

IMPERIAL

Real-Time Ammonia Quantification in Electrochemical Nitrogen Reduction

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A thesis submitted in fulfilment of the requirements for the
degree of Doctor of Philosophy (PhD)

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Statement of Originality

I hereby declare that this thesis and the work reported herein are the result of my own research and have been written by me in their entirety. Contributions from collaborators and colleagues have been appropriately acknowledged, and any data collected by others is clearly credited. Information and ideas derived from the published and unpublished work of others have been properly cited in the text, with full references provided in the final section of this manuscript.

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Abstract

Ammonia synthesis is a cornerstone of global agriculture, yet the conventional Haber–Bosch process relies on high temperatures and pressures, operates at large centralised facilities, and is a major contributor to global CO₂ emissions. Electrochemical approaches, particularly lithium-mediated nitrogen reduction, offer a promising and potentially sustainable alternative, enabling ammonia production under ambient conditions with decentralised, renewable-powered operation. However, despite recent advances, the lithium-mediated system remains limited by key challenges, including electrolyte instability, parasitic side reactions, and low ammonia yields, all of which hinder its commercial viability. This thesis aims to enhance the accuracy and consistency of ammonia quantification techniques, specifically UV–Vis colorimetry and electrochemistry–mass spectrometry (ECMS), and apply them to investigate the mechanisms of electrolyte degradation and acidification, as well as their impact on system performance and stability. This work demonstrates that conventional calibration curves are unsuitable for colorimetric detection of ammonia in lithium-mediated electrolytes due to large variations in calibration curve gradients. Additionally, real-time detection of gas-phase ammonia using ECMS was found to be highly sensitive to electrolyte acidity, which primarily arises from anodic solvent oxidation. This work establishes a rigorous methodology for real-time ammonia quantification using ECMS, addressing a critical gap in literature for standardisation and technique development. Through this framework, the project provides new mechanistic insight into electrolyte decomposition processes in lithium-mediated nitrogen reduction, highlighting the role of solvent breakdown and gas evolution. Furthermore, it elucidates how electrolyte acidification, driven by anodic reactions, affects ammonia yield & distribution and system stability. Together, these contributions advance the analytical and mechanistic understanding of the lithium-mediated system and inform the design of more robust, efficient electrochemical ammonia synthesis platforms.

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Nomenclature

CA – Chronoamperometry

CE – Counter Electrode

CP – Chronopotentiometry

ECMS – Electrochemistry-Mass Spectrometry

EIS – Electrochemical Impedance

Ethanol – Ethanol

FE – Faradaic Efficiency

HER – Hydrogen Evolution Reaction

Li-NRR – Lithium-Mediated Nitrogen Reduction

LiTFSI – Lithium bis(trifluoromethanesulfonyl)imide

LFP – Lithium Iron Phosphate (LiFePO_4)

LSV – Linear Sweep Voltammetry

NMR – Nuclear Magnetic Resonance

OCV – Open Circuit Voltage

OCP – Open Circuit Potential

PEEK – Polyetheretherketone

PTFE – Polytetrafluoroethylene

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

RE – Reference Electrode

RHE – Reversible Hydrogen Electrode

SEI – Solid Electrolyte Interphase

SHE – Standard Hydrogen Electrode

THF – Tetrahydrofuran

WE – Working Electrode

Contents

Abstract	iii
Acknowledgements	iv
Academic Contributions	v
<u>Peer-Reviewed Publications</u>	<u>v</u>
<u>Preprints.....</u>	<u>v</u>
<u>Manuscripts in Preparation</u>	<u>v</u>
<u>Conference Presentations.....</u>	<u>v</u>
<u>Awards & Grants</u>	<u>vi</u>
Nomenclature	vii
Contents	viii
1 Introduction	1
<u>1.1 Background</u>	<u>1</u>
<u>1.2 Scope</u>	<u>4</u>
<u>1.3 The Lithium-Mediated System</u>	<u>5</u>
1.3.1 State-of-the-Art.....	7
<u>1.4 Key Aspects of the Lithium-Mediated System</u>	<u>8</u>
1.4.1 The Solid-Electrolyte Interphase (SEI).....	8
1.4.2 The Importance of Electrolyte Composition	9
1.4.3 The Role of Ethanol	13
1.4.4 Electrolyte Decomposition & Acidification	15
1.4.5 Electrode Crosstalk	17
<u>1.5 Quantification of Dissolved Ammonia using Colorimetry.....</u>	<u>18</u>
<u>1.6 Real-Time Quantification Through Mass Spectrometry</u>	<u>20</u>
1.6.1 Membrane Inlet Mass Spectrometry (MIMS)	21
1.6.2 Differential Electrochemical Mass Spectrometry (DEMS)	21
1.6.3 On-Line Electrochemical Mass Spectrometry (OLEMS)	22
1.6.4 Summary of the Established Techniques	23
<u>1.7 Electrochemistry-Mass Spectrometry (ECMS).....</u>	<u>24</u>
1.7.1 Introduction	24
1.7.2 Adaptation for Non-Aqueous Electrochemistry	25
1.7.3 Use in Lithium-Mediated Nitrogen Reduction	26
<u>1.8 Summary</u>	<u>27</u>
2 Experimental Methods	29
<u>2.1 Theoretical Background</u>	<u>29</u>
2.1.1 Electrochemistry	29
2.1.2 Colorimetry	31

2.1.3 Electrochemistry-Mass Spectrometry (ECMS)	32
2.2 Methodology	35
2.2.1 Colorimetry	35
2.2.2 Electrochemistry-Mass Spectrometry (ECMS)	38
3 Quantification of Dissolved Ammonia (Colorimetry)	42
3.1 Introduction	42
3.2 Quantification with Phenol vs Salicylate	42
3.3 Quantification using Calibration Curves vs Standard Addition	45
3.4 Reducing Organic Interference through Evaporation vs Dilution	47
3.5 Improving Accuracy and Reliability of the Salicylate Method	51
3.5.1 Determining Optimal Concentration Range	51
3.5.2 Quantification of Adventitious Ammonia	52
3.5.3 Identification of Appropriate Signal Background	53
3.6 Conclusion	53
4 Quantification of Gas Phase Ammonia (Mass-Spectrometry)	55
4.1 Introduction	55
4.1.1 Challenges of Gas Phase Ammonia Detection Using ECMS	55
4.1.2 Challenges of Electrochemical Ammonia Generation in the ECMS Cell	56
4.1.3 Challenges of Real-Time Detection of in-situ Generated Gas Phase Ammonia	56
4.1.4 Overview of Cell Configurations Used	57
4.2 Validation of Gas-Phase Ammonia Detection Using ECMS	59
4.3 Verification of Electrochemical Ammonia Generation in the ECMS Cell	61
4.3.1 False Positive (Methane)	61
4.3.2 Increasing Ammonia Yield	63
4.3.3 Investigating Acidification from Anodic Solvent Oxidation	65
4.4 Confirmation of Real-Time Detection of in-situ Generated Gas Phase Ammonia	69
4.5 Conclusion	71
5 Investigating Electrolyte Degradation, Acidification and Crosstalk	73
5.1 Introduction	73
5.2 Insights into Electrolyte Degradation Mechanisms	74
5.3 Overview of Cell Configuration Effects	77
5.4 Evidence for Acidity Trend	78
5.4.1 Hydrogen Evolution Evidence	78
5.4.2 Electrochemistry Evidence	80
5.5 Effect on Performance (Ammonia vs other gas products)	81
5.6 Effect on Stability (Solvent Degradation)	82
5.7 Conclusion	83

Conclusion & Outlook.....	85
References	86

1 Introduction

1.1 Background

Ammonia is a critical compound for modern civilisation, primarily due to its role in fertiliser production, which supports nearly half of global food output. Since the 1940s, demand for ammonia-based fertilisers has risen steadily, reaching approximately 118 million tonnes in 2020 [1]. The global population has become increasingly reliant on Haber-Bosch-derived nitrogen as seen in Figure 1.1. With the global population projected to surpass 9.7 billion by 2050, the need for sustainable and accessible fertiliser will only intensify [2]. In parallel, ammonia is gaining increasing attention as a potential zero-carbon energy carrier. Its high hydrogen content established transport infrastructure, and ability to be combusted or used in fuel cells make it an attractive candidate for decarbonising sectors such as shipping, power generation, and long-distance transport [3], [4]. The International Energy Agency (IEA) projects that low-carbon ammonia could account for nearly 45% of global ammonia production by 2050 under net-zero scenarios, with significant demand from both fertiliser and energy sectors [5]. These dual roles (in agriculture and clean energy) mean that global ammonia demand is expected to increase dramatically. Meeting this demand sustainably, without the heavy carbon footprint of current production methods, is one of the major technological and environmental challenges of the coming decades.

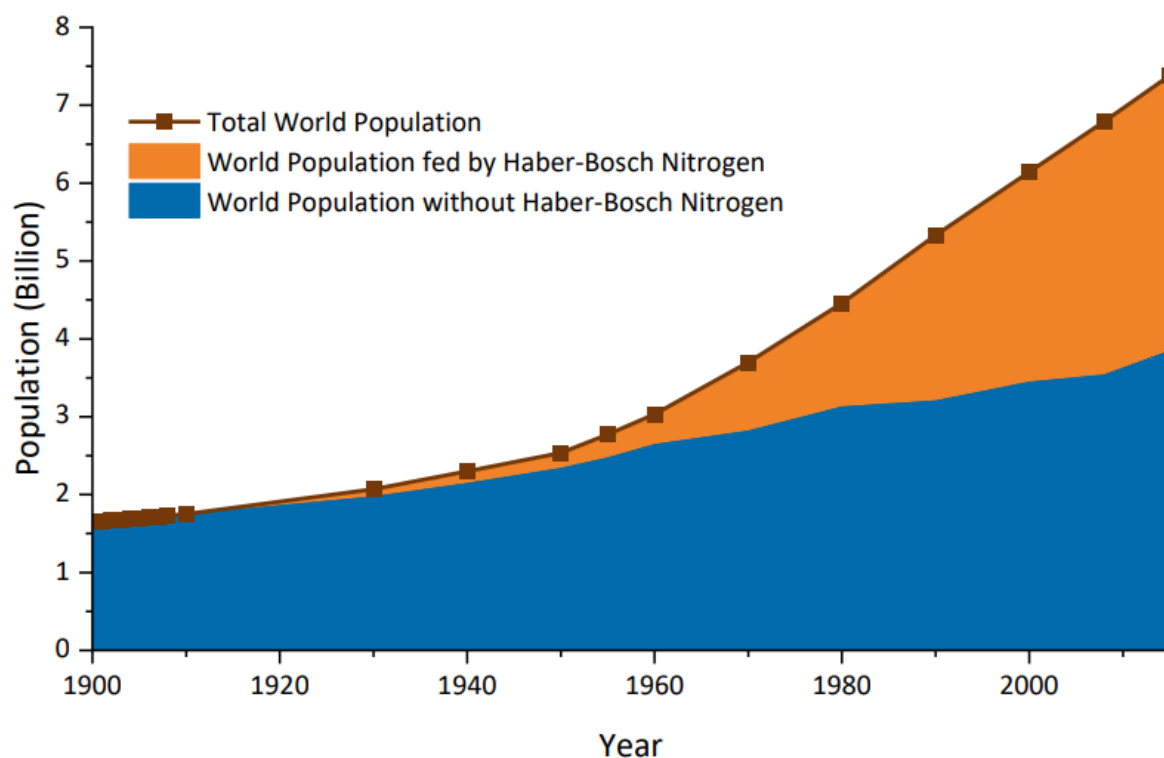


Figure 1.1: Estimated proportion of the global population sustained by Haber–Bosch-derived nitrogen fertiliser from 1900 to present. By 2020, it is estimated that nearly half of the global population was fed by food produced using synthetic nitrogen fertilisers. Figure reproduced from [6].

The Haber–Bosch process has dominated ammonia (NH_3) production for over a century and remains the cornerstone of global fertiliser manufacturing [7]. Its success lies in its ability to produce ammonia at scale and relatively low cost, with global output exceeding 170 million tonnes in 2020 [1]. However, the process presents significant environmental and logistical drawbacks that are increasingly incompatible with global sustainability targets. It operates under extreme conditions (typically 400 to 500 °C and pressures of 150 to 200 bar) which require substantial energy input and complex industrial infrastructure [8]. Most critically, the hydrogen used in the process is primarily derived from steam methane reforming, a fossil-fuel-based route that alone consumes around 1% of the world’s total energy and emits more than 450 million tonnes of CO_2 annually [9], [10]. Figure 1.2 highlights the sources of CO_2 emissions in the Haber–Bosch process. Additionally, due to the need for economies of scale, the Haber–Bosch process is only economically viable in large, centralised plants. This necessitates ammonia distribution over long distances, adding further CO_2 emissions, raising costs, and limiting access in regions lacking robust transport infrastructure, particularly in developing nations [11], [12]. As a result, there is a growing imperative to develop decentralised and low-carbon alternatives to Haber–Bosch ammonia synthesis.

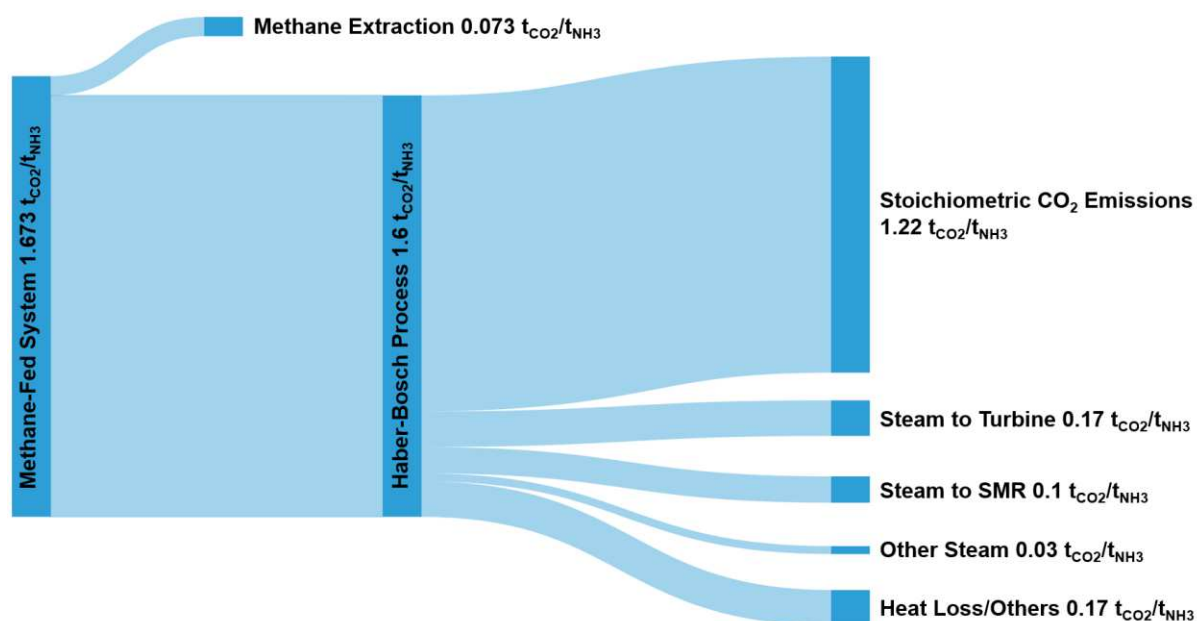


Figure 1.2: Sankey diagram showing the attributions of $\text{CO}_{2\text{-eq}}$ emissions arising from the methane-fed Haber–Bosch process. Figure adapted from [7] with permission from the Royal Society of Chemistry.

A big contender for replacing the current Haber–Bosch process is the green Haber–Bosch process which would utilise renewable hydrogen [7]. However, this does not address the high temperatures and high pressures utilised and the need for distribution infrastructure due to large scale centralised production. This would make green Haber–Bosch an incremental improvement. Continuous electrochemical nitrogen reduction to ammonia on the other hand, is a completely different system which is not limited to the same drawbacks of the Haber–Bosch. The system would utilise electrons from renewable electricity, nitrogen from the air and protons from water to make sustainable ammonia that can be made under ambient conditions (as illustrated in Figure 1.3 and described by Equation (1.1)) [13]. Furthermore, the feasibility of the system is not tied to a large scale, making de-centralised production viable.

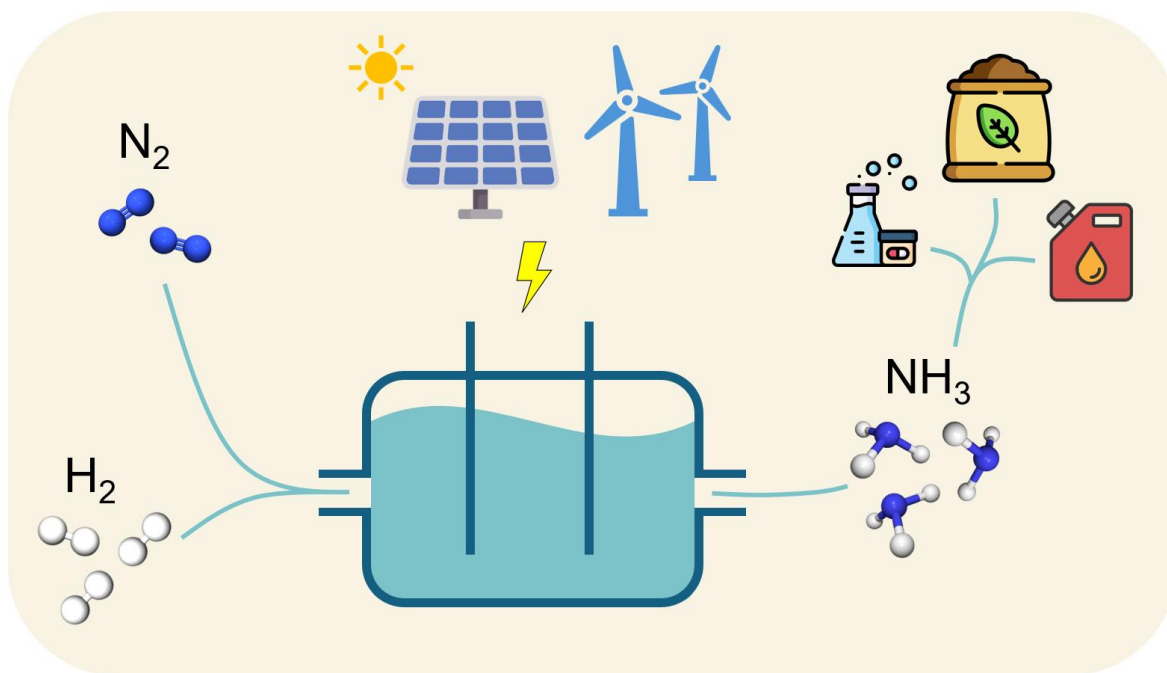


Figure 1.3: Schematic illustration of sustainable electrochemical nitrogen reduction. Renewable electricity is used to drive the reduction of nitrogen and oxidation of hydrogen from water to synthesise ammonia (NH_3) under mild conditions.



Many electrocatalysts and systems have been studied for ambient condition electrochemical nitrogen reduction, including Fe in alkaline aqueous conditions [14], Ru in acidic aqueous conditions [15] and Au in aqueous alkaline conditions [16] with varying reported successes [16], [17], [18], [19]. In 2019, Andersen et al. developed a rigorous ammonia quantification protocol using isotope labelling and systemically verified the various systems [20]. It was found that only the non-aqueous lithium-mediated system as first reported by Tsuneto et al. [21] was able to synthesise ammonia via electroreduction of nitrogen gas at ambient conditions. In this system, lithium ions are electrochemically reduced to metallic lithium at the cathode surface, which then reacts chemically with nitrogen gas to form lithium nitride (Li_3N). The Li_3N is subsequently protonated by a proton donor (ethanol) to release ammonia. In recent years, a number of studies have focused on other mediators such as Mg or Ca for continuous electrochemical nitrogen reduction [22], [23], [24]. While successful, these chemistries are very novel and require a lot of further development. Therefore, the lithium-mediated system remains the most promising candidate for continuous electrochemical nitrogen reduction to ammonia for now.

While the system is promising, there remain key challenges to overcome before this system becomes commercially viable. A faradaic efficiency of nearly 100% has been achieved using lithium-mediated nitrogen reduction [25]. However, this was achieved using a 15 bar nitrogen atmosphere, further advancement are required to achieve similar faradaic efficiencies under ambient conditions. Under ambient conditions, parasitic hydrogen evolution remains a key side reaction that limits faradaic efficiency. Another major challenge to overcome is the low current densities that are currently achievable. Current state-of-the-art ambient lithium-mediated nitrogen reduction has been able to achieve a current density of 6 mA/cm^2 [26]. However, this

is far from the required 100 mA/cm^2 reported by a recent techno-economic analysis [27] and 300 mA/cm^2 reported by the US Department of Energy's REFUEL Program [28]. Furthermore, due to the large magnitude of the potential needed to plate lithium (-3.04 V vs SHE), the overall energy efficiency is limited to around 28% (this assumes H_2 oxidation at the anode and N_2 reduction at the cathode and accounts for the energy required to split water to produce H_2) [29]. Finally the degradation of electrolyte in the system continues to be a key issue and has been a widely discussed topic [30] due to the negative impact it has on the performance [31] and stability [32], [33], [34].

1.2 Scope

This thesis aims to investigate the lithium-mediated nitrogen reduction (Li-NRR) system using Electrochemistry–Mass Spectrometry (ECMS) to monitor gas-phase product evolution in real time. ECMS is a powerful analytical technique that enables quantitative, time-resolved detection of volatile species with exceptional sensitivity (0.3 pmol/s for NH_3) and rapid response times ($<1 \text{ s}$ for H_2), making it uniquely suited for probing the dynamic behaviour of lithium-mediated systems. The project focused on three primary objectives:

1. Development of a reliable method for quantifying dissolved ammonia in non-aqueous electrolytes. While ECMS enables real-time detection of gas phase ammonia, it does not capture ammonia retained in the electrolyte (either as dissolved NH_3 or protonated NH_4^+). Accurate quantification of this fraction is essential to fully account for total ammonia production and determine ammonia distribution across phases. This objective involved developing and validating a sensitive, consistent, and accurate UV–Vis colorimetric method for measuring ammonia concentrations in electrolyte samples.
2. Establishment of a robust methodology for consistent gas phase ammonia generation and detection using ECMS. Although ECMS has previously been used to detect gas-phase ammonia in lithium-mediated nitrogen reduction [35], [36], its application remains limited due to challenges in reproducibility. Building on prior work, this project aimed to systematically evaluate and optimise the ECMS system for real-time ammonia detection. The goal was to understand the key variables influencing gas phase ammonia liberation and detection, ultimately creating a reproducible and generalisable framework for ECMS-based quantification.
3. Investigation of electrolyte degradation, acidification, and ammonia distribution, with emphasis on mechanistic understanding. One of the most underexplored aspects of lithium-mediated nitrogen reduction is the acidification of the electrolyte, which arises from anodic oxidation reactions. This acidification can alter the ammonia/ammonium equilibrium, enhance parasitic hydrogen evolution, and degrade the SEI, thereby reducing system stability and selectivity. Using ECMS, the project probed the gas phase products of degradation, while also quantifying changes in ammonia distribution between gas and liquid phases. By correlating electrolyte composition, acidity changes, and ammonia distribution, the project sought to provide mechanistic insight into how electrolyte decomposition affects performance and stability.

1.3 The Lithium-Mediated System

A key challenge in electrochemical nitrogen reduction is achieving sufficient selectivity toward ammonia over the parasitic hydrogen evolution reaction (HER). Theoretical studies led by Nørskov and colleagues have shown that this selectivity is fundamentally constrained by the scaling relationships that govern surface catalysis: most surfaces that bind N_2 strongly also tend to bind protons strongly, making it difficult to activate dinitrogen without simultaneously promoting HER [37]. This challenge was further emphasised by Bagger et al., who demonstrated there is no known catalyst surface that offers both strong N_2 adsorption and weak H^+ binding, presenting a critical limitation for conventional aqueous systems [38]. Unlike aqueous systems, which suffer from the dominant HER, the lithium-mediated system utilises a non-aqueous electrolyte to limit proton activity and thus suppress HER [39].

The lithium-mediated nitrogen reduction (Li-NRR) system offers a fundamentally distinct approach to ammonia synthesis, leveraging the unique reactivity of lithium in non-aqueous environments. In this system, lithium ions from a lithium salt dissolved in an organic solvent (typically ethers such as tetrahydrofuran (THF) or diglyme) are electrochemically reduced at the working electrode to deposit metallic lithium [26]. This highly reactive lithium spontaneously reacts with dinitrogen (N_2) under ambient conditions to form lithium nitride (Li_3N), a key intermediate in the process [39]. The Li_3N is subsequently protonated by a suitable proton donor (typically ethanol) to form ammonia (NH_3), completing the nitrogen reduction cycle (as illustrated in Figure 1.4). A crucial component of this system is the formation of a solid–electrolyte interphase (SEI) on the electrode surface [40]. This interfacial layer, formed via reductive decomposition of the electrolyte, plays a vital role in maintaining selective and stable operation. It regulates lithium ion transport, protects the electrode from further degradation, and influences both the rate and selectivity of the reaction by modulating access of nitrogen and protons to reactive sites [40]. The formation, composition, and properties of the SEI remain active areas of research, as they critically affect the efficiency and long-term stability of the Li-NRR system.

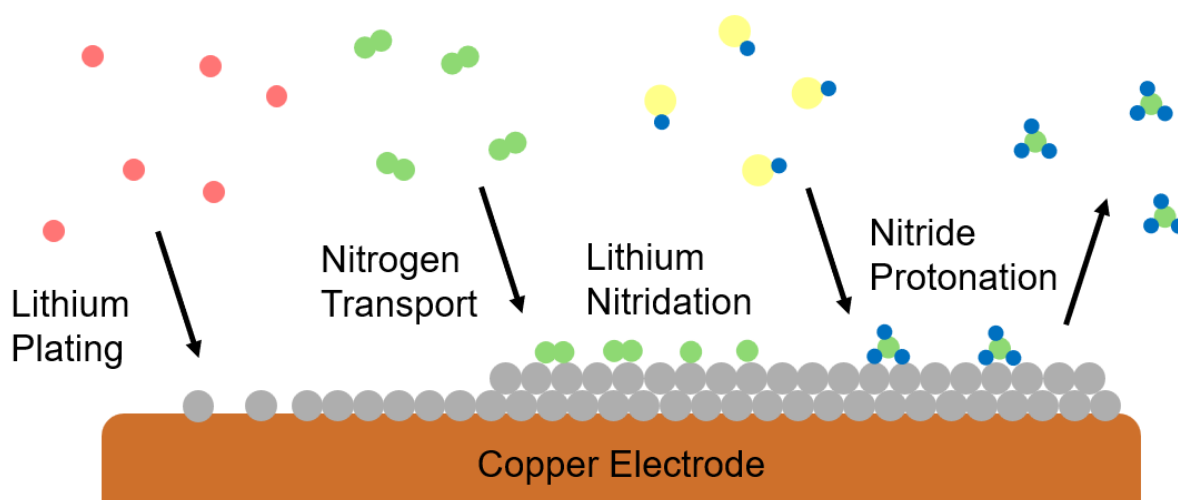


Figure 1.4: Schematic diagram of electrochemical lithium-mediated nitrogen reduction. Figure adapted with permission from [41].

Such a system was realised in the seminal lithium-mediated nitrogen reduction work published by Tsuneto et al. in 1993, which used a 0.2 M lithium perchlorate (LiClO_4) in THF with 1 vol%

ethanol electrolyte in a single compartment cell to achieve a faradaic efficiency of 8% towards ammonia [21]. However, it was not until several decades after Tsuneto et al.'s pioneering study that the lithium-mediated nitrogen reduction system was rigorously verified. This was accomplished by Andersen et al., who developed a comprehensive experimental protocol that marked a turning point in the field [20]. Their methodology included control experiments substituting argon for nitrogen to account for background ammonia, as well as open-circuit N_2 experiments to identify contamination from the gas stream. Most importantly, they employed $^{15}N_2$ isotopic labelling with quantitative detection of $^{15}NH_3$ to unambiguously confirm the nitrogen source. This protocol established a new benchmark for validating electrochemical nitrogen reduction systems, ensuring that reported ammonia truly originates from N_2 reduction rather than from adventitious sources such as atmospheric ammonia, NO_x impurities, or experimental materials. By setting this standard for experimental rigor, Andersen et al. provided a foundation for reproducible and credible research in the field.

In the years following the work of Andersen et al., the performance of the lithium-mediated system improved significantly, largely due to advances in electrolyte composition (key breakthroughs are illustrated in Figure 1.5). Initial progress was made by increasing the concentration of lithium salt in the electrolyte, which enhanced ionic conductivity and contributed to a more stable SEI layer [42]. Researchers then shifted from using $LiClO_4$ to lithium bis(trifluoromethanesulfonyl)imide ($LiTFSI$), which provided higher faradaic efficiencies [25], [43]. A further breakthrough came with the replacement of the solvent tetrahydrofuran (THF) with diglyme (DG), and the use of lithium tetrafluoroborate ($LiBF_4$) as the salt [26], [29]. This combination resulted in superior SEI properties, reduced solvent volatility, and enabled sustained ammonia synthesis over extended operation times, marking a significant advancement in system performance.

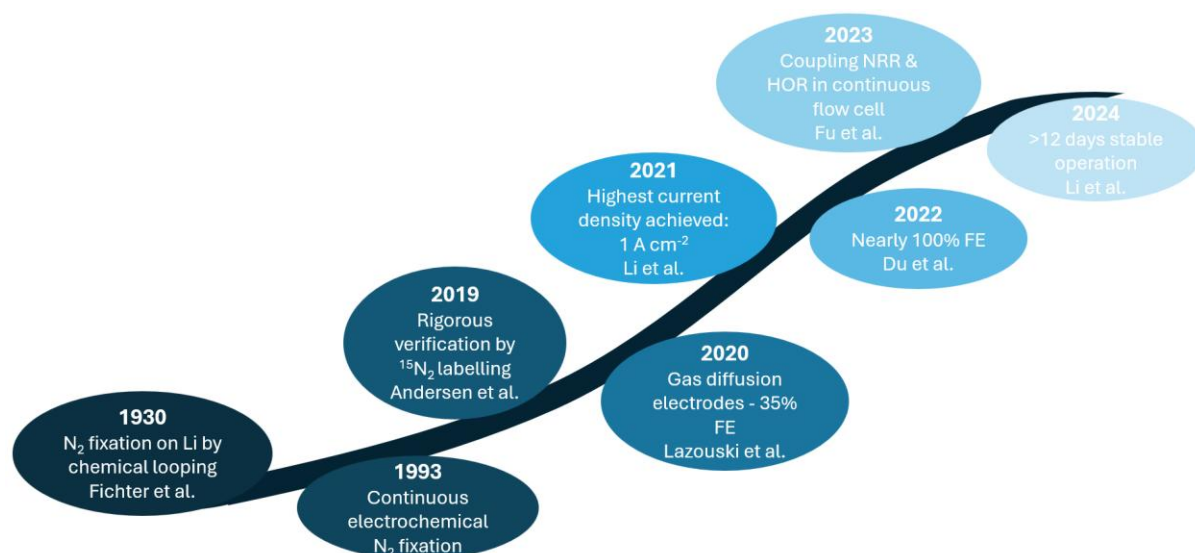


Figure 1.5: Timeline of technological breakthrough made in the field of Li-mediated ammonia synthesis. Figure adapted from [6].

Several important achievements have been made in the lithium-mediated system in recent years. Du et al. were able to achieve a faradaic efficiency of 99% using 2 M $LiTFSI$ in THF with 0.1 M ethanol (0.58 vol%) and a 15 bar N_2 atmosphere [25]. Li et al. were able to achieve a current density of $1 A/cm^2_{geo}$ with a faradaic efficiency of 71% using 2 M $LiBF_4$ in THF with 1 vol% ethanol and a 20 bar N_2 atmosphere [44]. These advancements are impressive and show

just how much progress has been made in developing the lithium-mediated system. However, achieving all of these performance metrics in one system that doesn't require a pressurised enclosure would be required to create a commercially viable product.

1.3.1 State-of-the-Art

While most early studies have employed batch-type reactors, these suffer from inherent limitations in scalability, stability, and control over mass transport. Recent developments in continuous-flow cell designs have marked a pivotal shift, positioning flow reactors as the state-of-the-art approach for Li-NRR [26], [29]. Initial challenges in Li-NRR stemmed from the use of sacrificial proton sources and unstable solvent systems [34]. Early systems often employed tetrahydrofuran (THF) as the electrolyte solvent [21], [42], but its low boiling point and tendency to undergo polymerisation rendered it unsuitable for long-term operation [45]. Additionally, sacrificial solvents as proton donors led to instability and inefficiency in sustained ammonia production.

To overcome these limitations, recent advances have coupled Li-NRR with the hydrogen oxidation reaction (HOR) at the anode, using molecular hydrogen as a sustainable proton source. Fu et al. introduced a continuous-flow electrolyser incorporating a PtAu alloy anode (see illustration in **Error! Reference source not found.**), which demonstrated exceptional stability and catalytic performance for HOR in organic solvents [29]. This alloy not only mitigated the decomposition of the electrolyte but also ensured steady proton delivery, achieving a faradaic efficiency (FE) of up to $61 \pm 1\%$ and an energy efficiency (EE) of $13 \pm 1\%$ at -6 mA cm^{-2} and 1 bar pressure [29].

Building upon this, Li et al. achieved the first long-term, gram-scale continuous ammonia synthesis using a chain-ether-based solvent (diglyme), in a 25 cm^2 gas diffusion electrode (GDE)-based flow reactor. Diglyme was found to be resistant to polymerisation, had a high boiling point, and formed a compact SEI layer that facilitated the release of ammonia in the gas phase. Using a controlled potential cycling strategy, they sustained continuous ammonia production for over 300 hours with an FE of $64 \pm 1\%$ and nearly 98% of the product distributed in the gas phase [26]. Producing ammonia in the gas phase is particularly important for practical applications, as it enables easier separation, collection, and integration into downstream processes compared to dissolved ammonia, thereby improving the overall efficiency and scalability of electrochemical nitrogen reduction systems.

Critically, the use of high-surface-area GDEs enabled efficient access of both N_2 and H_2 to the reactive interface, overcoming the mass transport limitations inherent in batch configurations. The reactor design also allowed for operation at higher current densities (up to -60 mA cm^{-2}) without compromising efficiency or selectivity [26]. These innovations represent a substantial leap forward in the development of scalable, high-performance systems for ammonia synthesis, with the startup Nitrovolt already planning to commercialise this technology.

1.4 Key Aspects of the Lithium-Mediated System

1.4.1 The Solid-Electrolyte Interphase (SEI)

The term SEI actually comes from the Li-ion battery field where many studies have been done on the battery SEI as its structure is critical to battery performance and longevity. The SEI is a passivating layer that forms on the graphite or Li metal anode (N.B. in battery literature, the conventional electrodes are switched, so the battery anode would be analogous to the Li-NRR cathode, where Li metal is deposited) due to electrolyte decomposition at negative potentials. Its formation is thermodynamically favourable below the reduction potential of the electrolyte components (typically <1 V vs Li^+/Li) [46]. In batteries, the SEI functions as an electrically insulated passivating layer, preventing continuous electrolyte reduction and protecting the underlying Li metal from parasitic side reactions, while still allowing Li^+ transport [47]. The battery SEI is composed of inorganic and organic components such as LiF , Li_2CO_3 and ROLi that come from the reductive decomposition of salt and solvent in the electrolyte [48], [49]. Battery SEI formation usually occurs in the first few cycles but can evolve over time through cracking, reforming and growth [50].

Similarly, the SEI in In Li-NRR, is formed at the electrode surface due to electrolyte decomposition, and acts as a chemically and electronically distinct layer that influences nearly every aspect of electrochemical performance. Figure 1.6 shows a schematic diagram of an SEI formed with LiBF_4 and the microscopy cross section of an SEI formed with 1 M LiNTf_2 in THF with 0.15 vol% ethanol. A functional SEI is critical for enabling selective and efficient ammonia production, serving several key roles. Firstly, it provides physical and chemical protection to the electrode surface, suppressing further electrolyte degradation and stabilising the interface [51], [52]. Secondly, it regulates ion transport by allowing lithium-ion conduction while limiting electron transfer, thereby maintaining the balance between electrochemical activity and chemical stability [9], [10]. Thirdly, the SEI directly impacts reaction pathways: McShane *et al.* demonstrated that modifying SEI composition can suppress parasitic hydrogen evolution, thereby enhancing selectivity for ammonia formation [53]. The SEI is not merely a passive byproduct of electrolysis but an active component that must be carefully understood and engineered to achieve high performance in lithium-mediated nitrogen reduction.

