***Dispersion of Nanocrystalline Fe_3O_4 within
Composite Electrodes: Insights on Battery Related
Electrochemistry***

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Submitted to the ACS Applied Materials & Interfaces

April 2016

Energy and Photon Sciences Directorate

Brookhaven National Laboratory

**U.S. Department of Energy
Office of Science, Basic Energy Sciences**

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Dispersion of Nanocrystalline Fe₃O₄ within Composite Electrodes: Insights on Battery Related Electrochemistry

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KEYWORDS

magnetite, composite, aggregate, EXAFS, lithium-ion battery, electrochemical impedance spectroscopy, TXM

ABSTRACT

Aggregation of nanosized materials in composite lithium ion battery electrodes can be a significant factor influencing electrochemical behavior. In this study, aggregation was controlled

in magnetite, Fe_3O_4 , composite electrodes via oleic acid capping and subsequent dispersion in a carbon black matrix. A heat treatment process was effective in removal of the oleic acid capping agent while preserving a high degree of Fe_3O_4 dispersion. Electrochemical testing showed that Fe_3O_4 dispersion is initially beneficial in delivering higher functional capacity, in agreement with continuum model simulations. However, increased capacity fade upon extended cycling was observed for the dispersed Fe_3O_4 relative to the aggregated Fe_3O_4 composites. X-ray absorption spectroscopy measurements of electrodes post cycling indicated that the dispersed Fe_3O_4 electrodes are more oxidized in the discharged state consistent with reduced reversibility compared with the aggregated sample. Higher charge transfer resistance for the dispersed sample after cycling suggests increased surface film formation on the dispersed, high surface area nanocrystalline Fe_3O_4 compared to the aggregated materials. This study provides insight into the specific effects of aggregation on electrochemistry through a multiscale view of mechanisms for magnetite composite electrodes.

INTRODUCTION

The demand for improved lithium ion battery technology is driven in part by the capacity, energy and power requirements of a variety of applications, including electric vehicles, renewable energy storage and portable electronics. A specific recent focus is the study of new materials with considerably higher capacity than those in current use.¹⁻² Ideally, these materials should also be inexpensive to manufacture, safe, and environmentally friendly. The iron oxide magnetite (Fe_3O_4), is a prime candidate due to its low toxicity, high theoretical gravimetric capacity (ca. 920 mAhg^{-1}) and natural abundance.³⁻⁴ The high energy density of Fe_3O_4 is owed to the both the close-packed inverse spinel crystal structure of the material as well as the

multielectron transfer reduction mechanisms which convert the original Fe^{3+} and Fe^{2+} centers to Fe^0 when fully lithiated.⁵⁻⁷

The particle size of active electrode materials can have a large effect on the cycling performance and rate capability of composite electrodes, in particular for materials such as magnetite which are limited by low ionic conductivity.⁸⁻¹⁰ For example, by reducing the crystallite dimension of magnetite, the total path length for Li^+ ions can be decreased, allowing for an increase in functional capacity at higher discharge currents by increasing the effective utilization of the active material.^{4, 11-16} Specifically, magnetite with a crystallite size of ~ 6 nm displayed a 30% increase in delivered capacity upon intermittent pulsatile discharge relative to magnetite with a crystallite size of ~ 10 nm.¹³⁻¹⁴

In addition to the size of individual crystallites, the size of aggregates can significantly impact the resulting application specific properties of nanomaterials, such as photoluminescence,¹⁷ catalysis,¹⁸⁻¹⁹ and electrochemical behavior.²⁰ Recently, mass transport diffusion coefficients for individual crystallites as well as crystallite aggregates were calculated by fitting simulated voltage recovery times to experimental data.²¹ Notably, transport limitations on the aggregate level and the crystallite level were both significant. The model was able to rationalize long voltage recovery times and utilization levels of Fe_3O_4 active material in composite electrodes with significant Fe_3O_4 aggregation.

Motivated by the performance model of Fe_3O_4 containing electrodes, the goals of this study are: 1) to reduce aggregation of Fe_3O_4 within composite electrodes through the use of oleic acid as a capping agent, 2) to prepare dispersed Fe_3O_4 composite electrodes with oleic acid retained and removed, and 3) to mechanistically probe the relationship among Fe_3O_4 dispersity, oleic acid capping effects, and delivered capacity. Fe_3O_4 was synthesized with a 9 nm crystallite

size, coated with oleic acid and then dispersed within a carbon black composite electrode. For some samples, the oleic acid was subsequently removed from the composite electrodes through heat treatment. A composite electrode was prepared for comparison where magnetite was physically mixed with the carbon black. The three composite electrodes (physically mixed Fe_3O_4 /carbon black, oleic acid capped Fe_3O_4 /carbon black, and heat treated oleic acid capped Fe_3O_4 /carbon black) were characterized by transmission electron microscopy (TEM) and transmission x-ray microscopy – x-ray absorption near edge structure (TXM-XANES) to determine the relative level of dispersion of Fe_3O_4 crystallites. An established synchrotron based technique, transmission X-ray microscopy (TXM) can provide submicron spatial resolution, with the opportunity to gain oxidation state information over a large sample area via XANES,²²⁻²³ as has been discussed in recent reviews.²⁴⁻²⁵ Electrochemical testing included galvanostatic cycling and electrochemical impedance spectroscopy. Results of continuum level simulations, x-ray absorption spectroscopy (XAS) measurements, and electrochemical impedance spectroscopy (EIS) data, facilitate a detailed mechanistic view of the dramatically different observed capacities over 25 cycles for the three types of composite electrodes. In particular, an understanding of the active material evolution and its relation to functional capacity upon extended discharge-charge cycling is described.

Within the past 5 years, research on Fe_3O_4 /carbon type composites as lithium ion batteries has increased substantially due to the high theoretical capacity of Fe_3O_4 as an anode material and its potential for implementation.²⁶ The physically mixed Fe_3O_4 /carbon black composite reported herein has comparable performance (840 mAh/g after 25 cycles, 0.125 C rate, 0.3 – 3.0 V) to various Fe_3O_4 /carbon composites (core-shell $\text{Fe}_3\text{O}_4@\text{C}$, Fe_3O_4 /graphene, Fe_3O_4 /carbon nanotubes) which have been summarized extensively in a recent review.²⁶

However, in comparison to these previous reports, the current study strives to fundamentally understand the performance effects of agglomeration versus dispersion in a mesoscale electrode while maintaining the same primary Fe_3O_4 particle size. Furthermore, to our knowledge, this is the first report which utilizes extended x-ray absorption fine structure (EXAFS) modeling and XANES techniques to characterize structural changes in cycled Fe_3O_4 composite electrodes. Thus, the data presented herein not only provide new insight into the effects of aggregation and capping agents, but also offer a template for investigating the mechanism of capacity fade in mesoscale composite electrodes.

EXPERIMENTAL METHODS

Synthesis and Characterization. A previously reported coprecipitation approach was used to synthesize magnetite, Fe_3O_4 .¹³⁻¹⁴ Briefly, stoichiometric quantities of iron (III) chloride hexahydrate and iron (II) chloride hexahydrate were dissolved in water and slowly added to aqueous triethylamine [$\text{N}(\text{CH}_2\text{CH}_3)_3$] under nitrogen. Precipitated Fe_3O_4 was isolated by centrifugation and dried.

