Original Article

Electrochemical Performance of Fe₂O₃/AB-Based Composite Electrode

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Abstract: In this study, Fe₂O₃ nanoparticles (nm) and microparticles (µm) were used as active materials and Acetylene Black carbon (AB) as an additive to prepare Fe₂O₃/AB composites to find a suitable material for Fe-air battery anode. The effects of grain size of iron oxide particles and additives on the electrochemical behavior of Fe₂O₃/AB composite electrodes in alkaline solution were investigated using cyclic voltammetry (CV), galvanostatic cycling and electrochemical impedance spectroscopy (EIS) measurements. The study results show that iron oxide nanoparticles provided better cyclability than iron oxide microparticles. The impedance of electrode increased during cycling, but the nm-Fe₂O₃/AB electrode gave smaller resistance than the µm-Fe₂O₃/AB one. The additives showed strong effects on the electrochemical behaviors of iron oxide electrodes. The AB additive enhanced the electric conductivity of Fe₂O₃/AB electrode and thus increased the redox reaction rate of iron oxide while K₂S interacted with and broke down the passive layer leading to improved cyclability and giving higher capacity for Fe₂O₃/AB electrodes.

Keywords: Fe₂O₃ nanoparticles, Fe₂O₃ microparticles, K₂S additive, Fe₂O₃/AB composite electrode, Fe-air battery anode

1. Introduction

High energy density for metal/air batteries has been the focus of attention in recent years for applications involving electric vehicles [1-3]. Iron is a potential candidate for metal/air battery anode and is also used in nickel/iron battery because of high theoretical energy (0.96 Ah/g) and low cost [4-
However, the problem of iron electrode is the passive layer of Fe(OH)$_2$ formed during cycling leading to a low utilization coefficient. Further, the potential of the Fe/Fe(OH)$_2$ couple is only slightly more negative than that of the hydrogen evolution potential in alkaline solution [5,7] thereby there is a simultaneous evolution of hydrogen during charging [8-9]. This is the cause of the low charge/discharge efficiency and high self-discharge rate of iron electrode. To overcome the limitations of the iron electrode, a number of additives are incorporated in the iron electrode during fabrication [6, 8-11] or in electrolyte [6, 10-14] or both [6, 10-11, 14]. To increase the active material surface area, in the present study, we prepared Fe$_2$O$_3/C$ using Acetylene Black carbon (AB) and iron oxide for use as anode in Fe/air battery. In addition, K$_2$S is used as an additive to electrolyte to improve the limitations of the iron electrode.

2. Experimental

Fe$_2$O$_3$ nanoparticle (nm-Fe$_2$O$_3$) and microparticles (μm-Fe$_2$O$_3$)(Wako Pure Chemical Co.) and acetylene black (AB, Denki Kagaku Co. Ltd.) were used as the iron sources and carbon additives to prepare the Fe$_2$O$_3$/AB materials by mixing of 50 : 50 wt% Fe$_2$O$_3$ and AB followed by ball milling. The Fe$_2$O$_3$/AB composite electrodes were fabricated by mixing 90 wt% Fe$_2$O$_3$/AB materials obtained after ball milling with 10wt%polytetrafluoroethylene (PTFE, Daikin Co.) binder followed by rolling and punching into the form of a pellet with 1 cm in diameter. Thus, in Fe$_2$O$_3$/AB composite electrodes, Fe$_2$O$_3$, AB and binder components are 45, 45 and 10 wt%, respectively.

