# Hydrothermal Synthesis of Ultrafine β-FeOOH Nanorods as Cathode Materials for Lithium Ion Batteries

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β-FeOOH nanorods with the diameter of only 10 nm were fabricated through a facile PEG-assisted hydrothermal synthetic route, which was the smallest dimension reported for the fabrication of β-FeOOH one-dimensional (1-D) nanostructures so far. The as-prepared ultrafine β-FeOOH nanorods were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and galvanostatic tests. Electrochemical tests on the as-obtained ultrafine β-FeOOH nanorods revealed that they exhibited excellent electrochemical properties with a large discharge capacity of 290 mA h g$^{-1}$ and good cycleability, which enabled them to be applied as superior cathode materials for lithium ion battery systems.

Novel materials for use as electrodes in lithium ion batteries have attracted much attention since Sony produced the first commercial lithium ion batteries in 1990.[1] Commercial lithium ion batteries today contain expensive and hazardous compounds, like lithium cobalt, nickel oxides, or combinations of them. It is desirable to replace them with other electrode materials which are potentially cheaper and less toxic. Among the new electrode materials developed recently, iron compounds seem to be attractive for the production of large-scale lithium batteries, because of their large natural abundance and low cost. Recently, β-FeOOH, which exhibits a tunnel-type structure in which iron atoms are strongly bonded to the framework constituting the tunnels, has been reported to be a promising cathode material for lithium batteries.[2–4] This material has a more stable structure in which the possibility of structural collapse is eliminated, and the large tunnel-type structure offers a good gate for the intercalation/deintercalation process of lithium ions during the charge/discharge cycles, which makes it a promising cathode material with a high theoretical discharge capacity (302 mA h g$^{-1}$).

Over the past decades, 1-D nanostructures have attracted wide interest for their potential uses in mesoscopic research and development of nanodevices.[5,6] In the electrochemical field, 1-D nanostructured electrode materials are regarded as the smallest dimension structures for efficient electron transport, which can be applied to detect the theoretical operating limits of lithium ion batteries.[7] Recently, there has been considerable interest in the fabrication of 1-D β-FeOOH nanostructures. Zhang et al. have synthesized β-FeOOH nanowire arrays by an electrochemical deposition route using porous anodized oxide (AAO) templates.[8] Xie et al. have obtained aligned β-FeOOH nanowires through a simple solution reaction from the complex precursor $[\mathrm{Fe(phen)_3}]^{2+}$.[9] A solvothermal synthetic method has been proposed to fabricate arrayed β-FeOOH nanorods by Qian et al.[10] Zhang et al. have obtained β-FeOOH nanorods with the diameter of 30 nm via a hydrothermal route.[11] However, to the best of our knowledge, there have been no report of the fabrication of β-FeOOH 1-D nanostructures with the diameter reduced to as low as 10 nm, which would certainly introduce superior electrochemical properties to facilitate their application as cathode materials. Herein, we report for the first time the fabrication of ultrafine β-FeOOH nanorods with the diameter of only 10 nm via a facile PEG-assisted hydrothermal synthetic route. Electrochemical tests on the as-obtained ultrafine β-FeOOH nanorods indicate that they are superior cathode materials for lithium ion battery systems.

All the reagents were of analytical grade purity and were used without further purification. In a typical synthetic procedure of β-FeOOH nanorods, 0.6-g $FeCl_3{\cdot}6H_2O$ and 1.0-g PEG-10000 (Polyethylene glycol) were dissolved into 40-mL distilled water by magnetic stirring. The as-prepared solution was transferred into a 50-mL Teflon-lined stainless-steel autoclave. The autoclave was sealed and maintained at 80 °C for 12 h, then cooled to room temperature naturally. The as-obtained yellow precipitate was collected and rinsed with distilled water and anhydrous alcohol several times, and finally dried in vacuum at 80 °C for 10 h.

The overall crystallinity and purity of as-fabricated sample were examined by XRD using a Philiphs X'Pert Super diffractometer with graphite monochromatized Cu K$\alpha$ radiation ($\lambda = 1.54178$ Å). The morphology and size distribution of the sample was examined by TEM using a Hitachi 800 TEM with the accelerating voltage of 200 kV. Teflon cells were made to study the electrochemical properties of the product. The cathode consisted of the prepared β-FeOOH nanorods (80 wt %), carbon black (10 wt %), and polyvinylidene fluoride (PVDF, 10 wt %). The cells were assembled in an argon-filled glove box in which both the moisture and the oxygen levels were less than 1 ppm. The electrochemical tests were made in the voltage range of 1.5–4.2 V at a current density of 0.2 mA cm$^{-2}$.

