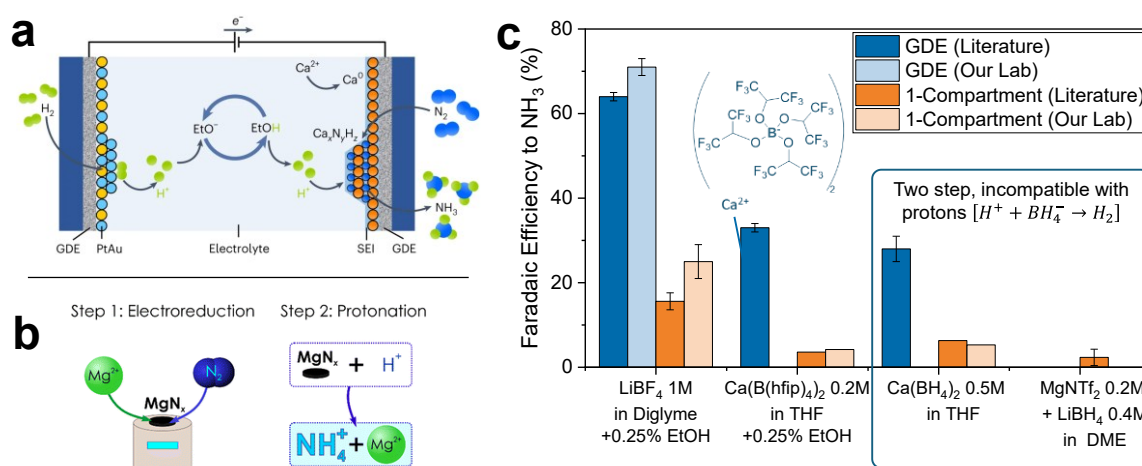


Figure 61. Ca- and Mg-mediated nitrogen fixation. (a) Electrochemical cell schematic for continuous Ca-mediated N_2 reduction to NH_3 . – Reproduced with permission from Fu *et al.*⁵⁴ © 2023, The Author(s),

under exclusive licence to Springer Nature Limited. **(b)** Schematic for the stepwise reduction of N_2 , (i) plating Mg or Ca in a proton-incompatible electrolyte and converting N_2 to a nitride (Mg_3N_2 , Ca_3N_2), (ii) isolating the electrode deposit and hydrolysing it to yield ammonia. Reproduced with permission from Krebsz *et al.*⁵⁶ © The Royal Society of Chemistry 2024. **(c)** Selectivity of state of the art metal mediated ammonia synthesis methods using Li, Ca or Mg, using a gas diffusion electrode (blue) or a single compartment cell (orange), comparing own lab results and original reports.^{54,56} GDE cell measurements for Li electrolytes courtesy of Craig Burdis.

Following the validation of calcium, Krebsz *et al.* suggested N_2 electrochemical fixation on magnesium in an analogous two step strategy (Figure 61b), where a $LiBH_4$ additive was added to the electrolyte we studied in the previous section ($Mg(NTf_2)_2$ 0.2 M in 1,2-dimethoxyethane (DME)).⁵⁶ Alike the Ca electrolyte used by Fu *et al.*, the as introduced BH_4^- anions act as scavengers for problematic electrolyte species (*e.g.* water, oxygen),²⁶⁶ or directly consuming passivating SEI species,²⁶⁷ to yield a Mg^0 -electrolyte interphase with less passivating species such as borohydrides of different sorts (B_xH_y). However, the presence of BH_4^- anions does not explain the improvement in reversibility of Mg plating since an electrolyte containing only $Mg(BH_4)_2$ did not result in significant plating/stripping currents. Rather, the role of lithium seems to be crucial for Mg plating in the proposed electrolyte. While its presence in the electrolyte and the operation at electrochemical potentials more negative than the equilibrium potential for Li^+/Li does throw some shade to the origin of the fixated nitrogen (Li mediated?), earlier work from the same group indicate that the role of Li^+ ions aid is solely to solvate the byproducts of the BH_4^- mediated reduction of passivating SEI species, providing a clean Mg^0 surface for further Mg plating.²⁶⁷ In these N_2 reduction experiments however, enough charge is passed to –in theory– reduce *all* Mg ions in solution. In an electrolyte completely depleted from Mg ions, Li ion reduction is likely to happen. XPS analysis of Mg-plated electrode deposits suggest that Li^+ is not being reduced to Li^0 alongside plated Mg, with no observable trace of Li on the electrode deposits.⁵⁶ However, the same XPS characterisation also suggests the absence of metallic Mg (only Mg^{2+}), attributing this observation to flaws in the sample handling process post electrochemistry. The same issue could have one miss the presence of metallic Li. In addition, despite the very clear correlation in $^{15}N/^{14}N$ isotopic ration between fed N_2 and produced NH_3 through this means, faradaic efficiency to fixated nitrogen is highly variable, ranging from <0.5 to 7 %. The amount of $^{15}NH_3$ observed could very well come from more labile N-containing impurities in the gas feed for example (section 1.3.2.1). While this work looks promising, more investigations are necessary to understand the underlying chemistry behind this process. Other reports suggest that both Ca and Mg can mediate N_2 reduction to ammonia

through the formation of metal nitrides,⁵⁵ but they also lack rigorous quantitative isotope labelled experimental proofs with regards of the origin of the as fixated nitrogen.

All in all, these works provide experimental confirmations of the hypotheses laid above with regards to Mg and Ca.^{54,56} They also offer alternatives in material sourcing sustainability considering the issues associated with the mining of lithium (Figure 56c). However, despite the lower standard reduction potential of Ca and Mg (especially for Mg, +0.684 V vs Li⁺/Li, Figure 56b), both systems experience voltage losses due to either charge transfer resistance (divalent cation slow desolvation kinetics), SEI resistance or electrolyte ohmic drop, eventually making them operate at potentials more negative than lithium-mediated ammonia synthesis does (Figure 62). Resistance to charge transfer could be decreased by selecting current collectors which favour Ca or Mg nucleation and growth,^{56,237} but most sources of loss may be alleviated through the development of electrolytes that ease cation desolvation and yield cation conducting SEIs, even in the presence of a source of protons.

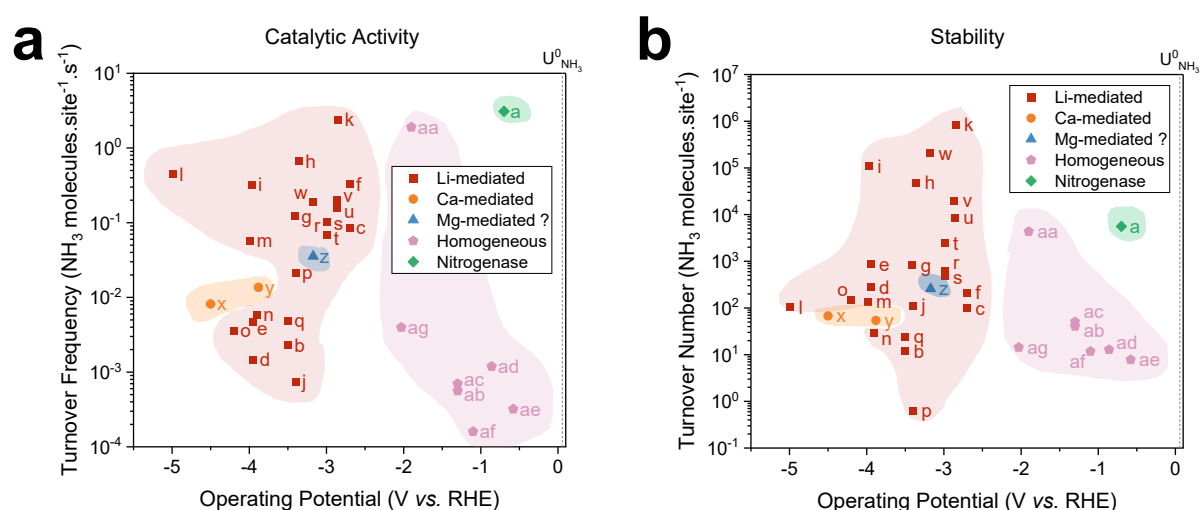


Figure 62. Evolution of performance in electrochemical ammonia synthesis. Comparing Ca-mediated, Li-mediated (and potentially Mg-mediated) ammonia synthesis against homogeneous electrocatalysts and nitrogenase on the basis of (a) catalytic activity (turnover frequency, TOF) and (b) stability (turnover number, TON), against operating potential. Data reproduced with permission from Westhead et al.³⁶ and references therein: a²¹⁷, b⁴⁹, c⁴⁸, d,e³⁹, f²¹⁸, g¹¹³, h,i⁶⁹ j⁷⁰, k⁸⁴, l,m⁸², n,o,q⁸⁰ p⁸¹, r,s,t¹⁰⁰, u,v,w⁹⁹, x,y⁵⁴, z⁵⁶, aa⁴¹. ab,ac²¹⁹, ad²²⁰, ae²²¹, af²²², ag²²³, © Springer Nature Limited 2023. The limitations of the hypotheses made in the definition of potentials against RHE discussed in appendices.

5.3.1.2. Toward Continuous Mg-Mediated N_2 Reduction

Following these works, we looked further into the prospects for continuous magnesium mediated nitrogen reduction to ammonia, by aiming at decreasing anion decomposition to insulating SEI species and accommodating for the presence of ethanol, which has inhibited Mg plating in formulations studied in this work (Figure 59)¹⁴⁷ and is incompatible with hydride-based electrolytes proposed by other groups.⁵⁶ Magnesium ions in $Mg(NTf_2)_2$ based electrolytes like the one studied here ($Mg(NTf_2)_2$ in DME) exist in relatively strong ion pairing with NTf_2^- ions, resulting in anions being reduced alongside Mg, to yield Mg^{2+} -insulating species in the SEI (MgF_2 , MgO , MgS , etc) and significant overpotentials to Mg plating, when it is possible at all (Figure 59).^{236,237} Li *et al.* circumvented this issue by displacing NTf_2^- ions from the solvation sheath of Mg^{2+} with a triethylphosphate additive.²⁶⁸ Triethylphosphate is suggested to weaken the $Mg^{2+} - NTf_2^-$ ion pairing, easing the desolvation of Mg^{2+} , in turn improving Mg plating kinetics and lowering the amount of NTf_2^- derived SEI species (MgO , $Mg(OH)_2$, MgS , MgF_2) which hinder Mg diffusion through the SEI (Figure 63a). This strategy resulted in >1 V decrease in overpotential for Mg plating and stripping, and largely improved coulombic efficiency.²⁶⁸ With such information in mind and the expectation that the triethylphosphate additive may displace the problematic ethanol in the same way, we formulated an electrolyte made of 0.4 M $Mg(NTf_2)_2$ + 0.4 M EtO_3PO in DME, with different amounts of EtOH, and subjected it to our usual nitrogen reduction protocol (linear potential sweep down to a potential where Mg plates, followed with constant current electrolysis passing 10 C of charge at -2 mA.cm^{-2}) (Figure 63).

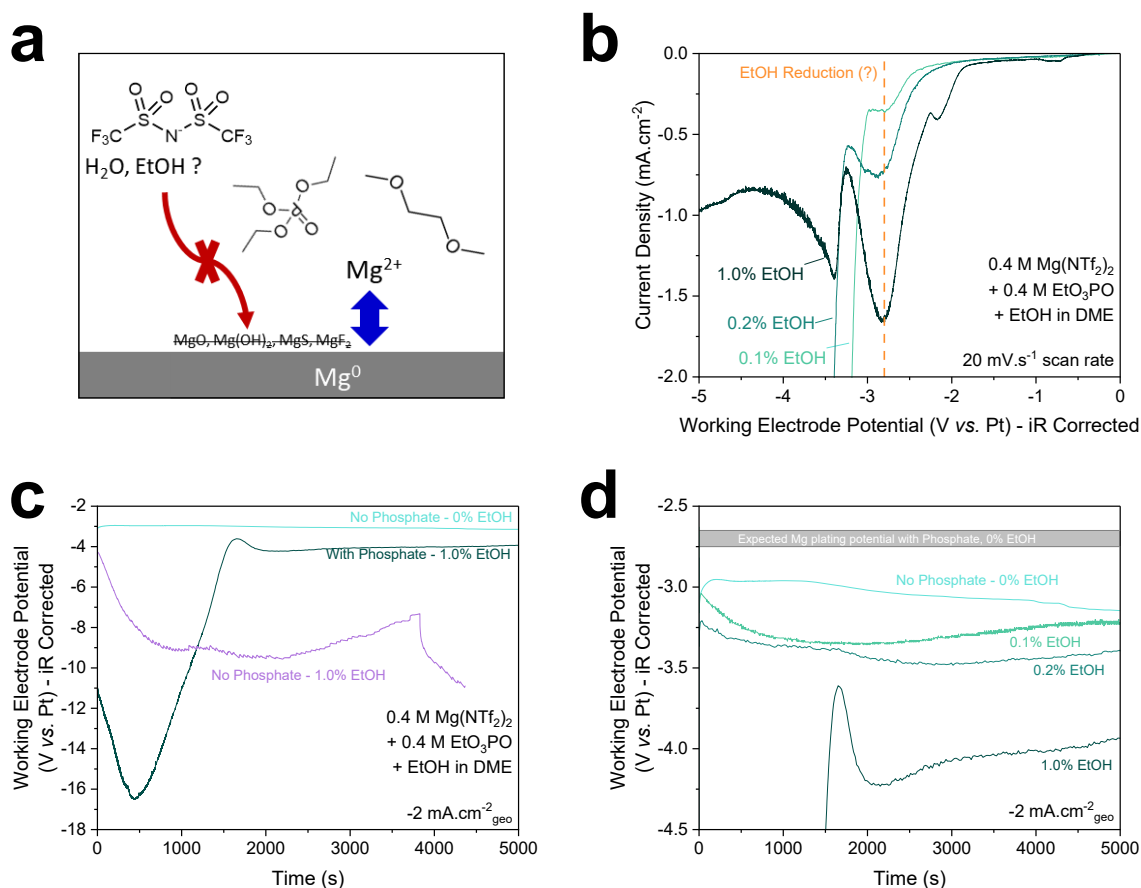
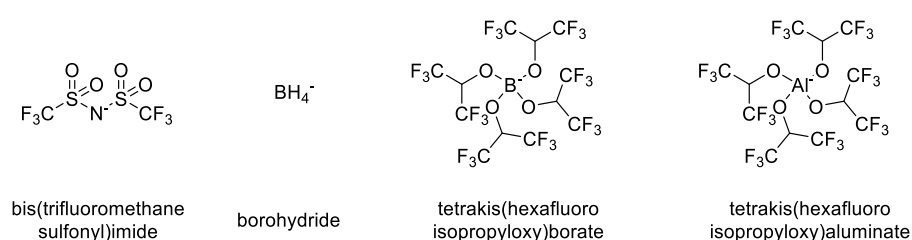


Figure 63. Incorporation of triethylphosphate in MgNTf_2 based electrolytes to accommodate for Mg plating in the presence of ethanol. **(a)** Schematic description of the role of triethylphosphate, reported to displace anions from the Mg-ion solvation sheath and preventing the formation of insulating Mg SEI components. Suggesting the same mechanism may help displace EtOH from Mg-ion solvation. **(b,c,d)** Electrochemical testing of $0.4\text{ M MgNTf}_2 + 0.4\text{ M}$ triethylphosphate in 1,2-dimethoxyethane electrolytes with different amounts of EtOH added. **(b)** Linear sweep voltammograms ($20\text{ mV}\cdot\text{s}^{-1}$ scan rate) followed with **(c)** constant current electrolysis passing 10 C charge at $-2\text{ mA}\cdot\text{cm}^{-2}$ (1 cm^2 Mo foil working electrode, $1\text{ cm}^2_{\text{geo}}$ Pt mesh counter electrode, Pt wire pseudo reference electrode, 10 ml electrolyte saturated with N_2 , stirred). **(d)** Region of more positive potentials zoomed in from (c).

