Rational Electrode–Electrolyte Design for Efficient Ammonia Electrosynthesis under Ambient Conditions

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ABSTRACT: Renewable energy-driven ammonia electrosynthesis by N₂ reduction reaction (NRR) at ambient conditions is vital for sustainability of both the global population and energy demand. However, NRR under ambient conditions to date has been plagued with a low yield rate and selectivity (<10%) due to the more favorable hydrogen evolution reaction (HER) in aqueous media. Herein, surface area enhanced α-Fe nanorods grown on carbon fiber paper were used as NRR cathodes in an aprotic fluorinated solvent—ionic liquid mixture. Through this design, significantly enhanced NRR activity with an NH₃ yield rate of ~2.35 × 10⁻¹¹ mol s⁻¹ cm⁻², (3.71 × 10⁻¹³ mol s⁻¹ cm⁻ECASA⁻) and selectivity of ~32% has been achieved under ambient conditions. This study reveals that the use of hydrophobic fluorinated aprotic electrolyte effectively limits the availability of protons and thus suppresses the competing HER. Therefore, electrode–electrolyte engineering is essential in advancing the NH₃ electrosynthesis technology.

Annually, an excess of 140 million tonnes of NH₃ is produced industrially via the Haber–Bosch process, and the demand is growing.¹,² Ammonia plays a vital role in supporting global population owing to its role as an essential precursor in fertilizer production. However, the process is energetically demanding and associated with low efficiencies. Typical reaction requires temperatures and pressures of ~500 °C and >200 atm and the use of Fe/Ru-based catalysts.³,⁴ Therefore, it is estimated that ~2% of the world’s energy budget is spent on NH₃ production.⁵ In addition, the process creates a substantial carbon footprint due to its dependence on steam reforming of natural gas.⁶

Electrochemical methods have a major role to play in the development of sustainable energy technologies. The method allows the direct conversion of renewable electricity (e.g., solar, wind) into chemical bonds.⁷ On the basis of this principle, N₂ could be converted into NH₃ through the 6e⁻ process. Due to the known sluggish nitrogen reduction reaction (NRR) kinetics, T > 100 °C is often necessary; for example, a selectivity, otherwise known as the Faradaic efficiency (FE), of 78% has been reported at 570 °C using a Pd-based catalyst operating in a perovskite-based solid electrolyte.⁸ Nevertheless, electrochemical studies reported to date have yet to prove the feasibility of NRR at room temperature and pressure conditions (RTP). Hitherto, studies on NRR at RTP suffer from the drawbacks of low FE and NRR current density (<5 μA cm⁻²), indicating low NH₃ yield rates of 10⁻¹¹–10⁻¹⁴ mol s⁻¹ cm⁻²).¹⁰⁻¹⁳ One of these studies was conducted by Kordali et al., in which Pt was used as the cathode, achieving an NH₃ yield rate of 3.1 × 10⁻¹² mol s⁻¹ cm⁻², with a FE of 0.3% at 20 °C.¹⁴ The main challenge for aqueous NRR is its low selectivity with respect to the HER due to the immediate availability of H⁺.¹⁵ In addition, although it remains debatable, the standard reduction potential of N₂ is close to that for HER.¹⁵ Therefore, HER is a greatly favored electrochemical reduction reaction in aqueous media. It is shown that materials that exhibit weak adsorption for H⁺ (ΔG°H > 0 eV) demonstrate improved activity for NRR. For example, Bao et al. used Au nanorods (NRs) (ΔG°M–H > 0.3 eV)¹⁶ as a NRR catalyst, delivering a maximum NH₃ yield rate of 2.7 × 10⁻¹¹ mol s⁻¹ cm⁻² and a FE of 4.0%.¹⁷ Further modifications of Au-based catalysts have demonstrated FEs as high as 10.1%.¹⁸,¹⁹ Other strategies include the use of alternate electrolyte media to enhance the NRR.²⁰–²² We have recently demonstrated the use of aprotic, highly fluorinated ionic liquids (ILs) to limit the availability of H⁺. In addition, the fluorinated IL also exhibits a high N₂ solubility, which therefore resulted in a highly efficient NRR with a FE as high as 60%. However, the NH₃ yield rate was found to be in the range of 10⁻¹² mol s⁻¹ cm⁻² due to the limited N₂ mass transport in the viscous IL.