The XRD pattern of the typical sample was given in Figure 1A. All the reflections in the pattern could be readily indexed to a tetragonal phase of β-FeOOH with lattice constants $a = 10.52 \pm 0.005$ Å, and $c = 3.02 \pm 0.005$ Å, which agrees well with the standard values (JCPDS Card 34-1266, $a = 10.53$ Å, $c = 3.03$ Å). No impurity phases are detected from the XRD pattern such as α-$Fe_2O_3$, α-, and γ-FeOOH, indicating that β-FeOOH nanorods with high purity were obtained under current synthetic conditions.

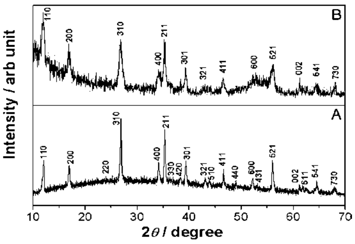

**Figure 1.** XRD patterns of the product (a) and the product after 40 charge/discharge cycles (b).

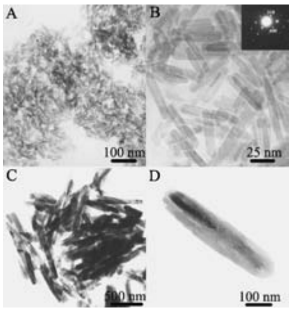

**Figure 2.** TEM images of as-obtained $\beta$-FeOOH nanorods using (A, B) 0.6-g $FeCl_3 \cdot 6H_2O$ and (C, D) 1.0-g $FeCl_3 \cdot 6H_2O$ as precursor. (Inset in Figure 2B: SAED pattern taken on a single $\beta$-FeOOH nanorod).

The morphology and size distribution of the as-obtained sample were investigated by TEM test, which were shown in Figure 2. Large amount of uniform $\beta$-FeOOH nanorods were obtained by our synthetic route. The diameter of the nanorods was 10 nm, which was the smallest dimensional 1-D nanostructures of $\beta$-FeOOH ever fabricated. The length of the $\beta$-FeOOH nanorods ranges from 40 to 60 nm, indicating a very narrow size distribution. Inset in Figure 2B showed the SAED pattern taken on a single nanorod, indicating that the as-fabricated $\beta$-FeOOH nanorods were well single crystallined.

PEG was believed to be one decisive factor in the fabrication of $\beta$-FeOOH nanorods. Firstly, according to Pearson's results,[12] the –O– of the ether group on the PEG chains has a strong basic property and possesses a pair of electrons, which facilitates the formation of $\beta$-FeOOH in the hydrothermal conditions, thus the reaction temperature is greatly lowered. Secondly, PEG is a nonionic polymer whose chain contains many hydrophilic (—O—) and hydrophobic ($-CH_2-CH_2-$) sites. And the chain has high flexibility so that the C–O bond is easy to rotate. The high flexibility of the chain and its ability as a donor of oxygen atoms enables it to couple with hydrated iron ions $Fe(H_2O)_6{}^{3+}$ and to form thermodynamically favorable polymer complex, which induces the growth of $\beta$-FeOOH nanorods under hydrothermal conditions. These extraordinary properties of PEG make it a superior surfactant for the fabrication of 1-D nanostructures,[13,14] exhibiting better growth direction ability than other surfactants such as CTAB, PVP, SDBS, and so on. Another decisive parameter in the fabrication of so small diameter $\beta$-FeOOH nanorods was the amount of $FeCl_3 \cdot 6H_2O$. Comparative experiment was done by increasing the dosage of $FeCl_3 \cdot 6H_2O$ to 1.0-g and keeping all other synthetic parameters stable. Figures 2C and 2D showed the TEM images of as-obtained sample. The product was also consisted of large area of $\beta$-FeOOH nanorods, but the diameter of these nanorods was greatly increased to around 60 nm. The above results firmly validated that the low concentration of precursor $FeCl_3 \cdot 6H_2O$ solution was indispensable for the fabrication of $\beta$-FeOOH nanorods with diameter as low as 10 nm.

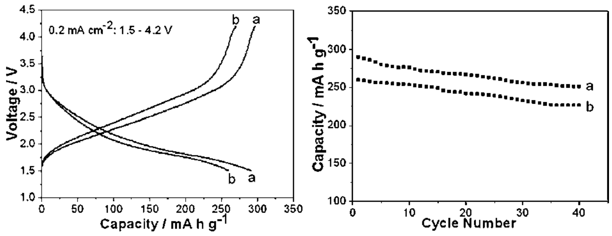

**Figure 3.** (A) First charge/discharge curve of as-fabricated $\beta$-FeOOH nanorods (a: 10-nm wide $\beta$-FeOOH nanorods; b: 100-nm wide $\beta$-FeOOH nanorods); (B) Cycle performance of $\beta$-FeOOH nanorods in the voltage range of 1.5–4.2 V.

