Electrochemical characters of α-Fe₂O₃ hexagonal platelets synthesized by a facile hydrothermal route

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Abstract. Fe₂O₃ materials with various morphologies were synthesized from iron (III) chloride (FeCl₃.6H₂O) by a facile hydrothermal route for Fe-air battery anodes. The crystal structure and morphology of the obtained Fe₂O₃ powder were studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The morphologies, shapes and sizes of Fe₂O₃ particles synthesized via the hydrothermal method were controllable by the concentration of precursors. The composite electrodes were fabricated by mixing the synthesized Fe₂O₃ powders with nanocarbon and were then subjected to electrochemical measurements. The results indicated that the shape and size of iron oxide affected the electrochemical properties of Fe₂O₃/carbon composite electrodes. The concentration of electrode components also significantly influenced the cyclability of Fe₂O₃/carbon composite electrodes.

1. Introduction

Rechargeable iron-based alkaline batteries are particularly attractive for large electrical energy storage because they have high theoretical capacity, long cycle life, and environment friendly [1–7]. In an alkaline solution, the iron electrode is oxidized from metallic iron to iron hydroxide (Eq. 1) and then further oxidized to iron oxyhydroxide (Eq. 2) and/or magnetite (Eq. 3):

\[ \text{Fe} + 2\text{OH}^- \rightleftharpoons \text{Fe(OH)}_2 + 2\text{e}^{-} \quad E^0 = -0.975 \text{ V vs. Hg/HgO} \ [8] \]  
\[ \text{Fe(OH)}_2 + \text{OH}^- \rightleftharpoons \text{FeOOH} + \text{H}_2\text{O} + \text{e}^{-} \quad E^0 = -0.658 \text{ V vs. Hg/HgO} \ [8] \]  
\[ 3 \text{Fe(OH)}_2 + 2\text{OH}^- \rightleftharpoons \text{Fe}_3\text{O}_4\text{H}_2\text{O} + 2\text{e}^{-} \quad E^0 = -0.758 \text{ V vs. Hg/HgO} \ [9, 10] \]  

The standard hydrogen evolution reaction potential is a little positive to that of iron electrode, the hydrogen evolution reaction occurs together with the reduction of iron hydroxide to iron (Eq. 1):

\[ 2\text{H}_2\text{O} + 2\text{e}^{-} \rightleftharpoons 2\text{OH}^- + \text{H}_2 \quad E^0 = -0.926 \text{ V vs. Hg/HgO} \ [11–13] \]  

The hydrogen evolution occurring simultaneously with the reduction reaction of iron during charging process reduces the charging efficiency of the iron electrode. In addition, the passivation caused by Fe(OH)₂ electrical insulator formed during discharge (Eq.1) restrict their practical applications. Numerous investigations have focused on improving the performance of iron [7, 14–19].

Our previous works showed that the cyclability of iron electrodes is significantly improved by the modification of the iron electrode structure and using additives [20–24]. We also demonstrated that morphology, shape and size of iron particles strongly affected on the electrochemical properties of Fe/C electrodes [25]. In this study, by changing the preparation conditions, iron oxide particles with...
the desired morphology and size were synthesized via a hydrothermal route. Nanocarbon was applied as an additive to improve the conductivity, cyclability, and cycle performance of iron electrodes.

2. Experimental

2.1. Synthesis of Fe₃O₄ powder
To synthesize Fe₃O₄ particles with various morphologies by hydrothermal method, we used analytical grade chemicals. Deionized water is used for dissolving the salts and rinsing the precipitates.

