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Defect Thermodynamics and Diffusion Mechanisms in Li_2CO_3 and Implications for the Solid Electrolyte Interphase in Li-Ion Batteries

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Abstract

Understanding and improving Li transport through crystalline Li_2CO_3, a stable component of the solid electrolyte interphase (SEI) films in Li-ion batteries, is critical to battery rate performance, capacity drop and power loss. Identification of the dominant diffusion carriers and their diffusion pathways in SEI films coated on anode and cathode surfaces is a necessary step towards the development of methods to increase Li conductivity. Therefore, we first predicted the dominant Li diffusion carriers in Li_2CO_3 over a voltage range (0 to 4.4V) by computing and comparing all seven Li-associated point defect thermodynamics with density functional theory (DFT). The main diffusion carriers in Li_2CO_3 below 0.98V are excess Li ion interstitials (Li_i^+), however, above 3.98V, Li ion vacancies (V_{Li}^-) become the dominant diffusion carrier type; and they have the same concentration in the voltage range of 0.98~3.98V. While the V_{Li}^- diffuses through *direct hopping*, the Li_i^+ diffuses by *knocking off* the Li^+ ion from a lattice. Although most Li_i^+ and V_{Li}^- diffuse independently, they can form a Li Frenkel pair with correlated diffusion when their distance is close to 3~5Å on the same (100) plane. Based on the concentration and diffusion barriers, the Li conductivity in Li_2CO_3 is mapped as a function of battery voltage and it is found to vary by ~7 orders of magnitude. Since the diffusion is limited by the concentration of diffusion carriers, various dopants were suggest to increasing the concentration of the main diffusion carriers (at different voltages) in order to enhance Li transport through Li_2CO_3 (and SEI) and improve battery rate performance. A possible mechanism is also proposed to explain electron leakage through an SEI film into the electrolyte by the diffusion of Li_i^0 interstitials, which can exist at low voltage. The methods employed in this study can be generalized to other solid electrolyte or Li ionic conductors.