Preparation of oleic acid capped Fe_3O_4 material was adapted from previously reports.²⁷⁻²⁸ Fe_3O_4 was first synthesized using the method described above. Prior to drying, the Fe_3O_4 was washed with acetone and oleic acid was added. The mixture was sonicated and mixed for several hours. Excess oleic acid was removed by washing with acetone. Oleic acid capped Fe_3O_4 was incorporated into carbon black in cyclohexane, isolated and dried. Heat treated OA- Fe_3O_4 /carbon black composite was prepared by heating under air at 250 °C for 2 hours in a tube furnace.

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3 X-ray diffraction data was collected using a Rigaku Smart Lab diffractometer with Cu K α
4 radiation. The crystallite size of the Fe₃O₄ was determined by applying the Scherrer equation to
5 the FWHM of the (311) peak where a LaB₆ standard was used to correct for instrumental
6 broadening.²⁹ Thermogravimetric analysis (TGA) data, from 40°C to 800 °C under air
7 atmosphere at a rate of 5°C/min, was collected to quantify levels of oleic acid, carbon black, and
8 Fe₃O₄ in the composites. Electron diffraction patterns and HRTEM images of heat treated OA-
9 Fe₃O₄ were recorded using a JEOL 2100F microscope.

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Electrochemical Methods. Electrodes were prepared on aluminum foil substrates with target ratios of 40% Fe₃O₄, 40% acetylene black carbon, and 20% polyvinylidene fluoride binder. Electrochemical tests were performed using coin-type experimental cells with lithium metal anodes and 1M LiPF₆ in 7:3 dimethyl carbonate: ethylene carbonate electrolyte. Comparison electrodes with 80% carbon black, 20% PVDF electrodes were also prepared. Cycling stability tests used C/8 (~58 mA/g Fe₃O₄ + C) or 1C (~460 mA/g Fe₃O₄ + C) with voltage limits of 0.3 and 3.0 V. Electrochemical Impedance Spectroscopy (EIS) measurements were collected using a Biologic VSP multichannel potentiostat with a 5 mV sinus amplitude and frequency range of 10 mHz to 1 MHz.

Performance Modeling. A previously validated multi-scale model^{21, 30} was used to simulate electrochemical performance of the coin-type cells. The model simulates the electrochemical performance of a single aggregate of nanocrystals by coupling ion transport on both length scales (aggregate and crystal) with descriptions of the thermodynamics and reaction kinetics. In this work, simulations were conducted without and with aggregate-scale transport resistance. Simulations without aggregate-scale resistance (*i.e.*, crystal only simulations) were conducted by using a fast aggregate-scale diffusion coefficient ($D_{\text{agg}} = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) as an input

parameter in the multi-scale model, which eliminated variations in lithium-ion concentration throughout the aggregate. Simulations with aggregate-scale transport resistance were conducted using the previously determined aggregate diffusion coefficient of $2.3 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$.²¹

Analysis of Electrode Samples. Electrodes were embedded in resin and 80 nm thickness were cut using a Reichert-Jung UltracutE ultramicrotome and placed on Formvar coated mesh copper grids. Sections were then viewed with a FEI Tecnai12 BioTwinG2 transmission electron microscope, and digital images were acquired with an AMT XR-60 CCD Digital Camera system.

Non-discharged electrodes were analyzed using transmission X-ray microscopy (TXM) in combination with (XANES) spectroscopy at Beamline X8C, NSLS I, Brookhaven National Laboratory. XANES image series were collected by scanning the Fe absorption K-edge from 7092 to 7192 eV, with 2 eV step size, and one image per step. Image series were collected with 20 s exposure time, and 2 x 2 pixels binned camera pixels, where each binned pixel is approximately 39 x 39 nm². Additional 2 x 2 binning was used during data processing resulting in 78 nm x 78 nm pixel resolution. The distributions of standard phases Fe₃O₄ and FeO were analyzed by least squares combination fitting using a customized MatLab program developed at Beamline X8C.

Coin cells were charged and discharged at a C/8 current rate to various dis(charge) and cycled states for XAS analysis. Specifically, electrodes were discharged to 0.9 V (460 mAh/g Fe₃O₄), 0.8 V (920 mAh/g Fe₃O₄), 0.3 V (1st full discharge), or discharged to 0.3 V then charged to 3.0 V (1st charge). Additional XAS samples were prepared after 25 cycles in both discharged and charged states. Full XAS spectra were collected at the Fe K-edge (7.112 keV) at sector 12-BM of the Advanced Photon Source at Argonne National Laboratory. Electrodes at specific depths of discharge were extracted from the coin cells, sealed between Kapton tape and stored in

an inert atmosphere environment until XAS measurements were collected. Each sample was measured in transmission mode with incident and transmission ion chambers. A Fe metal foil was used for initial X-ray beam energy calibration and was also measured simultaneously with each sample to ensure proper energy alignment of multiple XAS scans during analysis. XAS spectra were aligned, merged and normalized using Athena.³¹⁻³² Spectra were fit using Artemis with theoretical models created by FEFF6³³⁻³⁴ of Fe₃O₄, FeO, and metallic Fe crystal structures. Fits were made using a k-range of 2 – 11 Å⁻¹ with a Hanning window in k, k² and k³ weighting simultaneously. An R-range of 1.0 – 3.0 Å was typically used to fully encompass both the first and second coordination shells.

RESULTS

Materials Synthesis and Characterization. Three types magnetite/carbon black composites were prepared for study: Fe₃O₄ physically mixed with carbon black (Fe₃O₄/C), oleic acid capped Fe₃O₄ incorporated into carbon black (OA-Fe₃O₄/C), and heat treated oleic acid-capped Fe₃O₄/carbon black (HT OA-Fe₃O₄/C). The Fe₃O₄ in the composite samples was characterized by X-ray diffraction (Figure 1A) and the patterns compare well with the reported reference pattern for Fe₃O₄.³⁵ The crystallite size of the Fe₃O₄ in the composites was calculated from the XRD data by applying the Scherrer equation²⁹ to the FWHM of the (311) peak. The Fe₃O₄ crystallite sizes determined using this technique are 9 nm for each sample indicating that the oleic acid capping and heat treatment procedures did not impact the Fe₃O₄ crystallite size. The patterns compare well with the reported reference pattern for Fe₃O₄³⁵ (PDF #01-088-0315), however, the pattern of iron oxide phase γ -Fe₂O₃³⁶ (PDF # 01-080-2186) is similar so further characterization was pursued.

Electron diffraction was used to further investigate the effect of the heat treatment step on the oleic acid capped Fe_3O_4 particles (Figure 2). Fe_3O_4 possesses an inverse spinel structure, as indicated by the diffraction patterns obtained from many aggregate areas (Figure 2A). After heat treatment, the majority of nanoparticles remained as Fe_3O_4 , as evidenced by the diffraction rings corresponding to pure Fe_3O_4 . However, a small fraction of the nanoparticles were transformed to $\gamma\text{-Fe}_2\text{O}_3$, as the diffraction spots of $\gamma\text{-Fe}_2\text{O}_3$ are observed (Figures 2B and 2C). The $\gamma\text{-Fe}_2\text{O}_3$ phase is not formed on the surface of Fe_3O_4 , as it was not detected in the diffraction pattern (Figure 2A). The HRTEM image of one single heat-treated Fe_3O_4 nanoparticle (Figure 2F) also shows a clear surface with uniform crystalline structure, eliminating the possibility of forming $\gamma\text{-Fe}_2\text{O}_3$ on the surface. Thus, the electron diffraction results indicated that a low percentage of the nanoparticles are converted from Fe_3O_4 to $\gamma\text{-Fe}_2\text{O}_3$ during the heat treatment, with the majority of particles remaining as Fe_3O_4 .

