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Proton Donors Induce a Differential Transport Effect for Selectivity toward Ammonia in Lithium-Mediated Nitrogen Reduction

Nikifar Lazouski, Katherine J. Steinberg, Michal L. Gala, Dilip Krishnamurthy, Venkatasubramanian Viswanathan, and Karthish Manthiram*

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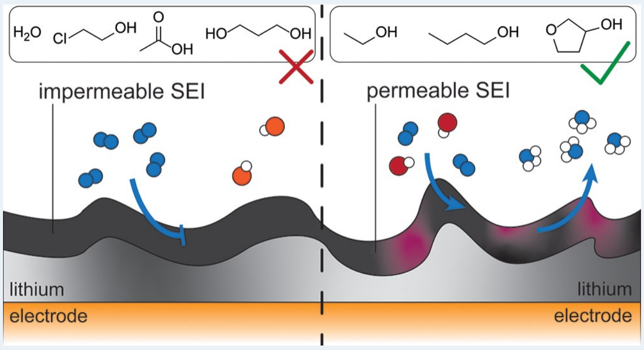

ABSTRACT: Alternative approaches for producing ammonia are necessary to reduce the environmental impact of its production. The lithium-mediated electrochemical nitrogen reduction reaction (LM-NRR) is one attractive alternative method for producing ammonia at small scales in a distributed process. This process requires a proton donor in the electrolyte to produce ammonia from nitrogen, but the role of the proton donor in selective ammonia production is not well understood. In this work, we experimentally tested several classes of proton donors for the ability to promote LM-NRR. We found that a wide array of alcohols can promote nitrogen reduction and that n-butanol leads to the highest ammonia Faradaic efficiencies. Among the tested proton donors, even slight changes in the proton donor structure can significantly affect the yield of ammonia. In addition, most active proton donors exhibit a thresholding behavior as a function of their concentration, where the selectivity toward ammonia increases dramatically above a certain concentration of the proton donor. We found evidence to imply that these effects could be due to the proton-donor-induced changes in the properties of the solid electrolyte interphase (SEI), which lead to changes in the diffusion of relevant species through the SEI to the reactive electrode. By selectively allowing for diffusion of nitrogen over the proton donor to the electrode, the SEI can promote selective nitrogen reduction to ammonia. A coupled kinetic transport model of the process was proposed to explain the observed trends and to predict ammonia production as a function of operating conditions.

KEYWORDS: electrochemistry, ammonia synthesis, lithium-mediated, nonaqueous, solid electrolyte interphase, proton donor

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INTRODUCTION

Ammonia (NH_3) is an important industrial chemical that is used in the production of various nitrogen-containing compounds, including fertilizers, pharmaceuticals, and polymers.[1,2] In addition to being a useful synthetic molecule, ammonia is also emerging as an attractive dense carbon-free energy and hydrogen carrier as, unlike gaseous hydrogen, it can be liquefied at moderate pressures (∼10 bar) or moderately low temperatures (−30 °C).[3,4] The volumetric energy density of liquid ammonia greatly exceeds that of lithium-ion batteries and is competitive with other chemical storage media, such as pressurized and liquid hydrogen.[5] NH_3 is typically produced via the Haber−Bosch process in which air-derived nitrogen and fossil fuel-derived hydrogen are reacted at high temperatures (450−500 °C) and pressures (up to 200 bar).[6] Because of its use of fossil fuels as sources of hydrogen, ammonia production accounts for up to 1.44% of the world's carbon dioxide emissions and is economically viable only in large, centralized plants.[3,6,7]

As the price of renewable energy decreases,[8] it is desirable to produce NH_3 using renewable electricity in a more distributed manner. Electrochemical methods could be one way to achieve this by interfacing production with intermittent sources of energy with no CO_2 emissions and low capital costs.[3] While a large number of chemistries and architectures have been proposed for electrochemical nitrogen reduction,[9,10] most of them report Faradaic efficiencies (FEs) and production rates too low for economical ammonia synthesis. In addition, numerous works highlight the need for reproducibility and rigorous controls in the electrochemical nitrogen reduction field,[11−15] implying that ammonia yields measured in some systems may come from adventitious sources.

Methods in which lithium metal acts as a mediator for nitrogen reduction report some of the highest FEs and absolute rates toward NH_3 synthesis, as well as strict and

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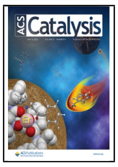

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reproducible controls.[16−20] In particular, the setup used in the present work has been confirmed to reduce nitrogen to ammonia through isotope labeling control experiments (Figure S4).[21] In the conventional, thermochemical lithium-mediated approach, lithium ions (Li^+) in an electrolyte are first electrochemically reduced to metallic lithium. This metallic lithium can spontaneously react with dinitrogen to produce lithium nitride,[22] which can then be protonated by a proton donor such as ethanol or water,[16,20,21,23,24] to form ammonia with the recovery of lithium ions (Figure 1a). The approach has been demonstrated to produce ammonia in both batchwise[17−19] and continuous operation systems.[11,16,20,23] However, the mechanism for ammonia formation may differ between continuous and batchwise systems.[20,23]

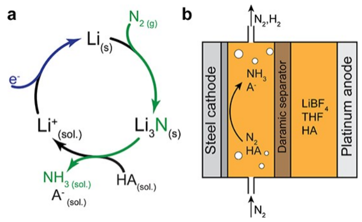

Figure 1. Lithium-mediated ammonia production from nitrogen. (a) Proposed lithium-mediated nitrogen reduction catalytic cycle. The flow of nitrogen through the cycle is highlighted in green. (b) Schematic diagram of the electrochemical cell setup used for studying the process of continuous ammonia production and the effects of proton donors.

In continuous systems, the primary role of the proton donor is the protonation of reduced nitrogen species to form ammonia. However, certain evidence suggests that the role of the proton donor goes beyond just being a source of hydrogen atoms in ammonia. For instance, it has been suggested that proton donors could have a role in activating the reaction between lithium and dinitrogen.[16,21,25,26] A previous theoretical analysis of a general electrochemical nitrogen reduction reaction demonstrated that the thermodynamic activity of the proton in solution is important for selective continuous nitrogen reduction.[27] The identity of the proton donor has been shown to have a profound effect on the FE toward ammonia in the lithium-mediated electrochemical nitrogen reduction reaction (LM-NRR).[16] For example, one study has used an ylide-based proton donor to improve the electrolyte conductivity and achieve high nitrogen reduction FEs, albeit at elevated pressures.[28] Other reduction reactions involving stoichiometric and buffering proton donors have been observed to be affected by the identity of the proton donor as well.[29−31] However, to date, no thorough study of the effect of the proton donor identity on LM-NRR has been performed. In addition, there is no consensus regarding the relationship between the concentration of the proton donor and ammonia FE at low donor concentrations.

