X-ray fluorescence mapping: Insights into mesoscale structure impact on battery functional electrochemistry

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Abstract

Electron transfer and ion transport occurs over multiple-length scales ranging from the atomic to mesoscale within battery materials and electrodes. Micro-X-ray fluorescence (μ -XRF) is an important characterization tool as it can resolve structural, compositional, and redox information while providing insight into the spatial distribution of an electroactive material. In this work, μ -XRF mapping is used to probe the distribution of iron within thin planar slurry-based and thick porous carbon nanotube (CNT)-based magnetite (Fe_3O_4) electrodes. Notably, the porous CNT-based electrode showed homogenous distribution of Fe within the electrode whereas the planar electrode demonstrated distinct Fe aggregates. This information was used to rationalize the electrochemistry observed by cyclic voltammetry and galvanostatic cycling. The thick porous electrode delivered 215% more capacity per gram of magnetite during the first discharge, consistent with increased electrode homogeneity enabling effective ion access and electron transfer.

Introduction

Understanding the ion and electron transport mechanisms within batteries is important to developing next-generation technologies [1]. While the active materials are crucial and determine the theoretical energy content and voltage of the devices [2], electrode design factors can significantly impact electrochemical function [3]. Using a tightly-focused primary X-ray beam to induce X-ray fluorescence emission as a sample is scanned, micro-X-ray fluorescence (μ -XRF) enables spatially resolved characterization of metal centers

and their oxidation states [4]. Synchrotron light sources are desirable for μ -XRF due to their high X-ray intensity, although benchtop and even portable solutions have been reported [5, 6].

This report focuses on use of μ -XRF mapping for characterization of magnetite (Fe_3O_4) electrodes. Fe_3O_4 is a naturally abundant, non-toxic iron oxide material with a theoretical capacity of 926 mAh/g, $\sim 3 \times$ that of graphite (~ 372 mAh/g) [7] and is thus an attractive material for lithium ion battery anodes. Unlike graphite, Fe_3O_4 electrodes undergo a multi-step electrochemical reduction, beginning with Li^+ insertion into the host spinel structure and ending with conversion reactions to FeO and Fe^0 [8, 9]. The first lithium equivalent inserts into an interstitial octahedral (16c) site. The second lithium equivalent inserts into the Fe_3O_4 lattice, displacing the Li^+ already situated in 16c sites while the two Li^+ are redistributed between 8a, 48f and 8b interstitial tetrahedral sites. The third and fourth lithium equivalents result in formation of $\text{Li}_2\text{O} \cdot \text{FeO}$ and then Fe^0 metal, where the overall half-reaction for Fe_3O_4 is:

Fe_3O_4 crystallite size has been shown to significantly influence the electrochemistry due to changes in the length of the lithium ion diffusion path [4, 8, 10–12]. μ -XRF mapping provided important findings on the charge transport

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within thin planar Fe_3O_4 electrodes prepared with different crystallite sized material where electrodes prepared with 12 nm Fe_3O_4 showed increased Fe aggregation relative to 30 nm Fe_3O_4 electrodes. Complimentary X-ray absorption near edge spectroscopy (XANES) analysis indicated greater reduction of smaller Fe aggregates within the 30 nm electrode, which correlated with decreased total heat generation measured by isothermal microcalorimetry [13]. X-ray absorption spectroscopy has been used to follow the lithiation and electrochemical reduction of Fe_3O_4 , with complementary density functional theory (DFT) to elucidate the four species involved in the whole intercalation–conversion process of Fe_3O_4 [14].

An alternative approach toward designing high energy, high power batteries is fabrication of three-dimensional thick porous electrodes that facilitate ion transport. Electroactive materials can be incorporated into carbon based substrates to achieve desirable mechanical and electrochemical properties. Recently, carbon nanofibers impregnated with Fe_3O_4 nanoparticles (NPs) were shown to function as flexible and high capacity negative electrodes for lithium-ion batteries, achieving a initial high discharge capacity of 1146 mAh/g [15]. Carbon nanotube (CNT) substrates can provide multiple advantages including increased electrical conductivity and strong sp^2 hybridization to buffer volumetric changes of conversion lithiation reactions [3]. *Operando* energy dispersive X-ray diffraction (EDXRD) demonstrated Fe_3O_4 lithiation can progress homogeneously throughout Fe_3O_4 –CNT electrodes, indicating effective electronic and ionic transport [16].

