Original Article

Characterization of Fe$_2$O$_3$ Nanopowder Synthesized by Sol-Gel Method for Energy Storage Applications

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Abstract: Fe$_2$O$_3$ nanopowder was synthesized by sol-gel method from the iron source material Fe(NO$_3$)$_3$.9H$_2$O and citric acid C$_6$H$_8$O$_7$.H$_2$O without any refined process. The structure and particles size of the synthesized materials were determined by X-ray diffraction and scanning electron microscopy. The obtained product is α-Fe$_2$O$_3$ with different shapes and sizes depending on the preparation conditions. α-Fe$_2$O$_3$ was applied as anode of iron-air battery. The cyclic voltammetry measurements showed that the size and morphology of Fe$_2$O$_3$ particles affect the electrochemical characteristics of the electrodes. Using K$_2$S as an electrolyte additive improved the electrochemical properties of mixing of Fe$_2$O$_3$ and carbon acetylene black (Fe$_2$O$_3$/AB) electrodes as evidenced by increased redox reaction rate of iron, increased capacity of Fe$_2$O$_3$/AB electrode and reduced H$_2$ evolution.

Keywords: Fe$_2$O$_3$ nanopowders, Fe$_2$O$_3$ nanoparticles, sol-gel, Fe$_2$O$_3$/AB electrode, energy storage.

1. Introduction

Rechargeable iron/air batteries have been attracting the attention of many researchers due to their high theoretical specific capacity (960 mAh/g), long cycle life, low cost and environmental friendliness [1-10]. Fe/air batteries can be used as a power supply for electric vehicles and hybrid electric vehicles. However, the practical applications of iron/air batteries are limited by the thermodynamic instability of iron in alkaline solution [11], the low discharge rate, high self-discharge, the hydrogen evolution reaction occurs simultaneously with the iron reduction reaction during the charging process, leading to
low discharge-charge efficiency of the battery [12-14]. In addition, the passivation caused by iron (II) hydroxide formed during the discharge prevents the oxidation reaction of the inner iron layer of the electrode.

To solve above mentioned problems of iron/air batteries, some additives for electrodes and electrolyte solutions have been used [6-11, 15-18]. Some researchers used conduction additives such as acetylene black to improve the conductivity of electrode, whereas others used sulfide additives to increases the anodic dissolution of iron metal and avoid the electrode passivation. There are also researchers who used both the carbon and sulfide additives: Sulfides suppressed the hydrogen evolution, accelerate the redox reaction of iron, helped the iron electrode to maintain high discharge current. Acetylene black helped to electrically connect up the insulating discharged product and therefore more active material can participate in the electrode reaction.

In iron/air batteries, the iron electrode plays an important role, deciding the capacity and performance of the battery. Finding a method to produce iron oxides with a low cost and a good quality is an important step to reduce the product price and improve the efficiency of iron/air batteries. Therefore, the objective of this work is to prepare Fe₃O₄ nanoparticles by sol-gel method and to identify the parameters controlling the particles size [19]. This is a simple and inexpensive method that can be used to produce large amounts of iron oxide per fabrication. The Fe₃O₄ powder synthesized by this method is expected to mitigate the existing limitations of iron electrodes and reducing production costs for iron/air batteries.

2. Experimental

2.1. Preparation of Fe₃O₄ Nanoparticles

Iron nitrate Fe(NO₃)₃.9H₂O (Aldrich 98%) was used as iron source and monohydrated citric acid C₆H₅O₇.H₂O (Aldrich 99%) as ligand molecules and distilled water as the solvent. All chemicals were used without further purification. 100 ml of iron nitrate solution was dropped into 100 ml citric acid solution with vigorous stirring. The obtained solution was then heated to 70 °C while maintaining vigorous stirring until the contained water was evaporated and the gel was formed. The dried gel was annealed at 400 °C to get Fe₃O₄ nanoparticles. The concentration of iron nitrate was kept at 0.1 M whereas citric acid concentration was changed from 0.05 M to 0.5 M to control the shape and size of iron oxide particles. The volume of citric acid was also increased to 800 ml at the concentration of 0.2 M to vary the product size. The preparation conditions of various sample were shown in the Table 1.

