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Shape Evolution of $\alpha$-Fe$_2$O$_3$ and Its Size-Dependent Electrochemical Properties for Lithium-Ion Batteries

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Crystalline $\alpha$-Fe$_2$O$_3$ with different particle shapes and sizes was selectively synthesized by a simple hydrothermal method. By carefully tuning the concentration of the reactants and the reaction time, $\alpha$-Fe$_2$O$_3$ cubic particles and nanowires can be obtained. Based on the evidence of electron microscope images, a shape evolution mechanism for the nanowire structure is proposed. Electrochemical performance as an anode material for lithium-ion batteries was further evaluated by cyclic voltammetry, electrochemical impedance, and charge-discharge measurements. It was demonstrated that both the morphology and the particle size had an influence on the performance. Compared with the electrode made from the cubic material, the nanowire electrode displayed higher discharge capacity and better cycling reversibility, which may be a result of the one-dimensional nanostructure and high surface area.

As the most stable iron oxide, hematite ($\alpha$-Fe$_2$O$_3$), based on hexagonal close packing of oxygen with iron in 2/3 of the octahedral vacancies, has been extensively used in the production of pigments, catalysts, gas sensors, magnetic recording media, and raw materials for hard and soft magnets, due to its low cost, environmental friendliness, and high resistance to corrosion. It has also been shown to act as a rechargeable conversion electrode material for hard and soft magnets, due to its low cost, environmental friendliness, and high resistance to corrosion. It has also been shown to be advantageous over other methods in homogeneity, chemical impedance, and charge–discharge measurements. It was demonstrated that both the morphology and the particle size had an influence on the performance. Compared with the electrode made from the cubic material, the nanowire electrode displayed higher discharge capacity and better cycling reversibility, which may be a result of the one-dimensional nanostructure and high surface area.

Table I. Experimental conditions for preparation of the $\alpha$-Fe$_2$O$_3$ materials.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Concentration of PEG-600 (mol/L)</th>
<th>Concentration of FeCl$_3$ (mol/L)</th>
<th>Reaction time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.4</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
<td>1</td>
<td>24</td>
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<tr>
<td>3</td>
<td>0.4</td>
<td>2</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>4</td>
<td>24</td>
</tr>
</tbody>
</table>

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Preparation of $\alpha$-Fe$_2$O$_3$ materials.—All of the chemical reagents were analytically pure and used without further purification. $\alpha$-Fe$_2$O$_3$ materials were prepared by a PEG precursor route. In a typical experimental procedure, PEG-600 (Aldrich) was dissolved in a methanol solution. An aqueous solution of FeCl$_3$ (BDH Laboratory Supplies, England) was added dropwise to an equivalent molar PEG-600 methanol solution under continuous stirring at room temperature to obtain a homogeneous solution. The solution was kept at 50°C for 12 h to form crystals, which were collected as precursors. A stoichiometric proportion of the precursors and NaOH (4 M) were added under stirring to a 15 mL Teflon-lined autoclave, which was filled to one-third by volume. The autoclave was sealed and heated to 160°C in an oven and then maintained at this temperature for a given period. After the reactions, the autoclaves were cooled naturally. The resulting products were separated by centrifugation, washed with ethanol and distilled water to ensure total removal of the inorganic ions, and then dried under vacuum at 80°C for 4 h.

In order to make the formation process of the $\alpha$-Fe$_2$O$_3$ materials clear, the detailed preparation conditions of the formed powders are shown in Table I.

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Sample characteristics.—X-ray powder diffraction analysis was conducted on a Philips 1730 X-ray diffractrometer (XRD) using Cu Kα radiation (λ = 1.54056 Å) with 2θ ranging from 20 to 80° at 1°/min to analyze the structure of the expected products. A JEOL JSM 6460A scanning electron microscope (SEM) was employed to examine the morphology.

A typical slurry was obtained by grinding a mixture of α-Fe2O3, carbon black, and poly(vinylidene fluoride) dissolved in N-methyl-2-pyrrolidinone with a weight ratio of 70:15:15. It was then pasted onto a copper foil (1 cm²) to form the electrode. After the electrode was dried at 100°C for 4 h under vacuum, it was compressed and then weighed. The electrochemical behavior of the materials was examined via CR2025 coin-type cells with lithium metal as the counter electrode. Celgard 2400 membrane as the separator, and an electrolyte composed of 1 M LiPF6 in a mixture of ethylene carbonate and dimethyl carbonate (1:1 by volume). The cells were assembled in an argon-filled glove box (Mbraun, Unilab, Germany). The charge–discharge measurements were conducted at ambient temperature on a multichannel battery cycler in the voltage range between 0.01 and 3.0 V at a current density of 20 mA g. The charge–discharge measurements were performed using a CHI660 electrochemical workstation (CH Instrument Co., USA). The scanning rate for CV was 0.1 mV/s. The electrochemical impedance measurements were carried out at the open-circuit voltage before and after the CV experiments by applying an ac voltage of 5 mV over the frequency range from 0.1 to 10⁵ Hz.

