Characterization and Quantification of Solid Electrolyte Interphases for Composition-Functionality Relationships at Lithium Metal Electrodes

By

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Lithium (Li) has the lowest electrochemical reduction potential and density of any metal, making it an exceptionally desirable anode material for batteries and a powerful chemical reductant. However, the reducing nature which makes Li so useful brings challenges: it is thermodynamically unstable in practical liquid electrolytes, driving the formation of a passivation film called the solid electrolyte interphase (SEI). The SEI mediates transport and reactivity at the Li surface, and in practical systems it both consumes active Li directly and leads to spatial heterogeneity in fluxes to and from the lithium surface, resulting in inefficiency in plating and stripping. Together, these effects make the SEI the most important factor determining the efficiency of Li electrochemistry, but its nanoscale, heterogeneous, and reactive nature make it extremely challenging to study experimentally. As a result, existing understanding of the impact of composition and structure on SEI functionality is limited. This thesis aims to enhance conceptual understanding in this space, combining multimodal characterization, the design and application of informative model systems, and the quantification of key phases to reveal mechanistic insights that advance understanding of composition-functionality relationships at Li interfaces.

To begin, this work focuses on the role of the SEI in Li-mediated electrochemical ammonia synthesis (LiMEAS), one of the most promising electrochemical pathways for nitrogen fixation. Here, quantification of major side products, multiscale imaging, and spectroscopic analysis were conducted methodically in four model systems, which introduced the presence of nitrogen gas and a proton donor separately. This study revealed that the electrolyte-derived SEI inhibits reactivity between Li and nitrogen, and that the proton donor is needed to disrupt this passivating interphase.

Next, focus shifted to Li metal battery anodes. Lithium carbonate has long been considered beneficial in anode SEI, but the field has lacked a mechanistic explanation for its effects. Here, lithium carbonate was studied through the development of two model systems, a model SEI formed by sequentially reacting oxygen and carbon dioxide with metallic lithium, and Li-Cu half cells saturated with either Ar or carbon dioxide. Through electrochemical impedance analysis on the model SEI, lithium carbonate was found to exhibit elevated conductivity compared to other common inorganic SEI materials. Cycling and subsequent titration analysis of Li-Cu cells revealed that carbon dioxide addition led to less inactive lithium formation during cycling, and that this avoided capacity loss was the driver behind increased Coulombic efficiency (CE) in numerous electrolytes.

Finally, an analysis was conducted to decipher unresolved materials in a set of techniques for the quantitative analysis of Li anode Coulombic inefficiencies. These techniques directly quantify capacity losses from formation of inactive lithium and several SEI materials, but lack the ability to delineate between residuals lost during cycling or sample processing, and SEI materials not yet resolvable by quantitative techniques. Here, a set of measurements was developed to explicitly measure material losses during sample processing steps. This work confirmed that

material losses do not alter broader trends between electrolytes, but revealed the uncertainty in specific material quantities.

Together, these studies illustrate a multimodal approach for deriving mechanistic insights into the relationships between SEI composition and electrode performance at Li metal electrodes. As part of a broader research movement toward accessing increasingly refined insights into the function of Li metal SEI, this work contributes to demystifying the role of SEI materials in two distinct Li electrochemical systems and improves the resolution of quantitative analysis techniques for identifying capacity losses at Li electrodes.

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