Sustainable ammonia synthesis: Just around the corner?

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Li-mediated electrochemical synthesis of ammonia has been put forward as a possible alternative to the Haber-Bosch process, which is harmful to the environment and requires centralized operation. However, it has historically been plagued by low Faradaic efficiency, rate, and current density. In this issue of Joule, Chorkendorff and co-workers present a version of the process that meets certain industrial benchmarks and unveil new insights into the reaction kinetics along the way. Their observations are borne out by a recent study in Nature from MacFarlane and co-workers which also demonstrates extremely high Faradaic efficiency and high rates toward ammonia synthesis.

Life on Earth as we know it could not be sustained without artificial ammonia synthesis.[1] Ammonia is an essential fertilizer; without the ammonia currently produced from nitrogen and hydrogen in the Haber-Bosch process, approximately 3 billion people would starve.[1] However, the Haber-Bosch process comes with costly downsides. It requires high temperatures (350C–450C) and extreme pressures (150–200 bar), necessitating capital-intensive plants and continuous operation.[2] Perhaps more importantly in this era of extreme climate change, it is also responsible for more than 1% of global CO_2 emissions; as of 2020, 2.6 tons CO_2 were produced per ton of ammonia in the Haber-Bosch process.[3] Thus, it is vital that an alternative that can operate at milder conditions and make use of renewable energy sources is developed.

One such alternative—lithium-mediated nitrogen reduction (LiNR)—has been recently thrust into the spotlight, as it is one of the only reproducible methods of electrochemical ammonia synthesis.[4,5] LiNR operates at ambient temperature and ambient or near-ambient pressures. A typical LiNR setup consists of a Li salt dissolved in an aprotic ether solvent such as THF and a small amount of some proton donor such as ethanol, into which nitrogen is bubbled. Upon application of electrical potential to the electrochemical cell, Li metal—which can split the nitrogen triple bond at ambient conditions—is plated out onto the cathode surface. Li nitride is then formed, which reacts with the proton donor in solution to give ammonia, as shown in Figure 1.[6] However, until quite recently the process suffered from low Faradaic efficiencies (FEs; around 5%–20%) and current densities (1–20 mA s^{1} cm^{2}), rendering it impractical at industrial scales.[7] In this issue of Joule, Chorkendorff and co-workers[7] solve this problem by utilizing a highly porous Cu electrode and tuning their electrolyte solution to achieve nearly 100% FE and a current density of 1 A cm^{2}.[7] Their work, in conjunction with a very recent communication in Nature from MacFarlane and co-workers in which 100% FE was also achieved, offers a promising path forward for sustainable electrochemical ammonia synthesis.[8]

Chorkendorff and co-workers[7] began their study by performing a theoretical analysis on the components of the solid-electrolyte interphase (SEI): a layer of electrolyte breakdown products that coats Li metal in solution and thus controls the rate at which nitrogen, proton donors, and Li ions diffuse to the surface to react. They found that a LiF-enriched SEI would allow for more homogeneous transport of Li ions to the surface and thus increase the amount of charge that can go to ammonia formation rather than Li plating. Based on this analysis, they tested three different Li salts and found that, as expected, $LiBF_4$ resulted in the highest FE toward ammonia. They also utilized porous Cu rather than Cu foil on the cathode. This material, which was reported by the group in a previous publication,[9] has an electrochemical surface area of over 300 times its geometric surface area. This approach allowed the authors to demonstrate the highest geometric current density toward ammonia synthesis to date.

A highlight of this study is the analysis of the SEI both by materials characterization and thermodynamic analysis. The authors hypothesized that a thicker layer of LiF within the SEI would cause the rate of horizontal (parallel to the cathode) Li^+ diffusion (r_h) to increase and the rate of vertical (orthogonal to the cathode) Li^+ diffusion (r_v) to decrease, as represented in Figure 2. This in turn would result in slower, more homogeneous Li plating, preventing uncontrolled Li reduction and thick SEI growth. They then used depth-profiling X-ray photoelectron spectroscopy (XPS) to confirm their hypothesis that $LiBF_4$—which resulted in a higher FE toward ammonia—gives a

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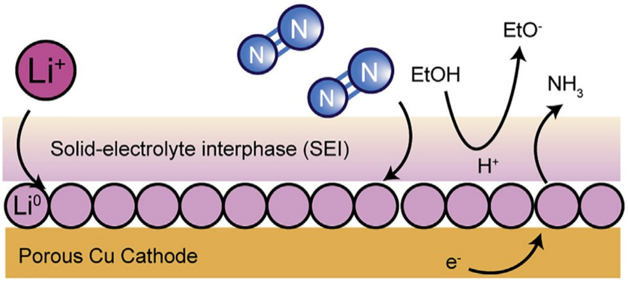

Figure 1. Mechanistic model for electrochemical Li-mediated ammonia synthesis

more LiF-enriched layer in the SEI than either of the other salts tested. Additionally, they showed that a more heavily inorganic (e.g., LiF-enriched) SEI traps less ammonia than a porous, organic SEI. This is an insight that will undoubtedly be useful when separation of ammonia in larger electrochemical settings becomes relevant.

