Electrochimica Acta 238 (2017) 384–396

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Simulations of Lithium-Magnetite Electrodes Incorporating Phase Change

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ARTICLE INFO

Article history:
Received 22 July 2016
Received in revised form 6 April 2017
Accepted 7 April 2017
Available online 9 April 2017

Keywords:
Nucleation and growth
voltage recovery
current interrupt
lithium-ion batteries
Avrami

ABSTRACT

The phase changes occurring in magnetite (Fe_3O_4) during lithiation and voltage recovery experiments are modeled using a model that simulates the electrochemical performance of a Fe_3O_4 electrode by coupling the lithium transport in the agglomerate and nano-crystal length-scales to thermodynamic and kinetic expressions. Phase changes are described using kinetic expressions based on the Avrami theory for nucleation and growth. Simulated results indicate that the slow, linear voltage change observed at long times during the voltage recovery experiments can be attributed to a slow phase change from α-$Li_xFe_3O_4$ to β-$Li_4Fe_3O_4$. In addition, the long voltage plateau at ~1.2 V observed during lithiation of electrodes is attributed to conversion from α-$Li_xFe_3O_4$ to γ-(4 Li_2O + 3 Fe). Simulations for the lithiation of 6 and 32 nm Fe_3O_4 suggest the rate of conversion to γ-(4 Li_2O + 3 Fe) decreases with decreasing crystal size.

1. Introduction

Two major factors limiting the widespread use of electric vehicles are the size and cost of the lithium-ion batteries used in the power system. To address these issues, next-generation batteries must contain active materials with high specific energy ($Wh\,L^{-1}$ or $Wh\,g^{-1}$), which can meet the required design specifications with smaller quantities of material. Currently, the specific energies of commercially available lithium-ion battery electrodes are limited by relatively low theoretical capacities – 140 to 200 $mAh\,g^{-1}$ and ~370 $mAh\,g^{-1}$ for positive and negative electrode materials, respectively [1,2]. These materials have low capacities because they can only accept ~1 mole of lithium per mole of host material (*e.g.*, C_6, CoO_2, and $FePO_4$). In an effort to expand the capacity of battery electrodes, new compounds are being investigated which undergo multiple electron transfers (MET) and can accommodate multiple moles of lithium per mole of host material. These compounds include metal oxides, fluorides, oxyfluorides, nitrides, and sulfides [3–9]. Unlike commercial lithium-ion electrode materials, which store and release energy through a (de)intercalation reaction, the MET compounds can undergo conversion reactions, which result in the structural rearrangement and phase change of the host material. The kinetics of formation and reversibility of these phase changes are important factors dictating the applicability of these new materials.

Among the new set of compounds, magnetite (Fe_3O_4) is of particular interest due to its low cost, safety, and high theoretical capacity (926 $mAh\,g^{-1}$), which is associated with its ability to accommodate 8 moles of lithium per mole of Fe_3O_4 [10–15]. During lithiation, magnetite first undergoes an intercalation process which results in the structural rearrangement of the material from an inverse spinel to a rock-salt-like structure [16–20]. Upon further lithiation, magnetite undergoes a conversion process to Li_2O and Fe metal [21–24]. Until recently, the performance of magnetite was limited by slow solid-state transport of lithium ions through the close-packed structure of the material. However, nanosizing has been utilized to shorten the path length for lithium ion diffusion, which has improved the rate capability and increased the utilization of the active material [13–15,25–27]. Further improvements in rate capability and utilization have been obtained using alternative electrode synthesis methods that reduce agglomeration of the nanocrystals [28,29]. Despite these improvements, it is still difficult to obtain the theoretical capacity of Fe_3O_4, especially during cycling. Recently, investigations of the

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http://dx.doi.org/10.1016/j.electacta.2017.04.041
0013-4686/

Nomenclature

a	specific surface area (cm^2 cm^{-3})
c_{agg}	lithium concentration in the agglomerate (mol cm^{-3})
$c^{\beta}_{\alpha,sat}$	concentration at which β begins to form from α (mol cm^{-3})
$c^{\gamma}_{\alpha,sat}$	concentration at which γ begins to form from α (mol cm^{-3})
c_0	bulk concentration in the electrolyte (mol cm^{-3})
c_x	total solid-state lithium concentration (mol cm^{-3})
$c_{\alpha,\max}$	maximum solid-state lithium concentration in α phase (mol cm^{-3})
D_{agg}	diffusion coefficient in the agglomerate (cm^2 s^{-1})
D_x	diffusion coefficient in crystal (cm^2 s^{-1})
F	Faraday's constant (96,485C mol^{-1})
i_{app}	applied current (A g^{-1})
i_{rxn}	reaction rate (A cm^{-2})
k_{β},k_{γ}	rate constant for phase formation (cm^{-3} mol^{-1} or cm^{-3} mol^{-1} s^{-1})
k_{rxn}	reaction rate constant (mol$^{-1/2}$ cm$^{-1/2}$ s^{-1})
r	radial position in the agglomerate (cm)
r_{agg}	agglomerate radius (cm)
R_G	ideal gas constant (8.314 J mol^{-1} K^{-1})
t	time (s)
T	temperature (K)
U	equilibrium potential (V)

