SYNTHESIS, AND STRUCTURAL, ELECTROCHEMICAL, AND MAGNETIC PROPERTY CHARACTERIZATION OF PROMISING ELECTRODE MATERIALS FOR LITHIUM-ION BATTERIES AND SODIUM-ION BATTERIES

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SYNTHESIS, AND STRUCTURAL, ELECTROCHEMICAL, AND MAGNETIC PROPERTY CHARACTERIZATION OF PROMISING ELECTRODE MATERIALS FOR LITHIUM-ION BATTERIES AND SODIUM-ION BATTERIES

THESIS

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the College of Arts and Sciences at the University of Kentucky

By
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2017
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ABSTRACT OF THESIS

SYNTHESIS, AND STRUCTURAL, ELECTROCHEMICAL, AND MAGNETIC PROPERTY CHARACTERIZATION OF PROMISING ELECTRODE MATERIALS FOR LITHIUM-ION BATTERIES AND SODIUM-ION BATTERIES

Iron oxides, have been widely studied as promising anode materials in lithium-ion batteries (LIBs) for their high capacity ($\approx 1000 \text{ mA h g}^{-1}$ for Fe$_2$O$_3$ and Fe$_3$O$_4$), non-toxicity, and low cost. In this work, $\beta$-FeOOH has been evaluated within a LIB half-cell showing an excellent capacity of $\approx 1500 \text{ mA h g}^{-1}$, superior to Fe$_2$O$_3$ or Fe$_3$O$_4$. Reaction mechanism has been proposed with the assistance of X-ray photoelectron spectroscopy (XPS). Various magnetic properties have been suggested for $\beta$-FeOOH such as superparamagnetism, antiferromagnetism and complex magnetism, for which, size of the material is believed to play a critical role. Here, we present a size-controlled synthesis of $\beta$-FeOOH nanorods. Co-existing superparamagnetism and antiferromagnetism have been revealed in $\beta$-FeOOH by using a Physical Property Measurement System (PPMS).

Compared with the high price of lithium in LIBs, sodium-ion batteries (SIBs) have attracted increasing attentions for lower cost. Recent studies have reported Na$_{0.44}$MnO$_2$ to be a promising candidate for cathode material of SIBs. This thesis has approached a novel solid-state synthesis of Na$_{0.44}$MnO$_2$ whiskers and a nano-scaled open cell for in situ TEM study. Preliminary results show the first-stage fabrication of the cell on a biasing protochip.

KEYWORDS: $\beta$-FeOOH, LIBs, magnetism, SIBs, in situ TEM

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December 11, 2017
SYNTHESIS, AND STRUCTURAL, ELECTROCHEMICAL, AND MAGNETIC
PROPERTY CHARACTERIZATION OF PROMISING ELECTRODE MATERIALS
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Chapter 1 Introduction and Background

1.1 Lithium Ion Battery

With the rapid growth of global populations, tremendous energy demand has led to an overwhelming consumption of fossil fuels, which have been the main energy sources for centuries.\textsuperscript{1,2} Global warming and air pollutions resulting from the combustion of fossil fuels are becoming urgent environmental concerns. Developing clean and sustainable new energy sources together with efficient energy conversion and storage systems will greatly alleviate the energy and environmental crisis.\textsuperscript{3} Rechargeable lithium-ion battery (LIBs) is one of the most successful technologies that can be applied not only to portable electronic devices but also in large-scale systems such as electric vehicles and stationary energy storage because of its high energy density, durability and environmental friendliness.\textsuperscript{4-5}

Typically, a rechargeable lithium ion battery shown in Figure 1.1. has a positive electrode (cathode upon discharge, e.g., LiCoO\textsubscript{2}) and a negative electrode (anode upon discharge, like graphite). Liquid/solid electrolyte is added to the cell offering transportation pathways for ionic species inside the cell and therefore driving the electrons through the external circuit. The cations travel from the negative to the positive electrode during the discharge.\textsuperscript{6} Upon charging, Li\textsuperscript{+} ions de-intercalate from the cathode and migrate through the electrolyte to the anode and end up intercalated into the anode material. Inversely, Li\textsuperscript{+} ions de-intercalate from the anode and then move to cathode upon discharging. The electrons always travel through the external circuit. The reversible intercalation and de-intercalation reaction of Li\textsuperscript{+} storage electrode materials enables the continuous conversion from chemical energy to electrical energy, and vice versa.\textsuperscript{7} Apparently, the choice of capable electrode materials will be crucial to make high-performance LIBs.
The conventional anode material for LIBs, graphite, is likely to be substituted by transition metal oxides due to its low theoretical capacity (372 mA h/g) and poor safety. Iron oxide based anode materials are intensively studied as highly potential candidates of LIBs electrodes owing to their high theoretical capacity (~ 1000 mA h/g), non-toxicity and earth-abundance. Among the iron oxide family, tunnel-structured $\beta$-FeOOH is very likely to be a high-performance anode material of LIBs for its ability to accommodate Li$^+$ ions in the square tunnels. However, rare electrochemistry studies have been done for $\beta$-FeOOH materials. In this report, electrochemical performance of 1-D $\beta$-FeOOH is evaluated in a half cell. A superior capacity of 1518 mA h/g has been achieved with $\beta$-FeOOH, comparable to that of popular anode materials, Fe$_2$O$_3$ or Fe$_3$O$_4$.

1.2 Magnetic Properties

Magnetic properties originate from the magnetic moment generated by the spins of unpaired electrons. According to the spin orientations, the common magnetic properties exerted by a material can be categorized into the following kinds: 1) paramagnetism 2) ferromagnetism 3) anti-ferromagnetism and 4) ferrimagnetism. The unpaired electrons’ spin orientation for each kind of magnetism is illustrated in Figure 1.2. In paramagnetism,
all unpaired spins’ orientations are randomized and the overall magnetic susceptibility is slightly positive which leads to an attractive interaction with the external applied field. In ferromagnetism, the spin orientations automatically align into one direction. This inherent uniform spin direction endows the ferromagnetism material a permanent magnet. More precisely, this permanent magnet originates from the so-called “magnetic domain”\textsuperscript{16-17} which refers to small regions with uniform spin orientation. It should be noticed that, although in one specific magnetic domain the spin orientations point to one direction, the direction is different from each other domain. In anti-ferromagnetism, the spin orientations are anti-parallel with the amounts of oppositely orientated spins equal. The overall magnetic moment is zero in anti-ferromagnetism. Lastly, ferrimagnetism is similar to anti-ferromagnetism except that the amounts of oppositely orientated spins are unequal, resulting a non-zero overall magnetic moment.

