Understanding the factors determining the faradaic efficiency and rate of the lithium redox-mediated $\text{N}_2$ reduction to ammonia

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ABSTRACT. The lithium mediated reduction of N₂ is one of the only available approaches to electrochemical ammonia production at significant yields under ambient conditions. However, much remains to be investigated about the various electrochemical processes and side reactions that are involved. Herein, we have examined the effects of parameters including electrode potential, convection, N₂ pressure and water content to refine and control the process. We demonstrate that a closely linear ammonia yield can be maintained during experiments up to 60 h in length, with approximately constant faradaic efficiency. This steady state operation appears to be preceded by a coating of the electrode surface with the products of the reductive electrolyte decomposition, such as LiF. We demonstrate ammonia yield rates above 1 nmol s⁻¹ cm⁻² and faradaic efficiencies as high as 60% through the improved control of the reaction conditions.
INTRODUCTION
Conversion of dinitrogen to ammonia mediated by the lithium$^{+/0}$ redox couple (Scheme 1) currently remains the only process that has been genuinely proven$^{1-3}$ to enable the electrochemical nitrogen reduction reaction (NRR) at yield rates and faradaic efficiencies that are sufficiently high to justify its further research and development into an NH$_3$ electrosynthesis system of applied significance.$^4$

Scheme 1. Putative reaction scheme of the lithium-mediated electroreduction of N$_2$ to NH$_3$. H$^+$ represents protons donated by a suitable proton source, *e.g.* C$_2$H$_5$OH, which is continuously transformed into its deprotonated state, *e.g.* C$_2$H$_5$O$^-$, during the cycle.

The importance of the Li-mediated NRR has been only recently recognized,$^1,3,5$ notwithstanding that the process was first demonstrated as early as in the 1930’s by Fichter *et al.*$^6$ and was also investigated in the 1990’s by Tsuneto and co-workers.$^7-8$ The latter studies, along with some of the recent work,$^3,5,9-10$ have majorly focused on maximizing the amount of ammonia generated in a constant current mode with little emphasis put on the electrode potentials required to maintain the reported reaction rates, which were trending more negative during the experiments. Uncontrolled potentials complicate the understanding of the kinetics and mechanism of the electrochemical processes involved, including the electrolyte breakdown and formation of various compounds on the electrode surface. Recently, Schwalbe *et al.*$^{10}$ identified a layer of lithium compounds on the electrode surface. They suggested, based on a density function theory analysis, a contribution of
the classical heterogeneous electrocatalytic N₂ reduction to NH₃ on the Li⁰, Li₃N, or LiH surfaces, as opposed to the redox-mediated electrochemical reaction (Scheme 1) that is otherwise considered to be the major source of ammonia generated in such a system. At the same time, a more recent publication by Andersen et al.⁹ demonstrates that periodic removal of this lithium-based layer through spontaneous decomposition under open circuit conditions is in fact advantageous in terms of improving the stability of the system and the faradaic efficiency of the process.

To further the current, far from complete, understanding of the lithium-mediated N₂ reduction process and identify the factors determining the faradaic efficiency and the yield rate of ammonia, the present work focuses on the underexplored effects of potential, N₂ pressure, convection and water concentration on the kinetics of the process at ambient temperature. Herein, lithium trifluoromethanesulfonate (LiOTf) was used as an electrolyte and lithium source, tetrahydrofuran (THF) was employed as a solvent, the working electrode was an electropolished copper wire with a nominally flat surface, while ethanol was added as a source of protons (see Methods for the complete description of experimental procedures). Quantification of ammonia was performed using the modified Berthelot spectrophotometric test and supported by ¹H NMR¹¹ to ensure reliability (we note in passing that the Berthelot method should not be directly applied to electrolysed tetrahydrofuran solutions, which strongly interfere with the indophenol chromophore in a hard to control manner; this can be resolved through the application of the standard additions method as described in Methods). Based on the new knowledge obtained, we demonstrate that even the unoptimized system investigated herein can continuously produce ammonia at a competitive faradaic efficiency and reasonable yield rates while keeping the potentials less negative than -1.5 V vs. the apparent reversible potential of the lithium(0/+ ) process (Li_app⁰/+).
METHODS