The present work seeks to determine the effect of the proton donor identity on ammonia production in LM-NRR. Through experimental testing, we find that aliphatic alcohols are typically active in LM-NRR, while most other classes of proton donors are inactive. Of the tested alcohols, 1-butanol can consistently produce ammonia at higher selectivities than state-of-the-art ethanol. While many proton donors containing alcohol groups were found to be active toward nitrogen reduction, no macroscopic properties were found to reliably predict the activity toward ammonia formation. We find that the observed experimental behaviors are consistent with the proton donor affecting the properties of the solid electrolyte interphase (SEI); the extent to and the manner in which the SEI is affected depend on the concentration and identity of the proton donor in the electrolyte. Based on this understanding, we propose a model based on previous literature in which the properties of the SEI change with electrolyte composition to conceptually describe the observed trends in the ability of proton donors to promote nitrogen reduction. The model can qualitatively reproduce the thresholding behavior for ammonia FE as a function of the proton donor concentration, as well as the existence of an optimal proton donor concentration. Within this framework, the diffusivity of nitrogen through the SEI was found to be the most important factor determining the maximum obtainable ammonia FE.

RESULTS

Experimental Characterization of Proton Donors for Ammonia Production. Regardless of the proposed nitrogen fixation mechanism, the presence of a source of protons, that is, a proton donor, in the electrolyte during LM-NRR is necessary for the formation of ammonia from dinitrogen. The proton donor could be mechanistically responsible for (1) protonating thermochemically formed lithium nitride (Figure 1a), (2) protonating the dinitrogen directly in an electrochemical reaction,[20] or (3) forming surface-bound hydrogen species (e.g., lithium hydride or adsorbed hydrogen), which then facilitate nitrogen reduction.[20,23] However, in experiments with low concentrations of ethanol (the proton donor) in the electrolyte, ammonia and other forms of fixed nitrogen (e.g., lithium nitride) are not detected following electrolysis (Figure S2);[16,21] instead, lithium metal or other solids are observed to accumulate on the surface. This suggests that ethanol, and likely any proton donor, plays an additional role in LM-NRR that goes beyond the possible pathways of stoichiometric proton addition outlined above. The proton donor likely promotes an early step involved in the activation of nitrogen reduction before stoichiometric proton donation. The ability of proton donors to promote reaction activation appears to depend on their chemical structure.[16]

To determine whether a given proton donor can promote LM-NRR, a number of candidate compounds were tested at flooded stainless steel electrodes[21] (Figure 1b) at a range of concentrations. Galvanostatic experiments were performed at both relatively low and high applied current densities, 3 and 20 mA cm^{-2}, respectively. Most of the proton donor surveys were performed at a high applied current density to better capture practically relevant conditions, while experiments at a lower applied current density were used for mechanistic studies. While we report the maximum FEs toward ammonia obtained for any given proton donor, we have also classified proton donors as "active" or "inactive" to simplify the analysis. We chose to classify a proton donor as "active" in LM-NRR if the FE toward ammonia in at least one operating condition exceeds 0.5%. If the ammonia FE in the none of the performed experiments exceeds 0.5%, then the proton donor is considered inactive. This threshold was chosen based on the quantification limits of the assay used (⍰0.1%) and the typical variation in FEs observed at low production rates (⍰0.1%). By using a threshold value of 0.5%, we reduce the risk of false-positive classification and the likelihood that the measured ammonia signal is spurious or comes from adventitious sources.[14,32−34]

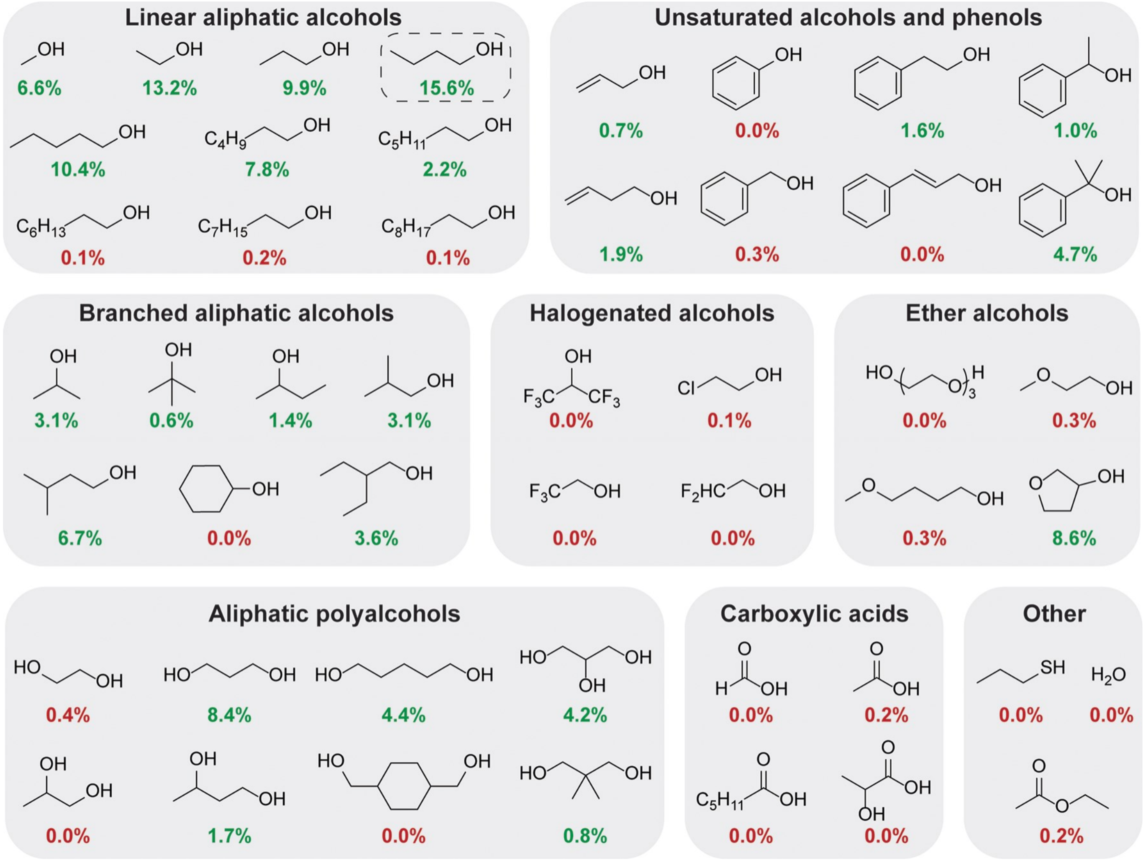

Figure 2. Maximum obtained ammonia FEs for a variety of tested proton donors. Some of these data have been presented in prior work.[35,36] Proton donors for which the FE values are given in green are classified as active (NH_3 FE > 0.5%) while those in red are classified as inactive (NH_3 FE < 0.5%). 1-Butanol is highlighted as it consistently resulted in the highest FEs of tested donors. The proton donor concentrations at which the maximum reported FEs were obtained vary between proton sources (Tables S2 and S3 and Figure S10).

Several classes of proton donors, including alcohols, carboxylic acids, phenols, thiols, and esters, were tested for their ability to promote LM-NRR. A large fraction of proton donors tested were aliphatic alcohols as they were found to be the most active group in preliminary studies.[16] Nitrogen-containing proton donors were excluded from the testing pool to avoid potential false positives, which could occur due to electrolyte decomposition or interference with the colorimetric assay used for ammonia quantification. Interference was observed in several experiments in which a nitrogen-containing donor was tested (Figure S3). Although some nitrogen-containing proton donors may have desirable properties and promote nitrogen reduction,[35] conclusively validating ammonia production when using them was deemed too resource-consuming due to the need for extensive isotope-labeling studies and is therefore outside the scope of this work.