![Image of magnetic orientation types](image_url)

**Figure 1.2.** Schematic of unpaired electrons’ spin orientation in common magnetic effects.

When placed in an external applied magnetic field, $H$, the magnetic flux density within the sample is given as:

$$B = \mu_0 H + \mu_0 M$$

where $\mu_0$ is permeability of free space and $M$ is the magnetization of sample in this field. Instead of using the total magnetic flux density, $B$, to characterize the material’s magnetic property, a new term called “magnetic susceptibility ($\chi$)” is more commonly used which is defined as the ratio of sample’s magnetization to external field:

$$\chi = \frac{M}{H}$$
χ indicates a sample’s response to external magnetic field and can serve as a main parameter to study magnetic properties. Different magnetic materials can be distinguished by their magnetic susceptibility dependence on temperature. This is because thermal energy could disrupt the unpaired electrons’ spin orientation. For example, in a ferro/ferri-magnetism material, above certain temperature, the thermal motions will overcome the low-energy well formed by ordered orientation and leads to a paramagnetic behavior with randomized spin orientations. This temperature is called Curie temperature of ferro/ferri-magnetism. Similarly, anti-ferromagnetism will become paramagnetic above certain temperature because of the disruption of perfect anti-parallel spin orientation by thermal motions, this temperature is called Néel temperature.

The above mentioned temperature dependence of χ can be described by the well-known Curie-Weiss equation:

\[ \chi = \frac{C}{T - \theta} \]

where \( \chi \) is magnetic susceptibility, \( T \) is absolute temperature, \( \theta \) is Weiss constant and \( C \) is Curie constant. The reciprocal form of the Curie-Weiss equation is often used to plot \( \frac{1}{\chi} \) against \( T \) (e.g. \( \frac{1}{\chi} = \frac{T}{C} - \frac{\theta}{C} \)), the typical plot is shown as Figure 1.3.
It is shown clearly from Figure 1.3 that both anti-ferromagnetism and ferro/ferri-magnetism lose their ordered spin orientation above Néel ($T_N$) and Curie ($T_C$) temperature, respectively.

Beside the four kinds of magnetism exerted in bulk materials stated above, some nanostructured materials are also able to show superparamagnetic behavior. When ferromagnetic/ferrimagnetic materials are in nanoparticle form, the magnetic anisotropy energy which ensures ordered spin orientation becomes comparable to thermal energy, at such circumstance the magnetic moment of each particle will flip due to temperature fluctuation. The time between two magnetic moment flips is called Néel relaxation time ($\Gamma_N$) and can be described by the Néel-Arrhenius equation:

$$\Gamma_N = \Gamma_0 \exp \left( \frac{KV}{k_b T} \right)$$

where $\Gamma_0$ is attempt time (characteristic of material), $K$ is magnetic moment anisotropy energy density and $V$ is volume of particle ($KV$ is thus the energy barrier for the flip of magnetic moment in each particle), $k_b$ is Boltzmann constant and $T$ is absolute temperature. From the Néel-Arrhenius we can see clearly that $\Gamma_N$ is determined by particle volume $V$ and temperature $T$: smaller particle size and higher temperature will result in more frequent magnetic moment flip (smaller $\Gamma_N$).
Assuming a constant time $\Gamma_m$ is need for one experimental magnetization measurement, if $\Gamma_N \ll \Gamma_m$, e.g., several magnetic moment flips has happened during one measurement, the overall measured magnetic moment is nearly zero and the nanoparticles will show superparamagnetism. In contrast, if $\Gamma_N \gg \Gamma_m$, within one measurement, the nanoparticles do not have magnetic moment flips and the measured magnetization are unchanged. At such circumstance, the election spins are “frozen.” The temperature at which $\Gamma_N = \Gamma_m$ is called blocking temperature, $T_B$.

Magnetic behavior of nano-sized $\beta$-FeOOH is still an open debate since different magnetic properties have been observed by previous studies including antiferromagnetic, superparamagnetic and complex magnetic behaviors as will be discussed in chapter 3. Size correlated magnetic property study of $\beta$-FeOOH is limited to amorphous phase or multi–shaped structures. We report the first study of the size-effect of the magnetic behavior of well-crystalized $\beta$-FeOOH.

1.3 Sodium-Ion Batteries (SIBs) Cathode Na$_{0.44}$MnO$_2$

LIBs are highly developed energy storage devices with high energy density and long life-span, which dominates the commercial battery markets. However, when designing for large-scale energy storage, high price of lithium metal has largely limited the feasibility of LIBs. Compared with LIBs, SIBs start gaining more attractions for the abundant availability and lower cost of sodium. Unlike well commercialized LIBs, exploitation of appropriate SIB electrodes material for high-performance SIBs is still challenging. So far, disordered carbon is mostly used as the anode material for SIBs because of the low cost and outstanding stability. The sodium manganese oxide family such as NaMnO$_2$, Na$_{0.44}$MnO$_2$, Na$_{0.7}$MnO$_2$ have been considered to be capable candidates for SIBs cathodes for their high capacity, low cost, and environmental benignancy.

Recently, Na$_{0.44}$MnO$_2$ with multi-shaped tunnels in the crystal structure have shown a desirable capacity of 130 mA h/g and a good stability. Na$_{0.44}$MnO$_2$ has been synthesized through diverse methods such as co-precipitation synthesis, polymer-pyrolysis, hydrothermal synthesis and solid state synthesis. An MnO$_2$ precursor based solid state
synthesis is reported here for the first time. Ultra-long Na$_{0.44}$MnO$_2$ whiskers were obtained and would be further used for fabrication of single-rod nano-sized open cell for *in situ* TEM study, which will be discussed in detail in chapter 4.

Assembly of the cell is still undergoing, but a dynamic study of sodiation and desodiation of the Na$_{0.44}$MnO$_2$ will be carried out with *in situ* TEM, which would provide a breakthrough of knowing the phase evolution and structural change behind the coin-cell level electrochemistry performance. Specific design and fabrication will be discussed later in Chapter 4.
Chapter 2 High Capacity β-FeOOH Nanorods Anode Materials for Lithium-Ion Batteries

2.1 Introduction

Lithium-ion batteries (LIBs) are widely used as energy storage devices; varying from portable electronics devices to high volume application such as electric vehicles.\textsuperscript{34} The growing demand of electronic devices would expect the next generation of LIBs to have higher energy capacity, better rate capability and higher cycling stability.\textsuperscript{35} The traditional commercial anode material, graphite, with a low theoretical capacity (372 mA h/g) would not meet the increasing need for high-performance LIBs.\textsuperscript{8}

In this context, many transition metal oxides, such as TiO\textsubscript{2}, Co\textsubscript{3}O\textsubscript{4}, Cu\textsubscript{2}O, and MoO\textsubscript{2},\textsuperscript{36-38} have gained interests as potential high-performance anode materials. Among these metal oxides, iron oxide anode materials, particularly Fe\textsubscript{2}O\textsubscript{3} or Fe\textsubscript{3}O\textsubscript{4}, have been considered as highly desirable electrode materials for their high theoretical capacity (1-2 times larger than that of graphite), high earth-abundance, inflammable nature, non-toxicity, and low cost.\textsuperscript{9-12}