Interestingly, what seems to be ethanol reduction (hydrogen evolution) still occurs in electrolytes containing triethylphosphate (Figure 63b), where a peak in current density at -2.8 V vs. Pt , previously attributed to ethanol reduction,⁴⁷ increases in intensity with an increase in ethanol concentration. The increase in EtOH concentration is also correlated with an increased overpotential to Mg plating, up to a point at which the electrode seems to passivate (1.0 % v/v EtOH) as an initial Mg plating current is

observed and quickly decays when the electrode potential is further decreased (Figure 63b). After this potential sweep, constant current electrolysis shows that Mg plating can accommodate for decent amounts of EtOH (0.1 and 0.2 % v/v) without a significant overpotential (Figure 63c,d). It is even true in the presence of 1.0 % v/v EtOH, which completely prevents Mg plating in a phosphate-free electrolyte. After an induction period where electrode potential decreases to extremely negative values, possibly due to passivation by insulating SEI species, the electrode recovers and Mg plating resumes. The reason for such transient behaviour is not explained thus far and may need to be repeated to confirm the observation, but it does leave scope for the introduction of ethanol in Mg-based electrolytes.

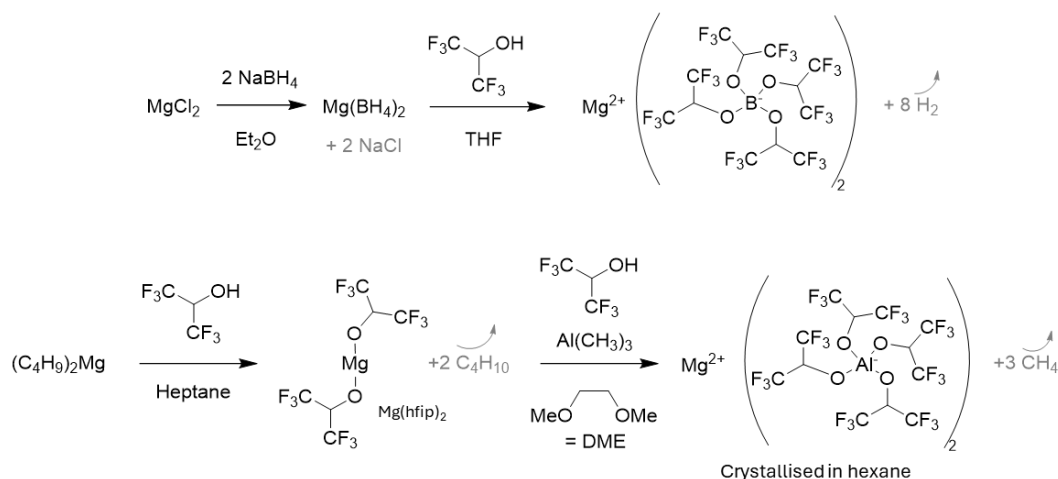
Other paths were taken to weaken ion pairing between Mg^{2+} and its anion (e.g. NTf_2^-), using strategies analogous to ones employed for calcium metal batteries. Electrolytes based on fluoroalkoxyborates have gained attention (e.g. magnesium tetrakis(hexafluoroisopropoxy)borate, $\text{Mg}[\text{B}(\text{hfp})_4]_2$, structure in Scheme 3) for their high performance with regards to oxidative stability, electrolyte ionic conductivity and most importantly for a record of high coulombic efficiency (>98 %) for Mg plating/stripping.^{269–272} Switching the Mg anion to a larger one with a more delocalised negative charge results in weaker ion pairing, to a point where Mg^{2+} ions are fully solvated by solvent molecules. This in turn limits the amount of ionic insulating MgF_2 produced from anion decomposition on the Mg metal surface,²⁶⁹ and eases Mg-ion desolvation (depending on solvent used),²⁷² overall facilitating Mg plating and stripping. Surprisingly, even better battery performance has been observed when the B centre is switched with an aluminium one, creating a tetrakis(hexafluoroisopropoxy)aluminate salt ($\text{Mg}[\text{Al}(\text{hfp})_4]_2$, structure in Scheme 3).^{273,274}



Scheme 3. Chemical structures of typical Mg salt anions

Under ideal conditions (pure electrolyte, minimised traces of water), performance is mostly better than the boron equivalent in terms of oxidative stability and Mg intercalation in battery cathodes.^{121,273,274} More interestingly to us, $\text{Mg}[\text{Al}(\text{hfp})_4]_2$ displays superior ionic conductivity and plates/strips at lower overpotentials (< 60 mV vs. Mg^{2+}/Mg) compared to $\text{Mg}[\text{B}(\text{hfp})_4]_2$ electrolytes,

and this with higher coulombic efficiency ($\sim 99.5\%$).^{121,274} What is especially interesting in the case of ammonia synthesis is the strong tolerance of $\text{Mg}[\text{Al}(\text{hfp})_4]_2$ to the presence of water in the electrolyte.¹²¹ When a typical $\text{Mg}(\text{NTf}_2)_2$ based electrolyte is contaminated with trace water (~ 10 s of ppm), $\text{MgO}/\text{Mg}(\text{OH})_2$ forms in contact with Mg metal and inhibits reversible plating/stripping, increasing overpotentials by $>2\text{ V}$.²⁷⁵ In contrast, $\text{Mg}[\text{Al}(\text{hfp})_4]_2$ based electrolytes can withstand much higher water contents (up to 1000 ppm) without significant overpotentials to plating/stripping. The coulombic efficiency of the first plating/stripping cycles decreased drastically but remained high in further cycles (98 %). The exact reason for the salt's high tolerance to impurities such as water remains unexplained but is affected by the methods through which such salt is synthesised. Indeed, the best performing $\text{Mg}[\text{Al}(\text{hfp})_4]_2$ electrolyte formulation come from synthesis methods employing organometallic compounds (*e.g.* $\text{Al}(\text{CH}_3)_3$) capable of scavenging impurities such as water.¹²⁰ Would the same tolerance be observed with the presence of ethanol (typically ≥ 1000 ppm) in the electrolyte? We attempted to synthesise $\text{Mg}[\text{B}(\text{hfp})_4]_2$ and $\text{Mg}[\text{Al}(\text{hfp})_4]_2$ following literature precedents (section 2.2, Scheme 4).^{120,270,276}



Scheme 4. Methods employed for the preparation of $\text{Mg}[\text{B}(\text{hfp})_4]_2$ and $\text{Mg}[\text{Al}(\text{hfp})_4]_2$ salts, synthesised by Andrijana Marojević.^{120,121,270}

Failing at the task for a lack of expertise and equipment, we turned to collaborators currently working on such salts for magnesium batteries (Andrijana Marojević, Dr Tjaša Pavčnik, Dr Jan Bitenc), who kindly sent us freshly made salt, and tested the effect of ethanol contamination on Mg plating/stripping in such electrolytes. Assembled battery Swagelok 2-electrode cells ($\text{Pt}|\text{glass fibre}|\text{Mg}$) were cycled by alternating Mg plating and stripping steps at constant current ($1\text{ mA}\cdot\text{cm}^{-2}$) in electrolytes containing either $0.1\text{--}0.2\text{ M}$ $\text{Mg}[\text{B}(\text{hfp})_4]_2$ or $\text{Mg}[\text{Al}(\text{hfp})_4]_2$ in diglyme (best

commercially available solvent for this chemistry),^{121,274} with 0, 0.1 or 1.0 % v/v EtOH (Figure 64a,b, experimental details and results alongside Figure 79).

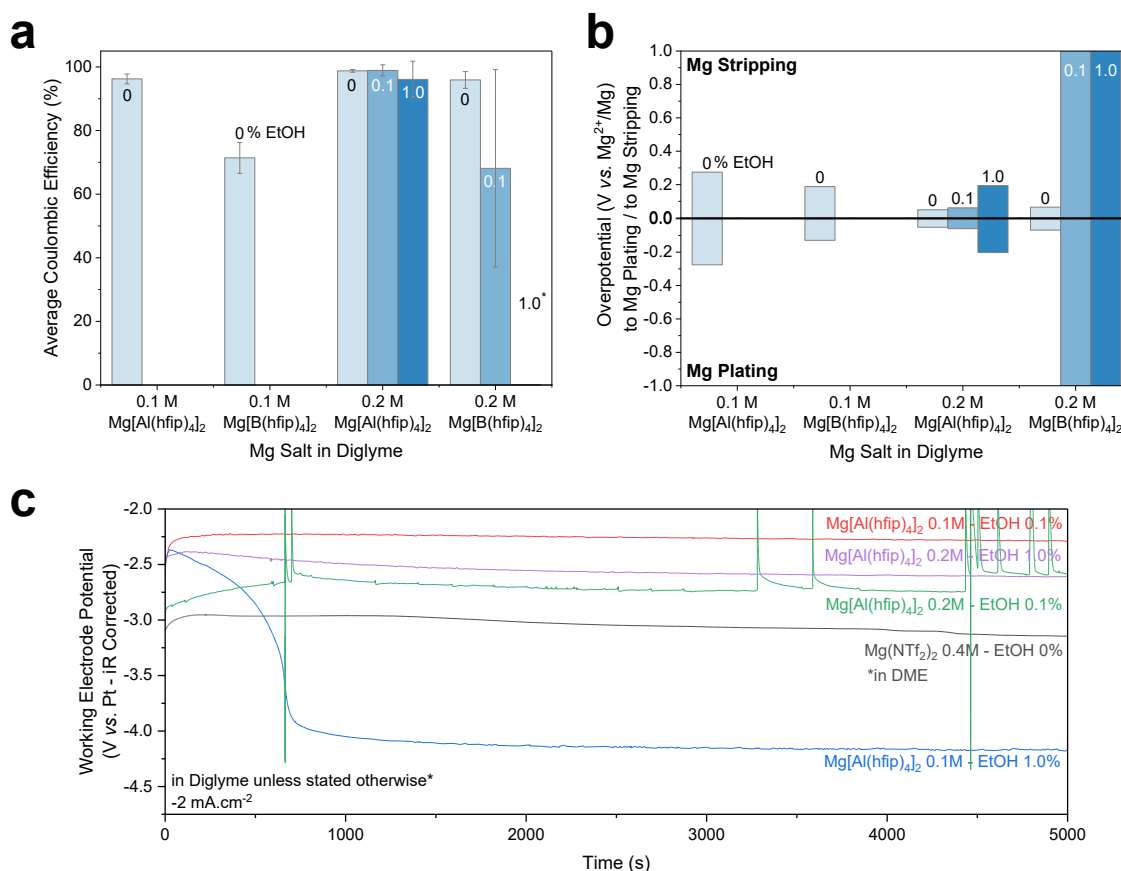


Figure 64. Investigation of Mg[Al(hfip)₄]₂ as an EtOH-tolerant electrolyte salt for ammonia synthesis. (a,b) Battery cycling performance comparison between electrolytes made of Mg[B(hfip)₄]₂ or Mg[Al(hfip)₄]₂ in diglyme with or without added ethanol, all performed by Pt|glass fibre|Mg Swagelok cells (100 µl electrolyte) were assembled and cycled in steps alternating between 1 hour of Mg plating on Pt at -1 mA.cm⁻², followed with Mg stripping at +1 mA.cm⁻² until a cut-off voltage of +2 V vs. Mg²⁺/Mg (no iR correction). The Mg salts were synthesised and tested in batteries by Andrijana Marojević. (a) Average coulombic efficiency of Mg plating/stripping steps in each electrolyte (*Mg[B(hfip)₄]₂ electrolytes with 1.0 % EtOH could only withstand one cycle of Mg plating/stripping). (b) Overpotentials (including both working and counter electrode reactions) measured for Mg plating and stripping in each electrolyte (> 1 V in Mg[B(hfip)₄]₂ electrolytes with added EtOH). (c) Constant current electrolysis of N₂ saturated Mg[Al(hfip)₄]₂ in diglyme electrolytes passing 10 C charge at -2 mA.cm⁻² (1 cm² Mo foil working electrode, 1 cm²_{geo} Pt mesh counter electrode, Pt wire pseudo reference electrode, 10 ml electrolyte, stirred, iR corrected) – *compared to a Mg(NTf₂)₂ in DME electrolyte.

Mg[B(hfip)₄]₂ based electrolytes severely suffered from the presence of EtOH. Only 0.1 % v/v added to 0.2 M Mg[B(hfip)₄]₂ in diglyme cuts the average Mg plating/stripping efficiency by 30 % with strong decrease observed in just a few cycles (Figure 79), and where both Mg plating and stripping operate at overpotentials >1 V vs. Mg²⁺/Mg. Increasing the amount of EtOH to 1.0 % v/v only made matters worse as assembled cells were only able to go through a single cycle of Mg plating/stripping before dying. In contrast, addition of 0.1 % and 1.0 % v/v EtOH to a 0.2 M Mg[Al(hfip)₄]₂ electrolyte resulted in only slight losses in plating/stripping coulombic efficiency (0 and 2 % loss, respectively) and little increase in plating/stripping overpotential (10 and 150 mV, respectively) compared to EtOH free conditions. Considering the increased robustness to EtOH of this latter electrolyte compared to electrolytes based on Mg(NTf₂)₂ or Mg[B(hfip)₄]₂, we subjected it to our usual nitrogen reduction protocol (linear potential sweep down to a potential where Mg plates, followed with constant current electrolysis passing 10 C of charge at -2 mA.cm⁻², see section 2.5.3, Figure 64c). 0.2 M Mg[Al(hfip)₄]₂ electrolytes operate at similar potentials no matter the amount of EtOH added, where part of the observed variations could be attributed to variations in the Pt *pseudo* reference electrode potential. Only when adding as much as 1.0 % EtOH to a 0.1 M electrolyte then some passivation is observed, where the working electrode potential drops down from -2.41 V to about -4.2 V vs. Pt, still operating, however.