Results and Discussion

Figure 1 shows the XRD patterns of as-synthesized powders prepared using the hydrothermal method under different conditions. It can be observed that the positions of the characteristic peaks of the products are consistent with the standard values for the hexagonal α-Fe2O3 phase (JCPDS card no. 33-0664), whereas the peak intensity differed from one to the other. The peak intensity of sample 1 is relatively higher than that of the other samples, especially the (116) peak, indicating its highly crystalline structure. Upon increasing the reaction time to 24 h (sample 2), the intensity of diffraction peaks decreased, suggesting a smaller crystalline size produced from a dissolution process over the longer time. Upon increasing the concentration of FeCl3 and PEG-600 and maintaining the time at 24 h, the relative intensity of the peaks for samples 3 and 4 gradually decreases, indicating that their crystalline size had become even smaller. So far as we know, there are few reports about the effects of reactant concentration on the particle size of α-Fe2O3, and we conclude that the particle size of the materials prepared by the hydrothermal reaction decreased with increasing reactant concentration, although the concrete reason for this phenomenon is still unclear.

It is possible that amorphous carbon was generated by the pyrolysis of excessive PEG-600 if the ratio of PEG-600 and FeCl3 in the precursors was raised or the reaction time was maintained for a longer period. Thus, the ratio of reagents and the reaction time must be carefully controlled.

To obtain a better understanding of the formation and shape evolution of α-Fe2O3 materials, the products produced under different reaction conditions were collected for SEM investigations. Figure 2 shows representative images of the samples. It can be seen that the powders prepared under different conditions display obvious differences in the particle shape and size. First, a reaction time-dependent morphology evolution study was conducted. Figures 2a and b show SEM images of the α-Fe2O3 sample obtained after a 12 h reaction at different magnifications, from which it can be seen that the product (sample 1) mainly contains cuboid platelets with a diameter of about 3–6 μm and a thickness of about 700 nm. The marked portion in Fig. 2b, which looks like a nanorod, is actually the side view of a cuboid, resulting from the different observation angle. Prolonging the reaction time to 24 h results in cuboids (sample 2) with smaller diameter (1–2 μm) and partially dissolved edges compared with Fig. 2b, as marked by the circle in Fig. 2c. Besides the reaction time, it was found that the concentrations of FeCl3 and PEG-600 significantly affect the shape and size of particles as well. Figure 2d shows a typical SEM image of sample 3, which was obtained by increasing the concentration of FeCl3 from 1 to 2 M. It can obviously be observed that some nanorods have formed on the sides of the cubes. By further increasing the concentration of FeCl3 from 2 to 4 M and the concentration of PEG-600 from 0.4 to 2 M, star-shaped nanowire clusters can be obtained. The primary nanowires are about 200 nm in diameter with a length of about 2 μm (sample 4), as shown in Fig. 2e. It seems that the influence of the concentration of reactants on the shape and the size of particles is more important than that of the reaction time. There also seem to be remarkable preferential coalescence directions for oriented aggregation, resulting in the formation of nanowires. Based on the above evidence of morphology evolution, a possible formation process for the nanowires can be proposed: under the hydrothermal conditions, nuclei grow quickly, followed by the growth of the nuclei into cuboid crystals. Afterward, secondary nucleation occurs on the edges and surfaces of these cube-shaped crystals by “dissolution” of the cube from the edges toward the interior along the long axis. The driving force is the high activity of the sharp edges, which are easily attacked by the hydroxyl radicals in the alkaline solution. Then, nanowires are formed by increasing the concentration of precursors via nanorods and semi-nanowires. Here we have to point out that although a formation process for the nanowires has been suggested, the intrinsic cause of the shape transformation from cubes to nanowires is still unclear. However, a clear evolutionary process for the particles is presented here through SEM images. The results we report indicate that a fully controllable synthesis could be achieved by tuning the synthesis parameters, such as reaction time and concentration.

Charge–discharge tests were performed to evaluate the electrochemical properties of the samples with different sizes and shapes. Figure 3 shows the charge–discharge curves of the electrodes made from sample 1 (cuboids) and sample 4 (nanowires) during the first and the fifth cycles. In the discharge curve of the first cycle, there is a weak potential slope located at 1.2–1.0 V and an obvious potential plateau at 0.9–0.8 V, corresponding to the respective reaction processes of the electrolyte and α-Fe2O3 with lithium. During the fifth cycle, only one discharge slope can be observed, in the range of 1.0–0.9 V, with a decrease of the discharge capacity. Compared with 1074.5 and 609.0 mAh/g for the cuboid electrode, the nanowire electrode exhibits higher discharge capacity, which is 1173.6 and 704.0 mAh/g for the first and fifth cycles, respectively. Moreover, the initial charge–discharge efficiency for the nanowire electrode

Figure 1. XRD patterns of as-prepared α-Fe2O3 sample (a) 1, (b) 2, (c) 3, and (d) 4.