TGA measurements were used to quantify the oleic acid on the surface of the Fe_3O_4 nanoparticles. Figure 1B shows thermogravimetric analysis of oleic acid, oleic acid capped $\text{Fe}_3\text{O}_4/\text{C}$, and heat treated oleic acid capped $\text{Fe}_3\text{O}_4/\text{C}$. From plots of the first derivative of the mass vs. temperature, dm/dT , (Figure 1C, 1D, 1E) the onset of mass loss due to oleic acid combustion is approximately 150°C . Low levels of mass loss (1-2%) prior to 150°C occur due to loss of trace moisture adsorbed onto the materials. The majority of oleic acid combustion occurs by 320°C , and additional mass loss from 320°C to 800°C is assigned to combustion of the carbon black component in the composite. The oleic acid capped $\text{Fe}_3\text{O}_4/\text{C}$ sample had 10% calculated percentage of oleic acid, defined as mass loss between 150°C and 320°C . Post heat treatment, the percentage of mass loss between 150°C and 320°C in the composite is 1%, indicating that the heat treatment is an effective means of removing the oleic acid from the

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3 composite. The plots of the first derivative of the mass vs. temperature confirm that the oleic acid
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6 is removed during the heat treatment step.
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8 Scanning transmission electron microscopy images of each composite type before
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10 incorporation into an electrode are shown in Figure 3. Before cycling, the physically mixed
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12 Fe_3O_4 /carbon black sample (Figures 3A, 3B) shows large aggregates of Fe_3O_4 (light contrast)
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14 mixed among carbon black (dark contrast). In contrast, for both the OA- Fe_3O_4 /C (Figures 3D,
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16 3E), and HT OA- Fe_3O_4 /C (Figures 3G, 3H), good dispersion of the Fe_3O_4 among the carbon
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18 black was observed. The particles remain dispersed on the carbon black after the heat treatment
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20 step. STEM images were also collected for composite electrodes after cycling 25x (Figure 3C,
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22 3F, 3I). Post cycling, the physically mixed Fe_3O_4 /C composite is still comprised of large
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24 aggregates of iron oxide particles. Individual iron oxide particles are still highly dispersed on the
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26 carbon in both OA- Fe_3O_4 /C and HT- Fe_3O_4 /C electrodes.
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32 The environment of the active Fe_3O_4 materials after preparation as electrodes was
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34 investigated where the electrodes were sectioned parallel to the plane of the electrode and
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36 imaged using TEM. Figures 4A-4C show bright-field TEM images of sectioned electrodes
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38 containing Fe_3O_4 /C, OA-capped Fe_3O_4 /C, and HT OA-capped Fe_3O_4 /C. There is a striking
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40 difference in appearance among the three types of Fe_3O_4 electrodes. The physically mixed
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42 Fe_3O_4 /C sample displays large, irregularly shaped aggregates (in dark contrast) of Fe_3O_4
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44 crystallites among the carbon black/PVDF matrix (light contrast). The average diameter of the
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46 aggregates in this composite was determined to be $1.1 \pm 1.3 \mu\text{m}$.³⁷ In comparison, electrodes
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48 prepared with OA- Fe_3O_4 /C and HT OA-capped Fe_3O_4 /C show good dispersion of the Fe_3O_4 in
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50 the carbon black/PVDF matrix, with few aggregates greater than 500 nm in diameter.
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Transmission x-ray microscopy – x-ray absorption near edge structure (TXM-XANES) was used to confirm relative levels of Fe_3O_4 dispersion in the prepared electrodes. TXM-XANES images of non-discharged electrodes containing physically mixed Fe_3O_4 /carbon black, oleic acid-capped Fe_3O_4 /carbon black, and heat treated oleic acid-capped Fe_3O_4 /carbon black composites are shown (Figures 4D-4F). Green and red pixels represent XANES spectra fit to the reference spectra for Fe_3O_4 and FeO , respectively. Predominantly green pixels in the non-discharged samples confirm that the oxidation state in each electrode is consistent with that of Fe_3O_4 . The electrode comprised of physically mixed Fe_3O_4 /carbon black shows the majority of the active material in aggregates. In contrast, the oleic acid-capped Fe_3O_4 /carbon black and heat treated oleic acid-capped Fe_3O_4 /carbon black composite electrodes display well dispersed Fe_3O_4 with no large aggregates.

Electrochemistry. Electrochemical performance was characterized using lithium metal based cells. Figures 5A and 5B show representative cyclic voltammograms of the three cell groups for the first and second cycle, respectively. In cycle 1, the cathodic process is characterized by three reduction peaks. The first of these peaks at 1.55 – 1.59 V is associated with initial insertion of the first Li^+ ion into the interstitial octahedral sites of the ccp Fe_3O_4 structure and reduction of 1 electron equivalent of Fe^{3+} to Fe^{2+} .³⁸ The second peak, at 1.01 – 1.03 V, corresponds to the second electron equivalent reduction of Fe^{3+} to Fe^{2+} and shifting of Fe ions from tetrahedral to octahedral sites as additional Li^+ insertion occurs and the material changes phase from inverse spinel Fe_3O_4 to a FeO-like rock salt structure.³⁸ The third reduction peak, centered at 0.60 V to 0.70 V, corresponds to the conversion process $\text{pf } 3\text{FeO} + 6\text{Li}^+ + 6\text{e}^- \rightarrow \text{Fe}^0 + 3\text{Li}_2\text{O}$, which occurs simultaneous to insertion of Li^+ into carbon black as well as formation of solid electrolyte

interphase. For the OA-Fe₃O₄ electrode all three reduction peaks occur at slightly lower voltages compared to Fe₃O₄/C and HT OA-Fe₃O₄/C electrodes, which is likely associated with an overpotential caused by slow Li⁺ mass transport through the oleic acid surface coating layer. During the 1st cycle anodic process, there are two overlapping peaks centered at approximately 1.6 V and 1.8 V, which correspond to conversion of Fe⁰ back to a FeO like structure and delithiation of the carbon black.

The cyclic voltammogram of cycle 2 and subsequent cycles is significantly different than the initial cycle. The reduction peaks associated with the initial Li⁺ insertion into the Fe₃O₄ host structure and phase change from Fe₃O₄ to FeO are no longer present. Only one large reduction peak centered at 0.8 V is visible, and is likely associated with the FeO to Fe⁰ metal conversion process and carbon lithiation/SEI formation. Thus, after the initial cycle, the reversible electrochemical reaction is $3\text{FeO} + 6\text{Li}^+ + 6\text{e}^- \rightleftharpoons \text{Fe}^0 + 3\text{Li}_2\text{O}$, which is consistent with a previous report.³⁸ Differential capacity dQ/dV plots (Figure S1) agree with the CV curves, with major reduction peaks centered at 1.5 V, 1.0V, and 0.8V occurring in the first cycle and only a single reduction peak at 0.85 V in the second cycle.