Now that a couple Mg electrolytes can withstand the presence of decent amounts of ethanol (Mg[Al(hfip)₄]₂ and Mg(NTf₂)₂ + EtO₃PO), we investigated their ability to mediate ammonia synthesis from N₂. Quantification of ammonia was done on the electrolyte previously subjected to N₂ electrolysis experiments (see section 2.8), to determine whether any N₂ had been reduced. Mg_xN_yH_z species, Mg metal, MgH₂ and MgO/Mg(OH)₂ were also quantified by titration of electrode deposits obtained from such electrolysis experiments with deuterated methanol (MeOD, see section 2.9). Results are displayed in Figure 65.

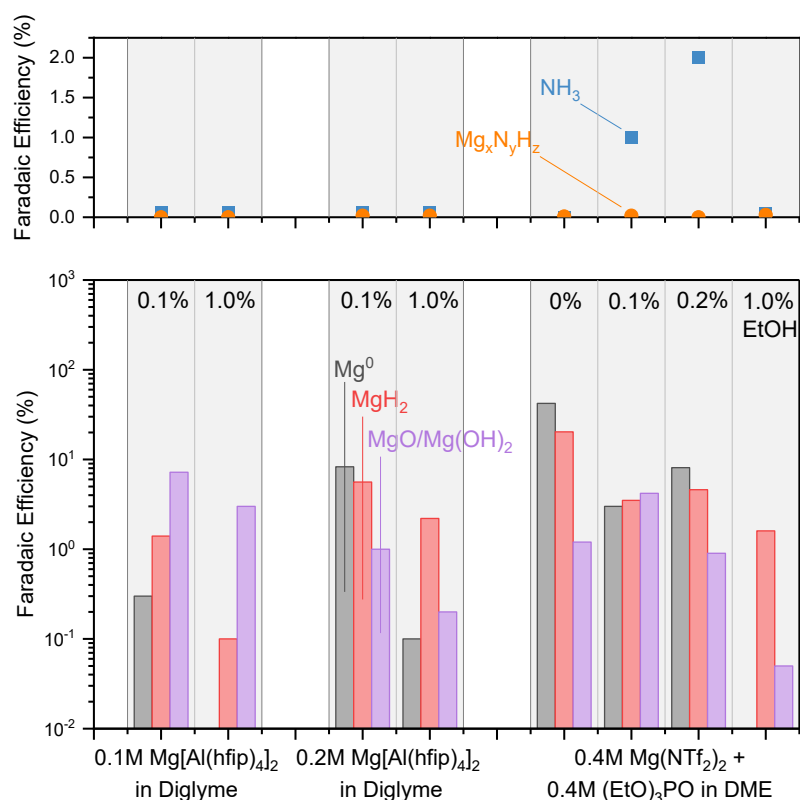


Figure 65. Investigation of the products formed in EtOH-tolerant Mg-based electrolytes tested for N_2 reduction. Faradaic efficiency to NH_3 from electrolysis of different N_2 saturated magnesium based electrolytes, and Faradaic efficiency to Mg/MgH_2 , $\text{Mg}_x\text{N}_y\text{H}_z$ and $\text{MgO}/\text{Mg(OH)}_2$ in electrode deposits, detected by titration of electrodes post electrolysis with MeOD.

$\text{Mg}_x\text{N}_y\text{H}_z$ seem to be present in all conditions, but in quantities close to background levels in the technique used and are therefore deemed insignificant. Ammonia is detected in the $\text{Mg}(\text{NTf}_2)_2$ + EtO_3PO based electrolytes with 0.1 and 0.2 % v/v EtOH. However, this ammonia most likely originates from the degradation of the NTf_2^- anion. Indeed, the quantities of ammonia generated are nearly identical to the amount of fixed nitrogen detected on electrodes following electrolysis of a phosphate-free and EtOH-free $\text{Mg}(\text{NTf}_2)_2$ in DME electrolyte previously tested for N_2 reduction (Figure 59c). Running electrolysis in Argon or $^{15}\text{N}_2$ saturated electrolytes would be required to confirm the adventitious nature of the produced. A step ammonia forward however is that now the detected fixed nitrogen is ammonia in the liquid phase rather than partially converted nitrogen in the electrode deposits. Interestingly, each one of the tested electrolytes yielded electrode deposits containing Mg, MgH_2 and $\text{MgO}/\text{Mg(OH)}_2$ in different amounts and different ratios, indicating a broad range of reactivities. It is also interesting to note that the magnitude and breadth of such species' quantities

match the ones observed in Li-mediated N_2 reduction systems (Figure 52). Surprisingly, $Mg[Al(hfip)_4]_2$ electrolytes that were deemed to reversibly deposit Mg metal with high current efficiencies (Figure 64a) end up with small quantities of metal deposits ($< 10\%$ Faradaic efficiency to Mg, Figure 65), implying that plated Mg reacts to yield other products during electrolysis.

These observations combined with the low overpotentials associated with Mg plating are indicative of an active Mg surface that is not passivated by insulating species and that can withstand the presence of proton carriers such as ethanol. So why is this system not able to convert N_2 to ammonia? We put forward a few possible reasons for it. With regards to the SEI formed, we only probed some of the chemical species present : a lot more could be missing, and it is irrespective of any morphological aspect that might be important.^{83,172,277} Second, $*N$ binding is more positive on Mg than it is on Li or Ca (Figure 57b). Higher N_2 partial pressure may be needed to favour N_2 activation, and testing in an electrochemical cell where N_2 diffusion is less of an impeding parameter (e.g. gas diffusion electrode, pressurised cell) is recommended. In fact, the reported N_2 activation on Mg has been performed at 15 bar N_2 pressure.⁵⁶ There are a couple potential issues specific to $Mg[Al(hfip)_4]_2$. The way $Mg[Al(hfip)_4]_2$ electrolytes are made (Scheme 4) results in the presence of proton scavengers in the electrolyte, such as $Al(CH_3)_3$ or $Mg(C_4H_9)_2$.¹²⁰ These scavengers have proven benefits for Mg plating in water contaminated electrolytes,¹²¹ but this advantage might turn out to be a drawback in the context of ammonia synthesis, where such reactive species may prevent ethanol from doing its part in carrying protons to the active surface, or even react to provide essential interphase components for selective N_2 activation.^{83,104} Finally, ^1H and ^{19}F NMR analysis of the as received $Mg[Al(hfip)_4]_2$ salt suggest that the as received salt quality was compromised, where peaks with chemical shifts attributable to free hexafluoroisopropanol are observed, suggesting partial hydrolysis of the aluminate anion before even being used in experiments. The presence of such a highly acidic proton carrier in the electrolyte may explain the concomitant null selectivity to ammonia and low amounts of Mg remaining on electrode deposits post electrolysis (Figure 65). Repeating these measurements with a clean electrolyte might have a different outcome. In conclusion, we identified and tested several Mg electrolyte formulations that proved successful at plating Mg without passivating in the presence of EtOH, producing a range of interphases with different reactivities. However, none were successful at reducing N_2 selectively, the reason remains unexplained although some were proposed.

5.3.2. Describing the Interface and Interphase from the Electrolyte Side

The investigations presented herein highlight the necessity of selecting the right electrolyte and making an SEI (or analogous structure) capable of regulating contact between key reactants and the active surface for ammonia synthesis. However, the specificities of the Li, Ca and Mg SEIs make it difficult to compare interfaces across the periodic table. The influence of metal ions' environment in the electrolyte, and in particular their (de)solvation,^{278–280} on the resulting SEI composition is well established. This principle also applies to Li-mediated ammonia synthesis.^{80,82} The behaviour of metal cations in their environment can be rationalised through Lewis acid/base interactions, where the metal cation acts as an acid binding to a base (*e.g.* solvent, anion). The Hard and Soft Acids and Bases (HSAB) principle classifies chemical species' acidity and basicity based on their atomic structure to describe their interactions and reactivity.²⁸¹ In metal-air batteries, solvent stability and effects on O₂ reduction have been rationalised using HSAB,^{282,283} and changes in lithium battery performance have been attributed to variations in metal cation acidity.²⁸⁴ In Li metal batteries, the incorporation of K⁺ ions altered the SEI composition due to their softer character.²⁸⁵ It seems reasonable to use the HSAB principle as a descriptor for interfaces and interphases. How can we scale this? Klopman quantified the acidity of acids through quantum mechanics calculation,²⁸⁶ providing a successful descriptor defined by the difference between the LUMO (Lowest Unoccupied Molecular Orbital) energy of the acid cation and its energy of desolvation from water (equation (39)).

$$(39) \quad \Delta E_{\text{acidity}} = E_{\text{LUMO}} - E_{\text{desolvation from H}_2\text{O}}$$

This formulation fits well in this context since metal plating and SEI formation are both regulated by the (re)activity of the metal cation (E_{LUMO}) and the desolvation of such metal ions from their environment ($E_{\text{desolvation from H}_2\text{O}}$). We therefore plotted elements on this scale against their metal nitride formation energy (Figure 66).

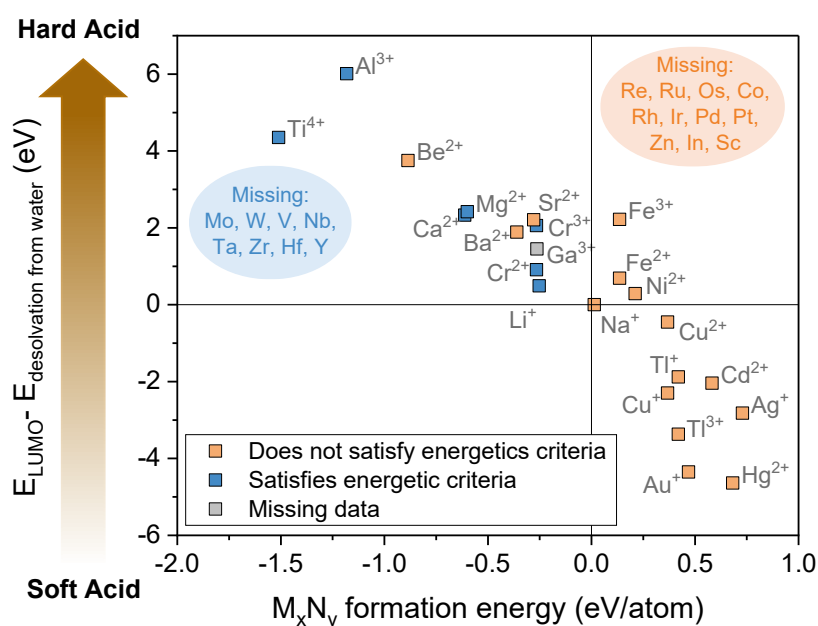


Figure 66. Using Hard and Soft Acids and Bases principle as a descriptor for the electrochemical interface and nitrogen fixation. Plotting Klopman's descriptor for acid hardness–softness²⁸⁶ against the formation energy of metal nitrides. An element satisfying energetic criteria (colour labelling) means concomitant negative *N binding energy and metal nitride formation energy, to a N-N cleaved phase. DFT calculations by Dr Alexander Bagger. Reproduced from my work,¹⁴⁷ © 2023 The Authors. Published by American Chemical Society.

The above correlation implies that the nitride formation energy is associated with the Hard and Soft Acids and Bases (HSAB) principle, in a way that we cannot confidently justify thus far. Interestingly, lithium exhibits the lowest acidity among elements satisfying the energetic criteria laid out in Figure 57, followed with Cr, and Ca or Mg which have now been proposed as mediators for ammonia synthesis beyond lithium.^{54–56} One must note that this analysis is not absolute, since the acidity scale illustrated in Figure 66 is based on ions solvated by water, a hard base. The hardness-softness of the environment in which ions evolve (e.g. solvent or salt anion used) will influence their acidity, making this scale dynamic.²⁸⁷ For instance, we have seen in section 4.2.1 that the electrochemical equilibrium potential of a metal with its ions (in this case $U_{\text{Li}^+/\text{Li}}$) will be dictated by the chemical environment of such ions.^{125,134} For example, switching the solvent from tetrahydrofuran (THF) to diglyme (a softer base) in a 1 M $\text{LiN}(\text{SO}_2\text{F})_2$ electrolyte results in a 90 mV shift towards a more negative Li equilibrium potential, attributable to changes in Li^+ acidity and interfacial reactivity.¹³⁴ Consequently, cations could shift substantially on this acidity scale when their environment is modified, potentially to a region

hypothesised to be more favourable for ammonia synthesis (*i.e.* closer to Li). Ca-mediated ammonia synthesis illustrates this point. Ca and Mg are both harder acids than Li. The introduction of a soft anion like B(hfp)₄⁻ or BH₄⁻ in the Ca²⁺ electrolyte may change its effective acidity on this scale, getting it closer to Li and making it successful at producing ammonia (as opposed to Ca(ClO₄)₂ or Ca(BF₄)₂).⁵⁴ Mg²⁺ is an even harder cation (smaller cation, more localised charge), making it more challenging to shift down on that scale. The introduction of LiBH₄, which is a combination of softer cation and anion, in a Mg(NTf₂)₂ based electrolyte is suggested to help achieve Mg-mediated N₂ fixation,⁵⁶ but we hope that further electrolyte engineering such as the one elaborated in this chapter (section 5.3.1.2) will succeed in achieving continuous Mg-mediated N₂ reduction at significant rates.

Other promising elements (*e.g.* Mo, W, Ta) are not depicted in Figure 66 due to their absence in the HSAB parameter dataset. Several research groups have employed Mo electrodes for the reduction of N₂ to NH₃,^{39,49,53,68,71,80,81,211} however, these reductions occur only at potentials sufficiently negative for Li deposition and produce equivalent amounts of ammonia as in an identical system using Cu as a current collector, indicating that Mo only serves the role of current collector.^{114,125} The apparent inactivity of Mo may be attributed to several factors. Firstly, the ability to form a nitride is necessary but not sufficient; an interphase that balances reagents at the active surface is also required.³⁹ Secondly, all studies to date have used Mo electrodes previously exposed to air, resulting in a native oxide layer with reactivity to N₂ distinct from metallic Mo.^{71,288}

In conclusion, we propose that Li, Ca and Mg are special in several ways: (i) they bind *N not too weakly nor too strongly; (ii) they favour N₂ dissociation to cleaved nitride phases which (iii) readily protonolyse to NH₃; (iv) they can form interphases that balances access of reagents and products, and protects the active surface from *H poisoning to yield ammonia selectively. Just like nitride formation and *N binding energies, we suggest this last feature to be generalisable across the periodic table using the HSAB principle, where Lewis acidity can guide the design of electrolytes forming optimal interfaces and interphases. Further investigations are encouraged to expand the prospects for N₂ reduction mediated by Ca, confirm the genuine origin of ammonia synthesis mediated by Mg and identify the appropriate interphase/interface that will selectively generate ammonia in a continuous fashion on these electrodes; but also explore new elements with significant potential for increased energy efficiency, such as Al, Mo, W, Cr or Ta for instance.