The hydrothermal process of synthesizing α-Fe₃O₄ was carried out as follows: 0.01 mol of FeCl₃·6H₂O was dissolved in 30 ml of deionized water to form a uniform solution. Then 15 ml NaOH 2M was added slowly to the above solution to form a Fe(OH)₃ suspension. The resultant mixture was continuously stirred to obtain the brown suspension. The brown Fe(OH)₃ precipitates are filtered and washed with deionized water several times to remove Cl⁻, Na⁺ ions. To synthesize the various morphologies of Fe₃O₄ materials, the brown Fe(OH)₃ precipitates were added to 40 ml NaOH aqueous solutions with various concentrations of 2.5, 7.5 and 15 M under stirring for 30 min to obtain various mixtures. Subsequently, the mixture has been transferred and sealed into a 100 mL Teflonlined stainless steel autoclave, maintained at 160 °C for 20 h in a typical hydrothermal process. Then the autoclave was cooled down gradually to room temperature. The reddish brown precipitates were collected by centrifugation, washed with deionized water and ethanol for several times to remove the remaining NaOH, and subsequently dried at 60 °C for 12 h to obtain the Fe₃O₄ powder.

2.2. Characterizations of Fe₃O₄ particles
The crystal structure of the synthesized powder was examined by an X-ray diffractometer (XRD; Rigaku). The morphologies and particle size of the as-prepared materials were observed by a scanning electron microscopy (SEM) using JEOL JSM-6060LA/VI (JEOL, Japan).

Two types of electrode, with and without acetylene black (AB) additive, were prepared to investigate the electrochemical properties of the synthesized Fe₃O₄ materials. The Fe₃O₄ electrode sheet free AB additive was fabricated by mixing of 90 wt% Fe₃O₄ and 10 wt.% polytetrafluoroethylene (PTFE; Daikin Co.) followed by rolling. The Fe₃O₄/AB composite electrodes were prepared by the same procedure with the mixing ratios of Fe₃O₄ : AB: PTFE = 45: 45: 10 wt.% and Fe₃O₄: AB: PTFE = 70: 20: 10 wt.%. The electrodes were punched into pellets with a diameter of 1 cm.

Cyclic voltammetry (CV) measurements were carried out using a three-electrode glass cell assembly with Fe₃O₄/AB composite as the working electrode, Pt mesh as the counter electrode, and Hg/HgO as the reference electrode. The electrolyte was 8 mol dm⁻³ aqueous KOH solution. The CV measurements were recorded at a scan rate of 2 mV s⁻¹ and within a range of -1.3 V to -0.1 V. All these measurements were described in our previous work [25].

3. Results and discussion

3.1. Morphological and structural properties of Fe₃O₄ particles
The X-ray patterns of the as-prepared materials synthesized at various concentrations of NaOH are presented in Figure 1. For convenience, the α-Fe₃O₄ samples synthesized at NaOH 2.5, 7.5 and 15 M are entitled as NaOH-2.5M, NaOH-7.5M and NaOH-15M. In all cases of various NaOH concentrations, the XRD patterns exhibit some typical diffraction peaks at 2 theta values of 24.15°, 33.16°, 35.63°, 40.86°, 49.46°, 54.07°, 62.44°, and 64.0°, which correspond to the (012), (104), (110), (113), (024), (116), (214), and (300) planes, respectively. These diffraction peaks are well matched with those of the α-Fe₃O₄ phase reported in ICSD No. 71194. No other peaks for impurities are observed in the XRD patterns, suggesting that the as-synthesized materials are pure α-Fe₃O₄.
Figure 1. XRD patterns of the as-prepared $\alpha$-$\text{Fe}_2\text{O}_3$ powders with various amounts of NaOH: (a) 2.5 M, (b) 7.5 M and (c) 15 M.

The size and shape of the synthesized materials were examined by SEM as shown in Figure 2. The as-prepared samples have a hexagonal platelet shape, un-uniform morphology and the dimension, thickness increases with increasing the NaOH amount. The diameter of most hexagonal platelets is less than 1 $\mu$m at NaOH 2.5 M, more than 1 $\mu$m at NaOH 7.5 M, and more than 2 $\mu$m at NaOH 15 M. The thickness of hexagonal platelets also increase when NaOH increases from 2.5 M to 15 M. Therefore, the size of $\text{Fe}_2\text{O}_3$ hexagonal platelets at NaOH 15 M is largest but they are relative uniform. These results demonstrated that the NaOH amount influenced on the morphology and dimension of the synthesized products. In this work, only amount of NaOH was changed while the other conditions were kept constantly. Thus, the size and shape of $\text{Fe}_2\text{O}_3$ synthesized via hydrothermal route can be controlled by changing NaOH amount.