The conclusions Chorkendorff and coworkers[7] drew from their studies are corroborated by a recent article in Nature from MacFarlane and co-workers.[8] This article also demonstrated LiNR at nearly 100% FE by utilizing a concentrated lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) electrolyte. Interestingly, their XPS studies also revealed LiF as one of the major SEI components and further found that thicker, uncontrolled Li deposition—which occurs at more negative overpotentials—was detrimental to ammonia production.

While these two papers together represent a key step forward for sustainable ammonia synthesis, many challenges remain before a practical LiNR system can be implemented. The system utilizes solvent oxidation as the anode reaction, which is unsustainable for continuous reactivity; however, this could conceivably be replaced with some appropriate oxidation reaction, such as hydrogen oxidation,[10] in a two-compartment cell in the future. Additionally, the difficulty of separating ammonia from the electrolyte and the high cost and safety issues associated with the use of both THF and hydrogen gas may prove a barrier to construction of small ammonia production sites. If these obstacles are overcome, sustainable ammonia synthesis could be just around the corner.

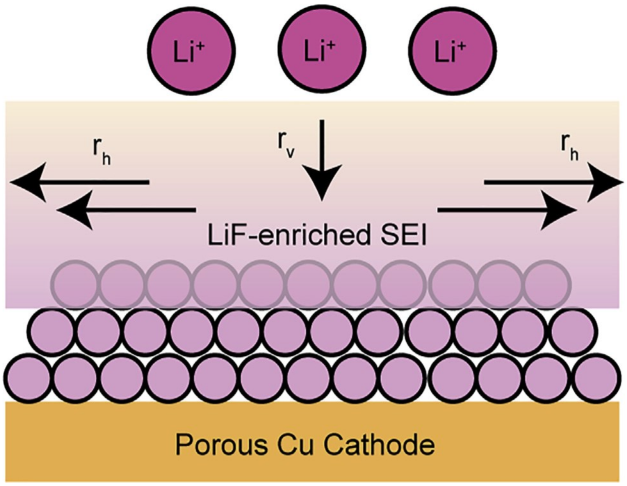

Figure 2. Representation of the effect of a fluoride-enriched SEI on Li^+ diffusion rate

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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Solid-electrolyte interphases enable efficient Li-mediated ammonia electrosynthesis

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The function and composition of solid-electrolyte interphases in lithium-mediated ammonia electrosynthesis are important yet largely unknown. Recently in Joule and Nature, Chorkendorff, Simonov, and their colleagues demonstrated that engineering the solid-electrolyte interphases is essential to boosting ammonia electrosynthesis up to a record-high rate and current efficiency.

As a landmark achievement in the modern chemical industry, the Haber-Bosch (H-B) process nowadays fixes around 150 million metric tons of atmospheric dinitrogen (N_2) annually into ammonia (NH_3),[1] accounting for 40% of the total N-nutrient circulated in the global nitrogen cycle.[2] Despite being highly energy-efficient, the traditional H-B process is becoming less and less suitable within the context of sustainability because the required hydrogen (H_2) reactant is derived from fossil fuels: either methane (via steam methane reforming) or coal. Operated under extremely harsh conditions (450C–550C and 250–350 bar) in centralized plants, the H-B process lacks the flexibility in economical deployment in smaller-scale facilities for the “distributed” NH_3 production—a long pursuit that aims to significantly bring down its transportation cost, especially for the less-developed regions of the world.

On that account, the electrochemical nitrogen reduction reaction (NRR) has been suggested as a promising alternative NH_3-producing process, since it does not rely on fossil-derived H_2. The past few years have witnessed a reckless “gold rush” on claiming a glut of electrocatalytic materials putatively active for aqueous NRR, but their performances are far from satisfactory due to sluggish NRR kinetics and the low N_2 solubility in aqueous electrolytes; more concerning is the validation of those subtle NRR activities as questioned by several individual reports.[3,4]

So far, this debate has led to a common recognition that currently only an indirect lithium (Li)-mediated approach (Figure 1) consistently manifests its validity in electrochemically reducing N_2 under varying conditions. In fact, Li is the only metal that is capable of cleaving the N h N bond under ambient conditions. This Li-mediated approach dates back to 1993 in the groundbreaking work by Sakata and colleagues.[5] As shown in Figure 1A, the three basic steps of Li-NRR can be brought together in the solid-electrolyte interphase (SEI) region of a single electrolytic cell in the presence of a Li^+-containing electrolyte, N_2 reactant, and a soluble proton carrier (HA). In traditional Li-ion batteries, SEI is a layer of material that forms between the negative electrode and the liquid electrolyte, and it is generated spontaneously by the breakdown of electrolyte compounds during the first few charging cycles under highly reducing potentials. SEI in those batteries provides the passivation of the negative electrode, inhibiting further electrolyte decomposition as well as suppressing the formation of lithium dendrites. A similar SEI may exist in Li-NRR system, but its composition and function are largely unknown.

In this issue of Joule, Chorkendorff and colleagues[6] reported an unprecedented NH_3 production rate of 2,500 nmol cm^{2} s^{1} with a current-to-NH_3 efficiency of 71% achieved with a stable SEI layer created by $LiBF_4$ electrolyte. Within the same month in Nature, Simonov and colleagues[7]

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