Chapter 6. Outlook

6.1. Thesis Summary and Conclusions

In less than 10 years, electrochemical nitrogen reduction to ammonia has leaped from a proof of concept to small-scale prototypes, producing gas phase ammonia at Faradaic efficiencies beyond expectation (60 to >99 %), operating steadily over weeks. However, the Li-mediated process that dominates the field suffers from a range of drawbacks that restrict its economic viability. We are just getting a glimpse at the interfacial processes guiding this challenging reaction and fundamental investigations are required to understand the unique interface of this non-aqueous system.

In Chapter 3, a true LiFePO_4 non-aqueous reference electrode was developed for this system. Unlike Pt *pseudo* references usually employed, this reference maintained a stable and reproducible potential during and across electrolysis experiments in different electrolytes, allowing the control and comparison of measured potentials. The LiFePO_4 reference electrode potential was unaffected by the saturation of electrolytes with Ar, N_2 and H_2 , while an analogous lithium titanate reference integrity was compromised in presence of H_2 . The LiFePO_4 reference quantified the origin of the overpotential caused by continuous operation at Li plating potential, suggesting that only altering that required reduction potential will succeed in improving energy efficiency significantly.¹²⁵ This reference electrode potential, being in equilibrium with Li-ions in solution, enabled the quantification of Li-ion activity changes *in situ*.

In Chapter 4, inspired by Li-metal battery research,¹³⁴ appropriate electrolyte engineering was demonstrated as a mean to alleviate the overpotential associated with Li plating through the modulation of the Li^+/Li equilibrium electrochemical potential ($U_{\text{Li}^+/\text{Li}}$), as well as the RHE potential (U_{RHE}), as observed by electrochemical measurements and Raman spectroscopy. Both parameters are a function of electrolyte solvation structure, and can be shifted by hundreds of mV. Such changes in Li-ion and proton activity impacted Faradaic efficiency of nitrogen reduction to ammonia, where a correlation was observed between the Faradaic efficiency to ammonia and its possible reaction intermediates (Li and $\text{Li}_x\text{N}_y\text{H}_z$), $U_{\text{Li}^+/\text{Li}}$, U_{RHE} and the mass transfer properties of N_2 in the electrolyte. This analysis does not refute the importance of SEI chemistry in describing selective ammonia production, it rather embeds it. Indeed, chemical titration of key SEI components ($\text{Li}_2\text{O}/\text{LiOH}$, LiF, LiH, Li-ions) in electrode deposits *post* electrolysis showed a peak-shaped relationship between

Faradaic efficiency to ammonia and $\text{Li}_2\text{O}/\text{LiOH}$ content, consistently with previous reports.^{70,80–82} An optimal kinetic passivation by $\text{Li}_2\text{O}/\text{LiOH}$ is proposed in this thesis as a mitigation to the reactivity of Li, in favour of NH_3 formation. Conversely, an increase in $U_{\text{Li}^+/\text{Li}}$ at roughly constant U_{RHE} resulted in the decrease of the $\text{Li}_2\text{O}/\text{LiOH}$ to Li metal ratio. Same went for a decrease in U_{RHE} at roughly constant $U_{\text{Li}^+/\text{Li}}$. Overall, closing the gap between $U_{\text{Li}^+/\text{Li}}$ and U_{RHE} resulted in optimally passivating interphases and high nitrogen reduction selectivity. In addition to this analysis, $U_{\text{Li}^+/\text{Li}}$ and U_{RHE} (and therefore the activity of Li-ions and protons, respectively) are hypothesised to account for a broader range of phenomena influencing ammonia synthesis, including but not limited to SEI chemical identity (Li and SEI morphology, SEI dynamics and the intrinsic reactivity of Li^+ , N_2 and H^+). Such descriptors may be more adequate to define suitable interfaces and identify new electrolytes for selective ammonia production. Finally, the above analysis pointed to the fact that the modulation of Li plating potential did not result in significant gains in voltage efficiency. In addition to changes in electrolyte conductivity, a correlation between $U_{\text{Li}^+/\text{Li}}$ and overpotential past Li plating was observed, likely caused by a mix of charge transfer resistance and SEI resistance, as evidenced by impedance measurements. This is likely caused by a systematically stronger ion pairing at higher $U_{\text{Li}^+/\text{Li}}$, and therefore slower desolvation of Li-ions from their solvation sheath. Electrolyte formulations were proposed to decorrelate these counteracting effects and increase the energy efficiency of Li-mediated ammonia synthesis. Failing that, bypassing the use of lithium may be the only way to significantly increase nitrogen reduction energy efficiency.

In Chapter 5, a theoretical framework was defined to identify new chemistries capable of splitting N_2 selectively, based on calculated descriptors such as $\ast\text{N}$ binding energy, metal nitride formation energy and hardness-softness of Lewis acids involved in such chemistries. This framework suggests that metals apparently analogous to Li (e.g. Na, K, Cs) may not activate N_2 for their weak $\ast\text{N}$ binding properties and the thermodynamically unfavourable formation of metal nitrides from N_2 . Several other elements including Ca, Mg, Al, Mo, Cr and W were identified as more likely candidates.¹⁴⁷ Our experimentations with Ca- and Mg-based electrolytes failed at reducing N_2 . Model experiments were performed in various electrolytes, including metal and metal nitride electroplating tests, nitride chemical dissolutions, *operando* electrochemistry mass spectrometry and *post-mortem* ToF-SIMS. All suggested that $\ast\text{N}$ binding and metal nitride formation energies were necessary but not sufficient criteria for the discovery of new electrochemical systems, but energetic descriptors were also required from the electrolyte-side. Indeed, with some electrolyte engineering, calcium-mediated N_2 reduction to ammonia was achieved in other laboratories.⁵⁴ Another report suggested that electrodeposited

magnesium could activate N_2 as well in the right electrolyte, albeit in a stepwise process.⁵⁶ In this work, experimental guidance is provided on how to possibly achieve continuous ammonia synthesis on magnesium, with a focus on accommodating for Mg plating in the presence of ethanol. The addition of triethylphosphate to the previously EtOH-incompatible MgNTf₂ based electrolytes allowed the inclusion of up to 1 % v/v EtOH while still plating Mg metal. Similarly, a magnesium tetrakis(hexafluoroisopropoxy)aluminate salt could equally accommodate for up to 1 % v/v EtOH without impeding Mg plating/stripping significantly, as opposed to a failing tetrakis(hexafluoroisopropoxy)borate salt, which was surprising considering the success of its calcium counterpart. Activating nitrogen in such kind of Mg electrolytes remains a challenge. We encourage further investigation of Mg electrolytes, as well as exploring electrochemical systems based on Al, Mo, Cr or W. Note that just like experienced with Ca and Mg in this thesis and other works, synthesising pure metallic salts that may be promising for metal mediated ammonia synthesis is a challenge in itself.^{54,120} Expertise in that regard will be crucial in discovering new chemistries capable of selectively reducing nitrogen.

With this in mind, we will end this discussion with the challenges awaiting electrochemical ammonia synthesis beyond the scope of this work (section 6.2), and debate its role in the broader context of nitrogen fertiliser utilisation and maintaining a sustainable nitrogen cycle (section 6.3).

6.2. Future Targets for Electrochemical Nitrogen Reduction

This work has discussed the extent to which non-aqueous nitrogen reduction to ammonia has evolved over the span of 10 years, where metal-mediated systems have drastically improved in selectivity, activity and stability (Figure 56),³⁶ but also scalability.^{289,290} However, the energy spent to sustain low reduction potentials, and maintain active metallic surfaces, forbids any competition with the highly integrated and energy efficient Haber-Bosch process.^{11,114} Nevertheless, such technologies have the potential to feed the market in places and times where Haber-Bosch derived ammonia is too expensive to produce or ship.

Several challenges lay ahead for the successful commercialisation of these low carbon technologies. The first one has to do with degradation of the system. In the case of the Li-mediated system, high current densities were achieved,¹¹³ but at the expense of undesired electrolyte solvent oxidation at the positive electrode taking over hydrogen oxidation, when the positive electrode reaches positive enough potentials to trigger it. The imbalance between the selectivity at the positive and negative

electrodes also drives progressive electrolyte acidification,¹⁰⁸ which in the long run may degrade performance of the electrochemical system, in the intrinsic reaction performance or product recovery rates. Achieving “full” selectivity and/or providing a buffer for acidity may solve this issue.⁶⁹

A second challenge comes with the sensitivity of the system to electrolyte modification and impurities. Indeed, it was shown that traces of water or oxygen (bound to contaminate large scale systems) can have drastic effects on the selectivity of the reaction.^{70,81} A small addition of each can improve performance, add a little more and performance is lost. In fact, this phenomenon is also observed in a range of experimental parameters, including alcohol acidity and concentration,^{53,102,104} or salt concentration. Flattening out all these volcano-shaped dependencies will increase robustness of the technology. It is possible that finding chemistries based on metals less reactive than Li, Ca or Mg will help in tuning this sensitivity down.

Thirdly, choice of feedstock and materials is also a key concern for applicability and sustainability (see illustrative discussion with the use of lithium page 207). In addition to the environmental impacts of the use of lithium, electrode current collectors are based off large slabs of metal, with high environmental impact. This could be alleviated by moving to carbon-based electrodes, just like in aqueous electrolytic systems. This may have other advantages, such as increased surface area and high current densities.²⁸⁹ Using organic electrolytes also comes with issues, such as flammability or potential product contamination. Devising solvent-free systems (*e.g.* membrane-electrode assemblies¹¹²) or using low vapour pressure solvents could attenuate this issue. In addition, the current technology relies on typically high concentrations of alkali metal salts, where best performing electrolytes are fluorinated.^{54,56,84,99} Fluorinated polymers and many fluorinated chemicals are expected to be banned from use in Europe due to their high potential for bioaccumulation and toxicity.^{291–293} Finding fluorine-free formulations has gained interest in battery research, and will need to be considered here too.^{90,294}

Finally, as mentioned in Chapter 5, energy efficiency has large room for improvement. Finding chemistries capable of activating nitrogen with a more positive intrinsic reduction potential than Li, Ca or Mg (*e.g.* Al, Mo, Cr, W, etc) will be key in alleviating the energy costs of ammonia synthesis as it is.^{11,147} State of the art devices rely on the oxidation of hydrogen at the counter electrode as a proton feed for ammonia synthesis. As such, hydrogen must either be shipped to the point of ammonia production (limiting the scope for decentralisation) or be made on site by upstream water electrolysis only to be oxidised back to protons in the nitrogen electrolyser, causing unnecessary energy losses at

each step. A better device would rely on nitrogen reduction directly coupled to water oxidation, which is so far unfeasible due to the sensitivity of nitrogen reduction to water. One needs to devise an electrolyser that accommodates for water at the positive electrode without compromising N_2 reduction, using proton conducting separators for instance.

All these challenges may seem daunting, but electrochemical nitrogen reduction is still at its early stages and a fast-progressing field. A lot of fundamental questions remain unanswered: How do protons, N_2 and NH_3 diffuse in and out of the SEI to the active sites? How dynamic is the SEI layer? Do we need high overpotentials such as the ones provided by Li and Ca metals to kinetically activate N_2 ? The work presented in this thesis provides an opinion on such questions and serves a basis for the development of electrolytes and new chemistries that may tackle some of the above laid challenges, toward economical, sustainable and globally accessible nitrogen fertiliser production.

6.3. Perspective for a Sustainable Nitrogen Cycle

It is one feat to produce ammonia sustainably, it is another to use it accordingly. We will conclude this thesis with perspectives for sustainably produced ammonia fertiliser and carbon-neutral fuels production, and the meaning of 'green' ammonia in the framework of a circular society. Electrochemical nitrogen reduction presents an attractive path to decarbonise fertiliser production, but should we make it this way? In this work, a lot of emphasis has been put on the need to reach high energy efficiencies to democratise this process. History has told us that the more energy efficient a process is, the more we use it, which backfires into more energy being used overall. This is the Jevons paradox, and it has two consequences. Firstly, we need to ensure that such energy supply is indeed renewable, and disseminating this process must be done alongside deployment of clean electricity. Secondly, we may well end up using more and more nitrogen fertiliser.

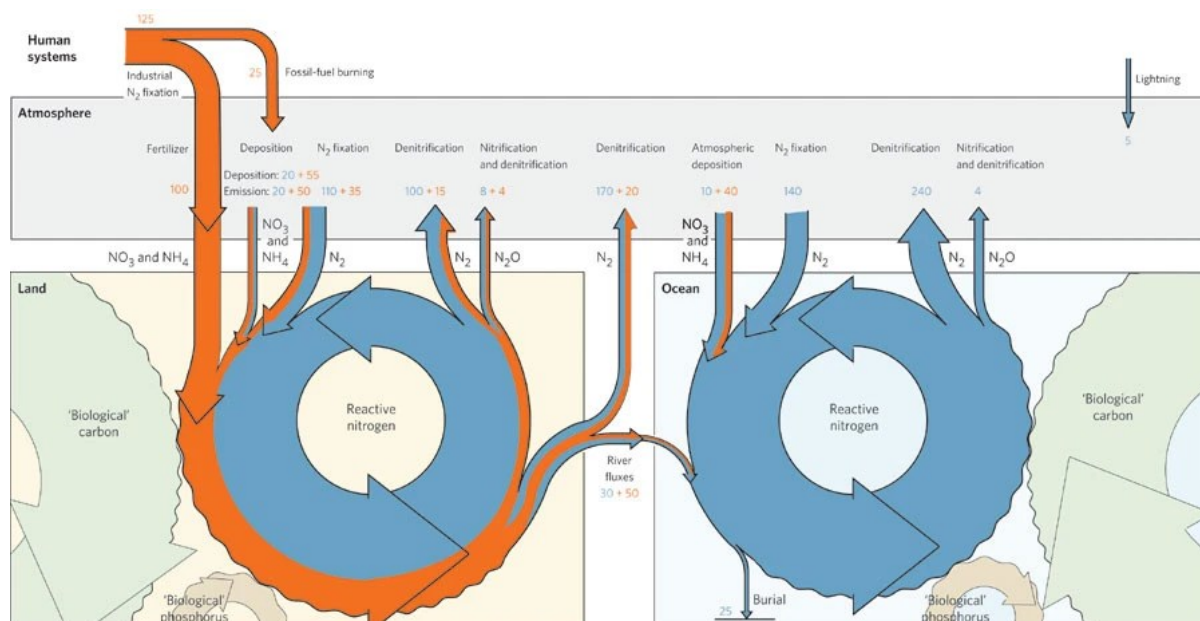


Figure 67. The Nitrogen cycle. Contribution of anthropogenic nitrogen fixation (orange) and all other biological fluxes (blue) to the nitrogen cycle in air, land and water. Displaying the intricate connection with the carbon and phosphorus cycles. Reproduced with permission from Gruber et al.²⁹⁵ © 2008, Springer Nature Limited.

