

First-Principles Study of the Influence of a Coherent Grain Boundary in Cathode Material LiCoO₂ on the Li-ion Battery Properties

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In all-solid-state LIBs, the liquid electrolyte is replaced by an inorganic Li-ion conducting solid. In these devices, solid-solid interfaces, specifically those between cathode and electrolyte, electrolyte and anode, and grain boundaries within each component, are expected to strongly affect battery performance. In this study, we report the structure and properties of a high-symmetry grain boundary of LiCoO₂, based on a combination of state-of-the-art experimental and theoretical techniques, namely scanning transmission electron microscopy and first-principles calculations. A high-symmetry twin boundary was observed in LiCoO₂ thin films (Fig. 1). The optimized twin structure from first-principles calculations is shown in Fig. 1b, and is in excellent agreement with the experimentally observed structure in Fig. 1a. Based on the identification of the zone axes of the two crystals and the interface plane from selected area electron diffraction patterns, the twin boundary was identified as being a near- $\Sigma 2$ $(1\bar{1}04) [\bar{1}\bar{1}20]_1 / (\bar{1}104) [11\bar{2}0]_2 \theta = 180^\circ$ twist boundary [1]. As LiCoO₂ is a 2D Li-ion conductor (with Li-ion hopping only possible parallel to the basal (0001) plane), to characterize Li-ion migration near the interface we need to consider Li migration in two directions, viz., across (oblique to) and along (parallel to) the twin boundary plane. Results of these calculations are plotted in Fig. 2. For the double-vacancy mechanism, which is likely the dominant mechanism for Li migration in LiCoO₂ in real battery systems, Li migration along the twin boundary has an activation energy, E_a , of 0.20 eV smaller than that in the bulk, while E_a for Li migration across the twin boundary is 0.40 eV. Noting that an activation energy difference of 0.20 eV corresponds to a change in diffusion constant of three orders of magnitude at the normal operating temperature of an LIB, even the highly symmetrical and coherent boundary studied here will have a significant impact on Li transport in LiCoO₂, and this effect will depend strongly on the orientation of the interface relative to the direction of the applied voltage. Assuming that more general boundaries with greater structural distortion are even less amenable to Li-ion transport than the high-coincidence, low-distortion $\Sigma 2$ twin boundary examined here, the presence of grain boundaries can be expected to severely impede the two dimensional diffusion of Li ions in LiCoO₂. The presence of internal interfaces is thus expected to have a noticeably detrimental effect on the charge-discharge rates of all-solid-state LIBs.

Reference

[1] H. Moriwake, et al., Adv. Mater., 25 (2013) 618.

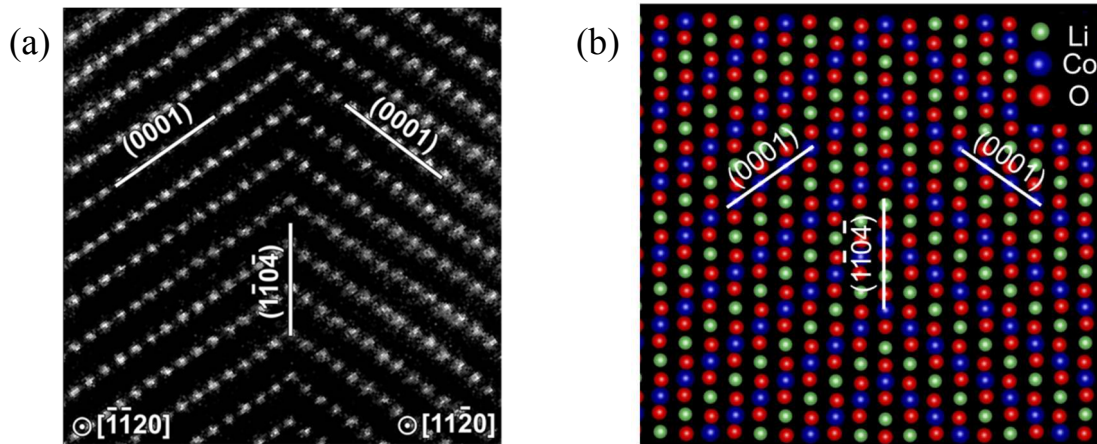


Fig. 1 Structure of a twin boundary in LiCoO_2 . (a) HAADF STEM image with bright spots corresponding to columns of Co atoms; (b) the stable structure obtained from DFT+ U calculations.

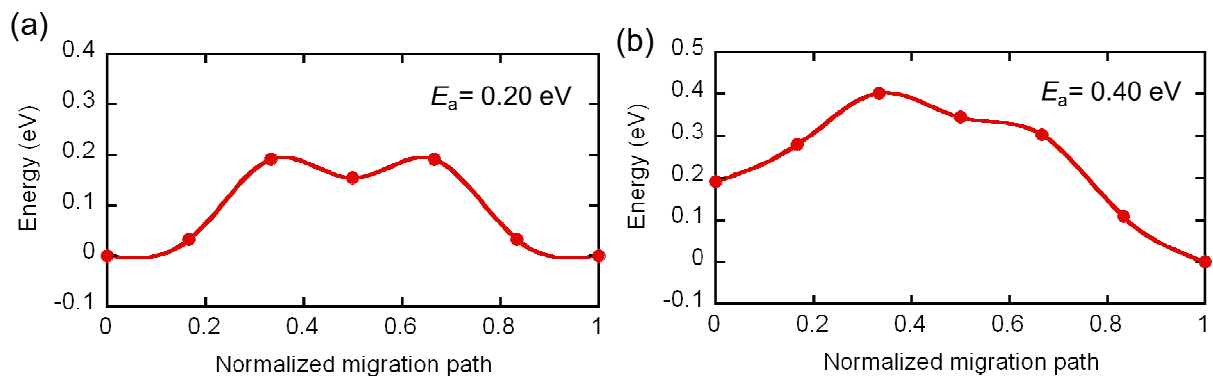


Fig. 2 Calculated potential surface for Li migration by the double-vacancy mechanism: (a) along the twin boundary; and (b) across the twin boundary. Li migration along the twin boundary has an activation energy, E_a , of 0.20 eV, while Li migration across the twin boundary has a higher E_a of 0.40 eV. An activation energy difference of about 0.20 eV corresponds to a diffusion constant difference of three orders of magnitude at normal operating temperature. Li migration across grain boundaries is expected to have a significant detrimental effect on the charge/discharge rates of all-solid-state LIBs.