To investigate the effect of Fe$_2$O$_3$ particle size as well as the K$_2$S additive on the electrochemical properties of the Fe$_2$O$_3$/AB electrodes, cyclic voltammetry (CV) studies have been carried out in three-electrode glass cells with Fe$_2$O$_3$/AB composite electrode as the working electrode, Pt mesh as the counter electrode and Hg/HgO as the reference electrode. The electrolyte was 8 moldm$^{-3}$ KOH aqueous solution or 7.99 moldm$^{-3}$ KOH + 0.01 moldm$^{-3}$ K$_2$S aqueous solution. CV measurements were taken at a scan rate of 2 mV s$^{-1}$ and within a voltage range of −1.3 V to −0.1 V. Charge/discharge measurements were conducted on three-electrode glass cells. In the charge course, the current density of 50 mA cm$^{-2}$ was used with a cutoff potential of −1.2 V whereas in the discharge course, a constant current density of 2.0 mA cm$^{-2}$ was applied with a cutoff potential of −0.1 V. The electrochemical impedance spectroscopy (EIS) studies have been performed on a three-electrode glass cell assembly using Auto Lab system. The impedance spectra were recorded after the cell was cycled and stopped at open circuit potential (OCP) followed by a rest period of 1 hour. The AC perturbation signal has been fixed at 10 mV, and the frequency range was from $10^2$ to $10^5$ Hz in the EIS. In all electrochemical measurements, we used fresh electrodes without pre-cycling.

3. Results and discussion

Nanoparticles (nm) and microparticles (μm) of Fe$_2$O$_3$ have been used as electrode active materials to investigate the effect of Fe$_2$O$_3$ particle size on their electrochemical properties. The SEM images of nm- Fe$_2$O$_3$ and μm-Fe$_2$O$_3$ samples are shown in Figs. 1a and 1b, respectively. The nm-Fe$_2$O$_3$ particles are less than 100 nm and relatively uniform. They look like little balls. Unlike the nm- Fe$_2$O$_3$ sample, the SEM image of the μm-Fe$_2$O$_3$ in Fig. 1b shows mixed particle size and shape. They consist of Fe$_2$O$_3$ flat flakes with dimensions ranging from several hundred nanometers to several ten micrometers. Different sizes and shapes of the nm-Fe$_2$O$_3$ and μm-Fe$_2$O$_3$ samples shall affect the electrochemical characterization of the Fe$_2$O$_3$ electrode.
3.1. Effect of particle size and shape of iron oxide and additive on the electrochemical behavior of \( \text{Fe}_2\text{O}_3/\text{AB} \) composite electrode

The cyclic voltammetry (CV) measurements of the nm-Fe\(_2\)O\(_3\)/AB composite electrode (Fe\(_2\)O\(_3\): AB: PTFE = 45:45: 10 wt%) are presented in Fig. 2a. On the oxidation scan from \(-1.3\) V to \(-0.1\) V, two oxidation peaks of \( \text{Fe}/\text{Fe(II)}(a_1) \), \( \text{Fe(II)}/\text{Fe(III)}(a_2) \) occur at about \(-0.9\) V and \(-0.4\) V, whereas on the reverse direction, only one reduction peak corresponding to \( \text{Fe (III)}/\text{Fe(II)}(c_1) \) occurs at about \(-1.0\) V along with the hydrogen evolution peak. The reduction peak of \( \text{Fe(II)}/\text{Fe(c2)} \) is completely masked by hydrogen evolution. Particularly, the oxidation peak \( a_2 \) is very large and broad compared to the \( a_1 \) peak. This may be due to the formation of \( \text{Fe(OH)}_2 \) which inhibits the oxidation of the inner layer of the iron leading to increase the overpotential of \( \text{Fe}/\text{Fe(II)} \) reaction. Consequently, \( a_2 \) peak includes oxidation reactions of both \( \text{Fe}/\text{Fe(II)} \) and \( \text{Fe(II)}/\text{Fe(III)} \). This is the reason why \( a_2 \) is a very large peak compared to \( a_1 \) peak. The redox peak currents increases during initial cycles and then decrease upon further cycling. In the first discharge, \( \text{Fe(OH)}_2 \) was formed on the surface of iron and carbon via an intermediate soluble species, \( \text{HFeO}_2 \). The passive layer \( \text{Fe(OH)}_2 \) inhibited the oxidation of inner iron and thus overpotential increased. In initial cycles, \( \text{Fe(OH)}_2 \) layer was thin, the oxidation reaction rate was high. Further cycling, insulated \( \text{Fe(OH)}_2 \) layer became thicker resulting in larger electrode resistance and consequently redox current decreased.

