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Lithium-mediated ammonia synthesis from water and nitrogen: a membrane-free approach enabled by an immiscible aqueous/organic hybrid electrolyte system†

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The lithium-mediated pathway provides a promising way for facile and selective dissociation of nitrogen for ammonia synthesis. However, the prevailing electro-deposition of lithium, especially when coupled to the anodic oxygen evolution from water or hydroxide, presents disadvantages including the use of expensive Li-ion conducting ceramics (LISICON) or high temperature operation of molten salts. In this study, a membrane-free approach based on the immiscibility of aqueous/organic electrolytes was adopted for lithium electro-deposition, which could be utilized for subsequent nitridation and ammonia synthesis. We found that a biphasic system of aqueous 1 M LiClO₄ and 1 M LiClO₄/propylene carbonate reinforced with PMMA (poly(methyl methacrylate)) acts the same as a LISICON-based aqueous/organic hybrid electrolyte system, but without any physical membrane. With a fairly high faradaic efficiency (FE) of 57.2% and a production rate of 1.21 × 10⁻⁹ mol cm⁻² s⁻¹ for ammonia synthesis, this membrane-free approach and its application to ammonia synthesis provide an innovative way to the advancements in next-generation energy storage technologies.

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Introduction

The Haber–Bosch process is a well-established ammonia (NH₃) synthesis technology which converts more than 170 million tons of nitrogen (N₂) to NH₃ every year.¹ This mature process, however, is exceedingly energy-intensive due to its harsh operational conditions, and suffers from extensive carbon emissions.^{2–6} In light of these shortcomings, the development of a more environmentally benign alternative is of absolute necessity.

Electrochemical synthesis is an attractive candidate because the energy consumption, if optimized, could be lowered com-

pared to the Haber–Bosch process while avoiding immediate carbon emissions.^{7–9} If the required electrical energy for the electro-synthesis is supplied from renewable sources, this approach will offer a way of energy storage into NH₃ as a next-generation, long-time energy carrier with an energy density higher than that of hydrogen, even close to that of fossil fuels.¹⁰ Provided that water serves as an electron donor for this N₂-reducing reaction, NH₃ synthesis can be possible with nature's abundant and eco-friendly resources, thereby achieving a truly sustainable and decentralized process. In the last three decades, such electrochemical processes have been widely developed.^{11–17} However, the faradaic efficiencies (FEs) were intolerably low in most cases because a significant fraction of the faradaic current becomes diverted toward an electron-stealing side reaction (*e.g.* hydrogen evolution), while the intended N₂ reduction is sluggish due to its inertness from the strong triple bond.^{18–23} The judicious choice of materials and an electrochemical configuration are therefore undoubtedly required to overcome such obstacles and eventually achieve excellent selectivity toward N₂ reduction.

Lithium (Li)-mediated reduction offers an innovative way of N₂ fixation. The Li metal, on account of the negative potential of Li⁺/Li (−3.04 V *vs.* SHE), spontaneously dissociates N₂ to form lithium nitride (Li₃N), a high energy precursor which is readily converted into NH₃ upon a reaction with protons or

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water.^{24–27} This Li-mediated approach, realized by a stepwise combination of Li deposition, nitridation, and NH₃ formation, gives advantageous features in that (1) from a material selection perspective, highly reactive surface Li, with small barriers of N₂ activation, is an excellent N₂-reducing agent²⁴ and (2) from an electrochemical process perspective, its configuration allows us to separate protic compounds (H₂O, H⁺ and OH[−]) from highly reactive cathodic surface Li by means of Li-ion conducting glass ceramics (LISICON)^{25,27} or porous alumina diffusion barriers,²⁴ thereby circumventing the self-discharge of Li and hydrogen evolution. Unfortunately, however, developing economic Li deposition processes is still challenging due to either high temperature (molten salt approach) or costly LISICON and its questionable chemical stability upon long-term operation.²⁸