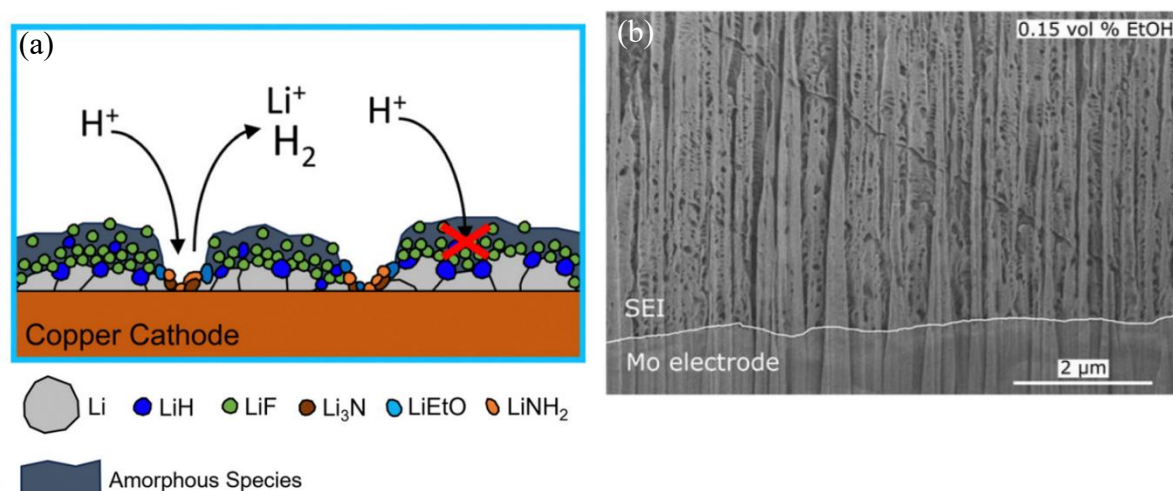


Figure 1.6: a) Schematic illustration of the SEI on a Cu working electrode in a LiBF_4 -based electrolyte with ethanol. Reproduced with permission from [54]. b) Scanning electron microscopy micrographs of

SEI cross section obtained in 1 M LiNTf₂, THF with 0.15 vol % ethanol electrolyte after -10 C was passed at a constant current of -2 mA.cm⁻² on a Mo working electrode. Figure reproduced from [40].

SEI formation occurs when lithium metal deposition potentials cause electrolyte reduction. Common components of the electrolytes used in lithium-mediated nitrogen reduction, such as ethers (like THF and diglyme) and salts (like LiTFSI), are particularly susceptible to decomposition under strongly reducing conditions [34], [36]. These decomposition reactions generate a heterogeneous mixture of inorganic and organic species that nucleate and grow to form the SEI. Deissler *et al.* used operando grazing incidence wide-angle X-ray scattering (GI WAXS) to identify SEI components and found that common inorganic components include LiF, Li₂CO₃, and LiOH [54], while Spry used in-situ infrared spectroscopy to determine that organic fragments were typically derived from solvent decomposition and included lithium alkoxides and polymerised ethers [55]. However, the composition and structure of the SEI can vary significantly depending on the electrolyte formulation, current density, and presence of additives like ethanol or water [53], [55].

A significant component of the SEI is metallic lithium which has been quantified using titrations by Tort [6] and seen with electron microscopy techniques by Westhead *et al.* and Steinberg *et al.* [40], [56]. Lithium buildup arises from continuous plating of lithium under strongly negative potentials [6] and is likely responsible for continued ammonia generation even after current is no longer supplied to the system, which has been reported by Andersen *et al.* and Krempel *et al.* [34], [35]. This phenomenon has led to the development of pulsed electrolysis, where current is applied intermittently to allow controlled lithium deposition. By tuning the duration and frequency of these pulses, it is possible to strike a balance between generating sufficient active lithium for effective nitrogen reduction while minimizing the accumulation of residual, inactive lithium. Li *et al.* utilise a strategy known as controlled cycling (where the length of the rest period of each pulse is determined by the electrode's potential) to improve the faradaic efficiency and longevity of a continuous lithium-mediated nitrogen reduction flow cell [26].

In summary, the SEI plays a critical role in enabling lithium-mediated nitrogen reduction by providing selective ion transport, protecting the electrode surface, and influencing interfacial reaction pathways. Its composition is highly sensitive to multiple factors, including the electrolyte formulation (solvents, salts, and additives) and operating potential. The SEI consists of inorganic and organic components such as LiF, Li₂CO₃, and LiOH, lithium alkoxides, and polymeric degradation products. Another key component is metallic lithium which remains chemically active, sustaining ammonia production even after electrolysis ceases. This has led to the development of intermittent current techniques (pulsing) to improve system performance and stability. By carefully tuning pulse parameters, these approaches aim to maximize ammonia yield while limiting lithium accumulation.

1.4.2 The Importance of Electrolyte Composition

Electrolyte composition is a critical factor that significantly influences the efficiency, selectivity, and stability of lithium-mediated nitrogen reduction system. A suitable electrolyte must support efficient lithium-ion transport and deposition, have high N₂ solubility and diffusivity, exhibit high ionic conductivity to minimize ohmic losses, remain electrochemically and chemically stable under strongly reducing and oxidizing conditions, and it must enable the

formation of a functional SEI. There are many parameters of electrolyte composition that can be varied to achieve these characteristics but the most studied so far are: choice of solvent, choice of proton source, choice of lithium salt, and the salt concentration. Each of these factors will be explored in greater detail.

Choice of Solvent

The vast majority of lithium-mediated reduction reaction studies have employed ether-based solvents due to their excellent ability to dissolve lithium salts and form stable coordination complexes with Li^+ ions [42]. The original solvent in this field is THF, used since the foundational work of Tsuneto et al. [33], and continues to be widely adopted in modern studies [25], [29], [40]. Despite its widespread use, THF poses two major limitations for long-term operation: volatility and tendency to polymerise. Under ambient conditions, THF's high vapor pressure leads to solvent loss in poorly sealed or long-duration experiments. More critically, THF is highly susceptible to cationic ring-opening polymerization, particularly when exposed to oxidative environments or strong Lewis acids [57], [58]. To overcome these drawbacks, chain ether (glyme) solvents have gained attention as promising alternatives. Notably, diglyme (diethylene glycol dimethyl ether) offers superior chemical and physical stability: it has a high boiling point ($\sim 162^\circ\text{C}$), is far less volatile, and is less prone to polymerization [26]. Glymes also resist oxidative decomposition better than THF due to the formation of more stable complexes with lithium ions [59]. While other solvents such as dimethoxyethane (DME)[26] have been used, THF and diglyme are the most used, with diglyme showing greater promise in the use of commercial systems.

Choice of Proton Source

The choice of proton source in Li-NRR is very important in determining system performance and stability. If the pK_a of the proton source is too low, the resulting high proton activity favours HER, which competes with and suppresses nitrogen reduction. Conversely, if the pK_a is too high, the limited proton availability can impede ammonia synthesis, leading to the accumulation of lithium metal and lithium nitride on the electrode surface [41]. The seminal work of Tsuneto et al. on the lithium-mediated system used ethanol as the proton source [21], but it was soon followed by a study that also tested acetic acid, water, methanol, 2-propanol, 1-propanol, and 2-methyl-2-propanol [60]. Of these, only 2-propanol showed performance comparable to ethanol. While 1-propanol, methanol, and water also produced ammonia, they did so with significantly lower faradaic efficiency. The difference in performance among these proton sources was attributed to their protic strength, with only 'moderately protic' sources yielding ammonia. Further, more comprehensive testing of various proton sources in the lithium-mediated system was performed by Lazouski [61], the results are shown in Figure 1.7. Lazouski found that linear aliphatic alcohols produced the highest faradaic efficiencies towards ammonia and attempted to correlate the performance of the proton sources tested with their pK_a values. They found no significant correlation between pK_a and faradaic efficiency towards ammonia, except that all proton sources that successfully produced ammonia were found within a narrow range of pK_a values. This suggests that pK_a is an important parameter in proton source selection but is not the only determinant of performance in Li-NRR. Although

significant opportunities remain for further investigation and optimisation of proton sources, the most commonly employed is still ethanol, which plays a multifaceted role in Li-NRR (see Section 1.4.3).

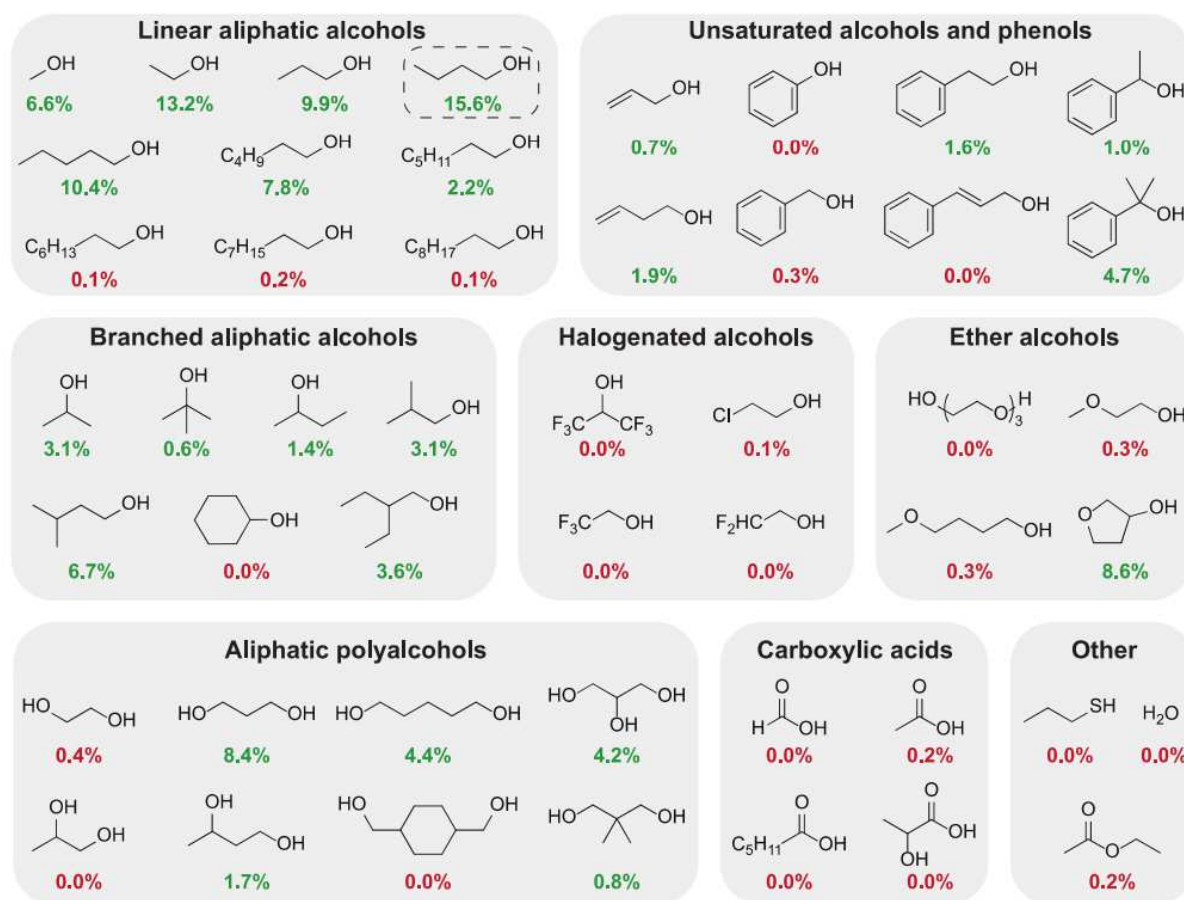


Figure 1.7: Maximum obtained ammonia Faradaic efficiencies for a variety of tested proton donors. Proton donors for which FE values are given in green are classified as active (NH_3 FE > 0.5%), while those in red are classified as inactive (NH_3 FE < 0.5%). Note that the conditions at which maximum reported FEs were obtained differ between proton sources but all utilised 1 M LiBF_4 in THF. Figure reproduced from [61].

Choice of Salt

The lithium salt plays a critical role in lithium-mediated nitrogen reduction by influencing ionic conductivity, solvation structure, SEI formation, and lithium deposition morphology. The most common salts used in lithium-mediated nitrogen reduction include lithium perchlorate (LiClO_4) [21], [42], lithium tetrafluoroborate (LiBF_4) [26], lithium hexafluorophosphate (LiPF_6) [31], lithium triflate (LiOTf) [35], and lithium bis(trifluoromethanesulfonyl)imide (LiNTf_2 or LiTFSI) [25]. Early studies, such as those by Tsuneto et al., employed LiClO_4 due to its high solubility in ether solvents like THF and its established use in non-aqueous electrochemistry. However, concerns over perchlorate's oxidative instability, coupled with the need for improved SEI properties, led researchers to explore alternative salts. This prompted a shift toward lithium LiTFSI , known for its higher ionic conductivity and favourable ion-pairing characteristics [31]. The bulky TFSI^- anion promotes the formation of Li^+ -rich SEIs containing stable inorganic species like LiF , which enhance interfacial stability and suppress solvent decomposition [40]. More recently, attention has turned to LiBF_4 which exhibits reasonable

solubility in ethers and facilitates the formation of a more compact SEI [31] which has led to systems with higher efficiencies, stability and higher proportion of gas phase ammonia [26]. A systematic comparison of lithium salts by Fu et al. highlighted the profound impact of salt identity on electrode surface chemistry, SEI morphology, and ammonia selectivity, reinforcing salt selection as a central design parameter in the development of high-performance lithium-mediated systems [31].

Effect of Salt Concentration

The salt concentration in electrolytes significantly influences the efficiency and stability of lithium-mediated nitrogen reduction. Westhead et al. systematically investigated this relationship, demonstrating that electrolyte stability, faradaic efficiency, and SEI composition are highly sensitive to changes in lithium salt concentration [42]. They found that salt concentration has a strong effect on system performance, as seen in the Figure 1.8a. Their study found that at low LiClO_4 concentrations (e.g., 0.2 M), the electrolyte exhibited substantial instability, evident through rapid electrode potential drift, which compromised electrochemical performance. Conversely, at moderate concentrations (~ 0.6 M), electrolyte stability markedly improved, alongside peak faradaic efficiencies of approximately 7.8%. These benefits stem from increased incorporation of salt anions into the lithium solvation shell, resulting in the formation of a predominantly inorganic and stable SEI. However, beyond this optimal concentration, further increases in salt content led to reduced ammonia yields due to decreased nitrogen solubility and diffusivity (see Figure 1.8b), alongside potentially enhanced lithium-ion transport favouring lithium plating over ammonia synthesis. These insights highlight the critical role of salt concentration in electrolyte design, balancing SEI stability with reactant transport properties to optimise the practical viability of lithium-mediated nitrogen reduction systems.

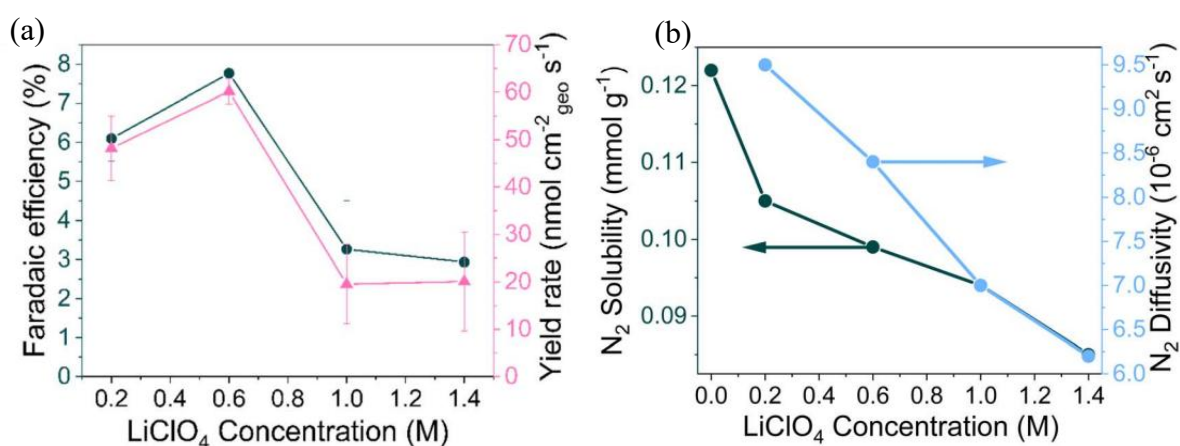


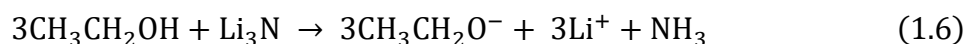
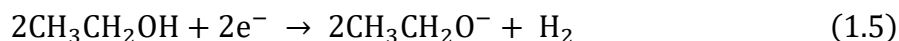
Figure 1.8: a) The change in faradaic efficiency and yield rate with LiClO_4 concentration ($n = 3$ separate experiments, error bar is standard error in the mean) for a chronopotentiometry experiment at an applied constant current of -2 mA cm^{-2} until -10C is passed. b) The change in N_2 solubility and diffusivity in THF at different concentrations of LiClO_4 . Reproduced from [42] with permission from the Royal Society of Chemistry.

1.4.3 The Role of Ethanol

Ethanol plays a multifaceted role in lithium-mediated nitrogen reduction, serving not only as a proton source but also as a key modulator of SEI composition and proton shuttle. In early work on the lithium-mediated system, ethanol was considered a sacrificial proton donor that was required to protonate lithium nitride to ammonia [33], [41], [60]. However, recent work has revealed that ethanol's role is far more complex. It strongly influences the composition and morphology of the SEI, affecting lithium accessibility, interfacial reactivity, and product selectivity.

Ethanol as a Proton Source

Ethanol can act as a direct proton source in the lithium-mediated system to either make H₂ or NH₃ at the cathode. Experimental evidence for this role comes from surface and spectroscopic analyses, which have consistently identified ethoxide as a component of the SEI [40], [53], [55], [62]. The presence of ethoxide confirms that ethanol undergoes deprotonation at the cathode surface. The key ethanol deprotonation reactions are shown in Equation 5 & 5 below.



To investigate the role of ethanol as a proton source further, Lazouski et al. varied ethanol concentration and measured the faradaic efficiency towards ammonia and H₂ in the lithium-mediated system [41]. They found a maximum in the faradaic efficiency towards ammonia with increasing ethanol concentration (as seen in Figure 1.9).

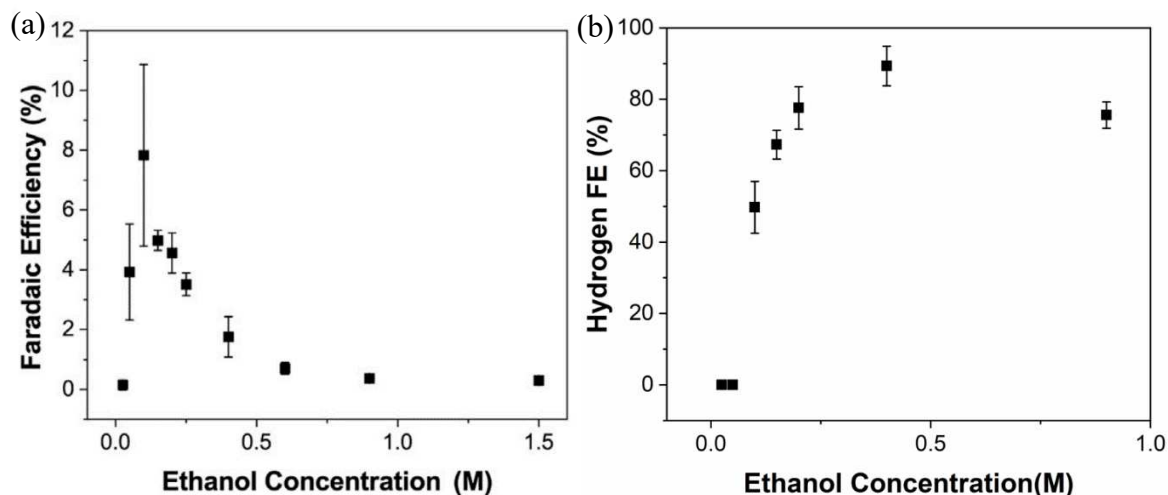


Figure 1.9: Faradaic efficiency towards a) ammonia (left) and b) hydrogen (right) as a function of ethanol concentration in a Li mediated system: 1 M LiBF₄ in THF, copper working electrode and platinum counter electrode. Reproduced with permission from [41].

At lower ethanol concentrations (below ~0.1 M), the faradaic efficiency toward ammonia increases with increasing ethanol concentration. This trend is primarily attributed to ethanol's role as a proton source: when proton availability is limited, intermediates such as Li₃N or

metallic lithium can accumulate on the electrode surface because they are formed more rapidly than they are consumed via protonation. In this regime, a significant portion of the current is diverted to lithium plating or nitridation rather than ammonia production. As ethanol concentration increases, more protons become available to protonate Li_3N , shifting the current toward ammonia formation. At higher ethanol concentrations, however, faradaic efficiency toward ammonia decreases. This is likely due to excess proton activity, which favours HER, thereby consuming the majority of the current. This study demonstrates ethanol's key role as a proton source, the concentration of which must be carefully optimised to ensure adequate protonation of Li_3N while avoiding excess HER.

Ethanol as an SEI Additive

Ethanol's impact on the SEI is particularly notable, Westhead et al investigated the effect of ethanol concentration (0-0.5 vol%) on SEI composition and morphology and how this related to system performance [40]. They found that a narrow optimal concentration window existed at around 0.15 vol% ethanol where the faradaic efficiency peaked to ~32% (Figure 1.10a). This volcano-type dependence can be attributed to two key regimes: at low ethanol concentrations, insufficient proton donor availability results in thick, passivating SEI layers composed largely of THF-derived polymeric species, which inhibit lithium reactivity and facilitate the accumulation of inactive, "dead" lithium; at higher ethanol concentrations, excess protons promote the competing HER, which reduces FE. Furthermore, the efficiency peak corresponded to an SEI composition enriched in LiF , LiH and $\text{Li}_2\text{O}/\text{LiOH}$, with minimal lithium metal (as seen in Figure 1.10b). The absence of ethanol resulted in an SEI that was thick, heterogeneous, and rich in inactive lithium species, leading to poor nitrogen reduction performance.

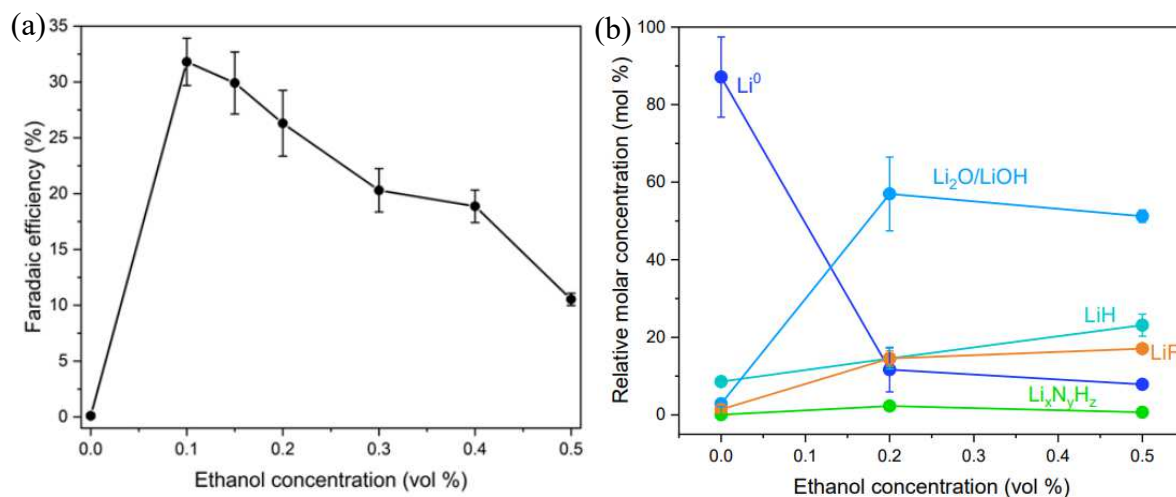


Figure 1.10: a) The variation in Faradaic efficiency towards ammonia after passing -10 C at a constant applied current density of $-2 \text{ mA}\cdot\text{cm}^{-2}$ ($n=3$). 1M LiTfSI in THF electrolyte (Working electrode = Mo foil, counter electrode = Pt mesh, reference electrode = Pt wire). b) Bulk composition of the SEI following its reactive dissolution post measurement and titration of produced analytes (so called SEI titration). Taken after -10 C of charge was passed at -2 mA cm^{-2} on a Mo working electrode in a 1 M LiNTf2 in THF electrolyte containing different ethanol concentrations. Error bars show the standard error in the mean from two separate electrochemical measurements. Figure reproduced from [40].

Supporting evidence from cryo-electron microscopy further corroborates ethanol's effect on SEI morphology. Figure 1.11 clearly demonstrates the substantial influence of ethanol concentration on SEI morphology. In the absence of ethanol, the SEI formed is extremely thick (on the order of tens of microns) and highly inhomogeneous, displaying voids, rough surface features, and possible deposits of 'dead' lithium (Figure 1.11a). This suggests uncontrolled electrolyte decomposition and poor regulation of reactant transport. In contrast, the presence of ethanol leads to a markedly thinner SEI (Figure 1.11b). These ethanol-containing SEIs are also far more uniform in texture and porosity, indicating a more controlled and stabilised interphase formation that likely facilitates balanced transport of lithium ions, nitrogen, and protons, and supports more efficient nitrogen reduction. Furthermore, Steinberg et al. showed that adding ethanol transforms the SEI from a dense, organic film into a more porous, reactive structure that sustains lithium activity toward both nitrogen and proton sources [56]. These structural changes explain the correlation between ethanol concentration and FE. Thus, ethanol functions as a critical SEI additive, tuning the interfacial environment to maintain lithium accessibility and optimize nitrogen reduction selectivity.

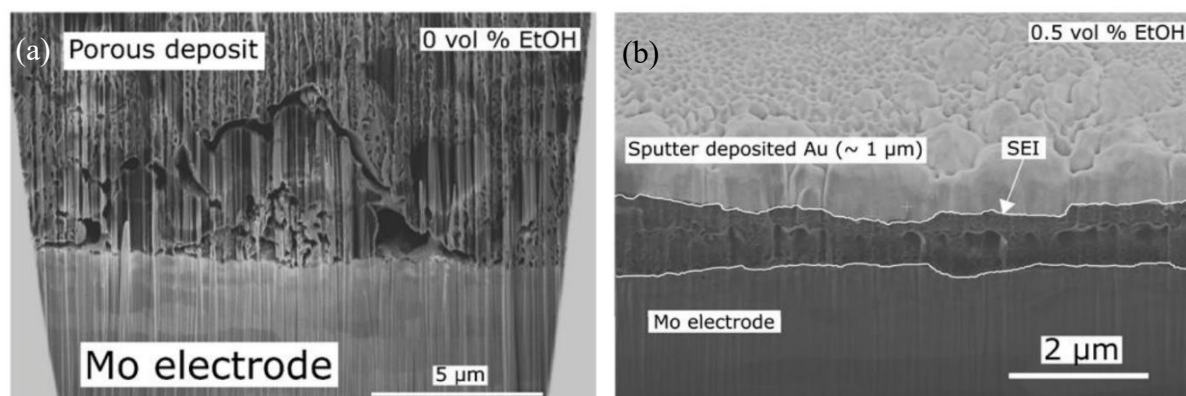


Figure 1.11: Scanning electron microscopy micrographs of solid electrolyte interphase (SEI) cross sections obtained by focussed ion beam milling in a) the 0 vol % ethanol condition (1 M LiNTf₂, THF as majority solvent) and b) 0.5 vol % ethanol electrolyte (1 M LiNTf₂, THF as majority solvent) after -10 C was passed at a constant current of -2 mA.cm⁻² on a Mo working electrode. Figure reproduced with permission from [40].

1.4.4 Electrolyte Decomposition & Acidification

Under the highly reducing conditions of lithium plating and the oxidizing conditions at the counter electrode, the organic electrolyte in lithium-mediated nitrogen reduction inevitably undergoes decomposition reactions. Understanding these reactions is critical because they consume electrolyte components (solvent, salt, ethanol), alter the SEI, can generate byproducts that poison the system and increase the acidity of the electrolyte. This section details the likely electrochemical and chemical decomposition pathways for key solvents (THF, diglyme & ethanol), drawing parallels to known processes in non-aqueous lithium battery electrolytes.

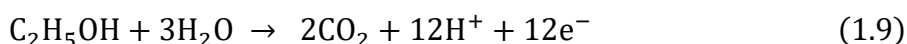
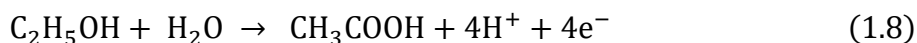
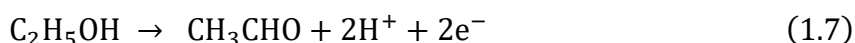
Reductive Decomposition

The reductive decomposition of THF, diglyme and ethanol on the cathode likely leads to deposition of alkoxides which constitute a substantial fraction of the SEI composition. Sažinas et al. used gas chromatography-mass spectrometry to detect the decomposition products of THF and diglyme (as well as DME) in lithium-mediated nitrogen reduction to reveal insights

into decomposition mechanisms. They found that both THF and diglyme were found to decompose through cleavage of ether bonds, driven by the chemical and electrochemical reactivity of metallic lithium under highly negative potentials [32]. Building on this, McShane et al. utilised NMR to analyse the composition of the SEI formed during lithium-mediated electrochemical nitrogen reduction. Their analysis revealed that lithium alkoxides were the dominant SEI constituents [53]. When combined, these studies indicate that the reductive decomposition of THF, diglyme, and ethanol likely proceed via ether bond cleavage, resulting in the formation of lithium alkoxides that accumulate in the SEI. In addition to the generation of alkoxides, diglyme may also reductively decompose to gaseous products as well. Goktas et al. demonstrated that the reduction of diglyme in sodium-based battery systems leads to the evolution of methane (CH₄) and ethylene (C₂H₄), highlighting significant side reactions that compromise electrolyte stability [63]. The researchers employed a combination of analytical techniques, including On-Line Electrochemical Mass Spectrometry (OLEMS, see Section 1.4.3 for further details on this technique), to systematically investigate the gas evolution and structural changes in both sodium metal and graphite electrodes. Their findings revealed that diglyme in the electrolyte is particularly prone to reductive decomposition to CH₄ and C₂H₄, especially when paired with NaTFSI as the salt [63].

Oxidative Decomposition

THF, diglyme, and ethanol can all undergo oxidation at the anode (typically platinum in lithium-mediated systems), and each of these oxidation pathways likely generates protons that contribute to electrolyte acidification. While the exact mechanisms are not known, a number of studies have suggested and provided evidence for likely reaction mechanisms. Firstly, let's consider the plausible mechanisms for ethanol oxidation, drawing on insights from studies performed in aqueous media. One of the most probable reaction pathways is presented in Equation 7, which describes the formation of acetaldehyde and protons without the involvement of additional reactants[64]. Evidence supporting this reaction pathway is provided by the work of Sažinas et al., who detected acetaldehyde in the electrolyte following ammonia electrosynthesis [32]. Further oxidation of ethanol is also possible, although it likely depends on the presence of trace amounts of water or oxygen in the non-aqueous electrolyte (which is plausible under typical experimental setups). The proposed mechanisms for this extended oxidation are shown in Equations 8 & 9, leading to the formation of acetic acid and carbon dioxide. The detection of acetic acid by Sažinas et al. provides supporting evidence for the occurrence of these pathways and implies the presence of trace water and/or oxygen in the system.



While electrochemical oxidation mechanisms of THF on platinum in non-aqueous systems remain relatively underexplored, Mygind et al. propose that THF can undergo anodic oxidation

(by the equation shown in Figure 1.12), potentially serving as a proton source in the absence of ethanol [36].

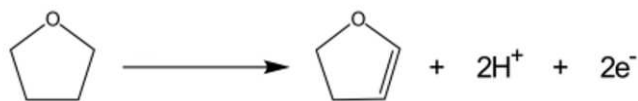


Figure 1.12: Proposed mechanism of THF oxidation at the anode in lithium-mediated nitrogen reduction, generating protons.

For the oxidation of diglyme, we can take inspiration from battery research [59], [63], [65]. The mechanisms of diglyme oxidation are numerous, complex and not well understood but likely involve C–H abstraction (generating protons) and C–O ether bond cleavage. Furthermore, these reactions are greatly accelerated by the presence of O₂ [63].

The effects of acidity in lithium-mediated systems are numerous, and understanding them is essential for improving both performance and stability. Acidity can drive electrolyte degradation, as exemplified by the polymerisation of THF, a reaction initiated by the presence of proton sources [45]. Once triggered, this polymerisation is self-propagating and can result in extensive degradation of the bulk electrolyte from the passage of only a small amount of charge [36]. Additionally, acidity can alter the structure of the SEI, often leading to a thinner and more porous morphology [56]. This can enhance the accessibility of nitrogen and protons to the electrode surface, potentially improving nitrogen reduction performance [40]. However, excessive acidity also accelerates HER, which competes with nitrogen reduction for electrons and thereby reduces the ammonia yield [44, 57]. Moreover, increased proton activity can lead to the protonation of NH₃ to NH₄⁺ [45], suppressing the formation of gas phase ammonia and complicating its extraction. Therefore, acidity is a critical parameter that must be carefully optimised and controlled to maximise the performance and stability of lithium-mediated nitrogen reduction systems.

1.4.5 *Electrode Crosstalk*

In electrochemical systems, crosstalk refers to the undesirable transfer of chemically active species from one electrode to the other, where they can interfere with the electrode reactions. In theory, a counter electrode should not interfere with the working electrode reaction, however, in practice no electrode satisfies this criterion [66]. In the context of lithium-mediated ammonia synthesis, the most significant crosstalk phenomena are ammonia or hydrogen (made at the cathode) diffusing to the anode and getting oxidised, as well as protons generated from anode reactions increasing the acidity of the working electrode environment (as discussed in Section 1.4.4). This can lower overall efficiency, increase the rate of side reactions and degrade the electrolyte (for example, acid-catalysed THF polymerisation). Crosstalk is a well-documented issue in battery systems. In lithium-ion batteries, for instance, transition metal ions such as Mn²⁺ can dissolve from the cathode, migrate through the electrolyte, and deposit onto the anode, where they interfere with the SEI [67], [68], [69], [70]. In this section, we discuss crosstalk phenomena relevant to the lithium-mediated system, namely ammonia oxidation and proton accumulation from anode reactions and these effects can be further exacerbated under high current densities, prolonged electrolysis, electrode proximity and low electrolyte volumes.

In a single-chamber cell, ammonia produced at the cathode is free to diffuse through the electrolyte and reach the anode where it can be oxidised. Ammonia is thermodynamically oxidizable at a relatively low potential, ammonia oxidation onset on platinum in alkaline conditions is around 0.5–0.6 V vs RHE [64], [71]. In an organic electrolyte, the exact potential will likely vary, but ammonia oxidation will likely remain favourable. The risk then becomes that the anode can act as an “ammonia burner”, which effectively creates a futile cycle where ammonia is generated at the cathode and lost at the anode, with no net ammonia accumulation and wasted current. Even partial oxidation of ammonia will lower the net faradaic efficiency. Furthermore, ammonium ions (NH_4^+) are often formed as a result of protonation of electrochemically produced ammonia. Ammonium may also be oxidised at the anode, studies on electrochemical wastewater treatment have shown that NH_4^+ can be oxidized on platinum anodes, yielding nitrogen species & protons [72], [73], [74]. This mechanism would contribute further to electrolyte acidification (as already discussed in Section 1.4.4). As already discussed, the anodic generation of protons can arise not only from ammonium oxidation, but also from hydrogen oxidation and the oxidative decomposition of solvents such as THF, diglyme and ethanol. These mechanisms can steadily increase the proton activity in the bulk electrolyte, which will lead to increased HER activity at the cathode, stabilisation of dissolved NH_3 to NH_4^+ , and disruption of the SEI [40].