Greek

α_a, α_c	anodic and cathodic charge transfer coefficients
ε	porosity
ϕ_1	potential in the solid (V)
$\rho_{Fe_3O_4}$	density of magnetite (g cm^{-3})
σ	conductivity of magnetite (S cm^{-1})
θ	volume fraction of phase

Subscript

agg	denotes agglomerate
α	denotes alpha phase ($Li_xFe_3O_4$)
β	denotes beta phase ($Li_4Fe_3O_4$)
γ	denotes gamma phase (4 Li_2O + 3 Fe)
x	denotes crystal

(de)lithiation process using synchrotron X-ray and transmission electron microscopy techniques have suggested that the poor capacity is caused by an inability to fully convert from Li_2O and Fe metal into the inverse-spinel phase (Fe_3O_4) during delithiation [21,24]. This suggests that further improvements in performance may result from a better understanding of the kinetics of structural rearrangement and phase change within the material.

This work seeks to complement recent experimental investigations by modeling the phase changes occurring within magnetite during lithiation and voltage recovery. In the battery field, modeling of phase change has been done in other materials (*e.g.* $FePO_4$ and FeF_2) using phase-field theory, which implements the Cahn-Hilliard equation to describe the concentration distribution of Li^+ within a crystal [30–34]. Phase-field modeling is capable of simulating phase-separation of materials into regions of high- and low-levels of lithiation by calculating the distribution of Li^+ which minimizes the free energy of the crystal. The concentration distributions agree well with experimental observations; however, the results are highly dependent on the use of a representation of the free energy of the system (often arising from regular solution theory and developed based on experimental observations), which often results in poor agreement between simulations and electrochemical performance data [33–37]. Other attempts to simulate the electrochemical performance of a material which undergoes phase change have utilized a "shrinking-core" model, which tracks the boundary separating the high- and low-lithium phases as it progresses from the surface of a crystal to the center during lithiation [38–40]. These models agree well with electrochemical data; however, they often only simulate the battery during lithiation of the electrode because modeling the subsequent delithiation is difficult due to the existence of multiple moving boundaries. In addition, shrinking-core models assume that both phases (high- and low- lithium) are already present at the start of the simulation. Therefore, they do not provide kinetic descriptions of the initial formation of the highly concentrated phase.

In this work, we seek to simulate the phase changes within magnetite during lithiation by incorporating the kinetics of nucleation and growth of new phases into a previously developed model [41–43]. The previously developed model, which did not include phase change, simulates the electrochemical performance of a Fe_3O_4 electrode by coupling the lithium transport in the agglomerate and crystal length-scales to thermodynamic and kinetic expressions. In previous work, the model without phase change was able to capture the electrochemical performance of an electrode at low levels of lithiation, where Fe_3O_4 undergoes an intercalation process [42]. To expand our understanding to higher levels of lithiation, the formation of new phases are incorporated into the previously developed model using kinetic expressions inspired by the Avrami theory for nucleation and growth [44–46]. Herein, simulations with phase change are used to explain the behavior of electrodes with "small" (~6 nm) and "large" (32 nm) crystals during lithiation and voltage recovery experiments.

2. Experimental

Nanocrystalline magnetite, Fe_3O_4, was synthesized using a co-precipitation approach, utilizing aqueous solutions of iron (III) chloride hexahydrate, iron (II) chloride hexahydrate, and base according to a previously reported method [14,15]. Larger sized nanocrystalline magnetite, ~32 nm, was purchased from Alfa Aesar. X-ray diffraction data was collected using a Rigaku Smart Lab diffractometer with Cu Kα radiation. The crystallite sizes of the Fe_3O_4 powders were calculated by applying the Scherrer equation to the FWHM of the (311) peak [47]. An instrumental broadening correction was applied using a LaB_6 standard.

Electrodes were prepared using magnetite, carbon, and polyvinylidene fluoride binder coated onto an aluminum foil substrate. Electrochemical tests were performed using two electrode coin-type experimental cells with lithium metal anodes and 1 M $LiPF_6$ in dimethyl carbonate:ethylene carbonate electrolyte (1:1 by volume). The electrode was comprised by weight of 90% Fe_3O_4, 5% acetylene carbon black, and 5% PVDF. For electrodes comprised of 6 and 32 nm crystals, lithiation was conducted under a C/200 rate to 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 electron equivalents per Fe_3O_4 and then allowed to rest under open circuit conditions for up to 30 days. For electrodes comprised of 8 nm crystals, similar experiments were conducted to 0.5, 1.0, 1.5, 2.0, 2.5, 3.25, 3.5, 4.0, 4.5, 5.0, 6.0, 7.0, and 8.0 electron equivalents per Fe_3O_4. All electrochemical testing was conducted at 30 °C.

3. Kinetics of Phase Change

This section describes the generic approach used to model the rearrangement of a material from "*a*" to "*b*," where *a* and *b* are unique phases of the same host material. Both *a* and *b* contain the same number of host atoms (*e.g.*, for a host material of Fe_3O_4 both