In this study, we employed a rational electrode–electrolyte design to improve the NRR selectivity, as supported by a

Received: March 25, 2018
Accepted: April 25, 2018
Published: April 25, 2018
Aprotic fluorinated solvent was used as an electrolyte in which the supply of H\(^+\) can be regulated to favor N\(_2\) adsorption onto the catalytic sites. Additionally, the fluorinated solvents used are known to be both highly fluid and to have high gas solubility (e.g., perfluorohexane has nearly twice the N\(_2\) solubility of heptane, 17 and 9.1 mmol L\(^{-1}\), respectively), while H\(_2\)O exhibits a significantly lower N\(_2\) solubility of 0.66 mmol L\(^{-1}\). However, these solvents generally show very poor solubility toward salts that are routinely used in aprotic electrolyte media. To counter this effect, a highly fluorinated IL salt, for example, 1-butyl-1-methylpyrrolidinium [tris(pentafluoroethyl)trifluorophosphate ([C\(_4\)mpyr][eFAP])] is shown to be highly soluble in the aprotic media in this work. Furthermore, the preparation of an Fe-based electrocatalyst by a direct hydrothermal deposition method is described. This minimizes the use of polymer binders that may disrupt electrocatalytic processes. The method also enables the achievement of a high-surface area Fe NR array structure, which is important for electrocatalysis.

Carbon fiber paper (CFP) was selected as an electrode substrate to grow the \(\beta\)-FeOOH NR due to the electrochemical inertness and its high porosity providing an enhanced active surface area (refer to the Supporting Information for details). Subsequently, \(\beta\)-FeOOH is reduced into a core–shell \(\alpha\)-Fe@Fe\(_3\)O\(_4\) by thermal annealing in a H\(_2\) atmosphere. The successful synthesis of \(\alpha\)-Fe@Fe\(_3\)O\(_4\) was validated by X-ray diffraction (XRD) (refer to the Supporting Information for further details). Scanning electron microscopy (SEM) reveals the morphology of the synthesized \(\beta\)-FeOOH and \(\alpha\)-Fe NR. As shown in Figure S1a,b, the \(\beta\)-FeOOH grows in a perpendicular direction against the CFP substrate, forming a dense array of NRs. The \(\beta\)-FeOOH exhibits an average diameter of \(\sim 100–150\) nm and length of \(\sim 500–1000\) nm. Following the thermal reduction to \(\alpha\)-Fe, the initially tubular NRs have transformed into an interconnected spherical particle morphology with a significantly reduced average diameter of \(\sim 40–60\) nm (Figure 1a,b). The significant size reductions suggest the removal of structural oxygen from the \(\beta\)-FeOOH crystal structure. Additionally, transmission electron microscopy (TEM) in Figure 1c,d validates the formation of a core–shell \(\alpha\)-Fe@Fe\(_3\)O\(_4\) structure, showing an oxide thickness of \(\sim 5\) nm.

Electrochemical measurements were conducted using the setup shown in Figure S2a. In designing the electrolyte for this work, we observed that [C\(_4\)mpyr][eFAP] was not miscible with some solvents (e.g., perfluoromethylcyclohexane); therefore, \(1H,1H,1H,1H\)-octafluoropentyl-1,1,2,2-tetrafluoroethyl (FPFE) was chosen to its high degree of fluorination and high miscibility with [C\(_4\)mpyr][eFAP] (Figure S2b). The physicochemical and electrochemical properties of FPFE, [C\(_4\)mpyr][eFAP], and their mixtures were characterized to determine the optimum solvent–IL ratio (X\(_{IL}\)) (please refer to section 3 of the Supporting Information for discussion). It is shown that the solvent–IL electrolyte system has a maximum conductivity of 1.95 mS cm\(^{-1}\) and electrochemical window of 3.40 V, ideal for NRR.

