



# Comparative Study of Li and Na Electrochemical Reactions with Iron Oxide Nanowires



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## ARTICLE INFO

### Article history:

Received 10 September 2013

Received in revised form 2 December 2013

Accepted 3 December 2013

Available online 17 December 2013

### Keywords:

lithium battery  
sodium battery  
iron oxide nanowire  
conversion reaction  
TEM investigation.

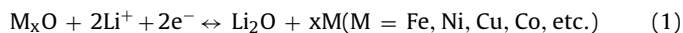
## ABSTRACT

This study emphasizes optimization of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  nanowire conversion electrodes by directly-growing them on current collectors, preparing them as single crystals, and coating their surfaces with conductive carbon coatings. The systems with the least polarization during Li-ion cycling are then tested as electrodes for Na-ion chemistry. Precipitation of nanograined material during the first cycle reduces the polarization associated with Li insertion upon subsequent cycles. After the first cycle, delithiation primarily contributes to polarization associated with the conversion reaction with lithiation occurring close to the equilibrium potential. The initial reduction reaction does not proceed to completion for Na chemistries. Electron microscopy reveals significant Na insertion that occurs along with the formation of defect networks. However, the results indicate that an insufficient amount is present to form critical nuclei necessary to induce the conversion reaction.

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## 1. Introduction

Conversion reactions possess the potential to greatly enhance the energy density of electrochemical storage technologies. Many conversion electrodes exhibit capacities in the range of  $500\text{--}1000\text{ mAhg}^{-1}$  and can achieve good cycle life.[1] Metal oxide based conversion reactions with Li typically proceed as follows [2]:



High capacity high voltage conversion cathodes based on metal fluorides show particular promise in improving Li-ion energy density.[3] Conversion reactions typically suffer from hysteresis that limits their round trip efficiency.[1] Since conversion reactions do not require intercalation, ideally they should be well suited to perform well as electrodes for Na-ion reactions. Developing high capacity Na-ion batteries is desirable because of Na's relative abundance and low cost. However, limited success has been achieved in applying conversion reaction electrodes to Na-ion systems.[4] This work investigates the rate limiting processes associated with Li-ion and Na-ion cycling of model iron oxides ( $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ) conversion reaction electrode materials.

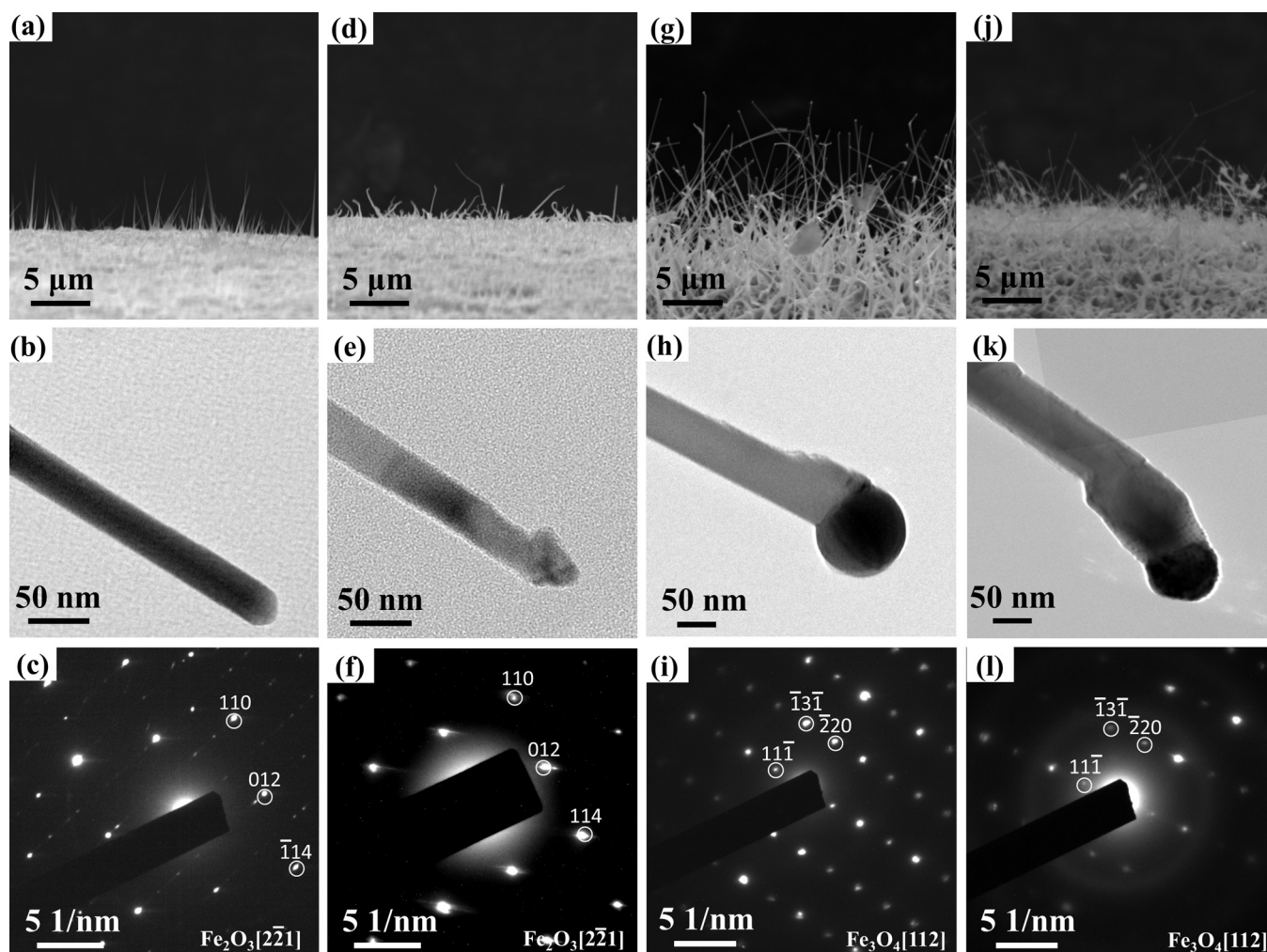
Iron oxides are interesting conversion reaction anodes due to the high capacity ( $1007\text{ mAh/g}$  for  $\text{Fe}_2\text{O}_3$  and  $900\text{ mAh/g}$  for  $\text{Fe}_3\text{O}_4$  [5,6]), abundance, low toxicity, and low cost. Similarly, iron fluorides could serve as ideal next-generation Li-ion cathodes [3].

