

Atomic-Level Characterization of Interfaces in LiCoO_2
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Cathode materials for conventional lithium ion batteries are typically prepared in nanocrystalline form to minimize transport distances and maximize electrolyte-electrode contact. For all-solid-state batteries, which are drawing significant interest as a next-generation of battery technology, electrodes are deposited as thin films [1]. In both cases, the structures of surfaces and particle morphologies and sizes strongly influence charge/mass transfer kinetics, affecting cell performance, particularly its cyclability and lifetime.

Many different materials have been proposed as cathode materials with improved energy densities, power densities and lifetimes. Layer-structured LiCoO_2 , despite its drawbacks, however, remains the most widely used, and as the prototypical cathode material an understanding of the structures of interfaces and the processes operating at a fundamental level is required if its properties are to be optimized.

One of the most powerful means of probing materials on the atomic level is the use of atomistic computer simulations [2]. Such simulations can provide detailed insights into transport phenomena, as well as the nature and constitution of defects at interfaces such as surfaces [3,4], grain boundaries [5,6], and domain boundaries [7] and. These atomic level simulations typically consist of either classical forcefield models or more detailed but computationally expensive first-principles calculations based on density functional theory (DFT) [8]. When possible it is useful to compare the results with structures observed using the advanced scanning transmission electron microscopy (STEM) [9], together with chemical information from electron energy loss spectroscopy and associated methods. Direct comparison is now possible thanks to the development of annular bright field detectors used in aberration-corrected STEMs that allow even the lightest elements to be visualized with sub-angstrom resolution in real time [10].

Atomistic simulations allow a detailed examination of the relative stabilities, coordination environments, and defect formation energetics. A common feature of the LiCoO_2 [3] and other related materials [11] is that cation antisite defects are readily formed in each case; initially predicted and quantified by computational methods, such defects have since been confirmed experimentally, and have been implicated in the degradation of cathode performance with cycling [11]. To date, only a few interfaces have been examined in such detail, including near- $\Sigma 2$ $(1\bar{1}0\bar{4})/[4\bar{4}0\bar{1}]$ $\theta=180^\circ$ twist grain boundaries (Fig. 1) and $(1\bar{1}00)$ antiphase inversion domain boundaries (Fig. 2) in LiCoO_2 . Typically the results of DFT calculations show excellent agreement with observed structures, at least for high-symmetry cases.

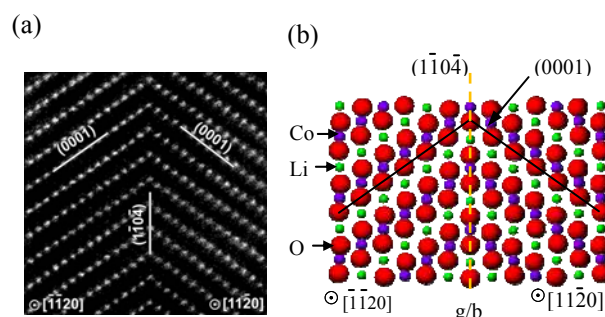
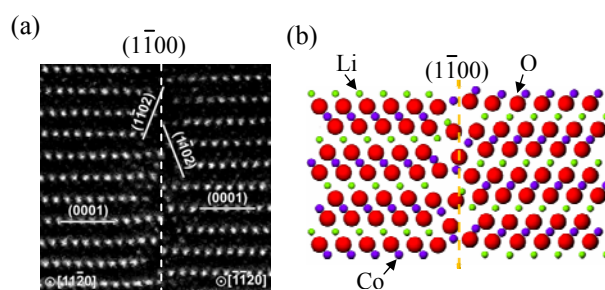


Figure 1. (a) HAADF-STEM micrograph of a twin boundary in polycrystalline LiCoO_2 ; (b) Calculated structure of a near- $\Sigma 2$ $(1\bar{1}0\bar{4})/[4\bar{4}0\bar{1}]$ $\theta=180^\circ$ twist grain boundary in LiCoO_2 using VASP [5].

Figure 2. Structure of antiphase inversion domain



boundary in epitaxial LiCoO_2 : (a) high-angle annular dark field STEM image showing Co ions only; (b) structure obtained from DFT calculations using VASP [5].

Although the study of interfaces in battery systems at the atomic level is still in its infancy, in this paper we will report on our recent progress in this area, with emphasis on the effects of interfaces on battery materials properties, particularly lithium-ion transport, based on a combination of computational and experimental results.

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