

***In-situ* Liquid Phase Transmission Electron Microscopy Study for Phase Evolution of α -Fe₂O₃ Nanorods upon Lithiation/delithiation Process**

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Iron oxide (Fe₂O₃) have attracted significant attention and intensively investigated for anode material in lithium-ion battery (LIB) owing to the high theoretical capacity (1007 mAh g⁻¹), low cost, low toxicity, and ease of fabrication [1,2]. Despite these advantages, a practical use of Fe₂O₃ anodes in LIB is still limited by some critical issues such as irreversible conversion reaction, and capacity loss, etc. The electrochemical reaction of Fe₂O₃ in LIB is simply known as Fe₂O₃ + 6Li ↔ 2Fe + 3Li₂O [3]. However, previous study shows that Fe₂O₃ nanoparticles undergo irreversible electrochemical process, resulting in large capacity fading in the first cycle [4], which indicates the fact that conversion mechanism of Fe₂O₃ in LIB is still not fully understood yet.

Liquid phase transmission electron microscopy (TEM) with microfluidic electrochemical cell extends our capability for characterizing microstructures in the liquid environment at nanoscale while measuring the electrochemical properties. Here, we investigate the structural changes of Fe₂O₃ nanorods during lithium insertion/extraction process using in-situ liquid phase TEM. Liquid flow in-situ TEM holder (Poseidon Select, Protochips Inc, USA) and silicon microchip device for electrochemistry are employed to perform structural characterization in the liquid electrolyte during electrochemical cycles. The microchip device is properly developed to realizing a nanoscale battery in the TEM.

Figure 1(a) and (b) show the ex-situ bright field TEM image and electron diffraction pattern of Fe₂O₃ nanorod which is sampled from the coin cell before a large reduction peak appears (at ~1.0 V vs Li) during the first cycle of discharging in the cyclic voltammogram. In this region, Fe₂O₃ nanorod still retains single crystalline phase. Some additional spots are observed which are not identified yet. After the first half cycle of discharge finishes, the single crystalline phase changes into polycrystalline phase, showing many nanograins as shown in Figure 1(c). After the 20th cycle, however, the nanorods undergo dramatic structural changes and the amorphous phase is observed as displayed in Figure 2.

In this work, we will show a phase evolution of Fe₂O₃ nanorods during electrochemical cycles and the correlation between microstructural changes and the electrochemical properties will be discussed. This study will provide crucial information for understanding of fundamental mechanism of lithiation/delithiation process of complex irreversible conversion reaction in transition metal oxides [5].

References:

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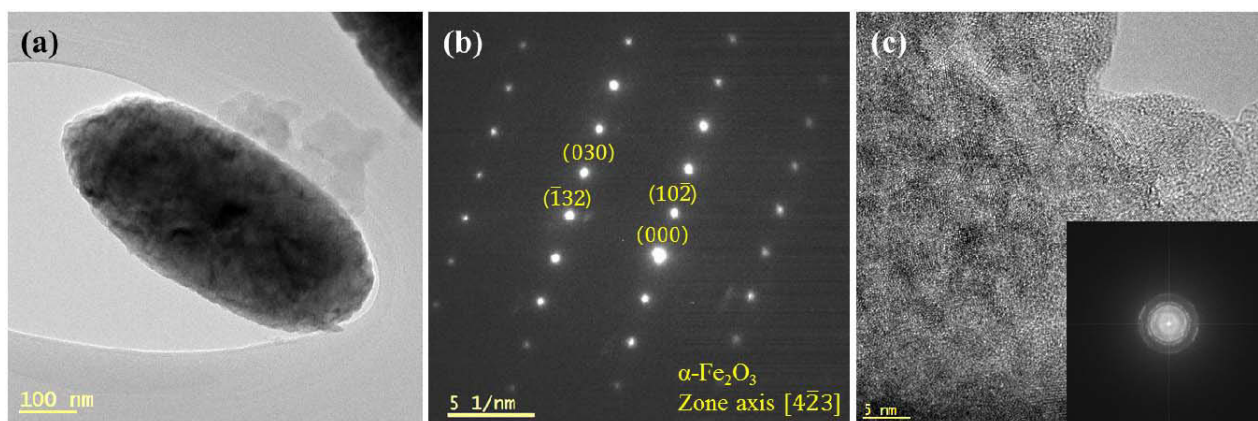


Figure 1. (a) Bright-field TEM image, (b) Electron diffraction pattern, (c) High-resolution image of lithiated nanorod after the first half cycle of discharging (inset: Fast Fourier Transform).

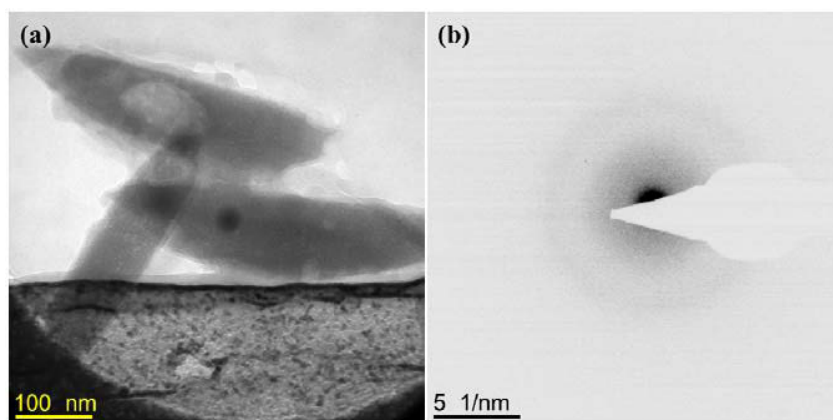


Figure 2. (a) Bright-field TEM image of iron oxide nanorods after the 20th cycle of discharging and charging, (b) Electron diffraction pattern.