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Full Communication

Electrolyte acidification from anode reactions during lithium mediated ammonia synthesis

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ABSTRACT

Li-mediated electrochemical ammonia synthesis (LiMEAS), a potential alternative to conventional thermochemical synthesis, is enabled by non-aqueous electrolytes with precisely controlled proton activity. However, the effects of proton generating anode reactions, such as hydrogen or electrolyte oxidation, is unknown but crucially important for enabling a steady-state LiMEAS without the need of sacrificial proton sources. By employing cyclic voltammetry on a platinum electrode, we demonstrate that protons are generated not only by hydrogen oxidation but also electrolyte oxidation, which has the consequence of a continuous acidification of the electrolyte over the course of a LiMEAS experiment. In addition, the cyclic voltammograms reveal that the generated protons show reactivity towards electrolyte components, which would disrupt the replenishment of the added proton source. We therefore suggest to design new electrolytes that also contain proton acceptors, ultimately resulting in a buffered electrolyte with a stable proton activity.

1. Introduction

Li-mediated electrochemical ammonia synthesis (LiMEAS) has recently gained much interest, as a process to unambiguously activate unreactive nitrogen and convert it into ammonia [1]. The Li-mediated nitrogen reduction process requires a non-aqueous electrolyte, such that the proton availability can be controlled by addition of appropriate amounts of a proton source [2]. In that regard, most reports on Li-mediated nitrogen reduction closely resemble the original reports by Tsuneto et al., who used tetrahydrofuran (THF) as a solvent and ethanol as proton source with a Li-containing electrolyte in a single compartment electrochemical cell [3]. Most studies have so far focused on the processes occurring at the ammonia producing cathode, such as solid-electrolyte-interface (SEI) formation [4] or Li-metal deposition and corrosion [5], as well as the effect of proton donor concentration or nitrogen pressure [6,7]. A fully integrated, steady-state LiMEAS as depicted in Fig. 1A however requires not only ammonia being produced at the cathode but also a suitable oxidation reaction on the anode, that is able to selectively regenerate the deprotonated proton source. For this purpose, Lazouski et al. have demonstrated the use of hydrogen oxidation reaction (HOR) in a separated gas-diffusion electrode set-up, which

can selectively provide protons and replace the electrolyte oxidation reactions encountered in single compartment cells when no hydrogen is provided [8]. In combination with a suitable proton donor/acceptor system, for example phosphonium ions [9], a steady-state LiMEAS can be imagined. While the HOR can conceptually provide protons necessary for this [10,11], the interaction of the generated protons with the electrolyte is rarely studied in the context of LiMEAS. In this letter, we present cyclic voltammetry studies on platinum disk electrodes of both anode reactions, electrolyte oxidation and HOR, in order to clarify their role in LiMEAS. We demonstrate that during anodic oxidation of electrolyte or hydrogen, readily reducible protons are formed, which accumulate in the electrolyte over the course of an experiment. Unlike the protons provided by ethanol itself, these readily reducible protons are at a significantly higher chemical potential leading to unwanted side reactions. Based on the results, we discuss the conditions that must be fulfilled to enable steady-state electrochemical LiMEAS in non-aqueous electrolytes and point out potential future research directions.

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2. Results and discussion

2.1. Oxidation and reduction features

As a first step, we measured cyclic voltammograms on a platinum disk electrode in a THF based 0.5 M LiClO₄ electrolyte under static electrolyte conditions (see [Supporting Information](#) for details) in order to take a closer look at the anode reaction in conventional single-compartment cells. In order to obtain the potential on an absolute scale and therefore allow comparison between different electrolytes, the Ag-wire pseudo-reference electrode was calibrated against the Fc/Fc⁺ redox couple after each measurement. As shown in [Fig. 1B](#), the first cathodic sweep does not show any redox features as expected for an aprotic electrolyte. Even with the addition of the proton source, [Fig. 1C](#), in this case ethanol, no reductive feature is observed in this potential range indicating that protons provided by ethanol are only reduced at more cathodic potentials. This is in line with the high pKa value of ethanol in non-aqueous solvents, which is significantly higher than in an aqueous system [12]. On the subsequent anodic sweep, the onset of electrolyte oxidation can be observed at around +0.3 V vs Fc/Fc⁺ with a less pronounced increase in oxidative current for the ethanol containing electrolyte. It appears that ethanol partly inhibits the anode reaction, which in this case is probably the anodic polymerization of THF [13,14]. At the same time, the oxidation of ethanol itself cannot be excluded. However, an important consequence of electrolyte oxidation