As a novel strategy in the Li-mediated NH₃ synthesis regime, a membraneless electrochemical cell for Li deposition was proposed which relies on the immiscible nature of aqueous/organic electrolytes. The biphasic interface serves as not only a Li-ion conductor but also a physical barrier, rendering expensive LISICON dispensable and therefore making the membraneless Li-mediated pathway (Fig. 1) more economically favorable. Herein, in an effort to realize this membraneless approach, we proved that an aqueous lithium perchlorate (LiClO₄) solution and an organic electrolyte, LiClO₄ in propylene carbonate (PC), are not miscible but instead form an interface, acting in the same manner as a LISICON-based hybrid aqueous/organic electrolyte system,²⁵ even without the use of LISICON. The LiClO₄/PC-based system was chosen as the model electrolyte for its well-understood interfacial chemistry (*e.g.* the reaction of metallic Li and PC) and already proven applicability toward nitridation and NH₃ synthesis.^{25,27} It is worth noting that, by taking advantage of the hydrophobic polymer poly(methyl methacrylate) (PMMA) in the organic phase,^{28,29} we successfully controlled the interfacial diffusion of water from the aqueous phase to the organic phase, thereby ensuring the water-proof nature of the organic solvent and stability of our biphasic system. Interestingly, the additional benefit of PMMA was that its incorporation into the organic

electrolyte enhanced Li plating performance and in turn, NH₃ synthesis efficiency.

Results and discussion

Electrochemical behavior of a biphasic system

Since the density of PC is higher than that of water ($\rho_{\text{PC}} = 1.2 \text{ g cm}^{-3}$ vs. $\rho_{\text{water}} = 0.997 \text{ g cm}^{-3}$), the aqueous phase floats on top of the organic electrolyte, thus spontaneously forming a biphasic system without being intermixed (Fig. 2(a)). In order to evaluate the general electrochemical behavior of this system, the aqueous/organic electrolytes were individually subjected to cyclic voltammetry (CV) in a three-electrode electrochemical cell (Fig. S1†) in the potential range of -0.45 to 1.45 V and 3.55 to 5.30 V (vs. Li⁺/Li) for the organic and aqueous phases, respectively. As shown in Fig. 2(b), the CV of the organic catholyte (red) exhibited a reversible behavior of Li plating and stripping, while the aqueous anolyte (blue) showed an increase in current density due to oxygen evolution. This result showed that the electrochemical windows for individual electrolytes were separated, demonstrating the immiscible nature of two electrolytes. The position of potentials in the CVs indicated a minimum cell voltage of 4.5 V for Li deposition by utilizing the two immiscible electrolyte systems. As shown in Fig. S5,† the required voltage for Li deposition at 5 mA cm^{-2} was about 5.3 V, which was 14.5% lower than the voltage requirement of LISICON-based Li deposition (6.2 V) at the same current density.²⁵

The effect of PMMA on the stability of a biphasic system

Controlling interfacial water diffusion from the aqueous to the organic phase is a prerequisite for ensuring the stability of the interface between the two immiscible electrolyte systems. As shown in Fig. 3(a), the contamination of the organic electrolyte with water caused an irreversible loss of metallic Li or electrons, resulting in hydrogen evolution ((i) $\text{H}_2\text{O} + \text{e}^- \rightarrow \text{OH}^- +$

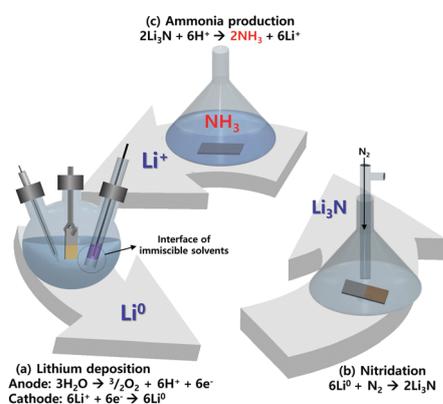


Fig. 1 A schematic representation of membrane-free Li-mediated NH₃ synthesis.