1.5 Quantification of Dissolved Ammonia using Colorimetry

As discussed in the scope of this thesis (Section 1.2), ammonia can escape in the gas phase or accumulate in the electrolyte as dissolved NH_3 or NH_4^+ . Therefore, reliable methods of quantifying dissolved ammonia are essential to provide a complete picture of the ammonia yield and distribution. The key challenges of detecting ammonia in the electrolytes used in lithium-mediated nitrogen reduction are low ammonia concentration and interference from organic species and lithium salts. The main techniques that are capable of detecting ammonia in the ppm and sub-ppm levels are NMR, ion chromatography, ion-selective electrode and colorimetric determination [75], [76], [77]. NMR and colorimetric determination are the most commonly used in the field of lithium-mediated nitrogen reduction due to their accessibility, sub-ppm detection levels and moderate resilience to interference from organics and lithium salts. In this project, colorimetric determination was chosen as the primary method of quantifying dissolved ammonia due to accessibility of equipment and existing knowledge of using this technique in the group.

Colorimetric determination of ammonia is usually based on either indophenol (Berthelot) or Nessler’s method [78]. Both methods rely on adding reagents to the sample solution that react with the dissolved ammonia to form coloured compounds that can be detected with a UV-Vis spectrophotometer. The indophenol (Berthelot) method is generally preferred because it is safer (Nessler’s reagent contains mercury) and less prone to interference from metal cations [79]. The Berthelot method was first described in 1859 and involves the formation of indophenol blue dye by the steps illustrated in Figure 1.13. It involves 1) reaction of ammonia with hypochlorite to form monochloramine, 2) reaction of monochloramine with phenol to form benzoquinone chloramine, 3) reaction of benzoquinone chloramine with phenol to form indophenol [80], [81]. A catalyst such as sodium nitroprusside or sodium nitroferrocyanide is typically employed to increase the kinetics. A notable modification to the method was developed in the 1970s and involved replacing phenol with salicylic acid/salicylate salt [82],

[83]. The substitution of phenol increases safety as phenol is highly toxic and reduces interference because of salicylate's lower reactivity decreasing the likelihood of reaction with species other than ammonia [78], [84]. However, the salicylate method is still prone to salt interference [85].

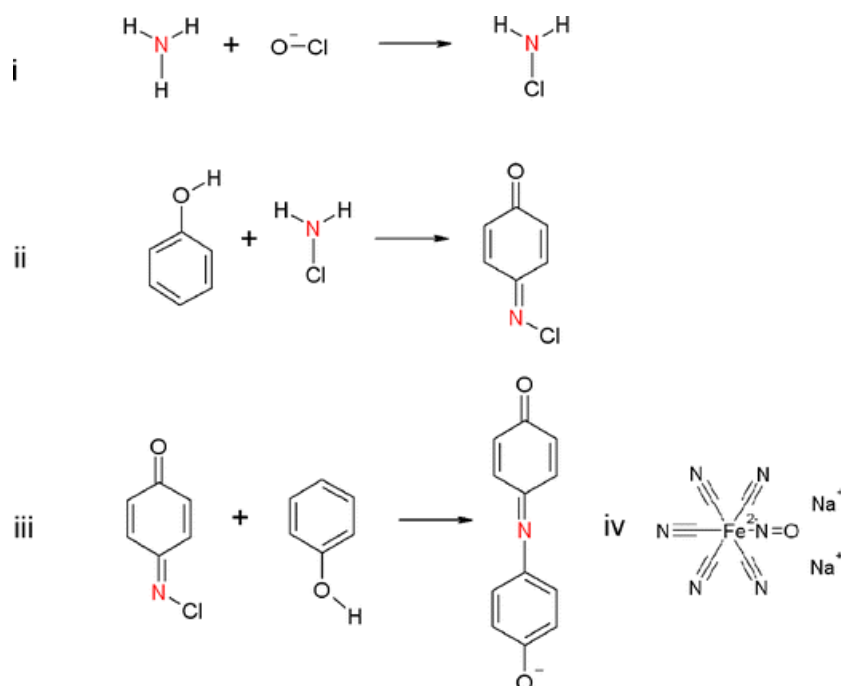


Figure 1.13: Diagram illustrating the steps involved in the Berthelot reaction: i) reaction of ammonia with hypochlorite to form monochloramine, ii) reaction of monochloramine with phenol to form benzoquinone chloramine, iii) reaction of benzoquinone chloramine with phenol to form indophenol and iv) the use of a catalyst, sodium nitroferricyanide here. Reproduced with permission from [80].

Unfortunately though, the Berthelot method was developed in aqueous media and cannot be applied directly to the non-aqueous electrolytes used in lithium-mediated nitrogen reduction. The non-aqueous electrolyte must either first be diluted with water or heated to first evaporate the organic solvent and the remaining solids then dissolved in water. Evaporation has the advantage of higher ammonia concentration (as dilution is not required) and less interference from organics but suffers from longer waiting times (evaporation can take hours) and possible ammonia loss from evaporation or reaction with electrolyte under heating. Dilution has the main advantage of being quicker but also less risk of degrading electrolyte components from heating.

Once the electrolyte has been diluted or evaporated and the chosen reagents added, the absorbance of the sample then needs to be related to a concentration through a standard NH_4^+ solution. This can be done through the use of a calibration curve or through standard additions, (Figure 1.14 graphically shows the differences between quantification using calibration curves vs standard additions). A calibration curve is made by preparing samples with known concentrations of NH_4^+ and measuring their absorbance, the absorbance of the sample is then measured and the corresponding concentration is taken from the calibration curve. Standard addition works by adding known concentrations of NH_4^+ to the sample, the increase in absorbance for a given increase in concentration is used to create a gradient which can be used to calculate the concentration from the absolute absorbance in the sample. The main advantage of the calibration curve method is the time saved by having to prepare less samples. A

calibration curve is only performed once (or once per reagent batch) and then only the absorption of the sample is needed. However, the calibration curve method relies on the assumption that the absorbance for a given NH_4^+ concentration is the same in the calibration solutions as in the sample solution, which is not always the case (see discussion on this later in Section 3.3). More sample have to be prepared each time for standard addition but this method ensures the gradient of absorbance/concentration is obtained in the sample solution, leading to higher accuracy and consistency [86], [87].

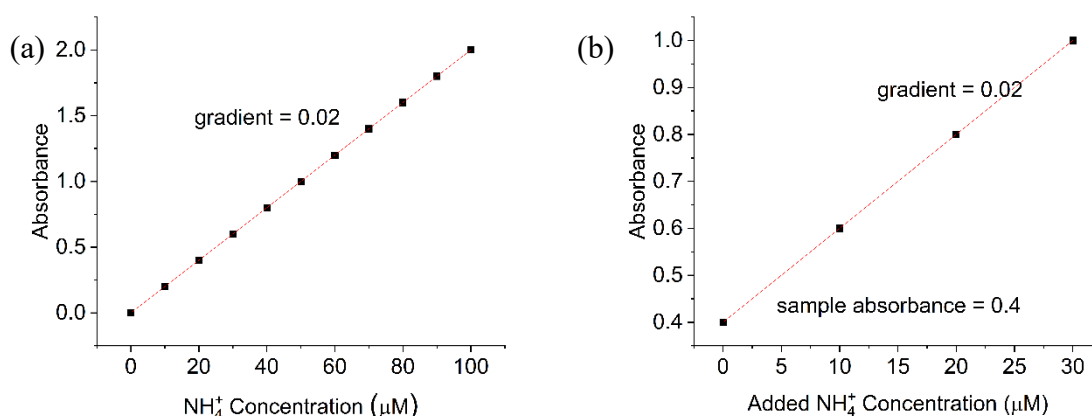


Figure 1.14: Example curves showing a) calibration curve and b) standard addition curve. In both cases, the sample concentration is determined by dividing sample absorbance by the gradient. The key difference is calibration curves are prepared with separate solutions and the sample solution is measured separately, whereas in standard addition, known amounts of NH_4^+ are added to the sample solution.

While the essentials of the Berthelot method have not changed significantly since 1859, several variations exist within the lithium-mediated nitrogen reduction community, the key ones being:

1. Using phenol vs salicylate
2. Diluting vs evaporating the electrolyte
3. Using calibration curves vs standard addition

Different combinations of these variations are used in the lithium-mediated nitrogen reduction community with the justifications not always stated. For example the Chorkendorff group use phenol, evaporation and calibration curves [20], [34], while the Macfarlane group use salicylic acid, dilution and standard addition [25], [88], and the Manthiram group use salicylate, dilution and calibration curves [41].

1.6 Real-Time Quantification Through Mass Spectrometry

Many electrochemical systems exhibit reactions involving gases and or volatile species. Often, these reactions are of great interest, either being the main reactions to be optimised (such as the hydrogen evolution reaction [89], CO_2 reduction reaction [90] or oxygen evolution reaction [91]) or the main parasitic reaction to be avoided (hydrogen evolution in electrodeposition [92] and battery technology [93], [94]). The ability to monitor gases/volatile species in electrochemical systems in real-time provides a unique insight into the mechanisms, thermodynamics and kinetics of these electrochemical reactions. Several techniques have been developed to enable real-time detection of gases/volatiles in electrochemical systems, most of

them utilise mass spectrometry. The key established techniques are Membrane Inlet Mass Spectrometry (MIMS), Differential Electrochemical Mass Spectrometry (DEMS) and On-Line Electrochemical Mass Spectrometry (OLEMS).

1.6.1 Membrane Inlet Mass Spectrometry (MIMS)

MIMS, developed in the 1960s, was the first mass spectrometry technique for detecting gaseous species evolved from liquids and was soon adapted for electrochemical systems [95]. It uses a non-porous, gas-permeable polymer membrane that separates a liquid phase from a vacuum connected to a mass spectrometer [96] (illustration shown in Figure 1.15). Gases diffuse through the membrane, are ionised, and detected. The choice of material for the non-porous polymer membrane strongly affects the relative permeability rates of different gases (CO_2 diffuses much faster than H_2 through polyethylene [96]), which means the membrane can be tailored for selectivity towards specific gases. However, this selectivity limits universal application and the thick non-porous membrane contributes to relatively slow response times (~ 10 s) due to slow diffusion [97], [98]. Despite these limitations, MIMS remains widely used and continues to evolve [98], [99], [100].

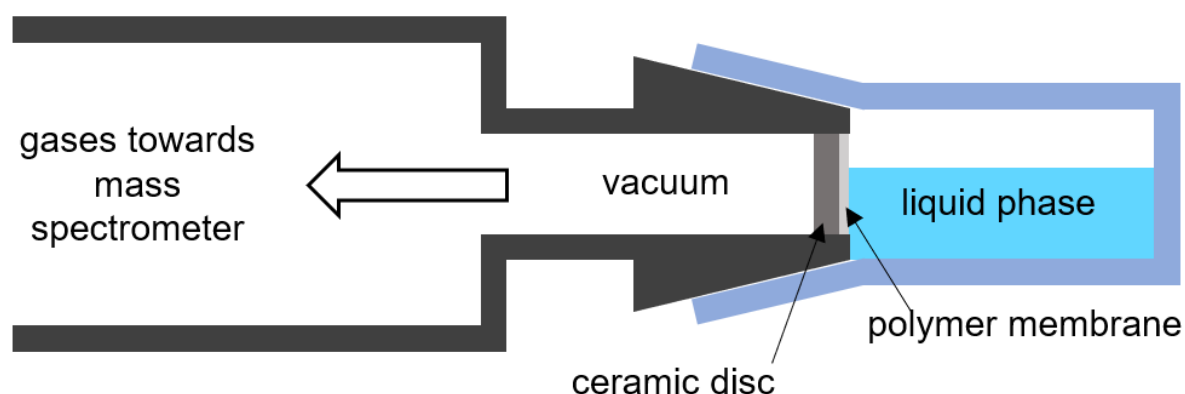


Figure 1.15: Schematic of a typical Membrane Inlet Mass Spectrometry (MIMS) setup. Gases produced in the liquid phase diffuse through a non-porous polymer membrane that is supported by a ceramic disc, and then enter the mass spectrometer for ionisation and detection. Figure recreated based on information from [96].

1.6.2 Differential Electrochemical Mass Spectrometry (DEMS)

The working principle of DEMS is similar to that of Membrane Inlet Mass Spectrometry, with the key distinction being the use of a porous membrane (typically Teflon). This allows for higher gas flux, significantly reduced diffusion times and faster response times (~ 1 s) [101]. However, the increased gas flux necessitates additional vacuum pumping to maintain the mass spectrometer's operating pressure. As shown in Figure 1.16, this additional pumping diverts some of the gas away from the detector, reducing both sensitivity and collection efficiency (the ratio of detected to generated gas). To minimise response time and maximise signal, the gap between the membrane and the working electrode must be small which is most commonly achieved by sputtering the electrode material directly onto a Teflon membrane. Various other configurations also exist, tailored to specific systems and electrode designs [80]. DEMS has

been widely applied to a range of electrochemical systems [85]–[89], notably lithium-ion batteries [88]–[91], demonstrating its suitability for non-aqueous systems as well.

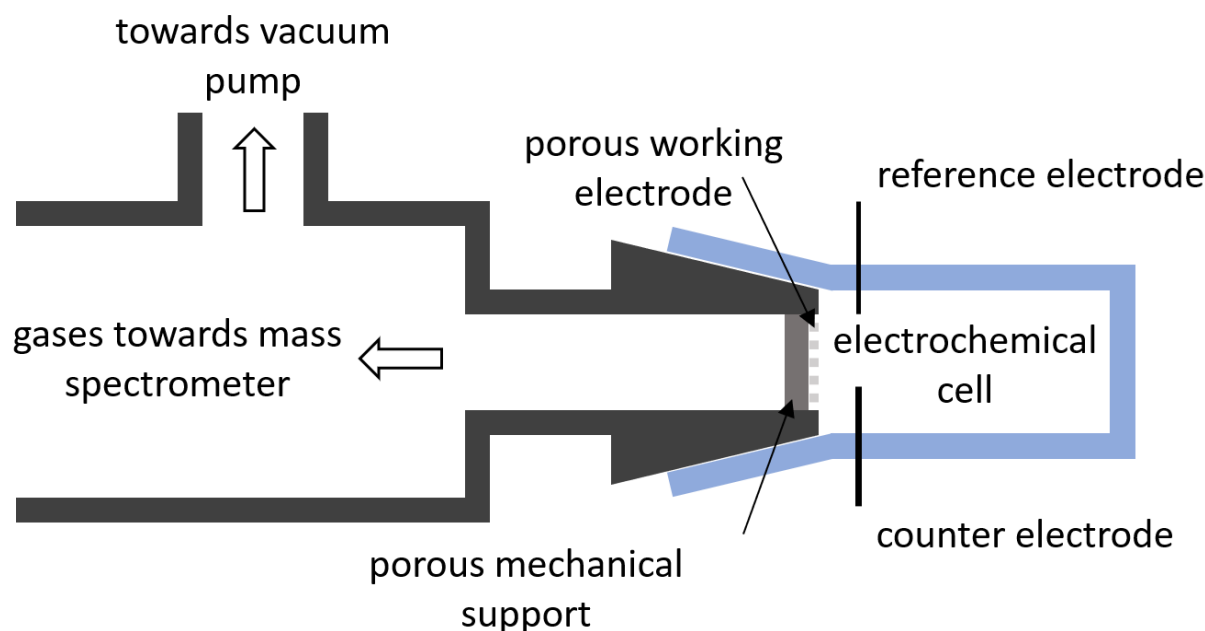


Figure 1.16: Schematic of a typical Differential Electrochemical Mass Spectrometry (DEMS) setup. Gases generated in the electrochemical cell pass through a porous Teflon membrane that is coated with the working electrode material, and then enter the mass spectrometer for ionisation and detection. A portion of the gas is diverted by the pump to maintain vacuum, while the remainder enters the mass spectrometer for detection. Figure recreated based on information from [101].

1.6.3 On-Line Electrochemical Mass Spectrometry (OLEMS)

OLEMS originated from a variation of DEMS called Scanning Differential Electrochemical Mass Spectrometry (SDEMS) in which a porous Teflon membrane sits inside a small capillary inlet which is held over the working electrode and samples the gases being evolved (as can be seen from Figure 1.17) [102]. The key variation that separates OLEMS from SDEMS is that the size of the inlet has been appropriately miniaturised to reduce the gas flux entering the vacuum side such that differential pumping is no longer required [103]. This allows for a reasonably fast response time (2-10 s) while eliminating the need for differential pumping. However, this comes at the cost of significantly reduced collection efficiency as only a portion of the gases generated enter the mass detector. Nevertheless, the technique has provided valuable information for the understanding of many electrochemical reactions such as CO₂ reduction and oxygen evolution [104], [105], [106], [107].

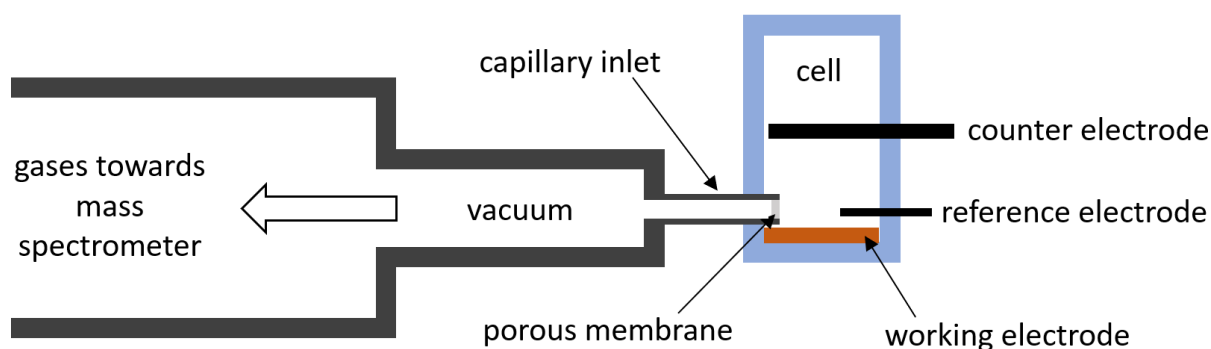


Figure 1.17: Schematic of a typical On-Line Electrochemical Mass Spectrometry (OLEMS) setup. Gases generated at the working electrode diffuse through a porous membrane in the capillary inlet, which enables fast response while limiting gas flux. This eliminates the need for differential pumping. The gases then enter the mass spectrometer for detection. Figure recreated based on information from [102], [103].

1.6.4 Summary of the Established Techniques

Table 1.1: Summary of the key differences between the different established electrochemical mass spectrometry techniques and their corresponding response times.

Technique	Approximate Response time	Summary
Membrane Inlet Mass Spectrometry	>10 s [97], [98]	Uses non-porous polymer membrane, whose selectivity can be tailored
Differential Electrochemical Mass Spectrometry	>1 s [101]	Uses porous electrode membrane, requires differential pumping which lowers collection efficiency
On-Line Electrochemical Mass Spectrometry	2-10 s [102]	Uses capillary inlet with porous membrane.

MIMS, DEMS, and OLEMS have proven invaluable for probing gas-evolving electrochemical systems. These methods enable real-time detection of gaseous products, offering key insights into reaction mechanisms, selectivity, and kinetics. Each technique, however, presents distinct trade-offs, which are summarised in Table 1. MIMS offers simplicity and selectivity but suffers from slow response times due to its non-porous membrane. DEMS improves time resolution using a porous membrane but requires differential pumping, which reduces sensitivity. OLEMS eliminates the need for additional pumping with a capillary-based inlet, but this can limit the total gas flux reaching the detector. These techniques leave a gap in fully capturing fast, transient gas-evolution dynamics with high sensitivity, highlighting the need for further innovation in real-time gas detection techniques for electrochemical systems.

1.7 Electrochemistry-Mass Spectrometry (ECMS)

1.7.1 *Introduction*

The established techniques discussed in the previous section have been used extensively over the last few decades to study electrochemical reactions involving gases. However, they often have collection efficiencies well below 100% and no single technique can be optimised for high collection efficiency, fast response time and low detection limit. Vesborg & coworkers at DTU physics recognised these limitations in real-time gas detection and spearheaded the development of a novel chip-based technique that allowed fast (<1 s for H_2) and sensitive (~ 0.3 pmol/s for NH_3) detection of volatile species evolved from electrochemical systems [108], [109], [110]. Importantly, the innovation was not confined to the lab, it led to a commercial venture: SpectroInlets, a company founded in Copenhagen, Denmark, which commercialised chip-based ECMS in 2016. Scott developed the technique further to utilise isotope-labelling to study the Oxygen Evolution Reaction (OER), demonstrating the remarkable capabilities of the ECMS system in uncovering mechanistic insights in electrochemical reaction [111]. The SpectroInlets EC-MS system is now used in various labs for *in-situ* electrochemical analysis and represents the current state-of-the-art in coupling electrochemistry with mass spectrometry. It achieves the long-sought combination of fast response, high sensitivity, 100% collection efficiency and quantitative accuracy, opening new possibilities for studying electrocatalytic reactions in real time.

Figure 1.18 shows a simplified diagram of the key elements in the ECMS system. Gases/volatile species evolved at the working electrode diffuse through the thin layer of electrolyte and enter the sampling volume in the chip via the surface pores. The sampling volume is pressurised by a ‘backing’ gas which stabilises the gas-liquid interface present at the surface of the membrane but can also be used to introduce reactive gas into the electrochemical system. A small capillary below the sampling volume directs gas flow to the mass spectrometer. This design, much like OLEMS, precisely tailors the gas flow to eliminate the need for differential pumping. The composition and pressure of the backing gas in the sampling volume is controlled externally with mass flow controllers and pressure controllers [110]. One of the unique advantages of this system is that the backing gas is not only used to support the liquid on top of the membrane but can also be used to dose the electrochemical cell with different gases. This is particularly useful if the electrochemical system under investigation utilises gaseous reactants or when gases can bind to the electrocatalytic surface and be used to probe it. Furthermore, the external control system allows fast switching between different gases which is incredibly useful for investigating the binding and poisoning properties of different gases on electrocatalytic surfaces. The numerous advantages of this system stem from its use of a uniquely engineered silicon membrane chip.

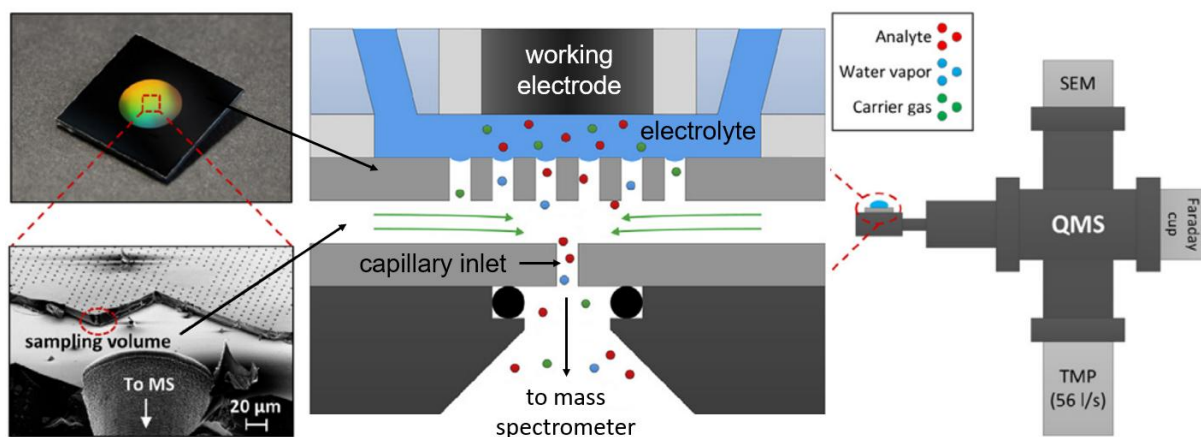


Figure 1.18: Simplified schematic of the stagnant thin-layer electrochemical cell, silicon membrane chip and mass spectrometer setup used in the ECMS system. Volatile species evolved at the working electrode diffuse through a thin ($\sim 100\ \mu\text{m}$) electrolyte layer and enter the chip's sampling volume via surface pores. The pressure within the sampling volume is stabilized by an externally controlled flow of a backing gas. This gas stream (containing analyte species, solvent vapor, and carrier gas) is directed through a microfabricated capillary to the mass spectrometer for detection. Adapted with permission from [110].

The membrane chip is manufactured using the same processes utilised in the semiconductor industry and include UV lithography, ion etching and molecular vapour deposition [110]. These processing techniques allow the creation of nanostructures with great control and customisation while being scalable. From Figure 1.18 it can be seen that the membrane chip consists of three main structures: the top surface pores which are $2.5\ \mu\text{m}$ in diameter; the sampling volume which is $3\ \mu\text{m}$ in height and the capillary inlet. The combination of a thin sampling volume and abundance of surface pores means that the liquid directly above the membrane equilibrates quickly with the sampling volume and the partial pressure of a gas/volatile species in the sampling volume is proportional to its concentration in the liquid above the membrane. The geometry of the capillary ensures that the total flux to the mass spectrometer is close to the maximum desired flux which is around $2\ \text{nmol s}^{-1}$. Since the flux to the mass spectrometer is fixed, quantification is possible when a calibration is used. By fixing the partial pressure of the species of interest and measuring the signal for the dominant mass fragment associated with it, the two can be related by a sensitivity factor. By repeating this for different species and different mass fragments, one can build up a sensitivity matrix which can be used to convert m/z signals back into partial pressures. The partial pressure can be converted to a concentration in the liquid directly above the membrane using Equation 6, where p^s is the partial pressure of species s in the sampling volume, K_H^s is the Henry's law volatility constant for species s and c^s is the concentration of species s in the electrolyte just above the membrane.

$$p^s = K_H^s c^s \quad (1.10)$$

1.7.2 Adaptation for Non-Aqueous Electrochemistry

Organic solvents typically have reduced surface tension compared to water. This means that the membrane chips used in traditional ECMS are unable to maintain the liquid-gas junction when organic solvents are used. To overcome this, Spectro Inlets designed a non-aqueous chip that comes with a polymer coating to stop the penetration of organic solvents into the chip's sampling volume. However, to maintain performance, these coating are very thin and highly

susceptible to scratching, which ruins their ability to resist organic electrolytes. Furthermore, the cell that is typically used with Spectro Inlets' system (shown in Figure 1.19a) has a relatively large distance between the working electrode and counter electrode which is not usually a problem for aqueous electrolytes with relatively low resistivities. However, for non-aqueous electrolytes, where resistivity is typically higher, the ohmic drop between the working and counter electrodes would be too great and the potentiostat would be unable to supply such a high compliance voltage. Furthermore, it is desirable to have the working and counter electrodes parallel to create a more even current density distribution around the working electrode which helps to create a more uniform SEI. These two factors make the cell unsuitable for the non-aqueous electrochemistry. Thornton et al. in our group (Interfacial Electrochemistry Group, Imperial College London) developed a new cell design that optimised the ECMS system for probing gas-evolving degradation mechanisms in lithium-ion batteries [112]. Several changes had to be made to the cell used in previous ECMS studies and can be seen from Figure 1.19b, which compare both cell designs. Firstly, the reference electrode is a wire that comes in through a port in the cell which allows it to be very close to the working electrode. The working electrode is a thin mesh (to allow gas diffusion towards the chip) that sits under the counter electrode with a separator in between to prevent short circuiting. The working electrode is contacted by a wire that comes in from the other port. Finally, another separator sits between the working electrode and membrane chip to prevent scratching the fragile coating of the chip. These alterations allow much higher current densities to be used and create a more uniform current distribution [113].

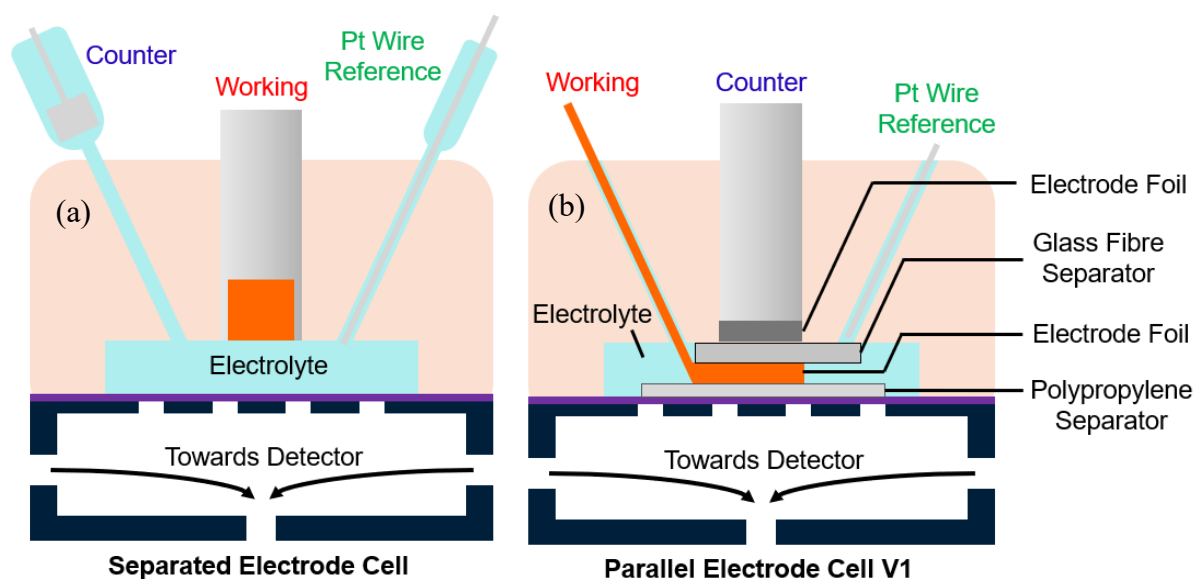


Figure 1.19: Schematic diagram of left) the original ECMS cell used for aqueous electrochemistry (referred to as the separated electrode cell and right) the modified ECMS cell, optimised for non-aqueous lithium-ion battery electrochemistry (referred to as the parallel electrode cell).

1.7.3 Use in Lithium-Mediated Nitrogen Reduction

The adaptation of the ECMS system for probing ammonia synthesis in the lithium-mediated system was pioneered by Krempel et al. [35]. The work utilised two counter electrodes in the separated electrode cell shown in Figure 1.19a, to improve the current distribution, however, the large distance between the working and counter electrodes still limited current densities.

Krempl et al. utilised soft ionisation and chamber heating to overcome the main challenges in real-time ammonia detection which were strong adsorption of ammonia on chamber walls and overlapping mass fragment signals with water.

In the field of mass spectrometry, ammonia is known to adsorb onto tubing, chamber walls and inlets, which interferes with accurate detection, especially for real-time detection as it can introduce significant response time delays [114], [115], [116]. In the case where only small amounts of ammonia are made, a majority portion of this could simply be adsorbed within the tubing of the detection system and only an insignificant amount would reach the detector, too low to detect. A potential solution is to heat the vacuum chamber to reduce the amount of ammonia adsorption and hence increase the amount reaching the detector.

The other main challenge is the interference from water. The mass spectra of water and ammonia (shown in Figure 1.20) share a common peak: m/z 17. The NH_3^+ fragment (17.03 amu) in the ammonia mass spectrum and the OH^+ (17.01) fragment in water cannot be distinguished with a quadrupole detector such as the one used in the ECMS system because the resolution is too low [108], [110], [117]. Therefore, if the amount of water in the mass spectrometer is significantly higher than the amount of ammonia, the ammonia signal may become overshadowed. Furthermore, a changing water signal may (falsely) be interpreted as ammonia evolution. A technique known as ‘soft ionisation’ can be used to overcome this interference [118], [119]. Soft ionisation involves lowering the ionisation energy of the emission which leads to significantly less fragmentation. In the ‘soft ionization’ ECMS technical note, lowering the ionisation energy to 20 eV eliminates the m/z 17 peak from the water mass spectrum [120]. Therefore, soft ionisation can significantly reduce or even eliminate (depending on the ionisation energy chosen) interference from water. Krempl et al. utilised both chamber heating and soft ionisation to successfully detect in-situ-synthesised gas phase ammonia in real-time using ECMS [35].

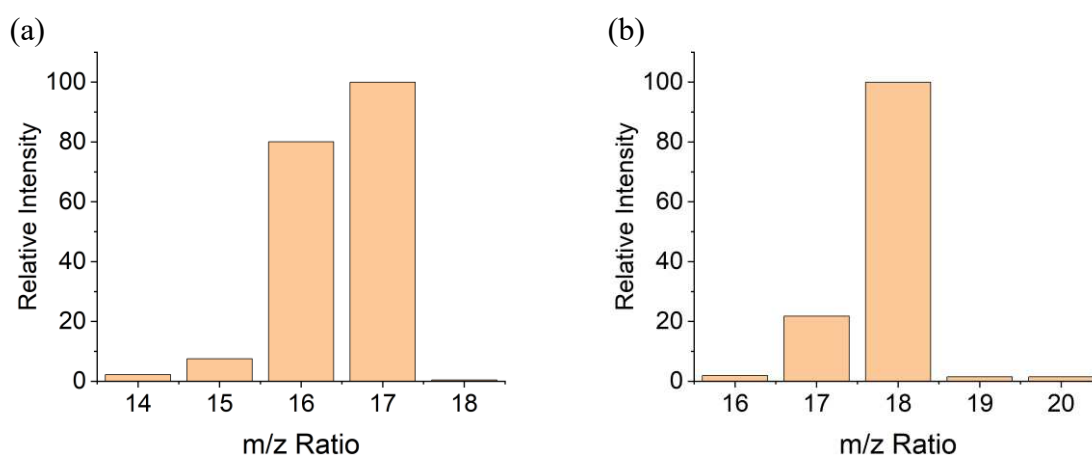


Figure 1.20: Reference mass spectrum for a) ammonia and b) water. Figure created from data taken from NIST database [121].

1.8 Summary

Lithium-mediated nitrogen reduction has emerged as a promising electrochemical route for ammonia synthesis under ambient conditions, offering a sustainable alternative to the Haber–Bosch process. The system's unique capability arises from the strong reducing power of lithium

metal, which facilitates dinitrogen (N_2) activation and promotes ammonia formation. In recent years, substantial progress has been made in understanding the fundamental components of lithium-mediated nitrogen reduction. Key research efforts have focused on SEI formation and composition, the importance of electrolyte formulation (including solvent and salt effects), the role of ethanol as a proton donor and SEI modifier, electrolyte decomposition pathways, and the development of analytical techniques for ammonia detection.

Despite these advancements, several critical gaps remain in the current understanding of the system. Firstly, the mechanisms underlying electrolyte decomposition, particularly the oxidative and reductive breakdown of common ether solvents such as THF and diglyme, remain poorly defined. Although several studies have proposed likely intermediates and degradation products, there is limited consensus on the dominant reaction pathways, their electrochemical onset potentials, or how decomposition impacts SEI integrity and system longevity. Secondly, the role of acidity in non-aqueous environments is not fully understood. Acidification arising from anode reactions, including hydrogen oxidation and solvent decomposition, alters electrolyte properties and can significantly affect side reactions such as HER. Furthermore, the influence of proton activity on the ammonia/ammonium equilibrium in non-aqueous solvents, such as THF and diglyme, has yet to be rigorously characterized. Thirdly, while ammonia detection techniques have been widely applied in the literature, there remains no universal consensus on best practices for quantifying dissolved versus gas phase ammonia in lithium-mediated systems.

This project aims to address these open questions about technique development and application. A primary objective is to refine and validate detection methodologies, particularly UV-Vis colorimetry and ECMS, for accurate quantification of both dissolved and gas phase ammonia. By systematically evaluating the limitations and error sources associated with these techniques, the project seeks to establish more rigorous, standardized protocols for ammonia measurement in lithium-mediated systems. Building on these improved detection capabilities, the project will also explore the mechanisms of electrolyte decomposition in lithium-mediated systems. This includes identifying the electrochemical conditions under which solvents like THF and diglyme degrade, characterizing their decomposition products, and assessing the likely mechanisms. Through this investigation, the project aims to generate new mechanistic insights that can inform the rational design of more stable systems, ultimately advancing the development of robust, high-performance lithium-mediated nitrogen reduction technologies.

