Oxidation of Fe₃N for a High-Energy-Density Anode in Lithium Ion Batteries

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In this work, the oxidation behaviors of Fe₃N with micro-polygonal structures are studied in detail. At 300 °C, its micro-polygonal structures can be well retained, although the oxidation of Fe₃N has taken place. The oxidation product should be composed of Fe₃O₄ and Fe₂O₃ according to all XRD data for samples oxidized in different temperatures from 300 to 500 °C. The electrochemical properties of Fe₃O₄-Fe₂O₃ on Fe₃N are analyzed by conventional electrochemical technologies, containing discharge/charge analysis, cyclic voltammogram (CV) and electrochemical impedance spectroscopy (EIS). The results indicate that the Fe₃N-O-300 sample oxidized at 300 °C exhibits an extraordinary capacity retention and good rate performance with Columbic efficiency nearly 100%. The interface between Fe₃O₄-Fe₂O₃ and Fe₃N is confirmed by EIS with two depressed semicircles.

Keywords: Oxidation; Fe₃N; High-energy-density; Electrochemical properties; Lithium ion batteries.

1. INTRODUCTION

High-energy-density materials that undergo conversion reactions hold promise for next-generation lithium ion batteries [1]. For example, Fe₃O₄ possesses a high theoretical specific capacity of 926 mA h g⁻¹ and undergoes a following conversion reaction [2].

Fe₃O₄ + 8 Li⁺ + 8 e⁻ → 8 Fe + 4 Li₂O (1)

However, their practical applications are inhibited by serious capacity attenuation, which results from volume change of the materials during charge/discharge processes [3-5]. Forming nanostructures [6-11] (such as nanopore, nanopillar, nanofiber and nanorod) and/or composites with
carbon materials [12-19] (such as porous carbon, carbon nanotube and graphene) are two efficient strategies to suppress capacity attenuation. Alternatively, utilizing the interface between two compounds may be another simple and efficient method. For example, a shell@core structured Fe₃O₄@Fe₃N nanoparticle exhibited an improved electrochemical performance [20].

In this work, a Fe₃O₄-Fe₂O₃ and Fe₃N interface was constructed by direct oxidation of Fe₃N foils in hot air, and it has demonstrated that such an interface indeed improve the capacity retention of the cheap iron-oxide materials.

2. EXPERIMENTAL

2.1 Preparation of Fe₃N foils

Fe foils, which possess polygonal crystals with microns size, were fabricated by electrodeposition according to the reference [21]. Then, the electrodeposited Fe foils were cut into disks with a diameter of 1.6 cm (~2.0 cm²).

To convert into Fe₃N foils, six Fe disks together with 1 g urea were put into a pipe stove (~ 2.5 L), then were annealed at 550 °C for 2 h in an atmosphere of N₂, and lastly were taken out after cooling to room temperature.

2.2 Oxidation of Fe₃N foils

The resultant Fe₃N disks were sintered for several hours in air atmosphere at 300 °C, 350 °C, 400 °C and 500 °C, respectively. For comparison, the Fe disks were also oxidized under above conditions. The weight increment of Fe₃N disks after oxidation was analyzed by a semimicro balance (readability: 0.01 mg, Mettler Toledo, MS105DU).

2.3 Characterizations

The morphologies of all samples were investigated by scanning electron microscopy (SEM, QUANTA 200, America FEI). Their X-ray diffraction (XRD) patterns were recorded using a D/max-TTRIII diffractometer with Cu Kα radiation over 2θ range of 10 °−90 °.