Recently, several studies have reported iron oxyhydroxides (α-phase, β-phase and amorphous FeOOH) to be promising candidates for LIBs anode materials since their capacities could be comparable to Fe\textsubscript{2}O\textsubscript{3} or Fe\textsubscript{3}O\textsubscript{4}.\textsuperscript{13-14,39} Typically, β-FeOOH has a tunnel-type structure as is shown in Figure 2.1. It has tetragonal lattice type with the space group of I 4/m. Tunnels are located along [001] direction within the $2 \times 2$ double FeO\textsubscript{6} octahedral chains, which enables lithium to be freely intercalated into or removed from the tunnels, providing sufficient pathways for charge mobility during battery discharge/charge. As a promising electrode material, the theoretical capacity of β-FeOOH in our case is calculated to be 905.96 mA h/g\textsuperscript{-1} through the equation below:

$$C = \frac{F \times z}{3600 \times M} = \frac{96485 \times 3}{3600 \times (55.8 + 2 \times 16 + 1)} = 905.96\text{mA h/g}$$

Where $C$ is the theoretical capacity (specific capacity) of β-FeOOH; $F$ is the Faraday Constant, $z$ is the number of electrons transferred in the reaction; and $M$ is the molecular weight of β-FeOOH.
Nanostructured materials have been proven to effectively enhance electrochemical performance of LIBs due to the larger electrode/electrolyte contact areas and shorter charge diffusion paths.\textsuperscript{40-42} One dimensional (1 D) \( \beta \)-FeOOH with nice single-crystal structure has rarely been studied as an electrode materials for LIBs. Besides, long-term cycling performance and fundamental understanding the lithium intercalation/extraction reactions are rather limited.

Herein, we developed 1D \( \beta \)-FeOOH nanorods as the anode material showing an impressive capacity as high as 1518 mA h/g, which is 50\% higher than that iron oxide (\( \text{Fe}_2\text{O}_3 \) and \( \text{Fe}_3\text{O}_4 \): about 1000 mA h/g). The high capacity attributes to both the multi-step lithiation reactions and existence of solid electrolyte interface (SEI) layers as well as the crystal structure-dominant properties. We proposed the reaction mechanism by employing X-ray photoelectron spectroscopy (XPS) analysis. Long-term cycling performance were conducted for 300 cycles, where the active material remains at a capacity of more than 500 mA h/g. Electrochemical impedance measurements were also carried out to further examine the reaction kinetics and structure evolution of the electrodes during discharge/charge. An equivalent circuit has also been proposed to analyze individual resistances.\textsuperscript{43-45}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2_1.png}
\caption{Schematic structure of \( \beta \)-FeOOH (the images were generated by VESTA46).}
\end{figure}
2.2 Experimental Methods

2.2.1 Preparation of β-FeOOH nanorods: β-FeOOH nanorods were synthesized via a hydrothermal method reported in the literature\textsuperscript{46}. 4 mmol of iron chloride (FeCl\textsubscript{3} 6H\textsubscript{2}O, Alfa Aesar) and 1.0 g of cetyl trimethylammonium bromide (CTAB, Alfa Aesar) were added to 40 ml of deionized water (DI water) followed by 30 min stirring to get complete dissolution. The solution was then transferred into a Teflon-lined stainless steel autoclave and was maintained at 80 °C for 12 h. The product was harvested by centrifugation and rinsing with DI water and methanol for several times, then dried at 60 °C overnight.

2.2.2 Characterization: The crystalline structures were confirmed by powder X-ray diffractometer (XRD, Bruker-AXS D8) with Cu Kα radiation (λ=1.5418 Å) at 2θ = 10° - 80°. The morphologies of β-FeOOH nanorods and electrodes was checked by scanning electron microscopy (SEM, S-4300SE, Hitachi) with an accelerating voltage of 10kV. The structures were also characterized by Transmission electron microscopy (TEM, JEOL 2010F) at 200 keV. The oxidation state change of the Fe was analyzed by X-ray photoelectron spectroscopy (XPS, K-Alpha system, ThermoScientific).

2.2.3 Electrochemical Measurement: The electrodes were prepared with β-FeOOH nanorods (70 wt.%), carbon black (CB, Super C65, TIMCAL, 20 wt.%) and binder (sodium carboxymethyl cellulose, CMC, SIMGA-ALDRICH, 10 wt.%). A planetary mixer (Mazerustar, KK-250S) was used to prepare uniform slurry. The slurry was casted on a battery grade Cu foil (thickness, 24 μm) with a blade (gap, 127 μm). The electrode was dried in a vacuum oven at 120°C for 12h. Electrode discs with a diameter of 12 mm were used for electrochemical tests. The β-FeOOH electrode and lithium (0.75 mm thick, Alfa Aesar) disks were assembled as the positive and negative electrodes, respectively in CR2025 type coin cells in an argon-filled glove box (<0.1 ppm of both oxygen and moisture, MBRAUN). Microporous polypropylene film, Celgard 2400, was used as the separator in each cell. The electrolyte was 1M LiPF6 in a mixture solution of ethylene carbonate.
and diethyl carbonate (EC: DEC = 1:1 wt%, BASF) with 10 wt% fluoroethylene carbonate (FEC, BASF) additive. Cycling tests and rate capability tests were conducted with a galvanostatic mode using Bio-Logic potentiostats (MPG-2 and VMP-3) at room temperature. C/10 is used for the first 2 cycles, and C/5 for the rest of the cycles. Cyclic voltammograms (CV) were carried out by using Bio-Logic potentiostats (MPG-2 and VMP-3) between 3.0 V and 0.01 V with a potential scanning rate of 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was measured after the electrodes reached the charging voltage (i.e., 3.0 V) after the 1st, 10th, 50th, and 100th cycles. The frequency ranges from 10 mHz to 100 kHz with an AC amplitude of 100 μA.

2.3 Preliminary Results and Discussion

![Figure 2.2](image)

Figure 2.2. (a) SEM image of as-synthesized β-FeOOH nanorods (inset: XRD pattern of as-synthesized β-FeOOH nanorods); (b) High-resolution TEM image of as-synthesise β-FeOOH nanorod.
Figure 2.2(a) shows the SEM image of the as-synthesized $\beta$-FeOOH nanorods, the length of the nanorods is about 430 nm whereas the diameter is around 120 nm. All the peaks from XRD (insert of Figure 2.2(a) could be indexed to a standard $\beta$-FeOOH diffraction pattern, indicating the as-synthesized material is phase-pure. High-resolution TEM image (Figure 2.2(b)) shows the well-defined crystal planes in a nanorod.
Figure 2.3. (a) The galvanostatic discharge/charge profiles of β-FeOOH-Li/Li+ cell; (b) CV curves of β-FeOOH-Li/Li+ cell with a scanning rate of 0.1mv/s.
Figure 2.3(a) shows the voltage-discharge capacity profiles of the β-FeOOH electrode. Three plateaus are shown in the first discharging curve including the first sloping plateau at around 1.87 V, the second plateau at around 1.47 V, and the third flat plateau at around 0.90 V. The first plateau corresponds to lithium intercalation in the β-FeOOH tunneling structure resulting in the reduction of β-FeOOH. While discharging to 1.47 V, LiFeOOH forms with the capacity of 215 mA h/g. It is less than the theoretical capacity (301.73 mA h/g) indicating the formation of Li_{0.7}FeOOH and relatively low utilization of β-FeOOH. The second sloping region (1.47 V-0.90 V) corresponds to the further intercalation of Li^+ and the formation of Li_{1.72}FeOOH since a capacity of 522 mA h/g is observed with respect to a theoretical capacity of 603.4 mA h/g for Li_2FeOOH. The third plateau at 0.66 V indicates the complete intercalation of Li^+ with the iron reduced to metal Fe (0). Meanwhile, SEI layer forms at this stage. The final discharging capacity 1518.3 mA h/g is larger than the theoretical capacity, which can be attributed to the formation of SEI.