Figure 3 shows the discharge curves of the electrodes made from sample 1 (cuboids) and sample 4 (nanowires) during the first and the fifth cycles. In the discharge curve of the first cycle, there is a weak potential slope located at 1.2–1.0 V and an obvious potential plateau at 0.9–0.8 V, corresponding to the respective reaction processes of the electrolyte and α-Fe2O3 with lithium. During the fifth cycle, only one discharge slope can be observed, in the range of 1.0–0.9 V, with a decrease of the discharge capacity. Compared with 1074.5 and 609.0 mAh/g for the cuboid electrode, the nanowire electrode exhibits higher discharge capacity, which is 1173.6 and 704.0 mAh/g for the first and fifth cycles, respectively. Moreover, the initial charge–discharge efficiency for the nanowire electrode...
is higher than for the cuboid electrode (65.3%). We believe that the electrochemical performance of the samples is related to the size effect.

The electrochemical performance of the materials with different sizes and shapes was further evaluated by CV, electrochemical impedance, and long-term cycling measurements. Figures 4a and b show the cyclic voltammetries of electrodes made from the as-prepared cuboid and nanowire samples, respectively. In the cathodic process of the first cycle, an obvious peak is observed, which is located at about 0.4 V and shifts to higher potential in the subsequent reduction process. It can be attributed to the reduction of Fe$^{3+}$ to Fe$^{0}$ and irreversible reaction with the electrolyte. Meanwhile, one main peak is recorded at about 1.8 V in the anodic process, corre-

Figure 2. SEM images of as-prepared $\alpha$-Fe$_2$O$_3$ samples: (a) and (b) 1 at different magnifications, (c) 2, (d) 3, and (e) 4.
sponding to the oxidation of Fe\(^0\) to Fe\(^{3+}\). During the subsequent cycles, the cathodic peak shifts to lower potentials and the anodic peak to higher potentials, revealing some irreversibility for the reaction process of Fe\(^3+\) and Fe\(^0\). Moreover, the gradually decreasing peak intensity indicates that the capacities of these electrodes could gradually decrease as the cycle number increases.

By comparing the CV curves for the first cycle, it was found that the current density for the nanowire electrode is larger than that of the cuboid electrode, revealing higher capacity and faster kinetics for transformation in the electrode. In addition, compared with the dramatically decreasing currents for the cuboid electrode, the shape of the CV curves in the following cycles remains similar to those of the fifth cycle, showing reversible reduction and oxidation of the nanowire electrode.

Figure 5 shows typical Nyquist plots obtained before and after the CV experiments for electrodes made of cuboid and nanowire material, respectively. The plots are similar to each other in shape, with a semicircle appearing in the high-frequency domain and a straight line in the low-frequency region. It can be seen that the semicircles for both samples become smaller after CV experiments, probably suggesting an easier reaction process after several CV cycles. The diameter of the semicircle for the nanowire electrode is smaller than that for the electrode made of cuboid particles, regardless of whether cycling occurred before or after the CV experiments, indicating a higher reactivity and lower polarization for the reaction of \(α-\text{Fe}_2\text{O}_3\) nanowire with Li.

It has been reported that the morphology and particle size of the materials have an obvious effect on the reactivity, not only in the initial charge/discharge cycles, but also in the subsequent cycles. Figure 6 compares the cycling behavior of \(α-\text{Fe}_2\text{O}_3\) cuboid and nanowire electrodes. Both electrodes show large reversible capacities in the first ten cycles, then the capacities gradually decrease, and the capacity fading rate from the 15th to the 30th cycle is much higher than that from the first to the 10th cycle. It is well known that a large surface area is important for the improvement of electrochemical performance, considering the introduction of lithium ions into the holes in the hematite surface. The capacity and affinity will be greatly enhanced when the surface area is high, because the diffusion length of the lithium ions is greatly shortened. Therefore, the materials with smaller size and higher surface area would exhibit higher discharge capacity. In this connection, we found that the nanowire electrode showed higher discharge capacity than the cuboid electrode. The electrode maintained 512.0 mAh/g after 30 cycles, corresponding to 63.2% of the second capacity, while the cuboid particle electrode only showed 51.5% capacity retention. Obviously, the nanowire electrode can maintain good cycling performance, indicating that the 1D nanostructures could lighten the stress caused by volume change during the charge–discharge cycles and suppress the degradation of the electrode.
Herein, we reported a feasible evolutionary synthesis of wirelike hematite nanocrystals by a convenient hydrothermal method. The experimental conditions were investigated, including concentration of the reactants and reaction time. It was concluded that the solution conditions had definite effects on particle size and shape of the powders. A possible evolutionary process from cuboids to nanowires was proposed in accordance with morphological investigations. The size-dependent electrochemical properties were also investigated. It was found that the $\alpha$-Fe$_2$O$_3$ nanowire electrodes exhibited better electrochemical performance, with an initial capacity of 1173.6 mAh/g and a capacity retention of 63.2% after 30 cycles.

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Figure 6. The discharge capacity vs cycle number curves of samples 1 and 4.