2.4 Electrochemical measurements

Galvanostatic discharge/charge measurements were carried out in CR2025 coin cells using the Land battery system (CT2001) with a potential window of 3.0−0.1 V v.s. Li⁺/Li. Cells were assembled in a high-purity argon-filled glovebox (Mikrouna, Super 1220/750). The oxidized Fe and Fe₃N disks were directly used as working electrode without any polymer binder. Lithium foils were used as both counter and reference electrodes, and Celgard 2320 was used as separator membrane. The electrolyte
was 1 M LiPF$_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume). Cyclic voltammogram (CV) measurements were performed with an electrochemical workstation (CHI 604D, Shanghai Chenhua) at a scanning rate of 0.5 mV/s. Electrochemical impedance spectroscopy (EIS) was recorded between 100 kHz to 10 mHz with an amplitude of 5 mV under an open circuit voltage.

3. RESULTS AND DISCUSSION

3.1 Nitridation of the electrodeposited Fe disk

![Figure 1. (a) XRD pattern and (b) SEM image of a nitrided Fe disk](image-url)
The nitridation of a transition metal requires the presence of active nitrogen atoms. NH$_3$ that decomposed from the urea at a high surrounding temperature can provide active nitrogen atoms according to the following reaction,

$$2 \text{NH}_3 + \text{Fe} \rightarrow 2 \text{N}^* + \text{Fe} + 3 \text{H}_2 \quad (2)$$

where, Fe takes a role of catalyzer. Then active nitrogen atoms penetrate into the Fe crystals and the resultant is a nitride according to the following reaction,

$$\text{N}^* + x \text{Fe} \rightarrow \text{Fe}_x\text{N} \quad (3)$$

Fig. 1 shows the XRD pattern and the SEM image of the nitride. As shown in Fig. 1 a, the diffraction peaks coincide with those from a hexagonal structure of Fe$_3$N (JCPDS No. 86-0232). The Fe diffraction peaks disappear, indicating enough Fe$_3$N to be converted into. From Fig. 1 b, it can be obviously seen that the polygonal structures of Fe crystals are retained after nitridation. However, in the inset with high magnification shown in Fig. 1 b, there are many pinholes in the Fe crystals. These pinholes may be some channels, by means of which nitrogen atoms are transported to the inner of Fe crystals.

### 3.2 Oxidation of Fe$_3$N

The weight increments ($\Delta m$) of Fe$_3$N disks ($\Phi$ 1.6 cm, $\sim$ 2.0 cm$^2$) changing with temperature and time are shown in Fig. 2. Below $\sim$ 450 °C, the oxidation rate of Fe$_3$N is faster than that of Fe (see Fig. 2 a). At 300 °C, the oxidation of Fe and Fe$_3$N had also taken place. It can be seen from Fig. 2 b that for Fe$_3$N the value of $\Delta m$ over 8 h is close to a constant, while for Fe the $\Delta m$ value increases slowly.
Figure 2. The relationships of (a) $\Delta m$ and temperature, (b) $\Delta m$ and time.

Figure 3. XRD patterns of four samples: $\text{Fe}_3\text{N}$-O-300, $\text{Fe}_3\text{N}$-O-350, $\text{Fe}_3\text{N}$-O-400 and $\text{Fe}_3\text{N}$-O-500.
Figure 4. SEM images of (a) Fe$_3$N-O-300, (b) Fe$_3$N-O-350, and (c) Fe$_3$N-O-400
The sample of Fe₃N oxidized at 300 °C for 8 h marked Fe₃N-O-300, and the samples oxidized for 2 h at 350 °C, 400 °C and 500 °C marked Fe₃N-O-350, Fe₃N-O-400 and Fe₃N-O-500, respectively. Their XRD patterns are shown in Fig. 3. At 300 °C, the oxidation product of Fe₃N is main Fe₃O₄ according to two weak diffraction peaks, at 2θ = 35.45 ° and 62.57 °, which are the two characteristic strong peaks of Fe₃O₄ (JCPDS No. 65-3107). The two peaks become strong with the increase of sinter temperature, indicating more Fe₃O₄ were formed. However, it can be clearly seen that four diffraction peaks located 2θ = 33.15 °, 49.48 °, 54.01 ° and 63.99 ° can be assigned to these of Fe₂O₃ (JCPDS No. 33-0664).