Materials
Lithium trifluoromethanesulfonate (96 %), ethanol (pure 200 proof), salicylic acid (99.0 %), sodium nitroferricyanide (99 %), sodium hypochlorite (5.3 wt.% solution), maleic acid (> 99 %), ammonium chloride (99.5 %) were purchased from Sigma-Aldrich. Orthophosphoric acid (85 %) and sodium hydroxide (analytical grade) were purchased from Merck. Trisodium citrate dihydrate (analytical grade) was purchased from Emsure. Tetrahydrofuran (BHT stabilized; 99.8 %) was purchased from Chem-Supply. Acetone (99.5 %), isopropanol (99.5 %), ethanol (absolute, 99.5 %), sulfuric acid (99.8 %) were purchased from Univar. Tetrabutylammonium hexafluorophosphate ([nBu4N][PF6], 98 %) was purchased from Sigma Aldrich and recrystallized seven times from ethanol : water (3 : 1 vol.) mixture prior to use. Dimethyl sulfoxide-d6 (D, 99.9 %; chemical purity 99.5 %) was purchased from Cambridge Isotope Laboratories Inc. Copper wire (1.25 mm diameter; 99.8 %) was purchased from Fisher Scientific. Zeolite 1.5-2.5 mm beads with an average pore size of 4 Å was sourced from High Vacuum Technologies PL. Argon (ultra-high purity grade, 99.999 %) and dinitrogen (ultra-high purity grade, 99.999 %) were purchased from BOC Australia. All aqueous solutions were prepared using high purity deionized water with a measured resistivity of 18.2 MΩ cm at 24 ± 1 °C derived from a Sartorius Arium Comfort I purification system equipped with a SARTOPORE 2 150 filter; the same grade of water was used for all experimental procedures.

Electrochemical procedures
In order to avoid any contamination by ammonia and other N-containing sources, all components of the electrochemical apparatus and labware were copiously washed with water, rinsed with ethanol and isopropanol and dried for at least 4 h at 80 °C in the oven before being used. The best
and most reproducible results (in particular, results in Figure 4 below) were obtained when a small quantity of lithium trifluoromethanesulfonate salt required to prepare 25 ml of the electrolyte solution (780 mg) was dried for at least 24 h under vacuum at 80 °C, while tetrahydrofuran and ethanol were dried over freshly calcined 4 Å zeolite for at least 48 h. Zeolite was preliminary washed several times with water and acetone and dried for 48 h under nitrogen flow at 300 °C. In the initial experiments (in particular, results in Figure 3 below), LiOTf was dried in larger portions of 5–10 g. All chemicals were kept in sealed containers in an Ar-filled dry box (KOREA KIYON Glovebox System). Electrochemical cell assembly and electrolyte preparation was performed inside the Ar-filled dry box as well.

Electrode preparation. Copper wire working electrodes were oxidatively electropolished in concentrated orthophosphoric acid solution while passing a current of 4 A for 4 min over the surface of ca. 1.5 cm². As a counter electrode for electropolishing, a high-surface area Cu wire coiled around the working electrode was used. After polishing, the electrodes were rinsed with water, ethanol and isopropanol.

As an auxiliary electrode for the NRR experiments, a flame-annealed platinum wire with a surface area of several cm² was used. A silver wire immersed in the working electrolyte solution but confined behind a ceramic frit was used as a quasi-reference electrode; prior to use, the silver wire was washed in ethanol and isopropanol, while the frit was sonicated in isopropanol for 5 min. Lowest changes in the potential of the quasi-reference electrode were achieved when the very low porosity frit (partially melted P4) was used to separate the Ag wire from the working electrode compartment. Electrodes were dried in the oven for at least 4 h at 80 °C and additionally dried under vacuum at 80 °C along with other components of the cell inside the Ar dry box antechamber for 20 min before assembly.
General electrochemical procedures. All electrochemical experiments were performed in a home-built air-tight single compartment polyether ether ketone (PEEK) high-pressure cell using a three-electrode configuration (Figure S1) at ambient temperature using a BioLogic VMP electrochemical workstation. A platinum wire auxiliary electrode was shaped as a spiral and arranged symmetrically around the working and reference electrodes. The volume of the electrolyte solution used in each experiment was 20 mL. Unless specifically mentioned, the solution in the cell was continuously agitated using a Teflon-lined magnetic stirrer at 600 rpm during all measurements. A typical electrolyte solution was 0.2 M LiOTf in THF (BHT stabilized) with the addition of specified quantities of ethanol when required. Fully assembled and filled with the electrolyte solution, the gas-tight sealed electrochemical cell was removed from the Ar-filled dry box and either used for the control experiments or pressurized with N\textsubscript{2} in a manner that excludes penetration of air inside. The pressurized cell was kept stirring for 30 min before conducting electrochemical tests to ensure the electrolyte solution has reached nitrogen saturation with the headspace. After electrochemical measurements, the excess N\textsubscript{2} pressure was slowly released to the atmosphere through a water trap, and the cell was returned to the Ar glove-box where it was disassembled and samples of the electrolyte solution and the working electrode were withdrawn for the analysis.