Control experiments detected no adventitious ammonia when using the same setup with nitrogen-free compounds in prior work.[21] In addition, significantly more ammonia was detected when N_2 was used as the feed gas than when argon (Ar) was used for all active proton donors. The measured FE toward NH_3 when using argon as the feed gas was <0.5% for all proton donors (Figure S5). Isotopic labeling experiments for selected proton donors confirmed that nitrogen is reduced to produce ammonia (Figure S4). Although pure proton donors could always be a source of ammonia or nitrogen contamination, we did not observe any contamination in our experiments (see the Supporting Information). Nitrogen-containing compounds (e.g., ethanolamine) in the catalysts or electrolytes may give false-positive results via the colorimetric assay (Figure S3). Though none were used in the present study, care must be taken when using nitrogen-containing proton donors.

In general, only a subset of compounds containing hydroxyl groups (alcohols) was found to be active for LM-NRR (Figure 2). When using 1-butanol as the proton donor, the FE toward ammonia was found to consistently exceed that obtainable by using ethanol as a proton donor, with FEs of ∼16 versus ∼13% at an applied current density of 20 mA cm^{-2} and optimized concentrations at a flooded stainless steel electrode. When using a gas diffusion electrode at the cathode with butanol as the proton donor,[24] a FE of 40.3 ± 3.9% is obtained at an applied current density of 25 mA cm^{-2}, which is higher than the 33.1 ± 4.8% FE reported with ethanol (Figure S6). We believe that 1-butanol should be used in future LM-NRR studies aimed at maximizing the yield of ammonia.

Even though 1-butanol had a consistently higher activity when compared to ethanol, as confirmed by a relatively large number of experiments (Figure S10), we would like to highlight that the reported maximum obtained FEs between most other proton donors should not be directly compared (Figure 2). The concentration in the electrolyte was not optimized for every proton donor as the goal of this study was to obtain a binary proton donor activity classification not to obtain a detailed relationship between the FE and concentration for all proton donors. The concentration at which the

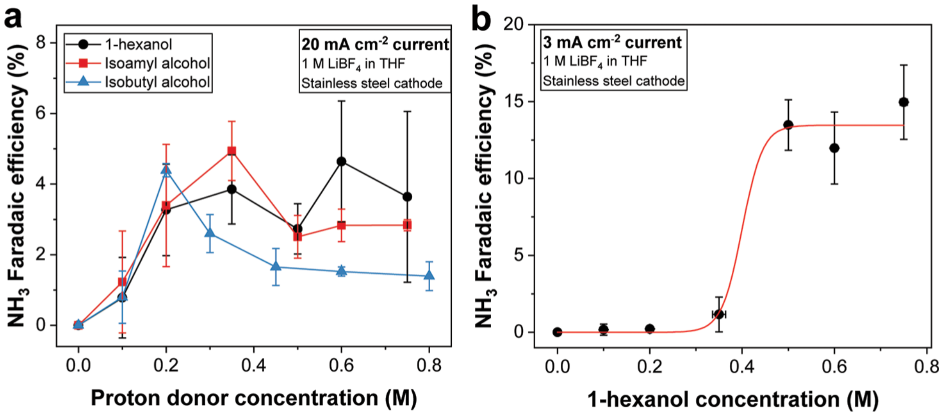

Figure 3. Relationship between the FE toward ammonia and the concentration of the proton donor. (a) NH_3 FE−concentration dependence for three proton donors at a 20 mA cm^{-2} applied current density at a polished stainless steel foil cathode. The error bars represent 1 standard deviation between replicates of identical experiments ($n \geq 2$). Note that the large standard deviations when using 1-hexanol and isoamyl alcohol are likely a result of stochastic behavior of the nitrogen reduction system and not experimental error as the error bars are much smaller when using isobutyl alcohol in the same setup. The confidence intervals contain zero because of several experiments that resulted in close-to-zero NH_3 yields (see Table S4). (b) FE−concentration dependence for 1-hexanol at a lower current density of 3 mA cm^{-2}. The error bars represent 1 standard deviation of replicates of identical experiments ($n = 2$). The red line is a logistic curve fit to the data and is meant to guide the eye.

highest measured FE was obtained varies with the proton donor identity (Table S2); the concentration at which FE is optimized likely also differs between proton donors.

The concentrations of certain proton donors must be higher in the electrolyte than in ethanol or butanol to promote ammonia formation (Table S2). Elevated concentrations of the proton donor in the electrolyte may increase hydrogen generation via proton donor reduction, which is an undesirable side reaction. However, maintaining high concentrations of the proton donor in the bulk electrolyte may be advantageous in systems producing ammonia at high rates, as they allow for higher diffusion-limited rates of proton-consuming reactions, of which ammonia production is one. High rates of proton donor diffusion may be important when nitrogen diffusion through the electrolyte is not rate limiting, such as when ammonia synthesis is performed at gas diffusion electrodes.[24] For these reasons, proton donors for LM-NRR which operate at higher concentrations could be practically relevant. In addition, the rate of proton donor reduction may be a function of the proton donor identity, likely being lower for proton donors with lower acidity. Thus, weakly acidic proton donors may still allow for the formation of ammonia via protonation of lithium nitride or other reduced nitrogen species in acid−base reactions if the nitrogen reduction reaction is sufficiently activated.

Relationship between Ammonia FEs and Proton Donor Concentrations. The FE toward ammonia increases sharply with low concentrations of ethanol (Figure S2). At an ethanol concentration of ⍰0.1 M (⍰0.6% v/v), the ammonia FE is maximized, and further increases in the proton donor concentration result in decreased FE.[16,21,23] Many other proton donors demonstrated the existence of an optimal concentration for maximizing the FE toward ammonia production (Table S3). The optimal concentration of the proton donor appears to be a strong function of the compound structure but typically lies in the range of 0.1−0.6 M, with many proton donors yielding peak ammonia FEs at concentrations in the range 0.1−0.2 M. Lower ammonia FEs at higher concentrations of the proton donor are typically attributed to increased competition from proton donor-derived hydrogen formation.[21,23] However, the nature of the relationship between the proton donor concentration and the yield of ammonia at low proton donor concentrations is less clear. A previous study hypothesized that at low concentrations of the proton donor, ammonia is not formed due to the low rate of proton diffusion through the SEI, which prevents protonation of reduced nitrogen species;[23] we believe that the data in the present work can reject this hypothesis (vide infra).

In order to more accurately measure the impact of the proton donor structure on the concentration that maximizes ammonia FE, and to study the relationship between the concentration and FE below the optimal concentration of the proton donor, we performed additional experiments for selected proton donors, varying the concentration of the proton donor in the electrolyte. Isobutanol, isoamyl alcohol, and 1-hexanol were used in these additional experiments because the optimal concentration for ammonia production appeared to be significantly higher than for ethanol (⍰0.1 M). When assessing the impact of the proton donor concentration in the experimental setup used in this work, it is important that the initial concentration of the proton donor is at least 0.1 M to maintain a low conversion of the proton donor. A low conversion of the proton donor ensures a relatively constant concentration in the electrolyte (see the Supporting Information). For the three aforementioned proton donors, the FE toward nitrogen reduction was measured at an applied current density of 20 mA cm^{-2}. The relationship between the 1-hexanol concentration and ammonia FE was also measured at a current density of 3 mA cm^{-2} to assess if the applied current density had any impact on nitrogen reduction. Additional experiments for a wide range of aliphatic alcohols at 3 mA cm^{-2} at copper electrodes were also performed (Figure S10).