2 Experimental Methods

2.1 Theoretical Background

2.1.1 *Electrochemistry*

This section provides a brief introduction into the most relevant concepts in electrochemistry, for a deeper exploration of the fundamentals, readers should consult the work of Bard & Faulkner [66]. Electrochemistry is the branch of physical chemistry concerned with the interplay between electrical energy and chemical change. It encompasses the study of redox reactions in which electrons are transferred between chemical species at the interface between an electronic conductor (typically a metal electrode) and an ionic conductor (the electrolyte). These electron-transfer reactions underlie a wide range of technologies, from batteries and fuel cells to corrosion and electrocatalysis. In an electrochemical cell, externally applied or internally generated electrical potentials can drive thermodynamically non-spontaneous reactions, enabling precise control over chemical transformations. At thermodynamic equilibrium, the equilibrium potential E_{eq} of an electrode is described by the Nernst equation (Equation (2.1)), which relates the potential to the concentrations (or more precisely, activities) of redox species involved in a half-reaction (Equation (2.2)).



$$E_{eq} = E^\circ - \frac{RT}{zF} \ln \left(\frac{\alpha_{\text{Red}}}{\alpha_{\text{Ox}}} \right) \quad (2.2)$$

Where E° is the standard electrode potential, z is the number of electrons, R is the universal ideal gas constant, T is temperature in Kelvin, F is Faraday's constant, α_{Red} is activity of the reaction product and α_{Ox} is the activity of the reagent. This equation defines the reversible potential of a redox couple under a given chemical environment. When a potential is applied and current flows, the system deviates from equilibrium. The resulting rate of electron transfer is governed by the Butler–Volmer equation (Equation (2.3)), which describes how the current density j varies with the overpotential η (which is the difference between the applied potential and the equilibrium potential E_{eq}).

$$j = j_0 \cdot \left\{ \exp \left[\frac{\alpha_a z F \eta}{RT} \right] - \exp \left[-\frac{\alpha_c z F \eta}{RT} \right] \right\} \quad (2.3)$$

Where j_0 is the exchange current density (a measure of the intrinsic reactivity of the electrode), α_a is the anodic charge transfer coefficient, and α_c is the cathodic charge transfer coefficient. In addition to thermodynamic considerations, the kinetics of electron transfer at the electrode interface are described by the **Butler–Volmer equation**, which accounts for the current/overpotential relationship in both forward and reverse directions of the redox reaction

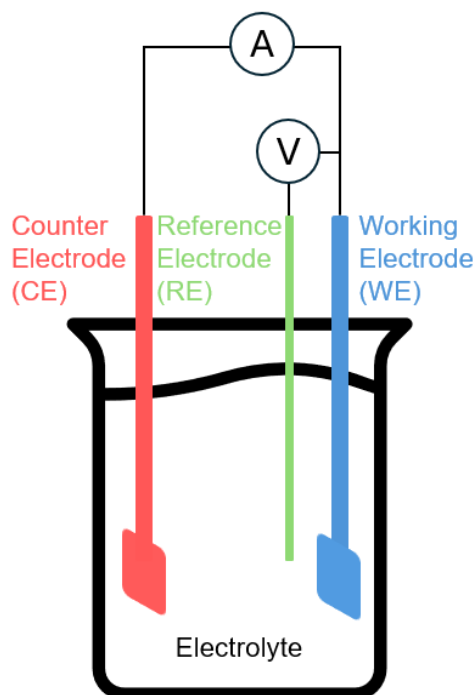


Figure 2.1: Schematic of a three-electrode electrochemical setup, consisting of a working electrode (WE), counter electrode (CE), and reference electrode (RE). In this configuration, current flows between the WE and CE, while the potential is measured between the WE and RE. This arrangement allows precise control of the electrode potential while isolating current-carrying pathways from the reference measurement, ensuring accurate and stable electrochemical measurements.

More practically, electrochemistry is usually carried out in a three-electrode setup (Figure 2.1), which is widely employed for studying electrode kinetics and performing controlled electrolysis. This system consists of three electrodes immersed in an electrolyte solution: a working electrode (WE), where the redox reaction of interest takes place; a counter electrode (CE), which serves to balance the current passed at the WE; and a reference electrode (RE), which provides a stable and reproducible reference potential. The critical design feature of this setup is that the reference electrode is positioned so that it does not carry any current, allowing accurate measurement of the working electrode potential without introducing a large iR (voltage) drop. A potentiostat is used to control the potential between the WE and RE while adjusting the current flowing through the CE accordingly. This configuration allows for precise control of electrochemical parameters and is especially important when investigating mechanisms, kinetics, and electrocatalytic activity. This setup forms the basis for many electrochemical techniques such as cyclic voltammetry (CV), linear sweep voltammetry (LSV), and chronopotentiometry (CP), and is indispensable in both aqueous and non-aqueous electrochemistry. A variety of electrochemical techniques are used to probe the thermodynamics, kinetics, and transport properties of redox systems. Each method provides different insights into the behaviour of electrochemical interfaces and reaction mechanisms. The techniques utilised in this work are:

Open Circuit Voltage (OCV): OCV refers to the potential difference between the working and reference electrodes when no current is applied to the system. It represents the equilibrium

potential of the electrochemical cell and serves as a baseline for interpreting other techniques. Measuring the OCV is crucial before starting controlled electrochemical experiments to ensure system stability and proper electrode conditioning.

Cyclic Voltammetry (CV): CV is a dynamic technique in which the working electrode potential is linearly swept back and forth between two set values while recording the resulting current. It is widely used to investigate redox couples, determine reaction reversibility, and identify electroactive species. The resulting cyclic voltammogram often exhibits characteristic oxidation and reduction peaks, the positions and shapes of which provide insight into electron transfer kinetics and mass transport. Cyclic voltammetry (CV) is arguably the most widely used electrochemical technique due to its combination of experimental simplicity, versatility, and the wealth of information it provides about redox processes, reaction kinetics, and electrode behaviour. For a comprehensive overview of best practices and data interpretation in cyclic voltammetry, readers are encouraged to consult the work of Elgrishi et al. [122].

Linear Sweep Voltammetry (LSV): LSV is similar to CV but involves a single, unidirectional potential sweep. It is commonly used to identify onset potentials for reactions (e.g., hydrogen evolution or nitrogen reduction) and to evaluate catalytic activity. LSV provides a simpler interpretation than CV when focusing on forward reactions only, without the added complexity of reverse scans.

Chronopotentiometry (CP): In CP, a constant current is applied to the working electrode, and the resulting potential is recorded over time. This technique is especially useful for driving electrochemical reactions such as electrolysis and for studying electrode stability under sustained operating conditions. The evolution of the working electrode potential reflects changes in surface processes, mass transport, or electrode degradation.

Electrochemical Impedance Spectroscopy (EIS): EIS involves applying a small-amplitude AC voltage over a range of frequencies and measuring the resulting current response. The frequency-dependent impedance provides detailed information about charge-transfer resistance, double-layer capacitance, diffusion processes, and interfacial kinetics. EIS is often represented in the form of Nyquist or Bode plots and is frequently used for mechanistic studies and modelling of electrode interfaces.

2.1.2 Colorimetry

UV-Vis colorimetry is a well-established analytical technique; therefore, only a brief overview is provided here. For a more comprehensive treatment of the underlying principles and applications, the reader is referred to [123]. UV-Vis colorimetry is a quantitative analytical technique used to determine the concentration of coloured species in solution based on their light absorbance in the ultraviolet and visible regions of the electromagnetic spectrum. The

method relies on the Beer–Lambert law, which relates absorbance A to the molar absorptivity ϵ , optical path length l , and analyte concentration c :

$$A = \epsilon lc \quad (2.4)$$

In the context of electrochemical nitrogen reduction, UV-Vis colorimetry is frequently employed to detect ammonia via derivatisation reactions that form chromophores, typically absorbing in the range of 630–660 nm. Common methods include the indophenol blue and salicylate assays, which produce stable, coloured complexes that enable high-sensitivity detection of trace ammonia. For more details on the indophenol blue and salicylate methods see Section 1.5. Absorbance is usually measured using a UV-Vis spectrophotometer, which consists of a light source, a monochromator or diffraction grating to select the desired wavelength, a sample holder (cuvette), and a photodetector to measure the transmitted light intensity. The instrument records the difference in light intensity before and after passing through the sample to calculate absorbance. The UV-Vis spectrophotometer used in this Thesis was an Agilent Cary 60 UV-Vis Spectrophotometer.

2.1.3 *Electrochemistry-Mass Spectrometry (ECMS)*

Electrochemistry–mass spectrometry (EC-MS) is a technique that enables real-time detection and quantification of volatile and gaseous products evolved during electrochemical reactions. It works by continuously sampling molecules that evaporate from the electrolyte near the electrode surface, transporting them into a mass spectrometer for molecular identification and analysis. EC-MS provides species-resolved insight into electrochemical processes by directly linking reaction products to mass signals. It was developed to overcome key limitations of earlier real-time MS techniques, namely MIMS, DEMS, and OLEMS. For a comprehensive overview of these prior methods, their constraints, and the development of EC-MS, see Sections 1.6 and 1.7. This section focuses specifically on the theoretical principles that underpin EC-MS operation, including evaporation from the electrolyte, analyte transport through the chip capillary, ionisation, and mass filtering/detection.

Evaporation

The first step in ECMS detection is the transition of analyte molecules from the liquid electrolyte phase to the gas phase, a process governed by Henry’s law of volatility (Equation (2.5)). At the liquid–membrane interface, volatile species equilibrate with the gas-phase sampling volume inside the membrane chip, where the partial pressure of a given species p^i becomes proportional to its concentration in the adjacent liquid c^i .

$$p^i = K_H^i \cdot c^i \quad (2.5)$$

Where, K_H^i is the Henry’s law constant for species i , a temperature-dependent parameter that quantifies the volatility of a solute in a given solvent. A significant challenge arises when applying this principle to non-aqueous systems because reliable values of K_H are often unavailable. This stage of evaporation is enhanced by the membrane chip design, which enables equilibration on sub-second timescales due to the small sampling volume and high density of

surface pores [110]. This facilitates high-sensitivity detection and supports real-time analysis of dynamic electrochemical processes.

Capillary Transport

Once volatilized at the liquid–gas interface, analyte molecules enter the sampling volume beneath the membrane and are transported through a microfabricated capillary integrated into the membrane chip. This capillary acts as a flow restrictor, precisely regulating the total gas flux from the sampling volume to the mass spectrometer. The capillary’s dimensions are engineered such that the flow rate remains close to the maximum permissible by the MS vacuum system, while avoiding overload and ensuring quantitative consistency. This well-defined and reproducible mass transport is a key advantage of the chip-based EC-MS system.

The total molecular flux through the capillary, is described by Equation (2.6), commonly referred to as the “capillary equation” [108], [109], [113]. This relationship allows one to calculate the total number of moles of gas entering the mass spectrometer per second $\dot{n}_{cap}$.

$$\dot{n}_{cap} = \frac{1}{RT} \frac{1}{l_{cap}} \left(\frac{\pi}{8\nu} a^4 \bar{p} + \frac{2\pi}{3} a^3 \bar{v} \frac{1 + 2 \frac{2\sqrt{2}}{\sqrt{\pi}} \frac{a}{\eta} \frac{\bar{p}}{\bar{v}}}{1 + 2.48 \frac{2\sqrt{2}}{\sqrt{\pi}} \frac{a}{\eta} \frac{\bar{p}}{\bar{v}}} \right) (p_1 - p_{tran}) + \frac{2\pi}{3} a^3 \bar{v} (p_{tran} - p_2) \quad (2.6)$$

Table 2.1: Definitions of the variables used in the capillary equation (Equation (2.6)). Reproduced with permission from [113].

Variable	Definition
p_1	Inlet pressure (usually 1 bar)
p_2	Outlet pressure (~ 0)
$p_{tran} = \frac{k_B T}{2\sqrt{2}\pi s^2 a}$	Pressure at which transition from viscous to molecular flow occurs. Where s is the molecular diameter of the gas.
$\bar{p} = \frac{p_1 + p_{tran}}{2}$	Average pressure in viscous flow regime
ν	Viscosity of the gas
a	Width and height of capillary
$\bar{v} = \sqrt{\frac{8k_B T}{\pi m}}$	Mean thermal velocity of the gas molecules
m	Molecular mass
l_{cap}	Capillary length

Thanks to this deterministic transport behaviour, the EC-MS system achieves near-100% collection efficiency for volatile species generated at the electrode. The precise knowledge of the molecular flow to the MS ensures that calibrated sensitivity factors can be reliably applied to convert measured ion currents into absolute production rates.

Ionisation

After passing through the chip capillary into the high-vacuum region of the mass spectrometer, analyte molecules undergo electron impact ionisation (EI). In this process, molecules are bombarded with high-energy electrons (typically 70 eV), which results in the ejection of an electron from the neutral molecule and often leads to its fragmentation into multiple ionised pieces. Each molecule produces a characteristic fragmentation pattern, with specific mass-to-charge (m/z) values and relative fragment intensities that serve as a unique “fingerprint” for identification. For instance, ammonia (NH_3) generates major fragments at $m/z = 17$ ($\text{NH}_3^+/\text{NH}_2^+$) and 16 (NH^+), while water primarily produces fragments at $m/z = 18$ (H_2O^+) and 17 (OH^+), which can interfere with ammonia detection if not properly resolved. The mass fragmentation patterns of ammonia and water are shown in Figure 1.20. These fragmentation patterns are essential for both qualitative identification and quantitative analysis, as the EC-MS system monitors one or more dominant m/z fragments per analyte.

Detection

Following ionisation, the resulting charged fragments are directed into a quadrupole mass spectrometer (QMS), which separates ions based on their mass-to-charge ratio (m/z). The quadrupole consists of four precisely arranged rods with oscillating electric fields that allow only ions of a specific m/z to pass through at any given time, while all others are destabilized and discarded (Diagram shown in Figure 2.2). By scanning across a range of m/z values or fixing on specific fragments of interest, the system can selectively detect analytes based on their unique fragmentation profiles.

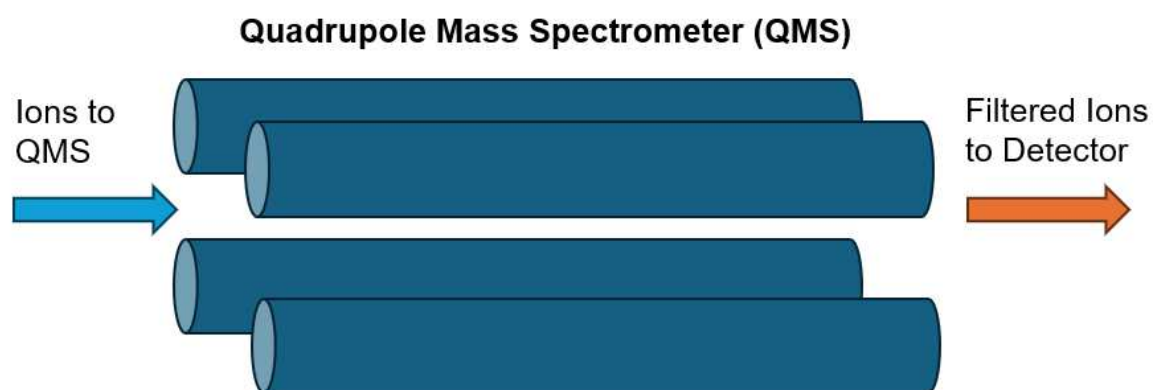


Figure 2.2: Schematic of a quadrupole mass spectrometer (QMS). Ionised analyte fragments enter the quadrupole filter, where four parallel rods generate oscillating electric fields that selectively stabilise ions of a specific mass-to-charge ratio (m/z). By varying the RF and DC voltages applied to the rods, ions of different m/z values can be sequentially transmitted to the detector. Filtered ions then enter the

detector. The entire process is conducted under high vacuum to ensure precise mass separation and detection.

After filtering, ions are collected and quantified using a Faraday cup detector, which measures the current generated by the impinging ions. The Faraday cup provides a stable and linear signal that is well-suited for quantitative analysis over long time periods, making it ideal for EC-MS applications involving calibration and real-time tracking of electrochemical products. For experiments requiring higher sensitivity, a secondary electron multiplier (SEM) can be employed in place of or alongside the Faraday cup. SEMs amplify the signal by initiating a cascade of electrons from a single ion impact, greatly enhancing detection limits. However, this increased sensitivity comes at the cost of long-term stability, as SEMs are more prone to drift, degradation, and variability in gain over time. Therefore, the Faraday cup detector is used for all experiments in this thesis.

2.2 Methodology

2.2.1 Colorimetry

Ammonia produced during electrochemical nitrogen reduction was quantified using UV-Vis colorimetric methods, specifically the indophenol blue (phenol) and salicylate reactions. Both methods rely on the formation of a coloured complex that absorbs visible light, with the absorbance intensity proportional to the concentration of ammonia in solution. As will be discussed in Chapter 3, a number of different variations to the quantification method were tested to determine the most accurate & consistent combination. This section outlines the procedures for all the different variations.

Sample Preparation

Before the quantification reagents could be added to the samples, they either had to be diluted or evaporated to reduce the organic content if the samples as this interferes with the quantification reaction (see Section 1.5 for more details).

Evaporation: Electrolyte samples were collected immediately following electrochemical experiments. Unless otherwise stated, 400 μL aliquots of the post-electrolysis electrolyte were drawn for each sample, alongside one 400 μL blank sample taken from freshly prepared (pristine) electrolyte and transferred to 7 mL glass vials. To stabilise the ammonia, 30 μL of 4 M aqueous HCl (Suprapur, Sigma-Aldrich) was added to each vial. Samples were then evaporated in a water bath at 70–90 $^{\circ}\text{C}$ (depending on solvent boiling point and viscosity) until dry, ensuring complete removal of organic solvents such as THF or diglyme. The remaining residue was redissolved in 2 mL of 18.2 M Ω water for spectrophotometric analysis.

Dilution: Electrolyte samples were collected immediately following electrochemical experiments. Aliquots of 100–400 μL were taken of the post-electrolysis electrolyte and from freshly prepared (pristine) electrolyte. Each aliquot was transferred to a 7 mL glass and diluted up to a total volume of 2 mL with 18.2 M Ω water for spectrophotometric analysis.

Reagent Preparation

Both the Indophenol Blue (Phenol) and Salicylate colorimetric methods were employed for the quantification of ammonia in electrolyte samples.

Stock Ammonia Solution: Stock ammonium chloride solutions of 3 mM & 2.56 mM were prepared by weighing and dissolving 8.02 mg & 6.85 mg (respectively) of NH_4Cl salt (99.99%, Sigma-Aldrich, dried in antechamber for 72 h, kept and measured out in Ar glovebox) in 18.2 M Ω water and then made up to 50 mL in volumetric flasks. The concentrations were chosen such that adding 10 μL of the stock ammonia solution to a sample would correspond to an increase of 10 μM in NH_4^+ (for the phenol and salicylate method respectively).

Indophenol Blue (Phenol) Method: For this method, a commercially available solution of phenol nitroprusside solution (Sigma-Aldrich) was used. Alkaline hypochlorite solution was prepared by the method described in the Supplemental Information of [41] using sodium hydroxide (AnalaR NormaPur (analytical grade), VWR) and sodium hypochlorite 14% solution (GPR Rectapur (analytical grade), VWR). To each 2 mL sample solution to be quantified, 500 μL of the alkaline hypochlorite solution was added, followed by 500 μL of phenol nitroprusside solution. Samples were incubated in a fume cupboard for **30 minutes** before spectrophotometric analysis. Method used as described in [20].

Salicylate Method: Alkaline hypochlorite solution & salicylate-catalyst solution were prepared by the method described in the Supplemental Information of [41] using sodium hydroxide (AnalaR NormaPur (analytical grade), VWR), sodium hypochlorite 14% solution (GPR Rectapur (analytical grade), VWR), sodium salicylate (*ReagentPlus*[®], $\geq 99.5\%$ (titration), Sigma-Aldrich) and sodium nitroprusside (ACS, 99.0-102.0%, Alfa Aesar). To each 2 mL sample solution to be quantified, 280 μL of the salicylate-catalyst solution was added, followed by 280 μL of alkaline hypochlorite solution. Samples were incubated in a fume cupboard for **45 minutes** before spectrophotometric analysis.

All reagents were stored at 4 °C and used within six months to minimize contamination and degradation. Following the incubation period, samples were transferred to PMMA macro cuvettes (VWR), and their absorbance spectra were recorded using an Agilent Cary 60 UV-Vis spectrophotometer over the 400–900 nm wavelength range. Figure 2.3 displays the appearance of the developed samples within the cuvettes.

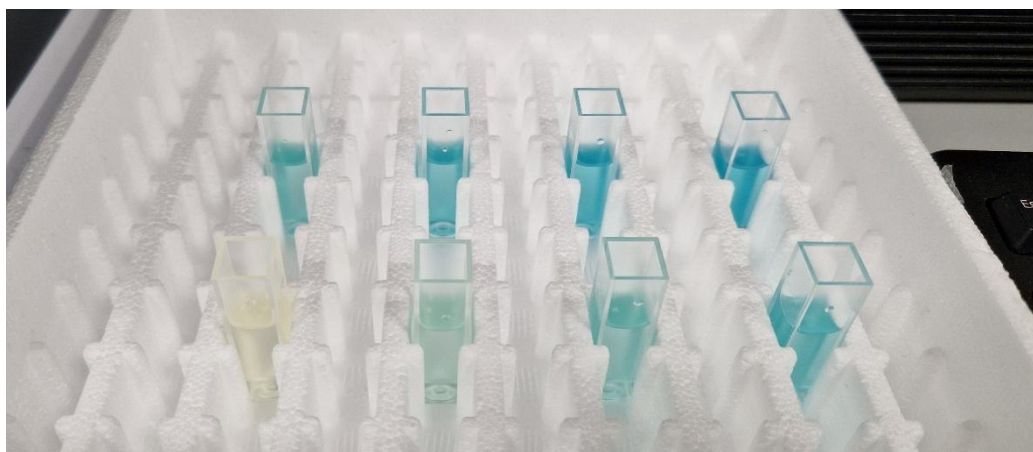


Figure 2.3: Cuvettes containing developed salicylate assays of ammonia-containing solutions. Each cuvette holds a fully developed colorimetric assay based on the salicylate method, used for the

quantification of ammonia. The intensity of the green-blue colour corresponds to the ammonia concentration in each sample, allowing for visual comparison prior to spectrophotometric measurement.

Quantification Methods

To determine the concentration of ammonia, two quantification approaches were used: the calibration curve method and the standard addition method. In all cases, ammonia concentration was measured in both the freshly prepared (pristine) electrolyte and the electrolyte collected after electrolysis. The net ammonia yield was then calculated by subtracting the ammonia content of the pristine electrolyte from that of the post-electrolysis sample. This step was essential to account for adventitious ammonia, which can vary between experiments due to trace contamination from reagents, solvents, or the glovebox environment. By directly quantifying and correcting for the background ammonia in each electrolyte batch, this method ensures more accurate and reproducible measurements of electrochemically produced ammonia.

Calibration Curve Method: To construct a calibration curve for ammonia quantification, a series of standard samples were prepared by spiking pristine (unused) electrolyte with increasing volumes of an aqueous ammonium chloride (NH_4Cl) stock solution of known concentration. After full colour development, the absorbance of each sample was measured by UV-Vis spectrophotometry, and the peak absorbance (typically ~ 650 nm for salicylate method and ~ 630 nm for phenol method), corrected by subtracting the baseline at 900 nm was plotted against the corresponding ammonia concentration. This produced a linear calibration curve, which was then used to determine the ammonia concentration in the sample electrolyte by interpolating its measured absorbance value (see Figure 1.14a in Section 1.5 for an example curve).

Standard Addition Method:

For the standard addition method, known volumes of a prepared ammonium chloride (NH_4Cl) stock solution were added to separate aliquots of the same sample electrolyte. Typically, a series of samples was prepared by spiking increasing amounts of the ammonia standard into identical volumes of the electrolyte, while one unspiked sample was retained as a reference. After full colour development, the absorbance of each sample was measured by UV-Vis spectrophotometry, and the peak absorbance (typically ~ 650 nm for salicylate method and ~ 630 nm for phenol method), corrected by subtracting the baseline at 900 nm was plotted against the number of moles of added ammonia. A linear regression was applied to the data, and the ammonia concentration was calculated by dividing the y-intercept by the gradient (see Figure 1.14b in Section 1.5 for an example curve).

Faradaic Efficiency Calculation

Once the concentration of ammonia in each sample was determined via UV-Vis colorimetry, the faradaic efficiency **FE** for dissolved ammonia could be calculated. First, the total amount of ammonia produced **n** was obtained by multiplying the measured concentration $[\text{NH}_4^+]$ by the total electrolyte V_{ele} and dividing by the cuvette volume V_{cuv} (Equation (2.7)).

$$n = [\text{NH}_4^+] \cdot \frac{V_{ele}}{V_{cuv}} \quad (2.7)$$

Next, the theoretical maximum amount of ammonia $n_{\max}$ that could be produced from the total charge passed Q during electrolysis was calculated using Faraday's law. As the reduction of nitrogen to ammonia requires 3 electrons per NH_3 molecule, the maximum yield is given by Equation (2.8).

$$n_{\max} = \frac{Q}{3F} \quad (2.8)$$

where F is the Faraday constant ($96,485 \text{ C mol}^{-1}$). Finally, the faradaic efficiency FE was determined by comparing the measured and theoretical values (Equation (2.9)).

$$FE = \frac{n}{n_{\max}} \times 100 = \frac{[\text{NH}_4^+] \cdot V_{ele} \cdot 3F}{Q \cdot V_{cuv}} \times 100 \quad (2.9)$$

2.2.2 Electrochemistry-Mass Spectrometry (ECMS)

All electrochemical mass spectrometry (EC-MS) experiments were performed using the Spectro Inlets EC-MS Professional system, which integrates a microchip-based electrochemical cell with a quadrupole mass spectrometer. The entire system, including the electrochemical cell, was fully enclosed within an Ar-filled glovebox to maintain an inert atmosphere and prevent contamination from ambient air (Figure 2.4).

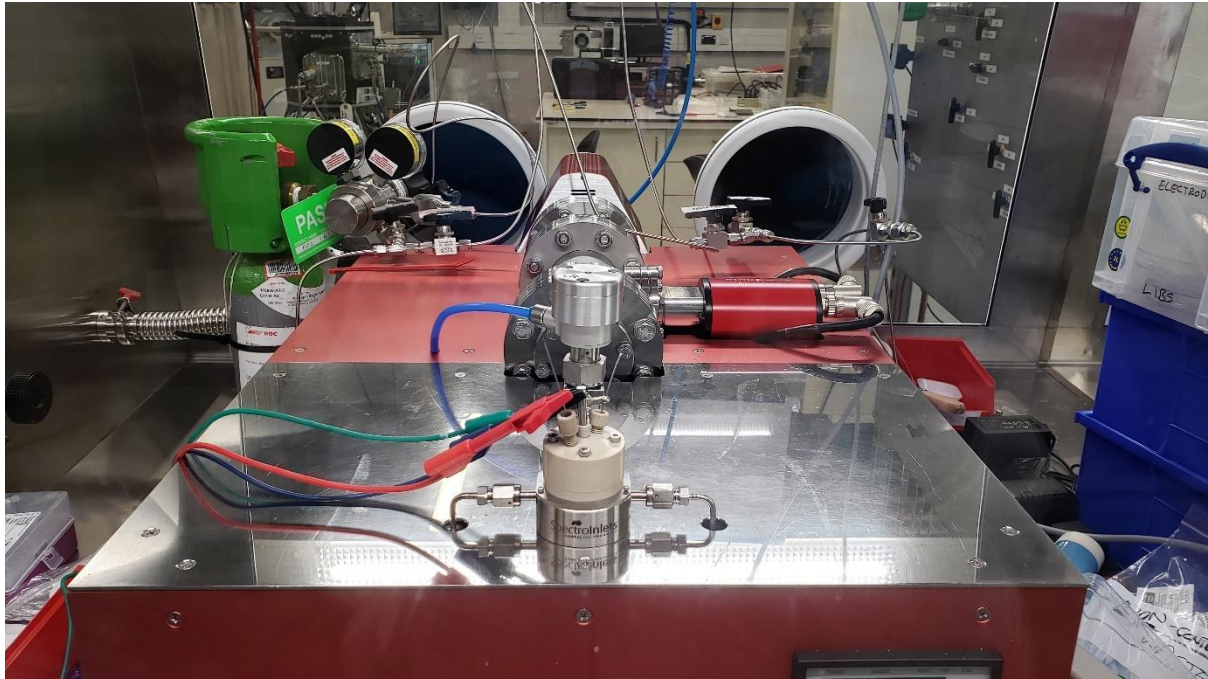


Figure 2.4: ECMS setup operated inside an argon-filled glovebox. The Spectro Inlets ECMS system is shown housed within an inert atmosphere glovebox to enable measurements in an oxygen- and moisture-free environment. The setup includes the electrochemical cell mounted above the membrane chip, connected to the mass spectrometer.

Calibration

The calibration procedure is essential to accurate quantitative analysis with ECMS and is used to relate the mass spectrometry signal to the actual flux of a given analyte. To achieve this, a calibration gas of known composition is introduced into the ECMS system under controlled conditions. By flowing a known concentration of a volatile species (e.g., ammonia, hydrogen, or carbon dioxide) through the backing gas stream and into the chip's sampling volume, the analyte flux into the mass spectrometer can be calculated using the chip equation (see Section 2.1.3). This calculated flux is then directly related to the measured ion current at the corresponding mass-to-charge ratio (m/z), allowing the determination of a sensitivity factor F_M^i , which links the signal intensity S_M (for a given m/z ratio, M) to the molecular flux $\dot{n}^i$ (of species i), by Equation (2.10)). An analyte molecule may produce several dominant mass fragments, each characterized by a distinct m/z ratio. A separate sensitivity factor is required for each unique analyte–fragment combination.

$$F_M^i = \frac{S_M}{\dot{n}^i} \quad (2.10)$$

Calibration procedures were performed by sealing the chip membrane from the external electrolyte environment, ensuring that the backing gas flowed exclusively into the mass spectrometer. This isolation was achieved either by assembling a glass slide–O-ring–chip sandwich as seen in Figure 2.5a or by applying epoxy directly over the membrane surface to block liquid contact (Figure 2.5b).

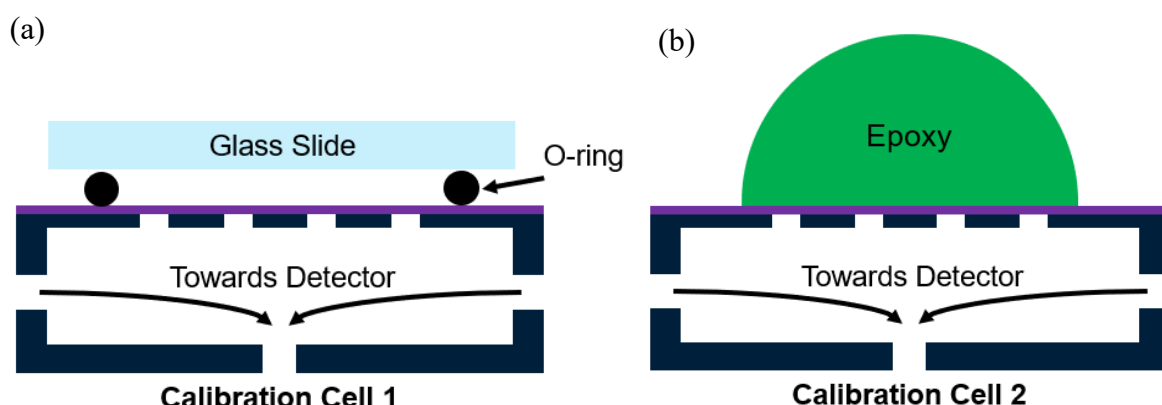


Figure 2.5: Calibration setups for isolating the chip sampling volume during EC-MS sensitivity determination. (a) Schematic of the calibration cell assembled using a glass slide–O-ring–chip sandwich, which physically seals the membrane from the electrolyte environment while allowing controlled gas flow to the mass spectrometer. (b) Chip membrane sealed with epoxy, effectively isolating the membrane surface to enable direct introduction of calibration gas into the sampling volume.

Calibrations for H_2 and C_2H_4 were performed using a 1000 ppm H_2 , 1000 ppm CO , 1000 ppm C_2H_4 & 1000 ppm O_2 in N6.0 Ar gas mixture (BOC). Calibration for NH_3 was performed using 1000 ppm NH_3 in N6.0 N_2 (BOC). Calibration for CH_4 was performed using 1000 ppm CH_4 in N6.0 Ar (BOC).

Setups

Three main cell configurations were used in the EC-MS experiments conducted in this thesis: the separated electrode cell (Figure 2.6a-b), parallel electrode cell V1 (Figure 2.6c-d), and parallel electrode cell V2 (Figure 2.6e-f). The second version of the parallel electrode cell (V2) was specifically developed to mitigate damage to the chip's highly sensitive membrane surface coating. This coating is critical for maintaining a stable gas-liquid interface; if scratched, it fails to repel the organic electrolyte, allowing liquid to enter the chip's sampling volume. This results in an excessive molecular flux into the mass spectrometer, often triggering an automatic system shutdown. For a detailed comparison of the advantages and limitations of each cell configuration, refer to Section 4.1.4. Electrochemical experiments were carried out using a Biologic SP-150 potentiostat (BioLogic Science Instruments) operated in three-electrode configuration and controlled via EC-Lab software. The reagents used for the preparation of the electrolytes in this study were THF (anhydrous, $\geq 99.9\%$, inhibitor-free, Sigma-Aldrich), Diglyme (anhydrous, 99.5%, Sigma-Aldrich), Ethanol (Extra Dry, absolute, *AcroSeal*[®], 99.5%, thermos scientific), LiClO₄ (anhydrous, 99.99%, Alfa Aesar), LiTFSI (99.9%, Solvionic) & LiBF₄ (99.99%, Stanford Advanced Materials).

Separated Electrode Cell: Separated electrode cell (Spectro Inlets) ChangeDisk RDE Tip (Pine Research), 5 mm Cu disk insert (99.99%, Pine Research) working electrode, 0.5 mm Pt reference wire (99.99%, Goodfellows), two 1 x 1 cm Pt foil square counter electrodes (99.99%, Goodfellows).

Parallel Electrode Cell V1: Parallel electrode cell (custom ordered from Spectro Inlets), 40 μm thick 5 mm Cu mesh disk (99.99%, EL-Cell), 20 μm Cu foil working electrode contact strip (99.99%, Goodfellow), 0.5 mm Pt reference wire (99.99%, Goodfellows), 20 μm 5 mm Pt foil disk (99.99%, Goodfellows), 25 μm thick Celgard 2500 microporous PP membrane 8 mm disk (Celgard), 6 mm glass microfibre filter disc (Whatman).

Parallel Electrode Cell V2: Parallel electrode cell (custom ordered from Spectro Inlets), 40 μm thick 5 mm Cu mesh disk (99.99%, EL-Cell), 20 μm Cu foil working electrode contact strip (99.99%, Goodfellow), 0.5 mm Pt reference wire (99.99%, Goodfellows), 20 μm 5 mm Pt foil disk (99.99%, Goodfellows), 5 mm glass microfibre filter disc (Whatman).

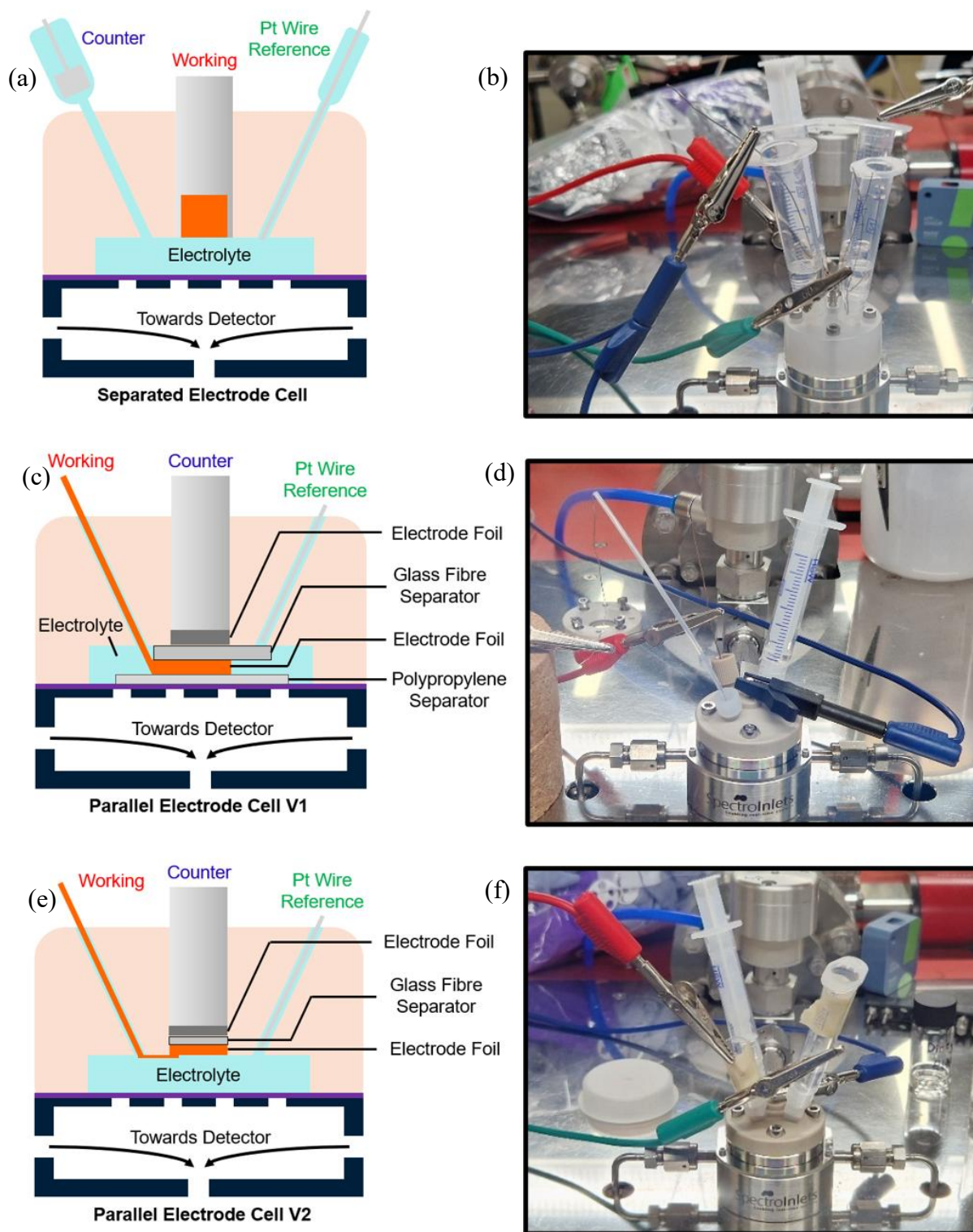


Figure 2.6: Comparison of EC-MS cell configurations used in this thesis. Separated electrode cell: a) schematic and b) photo of corresponding experimental setup. Parallel electrode cell V1: c) schematic and d) photo of corresponding experimental setup. Parallel electrode cell V2: e) schematic and f) photo of corresponding experimental setup.

