LITHIUM-ION BATTERIES

Mapping charge-transfer landscapes

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Charge transfer is ubiquitous in lithium (Li)-ion battery operations. The most fundamental charge-transfer reactions at a Li metal anode involve the dissolution of Li ions into an electrolyte and the deposition of Li atoms, produced from electrolyte decomposition, onto the anode, commonly known as Li stripping and plating, respectively. These processes, along with the solid-electrolyte interface (SEI) that forms in situ, govern the battery performance. Despite their importance, fundamental understanding of these processes is difficult to acquire from experiments. There are also challenges for computational approaches, because the size of the SEI is often larger than what a typical quantum calculation affords and it is nontrivial to implement electrochemical potentials in modelling. Now, Yunsong Li and Yue Qi at Michigan State University have developed a Li/SEI/electrolyte half-cell model, and using combined density functional theory and tight-binding methods they are able to obtain the charge-transfer and energy profile across the interface.

The calculation produces detailed charge variations across the half-cell during Li stripping and plating. To understand the kinetics of these charge-transfer processes, the researchers investigated two ion transport paths — Li ions moving from the electrolyte to the SEI and their diffusion in the SEI. In the former case, the activation energy for Li ion desolvation is found to be strongly dependent on the electric potential exerted by the charged electrode surface. In contrast, the Li ion diffusion through the SEI is found to be mainly determined by the crystalline formation energy of Li ions in the SEI. The overall energy profile across the interface allowed the researchers to derive the charge-transfer coefficient in the well-known Butler–Volmer equation that governs the battery kinetics. The obtained charge-transfer coefficient is in broad agreement with experimental measurements.

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