Anthropogenic nitrogen fixation through fertiliser production and fossil fuel combustion has kept increasing over the years, accounting now for more than 200 Tg_N each year (*i.e.* more than all other natural fluxes combined).⁷ With the advent of carbon neutral nitrogen fixation, new markets are opening for decarbonisation, such as grid energy storage, hydrogen storage and transport, marine shipping or heating and cooling.²⁹⁶ Given the expected global population increase and these new applications, anthropogenic fixation will likely keep increasing. Why would that be a problem? Sustainability is not just about patching the carbon cycle. There are more biological cycles that take part in regulating our environment. The nitrogen cycle is one, and the extent of anthropogenic nitrogen fixation disturbs that cycle significantly (Figure 67).^{7,295} Excess reactive nitrogen (NH₄⁺, NO_x, etc.) released in air, water and soils may affect the environment in ways that are still uncertain. For instance, excess nitrogen fertiliser in crops may be washed away and acidify water streams, leading to the eutrophication of soils and major perturbation of biospheres.^{295,297} Same goes for future use as a fuel: NH₃ and NO_x leaks from ships can acidify waters and reduce their CO₂ buffering ability. In addition, combustion of ammonia can yield N₂O, a greenhouse gas which, in large enough quantity, may counteract the benefits of a carbon neutral fuel.²⁹⁸

Within European arable lands, reactive nitrogen use efficiency (fertiliser to food) was estimated at around 10 to 40% in 2008 depending on countries.²⁹⁹ This results from the advent of large scale yield-focused intensive agriculture and strong incentives from the agri-food industry. Hereby quoting Thibaut Decolle, an agronomist I was lucky to interview, farmers have always been told that *“the last thing you would want is your crops running out of nitrogen. Your plants need nitrogen to grow healthy leaves, full of active chlorophyll, and be robust until the harvest”*. This is true, but this simple message leads to overuse. In addition to the above listed effects, fertilisers (and pesticides) overuse has long term damaging effects on soils. This increases soil erosion and reduces soil fertility (the capability of microorganisms such as bacteria and mycelium to help accumulate nutrients), nurturing a negative feedback loop between fertiliser use and crop yields.^{300–302} There are methods to limit reactive nitrogen leaks from crops³⁰³, but their implementation will need solid policy backing failing an economic incentive. Electrochemical ammonia synthesis may help in that regard, for its potential for decentralisation. In addition to evening out offer and demand across the globe, onsite production of fertiliser may give farmers ownership for their use of fertiliser, with more tools, giving them a better idea of how much nitrogen is enough to secure necessary yields while keeping their land healthy.

The effects of fertiliser overuse may take time to be counteracted considering the slow dynamics of soil recovery and denitrification. However, with evolving mindsets and the right policies and actions taken, decentralised fertiliser production may help in balancing both the nitrogen and carbon cycles, and turn back the tide.

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Appendices

Supporting Figures

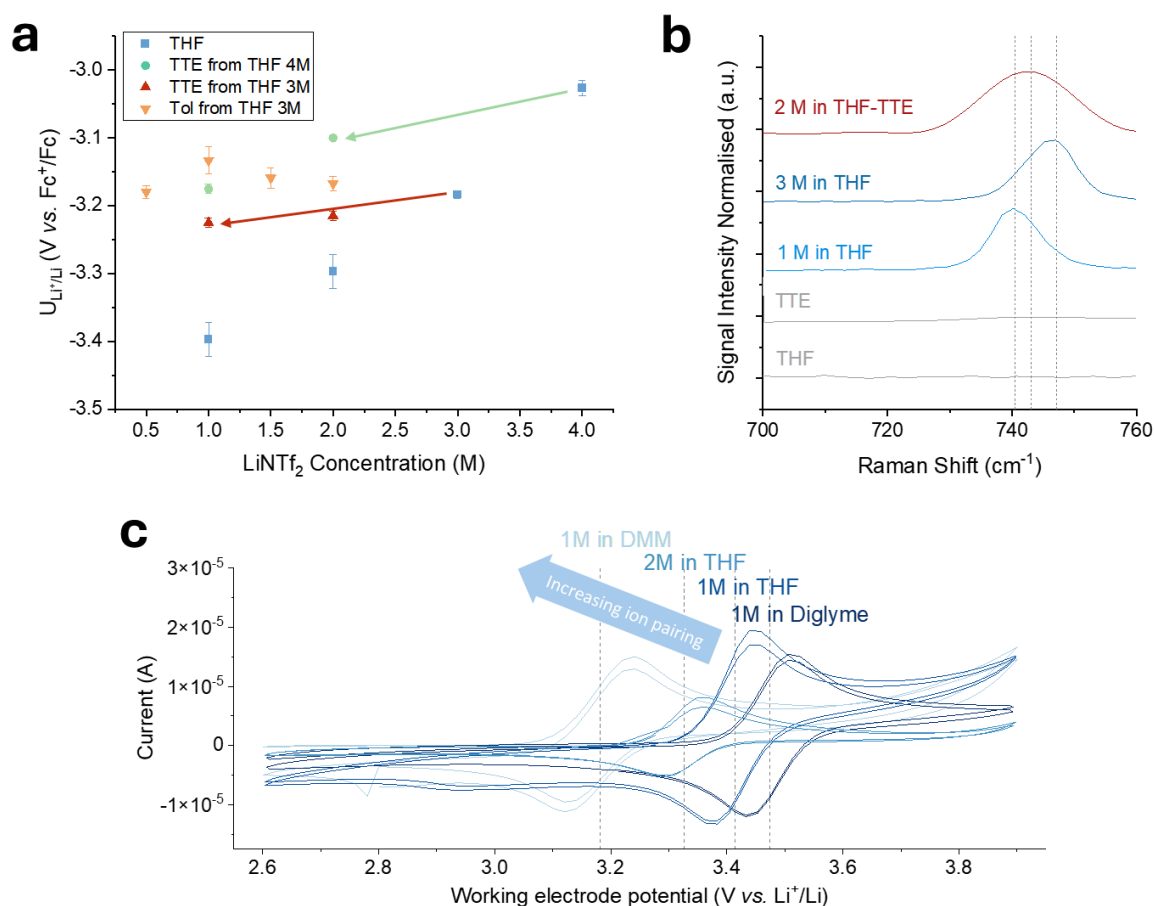


Figure 68. Li-ion activity studies by electrochemical $U_{Li^+/Li}$ measurement and Raman spectroscopy. **(a)** Recorded $U_{Li^+/Li}$ (method in experimental section 2.5.6) in various electrolyte compositions using $LiNTf_2$ in THF (blue squares), in THF-TTE (green circles and red triangles) or THF-toluene (orange triangles); showing a maintained high potential in THF electrolytes diluted with toluene, while losses are observed when diluting THF electrolytes with TTE. **(b)** Raman spectra for electrolytes of $LiNTf_2$ in THF (blue), and an electrolyte made of $LiNTf_2$ 3M in THF diluted to 2 M with TTE, displaying an upshift for the S-N-S bonds of the NTf_2^- anion as concentration is increased from 1 to 3 M, but is not fully retained as this 3 M electrolyte is diluted with TTE. **(c)** Cyclic voltammograms of 1 mM ferrocene in 5 ml $LiNTf_2$ in said solvent, recorded in a three-electrode setup installed in a temperature-controlled chamber at 25 °C (0.03 cm^2 Pt disc working electrode, Li wire reference electrode, Li foil counter

electrode, no iR correction), at a scan rate of 1 mV.s^{-1} . Electrolytes containing TTE were characterised by Guanglei Chen.

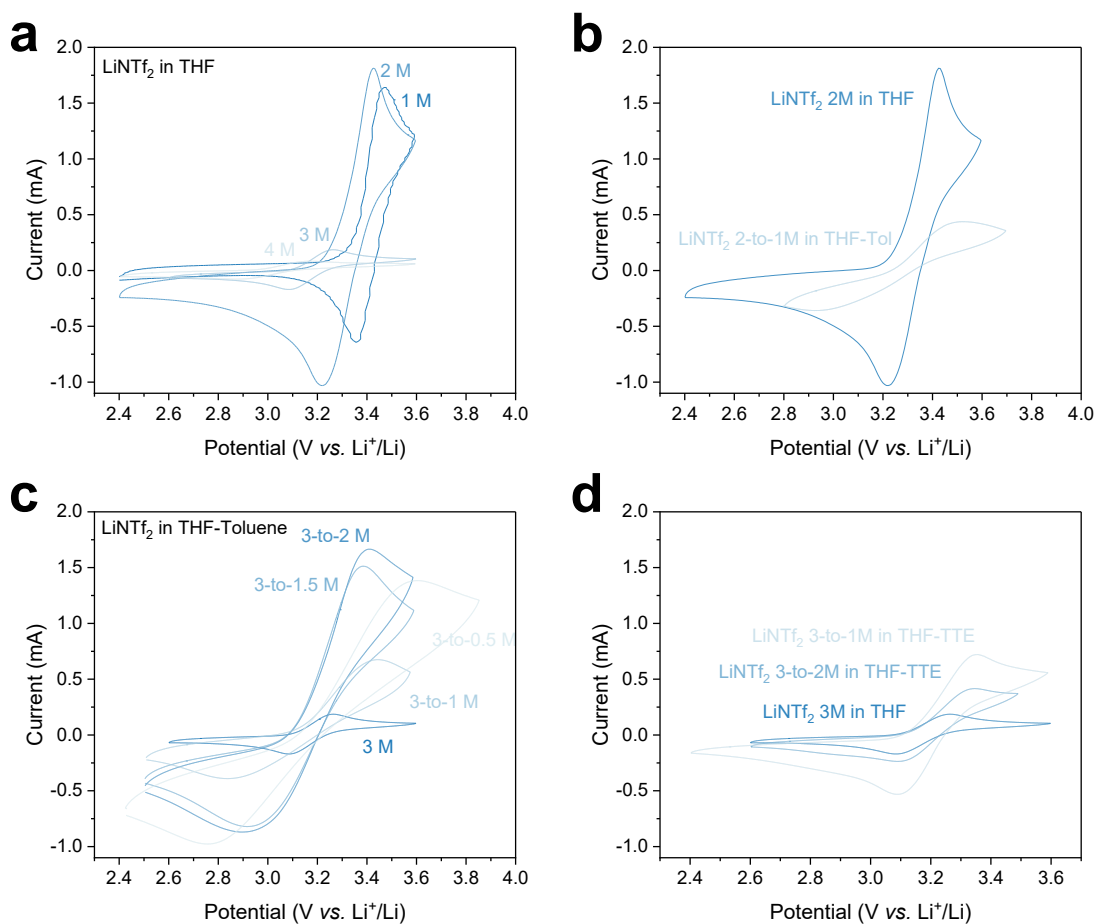


Figure 69. Ferrocene redox and $U_{\text{Li}^+/\text{Li}}$ measurements by cyclic voltammetry in coin cells. **(a)** LiNTf_2 in THF, 1 to 4 M. **(b)** LiNTf_2 2 M in THF compared with the same electrolyte diluted to 1 M with toluene. **(c)** LiNTf_2 3 M in THF compared to dilutions of this same electrolyte with toluene. **(d)** LiNTf_2 3 M in THF compared to dilutions of this same electrolyte with TTE. Method described in section 2.5.6.

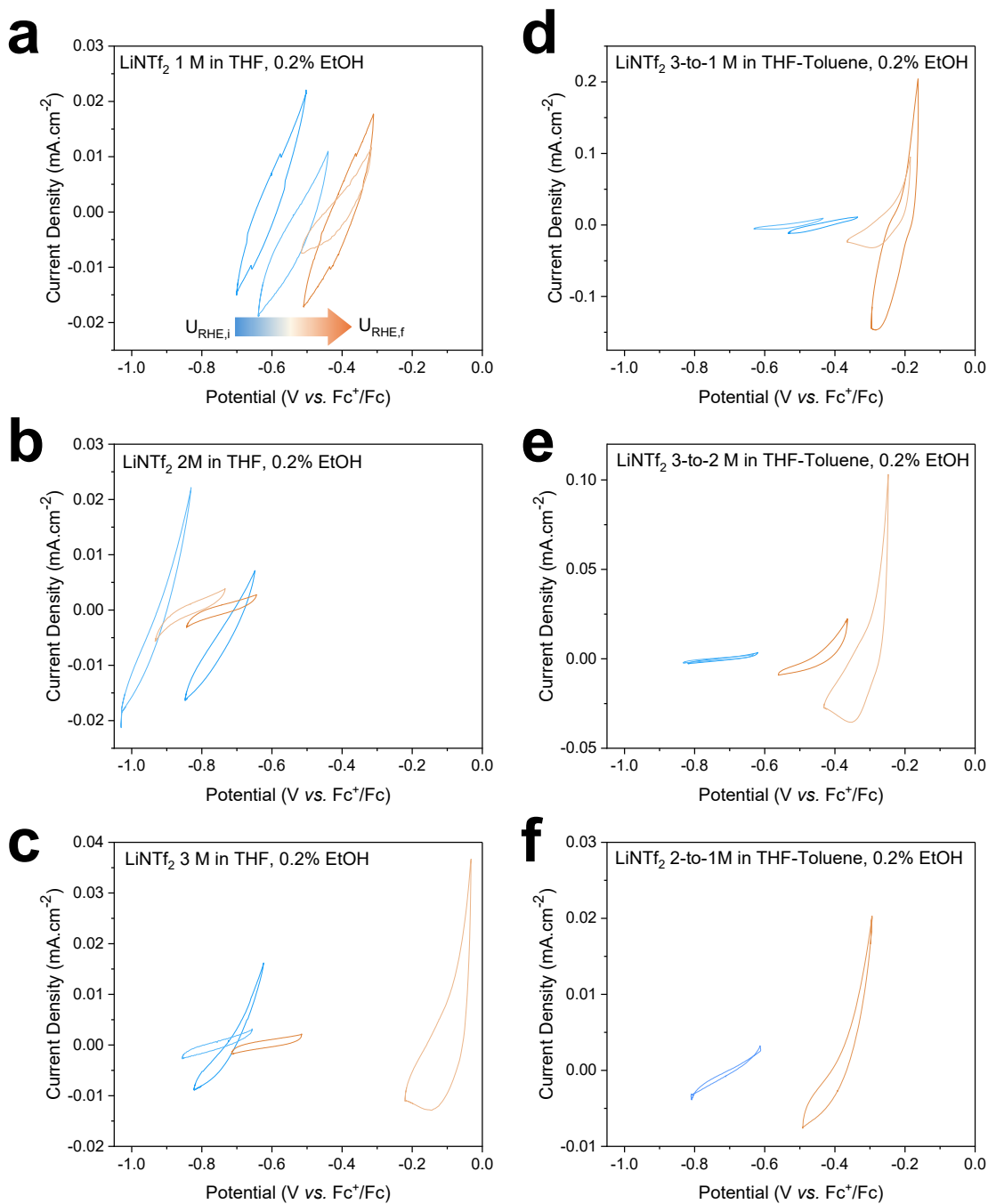


Figure 70. RHE potential measurement by cyclic voltammetry, before and after N_2 electrolysis. (a-f) For each electrolyte tested for N_2 reduction using a LFP reference electrode (2 repeats each), RHE potential was recorded before (blue) and after (orange) electrolysis.