Reference electrodes and reference potentials. In contrast to the conventional Li electrochemistry field, the use of an internal lithium-metal reference is not possible in the NRR context because of the spontaneous reaction of lithium metal with N\textsubscript{2} and C\textsubscript{2}H\textsubscript{5}OH. This urged us to use a quasi-reference electrode which consisted of a Ag wire placed in a fritted tube filled with the same solution as in the working electrode compartment. The use of a robust reference system with AgOTf added to this solution was not possible with the frits currently available to us as those could not prevent leakage of Ag\textsuperscript{+} into the main electrolyte solution on a timescale of hours and days as
required in our NRR experiments. As a reference for the internal calibration of the employed quasi-reference electrode, we used an apparent potential of the Li$^{0/+}$ process, which was approximated from comparatively slow (scan rate 0.020 V s$^{-1}$) cyclic voltammograms recorded at the start of the experiments. Since intersection of the forward and backward sweeps, which provides the most reliable estimate of Li$^{0/+}_{\text{app}}$, was not always observed in voltammetric curves when ethanol was present in solutions, the apparent lithium(0/+) potential was approximated as a potential where the backward (oxidative) sweep crosses $j = 0$ mA cm$^{-2}$. Given that this potential (i) is dynamic, (ii) is affected by the double-layer charging, and (iii) corresponds to a quasi-equilibrium of a currently unknown surface state involving Li$^0$, Li$_3$N, LiH and other electrolyte reduction products, the Li$^{0/+}_{\text{app}}$ used herein should not be regarded as a true reversible potential of the lithium(0/+) process.

In some experiments, the drift of the quasi-reference electrode was estimated by measuring its potential against a stable Ag|20 mM AgOTf (THF) master reference electrode inside the Ar-filled glove-box just before filling with N$_2$ and after opening the cell that was used for a 12 h NRR run. The master reference electrode was calibrated against the Fc$^{0/+}$ (Fc = ferrocene) redox couple potential ($E_{\text{Ag/Ag}} = 0.24$ V vs. Fc$^{0/+}$) by recording cyclic voltammograms for the oxidation of 0.2 mM ferrocene in 0.5 M $n$Bu$_4$NPF$_6$ (THF) using a Pt disk (Ø 1 mm) working electrode and a Pt wire auxiliary electrode. Based on the above calibration, the Li$^{0/+}_{\text{app}}$ reference point under the NRR conditions (i.e. with ethanol and N$_2$ present) reported in the discussions below and also summarized in Tables S1 and S2 can be approximated as -3.6 V vs. Fc$^{0/+}$, although we note that this value was somewhat variable and should not be used for high-precision comparisons with other published data.
Water content in the electrolyte solutions was measured via coulometric Karl Fisher titration using coulometer model KF-31 sourced from Mitsubishi Chemical Analytech Co. LTD. For each sample, 3 replicate injections were made, with the injection amount ranging from 0.100 to 0.300 g.

Ammonia quantification
Spectrophotometric analysis. The modified Berthelot spectrophotometric test was used for the determination of the amount of ammonia produced during experiments in the electrolyte solution. Rather than using standard NH$_4$Cl solutions to construct a traditional calibration curve for determining the concentration of NH$_4^+$ in the analyte solutions, a method of standard additions was used instead. This is designed to eliminate any interfering effects$^{12}$ of the electrolyte solution, which composition significantly changes during the NRR tests. In a typical procedure, minimum six analyte solutions of identical total volume (2 mL) containing the same amount of at least five times diluted electrolyte sample (1 mL) and different known amounts of the 102 μM NH$_4$Cl standard mixed with water (total 1 mL) were prepared. Next, 500 μL aliquots withdrawn from each freshly prepared analyte solution were added to 1.7 mL Axygen microtubes and mixed with 400 μL of the solution of 5 wt.% salicylic acid and 5 wt.% trisodium citrate in 1 M NaOH. Further, 100 μL of 0.05 M NaClO$_{(aq)}$ and 30 μL of 1 wt.% sodium nitroferricyanide in water were added. The resulting solutions were incubated in the dark for 2 h at ambient temperature. Finally, the derivatized solutions were transferred into polystyrol/polystyrene 10 mm cuvettes (Sarstedt), and the absorption spectra were recorded in a 500–1000 nm range using a Cary UV–vis spectrophotometer. The maximal absorption at ca 655 nm ($A$) vs. the amount of added ammonium was plotted and subjected to the linear regression analysis (equations 1-7) to determine the y-axis intercept ($b$) and the slope ($m$), which ratio defines the amount of ammonia in the analyzed sample (equation 8).$^{13}$ The extrapolation method was used
to estimate the precision $s_c$ (equation 10) of the standard additions analysis at 95% confidence limit using $t$-critical value for the apparent degrees of freedom ($N - 2$, where $N$ is the number of analyzed solutions).^{13-14}

$$\bar{x} = \frac{\sum x_i}{N}$$  \hspace{1cm} (1)

$$\bar{y} = \frac{\sum y_i}{N}$$  \hspace{1cm} (2)

$$S_{xx} = \sum x_i^2 - N(\bar{x})^2$$  \hspace{1cm} (3)