3 Quantification of Dissolved Ammonia (Colorimetry)

3.1 Introduction

Accurate, consistent, and reproducible quantification of dissolved ammonia in the electrolyte is essential for generating meaningful insights in lithium-mediated nitrogen reduction (Li-NRR) studies. Due to the typically low faradaic efficiencies and small ammonia yields associated with Li-NRR [20], detection methods must be highly sensitive and reliable. Without robust quantification, it is impossible to determine whether observed variations in ammonia yield stem from true experimental differences or from inconsistencies in the analytical method. Inaccurate measurements undermine the ability to draw mechanistic conclusions, compare results across studies, or evaluate the effects of variables such as electrolyte composition, operating conditions, or cell design.

Colorimetric detection using UV–Vis spectroscopy is widely adopted for ammonia quantification due to its accessibility, low cost, and sensitivity in the low ppm range [20], [41], [42]. Among these methods, the salicylate and indophenol blue (phenol) methods are most used. In addition to differences in chemical reagents, there is significant variation in how these assays are applied, particularly with regard to calibration strategies, some studies use external calibration curves [20], while others rely on standard addition methods to account for matrix effects [25]. Similarly, approaches for preparing non-aqueous samples vary, with both direct dilution into water [25] and solvent evaporation followed by aqueous reconstitution commonly reported [42]. These methodological differences can significantly affect the colour development reaction and, consequently, the measured absorbance. In Li-NRR systems, where solvents like THF or diglyme may interfere with the assay chemistry, these variations introduce uncertainty and make it difficult to compare results across studies. Despite the widespread use of UV–Vis colorimetry, there remains no universally accepted or validated protocol optimised for ammonia detection in lithium-mediated electrolytes.

This chapter presents a systematic comparison of key methodological choices in UV–Vis colorimetric ammonia detection, including the use of the phenol vs. the salicylate method, calibration curves vs. standard addition techniques, and sample preparation by solvent evaporation vs. direct dilution. Each approach was evaluated for its reproducibility, accuracy and sensitivity in lithium-mediated nitrogen reduction electrolytes. By identifying the limitations and variability associated with each method, this work establishes a robust and internally consistent quantification protocol tailored to non-aqueous systems. The methodology developed here not only underpins the analytical reliability of the subsequent experimental chapters but also contributes to the broader effort to standardise ammonia quantification practices within the Li-NRR research community.

3.2 Quantification with Phenol vs Salicylate

To assess the accuracy and consistency of the salicylate and phenol methods, calibration curves were prepared using a representative electrolyte (0.2 M LiClO₄ in THF, one of the most commonly used electrolytes during early Li-NRR work [33]). The electrolyte was first evaporated, and the remaining solids were re-dissolved in 18.2 MΩ deionised water. Known

amounts of NH_4^+ (added as NH_4Cl) were then introduced, and the absorbance of each sample was measured using a UV–Vis spectrophotometer. To further evaluate the performance and kinetics of the salicylate and phenol assays, the absorbance of the calibration standards was monitored over time to observe the evolution of the colour development reaction.

The resulting time-resolved calibration curves for both methods are shown in Figure 3.1. It is evident that the phenol-based calibration stabilises significantly faster than the salicylate-based one. The phenol method reaches a stable absorbance within 15–30 minutes, with negligible changes thereafter. In contrast, the salicylate calibration curve continues to evolve, showing measurable changes even between 75 and 90 minutes. This slower stabilisation is likely due to the lower reactivity of salicylate compared to phenol, resulting in slower reaction kinetic [78], [84].

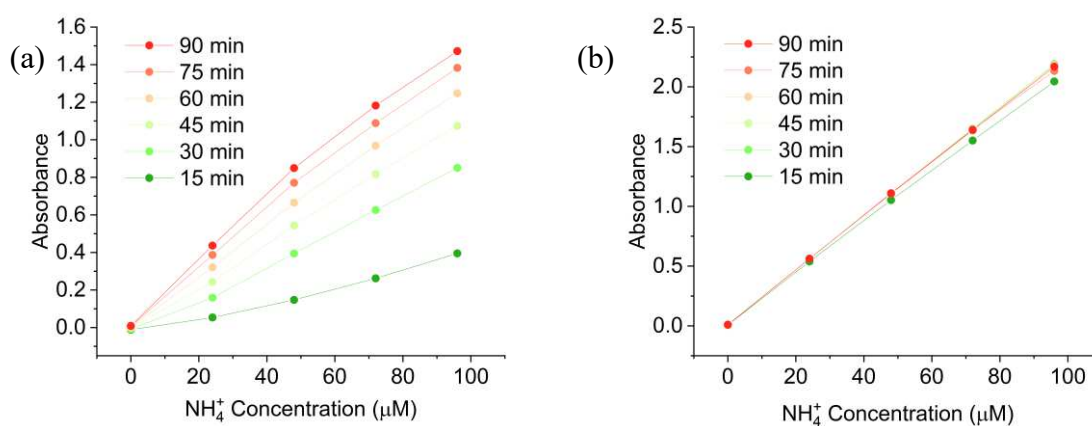


Figure 3.1: Calibration curves for NH_4^+ quantification in 0.2 M LiClO_4 in THF using (a) salicylate and (b) phenol detection methods. Calibration samples were prepared by evaporating 400 μL of 0.2 M LiClO_4 in THF, followed by re-dissolution of the residue in 18.2 $\text{M}\Omega\cdot\text{cm}$ deionised water. Each 2 mL sample contained the equivalent of 400 μL of electrolyte. Known concentrations of NH_4^+ were added as NH_4Cl , followed by 280 μL of alkaline hypochlorite solution and 280 μL of either salicylate or phenol catalyst solution.

Another key difference between the phenol and salicylate methods, as shown in Figure 3.1, is the markedly reduced linearity of the salicylate calibration curves. With the exception of the earliest 15 min data, the phenol-based calibration curves exhibit excellent linearity, with Pearson's r values consistently greater than 0.9999. In contrast, the salicylate calibration curve initially displays a convex profile, which gradually transitions to a concave shape over time. The most linear response is observed at 45 minutes, with a Pearson's r value exceeding 0.999. However, even at this time point, the curve deviates from ideal linearity, particularly around an NH_4^+ concentration of approximately 20 μM , where a clear change in gradient is observed.

The underlying cause of this evolving non-linearity in the salicylate calibration curves is not yet fully understood. One possible explanation draws from the work of Willis et al. [124], who showed that increasing the time interval between the addition of the catalyst solution and the alkaline hypochlorite reagent led to a measurable decrease in the final absorbance. In the present work, samples were prepared sequentially, meaning that the time delay between reagent additions increased for each successive sample. This could result in lower-than-expected final absorbance values for samples with higher NH_4^+ concentrations, particularly in the later timepoints of 45 minutes and beyond.

However, this alone does not explain the opposite trend observed in the earlier calibration curves taken at or before 30 minutes, where higher concentrations show disproportionately higher absorbance values. This may be attributed to reaction kinetics, specifically that higher ammonia concentrations lead to faster initial reaction rates and more rapid colour development. This effect is clearly illustrated in Figure 3.2, which shows the absorbance evolution over time for two NH_4^+ concentrations. The higher concentration reaches saturation more rapidly than the lower one. The combined influence of delayed reagent addition, which reduces final absorbance at higher concentrations, and concentration-dependent kinetics, which accelerate initial colour development at higher concentrations, likely explains both the initial convex shape and the gradual transition to a concave profile in the salicylate calibration curves over time.

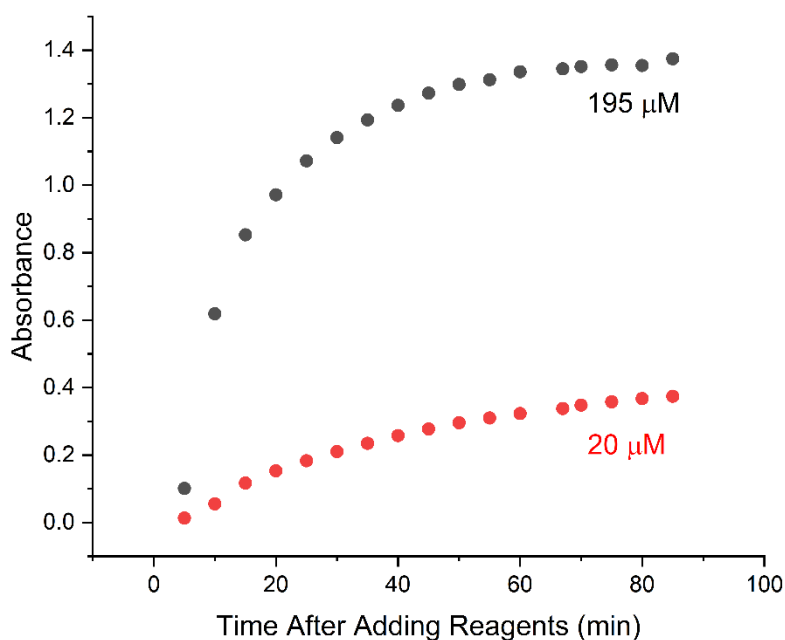


Figure 3.2: Absorbance vs time profiles for 20 μM and 195 μM NH_4^+ . samples were prepared by evaporating 100 μL of 1 M LiClO_4 in THF, followed by re-dissolution of the residue in 18.2 $\text{M}\Omega\cdot\text{cm}$ deionised water. Known concentrations of NH_4^+ were added as NH_4Cl , (to achieve the final concentrations), followed by 280 μL of alkaline hypochlorite solution and 280 μL of either salicylate or phenol catalyst solution.

To gain further insight into how the slower colour development and reduced linearity of the salicylate calibration curves affect ammonia quantification, an electrolyte sample from a typical lithium-mediated nitrogen reduction experiment was analysed using both the phenol and salicylate methods. The sample was prepared by passing 10 C of charge at a current density of 2 mA cm^{-2} in a 1 M LiTFSI in THF electrolyte containing 0.15 vol% ethanol, using a Cu working electrode, lithium iron phosphate (LFP) counter electrode, and a Pt wire pseudo-reference electrode. The electrolyte composition was based on the work of Westhead et al. in our group, who demonstrated that this formulation could achieve Faradaic efficiencies exceeding 30% [40].

The standard addition calibration curves obtained from both methods are shown in Figure 3.3. Both the salicylate and phenol curves exhibited excellent linearity, with Pearson's r values greater than 0.999. The phenol method showed slightly higher linearity overall, as indicated by a marginally higher Pearson's r coefficient.

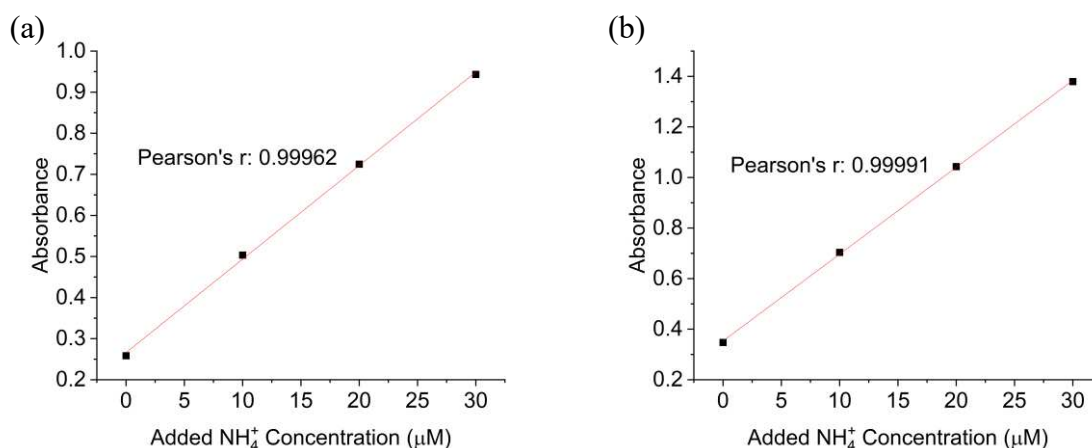


Figure 3.3: Standard addition curves for 1 M LiTFSI in THF containing 0.15 vol % Ethanol, following electrolysis (10 C passed at 2 mA cm⁻²) using a Cu working electrode, LFP counter electrode, and Pt wire pseudo-reference electrode. Samples were quantified using (a) salicylate and (b) phenol detection chemistries. The electrolyte was diluted with 18.2 MΩ·cm deionised water at a final dilution ratio of 25.6. Known amounts of NH₄⁺ were added as NH₄Cl, followed by 280 μL of alkaline hypochlorite solution and 280 μL of either salicylate or phenol catalyst solution. Absorbance was measured 45 min after reagent addition.

Despite the high linearity observed in both the salicylate and phenol standard addition curves (measured at 45 min), the ammonia concentration determined using the salicylate method was approximately 10% higher than that obtained with the phenol method. This discrepancy can be attributed to the gradient change in the 45 min salicylate calibration curve shown in Figure 3.1a. The steeper slope beyond approximately 20 μM results in an overestimation of the ammonia concentration at higher concentrations.

Although the phenol method demonstrated superior accuracy and performance, the salicylate method was ultimately selected for use throughout this work to ensure consistency with the broader dataset generated within the research group. Given the collective effort to standardise analytical protocols across related experiments, the use of the salicylate method enabled direct comparison despite the drawbacks discovered here. Furthermore, the salicylate method poses significantly lower toxicity. Given that quantifications were performed regularly and required sample transport between rooms and handling near a tabletop spectrophotometer, minimising health risks was a key factor. Additional benefits of the salicylate method include reports of lower chemical interference [125] and greater reagent stability over time [81]. Moreover, the performance of the salicylate method can be further enhanced through additional protocol optimisation as discussed in Section 3.5.

3.3 Quantification using Calibration Curves vs Standard Addition

The primary advantage of the calibration curve method lies in its efficiency. Although generating the calibration curve requires time and effort initially, once established, only the absorbance of each sample needs to be measured to determine its ammonia concentration. However, this approach assumes that the absorbance-to-concentration gradient in the calibration curve is identical to that in the sample matrix. Since this gradient is not directly measured in the sample itself, the accuracy of the result depends on an assumption that may not hold, especially in complex or variable electrolyte environments.

In contrast, the standard addition method involves adding known quantities of ammonia directly to the sample solution. This allows the absorbance-to-concentration gradient to be determined within the actual sample matrix, accounting for any matrix-specific effects and eliminating the need for a separate calibration curve. The trade-off is that this method requires the preparation and analysis of multiple samples per quantification, increasing both time and material consumption.

Several factors are known to influence the gradient of a calibration curve, including colour development time, light exposure, pH, and chemical interferents such as alkali metal salts [84], [85]. Within the context of this project, the two most significant factors were found to be the colour development time and the concentration of alkali metal salts. To evaluate the influence of these variables, calibration curves were prepared using two different salt concentrations and monitored over time. The results are presented in Figure 3.4.

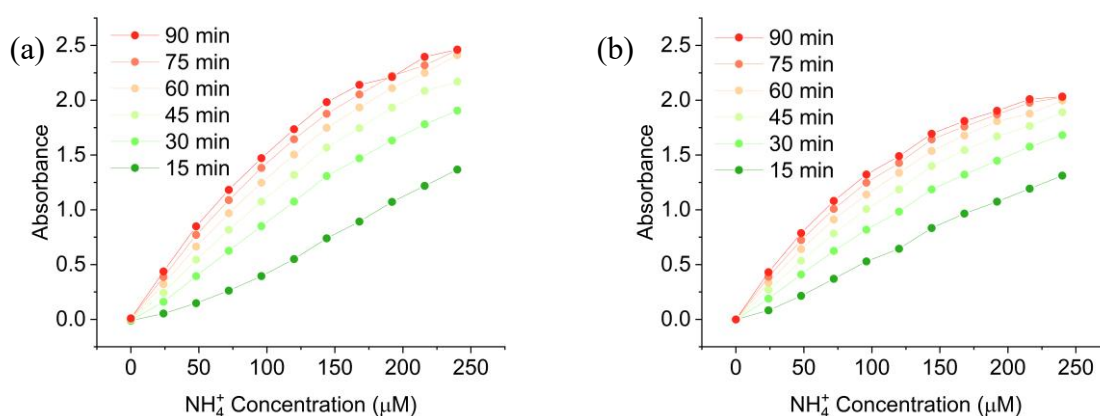


Figure 3.4: Calibration curves vs time for evaporated (a) 0.2 M LiClO_4 and (b) 1 M LiClO_4 in THF. Calibration samples were prepared by evaporating the respective electrolytes and re-dissolving the resulting residues in 18.2 $\text{M}\Omega\cdot\text{cm}$ deionised water. Each 2 mL sample contained the equivalent of 400 μL of electrolyte. Known amounts of NH_4^+ were added as NH_4Cl , followed by 280 μL of salicylate catalyst solution and 280 μL of alkaline hypochlorite solution.

The shape, linearity, and gradient of both the 0.2 M and 1 M LiClO_4 calibration curves shown in Figure 3.4 change significantly with time. As discussed earlier Section 3.2, these time-dependent variations are primarily attributed to differences in colour development kinetics and matrix effects. The key insight from this data is a quantitative assessment of the variability that can arise under typical experimental conditions. For example, if the absorbance of a 24 μM NH_4^+ sample in 0.2 M LiClO_4 were measured at 50 min but compared to a calibration curve generated at 45 min, the resulting ammonia concentration would be overestimated by approximately 11% (based on Figure 3.4a). This illustrates that even a small 5 min timing difference (well within the range of typical variation during reagent handling and measurement) can have a substantial impact on the calculated concentration.

This variability is further compounded by changes in alkali metal salt concentration. From Figure 3.4, it is evident that the absorbance values for the 1 M calibration curve are consistently lower than those of the 0.2 M curve. This suppression effect is consistent with the findings of Giner-Sanz et al. [85], who attributed it to the interaction between alkali metal cations and the indophenol dye, which alters the colour development reaction by forming coordination complexes in solution.

Understanding the influence of salt concentration is particularly important in lithium-mediated nitrogen reduction systems, where the use of volatile organic solvents such as THF can lead to changes in electrolyte concentration over the course of an experiment. For instance, partial evaporation of a 0.2 M LiClO_4 electrolyte could increase the salt concentration to around 0.3 M. While this change may only lead to an estimated 2% decrease in the measured ammonia concentration, such discrepancies, when combined with timing variability and other matrix effects, can introduce significant random error into the calibration curve method.

Ultimately, the magnitude of variability observed when using calibration curves with the salicylate reagent was deemed too large to ensure accurate and reliable ammonia quantification. Therefore, despite requiring more sample preparation, the standard addition method was selected for this project due to its robustness and greater resistance to matrix-dependent variability.

3.4 Reducing Organic Interference through Evaporation vs Dilution

Dilution offers the advantage of faster sample preparation but is more susceptible to interference from organic solvents present in the electrolyte. In contrast, evaporation can significantly reduce interference from organics by removing volatile components, but it is more time-consuming and carries the risk of ammonia loss during the evaporation process, potentially leading to underestimation. To evaluate the viability of these two approaches, the magnitude of their respective drawbacks was systematically assessed.

In particular, ammonia loss during evaporation was investigated by adding known amounts of NH_4^+ to a 0.2 M LiClO_4 in THF electrolyte both before and after evaporation. Following this, quantification was performed using the salicylate method, and the resulting absorbance values were compared. The outcomes of this comparison are presented in Figure 3.5a.

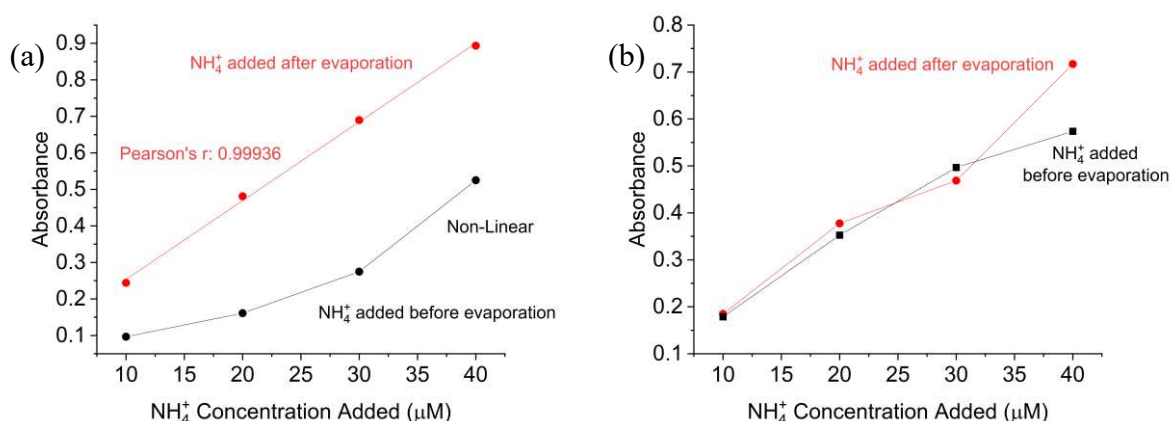


Figure 3.5: Calibration curves for 0.2 M LiClO_4 in THF with (a) no HCl and (b) with HCl added prior to evaporation. For the “before” samples, aqueous NH_4Cl solution was added to 400 μL aliquots of electrolyte, followed by evaporation and re-dissolution of the resulting solids in 18.2 $\text{M}\Omega\cdot\text{cm}$ deionised water. For the “after” samples, 400 μL of electrolyte was first evaporated, the remaining solids re-dissolved in 18.2 $\text{M}\Omega\cdot\text{cm}$ deionized water, and then aqueous NH_4Cl solution was added. All samples were made up to a final volume of 2 mL, followed by the sequential addition of 280 μL of salicylate catalyst solution and 280 μL of alkaline hypochlorite solution. Absorbance was measured 45 min after reagent addition.

Figure 3.5a clearly shows that the absorbance of samples with ammonia added **before** evaporation is substantially lower than that of samples with ammonia added **after** evaporation. Since the final solutions are otherwise nearly identical, this suggests that a significant amount of ammonia was lost during the evaporation process. Moreover, the proportion of ammonia lost does not follow a consistent trend with initial concentration, making it difficult to correct for or predict. This introduces substantial uncertainty and renders the method unsuitable in its unmodified form.

Giner-Sanz et al. also reported considerable ammonia loss during evaporation, attributing it to the presence of ammonia in its volatile NH_3 form. They proposed that adding hydrochloric acid (HCl) prior to evaporation could stabilise ammonia as NH_4^+ , thereby preventing its loss [84]. To test this, the above experiment was repeated with HCl added alongside NH_4Cl before the evaporation step. As shown in Figure 3.5b, the absorbance of samples with ammonia added before evaporation closely matched those with ammonia added afterward, with the exception of the $40\ \mu\text{M}$ sample, which likely deviated due to pipetting error. These results confirm that acidifying the solution with HCl successfully stabilises ammonia as NH_4^+ , effectively eliminating losses during evaporation.

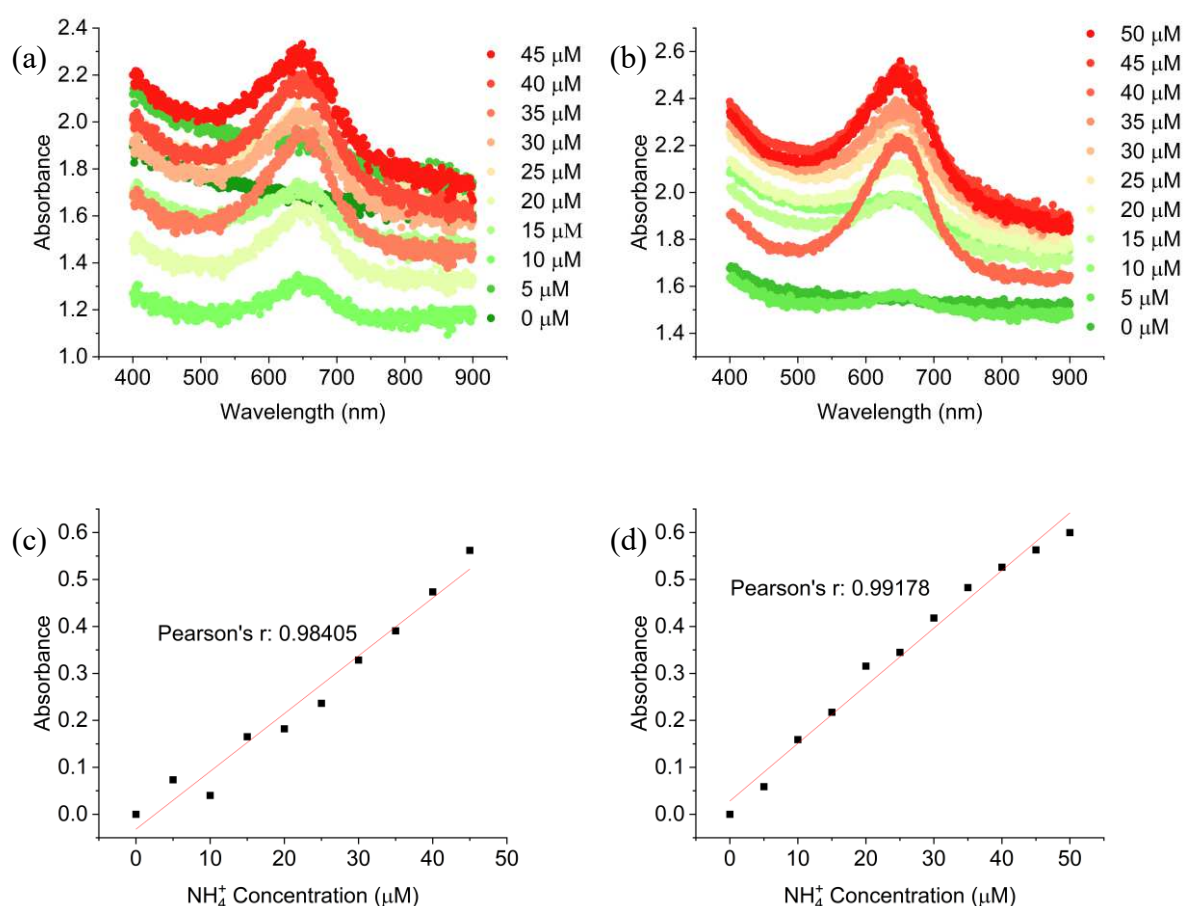


Figure 3.6: Absorbance spectra of 400 μL samples of (a) $0.2\ \text{M}\ \text{LiClO}_4$ in THF and (b) pure THF. Corresponding calibration curves (c) and (d) were obtained by measuring the peak absorbance of each spectrum and subtracting the baseline absorbance at 900 nm. For each sample, 400 μL of electrolyte or solvent was diluted to 2 mL with $18.2\ \text{M}\Omega\cdot\text{cm}$ deionised water. Known amounts of NH_4^+ were added as NH_4Cl , followed by 280 μL of salicylate catalyst solution and 280 μL of alkaline hypochlorite solution. Absorbance was measured 45 min after reagent addition.

While these results demonstrate that the evaporation method can be made accurate and reliable with appropriate acidification, its primary limitation remains long processing times. If the dilution method can be shown to offer comparable accuracy and resistance to interference, it would be the preferred approach due to its faster turnaround. To evaluate the potential impact of organic solvent interference on the dilution method, calibration curves were prepared using both 0.2 M LiClO₄ in THF and pure THF, as shown in Figure 3.6.

Figure 3.6a and Figure 3.6b highlight two major issues encountered when using the dilution method to generate calibration curves: a high and inconsistent background signal, and a low signal-to-noise ratio. Both factors introduce substantial uncertainty into the absorbance measurement, which is calculated by subtracting the background absorbance (typically taken at 900 nm) from the peak height. These issues are further reflected in Figure 3.6c and Figure 3.6d, where the resulting calibration curves show suboptimal linearity.

The elevated background signal and increased noise are almost certainly caused by interference from organic components in the electrolyte, although the precise mechanisms responsible were not fully understood at the time of experimentation. Several studies have reported that organic solvents can interfere with colorimetric Berthelot-type assays for ammonia, either by inhibiting the formation of the indophenol dye or by promoting its decomposition [78], [84], [126]. However, the exact chemical interactions underlying these effects are not well established.

To better understand the nature of this interference, the absorbance of a 30 μM NH₄⁺ sample (prepared by diluting a 0.2 M LiClO₄ in THF solution with water) was monitored over time.

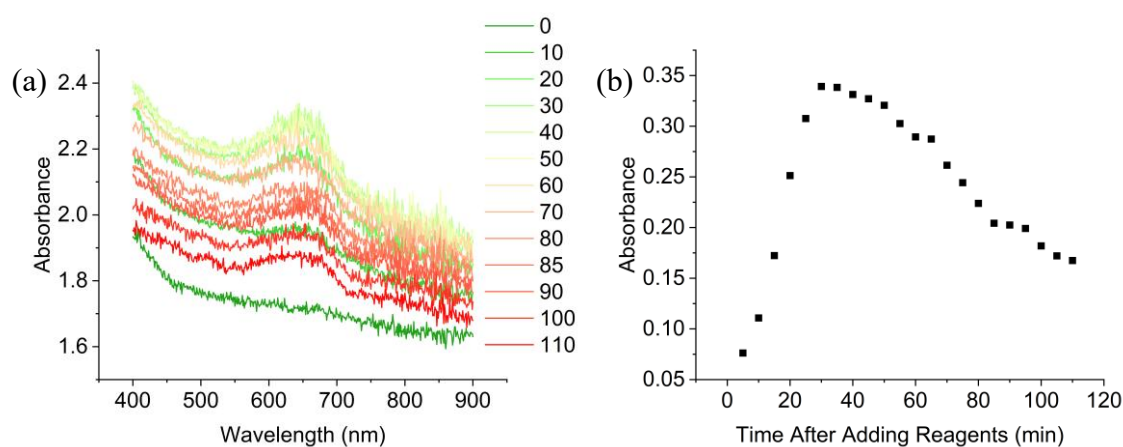


Figure 3.7: (a) Absorbance spectra of a 30 μM NH₄⁺ sample prepared from 400 μL of 0.2 M LiClO₄ in THF, made up to 2 mL with 18.2 M $\Omega\cdot\text{cm}$ deionised water. (b) Corresponding peak absorbance (background at 900 nm subtracted) plotted as a function of time. To each sample, 280 μL of salicylate catalyst solution was added, followed by 280 μL of alkaline hypochlorite solution. Absorbance was recorded at defined time intervals following reagent addition.

The absorbance spectra shown in Figure 3.7a exhibit the same issues observed in the dilution-based calibration curves in Figure 3.6: a high and inconsistent background signal, along with significant spectral noise. These artefacts introduce substantial error in determining the true peak absorbance. As shown in Figure 3.7b, the measured peak absorbance increases approximately linearly over the first 30 min, after which it begins to decline. This trend supports the hypothesis that organic solvents such as THF may chemically degrade the indophenol dye molecule over time. While this observation is consistent with prior reports of organic interference in Berthelot-based assays, no specific literature was found detailing the

interaction between THF and the indophenol complex. Investigating the underlying decomposition mechanism remains outside the scope of this work.

Importantly, the potential degradation of the indophenol dye by THF does not explain the high and inconsistent baseline observed in the absorbance spectra of diluted samples. No published studies addressing this phenomenon could be found. The source of this background interference was in fact identified serendipitously. It was observed that the plastic cuvettes used to hold the samples became visibly opaque upon the addition of the organic electrolyte. This was traced to the solvent–material interaction, as THF is known to dissolve polymethyl methacrylate (PMMA) [127]. THF is commonly used to dissolve PMMA during nanoparticle preparation, which supports the observed alteration in the structure and optical clarity of the cuvettes [128], [129].

To mitigate this issue, samples were instead prepared in glass vials and only transferred to cuvettes immediately before absorbance measurement. This simple adjustment resulted in significantly lower baseline signals and reduced spectral noise. The calibration curve shown previously in Figure 3.6a and Figure 3.6c was repeated using this improved protocol. The updated results are presented in Figure 3.8.

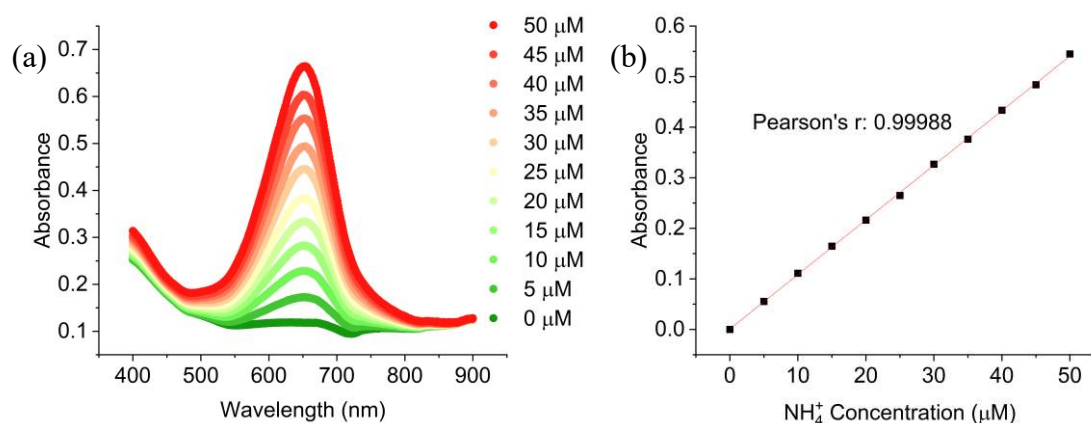


Figure 3.8: Absorbance spectra of 400 μL samples of 0.2 M LiClO_4 in THF, and (b) the corresponding calibration curve obtained by measuring the peak absorbance with background subtraction at 900 nm. Each 400 μL sample was made up to 2 mL with 18.2 $\text{M}\Omega\cdot\text{cm}$ deionised water. Known amounts of NH_4^+ were added as NH_4Cl , followed by the addition of 280 μL of salicylate catalyst solution and 280 μL of alkaline hypochlorite solution. Samples were prepared in glass vials and transferred to cuvettes after 30 minutes. Absorbance measurements were recorded after 45 minutes.

In contrast to the results shown in Figure 3.6, the absorbance spectra in Figure 3.8 (obtained using the modified sample preparation method) exhibit a substantially lower and more consistent background signal, as indicated by the absorbance at 900 nm. Additionally, the signal-to-noise ratio is significantly improved, resulting in excellent linearity in the calibration curve, with a Pearson's r value exceeding 0.999 (Figure 3.8b). This modification to the dilution method brings its accuracy in line with that of the evaporation approach. Given its shorter preparation time and operational simplicity, the improved dilution method was selected over evaporation for all subsequent ammonia quantification experiments.

3.5 Improving Accuracy and Reliability of the Salicylate Method

As discussed in Section 3.2, the phenol method demonstrated superior performance and accuracy compared to salicylate. Nevertheless, salicylate was chosen for this study to be consistent within the research group and allow direct comparison of datasets. This section focuses on identifying and addressing other major sources of error within the quantification procedure. The aim is to optimise the overall methodology so that high accuracy can still be achieved, despite the inherent limitations of the salicylate reagent.