Table 1. Samples and their preparation conditions by sol-gel method

<table>
<thead>
<tr>
<th>No</th>
<th>Sample name of Fe₃O₄</th>
<th>Preparation conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100 ml-0.05 M</td>
<td>100 ml Fe(NO₃)₃ 0.1 M + 100 ml C₆H₅O₇·0.05 M, T=400 °C</td>
</tr>
<tr>
<td>2</td>
<td>100 ml-0.2 M</td>
<td>100 ml Fe(NO₃)₃ 0.1 M + 100 ml C₆H₅O₇·0.2 M, T=400 °C</td>
</tr>
<tr>
<td>3</td>
<td>100 ml-0.5 M</td>
<td>100 ml Fe(NO₃)₃ 0.1 M + 100 ml C₆H₅O₇·0.5 M, T=400 °C</td>
</tr>
<tr>
<td>4</td>
<td>800 ml-0.2 M</td>
<td>100 ml Fe(NO₃)₃ 0.1 M + 800 ml C₆H₅O₇·0.2 M, T=400 °C</td>
</tr>
</tbody>
</table>

2.2. Characterisation

The crystalline structure of synthesized α-Fe₃O₄ nanopowder was characterized by X-ray diffraction (XRD; Rigaku), using CuKα radiation (λKα = 0.15406 nm, U = 40 kV, I = 150 mA) and 2θ range of 20
to 80°. The particles size and morphologies of the as-prepared materials were examined by a Field-Emission scanning electron microscopy (FE-SEM, Hitachi-4800).

To determine the electrochemical behavior of synthesized α-Fe₂O₃ materials, the electrode sheet was fabricated by mixing 45 wt.% of the respective Fe₂O₃, 45 wt.% of the carbon acetylene black (AB) as additive and 10 wt.% polytetrafluoroethylene (PTFE; Daikin Co.) as binder, and then rolling. The Fe₂O₃/AB electrodes were punched from electrode sheets into pellets of 1 cm diameter and then pressed onto the Titanium mesh with a pressure of about 150 kg cm⁻².

Cyclic voltammetry (CV) measurements were performed using a three-electrode glass cell with Fe₂O₃/AB as the working electrode (WE), Pt mesh as the counter electrode (CE) and Hg/HgO as the reference electrode (RE). The electrolyte was 8 mol dm⁻³ aqueous KOH solution. The effect of electrolyte additive K₂S was investigated using electrolyte containing 7.99 M KOH and 0.01 M K₂S aqueous solution. The CV measurements were taken at a scan rate of 5 mV s⁻¹ and within a range of −1.3 V to −0.1 V.

3. Results and Discussion

3.1. Crystal Structure and Morphology of Synthesized Materials

The X-ray patterns of the synthesized Fe₂O₃ powder are presented in Fig. 1. In all cases from 0.05 M to 0.50 M citric acid, XRD patterns exhibit characteristic diffraction peaks at 20 values of 24.13°; 33.11°; 35.61°; 40.83°; 49.41°; 53.99°; 57.49°; 62.38° and 63.96° corresponding to (012), (104), (110), (113), (024), (116), (018), (214) and (300) crystalline planes, respectively. These diffraction peaks match with patterns of the α-Fe₂O₃ phase reported in ICSD No.033-0664. No other reflections are detected in the XRD patterns, thereby one can suggest that the synthesized products are pure α-Fe₂O₃. Therefore, α-Fe₂O₃ powder was successfully prepared by the sol-gel method.

![Figure 1. X-ray patterns of the synthesized α-Fe₂O₃ with (a) 100 ml-0.05 M, (b) 100 ml-0.2 M, (c) 100 ml-0.5 M and (d) 800 ml-0.2 M citric acid.](image-url)
FE-SEM was used to investigate the particles size and surface morphology of α-Fe₂O₃. The obtained results are shown in Fig. 2. The effects of citric acid concentration on the size and shape of α-Fe₂O₃ particles under the same experimental conditions were clearly shown in Fig. 2. Using low citric acid concentration, i.e. 0.05 M, α-Fe₂O₃ look like polyhedral particles (Fig. 2a). Increasing citric acid to 0.2 M and 0.5 M, a cubic (Fig. 2b) and spherical shape (Fig. 2c) of α-Fe₂O₃ were formed, respectively. Keep the concentration of citric acid at 0.2 M and increasing amount from 100 ml to 800 ml, the aggregation of Fe₂O₃ nanoparticles occurred resulting in larger Fe₂O₃ particles (Fig. 2d). Fe₂O₃ particles with different sizes and shapes will have different effects on the electrochemical properties of the Fe₂O₃ electrode. By changing the synthesis conditions during the sol-gel process, one can control the shape and size of the Fe₂O₃ particles to achieve the desired particle size and shape.