The three cell groups were galvanostatically cycled at a C/8 rate between 3.0 V and 0.3 V (Figure 5C) where capacity was calculated based on the mass of Fe₃O₄. In the initial cycle, Fe₃O₄/C, OA-Fe₃O₄/C and HT OA-Fe₃O₄/C electrodes have discharge capacities of 1810, 1430 and 1870 mAh/g, respectively. In the following charge, capacities are lower (920, 850 and 1140 mAh/g for Fe₃O₄/C, OA-Fe₃O₄/C and HT OA-Fe₃O₄/C, respectively). The HT OA-Fe₃O₄ electrodes exhibit higher discharge/charge capacities relative to Fe₃O₄/C electrodes through the first 11 cycles. The performance is attributed to the greater level of dispersion among Fe₃O₄ nanoparticles in the HT OA-Fe₃O₄/C electrode, which reduces transport limitations at the

aggregate level and thus promotes a high level of active material utilization.^{21, 30} To confirm this hypothesis, two simulations of the discharge behavior were conducted using the multi-scale model: one assuming the nanocrystals did not form aggregates and one assuming an effective aggregate diameter of 0.4 μm , which is within the range of experimentally observed values. For both simulations, the magnetite was assumed to be fully delithiated at the start of discharge. Simulations were conducted at a rate of 115 mA/g Fe_3O_4 to a cutoff voltage of 1.0 V to remain in the validated range of the model. A comparison of these simulations with discharge data from the 5th discharge of the coin-type cells comprised of $\text{Fe}_3\text{O}_4/\text{C}$ and HT OA- $\text{Fe}_3\text{O}_4/\text{C}$ is shown (Figure 6). The 5th discharge was selected to minimize uncertainties associated with irreversible processes which occur during the first few cycles which may be partially attributed to formation of a solid electrolyte interphase layer.³⁹⁻⁴¹ Agreement between the simulations and experiments is compelling, especially when considering that porous electrode effects and intercalation into the carbon black are not incorporated into the simulations. The cell with the HT OA- $\text{Fe}_3\text{O}_4/\text{C}$ electrode has a similar performance to the simulation without aggregates, while the cell with the $\text{Fe}_3\text{O}_4/\text{C}$ electrode has a similar performance to the simulation with the aggregates. These results support that the higher capacity of the HT OA- $\text{Fe}_3\text{O}_4/\text{C}$ is due to greater dispersion.

Although the HT OA- Fe_3O_4 electrodes exhibit higher capacity over the first ~ 10 cycles, the capacity fade in the HT OA- $\text{Fe}_3\text{O}_4/\text{C}$ is more notable relative to the $\text{Fe}_3\text{O}_4/\text{C}$ electrode such that by cycle 25 the discharge capacities of $\text{Fe}_3\text{O}_4/\text{C}$ and HT OA- $\text{Fe}_3\text{O}_4/\text{C}$ are 840 and 650 mAh/g, respectively. The OA- Fe_3O_4 electrode exhibits even more pronounced capacity fade, with the discharge capacity dropping to 520 mAh/g by cycle 5 and 190 mAh/g at cycle 25. Cycling data at a 1C rate (Figure S2) show the same general trends with the rank order of performance in the initial cycles as HT OA- $\text{Fe}_3\text{O}_4/\text{C}$ > $\text{Fe}_3\text{O}_4/\text{C}$ > OA- $\text{Fe}_3\text{O}_4/\text{C}$. The difference

in capacity between HT OA- $\text{Fe}_3\text{O}_4/\text{C}$ and $\text{Fe}_3\text{O}_4/\text{C}$ electrodes in the first few cycles is more pronounced (130 mAh/g difference at cycle 1, 317 mAh/g difference at cycle 5) compared to the results at a C/8 rate (60 mAh/g difference at cycle 1, 220 mAh/g difference at cycle 5), consistent with Li^+ transport limitations for the aggregated sample more manifest at the 1C rate. To further validate that the higher initial capacity of HT OA- $\text{Fe}_3\text{O}_4/\text{C}$ electrodes results from improved dispersion rather than Fe_3O_4 oxidation during the heat treatment process, oleic acid capped Fe_3O_4 was heat treated prior to electrode preparation. The aggregated heat treated oleic acid capped Fe_3O_4 performed similarly to the physically mixed $\text{Fe}_3\text{O}_4/\text{C}$ sample (Figure S3), demonstrating that the heat treatment process alone does not significantly affect the electrochemical performance of Fe_3O_4 .

The physically mixed $\text{Fe}_3\text{O}_4/\text{C}$ composite exhibits 840 mAh/g (based on Fe_3O_4 mass only) at cycle 25 at C/8. The capacity contribution of carbon black in the composite electrodes was determined by cycling 80% carbon black, 20% PVDF electrodes using the same discharge parameters (Figure S4). Subtracting out the contribution of the carbon black, the capacity of the Fe_3O_4 in the electrode is estimated to be 690 mAh/g. The data suggest that the Fe atoms fully reduced to Fe^0 during discharge are reoxidized to the +2 oxidation state upon charge, rather than an average oxidation state of +2.66 in Fe_3O_4 , consistent with the formation of FeO .³⁸

Electrochemical Impedance Spectroscopy. Electrochemical impedance spectroscopy (EIS) was performed on cells in the as prepared state and after cycling 25 times and can be a useful tool for assessing lithium ion transport in Fe_3O_4 .⁴²⁻⁴⁷ Figures 5E and 5F show EIS data both before and after cycling. All impedance spectra were fit to the equivalent circuit model (Figure S5).⁴⁸ The equivalent circuit is a modified version of the Randles circuit⁴⁹ with: R_s representing ohmic

resistances, a R_{CT} representing charge transfer resistances at the electrode/electrolyte interface, constant phase element (CPE) representing electrode double layer capacitance, and a Warburg element W_o representing Li^+ diffusion in the electrode. In the low frequency region, the Warburg coefficient (σ_w), which is inversely proportional to ion diffusion coefficient, was determined from slope of Z' vs. $\omega^{-1/2}$.⁵⁰⁻⁵¹

Before discharge, Fe_3O_4/C and HT- Fe_3O_4/C electrode containing cells exhibit similar impedance spectra with calculated R_{CT} values between 12-14 Ω (Table S1). In contrast, the impedance of OA- Fe_3O_4/C containing cells was significantly higher with R_{CT} values of 240-300 Ω . Further, calculated σ_w values were ca. 5x higher for OA- Fe_3O_4/C electrodes, indicating slower ion diffusion kinetics. Calculated ohmic resistances were ~1 ohm in all cases. These results indicate that: (1) the oleic acid layer on the surface of the Fe_3O_4 nanoparticles slows the kinetics of lithium ion transfer and diffusion, and (2) the detrimental effects of the oleic acid coating are eliminated in the HT- Fe_3O_4/C electrodes.

