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# Developing an understanding of dynamic SEI formation during electrochemical N<sub>2</sub> reduction via combined, time-resolved in situ neutron reflectometry and X-ray diffraction

The production of ammonia-based fertilizers is essential to supporting the food supply for an increasing global population. However, the industrial production of ammonia proceeds via the highly resource- and energy-intensive Haber-Bosch process, consuming more than 1% of the global energy supply and releasing more than 450 million metric tons of CO<sub>2</sub> per year. One proposed alternative to this process is the electrochemical reduction of nitrogen (eN<sub>2</sub>R) to NH<sub>3</sub>, which would enable point-of-use NH<sub>3</sub> production at ambient temperatures and pressures. Non-aqueous, Li-mediated electrochemical nitrogen reduction reaction (Li-NRR) systems are particularly promising, as limiting proton availability has been demonstrated to significantly increase selectivity toward NH<sub>3</sub> relative to aqueous systems. In particular, cycling the current driving the reaction between open-circuit conditions and periods of applied current density has been shown to significantly improve Li-NRR performance. However, our understanding of the dynamic Li-plating and solid electrolyte interphase (SEI) processes under such conditions and their relation to Faradaic efficiency toward NH<sub>3</sub> (FENH<sub>3</sub>) remains limited and difficult to achieve due to the reactivity of Li-containing materials, which renders ex situ characterization unrepresentative of the electrode surface during electrochemistry, and the amorphous nature of certain SEI species.

In this talk, I will discuss our investigation of the dynamics of the electrode-electrolyte interface under Li-NRR conditions during current cycling using in situ time-resolved neutron reflectometry and grazing-incidence synchrotron X-ray diffraction. During cycling, measured neutron reflectivity curves indicated bilayer formation in which Li-containing species such as LiOH, Li<sub>2</sub>O, and small quantities of Li<sub>3</sub>N and metallic Li primarily appeared in a thin layer at the cathode surface, above which formed a much larger, porous, 'solid-electrolyte interface' (SEI) layer. Upon return to open-circuit conditions, Li-containing species quickly moved out of the thin layer, leaving a compact, stable layer of decomposition products underneath the SEI layer. This SEI layer concomitantly filled with electrolyte or dissolved, becoming indistinguishable from the electrolyte. These time-resolved observations of SEI and plated layers during current cycling suggest that benefits associated with return to open-circuit conditions between periods of applied current density may be related to the concomitant loss of Li-containing species from a thin layer at the cathode surface into a porous SEI layer that becomes filled with electrolyte or dissolves. Ultimately, this interface was found to be highly dynamic, and a combination of in situ techniques will be required to continue to unravel the complexities associated with SEI formation during Li-NRR.

## Topic

Energy Transfer

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