![Figure 2. FE-SEM images of the synthesized α-Fe₂O₃ with (a) 100 ml-0.05 M, (b) 100 ml-0.2 M, (c) 100 ml-0.5 M and (d) 800 ml-0.2 M citric acid.](image)

3.2. Electrochemical Characterization

The CV profiles of the Fe₂O₃/AB electrodes using Fe₂O₃ synthesized by sol-gel method as active material and AB as carbon additive are shown in Fig. 3. When scanning from −1.3 V to −0.1 V, three oxidation peaks appear at about −1.0 V (a₀), −0.75 V (a₁), −0.6 V (a₂) and two reduction peaks appears at about −1.1 V (c₂) and −1.2 V (c₁) in reverse scan but c₁ reduction peak is almost overlapped by H₂ evolution peak. The small a₀ peak is due to the OH⁻ group adsorption of the iron electrode to form...
[Fe(OH)$_{ad}$] before being oxidized to Fe(OH)$_2$. The anodic peak ($a_1$) is attributed to the oxidation of Fe to Fe(OH)$_2$ and anodic peak ($a_2$) is attributed to the oxidation of Fe(OH)$_2$ to Fe(III). Thus, the anodic peak $a_1$ and cathodic peak $c_1$ correspond to the Fe/Fe(II) redox couple (Eq. 1), and the anodic peak ($a_2$) and the cathodic peak ($c_2$) correspond to the Fe(II)/Fe(III) redox couple (Eqs. 2 and/or 3).

$$Fe + 2OH^- \rightleftharpoons Fe(OH)_2 + 2e \quad (1) \quad (E^0 = -0.975 \text{ V vs. Hg/HgO}) [20]$$
$$Fe(OH)_2 + OH^- \rightleftharpoons FeOOH + H_2O + e \quad (2) \quad (E^0 = -0.658 \text{ V vs. Hg/HgO}) [20]$$
and/or
$$3Fe(OH)_2 + 2OH^- \rightleftharpoons Fe_3O_4 \cdot 4H_2O + 2e \quad (3) \quad (E^0 = -0.758 \text{ V vs. Hg/HgO}) [21]$$

The cathodic peak corresponding to reduction of Fe(OH)$_2$ to Fe ($c_2$) is not visible, probably because it was superimposed on the current for the hydrogen evolution reaction. The hydrogen evolution reaction competes with the electrode charge reaction and results in low cycling efficiency of Fe$_3$O$_4$ electrode.

The oxidation peaks shifted towards the negative potential while the reduction peaks moved to the more positive side when repeated cycling, indicating that the overpotential of the redox reaction of iron reduced. This behavior will give positive effects on the cycling of the iron electrode. However, the redox current reduced with the increased number of cycles.

Figure 3. CV profiles of Fe$_3$O$_4$/AB composite electrodes with Fe$_3$O$_4$:AB:PTFE = 45:45:10 wt.% in KOH solution with Fe$_3$O$_4$ synthesized at (a) 100 ml-0.05 M, (b) 100 ml-0.2 M, (c) 100 ml-0.5 M and (d) 800 ml-0.2 M citric acid.
Comparing the CV profiles of all the samples each other shows that the Fe$_2$O$_3$ samples synthesized at citric acid concentration of 100 ml-0.05 M (Fig. 3a) and 800 ml-0.2 M (Fig. 3d) give higher $a_2/c_2$ redox couple peak than the other samples, demonstrating that they have better cyclability than others. FE-SEM images of the samples in Fig. 2 show that at the citric acid concentration of 100 ml-0.2 M (Fig. 2b) and 100 ml-0.5 M (Fig. 2c) Fe$_2$O$_3$ particles have relatively uniform cubic and spherical shape, respectively, but the sample of 100 ml-0.05 M (Fig. 2a) and 800 ml-0.2 M (Fig. 2d) have polyhedral shape and larger particle size. This result proved that the shape and size of the Fe$_2$O$_3$ particles have a strong effect on their cyclability. Due to the agglomeration of small Fe$_2$O$_3$ to form larger particles, the internal resistance of these samples is smaller than that of samples which have smaller Fe$_2$O$_3$ leading to their higher redox current.

Figure 4. CV profiles of Fe$_2$O$_3$/AB composite electrodes with Fe$_2$O$_3$:AB:PTFE = 45:45:10 wt. % in KOH+K$_2$S solution with Fe$_2$O$_3$ synthesized at (a) 100 ml-0.05 M, (b) 100 ml-0.2 M, (c) 100 ml-0.5 M and (d) 800 ml-0.2 M citric acid.