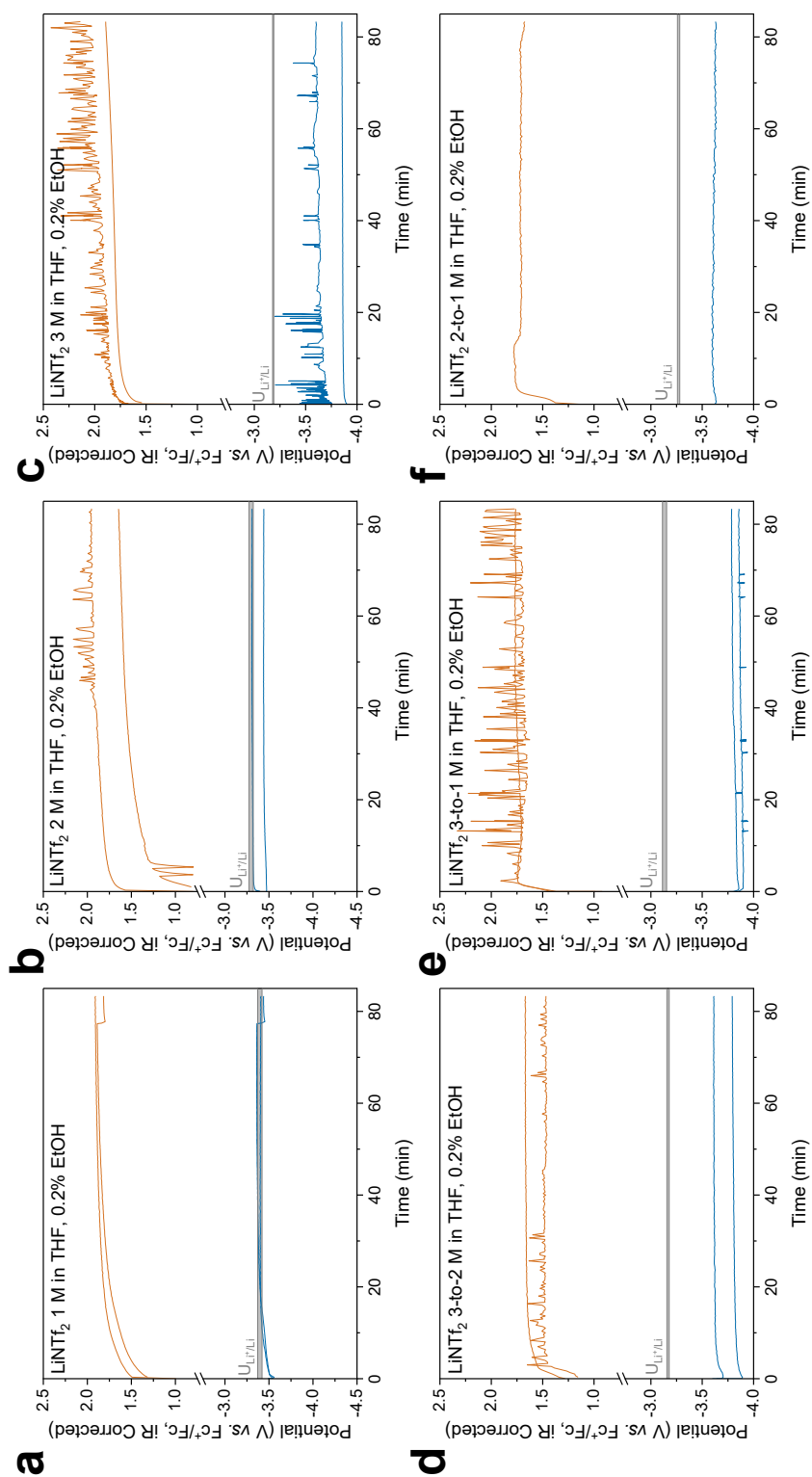


Figure 71. Nitrogen reduction experiments and working and counter electrode potentials measurements reported against the ferrocene scale. Each insert represents two repeats of the measurements recorded against a LFP reference, and reported back to the ferrocene scale. Li metal potential reported in grey for reference. Method in section 2.5.3.

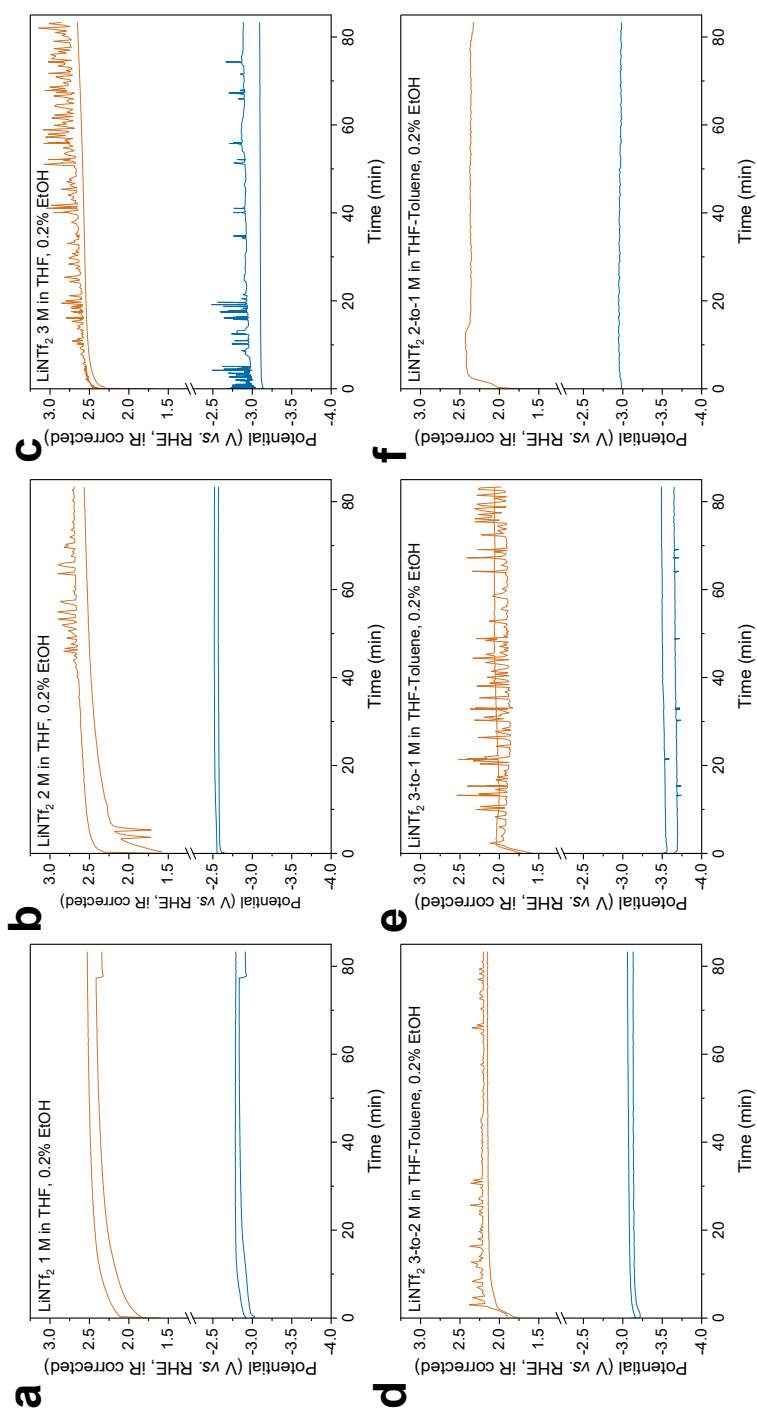


Figure 72. Nitrogen reduction experiments and working and counter electrode potentials measurements reported against RHE potential measured in each experiment. Nitrogen reduction experiments and working and counter electrode potentials measurements reported against the ferrocene scale. Each insert represents two repeats of the measurements recorded against a LFP reference, and reported back to the RHE scale by assuming a linear increase in RHE potential as measured before and after each experiment. Method in section 2.5.3.

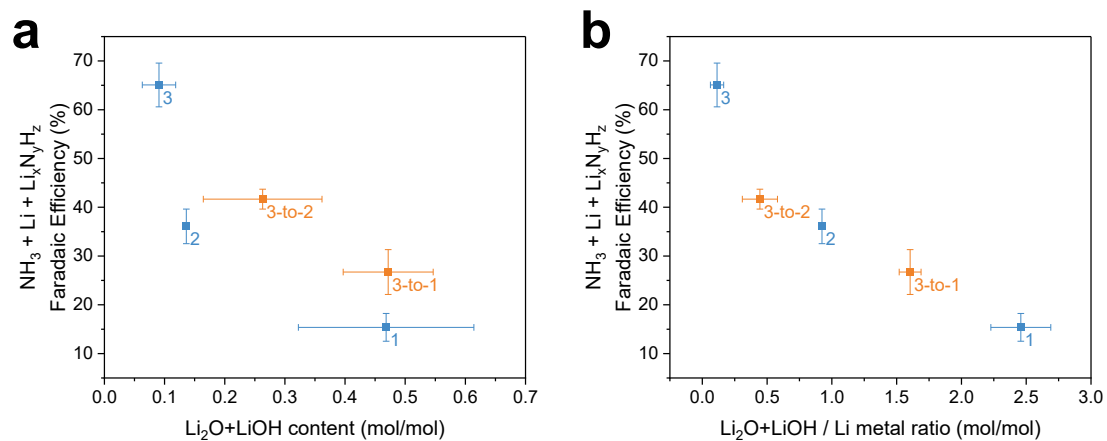


Figure 73. Correlation between Faradaic efficiency to $NH_3 + Li_xN_yH_z + Li$ in each electrolyte and (a) the $Li_2O/LiOH$ content or (b) the ratio of $Li_2O/LiOH$ to Li metal in the electrode deposits titrated post N_2 reduction experiments.

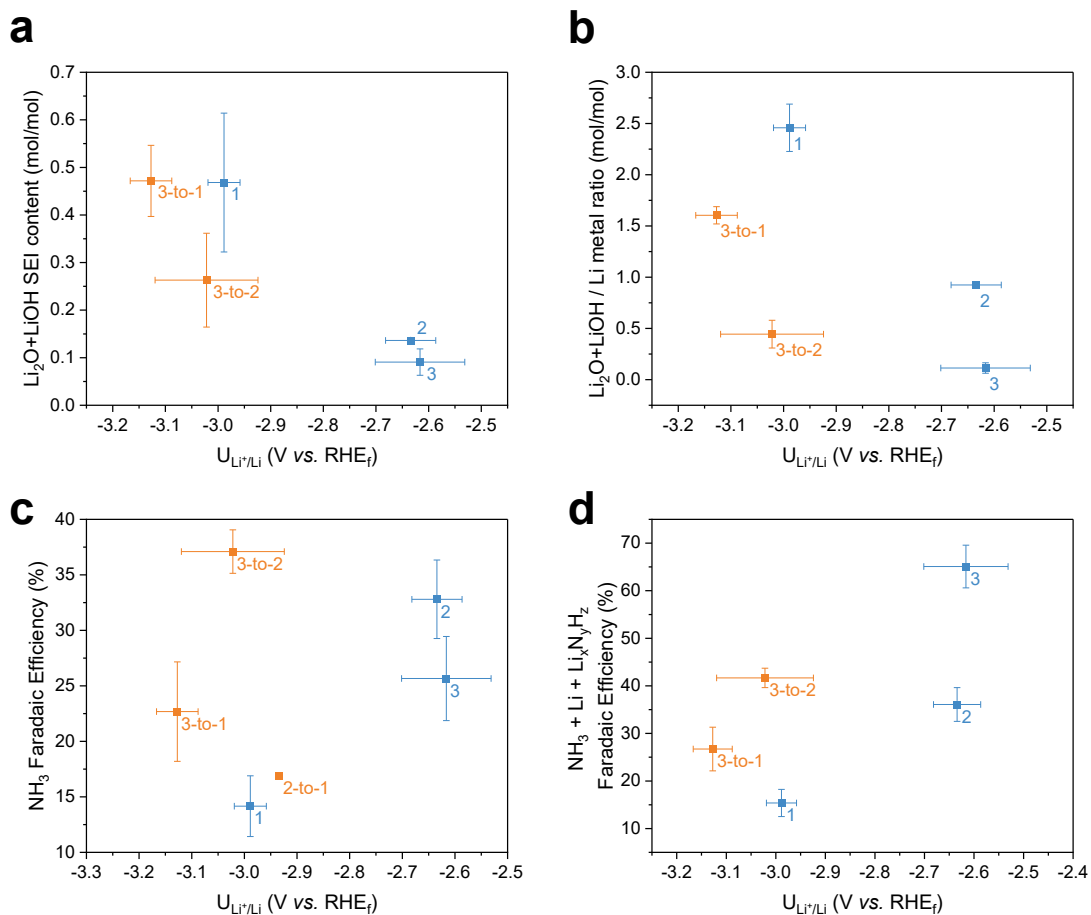


Figure 74. Correlations between SEI key chemistries, species activities post electrolysis and selectivity to ammonia and its intermediates. **(a)** Weak correlations between Li_2O content in the SEI and $U_{\text{Li}^+/\text{Li}} - U_{\text{RHE},f}$. **(b)** Absence of correlation between $\text{Li}_2\text{O}+\text{LiOH}$ to Li ratio and $U_{\text{Li}^+/\text{Li}} - U_{\text{RHE},f}$. **(c)** Absence of correlation between Faradaic efficiency to ammonia and $U_{\text{Li}^+/\text{Li}} - U_{\text{RHE},f}$. **(d)** Weak correlation between Faradaic efficiency to $\text{NH}_3+\text{Li}+\text{Li}_x\text{N}_y\text{H}_z$ and $U_{\text{Li}^+/\text{Li}} - U_{\text{RHE},f}$.