The FE increases fairly linearly with concentration in the range of 0−0.2 M at high applied current densities for the three proton donors tested (Figure 3a). At isobutanol concentrations above 0.2 M, the FE toward ammonia decreases monotonically with highly reproducible experiments (Figure 3a and Tables S3 and S4). When 1-hexanol and isoamyl alcohol were used as proton donors, however, the average FE remained fairly constant up to the highest tested concentration of 0.75 M, though there was a considerable

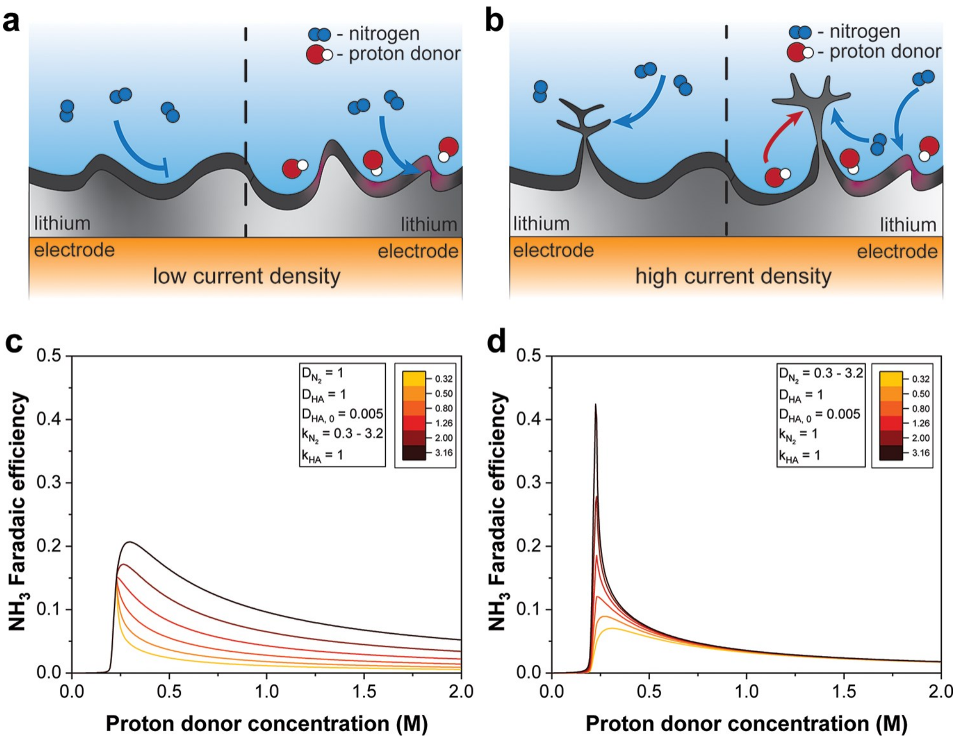

Figure 4. Proposed SEI-based mechanism for nitrogen reduction by lithium in the presence of a proton donor. (a) Behavior of the SEI (dark gray) in the absence and presence of a proton donor at low applied current densities. When a proton donor is present in the electrolyte, the SEI is more permeable (shown with shades of red), which allows nitrogen and an additional proton donor to diffuse through it and react with the underlying lithium metal. (b) Lithium morphology and SEI behavior at high applied current densities. At high current densities, some of the lithium may form dendrites that can physically disrupt the SEI, leaving local portions of lithium metal not covered by a layer of SEI. This uncovered lithium can react with nitrogen regardless of proton donor availability. (c,d) FEs toward ammonia as a function of the proton donor concentration as predicted by the kinetic diffusion model at different nitrogen (c) kinetic reactivities and (d) through SEI diffusivities.

spread in the ammonia FE for individual experimental runs. This large spread suggests that the nitrogen reduction process is more stochastic when using 1-hexanol and isoamyl alcohol than when using isobutanol as the proton donor as the experimental procedure is identical for all the three proton donors.

At a lower applied current density (3 mA cm^{-2}), the relationship between the ammonia FE and 1-hexanol concentration was markedly different (Figure 3b). At concentrations of 1-hexanol below 0.4 M, little ammonia was detected in the electrolyte. Under these conditions, the surface of the electrode was completely covered in a uniform layer of lithium metal or other solid species after the application of current (Figure S11). No appreciable amount of reduced nitrogen species, for example, lithium nitride, was detected in the solid material remaining on the electrode (Figure S12). These results suggest that no nitrogen reduction occurs, either to ammonia or other reduced forms of nitrogen at low applied current densities and concentrations of 1-hexanol below 0.4 M. However, at concentrations even slightly above 0.4 M, the FE toward ammonia increases dramatically (Figure 3b). The average ammonia FEs exceed 10% for all the tested concentrations above 0.4 M and reaches 15.0 ± 2.4% at 0.75 M 1-hexanol in the electrolyte (Figure 3b). Unlike under high current density conditions, where some ammonia is produced at all tested proton donor concentrations greater than zero, there exists a non-zero threshold concentration of 1-hexanol that is necessary to produce any amount of ammonia at low applied current densities.

DISCUSSION

Appropriate Descriptors for Predicting Proton Donor Activity. As ammonia FEs have been shown to vary greatly with the proton donor structure in LM-NRR, it would be desirable to be able to predict the activity toward LM-NRR as a function of proton donor properties. While a data-driven approach for elucidating property−activity relationships could be attractive, it is outside the scope of the present work and has been pursued elsewhere.[35] Instead, the existing mechanistic models can be used to propose the predictors of proton donor activity. By examining several models in the literature (see the Supporting Information for details),[20,21,23] it is reasonable to posit that the diffusivities and acidities (pK_a) of proton donors can be correlated with their activity. The proton donor property data were obtained either by using correlations or by compiling experimental data from PubChem.[37,38] However, we found that neither property could predict the proton donor activity well, though the pK_a values of proton donors that promote LM-NRR were found to lie in a relatively narrow range (Figures S13 and S14).

Because subtle differences in the proton donor structure are observed to have large impacts on ammonia generation, bulk properties of proton donors are likely to be poor predictors for their activity in LM-NRR. For example, 1,2-propanediol and 1,3-propanediol exhibit very different behaviors in LM-NRR; the peak ammonia FEs for the two proton donors are 0 and 8.2%, respectively (Figure 2). This stark difference occurs despite the compounds likely having very similar acidities and practically identical diffusion coefficients. Therefore, a nitrogen reduction model potentially sensitive to the proton donor structure, not just its macroscopic properties, is necessary to describe and understand trends in ammonia yields.

