Nitrogen Reduction to Ammonia at High Efficiency and Rates Based on a Phosphonium Proton Shuttle

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Abstract

Ammonia is a globally important commodity for fertilizer production, but its synthesis by the Haber-Bosch process causes significant emissions of CO\textsubscript{2}. Alternative, zero-carbon emission NH\textsubscript{3} synthesis methods being explored include the promising electrochemical lithium-mediated nitrogen reduction reaction, which has nonetheless required sacrificial sources of protons. Herein, a phosphonium salt is introduced as a proton shuttle to help resolve this limitation. The salt also provides additional ionic conductivity, enabling high NH\textsubscript{3} production rates of 53 \pm 1 \text{nmol s}^{-1} \text{cm}^{-2} at 69 \pm 1 \text{% faradaic efficiency in 20-hour experiments under 0.5 bar H}_2 \text{ and 19.5 bar N}_2. Continuous operation for more than 3 days is demonstrated.
Main text

In 2019, the total global production of ammonia (NH$_3$) reached 150 million metric tons per year, making it the second most produced chemical commodity in the world (1). Ammonia is an essential source of the so-called “fixed nitrogen” for agriculture and more than 80% of the produced NH$_3$ is today used for fertilizer production. With increasing global population, the demand for ammonia is expected to reach 350 million metric tons per year by 2050 (2). Furthermore, additional growth in the demand for NH$_3$ is expected due to the growing interest in its use as an energy carrier (3).

Ammonia is currently produced via a metal-catalyzed reaction between nitrogen and hydrogen gases, using an established technology known as the Haber-Bosch process. H$_2$ used in this reaction is currently generated from natural gas, and production of each metric ton of ammonia is accompanied by emission of 1.9 metric tons of CO$_2$ (4). As a result, the process accounts for roughly 1.8% of the global CO$_2$ emissions (5). Moreover, it also requires high temperatures (300-500 °C) and pressures (200-300 bar) and can only be feasibly achieved in large reactors at large industrial plants. Therefore, increasing the current Haber-Bosch production capability to meet growing ammonia demand beyond its use in the fertilizer industry is a capital-intensive, CO$_2$ producing prospect.

Decarbonization of ammonia production is a clear and achievable short-term goal (6). The methane-derived H$_2$ can be gradually substituted by H$_2$ generated from water electrolysis powered by renewable energy. However, the Haber-Bosch reactor is typically operated continuously to prevent damaging the catalyst, and consequently is incompatible with the fluctuating nature of renewable electricity supplies. Therefore, a better solution would be the development of a N$_2$ fixation process that directly uses renewably generated electricity in a small and robust electrolytic
device (7). This technology will be compatible with smaller scale, distributed production facilities, with less demanding infrastructure and capital requirements (8).

In this vein, the electrochemical nitrogen reduction reaction (NRR) has garnered substantial interest, as a means of directly reducing N₂ to NH₃ at significantly lower temperatures and pressures than required for N₂ and H₂ to react directly (9). However, most reports concerning this reaction only demonstrate production rates less than 1 nmol s⁻¹ cm⁻² (hereinafter, rates and currents are normalized to the geometric surface area of the electrode) (10-12), which is at least two orders of magnitude lower than the industrial targets for this process (13). Among the investigated modes of the NRR, a lithium-mediated process currently appears to be the most promising method in terms of ammonia yield rates (14). Typically, the reaction is undertaken in tetrahydrofuran solvent, which can dissolve reasonably high amounts of N₂ (5.2 mM at 25°C) (15). The mechanism of this electrochemical process is hypothesized to rely on the reduction of Li⁺ in the presence of N₂ to form lithium nitride (Li₃N) at the cathode of the electrochemical cell, followed by reaction of this transient species with a proton source to form NH₃ via:

\[
\text{Li}_3\text{N} + 3 \text{H}^+ \rightarrow 3 \text{Li}^+ + \text{NH}_3
\]  

In a practical process, the source of the protons must be from oxidation of either renewably-derived H₂ or H₂O at the anode of the electrochemical cell, with a proton shuttle molecule delivering H⁺ from the anode to the cathode to participate in reaction 1. In laboratory reports of the process, ethanol is typically used as a sacrificial proton donor in the electrolyte; sacrificial in the sense that it is not expected to be fully regenerated at the anode.