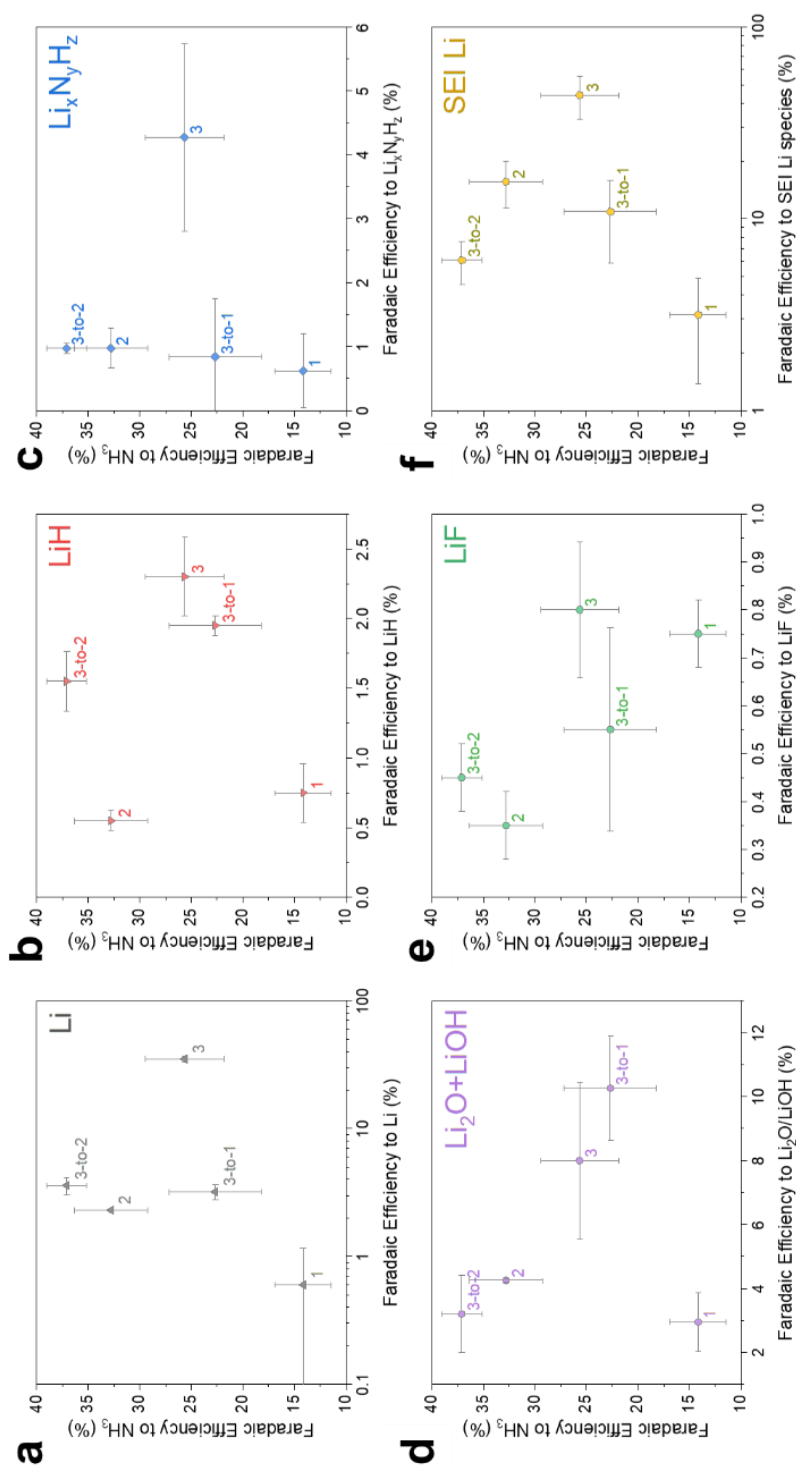


Figure 75. Faradaic efficiency toward ammonia plotted against the Faradaic efficiency to SEI components. (a) Li, (b) LiH, (c) $\text{Li}_x\text{N}_y\text{H}_z$, (d) $\text{Li}_2\text{O}/\text{LiOH}$, (e) LiF and (f) SEI Li species from a N_2 electrolysis experiment (2 repeats for LiF, 3 repeats for $\text{Li}_2\text{O}/\text{LiOH}$ and SEI Li species, 5 repeats for Li, LiH and $\text{Li}_x\text{N}_y\text{H}_z$).

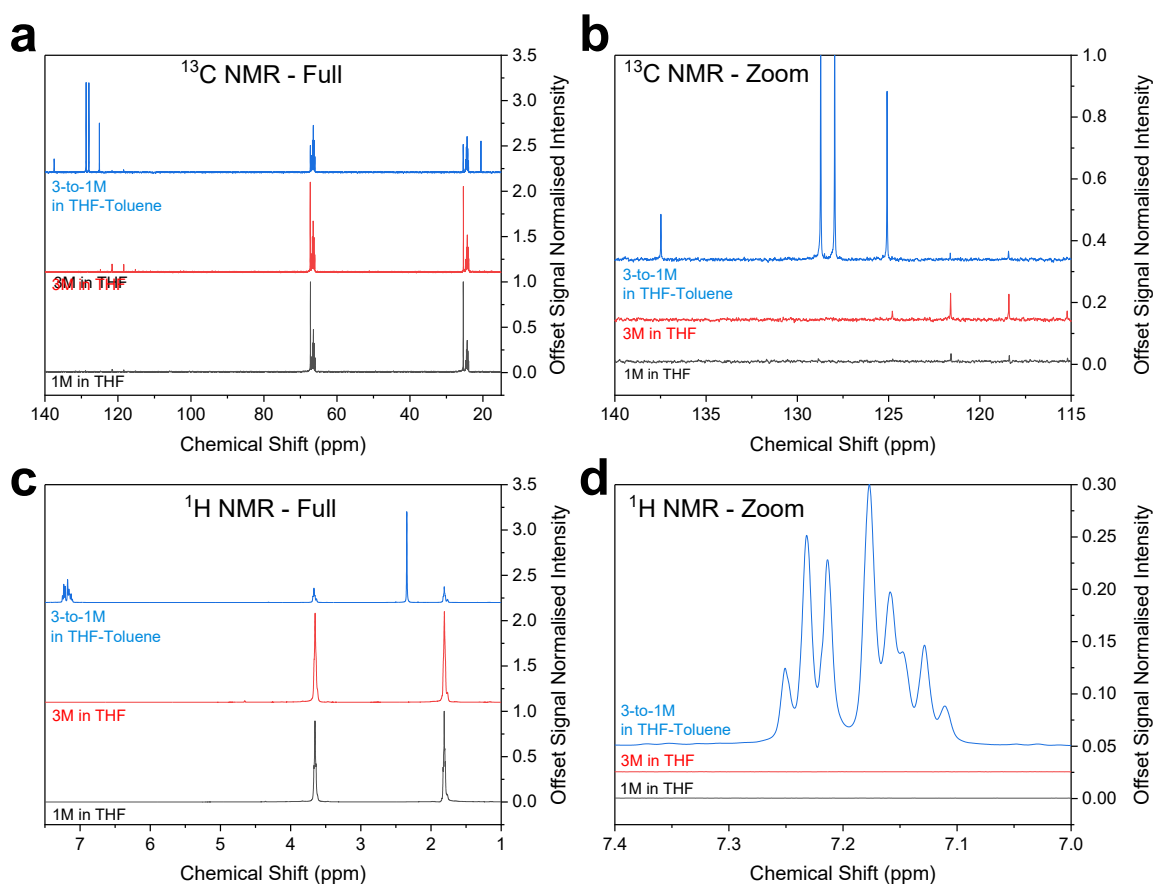


Figure 76. ^1H and ^{13}C NMR of electrolytes after a nitrogen reduction experiment, using electrolyte samples diluted with $d_8\text{-THF}$ to 1/10 v/v and recorded within 20 min of the nitrogen reduction experiment being conducted. **(a,b)** ^{13}C NMR in full (a), and with a zoom on the aromatic carbons region (b), showing an unidentified quadruplet at ~ 120 ppm in experiments with or without toluene. **(c,d)** ^1H NMR in full (c), and with a zoom on the aromatic carbons region (d), showing a doublet overlapping with a doublet of triplet, an expected signal for toluene.

Nearly all peaks observed by NMR can be assigned to either THF or toluene, except for a ^{13}C NMR quadruplet at 120ppm which could be attributed to an unsaturated THF-oxidation product, such as 2,3-dihydrofuran. However, sensitivity of such NMR analysis is limited and degradation in low quantities may be omitted.

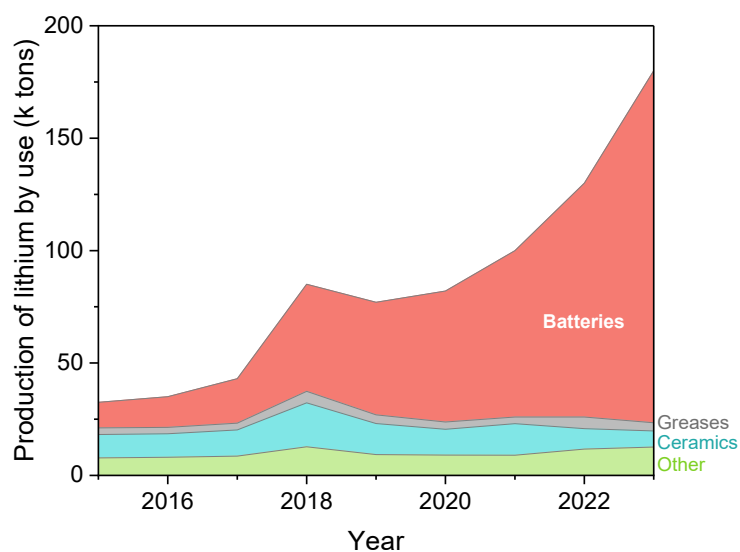


Figure 77. The evolution of lithium production over time, with detailed contribution by end use. Showing an increasing demand for the global battery market. Data collected from the US Geological Survey Mineral Commodity Summaries 2016 to 2024.²²⁵

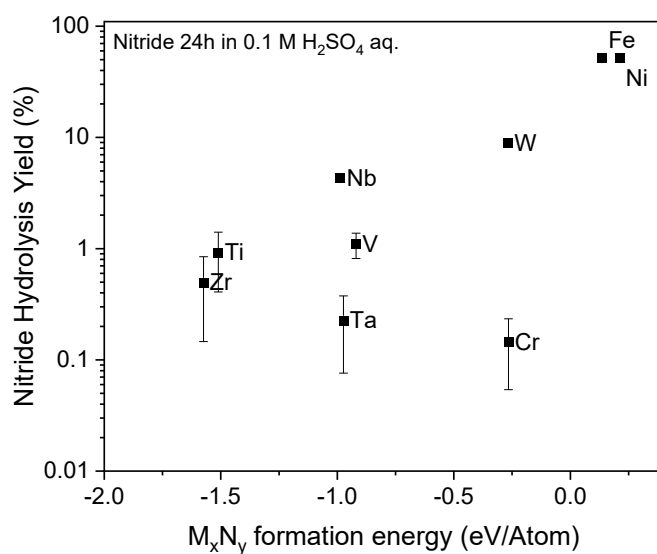


Figure 78. Yield of hydrolysis of metal nitrides suspended in dilute sulfuric acid as measured by Peng et al.²⁶¹, and plotted against the formation energy of each nitride from their respective metal and N_2 calculated by DFT simulation by Dr Alexander Bagger (see in section 2.12)

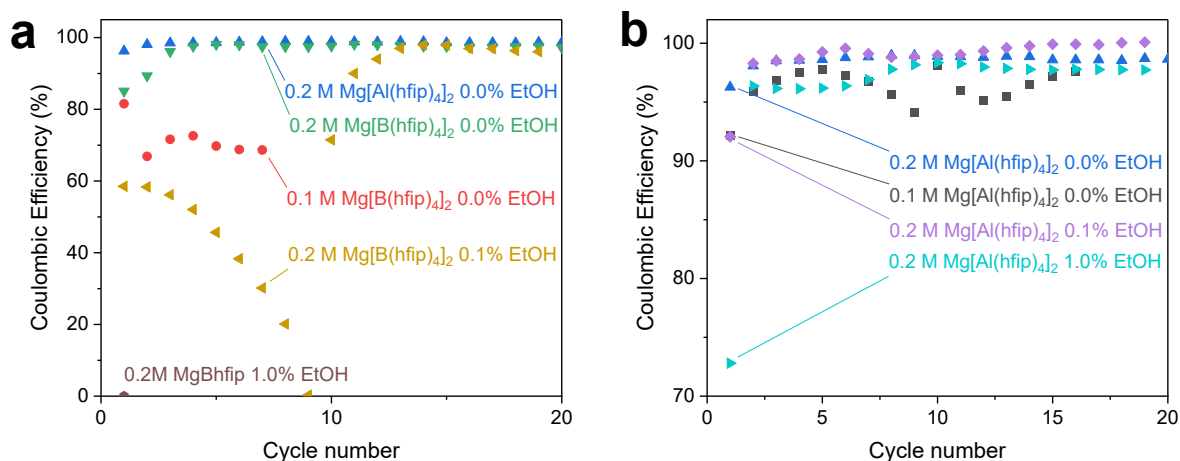


Figure 79. Coulombic efficiency of Mg plating and stripping in the presence of ethanol, using (a) $\text{Mg}[\text{B}(\text{hfip})_4]_2$ and (b) $\text{Mg}[\text{Al}(\text{hfip})_4]_2$ electrolytes in Diglyme with noted amounts of added ethanol. Measurements performed by Andrijana Marojević.

The Mg salts were synthesised and tested electrochemically by Andrijana Marojević, using a Swagelok two electrode cell with a Pt foil working electrode, a brushed Mg foil counter electrode, spaced by three glassy fiber separators wetted with 100 μl of electrolyte. Each cycle consists of constant current Mg plating at $-1 \text{ mA}\cdot\text{cm}^{-2}$ for 1 h, followed with Mg stripping at $+1 \text{ mA}\cdot\text{cm}^{-2}$ until a cut-off voltage of +2 V vs. Mg (no iR drop correction).

Supporting Tables

Table 4. Comparison of Faradaic efficiency to ammonia in the presence of different reference electrodes (Pt, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ or LiFePO_4), resulting from the electrolysis of a 1 M LiNTf_2 electrolyte in THF/EtOH 99:1 v/v at $2\text{mA}\cdot\text{cm}^{-2}$ passing 10 C of charge – Showing the interference of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in N_2 reduction experiments.