After 25 cycles, the relative magnitude of R_{CT} is in the order $Fe_3O_4/C < HT-Fe_3O_4/C < OA-Fe_3O_4/C$, reflecting the relative capacities of the three groups. Interestingly, for OA- Fe_3O_4/C electrodes, calculated R_{CT} values decreased after cycling, indicating that the resistive oleic acid layer may be somewhat disrupted after repeated lithiation/delithiation events, but were still significantly higher than the other two groups. R_{CT} values increased from 12-14 Ω to 25-26 Ω after 25 cycles for Fe_3O_4/C electrodes and from 12-14 Ω to 47-49 Ω for HT OA- Fe_3O_4/C electrodes. The higher charge transfer resistances of the HT- Fe_3O_4/C electrodes after cycling relative to Fe_3O_4/C correlate with the higher level of capacity fade observed in HT- Fe_3O_4/C electrodes. The data suggest that a greater level of surface film formation may occur over multiple cycles in the highly dispersed Fe_3O_4 particles of the HT- Fe_3O_4/C electrodes relative to

the aggregated $\text{Fe}_3\text{O}_4/\text{C}$ electrodes due to higher effective surface area in contact with the electrolyte. SEI formation has been shown to occur in iron oxides with high surface area and thus greater exposure to electrolyte and has been implicated as a significant cause of capacity fade.⁴¹

X-ray Absorption Spectroscopy - XANES. X-ray Absorption Spectroscopy (XAS) is an element specific technique that can be used to characterize both crystalline, amorphous or nanocrystalline phases within a sample and thus, does not rely on a long range periodic structure to obtain spectra, such as XRD.⁵²⁻⁵⁴ Specifically, X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) provide detailed information about the local electronic and atomic structural information respectively. These techniques also allow effective interrogation of amorphous or nanocrystalline materials.⁵⁵⁻⁵⁷

Coin cells were charged and discharged at the C/8 current rate to various dis(charge) and cycled states for XAS analysis, indicated as orange markers in Figure 5D. Electrodes were discharged to 0.9 V, 0.8 V, and 0.3 V (1st full discharge) and then charged to 3.0 V (1st charge). The results from the EXAFS study of Fe_3O_4 electrodes in various discharged, fully charged, and 25 times cycled states are presented in Figure 7 as XANES and Figure 8 as R-space plots (Fourier transforms of $k^2|\chi(R)|$). The three electrode types begin in the same oxidation states as the position of the XANES are consistent across all the undischarged electrodes (Figure 7), indicating that the oleic acid capping and the heat treatment processes do not significantly alter the average Fe oxidation state. Upon full discharge, the XANES of all three electrode types mimic the standard Fe metal XANES profile, indicating a dominant Fe^0 oxidation state. Minor discrepancies in the absorption edge profile between the three Fe_3O_4 samples likely indicating

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slight variations in the local atomic environment.⁵⁸⁻⁵⁹ Upon charge, all three Fe₃O₄ sample types revert to a FeO-like electronic state as evidenced by the shifts in the XANES profiles back to ca. 7.124 keV (FeO has an edge position of ca. 7.121 keV). There are slight differences between the highly dispersed samples (OA-Fe₃O₄/C and HT OA-Fe₃O₄) and the conventionally mixed Fe₃O₄/C, with the XANES of the highly dispersed electrodes slightly shifted to higher energy indicating more complete oxidation.

The 25th cycle discharged samples show a significant difference between the Fe₃O₄/C, the OA-Fe₃O₄/C and the HT OA-Fe₃O₄/C XANES spectra. The Fe₃O₄/C and HT OA-Fe₃O₄/C samples exhibit reversibility between the 25th discharged and charged states, demonstrating a charged FeO-like charged state and a metal Fe⁰ discharged state. However, in the 25th discharged state, HT OA-Fe₃O₄/C is more oxidized compared to the Fe₃O₄/C, as evidenced by the slight separation in the XANES spectra at ca. 7.115 keV (Figure 7) suggesting different local atomic environments between these two electrode types. The OA-Fe₃O₄/C remains in a FeO-like oxidation state similar to what was observed in the 1st charged state, regardless of discharged or charge on the 25th cycle.

X-ray Absorption Spectroscopy - EXAFS. In the undischarged state, the EXAFS spectra consist of two major peaks centered at ca. 1.4 Å and 2.6 Å for all three electrode types (Figure 8). These distances are not corrected for phase shifts and are ca. 0.3-0.4 Å shorter than the interatomic distances determined from theoretical EXAFS modeling. The peak at 1.4 Å originates from neighboring oxygen atoms, while the peak at 2.6 Å is primarily from neighboring iron atoms. As the discharge progresses, the peaks shift in position as well as evolve in shape, converting into two narrow peaks at ca. 1.4 and 2.3 Å when discharged to 0.9 and 0.8 V and eventually form a

single broad peak centered at ca. 2.1 Å in the fully discharged state, suggesting a significant phase transformation. The EXAFS spectra continue to shift upon recharge and cycling, with more significant differences between electrode types for the samples cycled 25 times and in the discharge state. Similar to observation in the XANES spectra (Figure 7), the Fe₃O₄/C and HT OA-Fe₃O₄/C maintain reversibility at the 25th discharge and charge states, mimicking the $|\chi(R)|$ observed on the initial cycle. The OA-Fe₃O₄/C sample, however, remains in a local atomic arrangement resembling the initial charged state no longer being able to discharge.

EXAFS spectra were fit using Artemis to quantify the differences in the interatomic distances and corresponding numbers of atoms present at each distance in the various discharged states (Figure 9). The structures of the undischarged Fe₃O₄ state are consistent among the three electrode types, confirming that the oleic acid capping and heat treatment processes do not disrupt the inverse-spinel Fe₃O₄ structure. In this state, Fe³⁺ ions occupy tetrahedral holes (Wyckoff position 8a) and both Fe³⁺ and Fe²⁺ ions occupy octahedral holes (Wyckoff position 16d) in a cubic close packed array of O²⁻ ions.⁶⁰ As such, both octahedral and tetrahedral iron atoms contribute to $|\chi(R)|$. A theoretical model of Fe₃O₄ with 8 distinct scattering paths was used to fit the EXAFS spectra for the non-discharged electrodes. There are two main features in $|\chi(R)|$ for the non-discharged state: a peak centered at approximately 1.4 Å in $|\chi(R)|$ consisting of nearest neighbor oxygen coordination shell contributions (Fe_{tet} - O, Fe_{oct} - O) and a second peak with maximum intensity at 2.6 Å in and a broad shoulder at 3.1 Å. The second peak is comprised of several Fe-Fe (Fe_{tet} - Fe_{tet}, Fe_{tet} - Fe_{oct}, Fe_{oct} - Fe_{tet}) and Fe-O (Fe_{tet} - O, Fe_{oct} - O) scattering contributions. Full EXAFS fitting results are tabulated in Tables S2-S9 and example EXAFS fits in $k^2 \chi(k)$ and $|\chi(R)|$ are shown in Figures S6-S14.