Role of Proton Donors in LM-NRR. In addition to being a source of hydrogen atoms in produced ammonia, the proton donor appears to have indirect effects on nitrogen reduction. Evidence of this can be found in experiments where dinitrogen and metallic lithium can coexist in an electrolyte where no proton donor is present with negligible rates of nitrogen fixation despite their thermodynamic and kinetic propensities to react (Figures S3 and S7).[21,39] Thus, there are two possible ways that the proton donor can affect the nitrogen reduction reaction: (1) either the proton donor directly activates a nitrogen-fixing reaction, which could be thermochemical or electrochemical, or (2) it deactivates an inhibitor of such a reaction. Note that these two options are not necessarily mutually exclusive. While it is difficult to distinguish these modes of action, several observations suggest that the proton donor is predominantly responsible for the deactivation of an inhibitor in LM-NRR.

First, gaseous nitrogen can react with dry lithium metal at ambient conditions without any proton donor present,[22] which suggests that the presence of a proton donor is not necessary for activating direct lithium nitridation. While it has been reported that small amounts of water vapor or oxygen in the gaseous nitrogen may accelerate lithium nitridation,[25,26,40] the effects of these impurities on the reaction are not well understood as the lithium surface morphology and composition in these experiments were not thoroughly controlled and studied. Lithium nitridation has been reported to be a both thermodynamically and kinetically facile reaction at room temperature.[41] This is further supported by experiments in which gas-phase lithium nitridation is shown to have a low effective activation energy,[25] which is consistent with the rate of the reaction being defined by the rate of diffusion of dinitrogen through solids present on the lithium surface.[25] In this case, the surface species can be treated as inhibitors of the otherwise rapid reaction between lithium metal and nitrogen. For these reasons, it is reasonable to posit that in LM-NRR, the proton donor can alter or remove surface species that are present on lithium, which inhibit the reduction of nitrogen.

An example of a potential surface inhibitor of LM-NRR is the SEI, which is often present in systems at highly reducing electrodes, such as on the surface of lithium metal.[42] Given its position between the electrolyte and the reactive lithium surface, the SEI could slow or completely prevent diffusion of dinitrogen and proton donors to the reactive electrode, thereby inhibiting the reduction of nitrogen (Figure 4a). Andersen et al. have proposed a detailed mechanistic model for LM-NRR that assumes that species slowly diffuse through the SEI.[23] This model highlights the important role that the SEI may play in LM-NRR and supports the idea that the SEI may act as an inhibitor of ammonia production. In the model, the relative diffusion rates of lithium ions, dinitrogen, and protons through the mass transport boundary layer and SEI to the reactive surface are assumed to influence the FE toward ammonia in the LM-NRR system. While not explicitly stated, the authors used a one-dimensional diffusion model in which constant species diffusivities were assumed when fitting the experimental data.[23] The constant diffusivity assumption also implicitly means that variations in the proton donor concentration cannot affect the diffusion rates of other species. As a result, a close-to-linear relationship was obtained between ammonia FEs and proton donor concentrations.[23] In the present work, an approximately linear relationship between ammonia FEs and proton donor concentrations was observed at high current densities and low proton donor concentrations (Figure 3a), validating parts of the model described by Andersen et al. However, a markedly different behavior was observed at low current densities (Figure 3b), which suggests that the model must be modified to accurately describe the experimental trends.

Refined Model for Explaining the Role of Proton Donors in LM-NRR. One possible modification to the model is to relax the implicit assumption that the diffusivity of species is constant with operating conditions. The rate of diffusion of species through the mass transport boundary layer is relatively constant with the proton donor concentration and applied current density as it is a function of species diffusivity and bulk solution hydrodynamics. Diffusion through the SEI, however, can change significantly as both the thickness and the properties of the SEI are strong functions of electrolyte composition.[43]

Stepwise factorial experiments offer evidence that the SEI properties change with the proton donor identity (Figure S7). To supplement this qualitative finding, we wanted to model this phenomenon in order to predict the effects of proton donors. Many possible models could represent this phenomenon, and they can be vetted with additional experiments and spectroscopic techniques. In our model, we assume that two distinct types of SEIs exist in the system, a permeable and an impermeable one, though in practice the permeability of the SEI can take a continuous range of values. In the absence of a proton donor, the SEI can be assumed to consist of products of reactions between THF, BF_4^-, and lithium metal. Because nitrogen reduction products are not detected in the absence of a proton donor, this type of SEI likely has a high resistance to nitrogen diffusion (Figure 4a) and is assumed to be mostly impermeable. When a proton donor is added to the electrolyte, the SEI may be partially composed of the products of the reaction between lithium and the proton donor as the proton donor is more reactive with lithium metal than either THF or BF_4^-. The change in SEI properties with the addition of a proton donor can be studied by impedance spectroscopy (Figure S8). This SEI could be less resistant to the transport of nitrogen (and likely proton donor), either by being thinner or being less dense, allowing for reactions that lead to ammonia synthesis to occur (Figure 4a).

The overall SEI permeability to various species is a function of the fractions of impermeable and permeable phases. These fractions, and therefore the overall SEI permeability, are likely a function of both proton donor identity and concentration, which could explain the observed differences in ammonia FEs when different proton donors are used (Figure 2), as well as the concentration dependence at low applied current densities (Figure 3b). While the exact functional form of SEI permeability as a function of the proton donor concentration is unknown, the behavior observed at low applied current densities suggests that it must exhibit a thresholding behavior, that is, the permeability increases rapidly above a certain threshold concentration, similar to a logistic function (Figures 3b, S2, and S10). Many mechanisms could result in thresholding behavior, including SEI formation described by percolation theory[44] and autocatalytic formation of a permeable SEI phase (see the Supporting Information). For the remainder of the work, we assumed that the fraction of the permeable SEI, defined as θ, can be derived from an autocatalytic formation model described in the Supporting Information Discussion and that the SEI permeability is constant in time after reaching dynamic equilibrium as long as the electrolyte composition is constant.

By using the relationship between the proton donor concentration and permeable SEI fraction (θ), the FEs toward hydrogen, ammonia, and residual metallic lithium can be predicted. The rates of hydrogen and ammonia formation can be obtained from the rates of diffusion of the proton donor and nitrogen through the SEI, respectively; these assumptions are similar to those made in the model proposed by Andersen et al.[23] The rate of diffusion of the proton donor is used in finding the rates of both ammonia and hydrogen formation. The proton donor is assumed to diffuse and act only as an undissociated species; the dissociation of proton donors to free protons is unlikely because the donors tested have high absolute pK_a values in THF.[45] While the presence of lithium ions in the electrolyte and SEI could lower the pK_a values, we believe that the concentration of free protons at the cathode and in the SEI is still negligible. We assume in the present model that the rate of lithium ion diffusion is fast and that it does not impact other processes in LM-NRR; this assumption is likely to not affect the model predictions as long as the lithium ion concentration profile, that is, its bulk concentration, remains constant.

The effective diffusivity of nitrogen and the proton donor through the SEI is assumed to be a strong function of θ in the present model. We will assume that the species of interest can diffuse through the impermeable SEI at small, yet non-zero rates, as well as through the permeable SEI at much higher rates. The total diffusion flux of species through the SEI (N_j) is given by the sum of the rates of diffusion through each type of SEI, weighted by the fraction of each type of SEI

$$N_j = (D_{j,\mathrm{i}}(1 - \theta) + D_{j,\mathrm{p}}\theta)\cdot(C_{j,\mathrm{bulk}} - C_{j,\mathrm{S}}),\ j \in \{\mathrm{N_2},\ \mathrm{HA}\} \tag{1}$$

The variable D_j captures both the diffusivity of species j through the SEI and the SEI thickness, making it an effective mass-transfer coefficient in units of length per unit time, the flux N_j is thus given in units of moles per unit area per unit time, $C_{j,\mathrm{bulk}}$ denotes the concentration of species j at the SEI, which is assumed to be equal to the bulk concentration for simplicity, while $C_{j,\mathrm{S}}$ is the concentration of species j at the reactive electrode surface beneath the SEI.

