Electrochemomechanics of solid electrolytes and critical currents

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Doped $Li_7La_3Zn_2O_{12}$ (LLZO) garnet has electrochemical stability and mechanical properties that make it promising for all solid-state batteries [1-3]. Although LLZO has shown long cycle life in low-current scenarios, dendrite nucleation occurs above a critical current [4], which restricts operating power below the range needed for many practical applications. LLZO is stiff enough to prevent dendrite nucleation due to morphological instability of the plane interface with lithium, so the mechanism of dendrite nucleation in LLZO remains to be established. This presentation develops a novel theory of dendrite nucleation that proves to be quantitatively consistent with a variety of independent experiments. We also provide a theoretical platform to guide the development of new all-solid-state battery prototypes.

Both theoretical research [5] and experimental observation [6] have drawn attention to the space-charge layers that develop in solid electrolytes near metal interfaces, and the importance of these layers in battery performance. Braun et al. [7] highlighted the impact of deformation stress within space-charge layers near biased blocking electrodes. For scenarios involving Faradaic currents, as well as interfacial screening, a clear picture of space-charge layers, especially the associated stress profile, is still missing. We fill this gap, providing comprehensive information about the complex electrochemical-mechanical environment at the lithium/solid electrolyte interface where dendrites initiate.

Newman's concentrated solution theory has been generalized [8] to form a dynamic electro-chemomechanical model of solid electrolytes. Inclusion of Poisson's equation releases Newman's local electroneutrality constraint. Thermodynamic driving forces, such as ion concentration, voltage, or pressure gradient, are related to current flow via Onsager–Stefan–Maxwell multicomponent diffusion theory. A momentum balance couples the mechanical, electrical, and electrochemical processes. This framework is applied to model the steady responses of galvanostatically polarized Li/LLZO/Li cells, including stress effects.

Deformation stress is found to have a profound impact on Li-ion concentration and voltage profiles in the space-charge layers. This discovery points to a novel mechanism of dendrite nucleation, which can be described by a formula for critical currents that connects several practically measurable properties, e.g., interfacial impedance, grain size, and ionic conductivity. Reducing interfacial resistance is shown to raise the critical current by tuning the balance of stresses caused by surface charges (tensile) and faradic currents (compressive). The temperature dependence of critical currents is compared with present experimental results quantitatively. Impacts of grain size on durability are also rationalized by the theory.

References:

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