Unfortunately, the performance of Li-mediated N₂ electroreduction has not progressed substantially over the past three decades. In 1994, Tsuneto et al. reported an ammonia production rate of ca 2 to 4 nmol s⁻¹ cm⁻² at 50 bar of N₂ pressure (16). The electrochemical selectivity of this
process towards ammonia, known as the faradaic efficiency (FE; calculated as a ratio of the amount of ammonia synthesized to the product of the Faraday constant, number of electrons \( n = 3 \) and the total measured charge passed in the experiment), was at best about 60%, indicating that a substantial fraction of the passed current was producing by-products such as lithium hydride (LiH) and \( \text{H}_2 \) \((17)\). Using a gas diffusion electrode design, Lazouski et al. showed a significant improvement in the yield rate to 30 nmol s\(^{-1}\) cm\(^{-2}\), but with a lower FE of \( \sim 35\% \) \((18)\). However, no study has been able to demonstrate, so far, stable operation on a reasonable timeframe at these high yield rates. Very recent work by Andersen et al. presents a stable operation of Li-mediated NRR through the implementation of an alternating “on/off” strategy, though at very modest yield rates below 1 nmol s\(^{-1}\) cm\(^{-2}\) and FE of \( \text{ca} \) 30\% \((19)\). A summary of the key results reported to date on the \( \text{N}_2 \) reduction to ammonia through a lithium-mediated process is provided in Table S1.

One factor limiting the performance and longevity of the Li-mediated NRR system is the chemical nature of the proton source participating in reaction 1 \((20)\). It is necessary that the proton shuttle in the electrolyte be completely recycled in the cell, if it is not to be consumed in the process; however, the recyclability of ethanol in this role is yet to be critically assessed, and its vulnerability to oxidation at the anode is potentially a major issue. It is therefore likely that ethanol is not suitable for a practical process and in the current research is used as a sacrificial material \((12)\). Hence, our goal in the present work was to develop a genuine recycling proton shuttle that is electrochemically stable such that there is minimal tendency for it to be oxidized or reduced at the electrodes.
Fig. 1. Schematic illustration of sustainable electrosynthesis of ammonia from H₂ and N₂. The cathode process involves the reduction of Li⁺ to lithium metal that rapidly reacts with N₂ to produce Li₃N, which is protonated to release the target product, NH₃. The proton carrier is the phosphonium cation, which forms an ylide structure in its deprotonated state; this cycles to the anode where it is regenerated back to the phosphonium form through the reaction with H⁺ derived from the oxidation of H₂.

Focusing on these criteria in the search for a proton shuttle for the NRR, we have investigated phosphonium based cations such as trihexyltetradecylphosphonium, which is denoted herein as [P₆,₆,₆,₁₄]⁺. These compounds are known to have good chemical, thermal and electrochemical stability (21). Some have also been explored previously as ionic liquid solvents in the context of the NRR (22) due to their high nitrogen solubility in certain cases (21), however the rates of the reaction in such solvents are impractically low (11). Equally important is the known reactivity of the protons situated on the carbons directly bonded to the phosphorus center of the cation (i.e. the α-carbons) (23). Reversible deprotonation of such cations produces an ylide structure (Fig. 1) that can be accessed through reaction with organolithium compounds as in the first step of the Wittig reaction (24); it has also been shown that the same mechanism occurs in basic phosphonium ionic liquids (25). Beyond the Wittig reaction, this phenomenon has been previously studied in the context of CO₂ capture (26, 27). The [P₆,₆,₆,₁₄]⁺ phosphonium cation used
herein is produced as the chloride salt in large quantities by several companies globally for a range of applications. Herein, we harness this chemistry of phosphonium salts to provide the proton shuttling mechanism required in a practical Li-mediated NRR (Fig. 1). In this process, reaction of the electrochemically generated lithium nitride with the phosphonium cation produces ammonia and an ylide; the latter is a very strong base that is readily re-protonated by H\(^+\) derived from the anodic oxidation reaction to regenerate the original phosphonium cation. Equally importantly, the salt is not consumed in the NRR process as demonstrated below.

