Recent Advances in Lithium Mediated Ammonia Synthesis

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Being one of the most indispensable feedstocks for the production of fertilizers, pharmaceuticals, and other valuable chemicals, developing a sustainable method to synthesize ammonia (NH_3) has drawn great interest from the scientific community. Currently, ammonia is produced predominantly through the Haber-Bosch process, in which, N_2 and H_2 gases are passed over an iron-based catalyst at high temperature (350-450 °C) and pressure (150-200 bar), requiring hefty capital investment for the centralized production.[1] This process of ammonia production annually consumes ~1% of the total global energy and is responsible for producing ~1.3% of the global CO_2 emission.[2] Hence, there is an obvious need to make ammonia production greener, by utilizing renewable energy sources, as well as decentralize the process to enable better distribution through smaller-scale devices.

This makes the electrochemical synthesis of ammonia, through the nitrogen reduction reaction (NRR), an attractive alternative as i) the electrical energy can be provided through renewable sources, such as wind or solar power,[3] ii) the harsh experimental conditions can be brought down to ambient scale,[4] iii) small scale synthesis can be actualized. Till today, numerous catalysts have been proposed and tested for electrochemical nitrogen reduction such as noble metals, metal oxides, metal sulfides, metal nitrides, boron and nitrogen-doped carbon, and lithium metal (Li). However, most of these catalysts suffer from low Faradaic efficiencies (FEs, often below 10%), low production rates of ammonia (~10^{-10} mol cm^{-2} s^{-1})[5], and lack of reproducibility. Recently, lithium mediated nitrogen reduction reaction (LiNRR) has been brought into the spotlight as one of the few reproducible methods for electrochemical ammonia synthesis which also has shown a potential to achieve higher faradaic efficiency compared to other methods.[6]

Li metal is capable of breaking the triple bond of dinitrogen under ambient conditions and forms lithium nitride (Li_3N). In a typical LiNRR setup, a lithium salt, e.g., lithium tetrafluoroborate ($LiBF_4$), is dissolved in an organic solvent, like tetrahydrofuran (THF), that serves as the electrolyte. It is hypothesized that Li^+ ions from the electrolyte get reduced to metallic lithium (Li^0) at the cathode and react with dinitrogen to form Li_3N at the solid
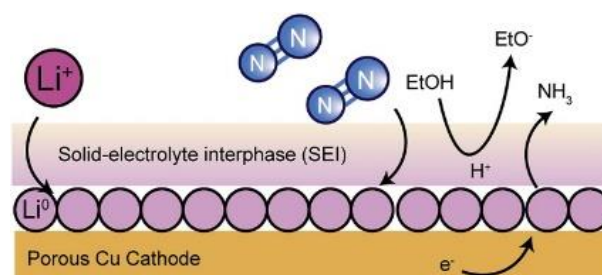

Fig. 1: Mechanistic model for electrochemical Li-mediated ammonia synthesis. Taken from reference 6.

electrolyte interface (SEI), which in the presence of a proton source (e.g., ethanol) generates NH_3 (Fig. 1). However, there are limitations to this process as well, such as irreversible oxidation of the organic solvent at the anode, use of sacrificial proton source (not fully regenerated), lower current density and FE than the target set by US Department of Energy (300 mA cm^{-2} and 90% respectively) for practical application of the process.[7] In the last few years, there have been several

significant progresses to address these issues, some of which have shown potential to reach the above-mentioned targeted values for practical application.

In 2021, Suryanto et. al. showed that by introducing a phosphonium-based salt, trihexyltetradecylphosphonium tris(pentafluoroethyl)trifluorophosphate ($[P_{6,6,6,14}]^+[eFAP]^-$), into the electrolyte it is indeed possible to mitigate the problem of the proton source being sacrificial as it acts as a recycling proton shuttle.[8] The proton carrier is the phosphonium cation, ($[P_{6,6,6,14}]^+$), in which the protons bonded to the α carbon (carbon directly bonded to the phosphorus center) get deprotonated generating a ylide (anion produced after deprotonation). Reversible deprotonation/protonation of this cation/ylide performs the proton shuttling during the NRR at the copper cathode.
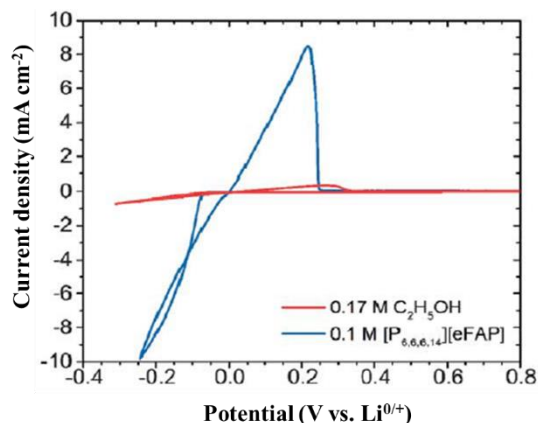

Fig. 2: Cyclic voltammetry with phosphonium salt (blue) and ethanol (red). Taken from reference 8.