In the second discharge process, the first plateau at around 1.87 V disappeared which indicates the poor reversibility of the first lithium intercalation reaction. The shape changes of the following two plateaus also reveal the low reversibility of the intercalation reactions. The significant capacity fading in ten cycles is probably due to the large volume change through the charge/discharge process. 47

Figure 2.3(b) shows the first ten cyclic voltammetry curves. From the first cycle, three reduction peaks are obtained at 1.70 V, 1.25 V and 0.68 V, which are correlated to the three plateau regions in the first discharge profile at 1.87 V, 1.43 V and 0.89 V, respectively. All oxidation and reduction peaks either become very weak or disappeared in the subsequent ten cycles, which indicates the poor reversibility of the reactions. The dropping of the peak 0.73 V is less notable than the other peaks meaning the relatively more reversibility of the final lithium intercalation reaction corresponding to the plateau around 0.89 V.
Figure 2.4. XRD patterns of the β-FeOOH electrode at different reaction stages: (a) As-made cathode, stars mark peaks of β-FeOOH; (b) After the first discharge at 0.01; and (c) After the first charge at 3.0 V.

The structure change of the β-FeOOH electrode after full lithiation/delithiation are further investigated by XRD. As shown in Figure 2.4(a), the most intensive peaks marked with stars (*) of the as-made electrode are attributed to β-FeOOH. As shown in Figure 2.4(b) and (c), no diffraction peaks were detected after the first cycle. Therefore, β-FeOOH transformed from a crystalline structure to amorphous. All three diffraction patterns have low peak intensities because the amount of electrode materials scraped off from the electrode is very small (~2 mg).
Figure 2.5. XPS spectrum of the electrode in the Fe 2p region, (a) After first discharge; (b) After first charge; (c) As-made electrode.

To further study the reactions that occurred in the charge and discharge process, XPS was carried out to analyze the as-made electrode as well as the electrode after first charge/discharge process by scanning the Fe 2p core-level spectrum. Figure 2.5(a) is the XPS spectrum at the end of first discharge process in which a low Fe oxidation state is expected. Two peaks are obtained by deconvolution in Figure 2.5(a) which are located at 713.72 and 707.0 eV corresponding to Fe 2p 3/2 in FeF$_3$ and Fe (0), respectively. This indicates the complete reduction from Fe$^{3+}$ to Fe metal during lithiation. Figure 2.5(b) is the XPS spectrum at the end of the first charge process in which high Fe oxidation state is expected. Deconvolution also resulted in two peaks in Figure 2.5(b): FeF$_3$ (715.02 eV) and Fe$_2$(III)O$_3$ (710.30 eV), consistent with another report. This suggests the irreversible oxidation of Fe into Fe$_2$(III)O$_3$ rather than the original β-FeOOH phase in the charge process, which agrees well with the electrochemical study. Figure 2.5(c) is the XPS spectrum of the as-made electrode which has two major peaks: 711.96 eV for Fe 2p 3/2 and 725.67 for Fe2p 1/2 corresponds well with previous reports.
Therefore, a three-step reaction mechanism accounting for lithiation can be proposed as:

1. $\beta$-FeOOH + Li$^+$ + e$^{-1}$ $\rightarrow$ LiFe(II)OOH

2. LiFe(II)OOH + Li$^+$ + e$^{-1}$ $\rightarrow$ Li$_2$Fe(I)OOH

3. Li$_2$Fe(I)OOH + Li$^+$ + e$^{-1}$ $\rightarrow$ Fe(0) + Li$_2$O + LiOH

Figure 2.6. SEM images of the $\beta$-FeOOH electrodes: (a) as-made, (b) after first discharge at 3.0 V and (c) after the first charge at 0.01 V.

SEM images could also confirm the morphology change of the $\beta$-FeOOH electrode changes during charge and discharge. The as-made electrode in Figure 2.6(a) consists of $\beta$-FeOOH nanorods and carbon black particles. For the electrode after the first discharge, an irregular flake-like morphology is present instead of the original rod-like structure of $\beta$-FeOOH. This drastic morphology change is due to the large volume swing during lithiation. For the electrode after first charge, the rod-like structure of $\beta$-FeOOH nanorods still exist but the surface become rough, which is also attributed to the volume expansion and structure damage during delithiation.
Figure 2.7. TEM images of the β-FeOOH electrode after (a-b) first discharge at 0.01 V and (c-d) after the first charge at 0.01 V.

Consistent with the SEM results, the crystal structure damage of the β-FeOOH electrode during lithiation and delithiation process are also detected by TEM. Figure 2.7(a-b) show the electrode after the first discharge. The β-FeOOH nanorods disappeared, leaving only the amorphous flakes and particles. From Figure 2.7(c-d), we can see that the well-defined crystal planes in the β-FeOOH nanorods (in comparison with Figure 2.2(b)) become porous and amorphous-like indicating the crystal structure damage after the lithiation/delithiation process.
Figure 2.8. (a) Cycling performance of the β-FeOOH electrode; (b) Rate capability of the β-FeOOH electrode. Current density (Ag-1): 0.1 (1st-4th cycle), 0.2 (5th-8th cycle), 0.5 (9th-12th cycle), 1 (13th-16th cycle), 2 (17th-20th cycle), 5 (21th-24th cycle), 0.1 (25th-28th cycle).
The cycling performance is shown in Figure 2.8(a). The β-FeOOH electrode exhibit a capacity higher than 500 mA h/g after 300 cycles with a stabilized Coulombic efficiency around 99%. Within the first five cycles, the capacity drops drastically from 1230.83 mA h/g to 814.84 mA h/g as a result of large volume change during lithiation and delithiation process, which is a normal phenomenon for high capacity electrode materials.\(^\text{47}\) The structure damage from the first cycle is confirmed by SEM images as mentioned above. Interestingly, the capacity begins to increase from 32th cycle with a lowest capacity of 650 mA h/g to 173th cycles with a highest capacity of 825.52 mA h/g. This increasing tendency is ascribed to an activation process.\(^\text{50}\) Through the charge-discharge process, the SEI layer gradually forms to cover the β-FeOOH nanorods leading to the alleviation of the volume swing.\(^\text{51}\) Due to the slow build-up of the SEI layer, the capacity experience an increase through 32th -173th cycle. At 173th cycle, the build-up of SEI layer is completed, followed by a continuous capacity decrease as a result of inevitable volume swing and crystal structure damage in the further cycling. The rate capability is evaluated after 100th cycle of charge-discharge is proceeded at different current density as is shown in Figure 2.8(b). The discharge capacity decreases as the current density increases. A fourth cycle specific capacity of 653.81 mA h/g at a current density of 0.1 A/g can be recovered to 644.14 mA h/g while restoring the current density back to 0.1 A/g, indicating a potentially high reversibility at 0.1 A/g.
Figure 2.9. Electrochemical impedance spectra (EIS) of the β-FeOOH electrode. (a) EIS of the electrode before cycling, after the 1st, 10th, 50th and 100th cycle; (b) EIS of the electrodes after 10th, 50th and 100th cycle; (c) the equivalent circuit: $R_1$ is the resistance
associated with the cell components; \( R_{\text{int}} \) is the interface resistance related to the SEI/active Fe interface; \( R_{\text{ct}} \) is the charge-transfer resistance; \( W \) is the Warburg impedance related to the diffusion of \( \text{Li}^+ \) into \( \text{Fe}_2\text{O}_3 \); \( C_1 \) is the double layer capacitor; \( Q_2 \) is the SEI/active materials interface capacitor.

Table 2.1 Charge-transfer resistance \( (R_{\text{ct}}) \) of \( \beta \)-FeOOH electrodes at delithiation state after different cycles.

<table>
<thead>
<tr>
<th>Cycle No.</th>
<th>Before cycle</th>
<th>1 cycle</th>
<th>10 cycles</th>
<th>50 cycles</th>
<th>100 cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{\text{ct}}/\text{Ohm} )</td>
<td>26</td>
<td>79.8</td>
<td>1.9</td>
<td>13.71</td>
<td>25.48</td>
</tr>
</tbody>
</table>

The Electrochemical impedance analysis was conducted to characterize the charge-transfer resistance of \( \beta \)-FeOOH electrode. The Nyquist impedance plots before and after cycling were shown in Fig8a. The equivalent circuit was shown in Fig. 8c. For this EIS study, we will focus on the charge transfer resistance, \( R_{\text{ct}} \), of the electrodes since it is the predominate parameters for lithiation/delithiation kinetics. Other impedance components, such as \( R_{\text{int}} \) and \( W \), are determined by reference electrode and cell configurations. For Nyquist based EIS analysis, the charge-transfer \( (R_{\text{ct}}) \) are the radius of the first semicircle (medium-frequency). It has been shown clearly from Figure 2.9(a) and Table 2.1 that \( R_{\text{ct}} \) changes with cycling number. Before cycling, \( R_{\text{ct}} \) was 26 Ohm and then reached a maximum as 79.8 Ohm after the first cycle, further cycling would first decrease and then increase \( R_{\text{ct}} \). The unsteady change tendency of \( R_{\text{ct}} \) of \( \beta \)-FeOOH electrodes may be attributed to the different oxidization products after different cycles.

2.4 Conclusions and Future Work

One dimensional \( \beta \)-FeOOH were fabricated as anode materials for LIBs. A significantly high capacity of 1500 mA h/g was obtained from \( \beta \)-FeOOH in the first cycle, which is higher than that of popular iron oxide electrodes, such as \( \text{Fe}_2\text{O}_3 \) and \( \text{Fe}_3\text{O}_4 \). A three-step lithiation mechanism was proposed based on XPS analysis and electrochemical
measurements. Long-term cycling performance of more than 300 cycles and rate capacity performance implied the durability of β-FeOOH nanorod electrode. This work paves the way for the application of β-FeOOH as an anode material in high capacity LIBs. Future work will focus on the full-cell performance of β-FeOOH anode with a cathode material of NMC (LiNiMnCoO₂).
Chapter 3 Size-effect Study of β-FeOOH Nanorods Magnetic Behaviors

3.1 Introduction

Magnetic materials have wide applications in various fields such as media storage,\textsuperscript{52} biosensor design,\textsuperscript{53-54} and drug delivery.\textsuperscript{55} The iron oxide family (includes iron oxides, iron hydroxides, iron oxyhydroxides) has drawn enormous attention for years because of their diverse magnetic properties including ferromagnetic, antiferromagnetic, superparamagnetic behaviors.\textsuperscript{56} Those complex magnetic properties are closely related to size and morphology of these materials, which have attracted numbers of researchers for much remaining controversy over the past few decades. Intensive size/morphology correlation property studies have been made on ferromagnetic materials but rare for antiferromagnetic ones.\textsuperscript{57}

β-FeOOH, a typical member of iron oxide family group with a known antiferromagnetic behavior in bulk phase, and a Néel transition temperature $T_N$ of 270 K-299K.\textsuperscript{58} For nanosized β-FeOOH, however, complex magnetic behaviors have been observed. Luna \textit{et al.} have synthesized ultrafine β-FeOOH nanoparticles with the size under 5 nm and observed frustrated antiferromagnetic behavior and acquired a Néel temperature of $T_N = 260$ K and a blocking temperature $T_B = 21$ K under an applied field of $H=100$ Oe.\textsuperscript{20} The frustration of antiferromagnetism arise from uncompensated spins due to surface effect. Kumar \textit{et al} have made β-FeOOH nanorods (length ~ 17 nm, diameter ~ 3.5 nm) and nanoparticle (size ~ 2.5 nm) mixture exhibiting superparamagnetic behavior with blocking temperature of 19 K at 500 Oe.\textsuperscript{21} Xue \textit{et al} have obtained amorphous-structured nanowires of different sizes (50 – 200 nm) showing consistent superparamagnetic behaviors and blocking temperatures ~ 20 K under 1000 Oe.\textsuperscript{22}

To the best of my knowledge, size-effect magnetic behavior study of well-crystalized β-FeOOH nanorods has never been reported. In this paper, β-FeOOH nanorods with high crystallinity as well as nice rod-shape structure have been synthesized. Size control synthesis of β-FeOOH nanorods were attempted in different ways. Magnetic properties of
β-FeOOH nanorods were discussed in detail. The size dependent magnetic property study is still in progress.

3.2 Experimental Methods

3.2.1 Preparation of β-FeOOH nanorods: β-FeOOH nanorods were synthesized via a hydrothermal method reported in the literature\textsuperscript{46}: 4 mmol of iron chloride (FeCl\textsubscript{3} \cdot 6H\textsubscript{2}O, Alfa Aesar) and 0 g, 0.25 g, 0.5 g, 1.0 g, 1.25 g, 1.5 g, 1.75 g, 2.0 g, and 3.0 g of cetyl trimethylammonium bromide (CTAB, Alfa Aesar) were added to 40 ml of deionized water (DI water) respectively, followed by 30 min stirring to get complete dissolution. The solution was then transferred into a Teflon-lined stainless steel autoclave and was maintained at 80ºC for 12 h. The product was harvested by centrifugation and rinsing with DI water and methanol for several times, then dried at 60ºC overnight.

3.2.2 Characterization: The crystalline structures were confirmed by powder X-ray diffractometer (XRD, Bruker-AXS D8) with Cu Kα radiation (λ=1.5418 Å) at 2θ = 10º - 80º. The morphologies of β-FeOOH nanorods and electrodes was checked by scanning electron microscopy (SEM, S-4300SE, Hitachi) with an accelerating voltage of 20kV. The lengths and diameters were measured out with “ImageJ” software.

3.2.3 Magnetic Properties Measurement: Physical Property Measurement System (PPMS) was applied to measure the magnetic properties of all samples using the Quantum Design PPMS 14 T with Vibrating SQUID Magnetometer (VSM). Field-Cool (FC) and Zero-Field-Cool (ZFC) data were collected under a constant external magnetic field of 100 Oe, while system temperature is increasing from 5 K to 300 K. Before collecting the data, the system was cooled down from 300 K to 5 K with an applied external magnetic field (FC) or without an applied external magnetic field (ZFC). The field dependence magnetism is measured at a constant temperature of 5 K for every sample.
3.3 Preliminary Results and Discussion

Figure 3.1. SEM image of as-synthesized β-FeOOH nanorods with increasing CTAB amount: (a) 0 g; (b) 0.25 g; (c) 0.5 g; (d) 1.0 g; (e) 1.25 g; (f) 1.5 g; (g) 1.75 g; (h) 2.0 g; (i) 3.0 g.
Figure 3.2. (a) XRD pattern of as-synthesized β-FeOOH nanorods with different amount of surfactant CTAB: 0.25 g, 0.5 g, 1.0 g, 1.25 g, 1.5 g, 1.75 g, 2.0 g, 3.0 g and standard β-FeOOH XRD pattern. (b) XRD pattern of as-synthesized β-FeOOH nanorods with no surfactant and standard β-FeOOH XRD pattern.

Figure 3.1. shows the SEM images of nine batches of β-FeOOH nanorods synthesized with variable amount of CTAB. All batches presented well-defined nanorod morphology. The size differences are hard to tell from the image and are further measured via software, ImageJ. The XRD patterns in Figure 3.2(a) confirmed all the batches of products are phase-pure β-FeOOH. Interestingly, when no CTAB is added, the synthetic approach gives β-FeOOH nanorod product as is shown in Figure 3.1(a) and 3.2(b).
I firstly attempted to control sizes of the nanorods by adjusting the amount of surfactant. After selecting the SEM images at the magnification of 50k (Figure 3.1), Sizes are measured through the software “ImageJ”, a maximum of ~40 whole nanorods can be visualized within each 50k SEM image. By manually selecting 40 individual nanorods and measuring their lengths and diameters with ImageJ, the average (mean) lengths, average (mean) diameters, minimum/maximum values and standard deviations are summarized out in table 3.1. We can see that the average lengths are ranging from 368 nm to 490 nm while the average diameters are varying from 87 nm to 116 nm, however, either is showing a simple increasing trend or decreasing trend. Average volumes are further calculated by the approximation of regarding all the nanorods as cylinders using the formula: \( V = \frac{4}{3} \pi \left( \frac{d}{2} \right)^3 \times l \), where \( V \) is the volume, \( d \) is average diameter of the nanorod and \( l \) is the average length of the nanorods.

<table>
<thead>
<tr>
<th>CTAB/g</th>
<th>Length (nm)</th>
<th>Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>SD</td>
</tr>
<tr>
<td>0</td>
<td>368.392</td>
<td>73.655</td>
</tr>
<tr>
<td>0.25</td>
<td>489.572</td>
<td>108.47</td>
</tr>
<tr>
<td>0.5</td>
<td>443.2</td>
<td>96.559</td>
</tr>
<tr>
<td>1</td>
<td>436.839</td>
<td>127.885</td>
</tr>
<tr>
<td>1.25</td>
<td>388.15</td>
<td>141.041</td>
</tr>
<tr>
<td>1.5</td>
<td>377.161</td>
<td>122.411</td>
</tr>
<tr>
<td>1.75</td>
<td>447.906</td>
<td>122.207</td>
</tr>
<tr>
<td>2</td>
<td>392.768</td>
<td>114.241</td>
</tr>
<tr>
<td>3</td>
<td>372.813</td>
<td>128.791</td>
</tr>
</tbody>
</table>
Figure 3.3. (a-c) size-surfactant amount relationship of nine groups of β-FeOOH nanorod products, (a): average length vs surfactant amount; (b): average width vs surfactant amount; (c): average volume vs surfactant amount; (d): aspect ratio (length/diameter) vs surfactant amount; (e) peak intensity ratio (040: 121) vs surfactant amount; (f): peak intensity ratio (040: 121) over aspect ratio vs surfactant amount.

Figure 3.4. (a)XRD pattern of as-synthesized β-FeOOH nanorods with different amount of surfactant CTAB, the circled peaks are from (040) and (121) planes.

Figure 3.3 describes different trials of exploring the size-surfactant relationship. (a-c) are average lengths, average diameters, and average volumes vs surfactant amount
respectively. They all present a fluctuant relationship between size and amount of CTAB, indicating CTAB amount might not be a critical issue for size-control synthesis of β-FeOOH nanorods. Aspect ratio, the ratio between length and diameter (L/D) was calculated for every sample, which also gives us a wavy tendency rather than a monotonic one in Figure 3.3(d). Moreover, a pair of peaks in each XRD pattern shows a unique intensity ratio as is shown in the circled area of Figure 3.4. Peaks are indexed by (040) and (121) crystal planes and the intensity ratio vs CTAB amount is plotted in Figure 3.3(e) but still gives a fluctuant trend. Lastly, values of peak intensity ratio divided by aspect ratio vs surfactant amount are studied in Figure 3.3(f), giving a complex trend too. All these surfactant-amount related tendencies prove that by simply adjusting CTAB in the solution cannot efficiently control the sizes of nanorods in our synthetic method.
Figure 3.5. FC-ZFC plots of as-synthesized β-FeOOH nanorods with increasing CTAB amount: (a) 0g; (b) 0.25g; (c) 0.5g; (d) 1.0g; (e) 1.25g; (f) 1.5g; (g) 1.75g; (h) 2.0g; (i) 3.0g from 5-300 K under the applied field of 100 Oe.