The electrochemical properties of the as-obtained $\beta$-FeOOH nanorods were studied by galvanostatic test. Figure 3A showed the initial charge/discharge curves of as-obtained $\beta$-FeOOH nanorods with different diameter. The initial discharge capacity of the 10-nm wide $\beta$-FeOOH nanorods (Figure 3A a) reached 290 mA h $g^{-1}$, which was very close to the theoretical capacity of $\beta$-FeOOH (302 mA h $g^{-1}$), while the 100-nm wide $\beta$-FeOOH nanorods (Figure 3A b) delivered an initial discharge capacity of 260 mA h $g^{-1}$. It was clear that the diameter of $\beta$-FeOOH nanorods played an important role on their electrochemical performances. The possible reason for this phenomenon could be that along with the decrease of the nanorod diameter, the specific surface of $\beta$-FeOOH nanorods was accordingly enlarged, leading to more $\beta$-FeOOH composites exposed to the electrolyte. As a result, the surface electrochemical reactivity between electrolyte and the electrode materials was greatly improved, causing the improvement of the electrochemical properties.[15] Meanwhile, the much smaller diameter offered a much shorter diffusion length for lithium ions. Since the insertion of lithium ions into the cathode materials is diffusion limited,[16] the shorter diffusion length is beneficial for the electrode kinetics and favors the charge-transport process in the charge/discharge cycles, thus the electrochemical properties of the samples were greatly improved. Forty charge/discharge cycles were tested to study the cycleability of the $\beta$-FeOOH nanorods. Figure 3B revealed the cycling behavior of the $\beta$-FeOOH/Li cells. About 80% of initial discharge capacity was reserved after 40 cycles, indicating that as-fabricated $\beta$-FeOOH nanorods have good cycleabilities for applications in lithium ion batteries. XRD test was applied on the typical sample after 40 cycles, and the result is shown in Figure 1B. The cycled sample remains mainly $\beta$-FeOOH structure, though the baseline is not as smooth as the sample before the galvanostatic test, indicating the good structure stability of as-fabricated $\beta$-FeOOH nanorods during the charge/discharge cycles.

In summary, $\beta$-FeOOH nanorods with the diameter of only 10 nm were successfully fabricated through a facile PEG-assisted hydrothermal synthetic route. The products were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and galvanostatic tests. The electrochemical performances of as-fabricated $\beta$-FeOOH nanorods were studied by galvanostatic tests, indicating them as superior cathode materials for application in the lithium ion battery industries.

### References

1 J. M. Tarascon, M. Armand, *Nature* **2001**, *414*, 359.
2 K. Amine, H. Yasuda, M. Yamachi, *J. Power Sources* **1999**, *81–82*, 221.
3 H. Sakaebe, S. Hiquchi, K. Kanamura, H. Fujimoto, Z. Takehara, *J. Electrochem. Soc.* **1995**, *142*, 360.
4 C. Benoit, C. Bourbon, P. Berthet, S. Franger, *J. Phys. Chem. Solids* **2006**, *67*, 1265.
5 S. Iijima, *Nature* **1991**, *354*, 56.
6 Z. W. Pan, Z. R. Dai, Z. L. Wang, *Science* **2001**, *291*, 1947.
7 B. Ammundsen, J. Paulsen, *Adv. Mater.* **2001**, *13*, 943.
8 L. Y. Zhang, D. S. Xue, J. Feng, *J. Magn. Magn. Mater.* **2006**, *305*, 228.
9 Y. J. Xiong, Y. Xie, S. W. Chen, Z. Q. Li, *Chem. Dur. J.* **2003**, *9*, 4991.
10 H. F. Shao, X. F. Qian, J. Yin, Z. K. Zhu, *J. Solid State Chem.* **2005**, *178*, 3130.
11 X. Wang, X. Y. Chen, L. S. Gao, H. G. Zheng, M. R. Ji, C. M. Tang, T. Shen, Z. D. Zhang, *J. Mater. Chem.* **2004**, *14*, 905.
12 P. G. Pearson, *J. Chem. Educ.* **1968**, *45*, 581.
13 Z. Q. Li, Y. J. Xiong, Y. Xie, *Inorg. Chem.* **2003**, *42*, 8105.
14 J. C. Go, L. H. Zhuo, F. Yang, B. Tang, L. Z. Wu, C. H. Tung, *J. Phys. Chem. B* **2006**, *110*, 17854.
15 D. R. Rolison, B. Dunn, *J. Mater. Chem.* **2001**, *11*, 963.
16 S. Nordlinder, J. Lindgren, T. Gustafsson, K. Edström, *J. Electrochem. Soc.* **2003**, *150*, E280.