Figure 2a shows the cyclic voltammograms (CVs) collected with the \(\alpha\)-Fe@Fe\(_3\)O\(_4\) NR cathode. The experiments were carried out at X\(_{IL}\) = 0.16, prepurged with either high-purity N\(_2\) gas (99.9999% purity, C\(_{O2}\) = \(\sim 20\) ppm) or Ar gas (99.9999% purity, C\(_{O2}\) = \(\sim 20\) ppm) for 45 min. Under a N\(_2\) atmosphere, the CV exhibited a cathodic shoulder with an onset of \(-0.60\) V vs NHE, while on the anodic sweep, an oxidation peak at \(-0.65\) V was observed. In contrast, the shoulder peak at \(-0.60\) V was not observed under an Ar atmosphere, signifying its ties to a N\(_2\) reduction event. However, the anodic peak at \(-0.65\) V was found to persist under Ar purging. To clarify the origin of the peak, CVs collected with different C\(_{O2}\) are also displayed. It is shown in Figure 2a that the anodic peak transforms proportionally with C\(_{O2}\) (Figure S3b) and is entirely absent in the dry Ar CV. The anodic peak can be related to the onset of HER at E = \(-1.18\) V. Therefore, this process can be associated with the oxidation of H\(_2\) generated by the HER process that occurs during the cathodic sweep.