$$S_{yy} = \sum y_i^2 - N(\bar{y})^2$$  \hspace{1cm} (4)

$$S_{xy} = \sum x_i y_i - N(\bar{x} \bar{y})$$  \hspace{1cm} (5)

$$m = \frac{S_{xy}}{S_{xx}}$$  \hspace{1cm} (6)

$$b = \bar{y} - m \bar{x}$$  \hspace{1cm} (7)

$$c_x = \frac{b}{m}$$  \hspace{1cm} (8)

$$s_y = \sqrt{\frac{S_{yy} - m^2 S_{xx}}{N-2}}$$  \hspace{1cm} (9)

$$s_c = \sqrt{\frac{s_y^2}{m^2} \left( \frac{1}{N} + \frac{\bar{y}^2}{m^2 S_{xx}} \right)}$$  \hspace{1cm} (10)

$^1H$ NMR analysis of ammonia. A series of calibration standards (0-2000 μM) were prepared in 0.2 M LiOTf (THF) – a base electrolyte solution used in the present study. A 125 μL aliquot of each standard was first combined with 50 μL of 4 M sulfuric acid solution in DMSO-d$_6$, then with 125 μL of 500 μM maleic acid standard solution in DMSO-d$_6$, 50 μL water and 700 μL DMSO-d$_6$ to make a final analysis volume of 1100 μL. Samples from the NRR experiments were prepared using the same procedure substituting 125 μL of the sample of interest for the 125 μL of standard solution.
Proton nuclear magnetic resonance measurements were conducted on a Bruker Avance III 600 (14.1 Tesla magnet) instrument with a 5 mm CPTC $^1H$-13C/15N/D autotuneable cryoprobe with Z-gradients and BACS 60 tube autosampler set to $^1$H at 600.27 MHz. The pulse sequence lc1pncwps was selected (504 scans, d1 = 1.5 s) and employed without further alteration.

For quantification, spectra were first processed with a multistep baseline correction, line broadening set to 3.00, and then normalized to the integral of the maleic acid peak (6.22 – 6.28 ppm), which was set to 2.00, indicative of the number of the associated protons. The ammonium signal was integrated within the 7.052 – 7.582 ppm range. Sample solutions were analyzed in the same manner, with the final concentration obtained using the calibration plot. Standard deviation was calculated via least squares regression.$^{15}$

**X-ray photoelectron spectroscopy**

XPS analysis of deposits formed on the copper wire working electrodes during 12 h chronoamperometric tests was performed using a Nexsa Surface Analysis System, ThermoFisher Scientific instrument with a monochromatic Al K$_\alpha$ source (1486.6 eV). X-ray spot size was set to 400 μm. The analysis chamber was maintained at a pressure of 1.0 × 10$^{-8}$ bar or less. Survey scans were recorded at a pass energy of 200 eV and a step size of 1 eV, while high resolution data were obtained at a pass energy of 50 eV and a step size of 0.1 eV. The samples were mounted onto a carbon tape in a manner that there was no electrical contact with the instrument ground and were charge neutralized before the analysis. Collected spectral data were energy corrected by adjusting the maximum of the C-C peak in C 1s spectra to 284.8 eV. When required, samples were transferred from the Ar-filled glove-box to the XPS analysis chamber using vacuum transfer module that excludes any exposure to air.
RESULTS AND DISCUSSIONS

To enable experiments at varied N\textsubscript{2} pressure, which defines the concentration of dinitrogen dissolved in the electrolyte solution, a high-pressure cell was employed (Figure S1). During the measurements, a static gas atmosphere was maintained inside the cell, i.e. no gas was flowing through. As a reproducible point of reference for the potentials reported in this work, the point of zero current in the backward (oxidative) voltammetric sweeps was used as a measure of the apparent Li\textsubscript{app}\textsuperscript{0/+} potential; however we recognise that the composition of the electrode surface is unknown at this stage and hence this apparent potential is likely not the same as the actual Li\textsuperscript{0/+} potential. To provide a more robust point of reference for future comparisons, we measured the Li\textsubscript{app}\textsuperscript{0/+} value in solutions containing N\textsubscript{2} and ethanol vs. the reversible potential of the ferrocene(0/+) redox couple (see “Reference electrodes and reference potentials” in Methods).