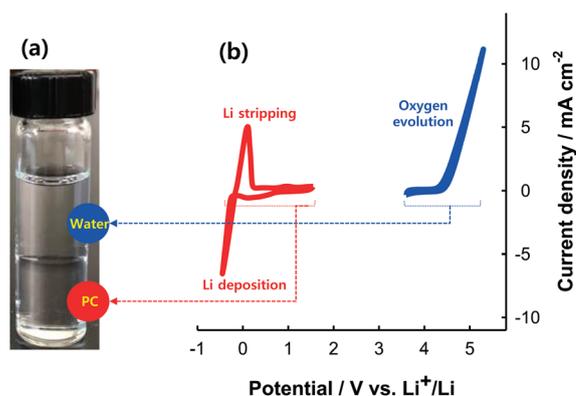


Fig. 2 (a) Immiscibility between water and propylene carbonate. (b) Cyclic voltammetry (CV) of Ni foil in the organic electrolyte (1 M LiClO₄/PC + 1 wt% PMMA, red) and the Pt wire anode in the aqueous electrolyte (1 M LiClO₄, blue) performed in the three-electrode electrochemical cell shown in Fig. S1† (scan rate: 50 mV s^{-1}).

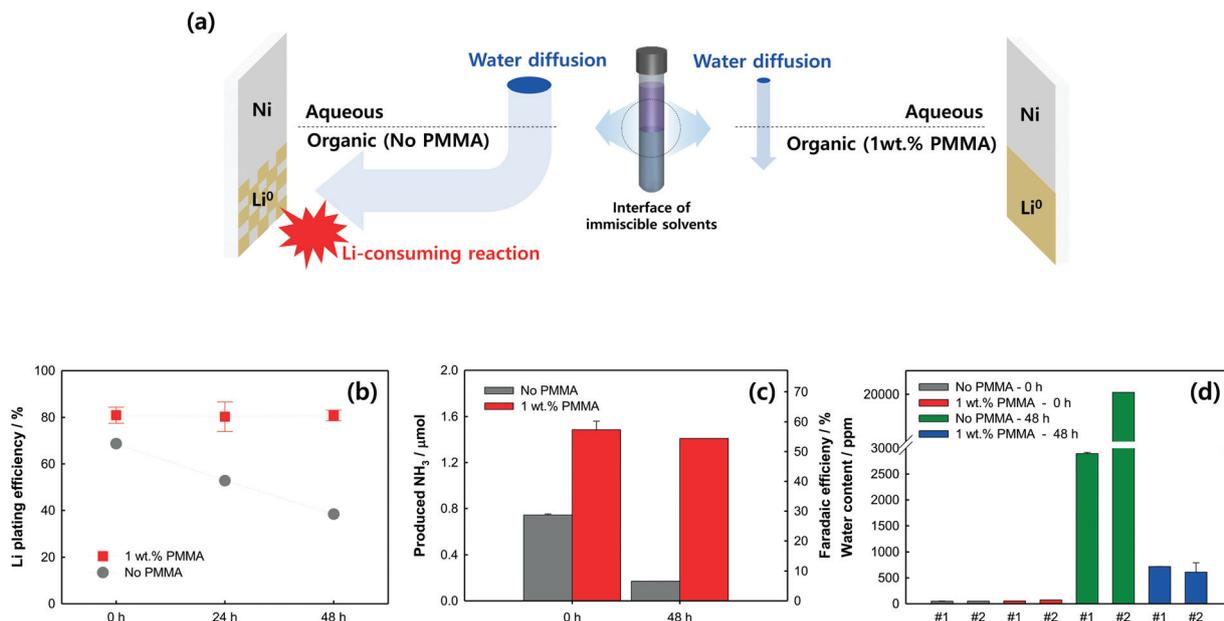


Fig. 3 (a) A schematic illustration showing water diffusion through the interface of the immiscible solvents and the resultant Li-consuming side reaction. (b) Li plating efficiencies of the organic electrolytes (1 M LiClO₄/PC) with no and 1 wt% PMMA after storage times of 0, 24, and 48 hours (see Fig. S6(a) and (b)† for voltage profiles, capacity: 0.83 mA h cm⁻²). (c) The amount of NH₃ and corresponding FEs using the organic electrolytes (1 M LiClO₄/PC) with no and 1 wt% PMMA after storage times of 0 and 48 hours (Li capacity: 0.83 mA h cm⁻²; Li was nitrated at 180 °C for 3 h). (d) Water contamination in the organic electrolytes measured by Karl-Fischer titration (see Table S1† for details).

1/2 H₂ or (ii) Li⁰ + H₂O → LiOH + 1/2 H₂) and thus lowering FE. On the other hand, the addition of hydrophobic polymer PMMA rendered the organic electrolyte water-proof and hence protected metallic Li from water-driven attacks (Fig. 3(a), right).²⁸ We firstly demonstrated this based on Li plating efficiencies and measured immediately after establishing the biphasic system and after storage times of 24 and 48 hours (Fig. 3(b), Fig. S6(a) and (b)†). The initial Li plating efficiencies were 68.7% and 81.0% for the organic electrolyte with no and 1 wt% PMMA, respectively. After a storage time of 48 h, it decreased to 38.4% without PMMA, while the initial efficiency was retained in the presence of 1 wt% PMMA, exhibiting 80.8%. Similar phenomena were also observed in CV analysis (see the caption of Fig. S6(c) and (d)†). Note that the Li plating efficiency is of great importance since only live metallic Li can be used in the subsequent nitridation and therefore determines the maximum attainable FEs for NH₃ synthesis.²⁵ As shown in Fig. 3(c), the corresponding NH₃ syntheses, obtained after the nitridation of Li deposit under a N₂ atmosphere, were in accordance with Li plating efficiency: the initial NH₃ syntheses were 7.43 × 10⁻⁷ mol and 1.49 × 10⁻⁶ mol for organic electrolytes with no PMMA and 1 wt% PMMA, which correspond to the FEs of 28.62% and 57.2%, respectively. After 48 h, the FE without PMMA diminished to 6.5%, while the organic medium with 1 wt% PMMA still showed an FE of 54.6%. All these results demonstrated that the incorporation of PMMA into the organic phase improves the stability of the interface between the two immiscible electrolytes. Karl-Fischer titration analysis supported our hypothesis on the PMMA-driven prevention of water contamination (Fig. 3(d) and Table S1†): at

0 h, the organic phases all exhibited their own dry nature (43.2–71.6 ppm). After 48 h, however, in the absence of PMMA, the organic phase was seriously contaminated with a relatively high concentration of water (2912.0–20 116.0 ppm), which diffused from the aqueous to the organic phase through the interface of the two immiscible electrolytes. Note that the water distribution in the bulky organic phase was inhomogeneous because water transport relied solely on diffusion through the confined interface. In contrast, the amount of water diffused was far lower (428.0–792.1 ppm) in the presence of 1 wt% PMMA due to the hydrophobicity of PMMA, which is in accordance with a previous report.²⁸ It is worth emphasizing that slight water contamination (*ca.* 800 ppm) in the PMMA-containing electrolyte had no impact on the performances in terms of Li plating efficiency and NH₃ synthesis (Fig. 3(b) and (c)), demonstrating the water-tolerant nature of the PMMA-based electrolyte.³⁰ Such a water-tolerant feature and the prevention of water contamination with PMMA addition are undeniable benefits with regard to the survival of metallic Li, especially in our presented membrane-free strategy.