3.2. Electrochemical characterization of synthesized $\text{Fe}_2\text{O}_3$

To define the effect of morphology and dimension of $\text{Fe}_2\text{O}_3$ particles on their electrochemical properties, the CV measurements were carried out with $\text{Fe}_2\text{O}_3$ electrodes using synthesized $\text{Fe}_2\text{O}_3$, the results are shown in Figure 3. A couple redox reaction peak was observed at around $-0.85$ V ($a_1$) upon oxidation and at around $-1.15$ V ($c_1$) upon reduction, together with a small couple peak at around $-0.65$ V ($a_2$) upon oxidation and around $-1.0$ V ($c_2$) upon reduction. The anodic peak ($a_1$) and cathodic peak ($c_1$) corresponds to the $\text{Fe/Fe(II)}$ redox couple (Eq.1) and peak couple ($a_2$)/($c_2$) corresponds to the $\text{Fe(II)/Fe(III)}$ redox couple (Eq. 2 and/or 3). A small oxidation peak $a_0$ observed at around $-1.0$ V was ascribed to the oxidation of iron to form $[\text{Fe(OH)}]_{\text{ads}}$ before forming $\text{Fe(II)}$ [10]. The hydrogen evolution appeared at around $-1.2$ V.

The $\text{Fe(II)/Fe(III)}$ ($a_2/c_2$) redox couple was smaller compared to the $\text{Fe/Fe(II)}$ ($a_1/c_1$) one. The iron deposition peak $\text{Fe(II)/Fe (c_1)}$ was completely covered by the hydrogen evolution peak in the samples NaOH-2.5M (Figure 3a) and NaOH-7.5M (Figure 3b), whereas it was separated from the hydrogen evolution peak in the samples NaOH-15M (Figure 3c).

Figure 2. SEM images of $\text{Fe}_2\text{O}_3$ powder synthesized at various amounts of NaOH in a typical hydrothermal process.
evolution in the sample NaOH-15M (Figure 3c). The separation of hydrogen evolution and Fe(II)/Fe reduction peak will support the charge efficiency and discharge capacity of the iron electrode. However, the redox current of the NaOH-7.5M sample decreased with cycling, whereas they increased in the case of NaOH-2.5M and NaOH-15M samples. As shown in SEM images in Figure 2, Fe$_3$O$_4$ particles synthesized at NaOH-15M are hexagonal platelets, relative uniform and thicker than those at NaOH-2.5M and 7.5M. These results demonstrated that shape and size of Fe$_3$O$_4$ particles influenced to their electrochemical characterizations.

**Figure 3.** Cyclic voltammograms of Fe$_3$O$_4$ electrodes (Fe$_3$O$_4$: PTFE = 90: 10 wt.%) using Fe$_3$O$_4$ synthesized at various NaOH amounts in KOH solution.

**Figure 4.** Cyclic voltammograms of Fe$_3$O$_4$/AB composite electrodes (Fe$_3$O$_4$:AB:PTFE=45:45:10 wt.%) using Fe$_3$O$_4$ synthesized at various NaOH amounts in KOH solution.