In this work, μ -XRF mapping was applied to determined Fe dispersion within traditional, planar slurry-based and thick porous CNT-based Fe_3O_4 electrodes. The goal was to compare the mesoscale structure of a conventional electrode (coated foil) prepared using the state of the art manufacturing process, to a new electrode type (3D porous electrode) prepared using a lower manufacturing readiness fabrication technique. Cyclic voltammetry (CV) and galvanostatic cycling tests were performed to compare the electrochemistry of the two electrode constructs.

Materials and Methods

Fe_3O_4 NPs were synthesized by oxidizing a basic FeCl_2 solution in air for 12 h adapted from a previously reported method [13]. Electron microscopy imaging of these Fe_3O_4 NPs has been provided previously [8, 9]. The sample was washed via centrifugation using water and freeze-dried overnight. X-ray powder diffraction (XRD) patterns were collected using a Rigaku smart lab X-ray powder diffractometer with Bragg–Brentano focusing geometry and $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Crystallite size was calculated using the

Scherrer equation based on the full-width half-maximum of the 220 diffraction peak after correcting for instrumental broadening using a lanthanum hexaboride standard [17]. Crystallite size was also determined via Rietveld refinement using GSAS-II [18].

CNT-based electrodes were prepared with Fe_3O_4 and CNTs in a 6:4 mass ratio. Thin planar electrodes were prepared by mixing Fe_3O_4 (42.5%), carbon (42.5), and polyvinylidene difluoride binder (15%) with *N*-methyl-2-pyrrolidone (NMP) and casting onto copper foil. Synchrotron-based X-ray fluorescence mapping of the pristine electrodes was collected at the SRX Beamline (5ID) within the National Synchrotron Light Source (NSLS-II) at Brookhaven National Laboratory. The $100 \times 100 \text{ }\mu\text{m}$ maps were collected using a step size of $2 \text{ }\mu\text{m}$ and 65 mm detector distance. Energy was tuned with a double-crystal monochromator and fluorescence intensity detected using a three-element Vortex ME3 silicon drift detector. During the maps, the monochromator was tuned to 7200 eV. Calibration was executed with a Fe reference foil. ImageJ software was utilized measure size of Fe aggregates within the maps [19].

Coin type cells were fabricated with the Fe_3O_4 electrodes, lithium metal anodes, 1 M LiPF_6 EC/DMC (3/7 v/v) electrolyte, and polypropylene separators. CV was conducted at 0.1 mV/s between 0.5 and 2.8 V for five cycles using a Biologic VSP potentiostat at 30 °C. Extended cycling tests using a constant current of 100 mA/g or 400 mA/g were executed using a Maccor battery tester at 30 °C from 0.3 to 3.0 V [20]. The average mass loadings for the thin and thick electrodes were 1.25 and 3.72 mg/cm², respectively.

Results

Rietveld refinement of the XRD pattern confirmed a $Fd\bar{3}m$ space group for the as-synthesized material group (Fig. S1; Table 1), consistent with the inverse spinel structure. A crystallite size of 30 nm was determined by the Scherrer equation.

μ -XRF mapping is an element specific technique used here to understand the spatial arrangement of Fe electroactive material within planar and CNT-based electrodes. Notably, the CNT-based electrodes (120 μm) are thicker than the planar (35 μm) electrodes, and thus, display significantly higher raw, absolute XRF intensities. Therefore, the μ -XRF maps of the two electrodes were compared using the same relative intensity range, rather than absolute XRF intensity. μ -XRF maps of the planar slurry-cast electrode (Fig. 1a) demonstrated clear regions of Fe aggregation; whereas, the Fe signal was more dispersed throughout Fe_3O_4 –CNT electrode (Fig. 2b), indicating increased homogeneity. Fe aggregate size was estimated by measuring the maximum distance of a visualized aggregate, which is denoted in Fig. 1c as

Fig. 1 μ -XRF mapping of **a** planar and **b** CNT- Fe_3O_4 electrodes. **c** Size distribution of aggregates

Fig. 2 Cycles 1 and 5 voltage profiles for the **a, d** planar and **b, e** CNT electrodes collected at **a, b** 100 mA/g and **d, e** 400 mA/g. Discharge (closed circles) and charge (open circles) capacities as a func-

tion of cycle number for the planar (red) and CNT (blue) Fe_3O_4 electrodes at **c** 100 mA/g and **f** 400 mA/g

Feret length. Aggregate size distributions of the planar and CNT electrodes (Fig. 1c) showed larger Fe aggregates within the planar electrode and smaller aggregates in the CNT electrode, indicating increased homogeneity of the Fe_3O_4 electroactive material within the CNT design.