becomes apparent on the second cathodic sweep in [Fig. 1B](#) and [1C](#), where a pronounced reduction feature appears that goes in hand with another oxidative feature on the subsequent anodic sweep. Hatsukade et al. have also shown similar behaviour in an ethylenecarbonate:ethylmethylcarbonate (EC:EMC) based electrolyte, and have ascribed the reductive feature to the reduction of protons formed during electrolyte oxidation [15]. In line with this, the oxidative feature on the subsequent anodic sweep would then be the hydrogen oxidation reaction (HOR). The difference in this oxidative feature between [Figure 1B](#) and [Figure 1C](#) is thereby most likely caused by the different voltage limits of the respective CVs.

To further substantiate that the redox feature appearing after electrolyte oxidation is associated with proton reduction and hydrogen oxidation, we also measured CVs in a hydrogen saturated electrolyte. In hydrogen, a clear duck-shaped voltammogram arises at the same potential as the redox couple observed after electrolyte oxidation, while under inert Ar gas the voltammogram remains featureless (see [Fig. 1D](#)) indicating the production of protons during electrolyte oxidation. This again is inline with earlier observations by Hatsukade et al., who also observe a duck-shaped voltammogram under hydrogen atmosphere. Unlike in the case of electrolyte oxidation, the presence of ethanol appears to improve the kinetics of the HOR since the separation between the anodic and cathodic peak, a measure for the degree of irreversibility of a redox couple, decreases [16]. A possible explanation for this could be the higher dielectric constant of ethanol compared to THF. The