To evaluate the applicability of synthesized Fe$_3$O$_4$ materials, the Fe$_3$O$_4$/AB composite electrodes with Fe$_3$O$_4$: AB: PTFE = 45: 45: 10% have been fabricated and measured CV, the results are shown in Figure 4. For all samples, the CV profiles depicted two pairs of redox peaks of Fe/Fe(II) ($a_1/c_1$) and Fe(II)/Fe(III) ($a_2/c_2$). The redox peaks of Fe/Fe(II) ($a_1/c_1$) were observed at around −0.8 V ($a_1$)/−1.2 V ($c_1$) on the forward and backward scan respectively while the redox couple of Fe(II)/Fe(III) ($a_2/c_2$) were seen at around −0.5 V ($a_2$) and −1.1 V ($c_2$), respectively. Along with the appearance of these peaks, a
small anodic peak $a_0$ was observed at around $-1.0$ V on the forward scan, and hydrogen evolution occurred at around $-1.25$ V. Opposite to the $\text{Fe}_2\text{O}_3$ electrode, the $\text{Fe}/\text{Fe(II)}$ ($a_1/c_1$) redox couple was very smaller compared to the $\text{Fe(II)}/\text{Fe(III)}$ ($a_2/c_2$) one. This suggests that $a_2/c_2$ couple contained both the redox reactions of $\text{Fe}/\text{Fe(II)}$ (Eq. 1) and $\text{Fe(II)}/\text{Fe(III)}$ (Eq. 2 and/or 3). However, the overpotential of two couples was increased and the reduction peak $c_1$ was still immerged in the hydrogen evolution when AB was added. This will cause the negative effect on the cycle performance of $\text{Fe}_2\text{O}_3$/AB electrode.

Comparison with the CV results of the $\text{Fe}_2\text{O}_3$ electrodes without AB (Figure 3), the redox peaks of the $\text{Fe}_2\text{O}_3$/AB electrodes (Figure 4) were higher and larger. This demonstrated that the reaction rate of $\text{Fe}/\text{Fe(II)}$ and $\text{Fe(II)}/\text{Fe(III)}$ couples increased in presence of AB and confirmed the positive effects of AB on the electrochemical behavior of $\text{Fe}_2\text{O}_3$. AB has good electrical conductivity, small particle size, and large actual surface area, thus it increased the conductivity of the $\text{Fe}_2\text{O}_3$/AB electrode and supported for redox reaction of $\text{Fe}_2\text{O}_3$.

During the discharge process, due to the dissolution-deposition mechanism of the redox reaction of iron (Eq. 1), the soluble $\text{HFeO}_2$ species, which were formed in the intermediate step of Eq. 1 would precipitate and distribute on the AB surface. This process reduced the passivity of the iron electrode caused by the $\text{Fe(OH)}_2$ layer, enhanced the reaction rate of the $\text{Fe}/\text{Fe(II)}$ and $\text{Fe(II)}/\text{Fe(III)}$ couples, and leads to improved cycleability of $\text{Fe}_2\text{O}_3$/AB electrode. Comparing CV results of these samples, we can see that there is a difference in CV profiles even though the sample composition and measuring conditions were the same. This confirmed that the shape and size of $\text{Fe}_2\text{O}_3$ particles affected the electrochemical properties of $\text{Fe}_2\text{O}_3$/AB electrodes.

To reduce the additive AB in electrode, the electrodes with 70 wt.% $\text{Fe}_2\text{O}_3$, 20 wt.% AB, and 10 wt.% PTFE were prepared and performed CV measurement, the results are showed in Figure 5. For the $\text{Fe}_2\text{O}_3$/-NaOH 2.5M and NaOH 7.5M samples, the oxidation peaks decreased rapidly with repeated cycling while the reduction peaks were completely covered by hydrogen evolution. The CV profiles of the $\text{Fe}_2\text{O}_3$/AB electrode using $\text{Fe}_2\text{O}_3$ synthesized at NaOH 15M with $\text{Fe}_2\text{O}_3$ 70 wt.% (Figure 5) are similar to those with $\text{Fe}_2\text{O}_3$ 45 wt.% (Figure 4). This result suggested that increasing the active material of the $\text{Fe}_2\text{O}_3$/AB electrode to 70 wt.% seems to be not suitable for these $\text{Fe}_2\text{O}_3$ products. It may be due to the conductivity of the $\text{Fe}_2\text{O}_3$/AB composite electrode decreased when reduced AB.