Upon discharge to 0.9 and 0.8 V, the general shape and position of both the first and second coordination shells change, indicating a phase transformation and $|\chi(R)|$ features are consistent among all three electrode types. At these discharge levels, the EXAFS spectra could no longer be modeled using the Fe_3O_4 crystal structure. Based on prior reports of phase conversion to FeO ^{5, 7, 38, 61}, the 0.9 and 0.8 V discharged states were initially fit using only Fe-O ($\text{Fe-O}_{\text{short}}$) and Fe-Fe contributions from a theoretical model based on the FeO crystal structure. However, this model resulted in fits with a residual signal in the second coordination shell, particularly at lower k-weights, indicating the presence of an additional low-Z element. This contribution was modeled as an additional oxygen pathway ($\text{Fe-O}_{\text{long}}$) at ca. $2.70 \pm 0.05 \text{ \AA}$ (for $\text{Fe}_3\text{O}_4/\text{C}$ electrode) presumably due to the formation of Li_2O upon discharge, and the resulting models produced fits with good agreement to the experimental spectra. The oxygen contribution from Li_2O is significant for the nanosize particles due to the high percentage of Fe atoms present on the particle surface. Thus, the fits at 0.9 and 0.8 V are comprised of a single oxygen contribution from the FeO crystal structure in the first coordination shell ($2.02 \pm 0.01 \text{ \AA}$ for $\text{Fe}_3\text{O}_4/\text{C}$ electrode), with the second shell comprised of the combination of both the Fe-Fe contribution from FeO ($3.02 \pm 0.01 \text{ \AA}$ for $\text{Fe}_3\text{O}_4/\text{C}$ electrode) and the additional $\text{Fe-O}_{\text{long}}$ path contributed by Li_2O . Both the number of near neighbors and the atomic distances are consistent across all three electrode types at 0.9 and 0.8 V, which corresponds well with similar electrochemical results at these levels of discharge.

In the fully discharged state (discharge to 0.3 V vs. Li/Li^+) the general shape of $|\chi(R)|$ evolves to a single broad peak. These EXAFS spectra were fit using both metallic Fe^{62} as well as the two Fe-O paths ($\text{Fe-O}_{\text{short}}$ at $1.93 \pm 0.02 \text{ \AA}$ and $\text{Fe-O}_{\text{long}}$ at $2.58 \pm 0.03 \text{ \AA}$ for the $\text{Fe}_3\text{O}_4/\text{C}$ electrode). It is evident that there is a dramatic shift in the Fe-Fe interatomic distance from ca.

3.0 Å to ca. 2.5 Å, signifying the transition from a FeO-like phase to Fe metal (Fe metal has a Fe-Fe interatomic distance of 2.54 Å). At the same time, the number of Fe-Fe near neighbors decreases from ca. 8 to ca. 3 Fe atoms. Previous TEM analysis indicates that the Fe metal nanoparticles that form during the conversion reaction from 9 nm Fe₃O₄ are approximately 1 nm in size, which aligns well with this data set.³⁸ Specifically, the particle size of Fe metal formed in all three fully discharged Fe₃O₄ samples is estimated to be ca. 1-3 nm, determined via a method developed to quantify the influence of atom packing, geometric arrangement of atoms and overall particle size on the observed number of neighboring atoms from EXAFS analysis.⁶³ With such small particle sizes, a significant number of Fe atoms are located on the surface of the particles, allowing a signal from surface oxides to be observed in EXAFS analysis, thus both the Fe-O_{short} and Fe-O_{long} contributions are still observed in the fully discharged state.

In the fully charged state (3.0 V vs. Li/Li⁺), there is a clear transformation to a FeO-like phase for all three electrode types. However, while Fe-O_{short} and Fe-Fe distances are similar to those observed in the FeO crystal structure (ca. 2.0 Å and 3.0 Å for Fe-O and Fe-Fe, respectively in the standard FeO crystal structure) the Fe-Fe contribution was significantly smaller in the charged electrodes, as evident by the lower number of Fe-Fe near neighbors (4.4 ± 0.9 in 1st charge state vs. 7.4 ± 1.9 in 0.8 V discharge state for Fe₃O₄/C electrode type). This reduction in neighboring iron atoms is likely due to disorder in the FeO-like phase. The similarity of the atomic structure of the three electrode types is consistent with the 1st charge electrochemical results.

Differences in the EXAFS spectra between Fe₃O₄/C, OA-Fe₃O₄/C and HT OA-Fe₃O₄/C electrodes becomes notable after 25 cycles and reflects the electrochemical cycling results, which show significant capacity fade for the OA-Fe₃O₄/C electrode (190 mAh/g), some capacity

decline for the HT OA-Fe₃O₄/C sample (650 mAh/g) and good capacity retention for the Fe₃O₄/C sample (840 mAh/g). In the discharged state, models of EXAFS spectra of the HT OA-Fe₃O₄/C and Fe₃O₄/C result in Fe-Fe interatomic distances and number of near neighbors the same as the 1st discharged state within error, however, there are clear differences in $|\chi(R)|$ between these two electrode types (Figure 8). EXAFS fitting results indicate structural disorder within the material, as quantified in the Debye-Waller factor, σ^2 , is higher in the HT OA-Fe₃O₄/C electrode (σ^2 of $0.0118 \pm 0.0052 \text{ \AA}^{-2}$) relative to Fe₃O₄/C (σ^2 of $0.0074 \pm 0.0017 \text{ \AA}^{-2}$). In addition, the HT OA-Fe₃O₄/C electrode shows the Fe-O_{short} scattering path with a significantly higher number of near neighbors relative to the Fe₃O₄/C electrode (1.9 ± 0.5 for HT OA-Fe₃O₄/C vs. 0.9 ± 0.1 for Fe₃O₄/C). When charged on the 25th cycle, both the HT OA-Fe₃O₄ and Fe₃O₄/C revert back to a FeO-like phase with Fe-O_{short} and Fe-Fe distances similar to those observed in the 1st charged state.

In contrast to Fe₃O₄/C and HT OA-Fe₃O₄/C electrodes, the OA-Fe₃O₄/C electrode remains in an FeO-like phase after discharge or charge in the 25th cycle, with characteristic Fe-Fe interatomic distance ($3.03 \pm 0.02 \text{ \AA}$) and number of Fe-Fe near neighbors (6.4 ± 1.1). This suggests that the majority of Fe within the electrode is no longer electrochemically active, as it remains in a FeO-like structure and does not convert to metallic Fe and Li₂O upon discharge. The minimal changes observed in the EXAFS spectra and XANES reflect the electrochemical cycling data, which show that in the 25th cycle the capacity of the OA-Fe₃O₄/C electrode is below 200 mAh/g.

DISCUSSION

The structural evolution observed for each of the three Fe_3O_4 electrode types upon extended cycling is different and reflects the observed electrochemical performance. The aggregated $\text{Fe}_3\text{O}_4/\text{C}$ electrode displayed the best capacity retention, with ca. 840 mAhg^{-1} for the 25th cycle. This is reflected in the EXAFS modeling, where the local structure on the 25th discharge is similar to that of the 1st discharge. On the 25th charge, there is a slight disordering in the structure as evidenced by the decreased number of neighboring Fe atoms from the FeO-like structure. However, it is clear from the results that the conversion reaction between the FeO-like structure and metallic Fe and Li_2O is reversible with no indications of structural degradation impacting the electrochemical performance within the first 25 cycles. Furthermore, EIS measurements indicate only a moderate increase in the charge transfer resistance after cycling compared with the undischarged electrodes. STEM of the electrode post-cycling (Figure 3C) shows that the iron oxide particles are still highly agglomerated in the composite.