The effect of PMMA on Li plating efficiency and NH₃ production

Interestingly, the presence of PMMA exhibited an additional benefit of enhancing Li plating efficiency and NH₃ synthesis; as shown in Fig. S7† (and Fig. 3(b) and (c)), a certain amount of PMMA inclusion (1 wt%) favored NH₃ synthesis, which diminished at higher PMMA concentrations (2 and 3 wt%). As can be inferred from the width of semicircles in the electrochemical impedance spectra (Fig. S8†), which is an indicator

of passive film resistance,^{31,32} the organic electrolytes with 2 and 3 wt% PMMA brought about the excessive growth of resistive and thick surface layers composed of a solid electrolyte interface (SEI) and/or PMMA during Li deposition.^{33,34} The excessive growth of such passivation layers is deemed to hinder the penetration of N₂ into the Li layer in the stage of nitridation, thereby leading to poor NH₃ synthesis.

To gain deep insights into how PMMA improved Li plating and NH₃ production, the morphologies of Li deposits with and without 1 wt% PMMA were visualized using SEM (Fig. 4(a) and (b)). The Li deposit without the addition of PMMA (Fig. 4(a)) exhibited sharp and needle-like dendrites mainly due to the locally enhanced electric field.^{35,36} It can be observed that sharp dendrites are prevailing over the entire Ni surface with a deposition capacity of 0.83 mA h cm⁻² (Fig. S9(a)†). The dendritic Li deposit with a large surface area can easily trigger the side reactions between metallic Li and the organic electrolyte PC, thereby forming an excessive SEI layer which is predominantly composed of Li₂CO₃ and/or ROCO₂Li (R = alkyl) and thus irreversibly decreasing the Li plating efficiency and FE for NH₃ synthesis.^{37,38} In contrast, the presence of 1 wt% PMMA obviously brought about a much different morphology (Fig. 4(b) and Fig. S9(b)†) though few dendritic structures were still observed: thicker Li particles were partially connected creating an overall flat and smooth layer, contrary to the rough and dendritic morphology in the absence of PMMA. The retarded formation of needle-like dendrites with 1 wt% PMMA therefore could reduce the side reactions between the Li metal and PC.³⁷ This was supported by the C 1s XPS spectra of the Li deposits (Fig. 4(c) and (d)). The carbon peak at 289.9 ± 0.1 eV (red), assigned to Li₂CO₃ and/or ROCO₂Li, decreased with the addition of 1 wt% PMMA, demonstrating that the Li-consum-

ing and carbonate-forming side reactions were largely inhibited in the presence of PMMA.³⁹