At the steady state, the rate of dinitrogen diffusion through the SEI equals the rate of the nitrogen reduction reaction. The rate of the nitrogen reduction reaction is assumed to be proportional to the average concentrations of nitrogen ($C_{\mathrm{N_2,S}}$) and lithium (C_{Li}) at the electrode surface beneath the SEI

$$r_{\mathrm{N_2}} = k_{\mathrm{N_2}}C_{\mathrm{N_2,S}}C_{\mathrm{Li}} = (D_{\mathrm{N_2,i}}(1 - \theta) + D_{\mathrm{N_2,p}}\theta)\cdot(C_{\mathrm{N_2,bulk}} - C_{\mathrm{N_2,S}}) = N_{\mathrm{N_2}} \tag{2}$$

Similarly, at the steady state, the rate of proton donor diffusion through the SEI is equal to the rates of all reactions involving the proton donor. The proton donor is consumed in two reactions: it can (1) be reduced to form hydrogen gas via proton reduction and (2) be deprotonated to form ammonia from a reduced nitrogen species. As direct electrochemical reduction of the proton donor to hydrogen does not appear to occur (Figure S16), hydrogen is likely evolved from the reaction between lithium and the proton donor.[21] For this reason, the rate of proton donor reduction to hydrogen ($r_{\mathrm{HA,red}}$) is assumed to be proportional to the product of the concentrations of the proton donor ($C_{\mathrm{HA,S}}$) and lithium at the electrode surface below the SEI

$$r_{\mathrm{HA,red}} = k_{\mathrm{HA}}C_{\mathrm{HA,S}}C_{\mathrm{Li}} \tag{3a}$$

Because the protonation of reduced nitrogen species is likely thermodynamically and kinetically facile, as it is an acid−base reaction, the rate of protonation ($r_{\mathrm{HA,prot}}$) is assumed to be given by the rate of nitrogen reduction. As six moles of the proton donor are necessary to protonate nitrogen species for every mole of dinitrogen reduced, the rate of protonation is given by

$$r_{\mathrm{HA,prot}} = 6k_{\mathrm{N_2}}C_{\mathrm{N_2,S}}C_{\mathrm{Li}} \tag{3b}$$

By setting the rates given by interfacial proton donor consumption equal to the rate of transport of donor through the SEI, we obtain

$$\begin{aligned} r_{\mathrm{HA}} &= r_{\mathrm{HA,red}} + r_{\mathrm{HA,prot}} = k_{\mathrm{HA}}C_{\mathrm{HA,S}}C_{\mathrm{Li}} + 6k_{\mathrm{N_2}}C_{\mathrm{N_2,S}}C_{\mathrm{Li}} \\ &= (D_{\mathrm{HA,i}}(1 - \theta) + D_{\mathrm{HA,p}}\theta)\cdot(C_{\mathrm{HA,bulk}} - C_{\mathrm{HA,S}}) = N_{\mathrm{HA}} \end{aligned} \tag{3c}$$

Similar to prior LM-NRR models,[21,23] we assumed an effective surface concentration of lithium that is used to define the rates of reactions involving lithium metal, namely, proton donor and nitrogen reduction. Unlike in a prior kinetic model,[21] the order with respect to lithium is assumed to be unity for all reactions; this simple assumption allows for more probable mechanistic interpretations, though more complex reaction orders may be used in the present model to represent other nitrogen reduction behaviors (Figure S18). The lithium activity or concentration used in rate expressions for nitrogen and proton donor reduction may not correspond to actual physical lithium. Instead, the lithium concentration may be a convenient way to account for electrons, which are passed in thermochemical reactions involving lithium (Figure S16) or direct electrochemical reactions. Nevertheless, a conservation of lithium mass equation can still be defined. The rate of accumulation of lithium can be found by taking the difference between the formation rate of lithium, which is deposited via application of current, and the rates of utilization in nitrogen and proton donor reduction reactions, whose rates are given in eqs 2 and 3a, respectively

$$F\frac{\mathrm{d}\,C_{\mathrm{Li}}}{\mathrm{d}\,t} = I - F(k_{\mathrm{HA}}C_{\mathrm{HA,S}}C_{\mathrm{Li}} - 6k_{\mathrm{N_2}}C_{\mathrm{N_2,S}}C_{\mathrm{Li}}) \geq 0 \tag{4}$$

Here, F is Faraday's constant, which is necessary to convert between molecular rates and current densities and I is a constant applied current density. In eq 4, a positive rate of change in lithium concentration represents an accumulation of bulk lithium on the electrode. Because the reactions in eqs 2 and 3a are assumed to be defined by the rate of diffusion of species through the SEI, they can be assumed to be fast. Because the reactions are fast, we can assume that the charge in the system is utilized efficiently; therefore, the amount of lithium accumulation should be minimized. By minimizing the rate of lithium accumulation in eq 4 subject to constraints given in eqs 2 and 3a, the surface concentrations of nitrogen, proton donor, and lithium metal can be found. This procedure was used to model a constant current process ($I > 0$). For systems in which the current is varied or cycled,[23] the lithium concentration can be solved for explicitly as a function of time using eqs 2−3b after assuming values for kinetic constants.

The rate of ammonia formation (r_{NH_3}) depends on the rate of diffusion of the limiting reactant; in most cases, the diffusion of nitrogen is rate limiting. However, in certain cases, the rate of proton diffusion may be insufficient to match the rate of nitrogen reduction, in which case the diffusion of the proton donor is rate limiting for ammonia production.[23] In eq 3cc, we implicitly assume that the proton donor will preferentially participate in the more facile acid−base reaction of protonating nitrogen species over the redox reaction of hydrogen generation. When accounting for reaction stoichiometry (N_2 to NH_3 is 1 to 2, while HA to NH_3 is 3 to 1), the rate of ammonia formation is given by[23]

$$r_{NH_3} = 2\cdot\min\left(\frac{r_{HA}}{6}, r_{N_2}\right) \tag{5}$$

The FE for ammonia, when accounting for the fact that ammonia formation is a three-electron process, is therefore defined as

$$FE_{NH_3} = \frac{3F\cdot r_{NH_3}}{I} \tag{6}$$

Accounting for the fact that proton donor reduction is a one-electron process and ammonia formation is a three-electron process while assuming that all proton donors that diffuse through the SEI that are not consumed in ammonia generation will form hydrogen, the FE for H_2 is given by

$$FE_{H_2} = \frac{F\cdot(r_{HA} - 3r_{NH_3})}{I} \tag{7}$$

This quantity may be equal to zero if the ammonia formation process is limited by proton diffusion. The exact distribution of FE toward other reactions, such as electrolyte decomposition, cannot be clearly described using the current assumptions. It is reasonable to assume that a large portion of the potentially unaccounted for current goes toward accumulating unreacted metallic lithium or SEI.