Magnetic properties of each sample has been measured to help us understand the potential behavior of β-FeOOH nanorods. From Figure 3.5, all FC-ZFC plots have gaps between the FC curve and the ZFC curve, meaning irreversible magnetic behavior of these materials.\(^{59}\) The irreversibility behavior is one of the characteristics of spin-glass-type materials.\(^{60}\) In our case, magnetic behaviors of nine samples can generally be separated into two distinct groups. First, superparamagnetic type: Figure 3.5(b), (d) and (f) corresponding to CTAB amount 0.25 g, 1 g, and 1.5 g, respectively. Those three samples exhibit maximum susceptibility ($\chi$) around 25 K in ZFC curve, namely a blocking temperature $T_B \approx 25$ K. When $T < T_B$ the magnetic spins are “frozen”, where the Néel relaxation time becomes longer, thus spin flipping cannot be captured during measurements. As the temperature raises before $T_B$, thermal energy positively assists the applied field to align the magnetic spins, giving a small susceptibility increasing regime up to $T_B$. In contrary to the regime $T > T_B$, all spins behave paramagnetic-like in alignment in which the Néel relaxation time is small enough to be captured within each measurement. With an increase in temperature after $T_B$, spin orientation is dominated by thermal energy which contributes to randomizing spin alignment, therefore reducing the susceptibility. When the temperature is further increased to about 260 K, merging of ZFC and FC curves is observed, indicating a complete transition to paramagnetic behavior. The merging point
is thus called Néel transition temperature, $T_N$. The rest six samples are categorized as antiferromagnetic type: Figure 3.5 (a) 0 g; (c) 0.5 g; (e) 1.25 g; (g) 1.75 g; (h) 2.0 g; (i) 3.0 g. All samples from this group only have a Néel transition temperature $T_N$ around 240 K, below which the perfect antiferromagnetic alignment will be disturbed by thermal energy, showing an increasing susceptibility up to $T_N$. When $T > T_N$, similarly to the first group, ZFC and FC curves merge together presenting a paramagnetic property. The sharp susceptibility decrease in the lower temperature range might be due to spin-glass behavior and need further examination.

![Figure 3.6](image)

Figure 3.6. (a) FC and (b) ZFC plots of all as-synthesized $\beta$-FeOOH nanorods with different amount of CTAB.

From FC curves in Figure 3.6(a), we observed higher susceptibility from three superparamagnetic samples at low temperature range ($T < 60$ K). As for ZFC curves in Figure 3.6 (b), blocking temperature maximum points are shown in superparamagnetic samples at low temperature (~25 K). Instead of a simple data trend, there are lots of intersections among the curves, which is a sign of independent magnetic behaviors from size or CTAB amount for each sample.
The field dependence magnetization plots of all samples are shown in Figure 3.7. Surprisingly, the coercive fields ($H_C$) for all samples are close to zero, revealing soft magnetization natures for all as-synthesized $\beta$-FeOOH nanorods. This observation is in contrast to previous discussion as we expect three superparamagnetic samples (with 0.25 g, 1 g and 1.5 g CTAB) $H_C$ values should be close to 0 while the rest anti-ferromagnetism samples have $H_C$ values modestly larger than 0. The discrepancy of field dependence behaver of anti-ferromagnetism samples may be due to the non-uniform size distribution of the nanorods. A stricter size-controlling synthesis method and detailed magnetism examinations may aid to find the reason of this discrepancy.
Figure 3.8. SEM image of size-control β-FeOOH nanorods with increasing iron chloride (FeCl$_3$·6H$_2$O) concentration: (a) 0.05 M; (b) 0.1 M; (c) 0.5 M; (d) 1.0 M.

Since, we figured out that size of β-FeOOH nanorods is independent from amount of CTAB, we thought to figure out another way to efficiently enable size-control synthesis of β-FeOOH nanorods. By controlling the concentration of starting material (FeCl$_3$·6H$_2$O) as 0.05 M, 0.1 M, 0.5 M and 1.0 M, while keeping other parameters exactly the same as described in the former synthetic method. Nanorods of different sizes were obtained: Figure 3.8(a) FeCl$_3$·6H$_2$O 0.05 M, length ~ 300 nm, diameter ~ 90 nm; aspect ratio 3.3; (b) FeCl$_3$·6H$_2$O 0.1 M, length ~ 400 nm, diameter ~ 100 nm; aspect ratio 4.0; (c) FeCl$_3$·6H$_2$O 0.5 M, length ~ 700 nm, diameter ~ 60 nm; aspect ratio 11.7; (d) FeCl$_3$·6H$_2$O 1 M, length ~ 700 nm, diameter ~ 60 nm; aspect ratio 16.0. A clear increase of aspect ratio of the nanorods will make each batch of sample distinct from each other, thus providing much stronger condition for size-dependence magnetic property study under way.
3.4 Conclusions and Future Work

Well-crystallized $\beta$-FeOOH nanorods have been synthesized. A size control synthesis has been achieved by controlling the concentration of starting materials rather than the amount of surfactant. Magnetic properties of $\beta$-FeOOH nanorods were categorized into two groups: superparamagnetic and anti-ferromagnetic. In a collaboration with University of Michigan, samples with a nice size distribution are under magnetic property measurement.
4.1 Introduction

As an emerging energy storage system, sodium-ion batteries (SIBs) are still facing challenges of developing more advanced electrode materials. Na$_{0.44}$MnO$_2$ has been considered as one of the outstanding cathode materials for its high theoretical capacity of 121 mA g$^{-1}$ and stability. As is illustrated in Figure 4.1, Na$_{0.44}$MnO$_2$ has orthorhombic structure built on corner-sharing MnO$_5$ pyramids and MnO$_6$ octahedra. The crystal structure is featured by two unique types of tunnels, S-shape tunnels and pentagon-shape tunnels. Na in pentagon tunnels are locked while those situated in the large S-shaped tunnels would be easily extracted or inserted. There are also two oxidation states of manganese ions, Mn$^{3+}$ and Mn$^{4+}$ ions. All Mn$^{4+}$ ions and half of the Mn$^{3+}$ ions are in octahedral coordination sites while the rest of Mn$^{3+}$ ions are in pyramidal sites. Two-step solid-state synthesis of Na$_{0.44}$MnO$_2$ whiskers has never been approached.

Figure 4.1. (a) Schematic crystal structure of Na$_{0.44}$MnO$_2$ (looking down the c-axis).

Cyclability is known to be one of the most important criteria to evaluate the performance of an electrode material. In other words, for lithium or sodium ion battery materials, a desirable electrode material would have the capability to host or relax Li$^+$ or Na$^+$ reversibly without structural degradation. Understanding the underlying phase and structural change mechanism during (de) lithiation/(de)sodiation would greatly help to design high
performance LIBs and SIBs. In situ TEM, a powerful tool to capture insight into the structural study upon the occurrence of battery reactions, has already been applied to investigate the phase evolution, as well as failure mechanism for various electrode materials.\textsuperscript{64-65} Lu et al. have employed in situ TEM to study Ge nanowires undergoing (de)sodiation, proving Ge nanowires are excellent candidates for SIB electrode by showing sodiation and desodiation at high rates.\textsuperscript{66} The experimental set-up is depicted below in Figure 4.2, a Ge nanowire act as the working electrode, pure sodium metal functions as counter electrode, and NaO\textsubscript{2} layer works as solid-state electrolyte. The contact between Na/NaO\textsubscript{2} electrode and Ge nanowire is achieved by a piezo-positioner. With the similar set up in Figure 4.2(b), Su et al has directly visualized structural evolution of Co\textsubscript{9}S\textsubscript{8}-filled carbon nanotubes using in situ TEM.\textsuperscript{67}

![Figure 4.2](image.png)

Figure 4.2. (a) and (b) Schematic illustrations of the experimental setup for in situ TEM analysis of nanoscale Na-ion battery.