The mechanism of PMMA-driven enhancement in Li plating efficiency

PMMA participates in the process of Li deposition and serves as a storage medium for Li-ions as shown in Fig. S10.†^{35,40} In the electrochemical reduction process, PMMA firstly undergoes one-electron transfer reduction and generates intramolecular cyclopentanone through a ring-closing reaction between two adjacent ester groups, accompanied by the irreversible elimination of lithium methoxide (CH₃OLi) (Fig. S10(a)†).⁴⁰ In the next step (Fig. S10(b)),† reversible lithiation and delithiation processes occur on the as-formed conjugate carbonyl groups through two-electron transfer reactions.⁴⁰ Such a Li-ion storage mechanism by PMMA alters the way Li is deposited, which is adequately proven in previous studies with Cu as the substrate.³⁵ In order to understand the role of PMMA specifically under our experimental conditions, electrochemical behaviors were first investigated using cyclic voltammetry within the voltage window of 0.35–2.4 V (vs. Li⁺/Li) at a scan rate of 10 mV s⁻¹ (Fig. S11(a)†). In the first negative scan, two cathodic peaks were found at 1.40 (peak A) and 0.58 V (peak B), while only one peak at 1.27 V was observed during the first anodic scan. In the second cycle, the sharp cathodic peak A at 1.40 V disappeared, but the cathodic/anodic peaks at 0.58 V and 1.27 V were still observed. Indeed, the sharp cathodic peak A at 1.40 V is ascribed to the formation of intramolecular cyclopentanone and the elimination of CH₃OLi as shown in Fig. S10(a),† and its irreversible nature is well reflected on the disappearance of peak A in the second negative sweep.⁴⁰ It is worth mentioning that the sharpness of peak A implies a fast kinetics of this ring-closing reaction.⁴⁰ The reduction/oxidation peaks at 0.58 V (peak B) and 1.27 V are due to the reversible lithiation and delithiation which occur on the *in situ* formed carbonyl groups *via* a two-electron transfer reaction, as depicted in Fig. S10(b).†⁴⁰ Likewise, during chronopotentiometry at a current density of 0.05 mA cm⁻² (Fig. S11(b)†), two voltage plateaus were found at about 1.35 and 0.63 V before Li deposition, which correspond to peaks A and B from CV analysis, respectively. All these were systematically confirmed and understood *via* Fourier transform infrared spectroscopy (FT-IR) using Ni electrodes obtained at different stages of charging during the chronopotentiometry experiment. As shown in Fig. S11(c),† the pristine electrode at open circuit potential exhibited strong vibration bands at 1735 and 1149 cm⁻¹, which can be assigned to the C=O stretching of the ester carbonyl group and C–O–C vibration, in good accordance with the structure of PMMA.⁴⁰ After being charged to 1.0 V (Fig. S11(c),† red), these two peaks disappeared, and two new peaks appeared at 1650 and 1100 cm⁻¹, which correspond to the keto carbonyl group and C–O vibration from CH₃OLi, respectively.^{35,40,41} The occurrence of these new peaks demonstrates the formation of intramolecular cyclopentanone and CH₃OLi (Fig. S10(a)†). After being further charged to 0.2 V (Fig. S11(c),† blue), an additional peak appeared at around

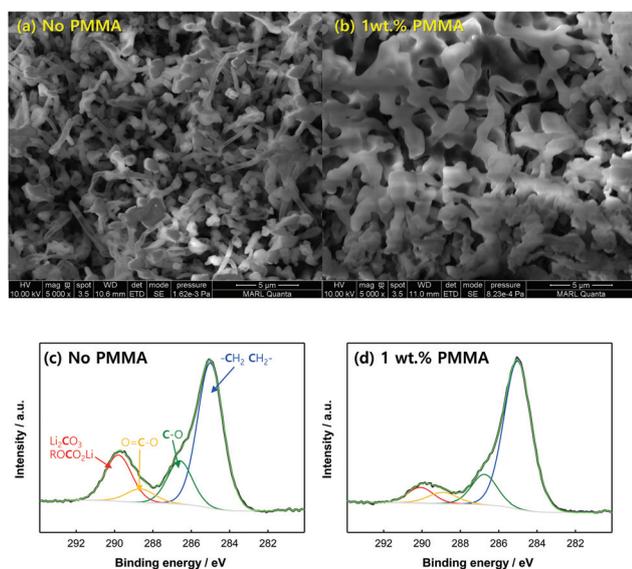


Fig. 4 SEM images of Li deposited (a) in the absence and (b) presence of 1 wt% PMMA. C 1s XPS spectra of Li deposited (c) in the absence and (d) presence of 1 wt% PMMA (deposition current density: 5 mA cm⁻²; Li capacity: 0.83 mA h cm⁻² for all cases).