Electrochemical optimization was first conducted at X\(_{IL}\) = 0.16, where the mixture exhibits a conductivity of 1.40 mS cm\(^{-1}\) (further discussions on conductivity and optimization are available in the sections 3 and 4 of the Supporting Information). NRR was carried out using controlled potential electrolysis (CPE). The possible NH\(_3\) contributions from impurities found in the IL, solutions, and gases, as well as possible electrochemical reduction of NO\(_x\), were initially determined by a series of control experiments, as shown in Supporting Information section 5 and Table S1. It is emphasized that such control/background experiments are vital in determining a reliable NH\(_3\) production rate in experiments such as these. CPE with different applied potentials ranging from \(-0.45\) to \(-0.75\) V vs NHE were carried out, and the current transients are shown in Figure 2b. The highest FE and NH\(_3\) yield rate of (11.0 \(\pm 0.6\)% and (0.74 \(\pm 0.06\)) \times 10^{-10} mol \(s^{-1} \text{cm}^{-2}\), respectively, were achieved at an applied potential of \(-0.65\) V. This potential is lower than the previously reported optimum NRR potential of \(-0.8\) V vs NHE on an electrodeposited Fe cathode in pure [C\(_4\)mpyr][eFAP]. The application of a more negative potential of \(-0.75\) V resulted in a diminished FE and ammonia yield rate of 6.6 \(\pm 0.7\)% and (0.65 \(\pm 0.06\)) \times 10^{-11} mol \(s^{-1} \text{cm}^{-2}\). The decreases can be ascribed to the increased selectivity toward proton reduction/hydrogen evolution reaction (HER) at more negative potentials.\(^{6,21}\)
Recognizing the role of the IL mole fraction ($X_{IL}$) on the physicochemical properties of the electrolyte mixture, the NRR performance of the system was then further optimized for $X_{IL}$. Figure 2c shows the typical current density ($j$) obtained in a range of different $X_{IL}$. At a low $X_{IL}$ of 0.16, an average current density of $\sim 1.5 \mu A \text{ cm}^{-2}$ was observed, while the lowest current density of $3.5 \mu A \text{ cm}^{-2}$ was exhibited at $X_{IL}$ of 0.46. A current density of $\sim 23 \mu A \text{ cm}^{-2}$ was achieved at an $X_{IL}$ of 0.23. The variation of the $j$ could be dictated by several factors such as viscosity, conductivity, and $N_2$ solubility. Figure 2d shows that the highest FE of 23.8 ± 0.8% with an $NH_3$ yield rate of 1.58 ± 0.05 $\times 10^{-11}$ mol $s^{-1} \text{ cm}^{-2}$ was achieved at $X_{IL}$ = 0.23 at the optimized potential of −0.65 V vs NHE. To provide insight on the activity of the catalyst, the electrochemical active surface area (ECSA) of the $\alpha$-Fe@Fe$_3$O$_4$ has been calculated (Figure S12), and the ECSA normalized $NH_3$ yield rate is provided in Table S4. The highest $X_{IL}$ tested in this series was 0.46, exhibiting a FE of 16.2 ± 1.2% and $NH_3$ yield rate of 0.27 ± 0.03 $\times 10^{-11}$ mol $s^{-1} \text{ cm}^{-2}$. The significant drop of NRR performance with increasing $X_{IL}$ signifies the important role of FPEE in supporting mass transport in this electrolyte. Other factors correlating FE to $X_{IL}$ include the presence of complex molecular interactions and/or different diffusion behavior of neutral $N_2$ molecules and polar $H_2O$ within the mixed electrolyte system. In addition, the electrochemical stability was also tested with CPE at the optimized condition, revealing a stable current profile for the testing period of 4 h, as shown in Figure S8. A FE as high as 30.8 ± 1.6% and $NH_3$ yield rate of $2.15 \pm 0.20 \times 10^{-11}$ mol $s^{-1} \text{ cm}^{-2}$ ($n = 4$ repeats, highest in the set = $2.35 \times 10^{-11}$ mol $s^{-1} \text{ cm}^{-2}$ and FE = 32%) could be achieved. It is worth noting that this value of the FE is significantly higher than most of the recent reports of NRR at RTP (Table S5). Finally, time-dependent NRR experiments shown by Figure S10 show that $NH_3$ can be continuously produced with the application of longer electrolysis periods. The amount of produced $NH_3$ is found to continuously increase at an approximately constant rate, after the first 30 min; the initial period may represent establishment of a steady state at the electrode. This result, in combination with the results of the control experiments listed in Table S1, validates the formation of $NH_3$ from NRR.

Density functional theory (DFT) investigations reveal that $\alpha$-Fe catalyzes the electrochemical conversion of $N_2$ to $NH_3$ at RTP; as shown in Figure 3a, NRR takes place on the (110) surface of $\alpha$-Fe via an associative distal pathway, entailing $N_2$ adsorption and its further reduction by successive transfers of six $H^+$ and e'. $N_2$ interaction on a flat $\alpha$-Fe(110) surface is estimated to be slightly physisorbed with a binding Gibbs free energy of $\sim 0.09$ eV and interatomic $N$–$Fe$ distance of 1.86 Å (at the RPBE level, see full computational details in the Supporting Information). As a result of this, adsorbed $N_2$ ($^*$$N_2$) experiences elongation of the $N\equiv N$ triple bond by 0.02 Å with respect to the calculated distance for an isolated $N_2$ molecule in the gas phase; this could result in its activation for the following hydrogenation steps. Accordingly, the reaction Gibbs free energy for the first hydrogenation step ($^*N_2 + H^+ + e^- \rightarrow ^*N_2H$) is estimated to be only 0.15 eV uphill after $N_2$ adsorption. In this sense and contrary what has been predicted by Skúlason el al., the inclusion of D3 dispersion effects seems to have an important role in stabilization of the adsorbed $N_2H$ species. This stabilization by dispersion effects has been also corroborated with other methods such as Grimme D2 and
Tkatchenko–Scheffler. This highlights the importance of the Fe-based catalytic process as compared with the first H+/e− pair transfer from N2 to N2H in the gas phase, which is found experimentally to be −3.2 V vs NHE and is usually the rate-limiting step of the whole reaction.