To confirm the capacity of \([\text{P}_{6,6,6,14}]^+\) to operate reversibly as a proton shuttle during the electrochemical nitrogen reduction, a series of chemical experiments simulating the transformation between the phosphonium cation and the ylide structure during the lithium-mediated NRR were performed and their progress monitored by \(^{31}\text{P}\) NMR and mass spectrometry (experimental details are provided in the Supplementary Materials). The \(^{31}\text{P}\) NMR spectrum of the phosphonium tris(pentafluoroethyl)trifluorophosphate ([eFAP]) salt features only a well-defined signal at 32.9 ppm that can be ascribed to the phosphonium cation (21) and a broad multiplet around -150 ppm due to the [eFAP]\(^-\) anion; the full spectrum is shown in Fig. S1, while Fig 2A focuses on the region between -10 and 40 ppm. To simulate the deprotonation process, the \([\text{P}_{6,6,6,14}][\text{eFAP}]\) solution was treated with excess Li\(_3\)N, pre-synthesized through the reaction of lithium metal with N\(_2\) (at 20 bar, 60 °C). The lithium nitride was observed to dissolve, and the initially colorless solution turned pale yellow, yet remained transparent. The \(^{31}\text{P}\) NMR spectrum of this solution shows almost full disappearance of the \([\text{P}_{6,6,6,14}]^+\) peak at 32.9 ppm, and exhibits a new signal at 9.4 ppm instead (Fig. 2B). The latter is assigned to the deprotonated form of the phosphonium cation according to previous, extensive studies of ylides (24, 28, 29).
Fig. 2. Chemical de-protonation/re-protonation cycling of a phosphonium proton carrier. The top panel (A) of the figure shows the $[\text{P}_{6,6,6,14}]^+$ cation and its $^{31}\text{P}$ NMR spectra in tetrahydrofuran solution, exhibiting a peak at 32.9 ppm; the second panel (B) shows the reaction of the cation with Li$_3$N to form an ylide, resulting in almost full disappearance of the cation peak and the appearance of a new peak at 9.3 ppm assigned to the ylide. On subsequent treatment (C) with acetic acid to reform the cation through re-protonation, the 32.9 ppm peak is recovered. Peaks labelled with an asterisk correspond to the PPh$_3$ external standard calibrated to $\delta_P = -6$ ppm. Experiments were undertaken at 24 ± 2 °C using a solution of 0.1 M $[\text{P}_{6,6,6,14}][\text{eFAP}]$ in tetrahydrofuran.

Re-protonation of the formed ylide achieved by the addition of a weak acid, in this case acetic acid, completely eliminated the signal at 9.4 ppm, fully regenerating the peak at 32.9 ppm (Fig. 2C). No other, new, species are visible in the $^{31}\text{P}$ NMR spectrum that might otherwise suggest side reactions. The integral of the regenerated $[\text{P}_{6,6,6,14}]^+$ signal matches closely that recorded in the initial solution. Additionally, recovery of the phosphonium cation was confirmed by mass spectroscopic analysis, which showed a sole, identical signal ($m/z = 483$) due to the $[\text{P}_{6,6,6,14}]^+$.
cation in the solution before and after the Li₃N / acetic acid cycle (Fig. S2 and Section 3 in the Supplementary Materials). The cycle from phosphonium cation to ylide and back was repeated 3 successive times, producing the same positive outcome, as shown in Fig. S1. Continuing this cycling further becomes difficult due to the build-up of the Li acetate by-product that accumulates in each cycle.

To test our hypothesis regarding the use of the phosphonium proton shuttle in the N₂ electroreduction process outlined in Fig. 1, the reaction was carried out in a single-compartment electrochemical cell using a standard three-electrode configuration that facilitates the control of the electrode potentials. The single compartment cell configuration enables uninterrupted proton shuttle cycling between the platinized titanium anode and the copper cathode. A silver wire was used as a reference electrode, and by calibration, as described in the Section 4 of the Supplementary Materials, the potentials are then reported here against the apparent potential of the lithium(0/+)

redox couple (Li⁰⁺). Unless otherwise stated, the electrochemical studies used 0.2 M LiBF₄ as electrolyte, dissolved in tetrahydrofuran along with 0.1 M of the [P₆,₆,₆,₁₄][eFAP] proton shuttle. The experiments were carried out at a range of N₂ pressures up to 20 bar in a static atmosphere, unstirred mode. Increased nitrogen gas pressure was employed to increase the concentration of dissolved N₂ available in the electrolyte solutions. A detailed description of the electrochemical setup and procedures is provided in Sections 4 – 6 and Figs S3 – S8 of the Supplementary Materials, including discussion of factors such as the active area of the working electrode.

