

# Phase-Field Modeling of Li Intercalation in Polycrystalline LiCoO<sub>2</sub>

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Li transition metal oxides are widely used as active materials for the positive electrode of Li-ion rechargeable batteries where intercalation of Li in the metal oxide is a fundamental phenomenon that determines the performance of the batteries. The intercalation process is significantly affected by the phase transition, the crystal anisotropy, and grain boundaries as shown in Fig. 1. Therefore, to improve the batteries, we believe that thorough understanding of the intercalation process on the nanometer length scale is essential.

To this end, we constructed a phase-field model [1] describing the diffusion of Li and the phase changes in polycrystalline Li<sub>x</sub>CoO<sub>2</sub>, as shown in Fig. 2. This model was based on formulation of thermodynamic energy functions. The Butler-Volmer equation was incorporated into this model to describe a charge-transfer reaction occurring across the Li<sub>x</sub>CoO<sub>2</sub>-electrolyte interface. The potential distribution in Li<sub>x</sub>CoO<sub>2</sub> and electrolyte, and the mass transport of Li ions in the electrolyte were calculated by using the conventional formulation. The thermodynamic parameters in the Gibbs energy functions of the individual phases in the Li<sub>x</sub>CoO<sub>2</sub> system were assessed, and a two-sublattice model [2] was adopted for the Li-vacancy ordered phase. The interaction parameter was determined so as to reproduce the formation entropy ( $\Delta H$ ) estimated from the first-principles calculations given in [3, 4]. An accuracy of the present simulation was verified via the comparison of the calculated equilibrium potential of Li, ( $U_{\text{LiCoO}_2}$ ) with the experimental result [5] as shown in Fig 3. The mean deviation is approximately 0.2 V. The major source of error may be lack of precise data for CoO<sub>2</sub>. On the other hand, the calculation has a sufficient accuracy about the partial derivative of the  $U_{\text{LiCoO}_2}$  with respect to the Li concentration, which validates the simulation of the Li diffusion in Li<sub>x</sub>CoO<sub>2</sub>.

We employed the phase-field model combined with the electrochemical model to study Li transport process in solid phase during a constant current discharge. Figure 4 shows Li concentration in polycrystalline Li<sub>x</sub>CoO<sub>2</sub>. The simulation results demonstrated that the discharge property is affected by the microstructure in material such as the crystallographic texture and crystallite size. When the angle  $\theta$  between the crystallite *c*-axis and the tangent line of the interface is large, Li segregation is increased. We also confirmed that the discharge properties were notably affected by the diffusivity at the grain boundary. Moreover, the rate-determining step may change from the internal diffusion to the surface reaction when the surface reaction resistance increases. Therefore, the balance of these rate-determining steps is crucial for the Li transport. Comparing the simulation results with the experimentally measured quantities that represent consequences of the multi-step process, leads to a quantitative understanding of each elemental step in the Li transport process.

## References

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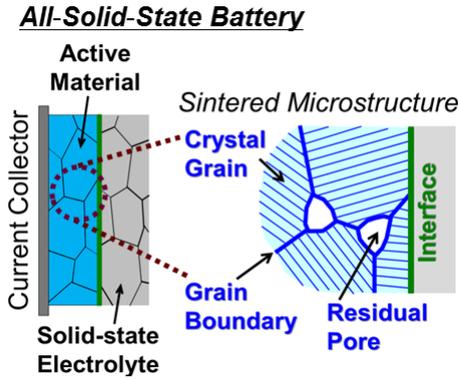


FIG. 1. Schematic illustration of microstructural characteristics treated in this simulation.

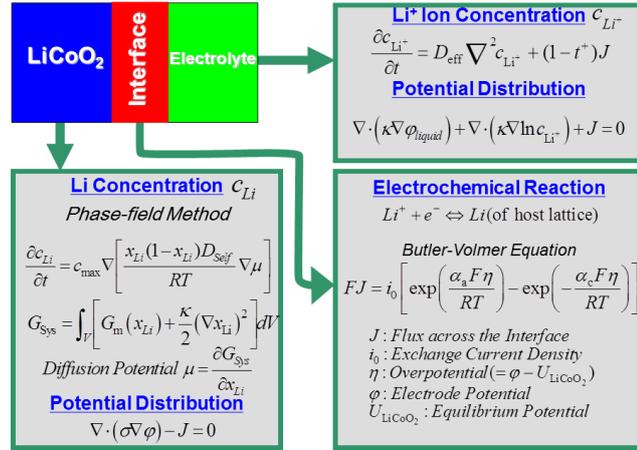


FIG. 2. Modelling of Li intercalation process.

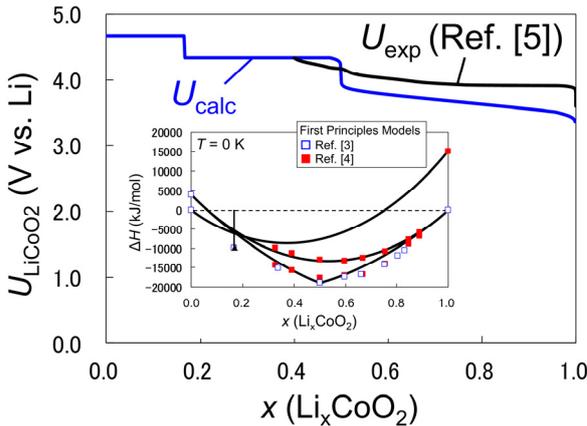


FIG. 3. Calculated equilibrium potential of  $LiCoO_2$ .

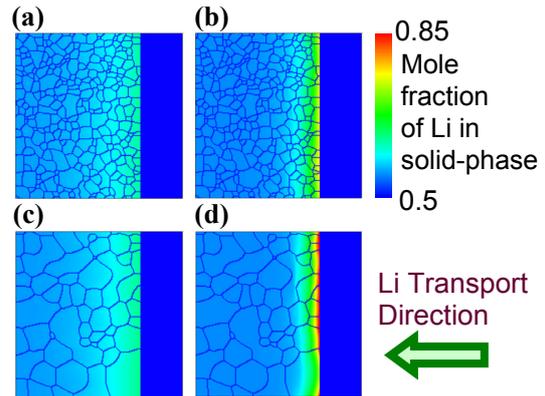


FIG. 4. Li concentration in each grain during a constant current discharge. The electrolyte nearby  $LiCoO_2$  is represented by a blue thin layer. The grains are oriented with their *c*-axis perpendicular to Li transport direction in (a) and (c) and parallel to that in (b) and (d).