Unfortunately, poor electronic conductivity and short characteristic diffusion lengths at room temperature handicaps iron oxides and limit their commercial applicability. Therefore, various approaches to nanostructuring have been married with carbon coating strategies to achieve reasonable performance [7–15]. Nanostructures grown directly on current collector are favored to reduce contact resistance and achieve optimal charge transport[16].

$\text{FeS}_2$ ,  $\text{Ni}_3\text{S}_2$  and  $\text{NiCo}_2\text{O}_4$  have been shown to function as conversion reaction electrodes for Na-ion batteries.[4,17–20] These reactions result in nanocrystalline metal surrounded by  $\text{Na}_2\text{O}$  or  $\text{Na}_2\text{S}$ . It has been suggested by some that iron oxides do not function as Na-ion conversion electrodes.[4] Na insertion was observed in  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  nanoparticles ranging from  $10\text{--}400\text{ nm}$  with increased capacity resulting from particle size reduction [21]. However, no conversion reaction was observed. Recent work demonstrates Na conversion reaction with  $\text{Fe}_3\text{O}_4$  in the particle size range from  $4\text{ to }10\text{ nm}$  [22]. However, much of the capacity achieved was in the range where Na intercalates into carbon, which was present in large amounts. The primary evidence for the reaction is the observation of  $\text{Na}_2\text{O}$  in electron diffraction and a single Fe ring that overlaps with  $\text{Fe}_3\text{O}_4$ . The  $\text{Na}_2\text{O}$  could possibly form upon exposure of the sample to air while loading it into the transmission electron microscope. However, the overall capacity does exceed what would be expected from the carbon alone. Hollow  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles with abundant cation vacancies have recently been reported to be promising electrode materials for Na-ion batteries in terms of the both capacity and cycle life [23]. The various results motivate further investigation into Na conversion reactions with Fe-based oxides.

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**Fig. 1.** SEM micrographs, TEM micrographs, and selected area electron diffraction (SAED) patterns of as-prepared nanowires:  $\alpha$ - $\text{Fe}_2\text{O}_3$  (a–c),  $\alpha$ - $\text{Fe}_2\text{O}_3$ -C (d–f),  $\text{Fe}_3\text{O}_4$ -C (g–i) and  $\text{Fe}_3\text{O}_4$  (j–l).

In this work, we grow  $\alpha$ - $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  single crystal nanowires with and without carbon coating directly on current collectors. The systems are optimized for Li-ion cycling and subsequently characterized as Na-ion hosts.

## 2. Experimental

### 2.1. Preparation of $\alpha$ - $\text{Fe}_2\text{O}_3$ single crystal nanowires without carbon coating

220  $\mu\text{m}$  diameter (99.99%, Goodfellow) 10 cm long iron wire was cleaned in dilute hydrochloric acid (2% in volume) and rinsed with acetone, alcohol, and deionized water. AC power ( $\sim 4\text{W}$  at 60 Hz) was then applied for  $\sim 10$  mins to promote surface oxidation during Joule heating [24]. Nanowire growth proceeds by rapid cation diffusion that emerges from grain boundaries of a thicker underlying oxide.

### 2.2. Preparation of $\alpha$ - $\text{Fe}_2\text{O}_3$ single crystal nanowires with carbon coating

The resulting  $\alpha$ - $\text{Fe}_2\text{O}_3$  single crystal nanowires were heated to  $500^\circ\text{C}$  for 5 h in a tube furnace containing Ar that had flowed through toluene. Decomposition of the toluene produces a carbon coating on the nanowires.

### 2.3. Preparation of $\text{Fe}_3\text{O}_4$ single crystal nanowires with carbon coating [25]

220  $\mu\text{m}$  diameter iron wire (99.99%, Goodfellow) was first cleaned as described above. It was pre-oxidized at  $250^\circ\text{C}$  for 0.5 h on the hotplate in ambient conditions. The samples were subsequently annealed at  $550^\circ\text{C}$  in a crucible also containing pure Cu. Annealing was performed in Ar that flowed through toluene prior to entering the furnace. During annealing Cu deposits on the Fe substrate and catalyzes the growth of  $\text{Fe}_3\text{O}_4$  nanowires. This process does not result in a thick underlying oxide typical of the  $\text{Fe}_2\text{O}_3$  growth process.

### 2.4. Preparation of $\text{Fe}_3\text{O}_4$ single crystal nanowires without carbon coating

Reactive ion etching in 5% oxygen and 95% argon for 40 sec was used to remove the carbon coating from the  $\text{Fe}_3\text{O}_4$  nanowires prepared as described above.

### 2.5. Electrochemical testing

The nanowires were tested in a vial cell within a dry Ar-filled glovebox (Mbraun Labstar). The iron wire substrate served as the electrode current collector. This was cycled against either a metallic lithium or sodium counter electrode in ethylene carbonate (EC)

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