When recorded under Ar at P = 1 bar, cyclic voltammograms of a Cu electrode in 0.2 M LiOTf (THF) electrolyte rapidly stabilized (Figure S2a) and exhibited a pattern of behaviour typical of a metal electroplating/stripping on/from the electrode surface (Figure 1a). By integrating the cathodic and anodic voltammetric sweeps, the coulombic efficiency of the lithium deposition/oxidation cycle was found to be essentially constant at ca 64 % (Figure 1b). This observation indicates that either a portion of the lithium metal is always irreversibly consumed, e.g. through the reaction with residual water, or that process(es) other than Li\textsuperscript{+} + e\textsuperscript{-} → Li\textsuperscript{0}, e.g. irreversible reduction of tetrahydrofuran,\textsuperscript{16} contribute substantially to the measured reductive currents. The latter is likely to be a dominant factor, since the coulombic efficiency in cyclic voltammograms improved to ca 90% when the switching potential was set to a less negative value (Figure S2b-c).
Figure 1. (a) Cyclic voltammograms (scan rate 0.020 V s\(^{-1}\)) recorded using a copper electrode in contact with stirred 0.2 M LiOTf tetrahydrofuran solution under 1 atm Ar (blue), 15 bar N\(_2\) (black), and 15 bar N\(_2\) with 0.086 M C\(_2\)H\(_5\)OH added to the solution (red). Currents are normalized to the geometric surface area of the electrode. Quasi-stabilized, 15\(^{th}\) voltammetric scans are shown. (b-d) Evolution of the cycling coulombic efficiency of the voltammetric experiments shown in panel (a) undertaken under (b) 1 atm Ar, (c) 15 bar N\(_2\), and (d) 15 bar N\(_2\) + 0.086 M C\(_2\)H\(_5\)OH; cyclic coulombic efficiency was calculated as a ratio of the oxidative charge to reductive charged passed within the whole potential range in each cycle.

Replacement of the argon atmosphere with 15 bar N\(_2\) did not induce notable changes to the voltammetric profile, which was still dominated by the apparent Li\(^{0/+}\) redox transformations (Figure 1a and Figure S3a) at the same level of coulombic cycling efficiency (Figure 1c). From a kinetic perspective, this finding indicates that the formation of lithium nitride (Li\(_3\)N), which should inevitably occur in a system where lithium metal and N\(_2\) are present,\(^{17-18}\) does not affect the rate of electroreduction notably under the conditions employed. It also suggests that the Li\(_3\)N oxidation
coincides with the peak for the lithium metal oxidation. Once ethanol is introduced to the system, the intensities of both reduction and oxidation processes are suppressed to some extent (Figure 1a and Figure S3b) and the cyclic coulombic efficiency drops by ca 20% (Figure 1d). This change is consistent with the irreversible conversion of the lithium-based reduced compounds, for example Li$_3$N, into soluble products that cannot be reoxidized within the examined potential range, e.g. NH$_3$ + LiOC$_2$H$_5$ (Scheme 1).

A minor peak within ca 0.0-0.5 V vs. Li$_{app}^{0/+}$ range, which precedes the major reduction wave in the cathodic sweeps, was found to be essentially identical under all conditions described above (Figure 1a). This process might be associated with the formation of lithium hydride as it appears to be coupled to the oxidation process of a similar intensity commencing at ca 2.4 V vs. Li$_{app}^{0/+}$ in the anodic sweeps (Figure 1a), which approximately coincides with the expected potential for LiH oxidation.$^{19}$ Previously, a similar cathodic signal was found to be enhanced upon increases in the C$_2$H$_5$OH concentration and ascribed to the reduction of protons dissociated from the ethanol hydroxyl group.$^{10}$ This is not consistent with our observations of no effects of the presence or absence of different ethanol concentrations on the reduction behaviour within 0.0-0.5 V vs. Li$_{app}^{0/+}$ range (Figure 1 and Figure S4). Therefore, we hypothesise that this process might be indeed associated with the reduction of H$^+$, but those derived from adventitious water rather than from ethanol. If not sufficiently dried, addition of different concentrations of C$_2$H$_5$OH will induce proportional changes in the amount of H$_2$O carried over to the electrolyte solution and thereby alter the intensity of the discussed signal. This was not the case under the optimised experimental conditions discussed herein.
Upon completion of the voltammetric characterization of the system in the presence of both N\textsubscript{2} and ethanol, chronoamperograms at potentials more negative than 0 V vs. Li\textsuperscript{0/+} were recorded. First of all, we note that provision of a favourable working-auxiliary electrode arrangement, as described in Experimental, allowed for a notable increase in the measured current densities and corresponding ammonia yield rates, as well as stability of the system operation (Figure S5). Further, it was found that the current transients were strongly affected by convection, viz. highly variable profiles were often obtained in quiescent solutions, in contrast to currents that commonly remained reasonably stable on a timescale of at least 12 h when the solutions were intensively stirred (exemplified for experiments at P\textsubscript{N\textsubscript{2}} = 15 bar in Figure S6). Variability in current densities observed with no forced convection provided suggests that the major reduction processes occurring in the system are reversibly suppressed by some of the products when they are not rapidly removed from the electrode surface. Deeper understanding of these effects would require the application of specialised \textit{in situ} techniques. At the same time, we were unable to identify any consistent effect of stirring on the ammonia yield rate or the faradaic efficiency.