The OA- $\text{Fe}_3\text{O}_4/\text{C}$ sample exhibits different behavior than the $\text{Fe}_3\text{O}_4/\text{C}$ electrode. During the initial discharge the OA- $\text{Fe}_3\text{O}_4/\text{C}$ follows the same trend as the other two Fe_3O_4 samples, a conversion to a FeO-like structure and then a phase transformation to metallic Fe^0 . Upon charge, the metallic Fe phase is converted to the FeO-like phase. However, after 25 cycles the local structure remains in the FeO-like phase, regardless of the electrochemical state of charge or discharge. Thus, the oleic acid capped Fe_3O_4 is initially electrochemically active, however the first cycle the capacity decreases from ca. 850 mAhg^{-1} to less than 200 mAhg^{-1} on the 25th cycle. EIS results show high R_{CT} and σ_w values for both undischarged and cycled OA- $\text{Fe}_3\text{O}_4/\text{C}$ electrodes, suggesting that the oleic acid coating on the surface of the Fe_3O_4 nanoparticles prevents effective lithiation/delithiation. After 25x cycles, the iron oxide particles are still well

dispersed on the carbon matrix (Figure 3F), suggesting that agglomeration of the material does not contribute to the capacity fade.

The HT OA-Fe₃O₄/C electrodes initially provide the highest capacity over the first ~ 10 cycles. However, the cells with these electrodes exhibit gradual capacity fade such that by cycle 25 their capacity has decreased to 650 mAh/g. EXAFS modeling of samples from the 25th cycle indicates reversibility between the metallic Fe state in the 25th discharge and a reversion to a FeO-like state in the subsequent charge. However, structural disorder, as quantified by σ^2 , is higher in the HT OA-Fe₃O₄/C electrode relative to the Fe₃O₄/C. XANES results indicate that the HT OA-Fe₃O₄/C electrode is more oxidized in the 25th discharge state compared with the aggregated Fe₃O₄/C electrode, suggesting reduced reversibility of the HT OA-Fe₃O₄/C after cycling compared to the non-dispersed sample. EIS measurements indicate that charge transfer resistance of HT OA-Fe₃O₄/C electrodes after cycling increase ca. 4 fold relative to the undischarged state. The increased structural disorder, retention of the FeO-like structure on discharge and high charge transfer resistance after 25 cycles reflect the increased loss of capacity on cycling. As observed with the cycled OA-Fe₃O₄ electrode, STEM of the electrode post cycling (Figure 3I) indicates that the individual iron oxide particles are still well dispersed on the carbon black matrix, and thus aggregation of the material is not believed to be a cause of the observed capacity fade.

Excessive growth of a surface solid electrolyte interphase (SEI) layer at the electrode/electrolyte interface has been implicated as a cause of capacity fade in iron oxides^{41, 64} and other conversion electrode materials.⁶⁵⁻⁶⁸ Ideally, once the SEI is formed, it protects the surface of the active material from continuous surface reaction, preventing further SEI growth while still allowing lithium ion migration.⁶⁹ However, formation of a stable SEI in conversion

electrode materials is complex. During conversion reactions large structural changes occur forming in new phases. As a result, the electrode surface in contact with the electrolyte is dynamic, where new active sites for additional electrolyte reduction during each cycle can be formed.^{67, 70} Additionally, the nanosized metal particles formed during reduction are catalytic in nature and appear to promote electrolyte decomposition^{66, 70-72} and may also facilitate decomposition of the SEI.⁷¹ The observed results were attributed to increased electrolyte degradation for materials with high surface area. A recent study on SEI layer evolution in iron fluoride conversion electrodes reports that capacity fade occurred due to growth of an SEI layer which increased in thickness with cycling and prevented ionic and electronic transport.⁶⁷ This is the first direct study comparing aggregated vs. highly dispersed conversion-type material nanoparticles. However, several papers have investigated the impact of particle size/morphology on cycling stability where worse capacity retention was reported for smaller particles and morphologies with higher surface area.^{66, 68, 73-76} The observed results were attributed to increased electrolyte degradation for materials with high surface area.

The results here show correlation among surface layer formation (measured as charge transfer resistance by EIS), increased structural disorder (determined through EXAFS fitting), reduced conversion between charged and discharged phases (determined through XANES), and capacity fade. Notably, the aggregated Fe₃O₄/C delivers ca. 840 mAhg⁻¹ after first few cycles and remains at that level through the 25th cycle. The electrodes with dispersed Fe₃O₄ nanoparticles show higher delivered capacity in the first several cycles, however, the capacity of the HT OA-Fe₃O₄/C decreases over 25 cycles. Impedance results suggest surface layer formation on the dispersed high surface area Fe₃O₄ nanoparticles with cycling resulting in capacity loss as the active material becomes more isolated. The Fe₃O₄ nanoparticles prepared

with an oleic acid coating do not provide efficient cycling performance due to significant resistance from the oleic acid.

Consideration of the surface area of the materials is illustrative. The measured BET surface area of 9 nm Fe₃O₄ is $136 \pm 7 \text{ m}^2/\text{g}$. Assuming spherical particles, the surface area value can be used to estimate an average Fe₃O₄ particle diameter of $8.5 \pm 0.4 \text{ nm}$ which is consistent with the data from TEM and XRD.³⁷ The results suggest that the BET measurement is a reasonable approximation of the surface area of the highly dispersed, non-aggregated Fe₃O₄ particles. In contrast, the surface area of the aggregates as observed in the physically mixed Fe₃O₄: carbon black electrodes can be estimated from the aggregate size distribution. Assuming spherical aggregates and a close packing density of 0.74 for primary particles within each aggregate, the surface area of the aggregates is estimated to be ca. $2 \text{ m}^2/\text{g}$. The continuum modeling results support the assertion that the aggregates are not rapidly and fully penetrated by electrolyte, which leads to the observed kinetic limitations.

Thus, we proposed the following mechanisms to rationalize the reported results. The highly dispersed HT OA-Fe₃O₄/C electrodes have Fe₃O₄ particles directly exposed to the electrolyte consistent with the higher delivered capacity over the first few cycles. However, the direct contact of the nanocrystalline Fe₃O₄ surfaces to electrolyte results in increased surface film formation resulting in isolation of the active material leading to capacity loss with extended cycling. XAS results indicate increased retention of the more oxidized FeO-like state on full reduction. In contrast, the aggregated Fe₃O₄/C electrodes demonstrate lower levels of surface film formation due to restricted electrolyte access to the core of the aggregate. The outcome is initially reduced delivered capacity, yet electrochemically good reversibility over 25 cycles, and

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3 is supported by the XAS results which indicate effective phase transformations during charge
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5 and discharge at the 25th cycle.
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10 CONCLUSION