3.5.1 *Determining Optimal Concentration Range*

Due to variations in background signal and the inherent sensitivity limitations of the spectrophotometer, the lower limit of quantification for this method is approximately 1 μM NH_4^+ . For this reason, samples should ideally contain ammonia concentrations above this threshold to ensure reliable detection. However, excessively high ammonia concentrations introduce other issues. As shown in Figure 3.9, which presents a calibration curve prepared using 0.2 M LiClO_4 in THF, two key problems arise at higher concentrations.

First, the linearity of the calibration curve begins to degrade, with the absorbance values of higher concentration samples falling below the expected trend. This deviation is consistent with the previously discussed effects in Section 3.2. Second, once the absorbance exceeds approximately 1.75, the spectral noise increases significantly. This occurs because less light reaches the detector at high absorbance values, bringing the signal closer to the noise floor of the instrument and thereby reducing the signal-to-noise ratio.

To minimise the impact of these two effects, the ammonia concentration in samples should ideally be maintained within the range of 1–100 μM , with optimal accuracy achieved between 10–50 μM . This can be consistently achieved through the application of appropriate dilution ratios during sample preparation.

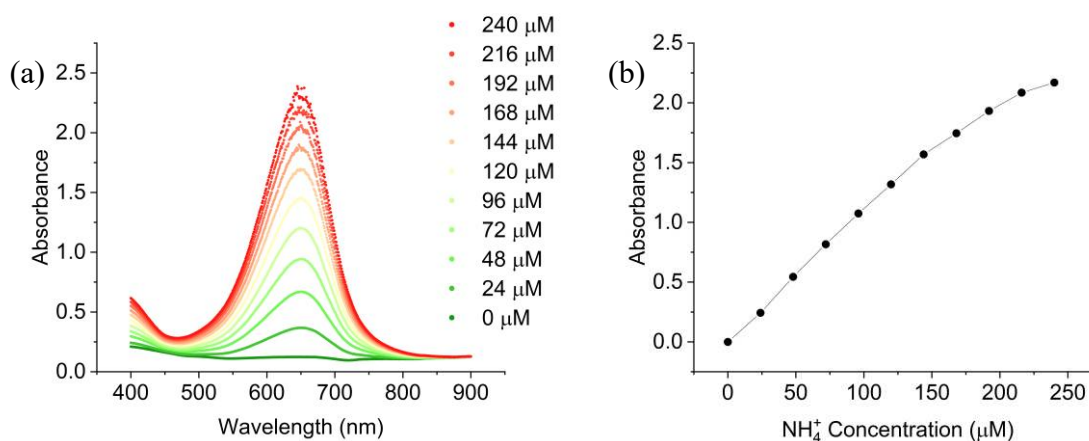


Figure 3.9: (a) Absorbance spectra of 400 μL samples of 0.2 M LiClO_4 in THF, and (b) the corresponding calibration curve obtained by measuring peak absorbance with background subtraction at 900 nm. Samples were prepared by evaporating the electrolyte and re-dissolving the remaining solids in 18.2 $\text{M}\Omega\text{-cm}$ deionised water. Each 2 mL sample contained the equivalent of 400 μL of electrolyte. Known amounts of NH_4^+ were added as NH_4Cl , followed by 280 μL of salicylate catalyst solution and 280 μL of alkaline hypochlorite solution. Absorbance was measured 45 minutes after reagent addition.

3.5.2 Quantification of Adventitious Ammonia

It is well established in the field of electrochemical nitrogen reduction that nitrogen-containing contaminants are commonly present in laboratory environments, and great care must be taken to minimise and account for these sources of error [20], [130]. Baseline levels of ammonia contamination can originate from reagents, storage containers, or ambient exposure, all of which may affect the accuracy of low-concentration measurements. To establish a baseline for expected contamination levels, standard addition quantification was performed on 18.2 M Ω deionised water using three salicylate reagent solutions of varying ages: one freshly prepared, one stored for three months, and another stored for nine months. The results of this analysis are presented in Figure 3.10a.

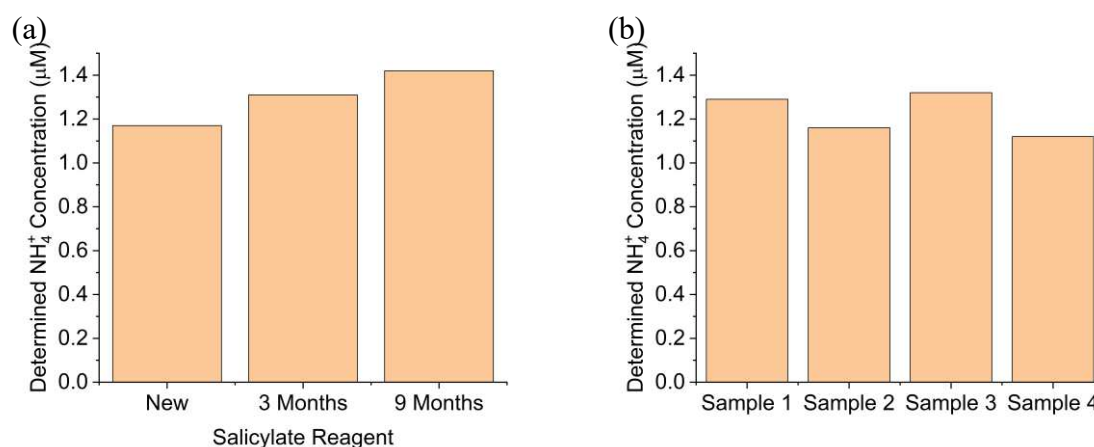


Figure 3.10: (a) NH_4^+ concentration determined using various salicylate reagent preparations with 18.2 M Ω -cm deionised water as the sample matrix, and (b) in 1 M LiBF_4 in diglyme electrolytes prepared using the same salicylate reagents on different days. Quantification was carried out via the salicylate method using standard additions and appropriate dilution.

Figure 3.10a shows that measurable amounts of ammonia are present even in samples prepared using 18.2 M Ω deionised water. This contamination likely originates from the quantification reagents themselves or from adventitious nitrogen-containing species that either generate ammonia or interfere with the assay by producing the indophenol dye directly. Figure 3.10b presents the results of ammonia quantification in 1 M LiBF_4 in diglyme electrolytes (current state-of-the-art electrolyte in continuous Li-NRR flow cells [26], [29]), all prepared from the same batch of reagents but on different days. The detected ammonia levels are comparable to those observed in the water-based controls, suggesting that the primary source of contamination is either the quantification reagents or ambient environmental exposure, rather than the electrolyte components themselves.

Notably, Figure 3.10b also highlights significant day-to-day variability in ammonia contamination, even when the same reagents are used. While the absolute concentration of ammonia may appear small, a contamination level of just 1 μM can correspond to a faradaic efficiency in the range of 1–10%, depending on the total charge passed during an experiment (e.g., 1–10 C). Therefore, to ensure accurate determination of ammonia yield and Faradaic efficiency, it is essential to quantify the baseline ammonia concentration present in the freshly prepared electrolyte and subtract this value from the final measured concentration in every experiment.

3.5.3 Identification of Appropriate Signal Background

In the field of lithium-mediated nitrogen reduction, various approaches are used to extract a single representative absorbance value from each UV–Vis spectrum. This typically involves calculating the difference between the peak absorbance and a corresponding background value. However, the methods used to determine these values vary across research groups. The wavelength of maximum absorbance generally falls near 650 nm but can shift by a few nanometres from day to day due to slight variations in reagent composition, temperature, or instrument calibration. As a result, it is more accurate to identify the peak absorbance directly from each individual spectrum rather than using a fixed wavelength value.

Similarly, the background signal can vary significantly between samples and measurement sessions, making background correction essential for accurate quantification. Common practice involves subtracting the absorbance at a baseline wavelength on either side of the main peak, typically around 475 nm or 850 nm [20], [41]. However, based on experimental observations in this work, 900 nm was consistently the most stable and invariant region across all spectra obtained using the salicylate assay and was therefore selected as the reference wavelength for background correction.

3.6 Conclusion

An accurate, consistent, and convenient method for quantifying ammonia in non-aqueous electrolytes is a critical foundation for the study of Li-NRR. Among the available methods, colorimetric detection based on the Berthelot reaction is widely used due to its high sensitivity, accessibility, operational simplicity, and moderate tolerance to interferents such as organic solvents. Despite its popularity, numerous variations in its implementation exist across the literature, and the relative advantages and limitations of each approach have not been clearly established. This study systematically investigated the performance of the most commonly used variations, focusing on three key methodological decisions: (1) the choice between phenol and salicylate as the quantification reagent, (2) the use of calibration curves vs. standard additions to relate absorbance to concentration, and (3) the use of dilution vs. solvent evaporation for sample preparation.

The phenol method was found to be more accurate and consistent than the salicylate method. However, to be consistent with the researcher group and allow direct comparison of datasets, the salicylate method was chosen for continued use in this project. Calibration curves, though widely employed in prior studies, were shown to be unreliable due to variability in the absorbance–concentration gradient, particularly with the salicylate method. This inconsistency calls into question the accuracy of quantitative results reported in earlier studies that relied solely on external calibration curves without accounting for time-dependent changes in reaction kinetics or matrix effects. As such, this study strongly supports the use of standard addition as a more robust and reliable approach for ammonia quantification in non-aqueous systems.

Sample dilution was found to perform comparably to solvent evaporation, provided that samples were initially stored in glass vials and only transferred to cuvettes immediately prior to absorbance measurement. Due to its significantly shorter turnaround time and reduced sample handling, dilution was selected as the preferred method. To further enhance the accuracy and consistency of the protocol, it was found that sample ammonia concentrations

should be maintained within 1–100 μM , ideally between 10–50 μM ; background ammonia levels in freshly prepared electrolyte should be measured and subtracted from final concentrations; and the peak absorbance value should be corrected by subtracting the baseline absorbance at 900 nm. Together, these optimisations establish a reliable, evidence-based methodology for ammonia quantification that underpins the subsequent chapters of this thesis and contributes toward standardising best practices in the field.

4 Quantification of Gas Phase Ammonia (Mass-Spectrometry)

4.1 Introduction

Ammonia generated during Li-NRR may remain dissolved in the electrolyte (referred to as ‘dissolved ammonia’ more generally but encompasses both $\text{NH}_{3(\text{non-aq})}$ and $\text{NH}_4^+_{(\text{non-aq})}$) but it can also volatilise and escape as gas phase ammonia (also referred to as gaseous ammonia or $\text{NH}_{3(\text{g})}$). Therefore, measuring the evolved gas phase ammonia in addition to the dissolved ammonia is essential to accurately measuring ammonia yields and hence system performance. Furthermore, the ratio between gas phase ammonia and dissolved ammonia (ammonia distribution) is of great interest. This distribution is important because in a commercial setting, gas phase ammonia would be much easier and cheaper to separate and extract from the system compared to dissolved ammonia [26], [29], [35], [44]. Therefore, understanding the mechanisms responsible for the ammonia distribution is essential for developing the applicability of the lithium-mediated system.

As discussed in the Section 1.7, ECMS is a very powerful technique and offers numerous advantages for the real-time detection of gas phase ammonia. The primary advantages include unprecedented sensitivity (pmol/s), quantitative in-situ monitoring with fast response times (~ 1 s) and the ability to continuously monitor multiple mass/charge signals. However, the development of a consistent and accurate methodology for detecting in situ gas phase ammonia in real time using ECMS remains highly challenging. To date, only a single publication by Krempl et al. has demonstrated successful real time detection under lithium-mediated conditions [4]. This chapter aims to address the challenges of real-time ammonia detection using ECMS by systematically developing a robust and reproducible protocol, guided by an evidence based approach. Through iterative experimentation and careful control of experimental parameters, this work seeks not only to establish a reliable method for detecting *in-situ* generated gas phase ammonia, but also to gain mechanistic insight into the factors that govern ammonia evolution, transport, and detection under lithium-mediated conditions.

This systematic approach to real time ammonia detection is structured around three key stages: 1) detection of gas phase ammonia using ECMS, 2) electrochemical generation of ammonia in the ECMS cell, and 3) real-time detection of *in-situ* generated gas phase ammonia. Together, these stages provide a robust foundation for future mechanistic studies and real time monitoring of ammonia in Li-NRR.

4.1.1 Challenges of Gas Phase Ammonia Detection Using ECMS

The first step was to determine whether the ECMS system could detect the extremely low concentrations of ammonia produced by Li-NRR, typically on the order of pmol/s. As discussed in the Section 1.7.3, two primary challenges affect sensitivity at this scale: ammonia adsorption and spectral overlap with water. Ammonia is known to adsorb onto tubing, chamber walls, and inlets within mass spectrometry systems, which can delay response times and significantly reduce the amount of ammonia reaching the detector [114], [115], [116]. In low yield experiments, this adsorption may prevent detection altogether. Heating the vacuum chamber can mitigate adsorption by promoting desorption and improving signal response.

The second challenge is spectral interference from water. Ammonia and water both produce a signal at m/z 17, corresponding to NH_3^+ (17.03 amu) and OH^+ (17.01 amu), respectively. With a quadrupole mass spectrometer, the resolution is insufficient to distinguish these fragments [108], [110], [117]. Consequently, elevated or fluctuating water levels can obscure or falsely resemble ammonia signals. This can be addressed using soft ionisation, a technique that lowers the ionisation energy to reduce fragmentation. At 20 eV, the m/z 17 peak from water is effectively suppressed, minimising interference [118], [119]. Krempel et al. successfully applied both chamber heating and soft ionisation to achieve real time detection of in situ generated ammonia using ECMS [35].

4.1.2 Challenges of Electrochemical Ammonia Generation in the ECMS Cell

While Li-NRR has been rigorously validated as a viable pathway for ammonia synthesis [20], several factors can still cause individual experiments to yield little or no ammonia. As discussed in Sections 1.4.4 and 1.4.5, electrolyte acidification and electrode crosstalk are two prominent mechanisms that can significantly suppress ammonia formation. These effects are particularly likely to be amplified in the ECMS cells used in this study due to their unique configuration.

Most previous studies have employed single compartment batch cells with working volumes between 1 and 20 mL [22], [42], [131], [132]. In contrast, the ECMS cell is a stagnant thin layer design with a working volume of approximately 20 μL . This extremely low volume, combined with a relatively high electrode area to electrolyte volume ratio, exacerbates electrolyte acidification because there is less electrolyte to dilute the fouling byproducts of electrolyte oxidation. In particular, protic species generated at the counter electrode can accumulate rapidly and poison the working electrode, inhibiting nitrogen reduction.

Another critical challenge associated with the small ECMS cells (0.15–0.2 cm^2 electrode area, ~ 20 μL volume) is the low ammonia yield. Li NRR inherently produces low quantities of ammonia, which already necessitates the use of highly sensitive detection techniques. In cells of this scale, the amount of ammonia generated may fall below the detection limits of ECMS or UV–Vis colorimetry, making it difficult to distinguish true electrochemical production from background contamination [20], [130].

In summary, the specialised ECMS cell configurations used in this work introduce several challenges for successful ammonia detection. Chief among them are enhanced electrolyte acidification and crosstalk due to the confined geometry, as well as reduced ammonia yield, which may be insufficient to exceed the threshold of detection.

4.1.3 Challenges of Real-Time Detection of in-situ Generated Gas Phase Ammonia

Although ammonia may be produced *in-situ* at the working electrode during Li-NRR several factors may prevent it from reaching the detector in the gas phase. One potential barrier is the trapping of synthesised ammonia within the separators used in the parallel electrode cell (Figure 4.1b). Previous studies have reported that separators and membranes can act as ammonia absorbers, thereby impeding its release into the gas phase [20]. Additionally,

ammonia formed at the working electrode may be oxidised at the counter electrode before it has a chance to escape the electrolyte.

Furthermore, researchers at DTU found that the ammonia produced in lithium-mediated systems is distributed among three primary forms: gas phase ammonia, dissolved ammonia in the electrolyte, and ammonia trapped within electrode surface deposits [26], [29], [44]. The relative distribution between these forms varies significantly depending on factors such as electrolyte composition, the application of current pulsing, and cell geometry. In the case of the ECMS cell used in this study, one of the most likely challenges is electrolyte acidification due to anodic solvent oxidation, which can stabilise ammonia as NH_4^+ and reduce its volatility.

In summary, the main obstacles to detecting gas phase ammonia in this system include oxidation of ammonia at the counter electrode, absorption by the separator, and electrolyte acidification leading to ammonia retention as dissolved NH_4^+ .

4.1.4 Overview of Cell Configurations Used

The original ECMS cell design, referred to in this work as the separated electrode cell, is shown in Figure 4.1c. This configuration features a dedicated chamber for the counter electrode, which effectively minimises diffusion between the electrodes. As a result, it enables isolated study of the working electrode. However, this design also introduces limitations, including uneven current distribution and significant ohmic resistance, both of which restrict the achievable current density.

An alternative design, the parallel electrode cell shown in Figure 4.1b, was developed in our group for Li-ion battery studies [112]. It offers improved current distribution and reduced ohmic drop due to the close spacing of the electrodes. However, it also introduces substantial crosstalk between electrodes, as discussed in Section 4.1.4.

The cell shown in Figure 4.1d is a modified version of the parallel electrode cell, engineered to reduce mechanical damage to the ECMS chip during assembly and operation. Finally, the configuration shown in Figure 4.1a is used for calibration experiments. In this setup, the chip is sealed with epoxy to create a closed system, allowing the backing gas to flow directly to the detector without dilution or leakage.

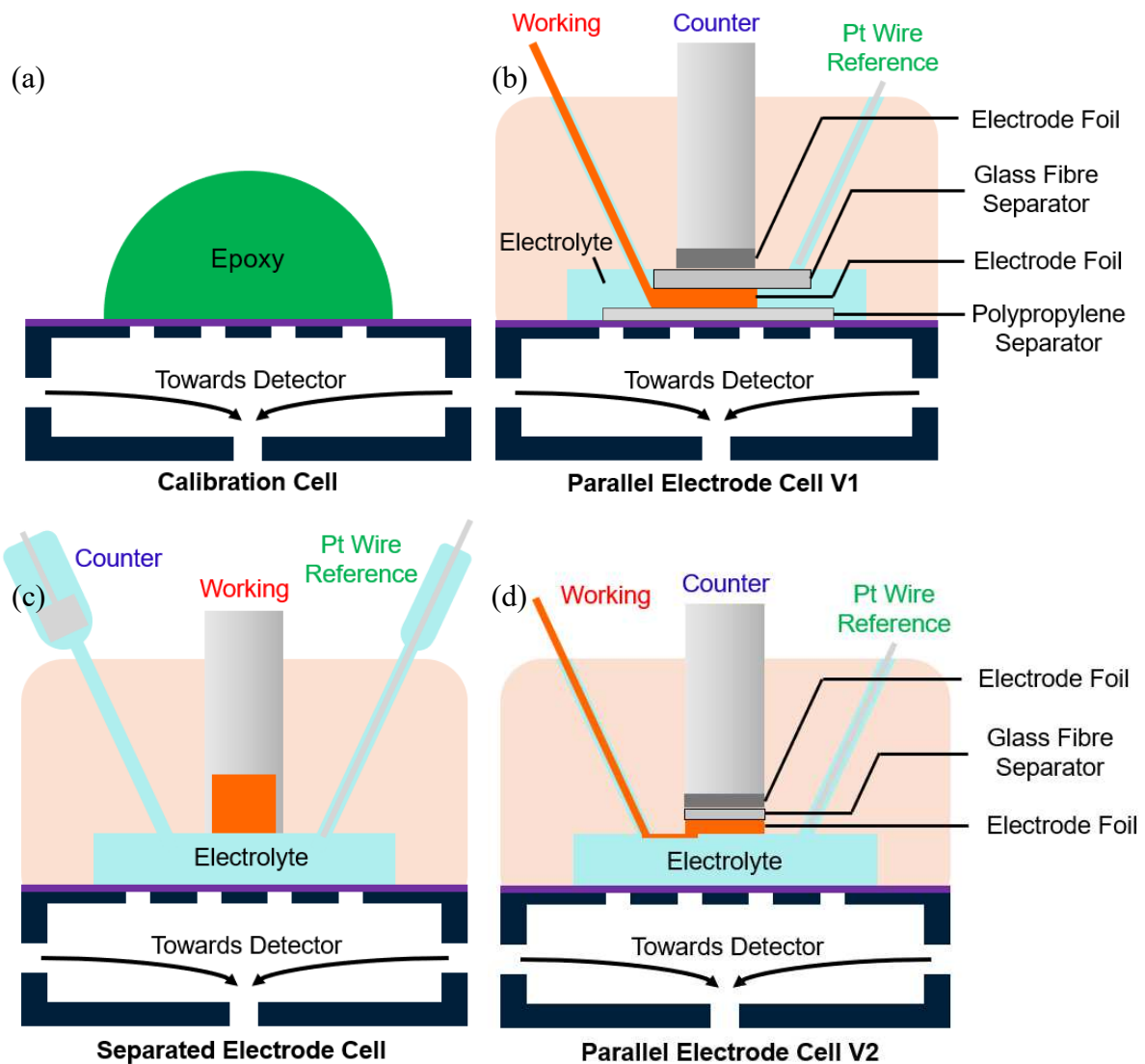


Figure 4.1: Diagrams of the ECMS cell configurations used in this project. (a) Chip sealed with epoxy to create a fully enclosed ECMS system for gas calibration experiments. (b) Version 1 of the parallel electrode cell assembly. (c) Separated electrode cell featuring four ports, with two counter electrodes used to enable more symmetric current distribution, similar to the configuration described by Krempel et al. [35]. (d) Version 2 of the parallel electrode cell, developed to prevent chip damage observed with version 1, which limited its reusability to one or two experiments.

4.2 Validation of Gas-Phase Ammonia Detection Using ECMS

Although Krempf et al. successfully demonstrated the real-time detection of gas phase ammonia ($\text{NH}_3(\text{g})$) using ECMS by employing both chamber heating and soft ionisation, no studies had evaluated whether ammonia could be detected using the default ECMS configuration without these modifications. In this work, the ECMS instrument was housed within an argon glovebox, providing a uniquely advantageous environment with ultra-low water and oxygen levels. Installing a chamber heater in the glovebox would have posed significant challenges, required extended instrument downtime, and risked compromising the glovebox atmosphere. Therefore, the aim was to determine whether $\text{NH}_3(\text{g})$ could be detected without any hardware modifications.

To introduce ammonia into the system in a controlled manner, a certified gas mixture containing 1000 ppm of ammonia in N6.0 purity nitrogen was used as the backing gas. The chip membrane was sealed with epoxy (as shown in Figure 4.1a) to create a closed configuration that forced the backing gas to flow directly into the detector. The chosen concentration of 1000 ppm was selected to yield an ammonia flux comparable to that expected from a typical Li-NRR experiment ($\sim 7 \text{ pmol s}^{-1}$).

To test the system's sensitivity, N6.0 nitrogen was first used as the backing gas, and the system was allowed to equilibrate for 40 hours to ensure stable baseline signals. At approximately 11,200 seconds (Figure 4.2a), the backing gas was switched to the 1000 ppm ammonia mixture. Following signal stabilisation, the gas was switched back to pure N_2 . Upon introduction of the ammonia mixture, the signals at m/z 17 and 16 rose well above the noise floor, m/z 15 increased slightly, and m/z 18 showed a small decrease, suggesting no significant interference from water. These results clearly demonstrate that the ECMS system is capable of detecting picomole-per-second levels of ammonia even without soft ionisation or chamber heating.

The successful detection without soft ionisation is likely due to the extremely low water content ($<1 \text{ ppm}$) in the glovebox. Soft ionisation is typically used to suppress the water-derived OH^+ signal at m/z 17, but with minimal water present, interference was negligible. This is confirmed in Figure 4.2a, where the baseline signal at m/z 17 prior to ammonia introduction is essentially zero.

Krempf et al. employed chamber heating to mitigate ammonia adsorption on the vacuum chamber walls, which they reported as a cause of slow signal response. Despite this, their system exhibited a gradual signal increase and did not fully stabilise even after 14 hours [35] (Figure 4.2c). By contrast, the unmodified ECMS setup used here showed significantly faster response dynamics, with a 10–90% rise time of 1850 seconds. While the ammonia concentration used in this work (1000 ppm) was higher than that used by Krempf et al. (315 ppm), this difference is unlikely to account for the substantially faster signal response observed, suggesting that system design and environmental conditions play a more dominant role in determining response time.

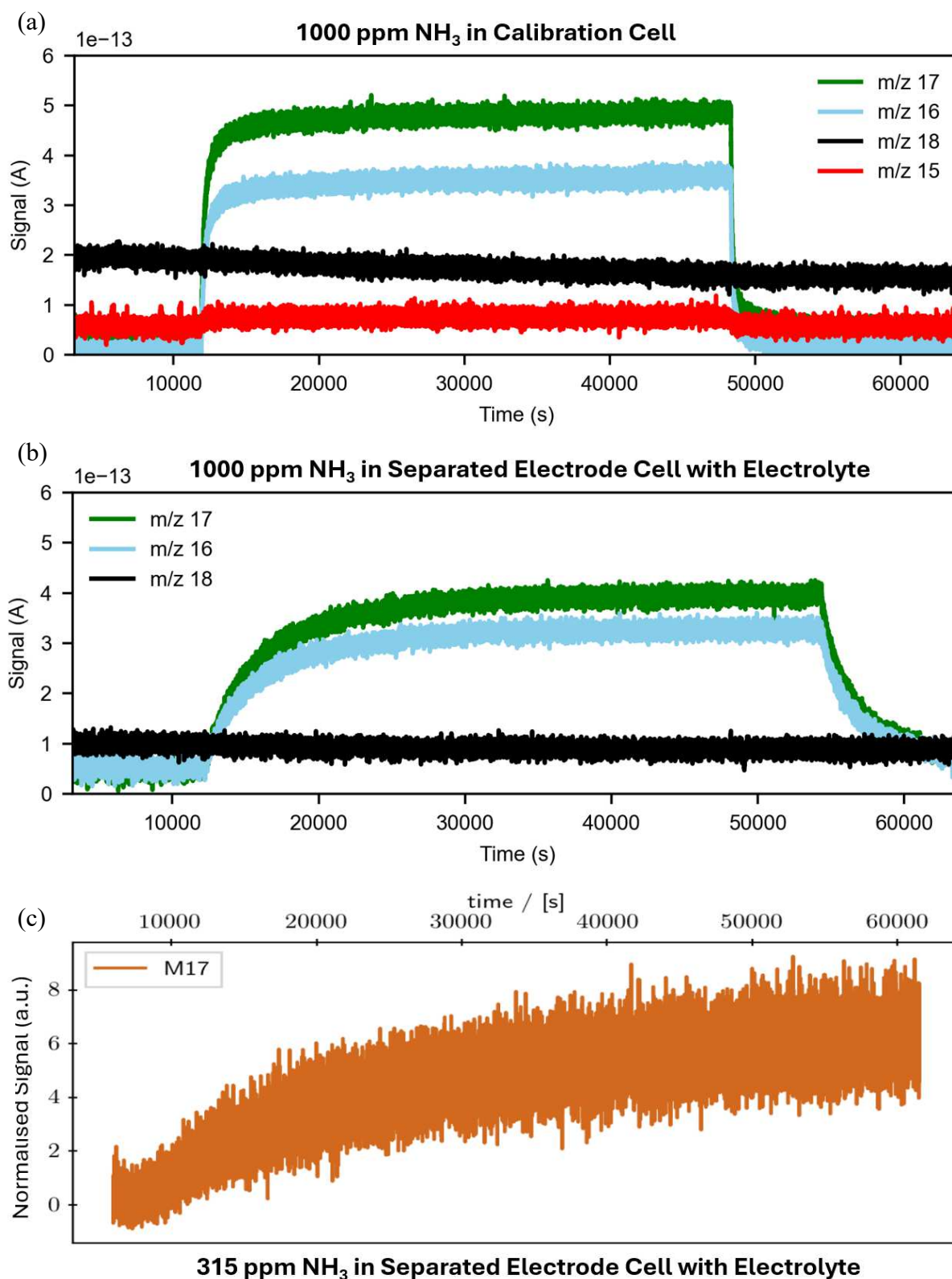


Figure 4.2: m/z signals associated with NH_3 shown as a function of time under different ECMS conditions: (a) 1000 ppm NH_3 in N_2 introduced into an ECMS system with an epoxy-sealed chip; (b) 1000 ppm NH_3 in N_2 introduced into an ECMS system with a parallel electrode cell filled with 1 M LiTFSI in diglyme containing 1 vol % Ethanol; and (c) 315 ppm NH_3 in N_2 introduced into an ECMS system containing 2 M LiOTf and 1 vol % Ethanol (Figure c reproduced with permission from [35]).

The significant difference in response time is likely attributable to the different cell configurations used in each study. In this work, the ammonia backing gas was introduced into a chip that had been sealed with epoxy, effectively minimising the risk of leaks and creating a direct path for ammonia to reach the detector. In contrast, Krempel et al. introduced ammonia into a system where an electrolyte-filled cell (similar to the one shown in Figure 4.1c) was positioned on top of the chip. In that configuration, the ammonia gas could follow two competing pathways: into the detector or into the electrolyte above the chip.

As a result, a portion of the introduced ammonia could dissolve into the electrolyte, delaying its detection in the gas phase. Only after the electrolyte became saturated with ammonia would the flux into the detector stabilise and reach its maximum. To test this hypothesis, the experiment was repeated using an electrolyte-filled cell mounted on the chip. The configuration shown in Figure 4.1b was used without electrodes or separators, and electrolyte-filled syringes were inserted into the inlet and outlet ports. The results are presented in Figure 4.2b.

As shown, the response time in the presence of electrolyte is significantly prolonged. The 10 to 90 percent rise time was measured at 10,820 seconds—approximately five times longer than that of the epoxy-sealed chip—confirming the influence of electrolyte absorption on response dynamics. These findings clearly demonstrate that ammonia can be successfully detected using the default ECMS configuration, without the need for soft ionisation or chamber heating, and with faster response times than previously reported by Krempel et al. [35].

4.3 Verification of Electrochemical Ammonia Generation in the ECMS Cell

4.3.1 *False Positive (Methane)*

Following the successful detection of gas phase ammonia using the ECMS, the next objective was to determine whether ammonia could be synthesised *in-situ* within the ECMS cell. For the initial trial, a commonly used electrolyte (0.6 M LiClO₄ in THF with 1 vol% ethanol, as reported by Westhead et al. in our group [40]) was employed in the parallel electrode ECMS cell (Figure 4.1b), using a Cu working electrode, Pt counter electrode, and a Pt wire pseudo reference electrode.

The rationale for selecting the parallel electrode configuration, as discussed in Section 4.1.4, lies in its ability to provide a more uniform current distribution and support higher current densities, in contrast to the separated electrode cell used by Krempel et al. [35] (Figure 4.1c). These advantages made the parallel configuration more suitable for ammonia synthesis.

After assembling the cell and injecting the electrolyte, the system was allowed to rest for 1 hour (not shown in Figure 4.3) to allow the mass spectrometry signals and electrochemical potentials to stabilise. The electrochemical protocol, illustrated in Figure 4.3, consisted of the following sequence: (1) a LSV scan from OCP to -1 mA cm^{-2} at a scan rate of 5 mV s^{-1} ; (2) a

CP step at -1 mA cm^{-2} for 2400 s; (3) PEIS at -3 V vs. the reference; and (4) a return to open circuit conditions.

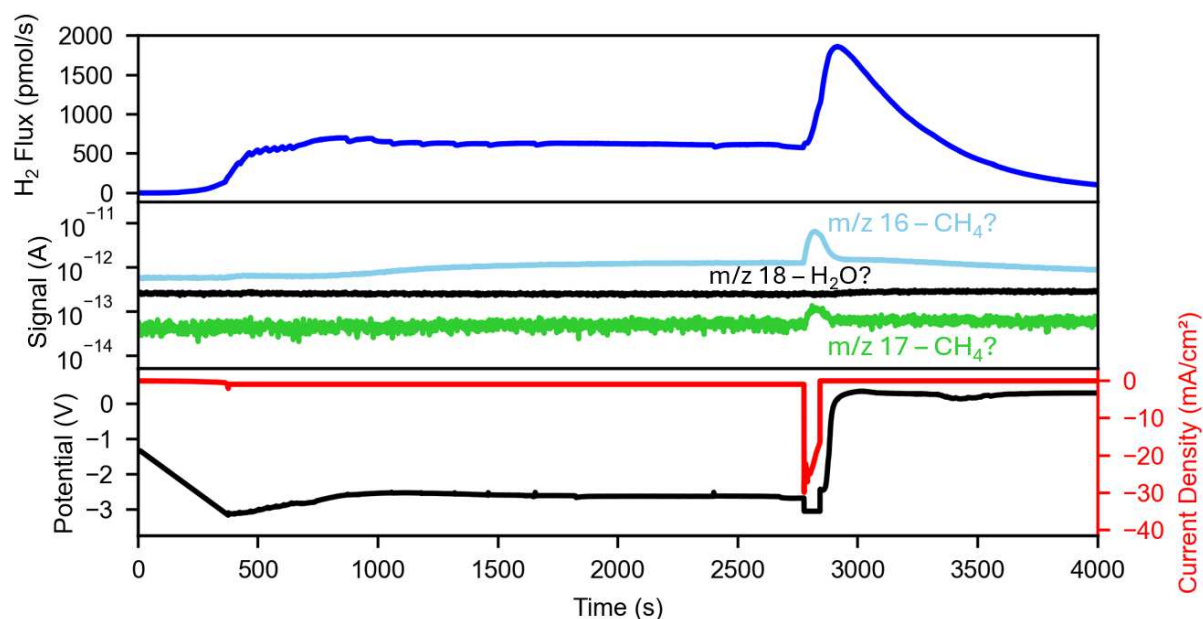


Figure 4.3 Li-NRR experiment conducted in a parallel electrode cell (shown in Figure 4.1b) using 0.6 M LiClO_4 in THF with 1 vol % Ethanol as the electrolyte. A Cu working electrode, Pt counter electrode, and Pt wire pseudo-reference electrode were employed. The electrochemical protocol consisted of: (1) linear sweep voltammetry (LSV) from open circuit potential (OCP) to -1 mA cm^{-2} at 5 mV s^{-1} ; (2) chronopotentiometry at -1 mA cm^{-2} for 2400 s; (3) potentiostatic electrochemical impedance spectroscopy (PEIS) at -3 V vs the reference; and (4) return to open circuit conditions. High-purity N6.0 N_2 was used as the backing gas.

The first noteworthy feature in Figure 4.3 is an OCP of -1.36 V which is untypically negative. The OCP depends on several factors like electrolyte composition, electrode material and cell configuration but is typically around $-0.2 \pm 0.4 \text{ V}$. The reason for this large OCP is unknown but is most likely due to an issue with the setup of the reference electrode. The issue did not seem to effect the Li plating potential (-3.1 V , which is fairly typical) and never occurred again in future experiments.

The m/z 2 signal is due to H_2 and has been quantified using calibration experiments (according to the procedure outlined in Section 2.2.2), while the other m/z signals could not be confidently identified and are thus plotted as raw signals. During the LSV, H_2 flux began to increase at around -2 V which is highly likely due to ethanol reduction. After around 500 s of -1 mA/cm^2 the m/z 16 signal began to increase, most likely due to methane evolution, however, m/z 17 stayed unchanged, indicating no ammonia being detected. At around 2700 s, PEIS was initiated at -3 V which caused a huge spike in current reaching a peak of -30 mA/cm^2 which caused a large increase in m/z 2, 16 and 17. The m/z 16/17 ratio and response time of m/z 17 did not match up with that of ammonia.

From the ammonia gas experiments performed above (Figure 4.2), the m/z 16/17 ratio of ammonia was measured to be 0.75 and corresponds well to the NIST database value of 0.8 [133]. The m/z 16/17 ratio measured from Figure 4.3 was 86, suggesting the evolution of a different gas, most likely methane. Furthermore, the m/z 17 signal in Figure 4.3 began to increase, peaked and fully decayed within 120 s. As seen from Figure 4.2b, ammonia typically has a much higher rise time of $\sim 10000 \text{ s}$. In addition, the electrolyte used in the experiment was

collected and the amount of ammonia in it was determined to be 3 nmol (using the colorimetry methods developed in Chapter 3), which corresponds to an essentially negligible faradaic efficiency of 0.05%. This data clearly shows that the first attempt was unsuccessful at generating ammonia.