A series of independent experiments undertaken on a timescale ranging from 4 to 60 h demonstrated a highly satisfactory linearity of yield with time (Figure 2a), indicating a steady rate of the NRR under the examined conditions. This is a noteworthy observation given the degradation in the performance of the continuous Li-mediated N\textsubscript{2} reduction reported in recent publications,\textsuperscript{3, 5, 9} although we also note slightly decreased faradaic efficiency (yet unaltered yield rate) in our 60 h experiment (Figure 2b). Another important observation is the much lower ammonia formation rate and selectivity of electroreduction found in the shorter (1 to 2 h) experiments (Figure 2). This indicates that the charge passed during these initial stages of the NRR is majorly spent on the reductive degradation of the electrolyte solution components, as well as the initial formation of
reduced lithium-based species, e.g. Li$^0$ and Li$_3$N, on the electrode surface. In principle, the latter can be still recovered to produce ammonia by allowing them to react with C$_2$H$_5$OH with no potential applied. To further investigate this possibility, chronoamperometric measurements were followed by monitoring the evolution of the open-circuit potential of the working electrode ($E_{oc}$) to estimate when the oxidative dissolution of the generated Li$^0$ species is complete. The $E_{oc}$ values measured immediately after the chronoamperograms were always very close to 0 V vs. Li$^{0/+}_{app}$, indicating that a layer of reduced materials was accumulated on the electrode surface, and then progressively changed to significantly more positive values, up to ca 3 V vs. Li$^{0/+}_{app}$ (Figure S7), attesting to their complete conversion into soluble products through reaction with C$_2$H$_5$OH. Andersen et al. have recently described an approach to long-term operation of the Li-mediated NRR that involves a periodic cycling between open circuit and constant current conditions, which was interestingly not required for a relatively stable operation under the conditions employed herein (Figure 2).
Figure 2. Effect of the duration of chronoamperometric reduction of stirred 0.2 M LiOTf + 0.17 M C$_2$H$_5$OH tetrahydrofuran solutions saturated with N$_2$ at 2 bar on the (a) amount of produced ammonia and (b) faradaic efficiency of the NRR. Dashed lines are guides to an eye showing (a) linear approximation to the data and (b) average faradaic efficiency (31 %) for the 4-12 h experiments. Errors bars show 95% confidence intervals for the method of standard additions (see Supporting Information). Extended data for these experiments are provided in Table S1.

In some experiments with both N$_2$ and C$_2$H$_5$OH present, cyclic voltammograms were recorded immediately after the chronoamperograms to reveal a purely resistance-controlled oxidation of the surface deposit on the electrode surface (Figure S8). The corresponding oxidative charge estimated based on such voltammetric experiments was \textit{ca} 0.3 C, which is notably small compared to charges of \textit{ca} 16 C typically passing during 12 h chronoamperograms. In another approach to estimate the amount of unreacted Li$^0$/Li$_3$N present on the surface, the electrode after the chronoamperogram was removed from the electrolyte solution and treated with H$_2$O as quickly as possible (see Experimental), where approximately 30 nmol of ammonia were found. By comparison, typical
yields in 12 h chronoamperometric experiments (Figure 2a) were of the order of 10000 nmol. Thus, the loss of charge due to the accumulation of the Li\(^0\)/Li\(_3\)N species on the electrode surface was not significant under conditions employed herein except at very short times (<4 h). This observation also suggests that, similar to the “solid-electrolyte interface” (SEI) layer formation observed in battery studies,\(^{20}\) the charge spent in the initial stages of the chronoamperometric reduction was majorly associated with the irreversible reductive formation of surface species, some of which are likely required to support the subsequent, stable operation of the system.

Visual examination of the electrodes after experiments consistently revealed the formation of a dark layer, which rapidly turned white when put in contact with air (Figure S9). X-ray photoelectron spectroscopic (XPS) analysis of the electrodes exposed to air after 12 h of electroreduction and resting at open circuit for 2.5 h until \(E_{oc}\) reached ca 2.8 V vs. Li\(_{app}\)\(^{0/+}\) showed no presence of Li\(^0\)/Li\(_3\)N, as expected (Figure S10a), but revealed a significant amount of Li\(_2\)CO\(_3\)^{21} (Figure S10b-d), which is most likely a product of reaction of Li\(_2\)O/LiOH with air CO\(_2\), as well as the original triflate salt (Figure S10e).\(^{22}\) Additionally, Li\(_2\)SO\(_3\) (Figure S10f)\(^{23}\) and small amounts of LiF (Figure S10e)\(^{24}\) were found, both being likely products of the reductive decomposition of the OTf\(^-\) anion.\(^{20, 22, 25}\) XPS analysis of the electrode that was withdrawn from the cell as fast as possible after a 12 h test, with no subsequent measurements/resting and no exposure to air, revealed a qualitatively very similar composition except for the presence of LiOH instead of carbonate (Figure S10). The N 1s spectra recorded for both electrodes were essentially identical with a low signal-to-noise ratio (Figure S10a), which attests to the absence of significant amounts of nitrogen containing species such as Li\(_3\)N on the surface after the reduction is stopped. This finding suggests that any nitride intermediate remaining in the topmost surface layers of the electrode accessible
for the XPS analysis is rapidly consumed by the reaction with a proton source while the electrode is being withdrawn from the cell.

