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EDITORIAL

A Decade of Electrochemical Ammonia Synthesis

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Racing to critical milestones is a favorite pastime of historical explorers and scientist. From the race to be the first to the North Pole to the discovery of the Haber−Bosch process, overcoming seemingly impossible goals often comes through persistent teams exploring creative solutions, while at the same time paying close attention to past failures. The race to develop electrochemical routes for ammonia synthesis is like these endeavors, as the path to the pole is long, not clear, and at times treacherous.

Over the past decade, researchers have made significant progress in improving electrochemical ammonia synthesis.[1] One critical challenge identified early was inaccurate product analyses. The low levels of ammonia reported were often in the same range as sources of lab-based adventitious ammonia and NOx.[2] This provided researchers several challenges with respect to identifying the true activity of a given catalyst. Thus, mitigating nitrogen contamination emerged as the critical problem to resolve within the field.[3,4]

Various research groups have converged on several suggested ammonia measurement methods which, if employed, can aid in ruling out contamination. Suggested controls which employ the use of isotopically labeled nitrogen gas and quantitative nuclear magnetic resonance spectroscopy allow researchers to discern adventitious nitrogen ($^{14}N_2$) from isotopically labeled nitrogen ($^{15}N_2$).[5] Beyond improving low-level ammonia measurements, movement toward operating conditions which increase ammonia yield well beyond the adventitious ammonia levels is also ideal. Specifically, moving to conditions where the $m_{product} \gg m_{system}$ and $C_{NH_3} > 100$ ppm is an important threshold identified which can provide confidence in each measurement.[6]

Interestingly, low ammonia levels and false positives are not a new occurrence. In fact, there are many cautionary tales within published scientific literature discussing this issue. For instance, the first observation of electrochemical N_2 fixation, in 1807, was later proven non-reproducible 90 years later,[7,8] and there were several passionate discussions on this subject which were published in the 1990s.[9−12]

Despite this setback, with solutions available for low-level ammonia measurements, there has been a significant growth in research centered around both aqueous-phase and non-aqueous-based electrocatalytic and photocatalytic systems.[13−15] Suppressing the hydrogen evolution reaction remains the critical bottleneck for aqueous-based catalytic systems. For these reasons, non-aqueous and lithium-mediated electrocatalytic approaches have emerged as the most likely routes to achieve technology-significant targets in terms of rate of production (current density) and product selectivity (Faradaic efficiency).[16]

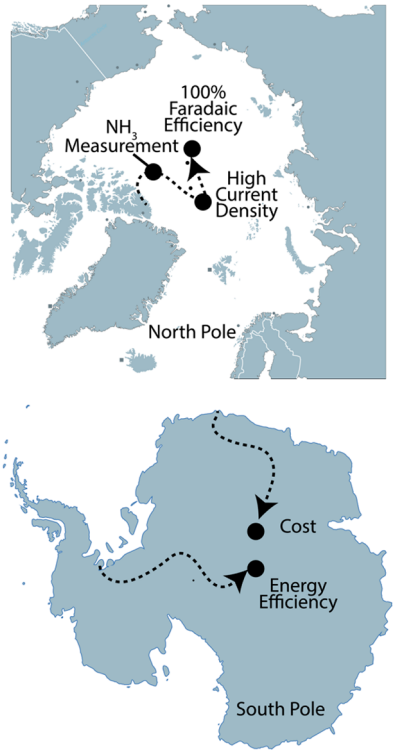

Figure 1. With electrosynthesis of ammonia reaching 100% Faradaic efficiency, will the next milestone be related to energy efficiency and cost?

Lithium-mediated nitrogen reduction (LiNR) most recently showed low Faradaic efficiencies (FE < 20%) and current densities ($I < 20$ mA cm^{-2}).[17,18] While significant, these values were well below the U.S. Department of Energy's feasibility

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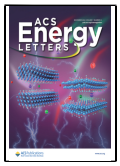

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targets (e.g., I = 300 mA cm^{-2} and FE = 90%). However, recent research findings by Simonov, MacFarlane, and colleagues and Chorkendorff and colleagues have for the first time demonstrated Faradaic efficiencies which approach 100% (Figure 1, top).[19] MacFarlane and Simonov and colleagues were able to suppress electrolyte decomposition through tuning the local physicochemical properties of the electrode−electrolyte interface with an imide-based lithium-salt electrolyte. Likewise, Chorkendorff and colleagues showed this is also possible through the use of a highly porous Cu electrode, at elevated current density (−1 A $cm_{geo\text{-}2}$).[20] This is the first demonstration of the lithium-mediated nitrogen reduction reaction at industrially relevant current densities.

With these impressive metrics, the field has undoubtedly reached a significant milestone, and in a sense has reached a "North Pole"-like discovery. With the "North Pole" in the rear-view mirror, eyes now are set on the "South Pole" (Figure 1, bottom). For ammonia electrosynthesis to compete with the Haber−Bosch process, significant work is needed to improve the energy efficiency, and several questions remain regarding the technoeconomics.[21] Furthermore, with growing materials criticality issues, will lithium remain a viable substrate, or will other materials emerge? I look forward to the next decade of electrochemical ammonia synthesis.

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Notes

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