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Galvanostatic interruption of lithium insertion into magnetite: Evidence of surface layer formation



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HIGHLIGHTS

- Surface layer formation on magnetite nanocrystals was investigated.
- Surface layer formation decreases the amount of active material.
- The decrease in active material is proportional to crystal surface area.
- The surface layer forms through a nucleation and growth process.
- Optimal crystal size balances active material loss and mass transport resistance.

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ABSTRACT

Magnetite is a known lithium intercalation material, and the loss of active, nanocrystalline magnetite can be inferred from the open-circuit potential relaxation. Specifically, for current interruption after relatively small amounts of lithium insertion, the potential first increases and then decreases, and the decrease is hypothesized to be due to a formation of a surface layer, which increases the solid-state lithium concentration in the remaining active material. Comparisons of simulation to experiment suggest that the reactions with the electrolyte result in the formation of a thin layer of electrochemically inactive material, which is best described by a nucleation and growth mechanism. Simulations are consistent with experimental results observed for 6, 8 and 32-nm crystals. Furthermore, simulations capture the experimental differences in lithiation behavior between the first and second cycles.

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1. Introduction

Nanostructuring of lithium-insertion materials may improve the performance of lithium-ion batteries by increasing the surface area to volume ratio and by lowering the solid-state diffusion resistances in the electrodes [1–9]. Increasing the surface area to volume ratio is beneficial because it provides more sites for the electrochemical reactions, thereby decreasing surface overpotential for a given nominal current density. However, extensive nanostructuring may have negative effects because it increases the

amount of active material that can be exposed to side reactions and surface layer formation [10–12]. For instance, during the first cycle(s) of a lithium-ion battery, reactions between the electrolyte and the electrodes may result in the formation of thin layers of material on the electrode surfaces, commonly referred to as the solid electrolyte interphase (SEI) for graphite anodes and the cathode electrolyte interphase for cathodes [13–15]. The formation of these layers typically involves the transformation of active material into a surface layer, thereby reducing theoretical capacity [13].

Herein, we compare simulations to experiments and hypothesize that the complex potential transients upon current interruption seen after a relatively small amount of lithium is inserted into magnetite ($x = 0.5, 1.0, \text{ and } 1.5$ in $\text{Li}_x\text{Fe}_3\text{O}_4$) is related to the

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formation of a thin layer of inactive material. In short, for small crystal sizes (6 and 8 nm) the potential initially increases due to relaxation of the concentration profile of reduced lithium, and then at longer times, decreases. Previous simulations capture the initial rise in potential caused by rearrangement of solid-state lithium [16,17], but the fall in potential during relaxation cannot be explained. We hypothesize that it is caused by transformation of the active material (Fe_3O_4) into inactive material. The transformation is confined to the crystal surface and occurs through a (as of yet unidentified) reaction, which increases the concentration of intercalated lithium in the remaining active material. The coupling of these effects - concentration profile relaxation by mass transport (rise) and increase of intercalated lithium (fall) - gives better experimental agreement. This paper uses the previously described mass-transfer model and incorporates a mechanism for surface layer formation. The formation of the surface layer appears to occur via nucleation and growth, which is qualitatively consistent with literature [18]. The Avrami model describes the formation of the surface layer [19–21].

2. Experimental

Experiments were conducted using electrodes comprised of nanocrystalline magnetite. Small crystals, 6 and 8 nm average diameter, were synthesized using a co-precipitation method previously reported by the authors [8,22]. Larger crystals, ~32 nm (data not shown), were purchased from Alpha Aesar. Electrodes were prepared using 90% magnetite, 5% carbon, and 5% polyvinylidene fluoride binder (by weight) coated onto an aluminum foil substrate. Each electrochemical test was performed using a two-electrode coin-type experimental cell with a lithium metal anode and 1 M LiPF_6 in 1:1 dimethyl carbonate: ethylene carbonate as the electrolyte. The electrodes had a nominal thickness of 50 μm and a nominal active mass loading of 4.1 mg cm^{-2} .

Galvanostatic interruption experiments were conducted for electrodes comprised of nanocrystalline magnetite with average diameters of 6, 8 and 32 nm. The experimental cells were first lithiated at a C/200 rate (4.63 mA g^{-1} of Fe_3O_4) to $x = 0.5, 1.0, 1.5$, and 2.0 electron equivalents per Fe_3O_4 and then held at open circuit for up to 30 days. After the rest period, the cells were delithiated to a cutoff voltage of 3.0 V using a C/200 rate, followed by a constant voltage oxidation at 3.0 V for two hours. Subsequently, a second experiment was performed, where the current interruption was applied after the reduction of a specified amount of charge, which was equivalent to the amount of charge passed during the first lithiation.