By varying the values of kinetic and diffusivity parameters in the above model, experimentally observed trends can be recovered for the relationship between ammonia FEs and proton donor concentrations (Figures 4c,d and S17). The rapid increase in the ammonia production rate above a threshold proton donor concentration can be explained by the increase in the permeability of the SEI. With increased SEI permeability, the rate of nitrogen diffusion through the SEI to the lithium surface is higher, which increases the potential rate of ammonia synthesis. As the permeability of SEI increases, the rate of proton donor diffusion through the SEI can also increase. At proton donor concentrations slightly above the threshold concentration, at which ammonia synthesis is rapid and most selective, most of the proton donors that diffuse through the SEI are used up to protonate the nitrogen species to produce ammonia. As a result, scant quantities of proton donor are available for reduction to form hydrogen; the FE toward hydrogen is therefore low and the FE toward ammonia is high. At proton donor concentrations above the threshold concentration, the rate of proton donor diffusion through the SEI increases due to both increased SEI permeability and the larger diffusion driving force across the SEI. This increased rate of proton donor diffusion leads to increased surface concentrations of the proton donor, so a larger fraction of the current goes toward hydrogen generation and the ammonia FE decreases. The exact shape of the ammonia FE curve depends strongly on the relative diffusivities of nitrogen and the proton donor, the reaction rate constants of the nitrogen and proton donor reduction reactions (Figure 4c,d), as well as on the dependence of SEI permeability on operating conditions. Notably, however, the peak FE for ammonia is a much stronger function of nitrogen diffusivity than of the reaction rate constant for nitrogen reduction (Figure 4c). In fact, the reaction rate constant for nitrogen reduction can be equal to or significantly lower than that for proton donor reduction while maintaining a high FE, so long that nitrogen diffusion is favored over proton donor diffusion. As the vast majority of proton donors are sterically bulkier than dinitrogen, the diffusivity of nitrogen through the SEI is likely to be higher than the diffusivity of proton donors. This suggests that the SEI acts as a protective layer that slows proton transfer and promotes selective ammonia synthesis through a differential transport effect. This is a mechanism of improving the selectivity of nitrogen reduction that has been previously suggested in the literature.[46] Differences in proton donor reactivity can explain the exact functional forms of ammonia FEs on proton donor concentrations (Figure S10). For example, if hydrogen generation using 1-hexanol is kinetically slow compared to nitrogen reduction, then the ammonia FE will not change significantly with the proton donor concentration (Figures 3b and 4c).

It is important to note that the proposed model has at least nine adjustable parameters: four parameters for species diffusivity, two kinetic parameters, and three parameters for defining the SEI permeability (θ) (see the Supporting Information). As the amount of experimental data is limited and the number of parameters is large, the model can be prone to overfitting the data. In addition, two physical phenomena in series (SEI formation and competitive transport of species through the SEI) are used in the model to describe one measured value (FE toward ammonia), which makes fitting all model parameters difficult. For this reason, the parameters in the model have not been explicitly fitted to experimental data; instead, the model was used to qualitatively explain many of the experimentally observed trends with relatively simple and literature-supported assumptions. If explicit data fitting is desired, certain assumptions may be made to constrain parameters to reduce overfitting. For instance, one may assume that the permeable SEI formation rates used to define θ in the present model are equal to the diffusivity of the proton donor used in the kinetic model (see the Supporting Information Discussion). Additional experimental data are necessary, particularly direct measurements of the SEI structure and properties, to further support the varying SEI permeability model. One possible method for measuring the SEI permeability and stability involves determining the rate of diffusion of a fluorescent dye through the SEI.[47] Many of the parameters in the model, particularly those related to the SEI permeability and formation, are likely strong functions of the proton donor structure, which could explain many of the differences in reactivity observed for different proton donor families (Figure 2).

We can postulate possible reasons that n-butanol demonstrates the highest ammonia FEs. One reason could be that the SEI formed by butanol is similar to the one formed by THF.

As THF could ring-open to form a butoxide-like moiety, the SEI may contain some butoxide.[48,49] Therefore, it is possible that any butoxide formed from n-butanol could change the composition of the SEI, while not significantly disrupting the overall SEI structure. This additional butoxide could avoid promoting the side reactions of lithium with the electrolyte, yet change the SEI properties enough to allow nitrogen to diffuse more readily to react with lithium. Other linear aliphatic alcohols may be active for similar reasons. In addition, while most ether-containing proton donors are not active (Figure 2), 3-hydroxytetrahydrofuran, which is very similar in structure to THF, is an active proton donor, which can reduce nitrogen at high FE.

We hypothesize that proton donors and additives that can form SEI species similar to the ones formed by THF lead to higher N_2 reduction efficiency. For this reason, linear and lightly branched aliphatic alcohols, as well as tetrahydrofuran and tetrahydropyran derivatives, likely make good proton donors. Ethers of short chain (two to six carbon atoms) aliphatic alcohols and tetrahydropyran could be non-proton-donating additives that promote the formation of desirable SEI structures; however, they may lower the conductivity of the electrolyte, making them undesirable for high ammonia production rates. A hexyl-based phosphonium additive was found to promote nitrogen reduction in THF,[28] which further supports the "similar-structure" hypothesis, as it could decompose to form SEIs similar to those formed by THF or hexanol.

The model in its current form does not completely explain the difference in the concentration−FE trends at low and high applied current densities. The present model can explain low current density behavior. A possible explanation for high current density behavior is that the lithium morphology becomes more dendritic.[50] Dendrites may produce cracks in the SEI, briefly exposing lithium that is completely free of SEI to the electrolyte (Figure 4b). This unprotected lithium can react with both nitrogen and the proton donor in the electrolyte at all proton donor concentrations. Because there is no SEI to allow for selective diffusion of nitrogen over the proton donor, the ammonia FEs obtained under these conditions are lower (Figure 3a). Stochastic breaking and reforming of the SEI by dendrites could also be the cause of the large spread in experimentally measured FEs for 1-hexanol and isoamyl alcohol (Figure 3a). However, the composition and properties of the SEI formed is still affected by the proton donor identity, which in turn has some effect on lithium plating and dendrite formation, as evidenced by the markedly different behavior observed in the case when isobutyl alcohol is used as the proton donor (Figure 3a). While it is possible to model this behavior qualitatively, for instance, by imposing that the current above a certain threshold reacts without diffusing through the SEI, we believe that the merit of adding such assumptions to the model is not well borne out by the experiment. The diffusion of lithium ions through the electrolyte and SEI was not explicitly modeled in the present work due to the low constant current assumed. However, modeling lithium ion transport is important for understanding the dynamic lithium morphology and SEI structure. In addition, a model accounting for lithium ion transport could describe the effect of the current density of ammonia yields with high fidelity. It is important to note that at the steady state, LM-NRR does not explicitly consume lithium ions; instead, a stable concentration profile with excess lithium at the cathode may be established. The transport of nitrogen and the proton donor from the bulk to the SEI can also be modeled and may be necessary for describing complex behaviors. While not included in the present model, this phenomenon may become rate-limiting at high applied currents, as evidenced by prior work.[21]