In-depth examination of the minimum-energy pathway (MEP) reveals that the second H+/e− pair transfer is produced on the unhydrogenated N, leading to *NHNH (adsorbed cis-diazene), with a Gibbs free energy change of −0.05 eV relative to *N2H. During the third H+/e− pair transfer, the *NHNH2 intermediate species requires 0.52 eV with respect to the adsorbed cis-diazene species. The first NH3 molecule is produced during the fourth H+/e− pair transfer as result of another hydrogenation on the NH2 moiety of *NHNH2.

Therefore, generation of the [Fe]NH motif entails an energy drop of 1.97 eV, indicating it to be a very stable entity during the NRR cycle. Subsequently, relative Gibbs free energies for the successive fifth and sixth H+/e− gains to reach *NH2 and the final adsorbed NH3 species are calculated as 0.52 and 0.15 eV, respectively. Finally, the reaction is completed by release of the second NH3 molecule, with an energy input of 0.27 eV.

For NRR, the first hydrogenation step (*N2 + H+/e− → *N2H) usually represents the rate-limiting step of the whole reaction. Our DFT calculations including D3 dispersion corrections indicate that *N2H formation is highly catalyzed by the α-Fe(110) surface, requiring only 0.15 eV. In this regard, dispersion effects have an important stabilizing role in N2H adsorption. It is hypothesized that the most endergonic steps on α-Fe(110) are instead the third (*NHNH + H+/e− → *NHNH2) and fifth (*NH + H+/e− → *NH2) hydrogenations, in both cases with relative reaction Gibbs free energies, ΔΔG, of 0.52 eV, as shown in Figure 3b.

In summary, we have shown that a high NRR FE of 32% and appreciable NH3 yield rate of 2.35 × 10−11 mol s−1 cm−2 was achieved at RTP by rational design of the electrode-electrolyte system. First, it is demonstrated that the ability to regulate H+ in an aprotic solvent greatly enhances the FE due to the improved NRR selectivity over HER. Second, both experimental and DFT results show that α-Fe(110) is an active surface for catalyzing NRR, and the core–shell structure of α-Fe@Fe3O4 minimizes the loss of charge in the initial reduction of the Fe3O4 passivating shell. The reduction of α-Fe@Fe3O4 to form the active α-Fe surface was also confirmed by post-NRR XRD characterization, Figure S11. DFT calculations have shown that N2 is slightly physisorbed on a flat α-Fe(110) surface, with a binding Gibbs free energy of −0.09 eV and interatomic N–Fe distance of 1.86 Å. More remarkable is the stabilization with an important dose of dispersion of the first reduced *N2H intermediate species, which is estimated to be only 0.15 eV uphill with respect N2 adsorption. Among the previous DFT studies for NRR mechanisms, α-Fe(110) exhibits one of the smoother energy profiles, which accounts
for the catalytic power of this material for electrochemical N\textsubscript{2} conversion. Finally, this study has demonstrated, for the first time, the effectiveness of using a highly fluorinated solvent in supporting highly efficient RTP NH\textsubscript{3} electrolys.

### ASSOCIATED CONTENT

#### Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.8b00487.

Experimental details, XRD characterizations, physicochemical and electrochemical properties of evaluations, NRR optimizations, control experiments, NRR performance of Fe\textsubscript{2}O\textsubscript{3} nanorods, supplementary figures, table of performance, and computational details (PDF)

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#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

The authors thank Monash Centre for Electron Microscopy (MCEM) for the provision of access to their instruments. L.M.A. and L.C. acknowledge King Abdullah University of Science and Technology (KAUST) for support. Gratitude is also due to the KAUST Supercomputing Laboratory using the supercomputer Shaheen II for providing the computational resources. This study was supported by an Australian Research Council (ARC) Discovery Grant (DP170102267). D.R.M. is grateful to the ARC for his Australian Laureate Fellowship.

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