Cyclic voltammetric analysis conducted at P(N₂) = 20 bar demonstrates that the reduction of lithium ions in the presence of the [P₆,₆,₆,₁₄]⁺ cation is highly efficient and achieves rates approaching -10 mA cm⁻² at -0.25 V vs. Li⁰⁺ (Fig. 3A) on a nominally flat electrode; similarly fast is the re-oxidation of the reduced species on the return cycle. These high rates compare very
favorably with the much lower currents observed in the same electrolyte solution containing the ethanol proton source instead of the phosphonium salt.

Fig. 3. Electrochemical analysis and metrics of the lithium-mediated NH₃ electrosynthesis. (A) Cyclic voltammetry (scan rate 0.020 V s⁻¹) in the presence of 0.1 M [P₆,₆,₆,₁₄][eFAP] (blue) or 0.17 M C₂H₅OH (red) at P(N₂) = 20 bar; evolution with cycling and voltammetric data recorded to more negative potentials are shown in Fig. S7. (B) Reproducibility of the current density vs. time dependencies (chronoamperograms) recorded at a constant potential of E = -0.75 V vs. Li⁰⁺ at P(N₂) = 20 bar (experiment index numbers correspond to details provided in Table S7). (C-D) Effects of (C) potential at P(N₂) = 20 bar and (D) N₂ pressure at E = -0.75 V vs. Li⁰⁺ on the ammonia yield rate and faradaic efficiency; data are presented as mean ± one standard deviation for n ≥ 3 replicate experiments or as individual measurements for n < 3 repeats (see Tables S7 and S9 for complete datasets). Unless otherwise indicated, all experiments were undertaken at ambient temperature (24 ± 2 °C) using unstirred N₂-saturated 0.2 M LiBF₄ + 0.1 M [P₆,₆,₆,₁₄][eFAP] solutions in tetrahydrofuran and a copper disk working electrode of area 0.012 cm².
This difference can be partially attributed to the higher ionic conductivity provided by the presence of 0.1 M [P$_{6,6,6,14}$][eFAP] salt (Fig. S6). Extending the negative voltammetric range down to -1 V vs. Li$^{0+/+}$ did not change the nearly linear, resistance-controlled increase of the reductive current with potential, and also did not induce a substantial increase in the oxidative peak (Fig. S7). The latter observation attests to a rapid chemical transformation of the reductively generated Li/Li$_3$N species, supported by the phosphonium cation.

The capability of the [P$_{6,6,6,14}$]$^+$ proton shuttle to sustain the generation of ammonia via reaction 1 was demonstrated by recording current density vs. time dependences (chronoamperograms) at a series of fixed potentials (Fig. 3B and Fig. S9). Except for the variations during the initial stages of the measurements, which are likely associated with the formation of a meta-stable reactive layer through a set of reductive transformations (commonly referred to as “solid-electrolyte interface” in battery research (30)), the chronoamperograms were well reproducible and did not demonstrate significant changes (within 20 %) on a 2 h timescale in most experiments. At every potential examined, a significant quantity of ammonia was detected in the electrolyte solutions (Fig. 3C), as quantified by the spectrophotometric Berthelot method and confirmed by $^1$H NMR spectroscopy (vide infra). The slight decrease in the faradaic efficiencies observed at more negative potentials is explained by the enhanced contribution from other reductive processes occurring in parallel with the NRR – a phenomenon typical of systems where several competing reactions take place (29); in the present case, these could include unproductive lithium or proton reduction. Under the examined conditions, the best system performance was achieved at around -0.75 V vs. Li$^{0+/+}$, where the N$_2$ electroreduction to ammonia occurred at a high FE of 69 ± 7 % (number of replicates, $n = 13$) at an average current density of ca -22.5 mA cm$^{-2}$. This corresponds to an ammonia yield rate of 58 ± 14 nmol s$^{-1}$ cm$^{-2}$. 


The N₂ pressure, which defines the amount of dissolved gas participating in the NRR, had a pronounced effect on the kinetics of the NH₃ generation facilitated by the phosphonium proton shuttle (Fig. 3D and Fig. S10). Within the investigated P(N₂) range (2 to 20 bar), the FE rose up to a limit at ~10 bar, while the ammonia yield rate demonstrated a progressive increase and also appeared to be reaching a maximum or limit. These trends indicate a kinetic effect (31) of the chemical reaction between Li⁰ and N₂ on the electrochemical lithium reduction and side processes occurring in the system (19). Also important is the indication that the nitrogen concentration strongly influences the kinetics of the reaction between N₂ and lithium metal, and that the rate of the reaction only becomes fast enough to overtake the electrochemical generation of Li⁰ when P(N₂) ≥ 10 bar, as reflected by the FE plateau at these pressures (Fig. 3D).