4.3.2 Increasing Ammonia Yield

Since the first attempt proved unsuccessful, the next step was to attempt to increase the amount of ammonia generated to increase the likelihood of overcoming the detection limit of the instrument. 1 M LiTFSI in THF with 0.1 vol% Ethanol was chosen as the electrolyte as it was one of the highest performing electrolytes reported by our group [40], with a typical faradaic efficiency of ~30% in a single compartment cell with a working volume of ~12 mL. To further increase the ammonia yield, the current density for the CP was increased to -2 mA/cm^2 .

After assembling the cell and injecting the electrolyte the system was left to rest until signals stabilised (20 min). The potential was then swept from OCP until Li plating was achieved (indicated by a sharp, large increase in current after around -3 V), followed by CP at -2 mA/cm^2 for 5000 s. The results are shown in Figure 4.4a.

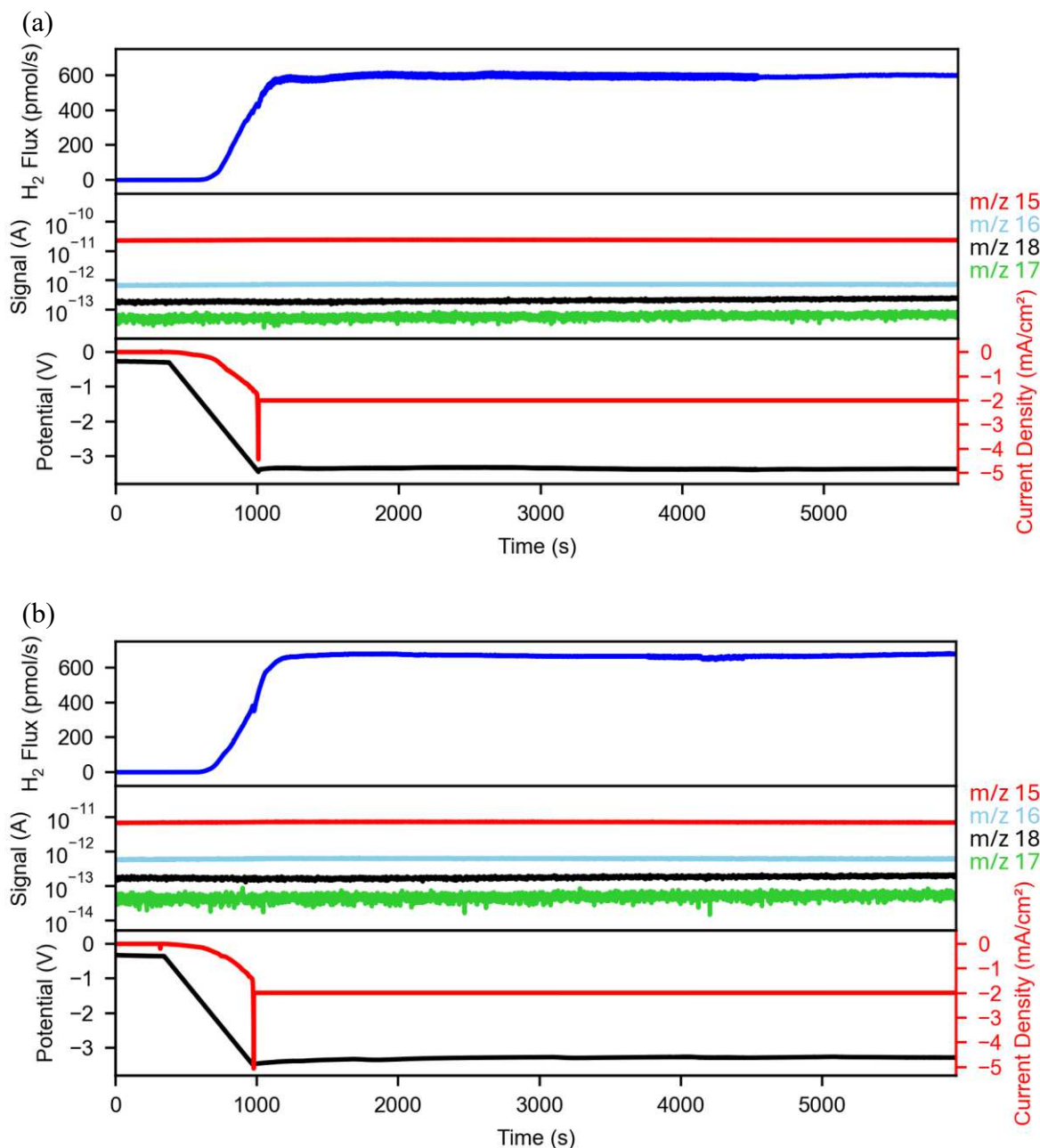


Figure 4.4: Li-NRR experiments conducted in a parallel electrode cell (shown in Figure 4.1b) using 1 M LiTFSI in THF with (a) 0.1 vol % Ethanol and (b) 0 vol % Ethanol as the electrolyte. A Cu working electrode, Pt counter electrode, and Pt wire pseudo-reference electrode were used. The electrochemical protocol consisted of: (1) linear sweep voltammetry (LSV) from open circuit potential (OCP) to the onset of lithium plating at a scan rate of 5 mV s⁻¹; and (2) chronopotentiometry at -2 mA cm⁻² for 4600 s. High-purity N6.0 N₂ was used as the backing gas.

Similar to the first attempt, only H₂ was detected during the LSV, with an onset potential of -1.2 V. During CP, the H₂ stabilised quickly and remained constant for the remainder of the experiments. All other signals did not change during the experiment indicating that only H₂ was produced. Furthermore, colorimetric quantification of the electrolyte after the experiment showed negligible amounts of ammonia. This was likely due to the substantial acidification of the electrolyte, which made the HER so thermodynamically favourable that it entirely outcompeted nitrogen reduction.

The fact that H_2 evolution stabilised quickly after the LSV and remained quite constant throughout the rest of the experiment is quite significant. H_2 evolution in the lithium-mediated system comes from the reduction of protic sources, either electrochemically at the working electrode or from reaction with Li metal. In the electrolyte prepared for the experiment above, the only protic source is Ethanol and around $0.7\ \mu\text{mol}$ of Ethanol was present in the working volume of the ECMS cell used. Assuming 2 mol of Ethanol are needed to evolve 1 mol of H_2 (by the equation shown below), $0.35\ \mu\text{mol}$ of H_2 can be evolved before the Ethanol is depleted. In the experiment above, a total of $3\ \mu\text{mol}$ of H_2 was evolved which means that the H_2 was coming from a protic source other than Ethanol. To confirm this, this experiment was repeated without Ethanol and the results are shown in Figure 4.4b. The experiment without Ethanol looks virtually identical with almost the same amount of H_2 being evolved, $3.36\ \mu\text{mol}$. This confirms that Ethanol played an insignificant role in the evolution of H_2 in these experiments and that some other protic source is responsible for the H_2 evolution in this setup. The most likely source of these protic species were the products from solvent oxidation at the counter electrode (see Section 1.4.4 for discussion on the likely mechanisms).

4.3.3 Investigating Acidification from Anodic Solvent Oxidation

To determine whether the reactions occurring at the counter electrode were playing a significant role in the evolution of H_2 and the acidity of the system, experiments were performed using different counter electrode materials. Three different materials were chosen: Pt, Li and Lithium Iron Phosphate (LFP). Pt was chosen to act as the baseline since this is what was used in the previous experiments and is the most common counter electrode material in Li-NRR [20], [21], [42]. Li metal was chosen because it was assumed that Li dissolution would be favoured over any other reactions on this electrode, thus eliminating (or at least reducing) the generation of protic species from solvent oxidation. However, in a typical Li-NRR system, Li cannot be used at the counter as it will just react with Ethanol in the electrolyte, for this reason LFP was also chosen as a counter electrode. It was thought that LFP would also favour Li dissolution over solvent oxidation while being more chemically stable than Li and hence wouldn't react with Ethanol in the electrolyte [132], [134]. Experiments were conducted using 1 M LiTFSI in THF with no Ethanol (because this would just react with the Li counter electrode). Results shown in Figure 4.5.

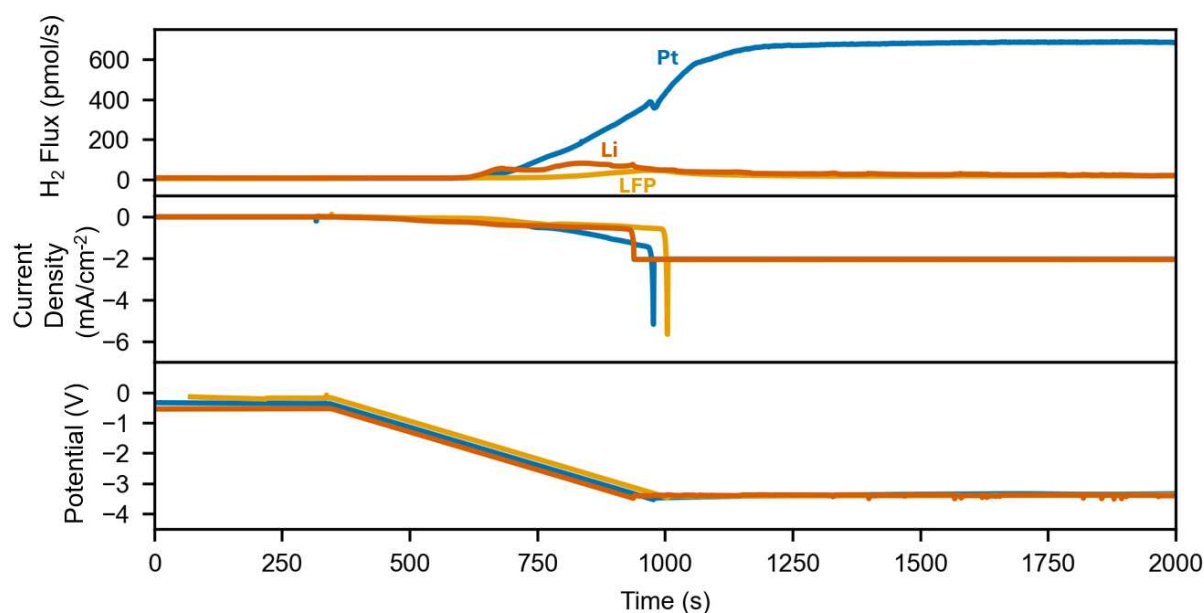


Figure 4.5: Hydrogen flux, current density, and potential as a function of time during NRR in a parallel electrode ECMS cell (Figure 4.1b) using 1 M LiTFSI in THF with 0 vol % Ethanol. Data are shown for three different counter electrode materials, co-plotted in each subplot as distinct coloured traces. A Cu working electrode, Pt wire pseudo-reference electrode, and one of either a Pt, Li, or LFP counter electrode were used. Working electrode area: 0.15 cm^2 . The electrochemical protocol consisted of: (1) linear sweep voltammetry (LSV) from open circuit potential (OCP) to the onset of lithium plating at a scan rate of 5 mV s^{-1} , and (2) chronopotentiometry at -2 mA cm^{-2} for 1200 s. High-purity N6.0 N_2 was used as the backing gas.

Figure 4.5a shows the H_2 flux vs potential during the LSV and Figure 4.5b shows the H_2 flux vs time during the CP that immediately followed. It can be clearly seen that substantially less H_2 was evolved in the LSV and CP when Li and LFP counters are used when compared to Pt. Furthermore, during the CP, H_2 flux kept increasing and then quickly stabilised when Pt was used. However, when Li or LFP were used, the H_2 flux continually decayed during the CP, reaching almost 0 after $\sim 400 \text{ s}$ for both.

The results shown in Figure 4.5 demonstrate that the choice of counter electrode material has a very significant impact on the H_2 evolution when Ethanol is absent from the system. However, as discussed in Section 1.4.3, ethanol plays an important role in Li-NRR and has been shown to greatly enhance performance. Therefore, to gain a more complete picture of the role of counter electrode material, LFP and Pt were compared in the presence of 0.5 vol% ethanol using the same electrolyte as before (results shown in Figure 4.6).

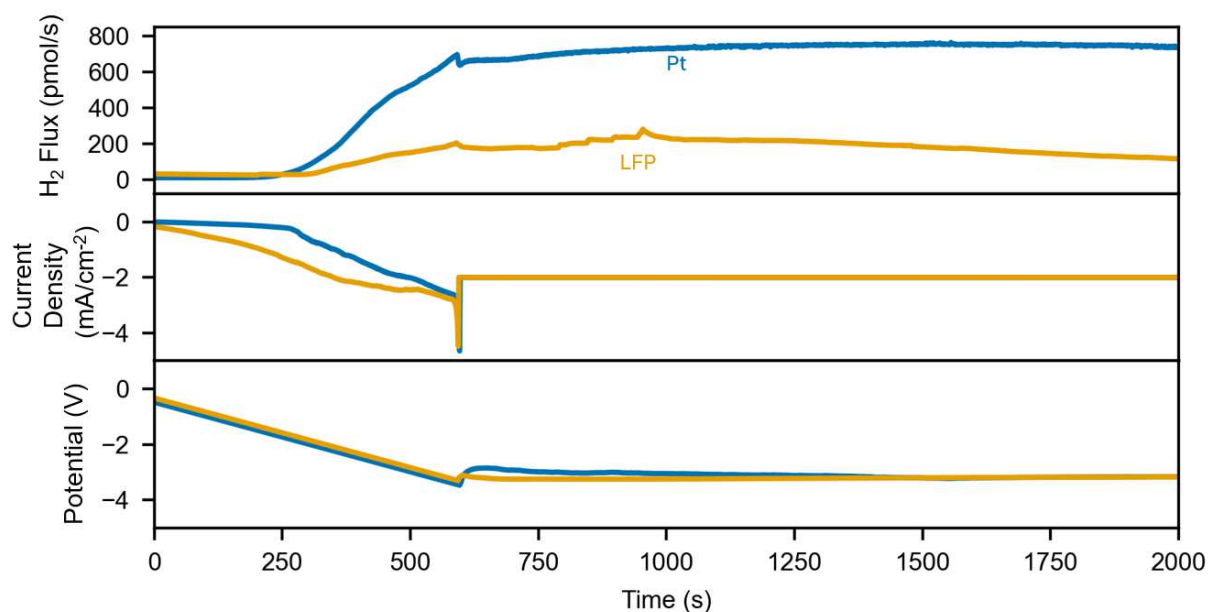


Figure 4.6: Hydrogen flux, current density, and potential as a function of time Li-NRR in a parallel electrode ECMS cell (Figure 4.1b) using 1 M LiTFSI in THF with 0.5 vol % Ethanol. Data are shown for three different counter electrode materials: Pt and LFP. A Cu working electrode and Pt wire pseudo-reference electrode were used in all cases. Working electrode area: 0.15 cm^2 . The electrochemical protocol consisted of: (1) linear sweep voltammetry (LSV) from open circuit potential (OCP) to the onset of lithium plating at a scan rate of 5 mV s^{-1} , followed by (2) chronopotentiometry at -2 mA cm^{-2} for 3000 s. High-purity N6.0 N_2 was used as the backing gas.

Figure 4.6 shows the H_2 flux during the LSV and CP for Pt and LFP (with two repeat experiments for each). As can be seen from Figure 4.6a & Figure 4.6b, the rate of H_2 evolution is lower when LFP is used (compared to Pt) in the LSV and CP, for both repeats. This once again demonstrates that the choice of counter electrode material plays a significant role in the amount of H_2 evolved even when the same electrolyte and cell configuration is used. As posited above, using LFP instead of Pt likely reduces the amount of protic species generated from solvent oxidation because an alternative, more favourable pathway is introduced: Li dissolution. Without the generation of additional protic species, the Ethanol in the system should get consumed and the amount of H_2 evolved should decrease. This decay in H_2 evolution can clearly be seen in Figure 4.6b for the two LFP experiments. By contrast, the rate of H_2 evolution stays relatively stable during the CP when Pt is used, further supporting the idea of continual generation of protic species that are then reduced to H_2 at the working electrode, given the proximity of the two electrodes. Previous Li-NRR experiments in the parallel electrode ECMS cell failed to generate any ammonia. The primary hypothesis for this was that protic species generated from solvent oxidation increased the proton activity of the electrolyte and made H_2 evolution much more favourable than nitrogen reduction. Therefore, by using LFP instead of Pt as the counter electrode, it was posited that the amount of protic species generated would be reduced, making nitrogen reduction more favourable and allowing ammonia to be synthesised. To test this, a nitrogen reduction experiment was carried out using 1 M LiTFSI with 0.5 vol% Ethanol in the parallel electrode ECMS cell with an LFP counter electrode. The results of this are shown in Figure 4.7.

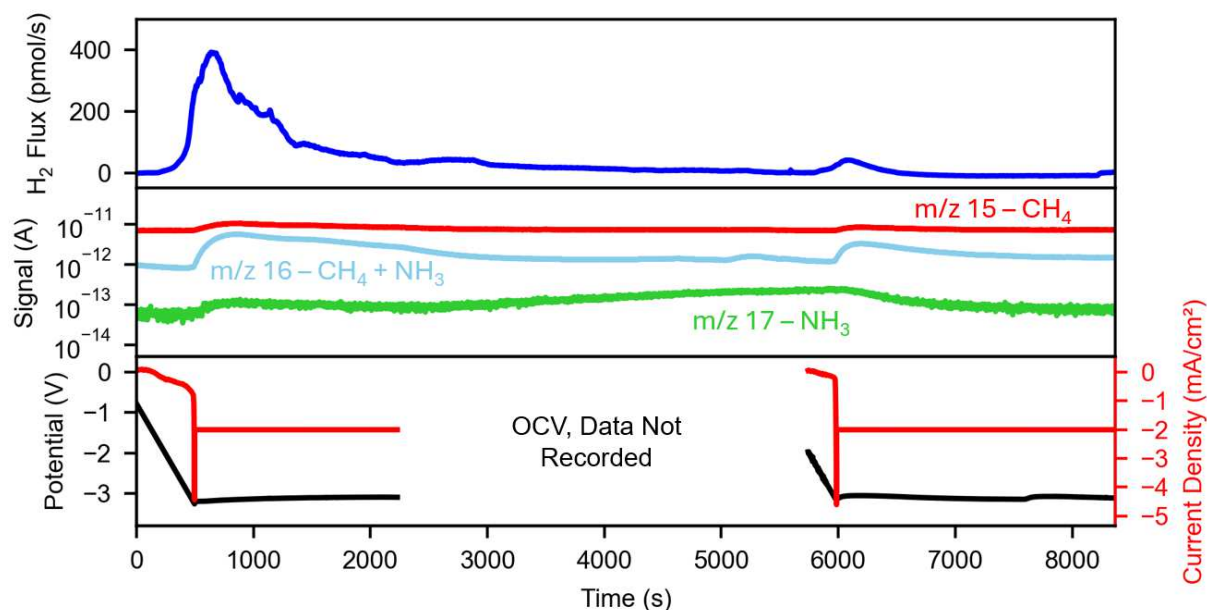


Figure 4.7: Li-NRR experiment using 1 M LiTFSI in THF with 0.5 vol % Ethanol in a parallel electrode ECMS cell (Figure 4.1b). Cu working electrode, LFP counter electrode, and Pt wire pseudo-reference electrode. Electrochemistry: (1) LSV from OCP to the onset of Li plating at 5 mV s⁻¹; (2) CP at -2 mA cm⁻² for 1737 s; (3) OCV for 3484 s (data not recorded); (4) LSV from OCP to Li plating at 5 mV s⁻¹; and (5) CP at -2 mA cm⁻² for 2360 s. High-purity N6.0 N₂ was used as the backing gas.

During the LSV only H₂ was evolved, however, after Li plating, signals m/z 15, 16 & 17 all increase initially and then gradually decay, the H₂ signal also decays but more rapidly. During the OCV immediately following the CP, the m/z 16 signal decays rapidly, however the m/z 17 signal increases slowly throughout the course of the OCV. Similar to the first LSV, only H₂ was evolved during the second LSV, however, when Li plating is achieved, m/z signals 2, 15 & 16 increase but m/z 17 actually decreases and continues to decay during the second CP. These results are surprising but can be explained by the following sequence of events. H₂ is the first gas product to be evolved because it likely comes from Ethanol reduction, which occurs at less negative potentials. When Li plating first occurs, m/z 15, 16 & 17 increase due to CH₄ evolution. Shortly after, the amount of H₂ begins to decay rapidly due to the consumption of Ethanol and the lack of solvent oxidation (due to LFP counter electrode being used) fails to replenish protic species that can also be reduced to H₂. The concurrent decay in m/z 15, 16 & 17 can be attributed to reduced CH₄ evolution which is likely a product of Ethanol reduction. The immediate decrease in m/z 16 following the end of the CP can be attributed to CH₄ no longer being generated. The parallel and continued increase in m/z 17 may be explained in two ways:

Hypothesis 1:

Ammonia is generated during CP but is also oxidised at the counter electrode. During OCV dissolved ammonia that accumulated in the electrolyte can then volatilise and reach the detector without being oxidised at the counter electrode.

Hypothesis 2:

Ammonia is generated during CP but is oxidised at the counter electrode. During OCV, ammonia continues to be generated due to leftover deposited Li reacting with N₂ and being protonated but is no longer oxidised at the counter electrode so the amount being detected increases.

Regardless of which hypothesis is correct, the key element is that ammonia is seemingly consumed during electrolysis. The idea of ammonia consumption during electrolysis is further corroborated when the m/z 17 signal goes down during the second CP, while m/z 2, 15 & 16 increase. These findings strongly suggest that ammonia was being consumed during electrolysis, likely through oxidation at the counter electrode, given its proximity to the working electrode. Furthermore, the m/z 16/17 ratio of around 1 and the slow response time of the m/z 17 signal, strongly suggest that ammonia was indeed successfully detected for the first time in this project. However, the fact that the detection only occurred during the OCV following electrolysis was an unusual finding and was further investigated.

4.4 Confirmation of Real-Time Detection of in-situ Generated Gas Phase Ammonia

As discussed in Section 4.3, ammonia was able to be detected successfully synthesised and detected in-situ using 1 M LiTFSI in THF with 0.5 vol% Ethanol in the parallel electrode cell (Figure 4.1b) using LFP as the counter electrode, but only during the OCV following electrolysis and not during the electrolysis itself. The likely reason for this was ammonia being oxidised at the counter electrode, given its close proximity to the working electrode. To confirm this, an experiment was conducted using a different cell configuration where the counter electrode sits in a different compartment and is connected to the working volume by a long narrow channel which makes the crossover between electrodes negligible (cell diagram shown in Figure 4.1c). This was the same cell configuration used by Krempel and all other parameters of the experiment (electrolyte composition and electrochemistry) were the same as that work [135]. The experiment was performed in both N₂ and Ar to confirm that the increase in m/z 17 was indeed coming from ammonia and not methane or other gas species. The results are shown in Figure 4.8.

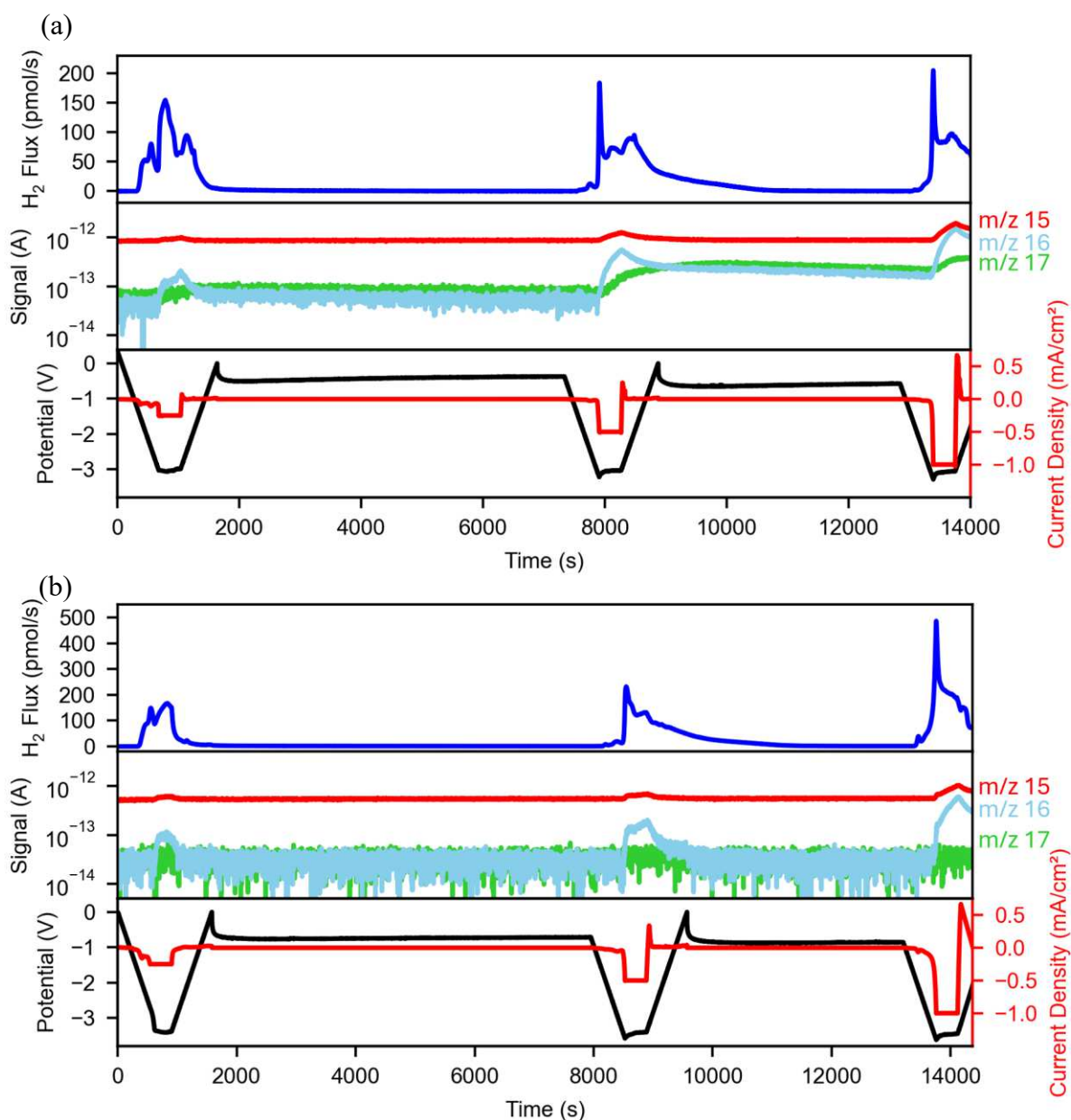


Figure 4.8: Li-NRR experiments under (a) N6.0 N₂ and (b) Ar atmospheres using 2 M LiOTf in diglyme with 1 vol % Ethanol in a separated electrode ECMS cell (Figure 4.1c). Cu working electrode, Pt counter electrode, and Pt wire pseudo-reference electrode. Electrochemistry: three consecutive pulses, each consisting of (1) LSV from OCP until the desired current (-0.25 , -0.5 , or -1 mA cm^{-2}) was reached at a scan rate of 5 mV s^{-1} ; (2) CP at the respective current for 360 s; and (3) LSV down to 0 V at 5 mV s^{-1} . The final LSV segment was terminated early due to a large oxidative current that triggered a potentiostat overload. EC parameters were adapted from the work of Kremp. [135].

As posited, the m/z 17 signal in Figure 4.8 began to increase almost immediately after the current pulse was initiated unlike in the previous experiment (Figure 4.7) where the m/z 17 signal due to ammonia only began to increase during OCV. This provides strong evidence for the occurrence of ammonia oxidation at the counter electrode in the parallel electrode cell and that the separated electrode cell configuration used here was able to successfully prevent ammonia consumption during electrolysis.

The most notable observation from Figure 4.8, however, is that the m/z 17 signal increases during the current pulses in N_2 but stays completely flat in the experiment with Ar, strongly suggesting that $NH_{3(g)}$ is synthesised and detected in-situ. Furthermore, the increase in m/z 17 in Figure 4.8a can be completely attributed to ammonia because the contribution from methane was negligible. Based on the increase in m/z 16, both experiments generate methane and in very similar amounts because the m/z 16 signal intensity is almost identical. However, no increase of m/z 17 is observed in the experiment with Ar and this can be explained by the m/z 16/17 ratio of methane being ~ 60 (this ratio changes depending on the ionisation energy used and other parameters of the mass spectrometry detection system, the value of 60 is taken from the NIST database [133]) and the signal detection limit of the ECMS being $\sim 1E^{-14}$ A. Therefore, even the peak m/z 16 signal of $6E^{-13}$ seen in Figure 4.8b would have an associated m/z 17 signal of $1E^{-14}$, right on the edge of the detection limit and hence why no m/z 17 signal is observed in Figure 4.8b. This provides good confidence that the increase of m/z 17 in Figure 4.8a is solely from ammonia.

From Figure 4.8a it is also evident that the m/z 16 signal comes from the convolution of methane and ammonia production. When a current pulse is first initiated, the m/z 16 signal quickly rises due to methane evolution while m/z 17 rises slowly due to ammonia evolution. Following the current pulse, m/z 16 begins to fall rapidly since methane is no longer being produced but m/z 17 continues increasing, after around 1000 s, the m/z 16 reaches a ratio of 0.8 and the two signals match each other since they are both only coming from ammonia.

Finally, in Figure 4.8a, m/z 16 starts to decrease immediately after the CP is terminated but m/z 17 continues increasing and only peaks around 1000 s later. This continued ammonia signal increase after electrolysis was observed in the previous experiment (Figure 4.7) and also by Kremp et al. [35]. Kremp et al. attributed this behaviour to residual Li that remains on the working electrode and continues to react with N_2 and produce ammonia [35]. However, as was observed in Figure 4.2, the response time of ammonia increases significantly (5 fold) when electrolyte is present above the chip. This is likely due to ammonia's low volatility and diffusion coefficient in the organic solvent. Therefore, the continued increase in ammonia signal after electrolysis could be from dissolved ammonia gradually escaping the solvent and reaching the detector as opposed to continued ammonia generation from residual lithium. However, both phenomena could be occurring, and it is not possible to determine which one or if both are occurring with the current setup and further investigation would be required to resolve this question.

4.5 Conclusion

The ability to detect gas phase ammonia alongside dissolved ammonia is essential in studies of Li NRR, as it enables a more comprehensive assessment of ammonia yield and distribution. From a practical standpoint, gas phase ammonia is far more desirable for commercial applications due to the ease of separation and collection. Therefore, maximising the proportion of ammonia produced in the gas phase is a key goal for system optimisation. Moreover, real time detection of gas phase ammonia provides a powerful tool for investigating the effects of dynamic operating conditions on system performance and reaction mechanisms.

Despite these advantages, the real time detection of in situ synthesised gas phase ammonia presents several challenges. In this work, these challenges were systematically addressed by

breaking down the overall task into three discrete stages: (1) detection of gas phase ammonia using ECMS, (2) electrochemical generation of ammonia in the ECMS cell, and (3) real-time detection of in-situ generated gas phase ammonia. This structured approach enabled a clearer understanding of the limitations at each stage and provided a pathway for progressive optimisation.

It was demonstrated that in-situ synthesised gas phase ammonia could indeed be detected in real time using both the separated and parallel electrode ECMS cells. In the parallel electrode cell, ammonia was only detectable in the gas phase when LFP was used as the counter electrode, likely due to its ability to suppress the generation of protic species from anodic solvent oxidation. When a Pt counter electrode was used, only dissolved ammonia was detected, suggesting that the ammonia formed at the working electrode was subsequently oxidised at the counter before it could enter the gas phase.

In contrast, the separated electrode configuration enabled successful real time detection of ammonia during electrolysis with minimal delay. However, the response was characterised by a long rise time, likely due to slow desorption and transport processes within the electrolyte compartment. These findings underscore the importance of cell design and electrode selection in enabling reliable ammonia detection and highlight ECMS as a promising platform for mechanistic studies and performance optimisation in Li NRR systems.

5 Investigating Electrolyte Degradation, Acidification and Crosstalk

5.1 Introduction

In developing real-time ammonia detection (see Chapter 4), it became increasingly evident that cell configuration and the choice of counter electrode material have a profound impact on both the yield and ammonia distribution (the ratio between gas phase and dissolved ammonia). These differences were strongly linked to variations in electrolyte acidification, arising from anodic solvent oxidation, and crosstalk between the working and counter electrodes.

Electrolyte degradation is a widely recognised issue in lithium-mediated nitrogen reduction (Li-NRR) [30], as it directly influences system performance [31] and long-term operational stability [32], [33], [136]. Moreover, electrolyte decomposition plays a critical role in shaping the composition and morphology of the solid-electrolyte interphase (SEI), which is central to maintaining lithium reactivity and suppressing parasitic reactions [54], [62], [137]. A clearer understanding of the mechanisms driving electrolyte degradation is therefore essential for optimising the Li-NRR system.

To explore the impact of cell design on electrolyte acidification, crosstalk, and ultimately ammonia generation, a series of real-time Li-NRR experiments were performed using three distinct ECMS cell configurations, illustrated in Figure 5.1. Each configuration was chosen to systematically vary the extent of electrolyte acidification and the degree of electrode crosstalk:

- **Separated Electrode Cell with Pt Counter Electrode** (Figure 5.1a): Features two Pt counter electrodes housed in separate compartments, isolating them from the working electrode. This setup was expected to produce significant electrolyte acidification due to solvent oxidation at the Pt surface, however, this was unlikely to reach the working electrode because of the large electrode separation. Crosstalk would, therefore, be minimal in this configuration.
- **Parallel Electrode Cell with LFP Counter Electrode** (Figure 5.1b): Utilises a parallel electrode arrangement with a LFP counter electrode and a $\sim 100\text{ }\mu\text{m}$ electrode separation. This setup was expected to reduce acidification due to reduced solvent oxidation at LFP, but allow significant crosstalk due to minimal spatial separation.
- **Parallel Electrode Cell with Pt Counter Electrode** (Figure 5.1c): Combines a Pt counter electrode with the parallel electrode geometry ($\sim 100\text{ }\mu\text{m}$ separation), and was thus anticipated to exhibit both high acidification and pronounced crosstalk.

Experiments were conducted using 1 M LiBF_4 in diglyme (a state-of-the-art electrolyte recently demonstrated to enable over 300 h of continuous operation in lithium-mediated flow cell systems [9]). This choice represents a deliberate departure from the THF-based electrolyte (2 M LiOTf in THF) used by Krempel et al. [138], offering improved oxidative stability and minimising complications from solvent polymerisation (see Section 1.4.4 for more details on electrolyte composition).

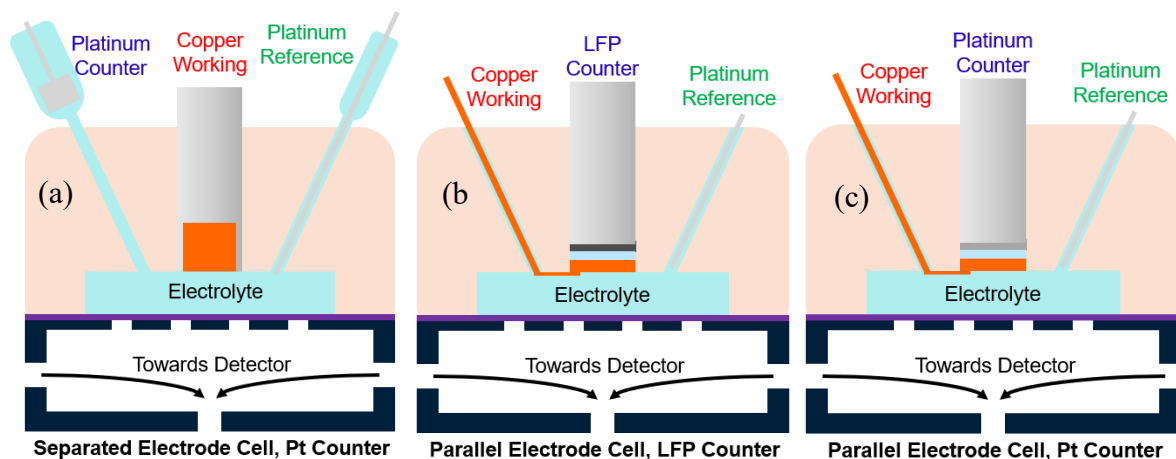


Figure 5.1: Schematics of the three ECMS cell configurations used to investigate electrolyte acidification and crosstalk. (a) Separated electrode cell with four equally spaced top ports around a central vertical axis; two counter electrodes are positioned opposite each other, with a reference electrode inserted into a third port. (b) Parallel electrode cell using LFP as the counter electrode. (c) Parallel electrode cell using Pt as the counter electrode.