To investigate the influence of K$_2$S additive on the electrochemical properties of the iron electrode, the CV measurement of Fe$_2$O$_3$/AB electrode with Fe$_2$O$_3$:AB:PTFE = 45:45:10 (%) was carried-out in
the electrolyte solution of 7.99 M KOH + 0.01 M K₂S, the results are shown in Fig. 4. With the presence of K₂S in the electrolyte solution, the sharp redox peaks appeared at the same potential range as Fe₂O₃/AB electrodes in KOH (Fig. 3). However, the oxidation peak a₀ was higher and especially the redox current under the Fe(II)/Fe(III)(a₂/c₂) couple peaks decreased more slowly with the cycling number. For the 100 ml-0.5 M citric acid sample (Fig. 4c), its redox current intensity was maintained when repeating 15 cycles. This result demonstrated the positive effect of K₂S additive on the redox reaction of iron. It may be due to the S²⁻ ion combines into the iron oxide and interacts with Fe(I), Fe(II) or Fe(III) in the oxide film to stimulate the decomposition of iron [22, 23] and increase the electric conductivity of the electrode [8, 13] thereby improving the cyclability of iron.

To evaluate the role of K₂S additive in the electrolyte solution for Fe₂O₃/AB electrode, the discharge capacity was calculated from the CV results of Fe₂O₃/AB electrodes in KOH (Fig. 3) and KOH + K₂S (Fig. 4), the results are shown in Fig. 5. Discharge capacities of all electrodes in KOH electrolyte solution (Fig. 5a) are lower than those in electrolyte solution containing K₂S (Fig. 5b) and rapidly decreased with repeated cycling. This confirmed that the presence of K₂S in the electrolyte increased the discharge capacity and improved the cyclability of the iron electrode.

Comparing the discharge capacities of samples prepared by sol-gel method in an electrolyte solution containing K₂S (Fig. 5b) each other, one can see that the 100ml-0.5M citric acid sample has a relatively stable specific capacity while the other samples have gradually decreased specific capacity with the number of cycles. SEM image of 100 ml-0.5 M citric acid sample (Fig. 2c) showed that Fe₂O₃ has spherical shape and their particles size is the smallest. This proves that the size and morphology of Fe₂O₃ particles have significant influence on their cyclability. Thus, among the Fe₂O₃ materials synthesized by sol-gel method, the sample produced at 100 ml-0.5 M citric acid gave the largest discharge capacity, thereby it is the most suitable material for iron-air batteries.

![Figure 5](image.png)

Figure 5. The variation of discharge capacity with the number of cycles of the Fe₂O₃/AB electrode in (a) KOH and (b) KOH + K₂S solutions.
One of the important roles of the K$_2$S additive in the electrolyte solution is to reduce the amount of H$_2$ generated during the charging process, leading to improve the efficiency, capacity, and energy of the electrode. To clarify this hypothesis, the amount of H$_2$ evolution was calculated from the CV measurement in KOH (Fig. 3) and KOH + K$_2$S (Fig. 4) and the results are shown in Fig. 6. The currents come from H$_2$ evolution at the electrodes in the electrolyte solution containing K$_2$S (Fig. 6b) are smaller than those in the electrolyte solution without K$_2$S additive (Fig. 6a). This demonstrates that in the presence of K$_2$S in the electrolyte solution, the amount of H$_2$ evolution has been reduced during the reaction. This is positive effect of K$_2$S on the capacity, as well as the discharge - charge efficiency of the Fe$_2$O$_3$/AB electrode.

![Figure 6](image-url)

**Figure 6.** The variation of hydrogen evolution with the number of cycles of the Fe$_2$O$_3$/C electrodes in (a) KOH and (b) KOH + K$_2$S solutions.

4. **Conclusion**

Nanostructured Fe$_2$O$_3$ powder materials with different particles sizes and shapes have been successfully synthesized by sol-gel method. Investigation of the electrochemical properties shows that the size and morphology of Fe$_2$O$_3$ particles strongly affect their cyclability. The size and morphology of Fe$_2$O$_3$ particles can be controlled by changing the concentration of precursors during sol-gel process to give the best electrochemical characteristics. The positive effect of K$_2$S additive on the electrochemical properties of Fe$_2$O$_3$/AB electrode is confirmed by the increase in both the redox reaction rate of iron and the capacity of Fe$_2$O$_3$/AB electrode, simultaneously the reduce of H$_2$ evolution. From the obtained results one can suggest that nanostructured Fe$_2$O$_3$ materials synthesized by sol-gel method can be a potential candidate for iron-air battery anode.

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References