Additional Considerations for Proton Donors in Practical Systems. While the proton donor in the electrolyte can likely influence the structure and composition of the SEI, and therefore should be appropriately selected to maximize the selectivity toward NH_3 in LM-NRR, there are additional considerations for the use of proton donors in practical systems. First, the proton donor should ideally only participate in SEI- and ammonia-forming reactions. Other reactions that use up the proton donor are undesirable as they increase the material costs for ammonia synthesis and may lead to the accumulation of undesirable side products. Of the proton donors tested (Figure 2), those with halogens in their structure consistently produced no ammonia in LM-NRR, even if unhalogenated analogues did. It is possible that the halogen of the proton donor reacts with lithium to form an inhibiting lithium halide layer on the electrode. This layer would not be affected by an additional proton donor, thus preventing ammonia formation. While being somewhat active toward LM-NRR, proton donors containing unsaturation also visibly showed signs of side reactions (i.e., dark, non-lithium accumulations on the electrode surface and unstable electrode potentials), which may make this class of proton donors non-ideal for further studies. The use of strong acids (e.g., carboxylic acids) as proton donors is also undesirable as they likely can get electrochemically reduced directly to form hydrogen, bypassing any lithium plating, which is necessary for ammonia formation.

An additional consideration that was not examined experimentally in the current study is the stability of proton donors and their deprotonated forms at the anode. In a practical ammonia-producing system using LM-NRR, the proton donor would react at the cathode to form its deprotonated form and ammonia (Figure 1b). The deprotonated form would react with the protons produced at the anode by an oxidation reaction, likely hydrogen oxidation, thereby recycling the proton donor.[24] If the proton donor or its deprotonated form is not stable at the anode (i.e., gets oxidized), then the lifetime of the overall process will be limited by proton donor oxidation, despite all advances to improve the stability of the cathode process. When selecting proton donors for anode stability, it may be desirable to use tertiary alcohols, which cannot be oxidized to carbonyl-containing compounds, unlike primary and secondary alcohols. An example of an attractive proton donor which is both reasonably active for LM-NRR at the cathode and likely stable at the anode is 2,2-diphenylpropan-2-ol (Figure 2). An ylide ionic-liquid-based proton donor has been proposed as an alternative to alcohols for proton cycling.[28] Further studies aimed at understanding and improving the anodic stability of proton donors are necessary.

The deprotonated form of the proton donor must also be sufficiently soluble in the electrolyte to be recycled in the cell. An example of a poorly cyclable proton donor is water. Water is inactive toward ammonia formation in LM-NRR, likely due to the formation of lithium hydroxide on the cathode, which is insoluble in the THF-based electrolyte. The effect of lithium hydroxide formation is twofold: it inhibits nitrogen diffusion to the electrode, and thus the LM-NRR reaction, and prevents the reformation of water at the anode as the hydroxide anion cannot diffuse to the other electrode. A similar phenomenon, though perhaps not as detrimental, was observed when using linear aliphatic alcohols as proton donors, whereby sparingly soluble alkoxides precipitated on the cathode (Figure S11). It is likely that a large majority of compounds would locally precipitate at the electrode due to elevated concentrations of deprotonated forms, high lithium ion concentration, and poor anion solvation by THF. However, as long as the precipitate does not actively impede surface reactions and instead acts as a medium through which nitrogen and the proton donor can diffuse, the proton donor is an acceptable choice for use in LM-NRR. In addition, the deprotonated form should be able to dynamically dissolve into the electrolyte solution to reach the anode. However, proton donors which are very soluble when deprotonated may actually be undesirable as they could make the permeable SEI that is necessary for efficient LM-NRR insufficiently long-lived for nitrogen reduction to occur.

CONCLUSIONS

In the present work, we tested several families of proton donors in lithium-mediated nitrogen reduction to determine the effect of the proton donor identity on ammonia FEs. We found that subtle differences in the proton donor structure can dramatically affect the ammonia yields. Of the families of proton donors tested, linear aliphatic alcohols were found to have the largest number of high-activity proton donors, with 1-butanol being the most effective proton donor for LM-NRR. In addition, a thresholding behavior for the rate of ammonia production with respect to the proton donor concentration was observed at low applied current densities, where no ammonia is produced when the concentration of the proton donor is below a certain threshold, while large amounts of ammonia are produced at proton donor concentrations above the threshold.

Because small differences in the proton donor structure can lead to large changes in activity in LM-NRR, simple macroscopic properties such as pK_a and bulk diffusivity are not able to describe and predict differences in activity. To qualitatively explain the observed trends, a detailed model was proposed and developed, in which nitrogen reduction occurs after it diffuses through the SEI, whose properties were assumed to vary with the proton donor identity and concentration. The model described in this work builds on prior LM-NRR models by assuming and demonstrating that the permeability of the SEI changes with the proton donor concentration.[23] The SEI becomes more permeable at higher concentrations of the proton donor in the electrolyte. A more permeable SEI allows for nitrogen or the proton donor to diffuse through it and participate in reactions at the electrode. The proposed model can predict the existence of the experimentally observed thresholding behavior, which arises as a consequence of changes in SEI permeability. The selectivity toward ammonia over hydrogen production was found to be a strong function of the relative mass-transfer coefficients of nitrogen and proton donors through the SEI. By allowing for differential transport of nitrogen over the proton donor to the electrode surface, the SEI can promote efficient ammonia production. The properties of the SEI depend on the proton donor identity as well as its concentration, which demonstrates that the proton donor plays an important and multifaceted role in lithium-mediated nitrogen reduction.

While the fact that the SEI properties can be altered by additives to the electrolyte is well known in the lithium battery literature, such additives are typically used with the intent of increasing the uniformity of lithium plating and the stability of the underlying lithium metal for use in the development of stable lithium−metal batteries for energy storage. In the present work, however, the electrolyte additives, proton donors, were shown to modify the SEI properties to instead increase the reactivity of lithium metal toward a useful synthetic reaction. The SEI was found to also act as a species-selective barrier, which allows for further tuning in reactivity and selectivity. We believe that continued development of the SEI in its capacity as a species-selective barrier can improve the yields toward ammonia in the lithium-mediated nitrogen reduction chemistry and could have potential applications in other chemistries of practical use.

ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.2c00389.

Additional experimental details, materials, methods, results, and discussion, including raw data and detailed description of the proposed nitrogen reduction model (PDF)

AUTHOR INFORMATION

Corresponding Author

Karthish Manthiram − Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States; orcid.org/0000-0001-9260-3391; Email: karthish@caltech.edu

Authors

Nikifar Lazouski − Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; orcid.org/0000-0002-4655-2041

Katherine J. Steinberg − Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; orcid.org/0000-0002-8232-7714

Michal L. Gala − Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Dilip Krishnamurthy − Department of Mechanical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States; orcid.org/0000-0001-8231-5492

Venkatasubramanian Viswanathan − Department of Mechanical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States; orcid.org/0000-0003-1060-5495

Complete contact information is available at: https://pubs.acs.org/10.1021/acscatal.2c00389

Notes

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Image processing software: Data were plotted in Origin 2018b (9.5). The plots obtained from Origin were compiled in Adobe Illustrator v 25.2. Diagrams were drawn in Adobe Illustrator.

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