Figure 1. SEM images of (a) nm-Fe\(_2\)O\(_3\) and (b) \( \mu \text{m-Fe}_2\text{O}_3 \) samples.
In order to investigate the effect of grain size and morphology of Fe$_2$O$_3$ on the electrochemical behaviors of Fe$_2$O$_3$/AB electrodes, CV measurements were carried out on the μm-Fe$_2$O$_3$/AB electrode (Fe$_2$O$_3$: AB: PTFE = 45:45: 10 wt%) and the results are presented in Fig. 3a. Similar to nm-Fe$_2$O$_3$/AB, the redox peaks $a_1$, $a_2$, $c_1$ also appear at around $-0.9$, $-0.5$ and $-0.95$ V respectively, and $c_2$ peak is masked by hydrogen peak. However, the current intensity of these peaks decreases with increasing cycle number.

Compared to nm-Fe$_2$O$_3$/AB sample (Fig. 2a), the redox peaks of μm-Fe$_2$O$_3$/AB (Fig. 3a) electrode are very small. This proves that the size and shape of Fe$_2$O$_3$ particles strongly influence their electrochemical properties. In this case, nm-Fe$_2$O$_3$ particles exhibit better cyclability than μm-Fe$_2$O$_3$. This could be explained in view of the Fe$_2$O$_3$ nanoparticles having a larger surface area than the Fe$_2$O$_3$ microparticles, so that the redox reaction rate of nm- Fe$_2$O$_3$ is greater than μm-Fe$_2$O$_3$ and therefore it has better cyclability.

Figure 2. CV profiles of nm-Fe$_2$O$_3$/AB composite electrodes(Fe$_2$O$_3$:AB:PTFE = 45:45:10 wt.%) in (a) KOH and (b) KOH+K$_2$S electrolyte solution.
The role of adding $K_2S$ in the electrolyte on the cyclability of the nm-$Fe_2O_3/AB$ and µm-$Fe_2O_3/AB$ electrodes have been investigated and the results are presented in Fig. 2b and 3b respectively. Comparing the CV results of the nm-$Fe_2O_3/AB$ sample in KOH solution (Fig. 2a) with those in KOH+$K_2S$ solution (Fig. 2b), it can be seen that adding $K_2S$ to the electrolyte solution (2b), beside the appearance $a_1$, $a_2$ and $c_1$ peaks, the reduction peak of $Fe (II)/Fe (c_2)$ is observable and it is separated from the hydrogen evolution peak. This demonstrates that the amount of hydrogen evolution is partially suppressed and the reaction rate of $Fe/Fe(II)$ couple is increased while its over-potential is decreased with the presence of $K_2S$ in the electrolyte solution. In other words, the reaction rate of $Fe/Fe(II)$ is increased and its overpotential is decreased by sulfide ion. There may be an effect of the adsorbed sulfide ion, which interacts strongly with Fe(I), Fe(II) or Fe(III) in the oxide film and promotes the dissolution of iron and enhance the bulk conductivity of the electrode, thereby improving cycleability [15-16].

![CV profiles of µm-$Fe_2O_3/AB$ composite electrodes](image)

Figure 3. CV profiles of µm-$Fe_2O_3/AB$ composite electrodes($Fe_2O_3:AB:PTFE = 45:45:10$ wt.%.) in (a) KOH and (b) KOH+$K_2S$ electrolyte solution.

Further cycling, the current under these peaks decreased and deposition peak of iron $c_2$ is gradually masked by hydrogen. This suggests that the inner resistance of the electrode was increased due to the insulating of $Fe(OH)_2$ layer forming during the oxidation. When $K_2S$ is present in the electrolyte solution, initially the reaction rates of the $Fe/Fe(II)$ and $Fe(II)/Fe$ (III) couples are increased, but on subsequent sweeping, the formed $Fe(OH)_2$ film is thicker, the passivation overwhelms the increase in the redox reaction rate supported by $K_2S$ thereby reducing the redox current. Consequently, $K_2S$ additive proved the positive effects on the electrochemical behaviors of nm-$Fe_2O_3/AB$ composite electrode.