A series of 12 h chronoamperometric NRR tests undertaken at varied applied potential \( E \) and nitrogen pressure \( P_{N_2} \) revealed, quite unexpectedly, an apparently insignificant influence of both parameters on the ammonia yield rate and the faradaic efficiency (exemplified for 14 experiments in Figure 3, Figure S11 and Table S2). For example, at \( E \approx -0.83 \) – \(-0.90 \) V vs. \( \text{Li}^{0/+} \text{app} \), increase in \( P_{N_2} \) from 2 to 10 bar did not change the faradaic efficiency and the rate of the \( \text{NH}_3 \) formation, which were within the 25 – 35 % and 0.2 – 0.4 nmol s\(^{-1}\) cm\(^{-2}\) ranges, respectively, regardless of the pressure (Figure 3a-b). Very similar metrics of the nitrogen reduction reaction were found in experiments undertaken at the same pressure, but at varied potentials (Figure 3c-d).

Examination of the data in Figure 3, as well as the lack of a pronounced effect of convection on the ammonia yield rate and faradaic efficiency mentioned above, indicate that the kinetics of the NRR under these conditions is controlled by a previously overlooked factor, other than the applied potential and \( \text{N}_2 \) concentration in the electrolyte solution. One might also note an apparent outlier in the presented dataset, demonstrating a distinctly better faradaic efficiency of \( \text{ca} \) 50% and yield rate of \( \text{ca} \) 0.62 nmol s\(^{-1}\) cm\(^{-2}\) achieved at \( E \approx -0.79 \) V vs. \( \text{Li}^{0/+} \text{app} \) and \( P_{N_2} = 4.5 \) bar, which indicates that the system under study can in principle be improved further.
Figure 3. Effects of (a-b) N₂ pressure and (c-d) potential on the (a, c) ammonia yield rate and (b, d) faradaic efficiency of the NRR during 12 h chronoamperometric reduction of stirred N₂-saturated 0.2 M LiOTf + 0.17 M C₂H₅OH tetrahydrofuran electrolyte solutions using a copper electrode. Faradaic efficiency and yield rate errors bars show 95% confidence intervals for the method of standard additions (see Supporting Information). Corresponding chronoamperograms and extended experimental data are provided in Figure S11 and Table S2.

We also observed that the potential of the quasi-reference electrode used in the present experiments could change during the chronoamperograms, by as much as 0.2 V in some of the experiments, as determined by measurements vs. a robust Ag|Ag⁺ reference electrode calibrated against ferrocene⁰⁺ (see Experimental). The use of the latter as a reference electrode in actual experiments was avoided, since small amounts of silver(I) inevitably leak through the frit on the timescale of the 12 h experiments. The impact of this reference electrode drift is to cause the actual potential controlled at the cathode to drift during the chronoamperometric experiments. To improve the
stability of the quasi-reference electrode, we employed less porous frits (details in Experimental) to better isolate the Ag wire quasi-reference from the continuously changing reaction environment; this enabled significantly decreased, less than 0.01 V, drift over 12 h.

Upon consideration of a range of parameters that could affect the NRR selectivity and rate most significantly and that had not been strictly controlled thus far in the exemplified set of measurements, we realized that the most plausible reason for the observed behaviour could be variable concentrations of residual H₂O. Water can be reduced both electrochemically and in a redox reaction with Li⁰ to produce LiH and/or H₂ along with insulating LiOH/Li₂O byproducts on the electrode surface and thereby substantially reduce the ammonia yield rate and faradaic efficiency of the lithium-mediated NRR. Although the tetrahydrofuran solvent and the electrolyte were dried, the variability in [H₂O] could arise from the added ethanol proton source. Indeed, when using as-received “anhydrous” C₂H₅OH, the [H₂O] in the electrolyte solutions was observed to vary from 0.0003 to as high as 0.003 M in Karl Fisher measurements. To resolve this, the ethanol was dried by using freshly calcined zeolite (see Experimental), which allowed us to bring [H₂O] in the electrolyte solutions down to a highly reproducible level of ≤0.0003 M. Moreover, to further alleviate the possible effects of water carried along by the ethanol proton source, its concentration was decreased by a factor of two down to 0.086 M in further experiments. Attempts to undertake the NRR at even lower ethanol concentration (0.017 M) resulted in significant deceleration of the process (yield rates of ca 0.05 nmol s⁻¹ cm⁻² and faradaic efficiency of only ca 7 %). We also found that drying LiOTf works best when applied to small portions of the salt, approximately of the amount required to prepare the electrolyte solution for one experiment (see Experimental). Implementation of these measures improved the performance of the system further (Figure 4), with a generally increasing yield rate at more negative potentials becoming apparent. Between -1.0 V
and - 1.5 V vs. Li_{app}^{0/+} a number of results exhibit yield rates above 1 nmol s\(^{-1}\) cm\(^{-2}\) and above 60% faradaic efficiency.