The phosphonium salt was added to the electrolyte solution (LiBF$_4$ in THF) and the overall performance of the system was compared to the case where ethanol was used as the proton source. An almost ~20-fold higher current density rate at -0.25 V versus Li$^{0/+}$ was observed, as evident from the cyclic voltammogram (scan rate 20 mV s^{-1}) (Fig. 2).[8] To test the longer-term operation of the system dihydrogen was oxidized at a platinized titanium anode to serve as the required source of proton (instead of solvent oxidation) in a 20 h constant current experiment (-22.5 mA cm^{-2}). The average NH$_3$ yield rate obtained was 53±1 nmol s^{-1} cm^{-2} with a FE of 69±1%, both of which were notable improvements compared to the best reported values (30 nmol s^{-1} cm^{-2}, FE of ~35%)[9] at the time. Continuous operation of the system for 93 h demonstrated that only one-quarter of the $[P_{6,6,6,14}]^+$ was consumed, showing long-term stability of the proton shuttle for efficient Li mediated NH$_3$ synthesis.

In another remarkable work by Du et. al., by investigating the effect of electrolytes in Li mediated NH$_3$ synthesis, almost 100% current to ammonia efficiency (FE) was achieved very recently.[10] A high concentration of an imide-based lithium salt was used as the electrolyte (2 M lithium bis(trifluoromethylsulfonyl)imide LiNTf$_2$), which showed superior performance over other conventional electrolytes such as lithium perchlorate, tetrafluoroborate, triflate, etc. This enhanced performance was attributed to several factors, such as the formation of a much more compact ionic assembly layer at the
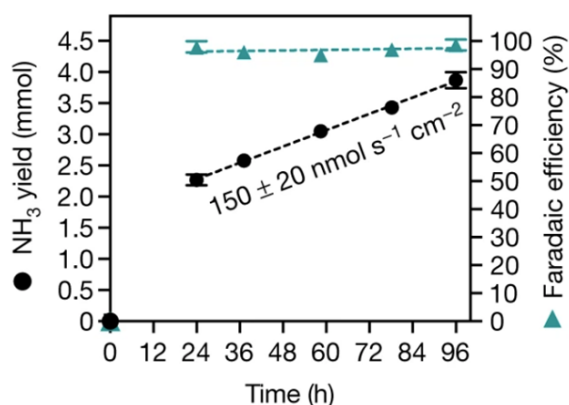

Fig. 3: Temporal evolution of the NH$_3$ yield Li-NRR faradaic efficiencies. Taken from reference 10.

electrode-electrolyte interface, minimal modification of the electrode surface through reductive degradation of the solvent and the electrolyte, resulting in a thin solid electrolyte interface (SEI), and high transference number of Li^+. In 96 h experiments (both continuous and interrupted) ammonia was produced with a FE of ~99% with a steady state NH_3 yield rate of 150 ± 20 nmol s^{-1} cm^{-2} after the current had stabilized at a very high value of 36 ± 12 mA cm^{-2} after 30 h (Fig. 3). As a preliminary demonstration of the scalability of the process, experiments with larger working electrode (active geometric surface area of 1.2 cm^2) were also performed, which showed FE of 90%. This further establishes the fact that achieving very high FE and ammonia yield rate through Li mediated pathway are fundamentally possible.

While these two works have demonstrated significant progress in terms of mitigating the issue of sacrificial proton source and achieving high FE through modification of the electrolyte, both were accomplished at high N_2 pressure (19.5 and 15 bar respectively) and in a batch-type electrochemical cell. Very recently, Fu and coworkers have actualized Li mediated N_2 reduction to ammonia (cathode) coupled with hydrogen oxidation reaction (HOR, anode) in a continuous-flow method under 1 bar of N_2 pressure.[11] A three-compartment continuous flow reactor was designed equipped with stainless steel cloth (SSC) based gas diffusion electrodes (GDE) positioned between the gas flow field and an electrolyte chamber as shown in Fig. 4. Nitrogen and hydrogen gases are directly fed into the GDE interface. A Platinum-Gold alloy was used as the catalyst on the SSC-based anode for HOR in organic solvent which showed long-term stability and superior performance compared to

Fig. 4: Expanded view of the continuous flow electrolyzer configuration. Taken from reference 11.

conventional Pt anode. 1 M $LiBF_4$ in THF with varying concentrations of EtOH was used as the electrolyte solution. Through operando mass spectrometry with Deuterium isotope studies on the system it was shown that as the experiment progressed, more and more D-containing products were formed, eventually producing fully deuterated ammonia (ND_3). This observation unambiguously proved that a coupled NRR and HOR was occurring and EtOH was acting as a proton shuttle. FE up to 67 ± 2% was achieved through this continuous flow method under 1 bar of N_2 pressure for the first time.
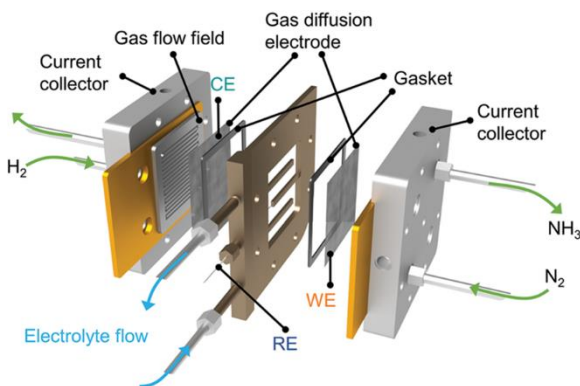
To summarize, three different limitations of lithium mediated ammonia synthesis were addressed in the discussed work providing solid foundation and guide for future exploration in the field. Though there still remain obstacles to overcome in terms of scaling up the synthesis, achieving high (>90%) FE in flow cell setup with high current density, these three works were indeed big steps forward in the path that can lead towards actualizing lithium mediated ammonia synthesis for real world applications.

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