The fabrication of a nano-sized open cell with single Na\textsubscript{0.44}MnO\textsubscript{2} rod and explore the in situ behavior during sodiation and desodiation will be an exciting and helpful study in SIBs development. In this report, Na\textsubscript{0.44}MnO\textsubscript{2} whiskers were first gained via a precursor derived two-step solid-state synthesis. A preliminary schematic design of in situ cell has been proposed as is displayed in Figure 4.3: a single Na\textsubscript{0.44}MnO\textsubscript{2} whisker will be chosen as the working electrode whereas pure Na metal will be the counter/reference electrode, both electrodes will be mounted onto the gold electrode on the E-chip. A thin Na\textsubscript{2}O layer will be formed by a short exposure of Na in air, working as solid-state electrolyte.
Figure 4.3. (a) Schematic illustrations of the experimental setup for in situ TEM analysis of single Na0.44MnO2 based nanoscale Na-ion battery.

Aduro TEM heating/biasing holder system (Figure 4.4(a)) is used to place the protochip, shown in the center of Figure 4.4(b). Biasing can be applied either between 2 & 3 or 1 & 4 electrodes while a sample is contacted to some of the electrodes. The wholes on the central part of the chip (Figure 4.4(c)) would provide vacuum area for imaging the sample under TEM.

Figure 4.4. (a) Protochips Aduro TEM holder; (b-c) illustrations of AEL-10 biasing E-chip.
4.2 Experimental Methods

4.2.1 Hydrothermal synthesis of MnO$_2$ nanowire precursor: MnO$_2$ nanowires were synthesized with the method reported in literature.\textsuperscript{68} Typically, 1.521 g MnSO$_4$·H$_2$O (SIGMA-ALDRICH) and 0.096 g NaClO$_3$ (SIGMA-ALDRICH) were added into 40 mL deionized water and stirred for 30 min followed by transferring into a Teflon-lined stainless steel autoclave. The autoclave was then sealed and maintained at 160 °C for 18 hours. After the system was cooled to room temperature, MnO$_2$ nanowire product was collected by centrifugation and washed with deionized water for several times. Finally, sample was dried in oven at 80 °C overnight.

4.2.2 Solid-state synthesis of Na$_{0.44}$MnO$_2$ whiskers: Na$_2$CO$_3$ and MnO$_2$ precursor were mixed with a (Na: Mn) molar ratio of 0.7:1 in 1 mL deionized water. Excess amount of NaCO$_3$ (Alfa Aesar) is added to ensure the sufficient Na diffusion into MnO$_2$ nanowires. The slurry was stirred for 30 min and then dried into a pellet at 60 °C for 5h in air. The pellet was then placed in a crucible and annealed in the muffle furnace at 800 °C for 40 hours. Right after the reaction time reaches 40 hours, the sample was taken out immediately and quenched in liquid nitrogen to lock the structure and the morphology from the high-temperature phase.

4.2.3 Single-rod open cell fabrication: Focused ion beam scanning electron microscope (FIB-SEM) were used to assemble a single whisker onto the AEL-10 protochip. A gas injection system (GIS) was used to deposit platinum onto two end of a rod/whisker in order to “glue” the rod on the electrodes. Then a Gallium liquid metal ion source (LMIS) was used to mill parts of the sample to the thickness less than 100 nm to endure the transmission of electrons under TEM.

4.2.4 Characterization: the crystal of structures Na$_{0.44}$MnO$_2$ whiskers were confirmed by powder X-ray diffractometer (XRD, Bruker-AXS D8) with Cu Kα radiation ($\lambda$=1.5418 Å) at 2θ = 10° - 80°. The morphologies of β- Na$_{0.44}$MnO$_2$ whiskers was checked by scanning electron microscopy (SEM, S-4300SE, Hitachi) with an accelerating voltage of 10 kV. The fabricated sample for \textit{in situ} biasing chip was imaged by Transmission electron microscopy (TEM, JEOL 2010F) at 200 keV.
4.3 Preliminary Results and Discussion

Figure 4.5. (a) SEM image of as-synthesized MnO2 nanowires; (b) XRD pattern of as-synthesized MnO2 nanowires.

Figure 4.6. (a) SEM images of as-synthesized Na\textsubscript{0.44}MnO\textsubscript{2} whiskers; (b) XRD pattern of as-synthesized Na\textsubscript{0.44}MnO\textsubscript{2} whiskers.

Figure 4.5(b) confirmed that phase-pure MnO\textsubscript{2} nanowires have been obtained with an average length:10-20 μm and average width: 50-200 nm. Figure 4.6(a) shows the as-synthesized whisker length: ~20 μm; width: 0.1-2 μm, which are significantly enlarged in volume compared with the precursors. This length will be super suitable for fabricating an open cell with a single rod/whisker on a protochip since the distance between two electrodes are 20 μm. The crystal structure of Na\textsubscript{0.44}MnO\textsubscript{2} is confirmed by XRD pattern in
Figure 4.6(b), except tiny amount of unreacted Mn$_2$O$_3$ and impurity, all peaks could be indexed by the standard pattern of Na$_{0.44}$MnO$_2$.

Figure 4.7. (a) TEM image of four electrodes on an AEL-10 biasing protochip with a single Na$_{0.44}$MnO$_2$ attached (b) a segment of the whisker on the whole at the magnification of 5 k; (b) high resolution image of red-squared area on the whisker.

Above TEM images provide the successful bridging of single rod/whisker between two electrodes. The preliminary fabrication is not a cell yet, but can be potentially used for observing sodium ion migration when applying a very low bias between two electrodes. The thickness of the whisker edge is thinned down by FIB and is small enough to see through under TEM. High resolution image reveals the fringes of the crystal planes. All these processes achieved so far would be important for us to carry out the in situ study of single-rod based open cell.

4.4 Conclusions and Future Work

Na$_{0.44}$MnO$_2$ whiskers have been synthesized via a two-step precursor – involved solid-state method. A single whisker was used to fabricate nano-sized open cell for in situ TEM study on a AEL-10 biasing protochip. FIB enabled the first-stage assembly where the rod is attached to two electrodes. A real-time dynamic study of sodiation and desodiation of the Na$_{0.44}$MnO$_2$ will be carried out with in situ TEM in the future after the cell has been well made.
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