**Figure 4.** Effects of potential on the (a) ammonia yield rate and (b) faradaic efficiency of the NRR during 12 h chronoamperometric reduction of stirred N\(_2\)-saturated (P\(_{N_2}\) = 15 bar) 0.2 M LiOTf + 0.086 M C\(_2\)H\(_5\)OH tetrahydrofuran solutions with [H\(_2\)O] \(\leq\) 0.0003 M using a copper electrode. Faradaic efficiency and yield rate errors bars show 95% confidence intervals for the method of standard additions (see Supporting Information). Lines are guides to an eye. Values in the plots show the mean \(\pm\) standard deviation calculated for data points highlighted within red dashed box. Examples of corresponding chronoamperograms are provided in Figure S12.

To ensure the reliability of these results, for selected experiments the amount of the ammonia synthesized was additionally quantified by \(^1\)H NMR,\(^{11}\) which produced values consistent with those derived from the Berthelot spectrophotometric technique with standard additions.
We also note that (i) the Li-mediated system has been previously confirmed to enable genuine conversion of dinitrogen to ammonia through the experiments involving the reduction of $^{15}$N$_2$,\textsuperscript{1,3} (ii) the NH$_3$ yield rates reported herein are comparable to those in the previous work,\textsuperscript{3,5,7-10} and (iii) no ammonia was produced in the absence of N$_2$ in our control experiments (Figure S14). On this basis, and in line with our recent recommendations,\textsuperscript{2} we concluded that the $^{15}$NRR controls are redundant in the present study.

As an indicator of the reproducibility of the experiments under improved conditions, one can consider a group of 3 results at -1.07 ± 0.01 V vs. Li$_{\text{app}}^{0/+/*}$ (outlined with a red box in Figure 4), which average performance corresponds to 54 ± 7% faradaic efficiency at a rate of 0.8 ± 0.2 nmol s$^{-1}$ cm$^{-2}$. This higher than desirable variability is also reflected in the scatter of the datapoints beyond the 95 % confidence interval of the analytical method employed. Hence, even though the overall performance in this dataset is comparable and, in some cases, exceeding the best thus far reported, we conclude that one of the important system parameters that affects the kinetics of the NRR and side processes, apart from those discussed and monitored above, remains uncontrolled. One prominent possibility are the products of the anode reaction that continuously accumulate in the electrolyte solution and likely interfere in a hard to predict manner with the cathode process on the experimental timescale considered herein.

CONCLUSIONS

In summary, the present communication investigates several practical parameters that affect the observed electrochemical selectivity and yield rate of the Li-redox mediated ammonia electrosynthesis from N$_2$. We describe the reliable ammonia quantification procedure for the electrolysed tetrahydrofuran solutions using the Berthelot method and demonstrate improved
reduction rates through the provision of the appropriate working-auxiliary electrode geometry. Further, the conditions employed herein required forced convection to ensure reasonable stability of the electroreduction rate, which was demonstrated to persist on a timescale of at least 60 h. It was also revealed that the rate of the ammonia formation is very low during the initial hours of operation, which are likely dominated by the electroreductive decomposition of the electrolyte solution components that produces the actual “active” layer on the electrode surface involving lithium fluoride that further sustains stable operation of the system. A relatively broad potential range enabling the best performance of the investigated system was identified, indicating that the chemical steps, as opposed to the electrochemical steps in Scheme 1, control the productivity under these conditions. Finally, and most importantly, the critical effect of water concentration in the electrolyte solution on the NRR metrics has been demonstrated. Minimisation of the H₂O content allows observation of faradaic efficiencies greater than 60% at ammonia yield rates in excess of 1 nmol s⁻¹ cm⁻². Based on the results reported herein, we conclude that future advancements in the Li-mediated NRR are likely to emerge through the design of improved electrolyte solution compositions, including consideration of the effects of the mass-transport of N₂ and also of the proton source.

**ASSOCIATED CONTENT**

**Supporting Information.** Photographs of the cell and electrodes, extended electrochemical data, X-ray photoelectron and ¹H NMR spectra.

**Notes**

The authors declare no competing financial interest.
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