Thus, the electrochemical characteristics of $\text{Fe}_2\text{O}_3$/AB electrode were affected by not only the shape and size of $\text{Fe}_2\text{O}_3$ particles, but also by the concentration of electrode components. The adequate ratio of the electrode components in this case is $\text{Fe}_2\text{O}_3$/AB:PTFE = 45:45:10 wt.%.
To find the most suitable Fe$_2$O$_3$ among the synthesized materials, the special discharge capacities of the Fe$_2$O$_3$/AB electrodes with Fe$_2$O$_3$ 45 wt.% are calculated from the CV profiles in Figure 4, the results are shown in Figure 6. Among the Fe$_2$O$_3$/AB electrodes, the electrode with Fe$_2$O$_3$ synthesized at NaOH 2.5M gave the largest capacities. As seen in the SEM images (Figure 2), the Fe$_2$O$_3$ material synthesized at NaOH 2.5 M has smaller dimension than those at NaOH 7.5 M and NaOH 15 M. In the Fe$_2$O$_3$/AB electrodes, all the electrode components are the same, only size and shape of Fe$_2$O$_3$ particles are different. In the case of Fe$_2$O$_3$/AB electrode using Fe$_2$O$_3$ synthesized at NaOH 2.5M, the distance between iron oxide and carbon species is expected to be shorter than those using Fe$_2$O$_3$ prepared at NaOH 7.5 M and 15 M, thus diffusion path of mobile iron between an iron particle and AB carbon is shorter resulting in the higher redox reaction rate, larger capacity. These results confirmed the size and shape of Fe$_2$O$_3$ significantly affected the cycle performance of Fe$_2$O$_3$/AB electrodes. This finding reveals that Fe$_2$O$_3$ sample synthesized at NaOH 2.5 M is the most suitable material for Fe$_2$O$_3$/AB electrode. The charge-discharge measurement was conducted on the Fe$_2$O$_3$/AB electrode using this active material, the result is shown in Figure 7. The discharge capacity increased in few initial cycles, achieved high value and then gradually decreased with subsequent cycling. Although the large discharge capacity obtained after few cycles, but the degradation of discharge capacity rapidly occurred. Optimization of fabrication conditions to further improve the capacity retention, hexagonal platelet shape α-Fe$_2$O$_3$ particles synthesized via a facile hydrothermal method are potential active materials for iron-air battery anodes.

![Figure 6. Discharge capacity of Fe$_2$O$_3$/AB electrodes (Fe$_2$O$_3$:AB:PTFE=45:45:10 wt.%) in KOH solution.](image1)

![Figure 7. Cycle performance of Fe$_2$O$_3$/AB electrodes (Fe$_2$O$_3$:AB:PTFE=45:45:10 wt.%) using Fe$_2$O$_3$-NaOH 2.5M in KOH+K$_2$S solution.](image2)

4. Conclusions

In this study, hexagonal platelet shape α-Fe$_2$O$_3$ particles with different dimension were synthesized via a facile hydrothermal route by changing the concentration of the precursors. SEM measurement showed that the size and morphological characteristics of α-Fe$_2$O$_3$ particles were dependent on the NaOH amount during the hydrothermal treatment.

Investigation of the electrochemical properties of the Fe$_2$O$_3$/AB composite electrodes using synthesized Fe$_2$O$_3$ showed that the electrochemical properties of Fe$_2$O$_3$/AB electrodes were affected by the shape and size of the Fe$_2$O$_3$ materials. Among the various synthesized α-Fe$_2$O$_3$, the sample obtained at NaOH 2.5 M provided the highest discharge capacity. These iron oxides are potential materials for iron-based rechargeable batteries when further improved capacity and cycle performance.
Acknowledgment

This research is funded by the Hanoi University of Science and Technology (HUST) under project number T2020-SAHEP-018.

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