530 cm^{-1} , which indicates that PMMA is lithiated and the Li ion is bound to the carbonyl oxygen.³⁵ Further characterization using XPS analysis well agreed with the FT-IR results (see the caption of Fig. S12†). All these characterization studies, along with the electrochemical analysis of CV profiles, led us to summarize as follows: (1) the formation of intramolecular cyclopentanedione at 1.40 V provides binding sites (carbonyl groups) for Li-ions, (2) Li-ions are bound to PMMA *via* carbonyl groups and thus immobilized during the reversible lithiation at about 0.58 V, and (3) the Li-ions bound to PMMA are preferentially deposited onto Li particles on the Ni substrate, providing “active sites” for subsequent deposition and serving to escort the way of next Li-ions to be deposited.³⁵ Considering that those “active sites” are distributed throughout the three-dimensional molecular structure of PMMA, the final morphology of Li deposit is patterned after the PMMA structure,³⁵ and this could explain the morphology of interconnected Li particles with a smooth surface (Fig. 4(b)), which is contrary to the needle-like individual dendrites due to the enhanced electric field in the absence of PMMA (Fig. 4(a)).

NH₃ synthesis performance and control experiments

During nitridation, a higher amount of NH₃ synthesis was obtained with increased nitridation temperature (Fig. S13†), which is in accordance with previous literature studies.^{24,25} As supported by the N 1s XPS spectrum (Fig. 5(a)), Li₃N was truly the intermediate of Li-mediated NH₃ synthesis (398.3 eV).⁴² Fig. 5(b) illustrates the NH₃ synthesis and corresponding FEs when Li deposit was nitrided at 180 °C for different time periods. The rate of NH₃ production decreased over time, as a consequence of decreasing accessibility of N₂ to the active Li metal, due to the hindrance by the SEI layer and the newly

formed Li₃N layer.²⁵ The maximum attainable FE after 3 h nitridation was 57.2% (Fig. 5(b)). We believe that the loss in FE is ascribed to (1) Li-consuming and carbonate-generating SEI formation, as reflected in the Li plating efficiency (Fig. 3(b)), and (2) the exposure of Li to the air especially during the transfer of Li from the electrochemical cell to the nitridation chamber. The NH₃ synthesis rate was calculated based on a nitridation time of 1 h (see section 1.5 of the ESI†); it turned out to be $1.21 \times 10^{-9} \text{ mol s}^{-1} \text{ cm}^{-2}$, but this can be further enhanced provided that the three sub-processes were operated simultaneously at higher current density for Li deposition.

In this study, particular attention was paid to systematically prove that N₂ is the dominant nitrogen source for NH₃ synthesis;^{43–45} we carried out several rigorous control and confirmatory experiments specifically in the stage of nitridation. As shown in Fig. 5(c), the replacement of Li deposit with pristine Ni or the replacement of N₂ flow with argon resulted in negligible NH₃ synthesis; only the exposure of N₂ to metallic Li led to NH₃ synthesis, confirming that the formation of Li₃N is unquestionably attributed to the bulk reaction between metallic Li and N₂. Most conclusively, as shown in the ¹H NMR spectra (Fig. 5(d)), the hydrolyzed Li₃N, prepared under the nitridation of Li using ¹⁵N₂, showed a doublet corresponding to ¹⁵N–¹H coupling, while only a triplet corresponding to ¹⁴N–¹H coupling was observed using ¹⁴N₂, qualitatively verifying that NH₃ originates from N₂.²⁶ Furthermore, isotope-labelled quantification agreed well with the colorimetric NH₃ assay using the indophenol blue method (Fig. S14†). All these stringent control experiments prove that the NH₃ synthesis is truly *via* a so-called Li-mediated pathway (Li⁺ → Li → Li₃N → NH₃).

