Understanding Ionic Transport in Energy Storage Devices

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Major challenges persist in the prediction of thermodynamic and kinetic properties of technologically important materials starting from the basic laws of Thermally activated atomic physics. processes often play a crucial role, especially in electrochemical energy storage devices. Any first-principles study of relevant materials properties in energy storage devices must rigorously account for temperature and entropy, requiring the use of statistical mechanical techniques to predict finite temperature phase stability, non-dilute diffusion and phase transformation mechanisms. These techniques have proven invaluable in shedding light on key materials processes in electrode materials for Li-ion batteries. In this talk, I will describe how modern statistical mechanical approaches can be used to explore and predict complex kinetic mechanisms in the next generation of energy storage devices.

Li ion batteries are an example of energy storage devices that rely on the shuttling of an ion between anode and cathode separated by an electronically insulating but ionically conducting electrolyte. The voltage profile of such a device is a purely thermodynamic property determined by the chemical potential difference of the shuttled ion between cathode and anode. Each charge and discharge cycle requires large variations of the electrode concentrations, which often results in phase transformations within the electrode materials. The electrode materials of most Li-ion batteries currently used and explored are intercalation compounds, made up of a crystalline host structure that can accommodate large variations in Li concentrations over interstitial sites. The rate of charge and discharge is in large part determined by the ion mobility within these host crystal structures, as well as the rate with which phase transformations can occur as the Li concentration is varied.

First-principles statistical mechanical approaches are now capable of predicting key electronic, thermodynamic and kinetic properties of Li-electrode materials. These types of approaches have been especially useful in elucidating the role of chemistry and crystal structure on Li mobility as a function of Li concentration in intercalation compounds. Experimental measurements of Li diffusion coefficients in electrode materials verv difficult and unreliable. are First-principles approaches, on the other hand, relying on effective Hamiltonians and kinetic Monte Carlo simulations evaluate to Kubo-Green expressions, have proven invaluable in predicting Li diffusion coefficients in technologically relevant electrode materials in the non-dilute limit. These theoretical studies have shown that crystal structure causes distinct concentration dependencies of Li diffusion coefficients and predict that Li diffusion in many two-dimensional lavered and three dimensional cubic electrode materials is mediated by divacancies and triple-vacancies.



Figure 1: Most Li batteries rely on intercalation compounds that can accommodate Li in interstitial sites. Variations in Li concentration during charge and discharge are often accompanied by phase transformations.



Figure 2: First-principles statistical mechanical approaches have provided crucial insight about the mechanisms of Li diffusion within different intercalation compounds, showing that crystal structure can play an important role in determining the concentration dependence of the Li diffusion coefficient.