The effect of the [P₆,₆,₆,₁₄][eFAP] concentration on the NRR kinetics was expected to be more complex than that of P(N₂), as the phosphonium salt provides additional ionic conductivity (Fig. S6 and Fig. S11A) and may also affect the electrodeposition of lithium. Indeed, decreasing the [P₆,₆,₆,₁₄]⁺ concentration from 0.1 to 0.01 M substantially suppressed the electroreduction kinetics (Fig. S11B-C), as well as the FE and the rate of the NH₃ electrosynthesis (Fig. S11D and Table S8). However, the use of a higher [P₆,₆,₆,₁₄]⁺ concentration (0.2 M) did not improve the performance. This can be explained by the altered kinetics of all reductive processes occurring in the system due to the changes in the conductivity and the activities of the phosphonium cation and [eFAP]⁻ anion. We also note that the concentration of the phosphonium (and any other) proton shuttle enabling the best performance is likely to be different for every system, especially in a “zero-gap” two-electrode configuration of an electrolyzer prototype, and is therefore a critical parameter that needs to be optimized on a case-by-case basis.
Nitrogen reduction verification

Notwithstanding previous validation of the Li-mediated nitrogen reduction route to ammonia (16, 19), we considered it critical to reconfirm that N₂ is the dominant source of the electrochemically generated NH₃ facilitated by the phosphonium salt. To this end, a recommended set of control experiments (11, 12, 32-34) was conducted to demonstrate that none of the possible nitrogen-containing contaminants (35), viz. NO₃⁻, NO₂⁻, gaseous NOₓ compounds and adventitious NH₃, contribute statistically significant amounts of ammonia to our main experiments. Colorimetric Berthelot and Griess tests, as well as gas chromatography were conducted to measure the purity of gases and electrolyte solutions used (full analysis details are provided in Section 8 and Figs S12 – S22 of the Supplementary Materials). The highest possible amount of N-containing contaminants that our ¹⁴N₂ gas supply can contribute at 20 bar is 0.02 μmol (Table S3). Fresh electrolyte solutions saturated with Ar at 2 bar contained only a very small amount of NH₃ (0.03 ± 0.02 μmol) and undetectable amounts of NO₃⁻ and NO₂⁻ (Fig. S19 and Table S4). Electroreduction of the electrolyte solutions under argon at 20 bar at -0.75 V vs. Li⁰/⁺ for 2 h produced a similarly small amount of NH₃ (0.1 ± 0.1 μmol, n = 3; Fig. S12 and Table S11). These contamination levels can be compared to the orders of magnitude higher NH₃ yields in our main experiments (Tables S7 – S10), ranging from 5 to as much as 60 μmol. This suggests negligible contributions, typically less than 1%, of extraneous N-sources to the amounts of the produced ammonia. As an ultimate proof of unambiguous NH₃ production from nitrogen gas, electroreduction of ¹⁵N₂ was undertaken (P(N₂) = 5 bar; t = 2 and 4 h) and the amounts of produced ¹⁵NH₄⁺ quantified by ¹H NMR (36) were proven to satisfactorily match the results of the ¹⁴N₂ reduction under the same conditions (Fig. S22, details in Section 8.4 of Supplementary Materials). The genuine nature of the Li-mediated NRR has been convincingly demonstrated by others before
and the main purpose of the $^{15}\text{N}_2$ reduction experiments herein was to prove that the new phosphonium proton shuttle does not introduce any extraneous contamination that can produce ammonia under the employed electroreductive conditions. The above results collectively verify that the $\text{N}_2$ gas is substantially the source of the ammonia produced in this work.