In addition, second lithiation experiments were conducted at a rate of C/100 (9.26 mA g^{-1} of Fe_3O_4) for electrodes made of 42.5% Fe_3O_4 , 42.5% acetylene carbon black, and 15% polyvinylidene fluoride binder (PVDF) by weight. The magnetite was lithiated at the C/100 rate until a charge of 100 mAh g^{-1} was passed. The magnetite was subsequently delithiated to a cut-off voltage of 3.0 V at the same C/100 rate and then held at 3.0 V for 1 hour, and lithiated again at C/100 to the same capacity, 100 mAh g^{-1} [23]. All voltage recovery experiments were conducted at 30 °C using a freshly fabricated cell.

3. Theory

This section provides an outline of the present model, which was developed by modifying a previously validated multi-scale model to include the effects of the transformation of active material [16,17]. Table 1 contains a comparison of the governing equations for the two models. Consistent with multi-scale simulation results for 6 and 8 nm crystals, the present model assumes mass

transport resistances only occur on the agglomerate length scale (i.e., no concentration variations within the crystals or across the bulk electrode). This assumption provides a valid approximation for the present experiments, where the focus is on understanding the complex voltage transients during the relaxation of electrodes comprised of crystals with diameters of 6 and 8 nm. The transport of lithium-ions in the agglomerate is simulated using dilute solution theory. The concentration of lithium-ions in the agglomerate is coupled to the concentration of solid-state lithium in the crystals through a Butler-Volmer kinetic expression. It is assumed that the formation of the surface layer has a negligible impact on the reaction kinetics. The thermodynamic potential as a function of lithium in the solid-state and in the agglomerate - $U(c_x, c_{agg})$ - was modeled by fitting a modified Nernst equation to experimental data.

The rate of change of solid-state lithium within the crystals, c_x , is calculated from the following material balance:

$$\frac{\partial(\epsilon_{active}c_x)}{\partial t} = -\frac{ai_{rxn}}{F} \quad (1)$$

When held at the open circuit, the local current density i_{rxn} may not be zero because the crystals within the agglomerate galvanically interact until the concentration variations completely relax. ϵ_{active} is the volume fraction of active material in the electrode. It is given by

$$\epsilon_{active} = (1 - \epsilon) \frac{V_{x,0} - \xi V_S}{V_{x,0}}, \quad V_{x,0} = \frac{4}{3} \pi r_x^3 \quad (2)$$

where ξ is the volume fraction of magnetite in the surface layer. For these simulations, $\xi = 50\%$ and it is assumed that $\epsilon = 0.26$, consistent with closed packed spheroidal crystals. Other volume fractions ξ were explored, and they did not have a significant impact on the simulated results. Equations (1) and (2) were formulated assuming the transformation of magnetite to an inactive phase does not alter the total amount of solid-state lithium within the remaining magnetite. This implies that the local concentration of solid-state lithium within the active material increases as a result of the loss of active magnetite.

3.1. Surface layer formation

The surface layer formation was initially modeled assuming a uniform, layer-by-layer growth. The results were able to capture some of the salient features of the OCP relaxation. However, better agreement was achieved by assuming a nucleation-and-growth mechanism, whereby the volume of the surface layer can be described through the Avrami model [19–21]:

$$V_S = V_{max,S} [1 - \exp(-k_S t^n)] \quad (3)$$

When the exponent $n = 1$, Equation (3) is consistent with a layer-by-layer growth mechanism. More generally, n is determined by the relative rate of nucleation to growth and the dimensionality of the growth (e.g., two-vs. three-dimensional). The value of $V_{max,S}$ is set by a final thickness of the surface layer:

$$V_{max,S} = \frac{4\pi}{3} (r_x^3 - (r_x - \lambda_{max})^3) \quad (4)$$

where λ_{max} is the maximum thickness of the surface layer, which was determined from the final measured open circuit potential.

Along with increasing the size of the crystals, the formation of the inactive layer is expected to increase the overall size of the agglomerate. In the present study, the agglomerate radius may, at

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