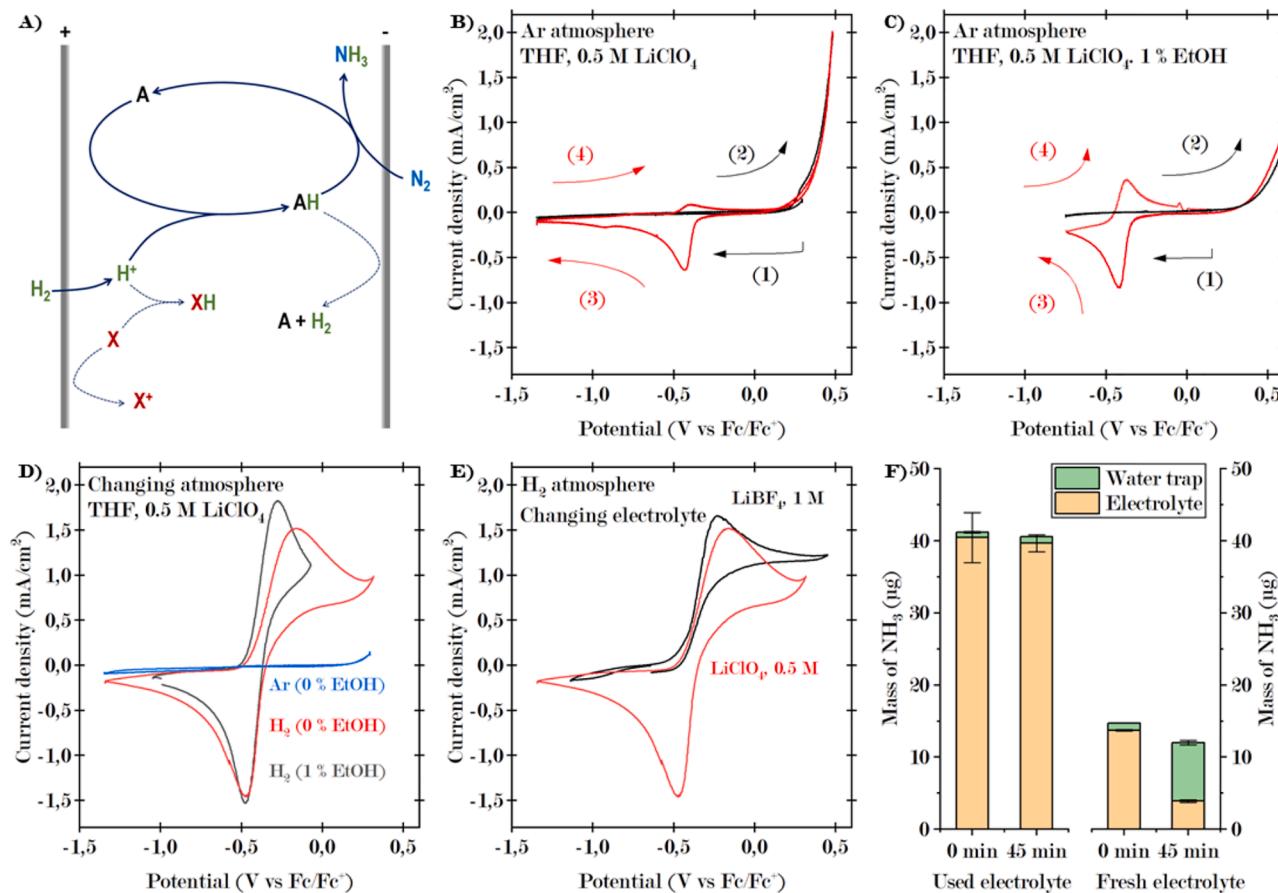


Fig. 1. (A) Potential reaction pathways for protons generated during hydrogen oxidation illustrating the selectivity challenge encountered in non-aqueous electrolytes. (B–E) CVs showing electrolyte oxidation and HOR/HER features in THF based electrolytes saturated with either Ar or H₂. (B) and (C): Appearance of an additional redox feature (red curve) at -0.4 V vs Fc/Fc⁺ after electrolyte oxidation in Ar saturated THF/LiClO₄ electrolyte with and without EtOH. (D): CVs in H₂ sat. THF/LiClO₄ electrolyte show the same feature as observed after electrolyte oxidation, while in Ar sat. electrolyte no feature is observed. (E): CV in HER/HOR region in THF based electrolyte with either LiBF₄ or LiClO₄. A cathodic HER peak is not seen in LiBF₄ containing electrolyte, while anodic peak is seen in both. (F) Amounts of NH₃ in electrolyte and in downstream water trap during evaporation experiments in used and fresh electrolyte demonstrating acidification of electrolyte.

addition of ethanol increases the dielectric constant of the solvent, which in turn leads to a better stabilization of the charged transition state during HOR. Moreover, measurements in EC:EMC based electrolyte carried out by Hatsukade et al., show an almost reversible redox behaviour for the HOR, which would be consistent with the substantially higher dielectric constant of organic carbonate solvents compared to THF. Another conclusion that can be drawn from these measurements is that the HOR provides protons to the electrolyte, similar to electrolyte oxidation. Moreover, the protons provided by electrolyte or hydrogen oxidation are at a substantially higher chemical potential than the protons provided by ethanol itself, since no reductive feature is observed without the presence of hydrogen in this potential range, Fig. 1D. A higher chemical potential of the generated protons, or in other words, a higher acidity of the generated protons can potentially also lead to higher effective reactivity [17]. This effective reactivity of the generated protons can be assessed by comparing the anodic and cathodic peak current densities of the cyclic voltammogram under hydrogen atmosphere. Since the cathodic peak (-1.53 mA/cm^2) is at lower current density than the anodic peak (1.82 mA/cm^2), it indicates that the generated protons are reacting with the electrolyte salt or solvent instead of being reduced. This is also in line with the observation of liquid decomposition products that can be detected in the electrolyte after long-term experiments [18]. For example, it is known that THF can undergo cationic polymerization when initiated with strong proton acids [19,20]. The instability of the generated protons becomes even more apparent when LiClO_4 is replaced by LiBF_4 , where no reductive feature can be observed at all, see Fig. 1E. Here, the generated protons most likely immediately react with the BF_4^- anion to form HF and BF_3 according to Eq. (2), a reaction that is observed for most fluoride based anions [21,22].