Reference used	FE to NH_3 (%) (run 1)	FE to NH_3 (%) (run 2)	FE to NH_3 (%) (run 3)	FE to NH_3 (%) (mean)
Pt wire	7.6 ± 0.5	6.9 ± 0.2	7.8 ± 0.9	7.4 ± 0.2
$\text{Li}_4\text{Ti}_5\text{O}_{12}$	4.1 ± 0.3	4.0 ± 0.4	3.6 ± 0.5	3.9 ± 0.1
LiFePO_4	7.8 ± 0.2	6.7 ± 1.0	7.0 ± 0.9	7.2 ± 0.3

*Table 5. Summary of the theoretical data gathered from the literature or calculated by Dr Alexander Bagger through DFT simulations. Metal nitrides-hydrides structures and Gibbs free energies of their formation and *N binding to metals were calculated by DFT by us. Elements representative minerals global productions were collected from the US Geological Survey – Mineral Commodity Summaries 2018 to 2023.²²⁵ SHE potentials were obtained from multiple references^{304–307}.*

Element	M_xH_y	M_xN_y	Cleaved Nitride?	M_xH_y Formation Energy (eV/atom)	M_xN_y Formation Energy (eV/atom)	*N binding energy (eV)	Global Mining (kton/year)	Standard Reduction Potential (V vs. SHE)
Ag	AgH	AgN_3	No	0.267	0.729	3.142	26	0.80
Al	AlH_3	AlN	Yes	0.036	-1.182	-0.703	70000	-1.66
Au	-	AuN_2	No		0.469	2.947	3	1.52
B	B_9H_{11}	BN	Yes	-0.084	-1.143		3400	-1.79
Ba	BaH_2	BaN_2	No	-0.461	-0.360	-1.302	8500	-2.91
Be	BeH_2	Be_3N_2	Yes	-0.006	-0.886	0.918	0.33	-1.85
Ca	CaH_2	Ca_3N_2	Yes	-0.472	-0.612	-1.715	430000	-2.87
Cd	CdH	CdN_6	No	0.511	0.583	1.579	23	-0.40
Co	Co_4H	CoN	Yes	0.039	0.306	0.275	230	-0.28
Cr	CrH	CrN	Yes	0.090577	-0.26548	-1.306	41000	-0.74
Cs	CsH	CsN_3	No	-0.113	-0.038	2.050		-3.03
Cu	CuH	Cu_3N	No	0.194	0.368	1.705	22000	0.34

Fe	FeH	FeN	Yes	0.101	0.136	-1.718	1300000	-0.44
Ga	GaH	GaN	Yes	0.504	-0.263		0.61	-0.53
Hf	HfH ₂	HfN	Yes	-0.372	-1.479	-2.618	0.043	-1.72
Hg	-	HgN ₃	No		0.682		1.2	0.85
In	InH	InN	Yes	0.500	0.232		0.99	-0.34
Ir	-	IrN ₃	No	0.504	0.573	0.270	0.027	1.00
K	KH	KN ₃	No	-0.159	-0.027	2.141	39000	-2.93
Li	LiH	Li ₃ N	Yes	-0.346	-0.252	-0.734	180	-3.04
Mg	MgH ₂	Mg ₃ N ₂	Yes	-0.124	-0.599	-0.355	22000	-2.37
Mn	Mn ₂₉ H ₂	MnN	Yes	0.018	-0.073		20000	-1.19
Mo	MoH	MoN	Yes	0.544	-0.231	-1.452	260	-0.15
Na	NaH	NaN ₃	No	-0.146	0.013	1.361	270000	-2.71
Nb	NbH ₂	NbN	Yes	-0.163	-0.987	-1.796	83	-1.10
Ni	NiH	Ni ₆ N ₂	Yes	0.068	0.211	-0.093	3600	-0.25
Os	-	OsN ₂	No	0.964	0.463	0.138	0.009	0.65
Pd	-	PdN ₂	No	-0.014	0.392	0.937	0.21	0.92
Pt	-	PtN ₂	No	0.405	0.690	0.718	0.18	1.19
Rb	RbH	RbN ₃	No	-0.112	-0.022	2.485		-2.98
Re	ReH ₃	ReN	Yes	0.611	0.191	-0.632	0.056	0.30
Rh	-	RhN ₂	No	0.139	0.597	0.302	0.018	0.76
Ru	-	RuN	Yes		0.404	0.217	0.091	0.46
Sc	ScH ₂	ScN	No	-0.584	-1.729	-2.250	0.27	-2.08
Sr	SrH ₂	SrN ₂	No	-0.455	-0.279	-1.047	520	-2.90
Ta	TaH ₂	TaN	Yes	-0.001	-0.973	-2.031	2.4	-0.60
Ti	TiH ₂	TiN	Yes	-0.392	-1.511	-2.430	330	-1.63
Tl	TlH	TlN ₃	No	0.455	0.420	2.256	2.1	-0.34
V	VH ₂	VN	Yes	-0.109	-0.920	-1.875	100	-1.13
W	-	W ₂ N ₃	Yes	0.224	-0.268	-1.669	78	-0.12
Y	YH ₂	YN	Yes	-0.627	-1.554	-2.080	0.27	-2.37
Zn	ZnH ₆	Zn ₃ N ₂	Yes	0.148	0.247	0.335	12000	-0.76
Zr	ZrH ₂	ZrN	Yes	-0.486	-1.573	-2.600	1.556	-1.45

Limitations of the RHE Scale Definition in Comparing Ammonia Synthesis Systems in Figure 56 and Figure 62

Figure 56 and Figure 62 were laid out by reproducing the data gathered by Westhead *et al.*³⁶ for which a few assumptions were required. While these assumptions were necessary in estimating the operating potentials vs. RHE and comparing the surveyed works on a similar scale, some assumptions may be wrong based on the findings of this work. It is important to note however that the analysis

proposed in the cited work is the best possible one with the state of knowledge and data available and a lot more work would be needed to correct this RHE scale for all datapoints. In addition, irrespective of such assumptions, this analysis proves the point that alkali metal based electrochemical systems lie far behind in voltage losses compared to nitrogenase and homogeneous systems. Indeed, a massive voltage gap exists between the best examples of metal mediated ammonia synthesis and the best (>2 V) or worst (>700 mV) homogeneous catalysts. In comparison, the work presented here estimates a range of variation in RHE potential across electrolytes of about 300 mV only (Figure 39b). However, definite scaling within Li/Ca/Mg-based systems is not possible in this way and one would need to measure the RHE potential and operating potential for each of these systems, against a stable reference electrode with a defined electrochemical equilibrium potential.

Assumption 1: “The variation in lithium plating potential for different concentrations of LiClO₄ in 1 vol% ethanol vs. a Pt pseudo reference was also measured. **The difference in lithium concentration should not vastly change the RHE potential, since the RHE potential depends on the activity of protons** as $U_{\text{RHE}} = U_{\text{RHE}}^0 + (RT/F) \cdot \ln(a_{\text{H}^+})$, and does not depend on the activity of the lithium ion. **This is of course a simplification**, given that the presence of lithium ions may affect proton activity due to their strong proton affinity.”

This assumption suggests that the RHE potential may not be affected by Li-ion concentration. However, this is indeed a simplification like acknowledged in the manuscript. Figure 49b shows that large shifts in RHE potential can result from a change in Li-ion concentration, up to roughly 300 mV in the space probed in this work. For the reported scale to be independent of Li-ion activity or concentration, measuring the RHE potential against a stable reference electrode with a defined electrochemical equilibrium potential would be required.

Assumption 2: “Fu and Pedersen et al also measured the reversible HER/HOR potential in a 1 M LiBF₄ in THF with no ethanol electrolyte as -0.05 V vs Pt. From my work examining the variation of the RHE potential with ethanol concentration, **there is little measurable difference in the HER/HOR potential between 0 and 1 vol% ethanol** (on the order of 10s of millivolts) for a 0.6 M LiClO₄ electrolyte [28]. Therefore, the RHE potential for Fu and Pedersen et al can be estimated as -0.05 V vs Pt in their working electrolyte (1 M LiBF₄, 0.25 vol % (0.04 M) ethanol).”

The absence of relation between the RHE potential and EtOH concentration claimed here is counterintuitive since the presence or absence of EtOH should affect proton activity. Figure 39b shows that platinum electrode potential can shift dramatically in the presence of organic compounds.¹⁷⁹

Because the RHE potential was measured on a platinum working electrode against a platinum *pseudo* reference electrode, it could be that both electrodes were equally affected by the presence of ethanol and virtually no shift was observed. Measuring the RHE potential against a reference electrode that is insensitive to such effects would be required to confirm or refute this hypothesis.

How Much Lithium Would Be Needed to Replace Haber-Bosch Derived Ammonia with Lithium Mediated Nitrogen Reduction?

Full reliance on lithium as a catalyst for electrochemical nitrogen reduction poses questions to the scalability of such technology, both because of the high electricity costs associated with continuous Li plating¹¹⁶, and because lithium is a critical mineral in direct competition with a growing battery market (Figure 77)²²⁴. However, a quick calculation detailed below suggests that the latter issue is expected to be a less significant one compared to electricity costs. Let us put forward an optimistic scenario where electrochemical ammonia synthesis was to replace 10% of present and future Haber-Bosch derived ammonia. With today's state of the art technology, this would require way more lithium than the mining industry can provide. However, with a few reasonable improvements in operating currents and system stability (see details below), the amount of lithium required to operate enough electrolyzers to cover ammonia production at scale is expected to be insignificant. The assumptions and calculations made in each scenario are listed below.

Comparison Metrics and Base Assumptions:

Today's ammonia production is estimated at 180 Mt.y⁻¹,²²⁵ and expected to increase by 40% by 2050 (252 Mt.y⁻¹)³⁰⁸. The amount of lithium required to match 10% of the Haber-Bosch nitrogen reduction scale (25.2 Mt.y⁻¹) will be calculated using this metric and compared against today's scale of global lithium mining. Global lithium mining today is estimated at 180 thousand tons a year, of which 87% is allocated to the battery market.

To realise the amount of lithium required to match such scale and compare it against available supply, one needs to define the yield rate defined by operating currents and Faradaic efficiency of the system (activity), electrolyser lifetime (stability), and amount of lithium required per cm² of electrode surface area. Each metric is dependent on the state of the technology (see specific assumptions below).

Overall, the amount of Li required to match the Haber-Bosch scale can be calculated by the following equations:

$$(40) \quad \text{electrochemical yield rate} \left(\frac{Mt_{NH_3}}{cm^2 \cdot y} \right) = \frac{\text{current} \left(\frac{C}{y \cdot cm^2} \right) * \text{Faradaic efficiency} (\%) * M(NH_3) \left(\frac{Mt}{mol} \right)}{3 * F}$$

$$(41) \quad \text{Li density} \left(\frac{t}{cm^2} \right) = [Li^+] \left(\frac{mol}{ml} \right) * M(Li^+) \left(\frac{t}{mol} \right) * V_{\text{electrolyte}} \left(\frac{ml}{cm^2} \right)$$

$$(42) \quad m_{Li} (t \cdot y^{-1}) = \frac{\text{Haber Bosch ammonia yield rate} \left(\frac{Mt_{NH_3}}{y} \right) * \text{Li density} \left(\frac{t}{cm^2} \right)}{\text{electrochemical yield rate} \left(\frac{Mt_{NH_3}}{cm^2 \cdot y} \right) * \text{electrolyser lifetime} (y)}$$

With: $[Li^+] = 1 \text{ mol} \cdot l^{-1} = 10^{-3} \text{ mol} \cdot ml^{-1}$, $M(NH_3) = 17 \text{ g} \cdot \text{mol}^{-1} = 1.7 * 10^{-11} \text{ Mt} \cdot \text{mol}^{-1}$, $M(Li^+) = 6.94 \text{ g} \cdot \text{mol}^{-1} = 6.94 * 10^{-6} \text{ t} \cdot \text{mol}^{-1}$, and $F = 96485 \text{ C} \cdot \text{mol}^{-1}$ the Faraday constant.

Today's state of the art:

State of the art metrics in performance are defined by the latest report from Li *et al.* using a gas diffusion flow cell reducing N_2 to ammonia on a stainless-steel mesh cathode and oxidising hydrogen to protons on a porous PtAu anode ($25 \text{ cm}^2_{\text{geo}}$ electrodes), both connected by an electrolyte made of $LiBF_4$ 1 M in diglyme and 0.25 % v/v EtOH.⁹⁹ This system was demonstrated to operate through a cycling protocol oscillating between equal periods of constant current Li plating at $-6 \text{ mA} \cdot \text{cm}^{-2}$ and relaxation at open circuit (average current density of $-3 \text{ mA} \cdot \text{cm}^{-2}$), with a Faradaic efficiency of $64 \pm 1\%$. Finally, the cathode and anode are separated by a 0.4 cm thick electrolyte chamber, meaning $V_{\text{electrolyte}} = 0.4 \text{ ml} \cdot \text{cm}^{-2}$ of electrolyte volume to electrode surface area.

With these assumptions in mind:

$$\text{Li density} = 10^{-3} * (6.94 * 10^{-6}) * 0.4 = 2.78 * 10^{-9} \text{ t} \cdot \text{cm}^{-2}$$

$$\text{e. yield rate} = \frac{(0.003 * 3600 * 24 * 365) * 0.64 * 1.7 * 10^{-11}}{3 * 96485} = 3.56 * 10^{-12} \text{ Mt}_{NH_3} \cdot \text{cm}^{-2} \cdot y^{-1}$$

$m_{Li} = \frac{25.2 * (2.78 * 10^{-9})}{(3.56 * 10^{-12}) * (\frac{300}{24 * 365})} = 574 \text{ kt} \cdot y^{-1}$ which corresponds to roughly 3.2 times the amount of lithium mined today (~ 3.7 times the battery market demand, see Figure 77). This is extremely far from practicality.

Tomorrow's target performance:

Since the technology is at its early stages, improvements in operating currents, Faradaic selectivity and stability can be expected. In a hypothetical future where the system operates at a current of 0.1 A.cm⁻² (an example operating at this current density already exists¹¹³), Faradaic efficiency of 90% (>99% already achieved⁸⁴), electrolyte chamber thickness of 1 mm and electrolyser lifetime of one year, the required amount of lithium supply can be expected as:

$$\text{Li density} = 10^{-3} * (6.94 * 10^{-6}) * 0.1 = 6.94 * 10^{-10} \text{ t.cm}^{-2}$$

$$\text{e.yield rate} = \frac{(0.1 * 3600 * 24 * 365) * 0.80 * 1.7 * 10^{-11}}{3 * 96485} = 1.48 * 10^{-10} \text{ Mt}_{\text{NH}_3}.\text{cm}^{-2}.\text{y}^{-1}$$

$$m_{\text{Li}} = \frac{25.2 * (6.94 * 10^{-10})}{(1.48 * 10^{-10}) * 1} = 118 \text{ t.y}^{-1} \text{ which corresponds to 0.07 \% of today's global lithium yearly supply, or 0.08 \% of the supply allocated to the battery market.}$$

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Vous avez tous contribué à l'aboutissement de ce travail, alors merci à tous.

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