Fig. 4 shows SEM images of Fe₃N oxidized at different temperatures. The polygonal crystal shape is still retained after oxidation at 300 °C, however the pinholes in Fe crystals disappear (see the inset in Fig. 4 a). The result implies that the oxidation products of Fe₃O₄ and Fe₂O₃ with bigger volume fill pinholes up. Over 300 °C, the crystal shape changes and the crystal boundaries become illegible. Moreover, many glass-like splinters appear. It can be observed from Fig. 4 b and c that the numbers as well as the size of the splinters grow as the sintered temperature increases, implying that there is a nucleation growth process during the transformation of Fe₃N to Fe₃O₄-Fe₂O₃.

3.3. Electrochemical Performances
Fig. 5 shows the discharge-charge voltage profiles of the Fe₃N, Fe-O-400 (Fe disks oxidized at 400 °C) and Fe₃N-O-300 at 0.2 mA in the range of 0.1−3.00 V. The Fe-O-400 was selected, because the Δm of Fe disks at 300 °C is few. As shown in Fig. 5 a, the nitriding material of Fe₃N exhibits a very low and attenuating capacity (< 0.1 mA h, ~10 mA h g⁻¹), while the Fe₃N, which was deposited by pulsed laser ablation of iron combined with N₂ gas DC discharge, exhibited a reversible discharge capacity of over 300 mA h g⁻¹ [22]. A possible reason is that the nitriding layer is too dense to insert Li⁺ ions into and the Fe₃N on the surface layer is only taking effect. Rapid capacity attenuation can be observed from Fig. 5 b, indicating that the interface of Fe and iron oxides is ineffective to improve their capacity retention. Interestingly, the capacity retention can be remarkably improved in the interface of Fe₃O₄-Fe₂O₃/Fe₃N as shown in Fig. 5 c, although the beginning several voltage profiles are the same as these of Fe-O-400. For example, a voltage plateau at 0.75 V followed by a sloping curve is exhibited in the first discharge, while it shifts to 0.98 V in subsequent discharge processes. And serious capacity degeneration in the second discharge process is also observed, which could be associated with the formation of a solid electrolyte interface (SEI) layer on the surface of the electrode. It is worth noting that the charge-discharge capacities of the 200th to 280th cycles are close to that of 2nd cycle, indicating an extraordinary capacity retention and cyclic behavior of the Fe₃O₄-Fe₂O₃/Fe₃N interface.

The durability of the Fe₃N-O-300 sample was estimated by cycling in the range of 0.1−3.00 V at stepwise current rates from 0.2 to 1.2 mA, then stepwise back to 0.2 mA for 200 cycles, lastly again stepwise current rates. It is clearly seen from Fig. 6 that the Fe₃N-O-300 sample exhibits extraordinary capacity retention with Columbic efficiency nearly 100%. After 350 cycling at different currents, the sample can still release a capacity of 0.41 mA h at the current of 0.2 mA, which is 83.67 % that of the second discharge capacity (0.49 mA h). From the 80th to 260th cycle at 0.2 mA, it is observed that the discharge/charge capacities rise with cycling. The capacity increasing phenomenon has been observed by other researchers on the interface of carbon/iron oxide [23, 24]. The cell exhibits also good rate performance, for example, still delivering 0.18 mA h at 1.2 mA (spending about 6 min).
Figure 6. Rate performance, cyclic behavior and Coulombic efficiency of the Fe$_3$N-O sample.
**Figure 7.** Discharge-charge voltage profiles of (a) Fe₃N-O-350, (b) Fe₃N-O-400, (c) Fe₃N-O-500

**Figure 8.** (a), (b) Cyclic voltammograms and (c), (d) Nyquist plots of the Fe₃N and Fe₃N-O-300 samples, respectively
The effect of oxidation temperatures on the capacity retention is shown in Fig. 7. Over 400 °C, the rapid capacity attenuation is observed from Fig. 7 b and c, similarly to that of Fe-O-400, although there is the interface of Fe₃N and Fe₃O₄-Fe₂O₃ according to the XRD data.