The CV results of µm-$Fe_2O_3/AB$ electrode in electrolyte containing $S^2$ are depicted in Fig. 3b. In comparison to CV results in KOH electrolyte (Fig.3a), the CV profiles in both cases are relatively similar. When $K_2S$ is introduced into the electrolyte solution (Fig. 3b), the $a_1$, $a_2$, and $c_1$ peaks still appear at the same potentials as in Figure 3a. As the number of sweeps increases, the current intensity in both couple peaks decreases. No significant differences are observed in the CV profiles of the µm-$Fe_2O_3/AB$ electrodes in KOH and KOH+$K_2S$. Thus, for the µm-$Fe_2O_3/AB$ composite sample, the presence of $K_2S$ in the electrolyte does not have a positive effect on the electrochemical behavior of µm-$Fe_2O_3$ as well as the cyclability of the µm-$Fe_2O_3/AB$ electrode.
3.2. Electrochemical Impedance spectroscopy (EIS) of nm-Fe₂O₃/AB and µm-Fe₂O₃/AB composite electrodes in electrolyte with and without additive

Electrode resistance was determined for nm-Fe₂O₃/AB and µm-Fe₂O₃/AB composite electrodes in KOH and KOH+K₂S electrolytes using electrochemical impedance spectroscopy (EIS). The EIS measurements were carried out before and after five initial cycles at open circuit potential (OCP) and the results are shown in Figs. 4 and 5 respectively. Before and after cycling, each spectrum consists of a semicircle in a high frequency region, which was assigned to the interfacial response, followed by a straight line in the lower frequency region corresponding to Warburg impedance. As the limitation of the apparatus was 100 Hz, straight line at lower frequencies is either short or not present.

Figure 4. Electrochemical impedance spectroscopy (EIS) of nm-Fe₂O₃/AB electrode (Fe₂O₃:AB:PTFE = 45:45:10 wt.%) in (a) KOH and (b) KOH + K₂S electrolyte solution

Figure 5. Electrochemical impedance spectroscopy (EIS) of µm-Fe₂O₃/AB electrode (Fe₂O₃:AB:PTFE = 45:45:10 wt.%) in (a) KOH and (b) KOH + K₂S electrolyte solution.

In the case of KOH electrolyte (Figs. 4a and 5a), before cycling, the semicircle was observed with a straight line in the lower frequency region. After cycling, the semicircle was observable but not completely and semicircle diameter of the electrode after cycling is larger than that before cycle. This suggested that the resistance of electrodes increased after cycling and gradually increased with increase in cycle number. The semicircle diameter of nm-Fe₂O₃/AB electrode is a little smaller than that of µm-Fe₂O₃/AB electrode in KOH suggests that nm-Fe₂O₃/AB electrode has lower resistance than µm-Fe₂O₃/AB. These results are consistent with the CV results (Figs.2 and 3), as the redox
current decreased with repeated cycling and nm-Fe$_2$O$_3$/AB electrodes have better cyclability than µm-Fe$_2$O$_3$/AB. This is reasonable since resistance of electrode gradually increased with repeated cycling and µm-Fe$_2$O$_3$/AB electrodes give larger resistance than nm-Fe$_2$O$_3$/AB electrode.