CV at 0.1 mV/s from 0.5 to 2.8 V was collected for five cycles to understand the reduction and oxidation mechanisms of planar (Fig. S2a) and CNT (Fig. S2b) Fe_3O_4 electrodes. During the first reduction, the both cell types showed three peaks at ~ 1.5 V, 1.0 V, and 0.5–0.7 V, indicating similar Fe_3O_4 reduction mechanism, consistent with the Li^+ insertion, FeO conversion and Fe^0 conversion reactions, respectively [9]. Notably, the CNT electrode generated

more mass normalized current during the FeO to Fe^0 conversion reaction at 0.5 V to 0.7 V, which may be attributed to decreased Fe_3O_4 aggregation within the electrode. During oxidation, the broad, two-peak feature from 1.5 to 2.0 V, indicates the oxidation of Fe^0 metal to the FeO rocksalt-like phase [9]. Upon cycles 2–5, one cathodic peak was identified at 1.0 V, consistent with a reduction of the FeO rock-salt structure back to Fe^0 . Both electrode designs demonstrated that the spinel structure was not recovered on delithiation.

Figure 2 compares the extended constant current cycling of $\text{Li}/\text{Fe}_3\text{O}_4$ cells containing the planar and CNT- Fe_3O_4 electrodes. Figure 2a–c were collected at a 100 mA/g current over 30 cycles while the data shown in Fig. 2d–f were

collected at a higher current of 400 mA/g. Voltage profiles for cycles 1 and 5 are shown for each current as a function of capacity. In the initial lithiation, both the planar and CNT electrodes demonstrated three voltage plateaus at 1.5 V, 1.0 V and 0.5 V, consistent with the CV results (Fig. S2). At the 100 mA/g rate, the planar electrode cells delivered 630 mAh/g upon lithiation to 0.3 V (Fig. 2a); while the CNT electrode delivered 1366 mAh/g (Fig. 2b). By cycle 5, the CNT electrodes reached a discharge capacity of 901 mAh/g, while the planar electrodes maintained a capacity of 468 mAh/g. The capacity retention after 30 cycles at 100 mA/g was 25% and 17% for the planar and CNT electrodes, respectively (Fig. 2c) indicating that both electrode architectures experienced capacity decreases on cycling. At the 400 mA/g rate, the first lithiation capacity for the planar electrode was 652 mAh/g (Fig. 2d) and the CNT electrode delivered 1256 mAh/g (Fig. 2e), suggesting an increase in rate does not significantly change first lithiation capacities for either the planar or CNT electrode. By cycle 5, the CNT electrodes reached a discharge capacity of 794 mAh/g, while the planar electrodes maintained a capacity of 446 mAh/g. After 30 cycles at 400 mA/g, the planar and CNT electrodes retained 18% and 13% capacity, respectively.

Discussion

In this report, μ -XRF mapping was collected on planar and CNT- Fe_3O_4 electrodes to elucidate the distribution of the Fe_3O_4 electroactive material within different electrode constructs. The CNT electrodes showed increased Fe homogeneity; whereas, the planar electrode showed clear regions of high Fe intensity, indicating aggregation. Statistical analysis of the Fe K -edge maps clearly demonstrated larger aggregate sizes within the planar electrode. CV indicated the initial reduction processes of the two electrodes were comparable, where three peaks present in initial cathodic scans, consistent with known lithium insertion and conversion reactions. Galvanostatic cycling results demonstrated significant differences between the planar and CNT electrodes, where the CNT electrode delivered 215% more capacity during cycle 1 lithiation at 100 mA/g and 400 mA/g rates consistent with decreased agglomeration observed by the μ -XRF mapping. Thus μ -XRF provides effective characterization of active material distributions and is well-suited for synergistic investigations that couple electrochemistry and other X-ray methods such as XANES.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1557/s43580-021-00150-w>.

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Data Availability Relevant data will be made available upon reasonable request to the corresponding authors.

Declarations

Conflict of interest The authors declare no conflicts of interest.

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