**Longer term operation**

As the next key step, we aimed to demonstrate the longer term stability of the $[\text{P}_{6,6,6,14}]^+$ proton shuttle system, which would distinguish it from the conventional approach using ethanol as the proton source. Such demonstration requires provision of a known and controlled anode reaction in a single compartment cell such as that used herein; otherwise, uncontrolled and destructive oxidation of the electrolyte solution components at the anode is the only alternative. Indeed, the potential of the platinum-based anode during the experiments under pure $\text{N}_2$ atmosphere was typically in the 4.0 to 4.4 V vs. $\text{Li}^{0/+}$ range, which suggests that the dominating process in this case was irreversible electrooxidation of the tetrahydrofuran solvent (37). In this regard, the introduction of $\text{H}_2$ into the cell provides a well-defined, proton-producing anodic process – the hydrogen oxidation reaction – to support the proposed cycle for continuous operation of the $[\text{P}_{6,6,6,14}]^+$ proton carrier (Fig. 1). Owing to the known reactivity of $\text{H}_2$ with lithium to produce the undesired $\text{LiH}$ by-product (38), the NRR performance was expected to be lower in the presence of hydrogen compared to that observed under pure $\text{N}_2$. Hence, the short-term ($t = 2$ h) performance of the investigated system at -0.75 V vs. $\text{Li}^{0/+}$ and 20 bar was first re-evaluated under a mixed atmosphere of 0.5 bar $\text{H}_2$ and 19.5 bar $\text{N}_2$ (Fig. S23). The introduction of 0.5 bar $\text{H}_2$ lowered the $\text{NH}_3$ yield rate and FE by small (though statistically insignificant) amounts, to $54 \pm 10$ nmol s$^{-1}$ cm$^{-2}$ and $66 \pm 9\%$ ($n = 6$ replicates), respectively. In practical devices, the anode and cathode
compartments would be separated by a suitable membrane or diaphragm to avoid this loss in performance. Time series testing was then carried out over 4, 8 and 20 h in a constant current mode (Fig. 4A, B) demonstrating very stable operation of the ammonia electrosynthesis system based on the phosphonium proton shuttle. We found that we needed to use a constant current mode to avoid the effect of drifts in the reference electrode potential over time, due to product build-up, that interfered with a controlled potential experiment. Multiple reproductions \((n = 3)\) of the 20 h tests produced an average \(\text{NH}_3\) yield rate of \(53 \pm 1\) \(\text{nmol s}^{-1} \text{cm}^{-2}\), at a FE of \(69 \pm 1\) %, which are a notable improvement upon the best reported thus far \((30\) \(\text{nmol s}^{-1} \text{cm}^{-2}\) and FE of \(\sim 35\) % \((18)\)). The cell also maintained a cell voltage of less than 5 V (Fig. 4B, Fig. S24 and Table S10) and no significant changes to the state of the working electrode surface after 20 h of the reaction were revealed by electrochemical impedance spectroscopy (Fig. S25).

**Fig. 4. Longer term ammonia electrosynthesis from \(\text{N}_2\) and \(\text{H}_2\).** (A) \(\text{NH}_3\) yield (blue symbols); and the faradaic efficiency of the process (orange) as a function of time; blue dashed line represents a linear fit that indicates a constant rate of \(53.7 \pm 0.4\) \(\text{nmol s}^{-1} \text{cm}^{-2}\). (B) corresponding evolution of the total cell potential (green) and potentials (vs. \(\text{Li}^{0+/+}\)) of the anode (pink) and cathode (blue) at a constant current density of \(-22.5 \text{ mA cm}^{-2}\) (normalized to the cathode surface area). Experiments were conducted in unstirred tetrahydrofuran solutions containing 0.2 M \(\text{LiBF}_4\) and 0.1 M \([\text{P}_{6,6,6,14}]\)[eFAP] under 0.5 bar \(\text{H}_2\) and 19.5 bar \(\text{N}_2\) pressure at 24 ± 2 °C. Data with error bars are mean and standard deviations of \(n \geq 3\) replicates. For 20 h experiments \(n = 3\), but standard deviations are smaller than symbols. For \(n < 3\), individual measurements are shown (details in Table S10).
A longer term stability test at a higher applied reductive current of -27.9 mA cm\(^{-2}\) for a total of 93 h was also carried out (Fig. S26 and Fig. S27). In experiments reported thus far the electrolyte was unstirred; however, to avoid build-up of tetrahydrofuran breakdown products at the electrodes, the electrolyte was stirred during this long running experiment. Stirring affects the mass-transport of all components in the system and thereby is likely to disturb the favorable balance between the kinetics of the NRR and side processes, which were optimized at this stage for the stationary electrolyte system. A 2 hour experiment was also conducted under these conditions as a point of comparison (Fig S27). The 93 h experiment was interrupted at 60 h for electrochemical analysis (cyclic voltammetry) and sampling, and then restarted. During the first 60 h the potential stabilized at around -1.4 V vs. Li\(^{0+/+}\) at a yield rate of 38 nmol s\(^{-1}\) cm\(^{-2}\) and FE of 38%; these values are lower than those of Fig. 2 due to the stirring and, more importantly, the more negative potentials involved. On restarting after the sampling, the potential returned to the previous starting potential, before slowly changing to the previously stabilized value. This behavior is similar to that observed by Andersen et al. (19), where a periodic return to open circuit potential was found to avoid build-up of interfering by-products. Fig S27 shows good linearity in yield with time in this experiment overall (yield rate 39 nmol s\(^{-1}\) cm\(^{-2}\) and FE of 38% over the whole 93 h experiment). However, even this long running experiment still only consumes ~0.5 mmol of H\(^{+}\), representing about one quarter of the [P\(_{6,6,6,14}\)]\(^{+}\) present (2 mmol). It is for this reason that we started out in our investigation with the chemical cycling test described above to verify the capability of the phosphonium cation as a proton shuttle.

To reinforce the above arguments on the stability of the described Li-mediated ammonia electrosynthesis system, we undertook additional characterization of the electrolyte solutions after the 20 h durability tests. The \(^{31}\)P NMR spectra featured one main peak at 32.9 ppm, which
corresponds to the phosphonium cation [P_{6,6,6,14}]^+, and the multiplet associated with the [eFAP]^- anion. A more detailed investigation by multinuclear NMR also did not reveal any side products arising due to the main electrochemical process (see Section 10 and Figs. S28-S34 of the Supplementary Materials).

At the same time, we conservatively note that although the potential of the anode during the described 20 h measurements was lowered by the presence of H_2 down to ca 4 V vs. Li^{0/+} (Fig. 4B and Fig. S24), it was still positive enough to induce the unwanted solvent oxidation (I8). Ideally, the anodic reaction should be strictly limited to the oxidation of hydrogen (or water in more advanced cells) only. This can be practically achieved through the optimization of the anode reaction to ensure a potential within the solvent stability zone, and/or the use of a more anodically stable solvent. These approaches are currently being explored by us and others (I8).

Changing the chemical nature of the anion of the phosphonium salt might also affect the way the system operates and thereby open the scope for further investigations. Equally important will be future optimizations of the mass-transport of the key system components including the proton shuttle in a practical cell where nitrogen is supplied to a gas-diffusion electrode integrated into a suitable electrolyte-electrode assembly. These observations open up a broad range of possibilities for future advancements which, when coupled with suitable engineering techniques, bring closer the prospect of an industrially feasible pathway for the electrochemical synthesis of green ammonia and fertilizers (6).
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**Acknowledgments:**

**Funding** for this work was provided by the Australian Renewable Energy Agency under grant 2018/RND009 DM015 and by the Australian Research Council (Centre of Excellence in Electromaterials Science CE140100012; Future Fellowship to ANS FT200100317; Discovery project DP200101878). **Author contributions:** BHRS conceived of and executed the electrochemical experiments, conceived of the chemical cycling experiments and contributed to the writing of the manuscript; KM conceived of the chemical cycling experiments, executed the NMR and Mass Spectrometry experiments and contributed to the writing of the manuscript; JC carried out confirmatory electrochemical experiments, conceived of and carried out the long term electrochemical tests and contributed to the writing of the manuscript; RYH conceived of and carried out the $^{14}$N$_2$ and $^{15}$N$_2$ NMR quantification measurements and contributed to the writing of the manuscript; HLD assisted with the larger electrode experiments; JMB carried out chemical synthesis and purity analysis; CK developed and optimised chemical synthesis and purification procedures; PVC conceived of the electrochemical cell design; ANS conceived of the experiments and contributed to the writing of the manuscript; DRM conceived of the experiments and contributed to the writing of the manuscript. **Competing interests:** BHRS, KM, PVC, ANS and DRM are inventors on Australian Provisional Patent Application No. 2020902696 entitled “A Method of Continuous Dinitrogen Reduction” filed by Monash University 31 July 2020 that covers aspects of the work reported here. DRM and ANS have management and consulting roles in Jupiter Ionics Pty Ltd. **Data and materials availability:** All data underlying the Figures are listed in Tables S2 – S11 of the supplementary materials.