Over the last few years, extensive efforts have been made for the improvement of electrochemical N₂ reduction, with the majority focusing on the development of novel electrocatalysts. The catalyst synthesis processes are usually complicated and rely on the use of toxic or hazardous compounds (*i.e.* pyromellitic dianhydride,¹⁴ cetyltrimethylammonium bromide,¹⁵ *N,N*-dimethylformamide,¹⁶ and ethylene glycol^{17,22}). Our Li-mediated process does not need a costly nanoparticle synthesis process, but just employs a green solvent PC,⁴⁶ whose production could even utilize carbon dioxide.⁴⁷ While the durability of electro-catalysts is questionable, PC can be reused, and in particular, Li salt could be efficiently recycled in the Li-mediated approach as demonstrated in XRD²⁴ and ICP²⁵ analyses. With its fairly high or comparable performance in terms of the synthesis rate and FE compared to the state-of-the-art technologies (Table S2†), this study proves the advantageous features as one of the most advanced and reliable electrochemical processes for N₂ fixation. Although the estimated energy consumption required for Li deposition is slightly larger than that of the matured Haber–Bosch process^{24,25,48} the Li-mediated NH₃ electrosynthesis route offers significant benefits compared to the traditional thermochemical process, such as no carbon emission (if powered by renewable wind and solar electricity, and indeed, carbon dioxide is utilized for the production of PC), no need for fossil

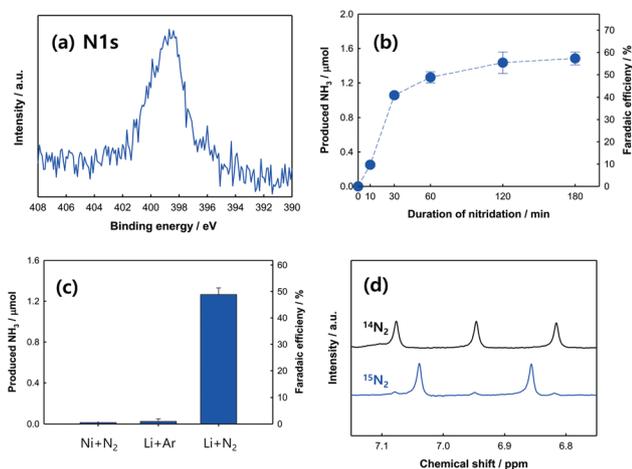


Fig. 5 (a) N 1s XPS spectra of the Li deposit nitrided at 180 °C. (b) The amounts of synthesized NH₃ and corresponding FEs using Li deposit nitrided at 180 °C over time. (c) The amount of synthesized NH₃ and corresponding FEs using Ni or Ar as a reactant in control experiments. (d) ¹H NMR spectra of the sulfuric acid solutions after the hydrolysis of Li₃N, which were generated during nitridation using ¹⁴N₂ and ¹⁵N₂. (Li was deposited from 1 M LiClO₄/PC + 1 wt% PMMA and the Li capacity was 0.83 mA h cm⁻² for all cases.)

sources such as hydrogen sources, milder operating conditions, and possibility of storing renewable energy, thereby enabling small scale, distributed, decentralized, onsite production of NH_3 , with reduced transportation and distribution costs.^{24,25}

Conclusion

In summary, we proposed a membrane-free approach for ambient Li deposition based on the immiscibility of aqueous/organic electrolytes and demonstrated the applicability of the biphasic system for the realization of Li-mediated NH_3 synthesis. The behavior of this system is the same as a LISICON-based cell,²⁵ especially thanks to the stability of the biphasic system. Rather, this system requires lower cell voltage (5.3 V in this study vs. 6.2 V in the LISICON-based cell at 5 mA cm^{-2}), even without the need for an expensive membrane, rendering it more economically favorable. The FE and NH_3 synthesis rate (57.2% and 1.21×10^{-9} mol cm^{-2} s^{-1} , respectively) obtained using a proof-of-concept electrochemical cell are higher or comparable with many of recent reports on NH_3 synthesis. This proof-of-concept has been realized merely using our model hybrid electrolyte system (LiClO_4 and $\text{PC-H}_2\text{O}$), but the use of the best optimized electrolytes with better biphasic stability, higher conductivity, higher stability against Li (lower SEI formation), and applicability to a continuous, integrated process will achieve further improvements in the novel Li-mediated NH_3 synthesis.

Conflicts of interest

The authors claim no conflicts of interest.

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