In the case of electrolyte solution containing K$_2$S additive (Fig. 4b and 5b), the semicircle diameters of the electrodes after cycling are also larger than those of the electrodes before cycle similar to that observed in KOH solution thereby implying that the electrode resistance also increases during cycling in additive electrolyte. Remarkably, the semicircle diameters of electrodes before and after cycling in the electrolyte containing K$_2$S (Figs. 4b and 5b) are larger than those in the base electrolyte (Figs. 4a and 5a). These results demonstrate that the resistance of the Fe$_2$O$_3$/AB electrode in the additive electrolyte is larger than that in the free additive electrolyte and can be ascribed to the S$^2-$ ion in the electrolyte solution adsorbed on the surface of the Fe$_2$O$_3$/AB electrode causing an increase in the contact resistance between the electrode surface and the electrolyte solution. However, the semicircle diameter of nm-Fe$_2$O$_3$/AB electrode before cycle is a little smaller than that after cycle while it is much smaller than that of µm-Fe$_2$O$_3$/AB electrode after cycle. This tendency is consistent with the CV profiles (Figs. 2b and 3b). In the case of nm-Fe$_2$O$_3$/AB electrode (Fig. 2b), the presence of the K$_2$S additive in the electrolyte enhances the redox reaction rate of the Fe$_2$O$_3$/AB electrode. Therefore, the presence of S$^2-$ in the electrolyte solution on the one hand increases the resistance of the Fe$_2$O$_3$/AB electrode, but on the other hand it also enhances the redox reaction rate of the electrode. However, the current intensity still decreased with increase in cycle number due to the passive layer Fe(OH)$_2$ formed during the discharge. Adding K$_2$S into the electrolyte solution, initially the reaction rate of the Fe/Fe(II) and Fe(II)/Fe(III) couples increases, but the Fe(OH)$_2$ layer becomes thicker upon repeated cycling, passivation dominates the increase in the reaction rate leading to reducing redox current. In the case of µm-Fe$_2$O$_3$/AB electrode, the presence of the K$_2$S additive in electrolyte did not provide any positive effect either in term of cyclability of iron (Fig. 3b) nor the impedance of electrode before and after cycling is too large (Fig. 5b) than that of nm-Fe$_2$O$_3$/AB electrode. Consequently, under these experimental conditions, nm-Fe$_2$O$_3$/AB electrode provided better cyclability, higher redox reaction rate than µm-Fe$_2$O$_3$/AB electrode.

3.3. Cycle performance of nm-Fe$_2$O$_3$/AB electrode

To obtain the cycle performance of nm-Fe$_2$O$_3$/AB electrode, the galvanostatic cycle measurement in KOH + K$_2$S solution was carried out, the results are presented in Figs. 6 and 7.
One oxidation plateau was observed at about $-0.65$ V in the discharge curves (Fig.6) correspondence to the oxidation reactions of Fe/Fe(II) and Fe(II)/Fe(III). The plateau was shortened when repeated cycling. These results suggest that the discharge capacity decreased with further cycling. The changing of discharge capacity of nm-Fe$_2$O$_3$/AB electrode was consistent with that of CV profiles (Fig. 2b).

Fig. 7 show the cycle performance of the nm-Fe$_2$O$_3$/AB electrode in KOH+K$_2$S solution. High discharge capacity attained at the initial cycle and then gradually decreased with further cycling. These results demonstrate the capacity retention was low at this cycling condition. To meet the actual application requirements the capacity retention still need further improvements.

4. Conclusion

The size and morphology of iron oxide strongly affected the electrochemical properties of Fe$_2$O$_3$/AB composite electrodes. Fe$_2$O$_3$ nanoparticles provided higher redox reaction rate and better cyclability than Fe$_2$O$_3$ microparticles. Besides that, nm-Fe$_2$O$_3$/AB composite electrodes gave smaller resistance than μm-Fe$_2$O$_3$/AB composite electrodes.

The nm-Fe$_2$O$_3$/AB composite electrodes in electrolyte containing K$_2$S additive showed the improved redox reaction rate of Fe/Fe(II) and Fe(II)/Fe(III) couples and significantly suppressed hydrogen evolution during cycling whereas μm-Fe$_2$O$_3$/AB composite electrodes did not show such behaviors. It revealed that K$_2$S has positive effects on the electrochemical properties of nm-Fe$_2$O$_3$/AB composite electrodes but negligibly affect on the μm-Fe$_2$O$_3$/AB one.

The resistance of the Fe$_2$O$_3$/AB composite electrodes after cycling is higher than that of before cycling in both electrolytes containing K$_2$S additive and free additive. The electrochemical impedance of the Fe$_2$O$_3$/AB electrodes in the electrolyte containing K$_2$S additive increased with respect to that in the basic KOH electrolyte. The nm-Fe$_2$O$_3$/AB composite electrode in electrolyte containing K$_2$S additive gave high discharge capacity at initial cycle and then gradually decreased with further cycling.
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References