![Figure 9. (a) XRD pattern and (b) SEM image of the Fe₃N-O-300 sample in charge state after 50 discharge/charge cycles](image)
The crystal shape change and glass-like splinters formation, which are observed from the SEM images shown in Fig. 4, may be responsible for the irreversible capacity loss. At 350 °C, the capacity attenuation become weak, and after the 100th cycle the discharge-charge capacities increase.

The first three cyclic voltammograms (CVs) of the Fe₃N and Fe₃N-O-300 samples were measured between 3.00 and 0.01 V at a scan rate of 0.5 mV s⁻¹, after they underwent 50 discharge/charge cycles. The data are shown in Fig. 8 a and b, respectively. The clear cathodic peaks of the Fe₃N and Fe₃N-O-300 samples are observed at potentials of 0.82 and 0.73 V, respectively. However, from Fig. 8 a, two overlap anodic peaks can be distinguished, locating at 1.60 and 1.91 V. The result suggests that there a two-step anodic process for the Fe₃N electrode. While only a wide anodic peak is distinguished from Fig. 8 b, implying a one-step anodic process for the Fe₃N-O-300 electrode. Comparing with the two-group CVs, the cathodic/anodic currents of the Fe₃N-O-300 are far bigger than those of Fe₃N, indicating the Fe₃N-O-300 sample possesses higher electrochemical activation. Hence, The Fe₃N-O-300 material can release more capacity as shown in Fig. 5.

The distinct different between two Nyquist plots of the Fe₃N and Fe₃N-O-300 samples is that two depressed semicircles are observed from Fig. 8 d. But no two- semicircle phenomenon was observed from nanostructured iron oxides and the composites of iron oxides and carbon materials [13, 15]. The result suggests that besides one electrode-electrolyte interface there is the other interface, which should be the Fe₃N/Fe₃O₄ interface. The interface charge transfer resistance can be estimated to about 20 Ω (for 2 cm²) from the EIS. Such an interface should be responsible for good electrochemical performances. Hence, when the Fe₃O₄-Fe₂O₃ layer become thick, which formed at a high temperature (for example 400 °C), a capacity loss with cycles can be observed due to weakening the interface effect.

The morphology and structure of the Fe₃N-O-300 sample in charge state were characterized after 100 discharge/charge cycles. As shown in Fig. 9 a, the main phase is still Fe₃N, however, all diffraction peaks became weak proportionally, implying that the Fe₃N was coated again by forming SEI and changing surface structure. At the same time, the original weak diffraction peaks of Fe₃O₄ are hardly observed after cycling, likely due to again spreading oxides on the Fe₃N reconstituting surface. Hence, as shown in Fig. 9 b the morphology changes seriously. The polygonal crystals disappear completely, for which irregular particles and sheets substitute. The morphology variation has been also observed in many redox-type electrodes [25, 26]. The structures consisted of microparticles and micronsheets increase the interface surface between Fe₃N and iron oxides, consequently increasing the capacity retention.

4. CONCLUSION

A Fe₃N material contained of polygonal crystals with micro-pores was prepared by nitriding on the electrodeposited Fe disks. Then, the interface of Fe₃N and Fe₃O₄-Fe₂O₃ on the polygonal crystal surface was constructed by a simple oxidation of Fe₃N in air at 300 °C. But the polygonal structure was destroyed in air above 350 °C. The EIS with two depressed semicircles verified the existence of the
Fe₃O₄-Fe₂O₃/Fe₃N interface. The Fe₃N-O-300 sample oxidized at 300 °C exhibited good capacity retention of 83.67 % and a reversible capacity of 0.41 mA h after 350 cycling at different currents.

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References

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