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12 Fe₃O₄ composite electrodes were prepared using oleic acid as a capping agent in a carbon
13 black matrix and exhibit significantly reduced aggregation, both before and after heat treatment,
14 compared with physically mixed composite electrodes. Heat treatment of the oleic acid capped
15 Fe₃O₄/ carbon black composites under air was effective in removing the oleic acid while
16 preserving a high level of Fe₃O₄ dispersion in the carbon black.
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24 EIS and XAS measurements were utilized as complementary techniques to gain insight
25 into the electrochemical mechanisms of composite electrode materials upon cycling. The
26 aggregated Fe₃O₄/C electrode exhibited the most reversible electrochemical performance, with
27 capacity loss of < 5% between cycles 5 and 25. EXAFS modeling results revealed the local
28 structure after the 25th discharge was analogous to the local atomic structure on the 1st discharge.
29 Additionally, only a minimal rise in impedance was observed after 25 cycles. The highly
30 dispersed HT OA-Fe₃O₄/C electrodes delivered higher capacity through the first 10 cycles in
31 agreement with a multiscale continuum model simulation. Upon cycling, however, the HT OA-
32 Fe₃O₄/C electrode cells exhibited a steady decrease in capacity and an increase in charge transfer
33 resistance. EXAFS results indicated retention of the FeO-like phase on discharge at the 25th
34 cycle consistent with diminished reversibility. The OA-capped electrode containing cells
35 showed high impedance from the oleic acid layer on the nanoparticle surface, preventing
36 effective lithiation/delithiation of the iron oxide.
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The following mechanisms are proposed to rationalize the results. The highly dispersed HT OA-Fe₃O₄/C electrodes have Fe₃O₄ particles directly exposed to the electrolyte consistent with the higher delivered capacity over the first few cycles. However, direct contact of the nanocrystalline Fe₃O₄ surfaces to electrolyte results in increased surface film formation resulting in isolation of the active material leading to capacity loss with extended cycling. XAS results indicate increased retention of the more oxidized FeO-like state on full reduction. In contrast, the aggregated Fe₃O₄/C electrodes demonstrate lower levels of surface film formation due to restricted electrolyte access to the core of the aggregate. The outcome is initially reduced delivered capacity, yet electrochemically good reversibility over 25 cycles supported by the XAS results which indicate effective phase transformations during charge and discharge at the 25th cycle. These results affirm that the size and architecture of the electrode over multiple length scales must be considered in conjunction with the active material to realize the desired electrochemical performance and offer new insight into the causes of degradation and capacity fade in magnetite composite electrodes. Further, since aggregation can significantly impact properties of nanocrystalline materials for a variety of applications, the methodologies described here for characterization and analysis of the composite electrodes should be broadly applicable.

ASSOCIATED CONTENT

Supporting Information Available: Additional electrochemistry and EXAFS modeling details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGEMENT

This work was supported as part of the Center for Mesoscale Transport Properties, an Energy Frontier Research Center supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under award #DE-SC0012673. This research used resources of the Center for Functional Nanomaterials, which is a US DOE Office of Science Facility, at Brookhaven National Laboratory under contract #DE-SC0012704. The use of NSLS-I was supported by the U.S. Department of Energy, Office of Basic Energy Science under contract #DE-AC02-98CH10886. The authors acknowledge the Transmission Electron Microscopy Facility in the Central Microscopy Imaging Center (C-MIC) at Stony Brook University, Stony Brook, New York for their contribution towards the TEM preparation and data collection. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. Use of APS Beamline 8BM is partially

supported by the National Synchrotron Light Source II, Brookhaven National Laboratory, under DOE Contract No. DE-SC0012704.

Figure 1. (A) Powder XRD patterns of Fe₃O₄/C, OA-capped Fe₃O₄/C, and HT OA-capped Fe₃O₄/C with reference patterns for Fe₃O₄ and γ-Fe₂O₃. (B) Thermogravimetric analysis and (C,D,E) first derivative of mass as a function of temperature for samples (C) oleic acid, (D) oleic acid capped Fe₃O₄, and (E) heat treated oleic acid capped Fe₃O₄/C.

Figure 2. Crystalline structures of heat treated oleic acid capped-Fe₃O₄ nanoparticles. (A) Typical diffraction pattern showing the pure inverse spinel structure of Fe₃O₄ nanoparticles. (B) Diffraction pattern obtained from the aggregate in (D), showing two additional diffraction spots which correspond to the {116} plane of γ-Fe₂O₃ phase. (C) Diffraction pattern obtained from the localized region in (E), showing the {216} plane of γ-Fe₂O₃ phase. (D,E) TEM images corresponding to (B,C) respectively. (F) HRTEM image of one single Fe₃O₄ nanoparticle oriented along [111] direction.

Figure 3. STEM images before cycling (A,B,D,E,G,H) and after 25 cycles (C,F,I) for electrodes prepared with (A,B,C) Fe₃O₄ physically mixed with carbon, (D,E,F) oleic acid capped Fe₃O₄ incorporated into carbon, (G, H, I) heat treated oleic acid capped Fe₃O₄ incorporated into carbon.

Figure 4. Cross sectional TEM (A,B,C) and TXM-XANES (D,E,F) images where green pixels are fit to a Fe_3O_4 standard and red pixels are fit to a FeO standard for non-discharged electrodes prepared with (A,D) Fe_3O_4 physically mixed with carbon, (B,E) oleic acid capped Fe_3O_4 incorporated into carbon, and (C,F) heat treated oleic acid capped Fe_3O_4 incorporated into carbon.

Figure 5. (A,B) Cyclic voltammograms of composite electrodes $\text{Fe}_3\text{O}_4/\text{C}$, $\text{OA-Fe}_3\text{O}_4/\text{C}$ and $\text{HT OA-Fe}_3\text{O}_4/\text{C}$ for (A) cycle 1 and (B) cycle 2 at a scan rate of 0.1 mV/s. (C) Specific capacity versus cycle number at C/8 rate with capacity calculated using the mass of Fe_3O_4 in the electrode. (D) Representative discharge profiles at cycle 1 and cycle 25. Orange markers indicate

the various discharge/charge states used for XAS analysis (undischarged, 0.9V discharged, 0.8 V discharged, 1st discharge, 1st charge, 25th discharge, 25th charge). (E,F) Nyquist plot of AC impedance response of cells (E) before discharge and (F) after 25 cycles. The insets show the high frequency region of the impedance spectra.

Figure 6. Comparison of multi-scale model simulations to the 5th discharge of the coin-type cells with Fe₃O₄/C and HT OA-Fe₃O₄/C electrodes. Simulations and experiments were conducted at a rate of 115 mA/g Fe₃O₄. For both simulations, the diffusion coefficient of the solid state lithium

(D_x) was $3.0 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1}$. The other aggregate simulation was conducted using the previously determined aggregate diffusion coefficient of $2.3 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$.²¹

Figure 7. XANES comparison of conventionally mixed Fe₃O₄/C, OA- Fe₃O₄/C, and HT OA-Fe₃O₄/C electrodes during 1st and 25th cycles.

Figure 8. k^2 weighted $|\chi(R)|$ comparison of conventionally mixed $\text{Fe}_3\text{O}_4/\text{C}$, $\text{OA-Fe}_3\text{O}_4/\text{C}$, and HT $\text{OA-Fe}_3\text{O}_4/\text{C}$ electrodes at various charge/discharge levels.

Figure 9. EXAFS fit results of number of interatomic distances (left) and number of near neighbors (right) for conventionally mixed $\text{Fe}_3\text{O}_4/\text{C}$ (black), HT $\text{OA-Fe}_3\text{O}_4/\text{C}$ (blue) and $\text{OA-Fe}_3\text{O}_4/\text{C}$ (red) during the first cycle and the 25th discharge and charge. Contributions from nearest neighboring oxygen ($\text{Fe-O}_{\text{short}}$), and iron (Fe-Fe) are shown.

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TOC Figure: