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The effect of surface-bulk potential difference on the kinetics of intercalation in core-shell active cathode particles

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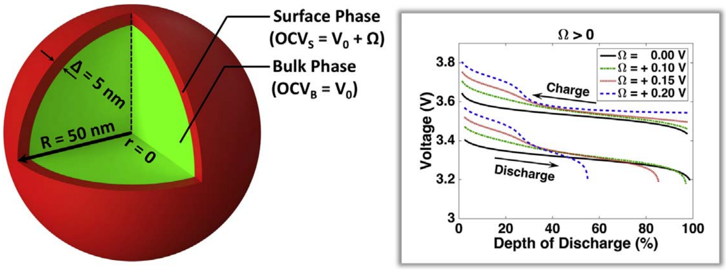
HIGHLIGHTS

- A model is developed to simulate the (dis)charge of core-shell cathode particles.
- The effect of surface-bulk OCV difference on the intercalation kinetics is studied.
- A charge/discharge asymmetry is observed in the galvanostatic voltage profiles.
- The accessible capacity of the particle is reduced due to transport limitations.
- Our findings shed light on the electrochemical behavior of hybrid cathode particles.

GRAPHICAL ABSTRACT



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ABSTRACT

Surface modification of active cathode particles is commonly observed in battery research as either a surface phase evolving during the cycling process, or intentionally engineered to improve capacity retention, rate capability, and/or thermal stability of the cathode material. Here, a continuum-scale model is developed to simulate the galvanostatic charge/discharge of a cathode particle with core-shell heterostructure. The particle is assumed to be comprised of a core material encapsulated by a thin layer of a second phase that has a different open-circuit voltage. The effect of the potential difference between the surface and bulk phases (Ω) on the kinetics of lithium intercalation and the galvanostatic charge/discharge profiles is studied at different values of Ω, C-rates, and exchange current densities. The difference between the Li chemical potential in the surface and bulk phases of the cathode particle results in a concentration difference between these two phases. This leads to a charge/discharge asymmetry in the galvanostatic voltage profiles, causing a decrease in the accessible capacity of the particle. These effects are more significant at higher magnitudes of surface-bulk potential difference. The proposed model provides detailed insight into the kinetics and voltage behavior of the intercalation/de-intercalation processes in core-shell heterostructure cathode particles.

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1. Introduction

During the past few decades, rechargeable batteries have received significant scientific attention since they show great promise as a reliable energy storage solution for a wide variety of applications ranging from electric powertrain systems to consumer portable electronics [1,2]. The scientific community has shown increasing interest in exploring new chemistries for lithium batteries such as lithium-sulfur [3,4] and lithium-air batteries [5–11]. Enhancing the performance of such rechargeable batteries requires material design for various battery components such as electrochemically stable electrolytes, high-capacity anodes, and high-voltage cathodes [12–14]. Developing new cathode materials with improved electrochemical performance, low cost, and enhanced cycle life is critically important in achieving the requirements for transportation applications [15].

Recent studies have confirmed that, in general, surface modification of the active cathode particles affects the capacity retention, rate capability and even thermal stability of the cathode materials for lithium-ion batteries [16–19]. This surface modification can be done by coating the particles with a protective layer, in which case, the coating must guard the core material against side reactions with the electrolyte and prevent the loss of transition-metal ions or oxygen, without significantly affecting the electronic and ionic conductivities [15,20].

In the field of lithium-ion battery research, nanoscale coatings or encapsulating phases on active cathode materials are ubiquitous, either by design to improve performance or through “in-situ” evolution [15,16,20–22]. For instance, carbon coating on $LiFePO_4$ is widely used to improve surface conductivity and electron transfer kinetics [16,23,24]. Jeong et al. [25] have recently used an oxide coating on $LiMn_2O_4$ spinel particles to mitigate the dissolution of Mn^{2+} into the electrolyte. The surface of the cathode particles can also be coated with another active material to create dual-active-material cathode particles with a core-shell heterostructure. For example, Shim et al. [26] have reported on the successful implementation of a thin spinel $Li_xCo_2O_4$-coated $LiCoO_2$ prepared by post-thermal treatment. They demonstrated that the high electrical conductivity of the coating layer enhances the charge transfer activity of the cathode material. In a recent study by Jing Li et al. [27] lithium-rich Ni-Mn-Co oxide core-shell electrodes with an Mn-rich shell were used to prevent the Ni from reacting with the electrolyte. Zaghib et al. [28] introduced a new cathode material by encapsulating $LiMnPO_4$ with $LiFePO_4$ to improve its thermal stability and to facilitate carbon coating of the particles.

Surface coating can also be used to decrease the rate of side reactions that lead to the degradation of the electrolyte or active electrode material. For instance, charged electrode materials such as delithiated cathodes tend to violently react with the non-aqueous electrolytes at elevated temperatures [29,30]. These side reactions can still occur slowly at room temperature, resulting in gradual degradation of cathode materials [16]. By creating an artificial physical barrier that increases the activation energy for such side reactions, it is possible to effectively decrease the rate of these reactions at ambient temperatures.

As mentioned, encapsulating phases on active cathode particles may form “in-situ.” For instance, Kikkawa et al. [31] observed $CoO_{2\text{-}\delta}$ $(0.67 < \delta < 1)$ forming on the surface of $LiCoO_2$ particles upon overcharge. Recently, Lee et al. introduced lithium-excess nickel titanium molybdenum oxides as a new class of high capacity cation-disordered oxides for use in rechargeable lithium battery cathodes [32]. They showed that $Li_{1.2}Ni_{1/3}Ti_{1/3}Mo_{2/15}O_2$ (LNTMO20) provides the best performance among Li-excess Ni-Ti-Mo oxides. However, galvanostatic discharge tests at different rates indicated that its discharge capacity decreases from 250 mAh/g to 120 mAh/g as the rate increases from 10 mA/g to 400 mA/g [32]. Lee at al [32]. showed that the surface phase that formed during the first charge of LNTMO20 particles was responsible for this reduction in capacity at high C-rates.

The formation of solid-electrolyte interphase (SEI) layer on the surface of cathode particles is another example of in-situ evolution of encapsulating phases that can potentially result in capacity reduction. For instance, Bian et al. [33] observed that a thick SEI layer (> 10 nm) forms on the surface of cycled $Li(Li_{0.18}Ni_{0.15}Co_{0.15}Mn_{0.52})O_2$ (LLMO) Li-excess cathode particles, which causes a significant capacity drop (~50%) after only 100 cycles at 0.2C rate. They also showed that BiOF-coated LLMO particles exhibit a dramatically reduced (~10%) capacity drop under the same conditions, which was attributed to very thin SEI layers (~3 nm) that formed on the BiOF-coated particles [33].

Identifying the sources of capacity drop in Li-excess compounds is crucial in the development of next-generation high-energy-density cathode materials [34]. In general, any difference in the material and geometrical properties of the surface and bulk phases, such as open-circuit voltage (OCV), Li diffusivity, reaction coefficient, and thickness, can potentially affect the charge/discharge behavior of core-shell cathode particles [35]. We hypothesize that the poor kinetic behavior of core-shell cathode particles is caused by either low diffusivity in the surface layer as shown by Lee et al. [32] in the case of Li-excess materials, or a shift in the OCV of the surface phase. While both mechanisms can occur simultaneously, in order to investigate which mechanism has a greater impact on the intercalation kinetics, the effect of each mechanism needs to be studied separately. Since the effect of a small Li diffusion coefficient on the kinetic behavior of core-shell cathode particles is more obvious, in this paper we focus on the effect of OCV shift in the surface phase. Below, a simple but general continuum model is formulated to study the lithium intercalation kinetics of a particle with a core-shell heterostructure. This model will allow us to evaluate the charge/discharge overpotential in dual-active-material core-shell cathode particles and to demonstrate that this shift in the surface-phase OCV may be responsible for the observed electrochemical behavior of high capacity Li-excess cathode materials.

2. Electrochemical model

The model particle with a core-shell heterostructure, illustrated schematically in Fig. 1 is comprised of two active materials: a core material with open circuit voltage V_o encapsulated by a thin layer of a second phase with a shifted open circuit voltage $V_o + \Omega$. The charge/discharge of a Li-ion battery cell is a result of multiple physical and chemical mechanisms that occur simultaneously in the electrode, liquid electrolyte and their interfaces. These mechanisms include i) ionic transport in the electrolyte, ii) current continuity in the ionically conductive electrolyte, iii) electrochemical reaction(s) at the particle-electrolyte interfaces, iv) Li ion transport in the electrode particles, and v) current continuity in the electronically conductive solid phases. The first two mechanisms take place in the electrolyte, while the last two processes occur in the cathode particles. The reaction (iii) arises on the interface between the electrolyte and cathode particles. The details and mathematical descriptions of these processes are described below.

During the discharge of a Li-ion battery, lithium is oxidized at the anode and the resulting Li ions travel through the electrolyte towards the cathode electrode. At the cathode-electrolyte interface, these Li ions react with the electrons and intercalate into the host crystal. The intercalation reaction is described by the chemical equation:

$$Li^+ + e^- + X \rightarrow LiX \tag{1}$$

where X represents the unit formula for the cathode host compound. The reverse reaction occurs when potential is applied to charge the cell. In this study, we do not consider side reactions such as those that form solid-electrolyte interphase (SEI) or that lead to decomposition of the electrode particles and/or the liquid electrolyte. We also assume the reaction-limited regime in the electrolyte (i.e., the mass transport in the electrolyte is rapid in comparison to the charge-transfer kinetics), and therefore ignore the diffuse double layers [36].

For simplicity and computational efficiency, we assume the geometry of the core-shell cathode particle to be spherical so that the dynamics can be described by one-dimensional (1D) equations in radial