For each configuration, three electrolyte/backing gas combinations were tested to isolate the role of ethanol and verify the generation of electrochemical ammonia through the use of an Ar blank: 1) 1 vol% Ethanol in N_2 , 2) No Ethanol in N_2 and 3) 1 vol% Ethanol in Ar.

Electrochemical parameters were inspired by the work of Krempel [138] but adapted to suit the cell geometries and objectives of this study. Each experiment included an LSV from OCP to -1 mA cm^{-2} , followed by three pulsed current steps at -1 mA cm^{-2} for 180 s, interspersed with 1 h OCV rest periods. ECMS was used to monitor the real-time evolution of gas phase NH_3 , CH_4 , C_2H_4 , and H_2 , with quantitative flux rates calculated using the calibration procedure described in Section 2.2.2. UV-Vis colorimetry was used to determine the amount of dissolved ammonia in the final electrolyte. In total, 11 experiments were conducted: 9 unique combinations of configuration and conditions, plus two technical repeats to assess reproducibility.

5.2 Insights into Electrolyte Degradation Mechanisms

Figure 5.2 presents the electrochemical data and corresponding gas evolution profiles for Li-NRR experiments conducted using the separated electrode cell with two Pt counter electrodes (Figure 5.1a), under two conditions: with and without ethanol. In this configuration, the counter electrodes are housed in isolated compartments connected to the working electrode chamber via narrow channels, effectively limiting crosstalk of reaction products. Therefore, it can be reasonably concluded that the detected gaseous species originate from cathodic processes occurring at the working electrode.

Notably, the onset of ammonia, methane (CH_4), and ethylene (C_2H_4) evolution coincides with the potential at which lithium plating begins, suggesting that these products are generated through lithium-mediated reduction pathways. The observation that CH_4 and C_2H_4 are produced in both the presence and absence of ethanol strongly implies that ethanol is not the source of these hydrocarbons. Instead, their presence under both conditions points toward

diglyme as the likely origin. This supports the hypothesis that diglyme undergoes cathodic degradation, giving rise to these smaller hydrocarbon products (as discussed in Section 1.4.4).

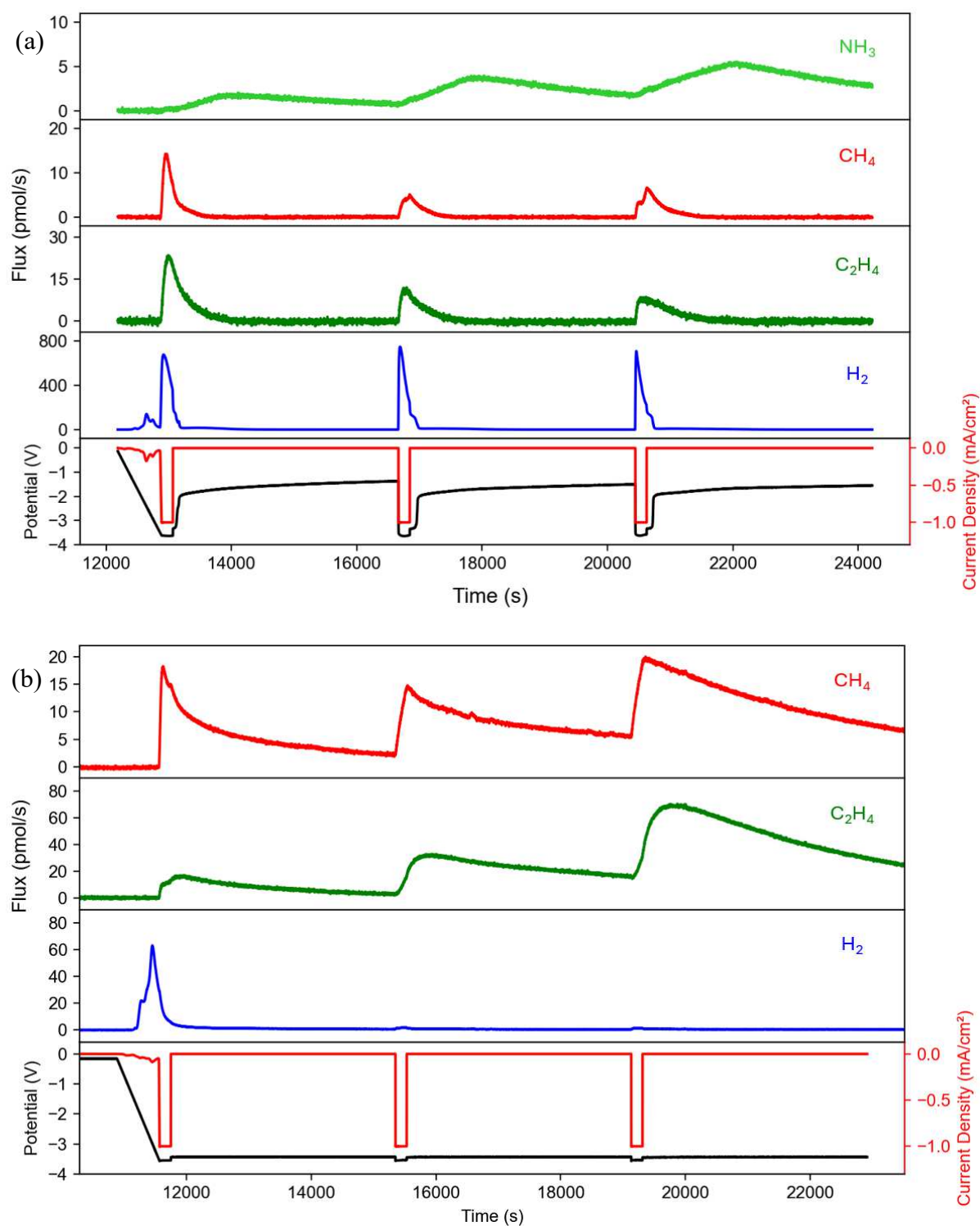


Figure 5.2: Lithium-mediated N_2 reduction experiments using separated electrode cell (Figure 5.1a) with 1 M $LiBF_4$ in diglyme containing (a) 1 vol % Ethanol and (b) 0 vol % Ethanol. N_2 was used as the backing gas. Cu working electrode, Pt counter electrode, and Pt reference electrode; voltages were not iR-compensated. The experiment consisted of LSV from OCP to -1 mA cm^{-2} at 5 mV s^{-1} , followed by three CP pulses at -1 mA cm^{-2} for 180 s each, with a 1 h rest period between pulses. Note: No NH_3 was detected in the absence of Ethanol, and the corresponding NH_3 signal is not shown.

Based on the findings presented above, and supported by previous studies indicating that diglyme decomposition predominantly occurs via ether C–O bond cleavage pathways (see Section 1.4.4), plausible mechanisms for the formation of methane and ethylene through reductive decomposition of diglyme are proposed in Figure 5.3.

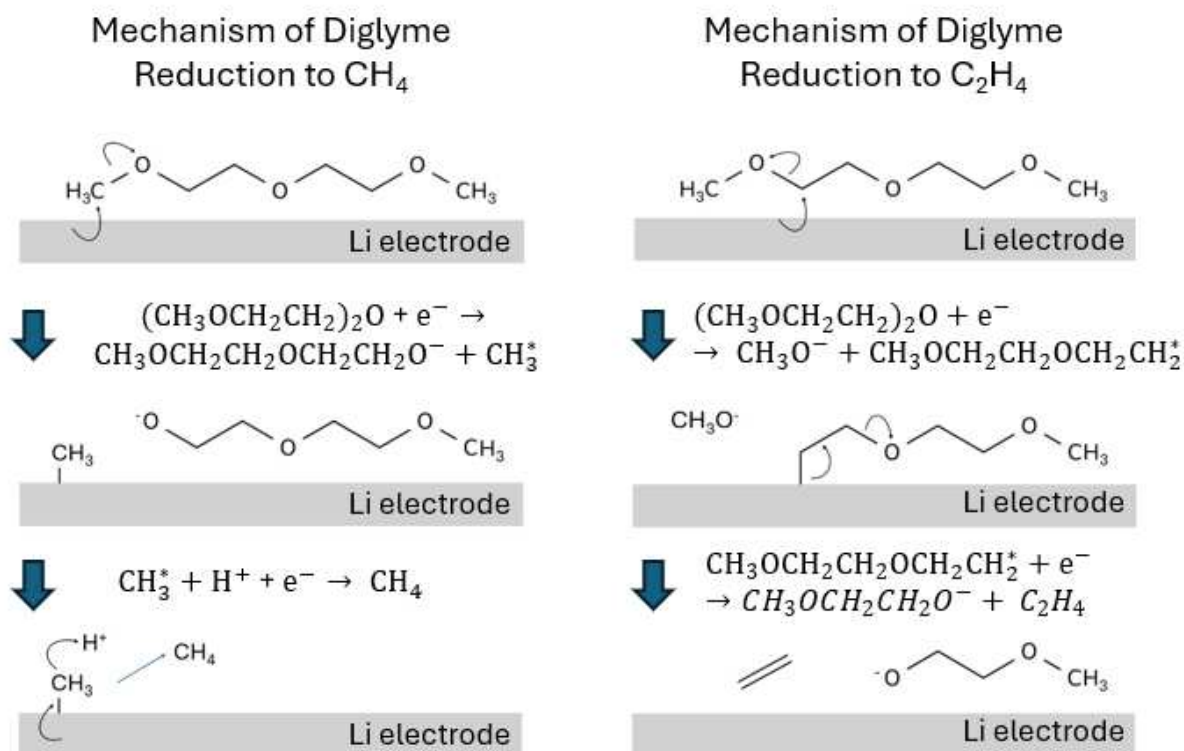
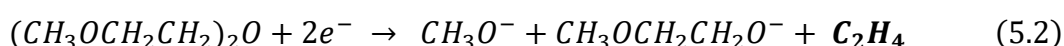
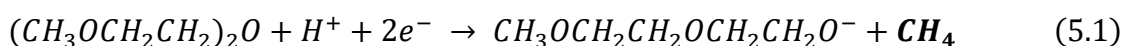


Figure 5.3: Schematics illustrating proposed pathways for CH₄ and C₂H₄ evolution from electrochemical diglyme reduction in the Li-NRR system. The proposed reaction pathways were developed in collaboration with Romain Tort, whose input is gratefully acknowledged.



Another notable finding from Figure 5.2 is that much more methane and ethylene are generated in the absence of ethanol. There are several likely reasons for this. Firstly, ethanol plays a critical role in SEI formation, therefore, its addition to the electrolyte likely leads to a more favourable SEI that reduces further electrolyte decomposition (as discussed in Section 1.4.1 & 1.4.3). Secondly, ethanol can be directly reduced to ethoxide and H₂ (see Section 1.4.4), providing a competing reaction to diglyme reduction. Furthermore, Schwalbe et al reported that ethanol reduction occurs at around 1.5 V positive of lithium plating [139], whereas diglyme reduction to methane and ethylene begins to occur only after lithium plating (as seen in Figure 5.2), suggesting that ethanol reduction is more favourable than diglyme reduction. Thirdly, as discussed in Section 1.4.3, ethanol is also a protic source, therefore, by adding it to the electrolyte, the bulk proton activity is increased, making HER more favourable, potentially reducing the amount of diglyme reduction.

5.3 Overview of Cell Configuration Effects

The integrated gas signals and the amount of dissolved ammonia for all the 11 experiments were converted into faradaic efficiencies for each experiment and the results are plotted in Figure 5.4. There are many trends that can be observed from these findings but perhaps the most obvious is that the total amount of detected gas products decreases between the configurations. This could be due to the formation liquid or solid products that cannot be detected by ECMS. Sažinas et al. detected many liquid phase products from electrolyte degradation in lithium-mediated nitrogen reduction [32]. Furthermore, several lithium-mediated nitrogen reduction studies report significant electrode deposits under certain conditions [6], [26], [29], [36], [44]. However, the more likely explanation for the reduced amount of detected gas products could be related to the amount of crosstalk within the different cell configurations. In the separated electrode configuration, the counter electrode sits in a separate chamber that is connected to the working volume by a long narrow channel so diffusion between the electrodes is very slow and so crosstalk is negligible. This explains why the detected gas products add up to almost 100% in the separated electrode configuration since they are unlikely to reach the counter electrode and be oxidised. In the parallel electrode, LFP counter configuration, the counter and working electrode are separated by a $\sim 100\ \mu\text{m}$ separator so diffusion between them is relatively fast. This explains why the total amount of detected gas products is much lower in this configuration. Finally, in the parallel electrode, Pt counter configuration, the electrodes are also close together, so diffusion between them is again relatively fast. However, the use of a Pt counter electrode, rather than LFP, is more likely to result in oxidation of cathodically generated gas products, as Pt lacks a favourable competing reaction such as lithium dissolution.

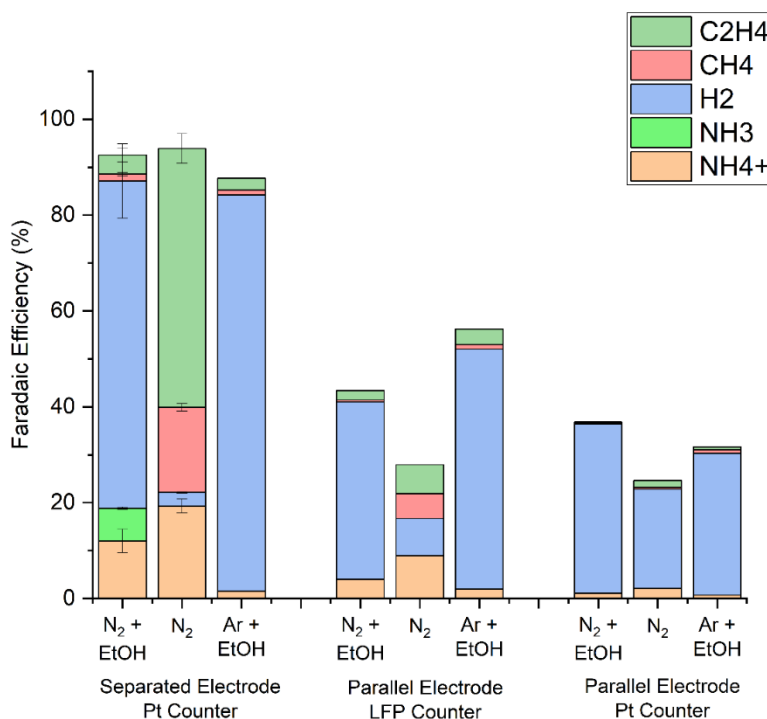


Figure 5.4: Selectivity plots for the three ECMS cell configurations shown in Figure 5.1. For each configuration, three experimental conditions were tested using 1 M LiBF₄ in diglyme as the electrolyte: (i) 1 vol % Ethanol with N₂ as the backing gas; (ii) 0 vol % Ethanol with N₂ as the backing gas; and (iii) 1 vol % Ethanol with Ar as the backing gas.

The other main trends observed in Figure 5.4 can be broadly categorised into those related to system performance and those associated with stability. These differences are likely governed by variations in electrolyte acidity across the different cell configurations. As discussed in Section 1.4.4, electrolyte acidification can arise from anodic solvent oxidation, particularly when using Pt as the counter electrode, and is further exacerbated in configurations with high degrees of electrode crosstalk. The following section outlines how acidity can be assessed across the different cell configurations, providing a basis for correlating acidity with system performance and stability.

5.4 Evidence for Acidity Trend

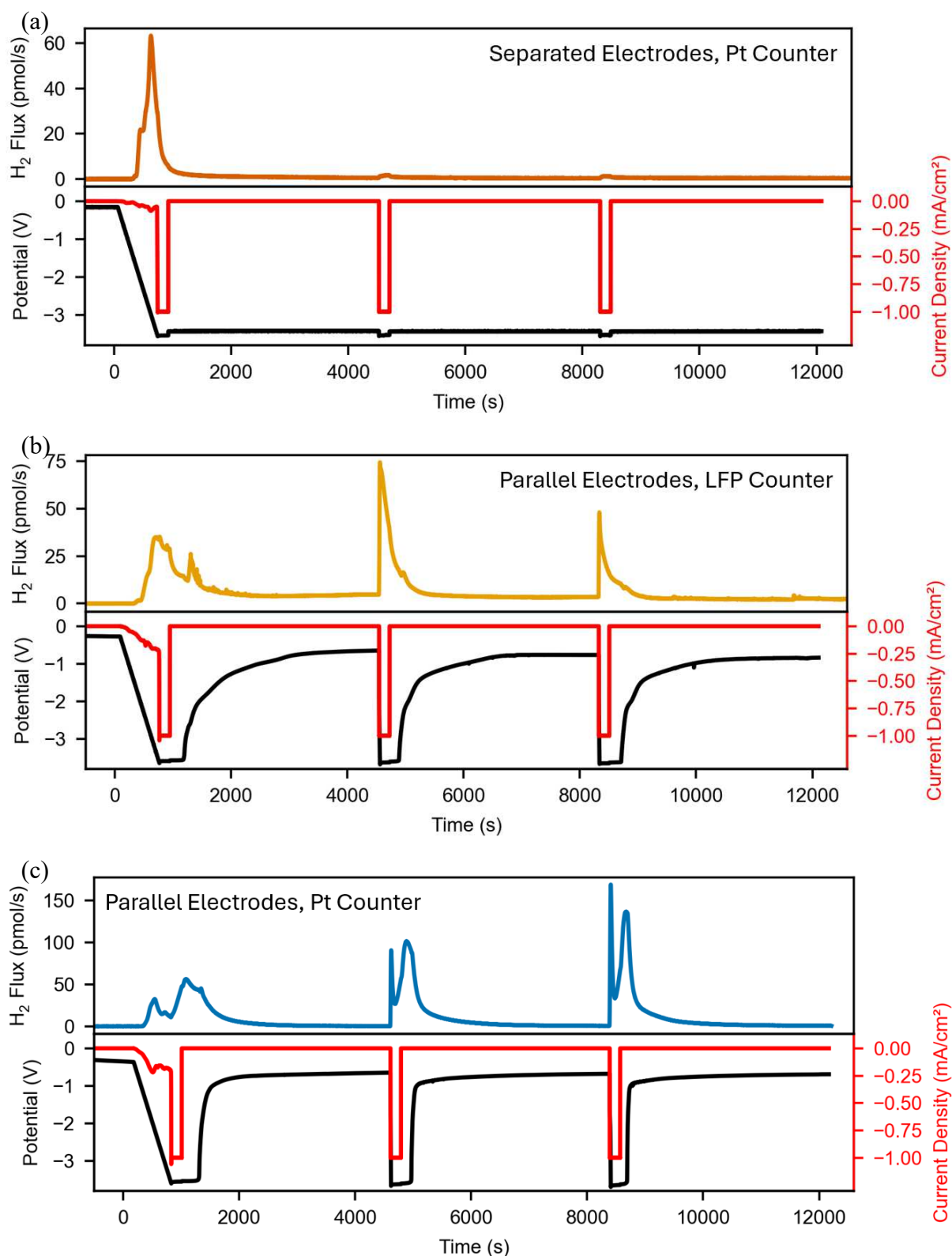
In non-aqueous systems, pH can be measured by comparing the voltage of a Reversible Hydrogen Electrode (RHE) to that of a stable reference electrode in that system [140], [141], [142]. However, the extremely small electrolyte volume used in ECMS cells ($\sim 20\ \mu\text{L}$) makes conventional RHE-based proton acidity measurements impractical. Instead, hydrogen evolution behaviour and electrochemical responses were used as indirect indicators of acidity across the three cell configurations.

5.4.1 *Hydrogen Evolution Evidence*

While not a direct or exclusive measure, the extent of hydrogen evolution can often correlate with the local proton activity in an electrochemical system. In general, higher proton activity (or acidity) increases the thermodynamic and kinetic favourability of proton reduction to H_2 , thereby diverting a greater portion of the current toward hydrogen evolution. However, it is important to note that hydrogen evolution is also influenced by additional factors, such as interfacial transport through the SEI and the kinetics of the HER, both of which can vary significantly between systems.

In the context of the Li-NRR experiments presented in this chapter, the local proton activity at the working electrode is influenced by multiple interrelated factors: (i) the bulk electrolyte proton donor concentration (e.g. ethanol), (ii) the generation of protic species at the counter electrode via anodic solvent oxidation (affected by the choice of counter electrode material) and (iii) the degree of electrode crosstalk, which governs the extent of proton transport from the anode to the cathode. In Li-NRR, protons are generated anodically and consumed cathodically. Therefore, the time-dependent profile of hydrogen evolution at the cathode can serve as a useful, though indirect, indicator of whether protons are accumulating locally (suggesting increasing acidity) or are being effectively consumed.

Figure 5.5 presents the measured H_2 flux for three the different cell configurations (without ethanol) to compare their respective proton environments: separated electrodes with Pt counter, parallel electrodes with LFP counter, and parallel electrodes with Pt counter. By analysing the differences in H_2 evolution across these setups, insights into the relative acidity and its impact on reaction selectivity and stability can be inferred.



In the separated electrode, Pt counter configuration, an initial H₂ evolution peak is observed during the first current pulse, followed by negligible H₂ generation in subsequent pulses. This initial peak is likely attributable to the rapid reduction of trace protic impurities such as residual water, as similarly demonstrated in acetonitrile by Ledezma-Yanez et al. [143]. In this configuration, anodically generated protons are largely confined to the counter electrode compartment, and limited crosstalk prevents their diffusion to the cathode. As a result, once the initial protic species are consumed, the system transitions to an aprotic environment where further H₂ evolution is suppressed.

In contrast, the parallel electrode, LFP counter configuration exhibits a more steady H₂ profile. A moderate initial H₂ peak is followed by a second, larger peak and then a third pulse similar in magnitude to the first. While the precise origin of this varying trend is not fully understood, the data suggest that proton generation persists at the counter electrode and that these protons are able to reach the cathode due to the short electrode separation. The LFP counter electrode does not contribute significantly to solvent oxidation, which may explain why proton accumulation is less pronounced than in the following Pt-based configuration.

The parallel electrode, Pt counter configuration displays a steadily increasing H₂ signal across all three current pulses. This trend is consistent with progressive acidification of the electrolyte due to anodic solvent oxidation on the Pt counter electrode. The close proximity between electrodes facilitates crosstalk, enabling the continuous transport of protons from the anode to the cathode, where they participate in hydrogen evolution. The increasing H₂ flux thus reflects the accumulation of protic species in the working volume over time.

In summary, these results indicate that the proton activity evolves throughout the course of a Li-NRR experiment and is strongly influenced by both electrode crosstalk and the choice of counter electrode material.

5.4.2 *Electrochemistry Evidence*

Another indirect method to gauge proton activity in Li-NRR systems is through careful analysis of the working electrode potential during electrochemical experiments. According to the Nernst equation (see Section 2.1.1), the electrode potential is closely linked to the surface species in equilibrium. When metallic lithium is plated onto the working electrode, the potential typically stabilises near the lithium redox potential, approximately -3.04 V vs SHE [66]. Once the lithium begins to dissolve or react, the potential shifts to more positive values.

One important mechanism for lithium removal is chemical reaction with protic species in the electrolyte. As such, the duration for which the electrode remains at the lithium plating potential can be used as a qualitative indicator of local proton activity. In electrolytes with low proton activity, lithium metal remains on the surface for longer, and the working electrode potential stays near the lithium plating value. In contrast, higher proton activity results in faster lithium consumption, leading to a more rapid shift in potential. However, it must be noted that the presence of passivation layers (such as the SEI) can stabilise the Li metal even in a protic environment.

Figure 5.6 presents the working electrode potential profiles for the three cell configurations studied in this chapter, using electrolyte without ethanol. The trends in working electrode potential stability are more readily observed in the absence of ethanol, as ethanol itself is a

protic species and can react with surface lithium, accelerating potential decay. The rate at which the potential deviates from the lithium plating value reflects differences in local proton availability, offering valuable insight into the dynamic acidity of the system under different geometric and electrochemical conditions.

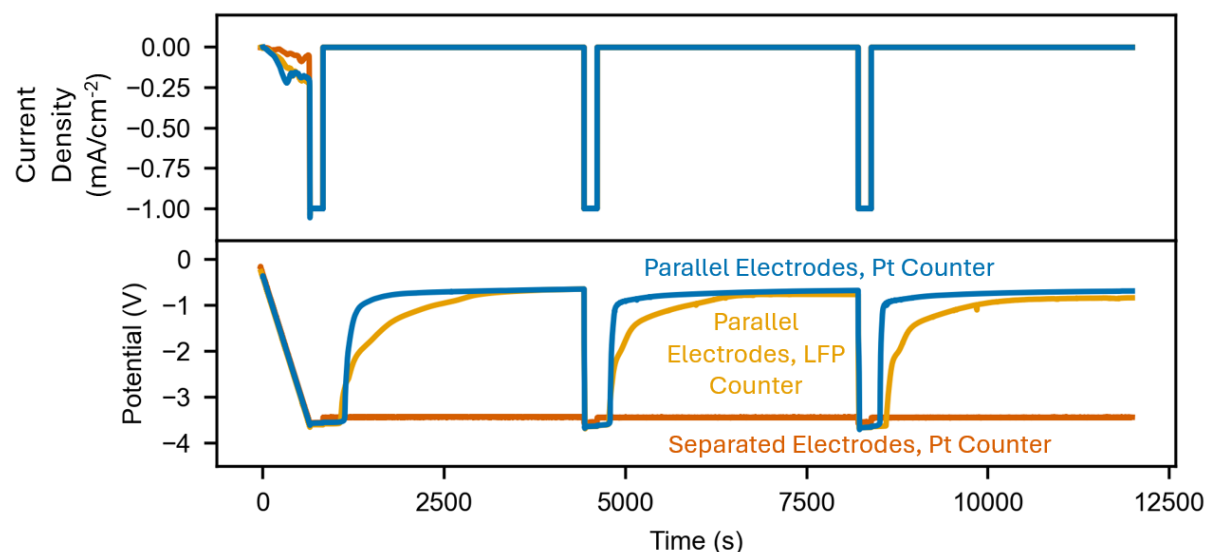


Figure 5.6: Potential and current density as a function of time during lithium-mediated N_2 reduction using 1 M $LiBF_4$ in diglyme with 0 vol % Ethanol and N6.0 N_2 as the backing gas. Data are shown for three ECMS cell configurations: (i) separated electrode cell with Pt counter electrode; (ii) parallel electrode cell with LFP counter electrode; and (iii) parallel electrode cell with Pt counter electrode. Cu working electrode and Pt wire pseudo-reference electrode were used in all cases; voltages are not iR -compensated. Electrochemistry consisted of LSV from OCP to -1 mA cm^{-2} at 5 mV s^{-1} , followed by three CP pulses at -1 mA cm^{-2} for 180 s each, with 1 h OCV between pulses.

As shown in Figure 5.6, the working electrode potential in the separated electrode, Pt counter configuration remains stable and flat between current pulses. This suggests that the plated lithium remains intact without significant chemical reaction, indicating a low local proton activity. In contrast, the potentials in the parallel electrode, LFP counter and parallel electrode, Pt counter configurations decay rapidly after each current pulse, implying that the deposited lithium is quickly consumed, most likely via chemical reaction with protic species in the electrolyte. The faster potential decay in the parallel electrode, Pt counter configuration compared to parallel configuration with LFP further supports the conclusion that proton activity is highest in the parallel electrode configuration with Pt as the counter.

These electrochemical observations are consistent with the hydrogen evolution trends discussed earlier and provide additional evidence that proton activity increases across the configurations. This reinforces the interpretation that cell geometry and counter electrode choice significantly influence local acidity and, in turn, impact system behaviour and performance.

5.5 Effect on Performance (Ammonia vs other gas products)

The performance of an electrochemical system is determined by several parameters, including energy efficiency, production rate, and faradaic efficiency. In this study, faradaic efficiency toward ammonia (both gas phase and dissolved), is the principal performance

metric. As discussed in Section 1.3.1, future commercial Li-NRR flow cells will require efficient gas phase ammonia production, as $\text{NH}_3(\text{g})$ is far easier to separate and extract than dissolved ammonia species. Thus, faradaic efficiency toward gas phase ammonia is the most relevant indicator of practical performance, though dissolved ammonia remains a valuable secondary metric for understanding system behaviour.

Among the nine unique experiments conducted, gas phase ammonia was detected in only one case: the separated electrode, Pt counter configuration with N_2 as the backing gas and 1 vol% ethanol in the electrolyte. This outcome is likely driven by two key factors: (i) the relatively optimal proton activity created by this specific cell configuration and (ii) ethanol's established role in facilitating Li-NRR. Producing ammonia in the gas phase requires a moderately low local proton activity, due to the acidity dependence of the $\text{NH}_3/\text{NH}_4^+$ equilibrium. If proton activity is too high, any NH_3 generated will be rapidly protonated to NH_4^+ and remain in solution. Conversely, if proton activity is too low, insufficient protons are available to complete the protonation of Li_3N , suppressing ammonia formation. Additionally, ethanol has been shown to contribute to SEI formation, potentially creating a more permeable interphase that facilitates ammonia escape into the gas phase [26], [40], [56].

Since gas phase ammonia was only observed in one experiment, dissolved ammonia was used as a comparative metric to examine trends in performance across the three configurations. A clear decrease in dissolved ammonia was observed between the configurations. This trend correlates with the likely increase in system acidity across configurations, which enhances the favourability of HER at the expense of nitrogen reduction. This is supported by the increasing proportion of H_2 flux in configurations with higher expected acidity (see Figure 5.4), indicating a shift in selectivity away from ammonia production. Moreover, increased electrode crosstalk between the configuration may exacerbate this effect by promoting the oxidation of cathodic gas products at the counter electrode, thereby reducing the amount of ammonia and hydrogen detected. This hypothesis is supported by the observed decrease in total gas products (including H_2) across the configurations.

Interestingly, the total ammonia yield was higher in experiments without ethanol, across all configurations. This observation contradicts much of the existing literature, which typically reports enhanced ammonia yields in the presence of ethanol (see Section 1.4.3). While this divergence is difficult to fully resolve, it may reflect the influence of the unique ECMS cell geometries used in this study, which use an exceptionally small electrolyte volume ($\sim 20\ \mu\text{L}$) and feature a particularly high electrode area-to-electrolyte volume ratio.

5.6 Effect on Stability (Solvent Degradation)

As discussed in Section 5.2, methane and ethylene can be key indicators of electrolyte degradation in Li-NRR, which are believed to result from the reductive breakdown of the diglyme solvent. Across the three cell configurations studied, a clear trend emerges: both the absolute and relative amounts of CH_4 and C_2H_4 decrease progressively across the cell configurations. In addition, in all three configurations, significantly more CH_4 and C_2H_4 are produced when ethanol is excluded from the electrolyte.

These trends can be rationalised by considering the influence of acidity on the competitive electrochemical pathways. As proton activity increases (due to greater anodic solvent oxidation

or the presence of ethanol) proton reduction to H_2 becomes increasingly favourable. This enhanced HER selectivity diverts current away from side reactions such as diglyme reduction, thereby suppressing the formation of methane and ethylene. In contrast, when ethanol is removed or when the degree of electrolyte acidification is limited (e.g. by using an LFP counter electrode or increasing electrode separation), proton availability is reduced. Under these conditions, the system becomes more prone to reductive degradation of the solvent, as evidenced by the greater production of CH_4 and C_2H_4 .

These findings suggest that higher proton activity may have a stabilising effect on the system, at least in terms of limiting cathodic solvent degradation. While excessive acidity can be detrimental to ammonia selectivity (by favouring HER and shifting the $\text{NH}_3/\text{NH}_4^+$ equilibrium), moderate increases in proton activity appear to reduce the extent of solvent breakdown. Therefore, achieving the right balance in proton activity is crucial not only for performance but also for maintaining electrolyte stability under extended operation.

5.7 Conclusion

This chapter investigated the effects of electrolyte acidification and electrode crosstalk on the performance and stability of Li-NRR by systematically varying cell configuration and monitoring gas products (NH_3 , H_2 , CH_4 , and C_2H_4) in real time using ECMS. Through this approach, several important insights into degradation pathways, electrolyte behaviour, and the role of acidity in Li-NRR were uncovered.

Firstly, the real-time evolution of CH_4 and C_2H_4 was shown to provide a direct and practical method for tracking electrolyte degradation. These species were identified as the dominant gaseous products arising from the reductive decomposition of diglyme, shedding light on possible degradation mechanisms that had previously been difficult to observe in operando. These findings highlight the utility of ECMS as a powerful diagnostic tool for studying dynamic chemical changes in Li-NRR systems.

Secondly, the study demonstrated that electrolyte acidity plays a central role in governing both performance and stability. An inferred acidity trend across the three cell configurations (from lowest in the separated electrode, Pt counter setup to highest in the parallel electrode, Pt counter setup) was supported by differences in H_2 evolution and working electrode potentials. Increasing acidity was found to suppress solvent degradation (likely by favouring HER over diglyme reduction) but also led to diminished ammonia yields, due to HER competing more effectively with the nitrogen reduction pathway and the acidification of NH_3 to NH_4^+ . These results emphasise the delicate balance required: while acidity can stabilise the electrolyte, excessive proton activity undermines faradaic efficiency and selectivity towards ammonia.

Importantly, this work provides a framework for tailoring and gauging proton activity in lithium-mediated systems. By tuning factors such as counter electrode material, electrode separation, and ethanol concentration, researchers can strategically influence local acidity to improve performance and longevity. Although indirect indicators such as H_2 evolution and working electrode potential proved useful, a key future direction will be to quantify acidity more directly, through the implementation of RHE-based measurements in appropriately designed cells.

In broader context, the insights from this chapter are highly relevant to the Li-NRR research community. They offer mechanistic understanding and practical strategies for mitigating degradation and optimising system performance. As the field progresses toward more scalable and stable Li-NRR systems, controlling and characterising electrolyte acidity will be vital. This study contributes new evidence and approaches to that ongoing effort.

Conclusion & Outlook

This thesis has addressed critical challenges in Li-NRR (Li-NRR) by developing robust analytical tools, uncovering degradation mechanisms, and elucidating the role of acidity in performance and stability. The work spans ammonia quantification, gas-phase detection, and electrolyte behaviour under varying cell configurations, offering both mechanistic insights and practical strategies to optimise the system.

Chapter 3 focused on improving the accuracy and reproducibility of colorimetry for ammonia detection. It was shown that conventional calibration curves [20] are unreliable in Li-NRR electrolytes due to solvent interactions and matrix effects. A systematic comparison of phenol and salicylate-based methods revealed that, while phenol offers greater accuracy, salicylate remains preferable due to lower toxicity. The final protocol combined standard addition with dilution-based sample preparation and was used consistently throughout the project.

Chapter 4 developed a methodology for real-time gas-phase ammonia detection using ECMS. Ammonia was successfully detected at picomolar fluxes without requiring chamber heating or soft ionisation (unlike previous work [35]), enabled by the ultra-dry glovebox environment. In situ ammonia generation and real-time detection were demonstrated, with performance shown to depend heavily on cell design and counter electrode material. This validated ECMS as a powerful tool for operando Li-NRR studies.

Chapter 5 examined how cell configuration influences electrolyte degradation, acidity, and crosstalk. Using real-time ECMS detection of NH_3 , H_2 , CH_4 , and C_2H_4 , methane and ethylene were identified as products of diglyme reduction and proposed as in situ markers of solvent breakdown. A key trade-off was observed: configurations that favoured lower acidity improved ammonia yield but increased solvent degradation, while more acidic environments suppressed degradation but reduced performance. These findings further demonstrate (in addition to [45]) that tailoring proton activity is crucial for optimising system efficiency and longevity.

This thesis has laid important groundwork for understanding electrolyte behaviour and quantifying ammonia in Li-NRR (Li-NRR), but several open questions remain that could benefit from further investigation. One key challenge is the direct and quantitative measurement of acidity in non-aqueous systems [140], [141]. This work relied on indirect proxies such as hydrogen evolution and working electrode potential decay, which provide only relative insight. Future efforts should explore absolute acidity measurements using non-aqueous RHE protocols, pKa benchmarking, or in situ spectroscopic techniques. More accurate acidity tracking would greatly enhance our understanding of ammonia speciation, SEI formation, and HER suppression.

Additionally, the ability to monitor gas evolution in real time using ECMS opens the door to studying the effects of dynamic operating strategies, such as current pulsing. Pulsing has been shown in recent literature to improve ammonia yield and system stability, yet the mechanistic reasons remain unclear [26], [34]. ECMS offers a unique opportunity to resolve this. Future studies could combine pulsed electrochemical protocols with real-time gas analysis and acidity measurements to investigate how pulsing effects performance and stability. A deeper mechanistic understanding of these effects will be essential to optimising the Li-NRR system and could lead to new design rules for electrolyte formulation and cell architecture.

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