2.2. Acidification of electrolyte

The formation of readily reducible protons through electrolyte oxidation, but also through hydrogen oxidation, at the anode, has important implications for LiMEAS experiments. First of all, the generation of protons at the anode can introduce non-steady-state conditions during ammonia synthesis experiments if they aren't neutralized by the deprotonated form of the proton source. This can for example be the case if substantial amounts of lithium metal are formed on the anode or if other parasitic decomposition reactions occur, which would lead to an acidification of the electrolyte. Using methyl orange as a colorimetric pH indicator solution, the used electrolyte was found to be more acidic compared to freshly prepared electrolyte (Fig. S6). Electrolyte acidification is also evident by the observation that synthesized ammonia can typically only be detected in the liquid electrolyte after an experiment and no NH_3 is recovered from the gas phase. Ammonia however is a volatile compound, with a Henry constant in water of 59 M bar^{-1} [23], and would be expected to evaporate, particularly if a high N_2 gas flow is used to saturate the electrochemical cell. To verify this, we spiked freshly prepared electrolyte with an ammonia containing solution of THF and purged it with an Ar gas flow for 45 min. As a result, the NH_3 was evaporated and could be recovered in a downstream water trap. On the other hand, if the same experiment is carried out with used electrolyte, the ammonia remains entirely in the liquid, see Fig. 1F and S5. The experimental details can be found in the Supporting Information. This indicates that the generated protons increase the acidity of the electrolyte over the course of the experiment such that NH_3 is protonated to form NH_4^+ ions, which do not evaporate into the gas phase. The acidification of the electrolyte by the anode reaction is therefore responsible that no NH_3 is lost through evaporation and accurate quantification can be performed by sampling the liquid electrolyte. It is

to be pointed out, that this however might not be the case for different cell geometries, where counter and working electrode are separated, or when the anode reaction is changed so that no acidic protons are generated. In addition, the effect of this acidification on ammonia synthesis rates can potentially be profound, as the acidity and concentration of the proton source are hypothesized to play a key role in enabling efficient LiMEAS [24].

Besides the protonation of synthesized ammonia, our CV measurements in the previous section also provide evidence for the protonation and subsequent decomposition of electrolyte components. This of course is in contrast to what would be required for a fully integrated steady-state LiMEAS system, where the generated protons should selectively recombine with the deprotonated form of the added proton source instead of with electrolyte components or with synthesized ammonia. In order to alleviate this issues and design a suitable electrolyte for a fully integrated steady-state LiMEAS, we believe it will be necessary to also provide a suitable proton acceptor in the electrolyte. As long as the proton acceptor is sufficiently stable in the electrolyte, this would result in a buffered system where protons can be effectively shuttled between working and counter electrode. Such proton acceptors should however be of high basicity, so that neither ammonia nor other electrolyte components are protonated. Moreover, the proton acceptors must not negatively affect the ammonia synthesis rate at the cathode, e.g. by altering the composition of the SEI. An added advantage of having a high basicity proton acceptor in the electrolyte would also be that the equilibrium potential for HOR is shifted to less oxidizing potentials compared to Li electroplating, which can potentially reduce the overall cell potential.

3. Conclusion

In summary, this study highlights the selectivity challenge encountered during proton generation for LiMEAS. We believe that further understanding of proton equilibria in non-aqueous electrolytes will play a crucial role in designing suitable electrolytes that allow for a fully integrated LiMEAS. In addition, the ability to precisely control proton activity in non-aqueous electrolytes can also open up new avenues for other reactions such as CO_2 reduction or organic electrosynthesis, where the proton chemical potential also plays an important role. The simple methodology based on cyclic voltammetry in hydrogen and Ar saturated electrolyte presented in this study, can give insight into the chemical potential but also into the stability of the protons in non-aqueous electrolytes. Applying this method to electrolytes typically used for LiMEAS, we uncovered the fate of anodically generated protons and showed that the interaction of protons with electrolyte components or ammonia itself must be considered when assessing the viability of the electrolyte for fully integrated LiMEAS. Based on the findings, we propose the addition of proton acceptors into the electrolyte in order to obtain a buffered system, which conceptually should provide a stable proton chemical potential and allow for effective shuttling of protons from the anode to the ammonia producing cathode.

Author contributions

KK ad JP contributed equally to the work, supervised by JK, PV and IC. All authors contributed to the editing of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.elecom.2021.107186>.

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