



THE INFLUENCE OF CARBON ADDITIVE ON THE ELECTROCHEMICAL BEHAVIORS OF Fe₂O₃/C ELECTRODES IN ALKALINE SOLUTION

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Abstract. In this study, Acetylene Black (AB) and Fe₂O₃ nanoparticles were used as the additive and active materials, respectively for preparing Fe₂O₃/AB composite electrode. The effects of carbon additive and binder content on the electrochemical properties of Fe₂O₃/AB electrodes in alkaline solution were investigated to find the suitable anode for the Fe/air battery. The results of electrochemical measurements showed that both the AB additive and binder content significantly affected on the electrochemical behaviors of Fe₂O₃/AB electrodes. AB additive improves in redox reaction of iron oxide. Increasing the binder content in electrode showed the negative effect in term of the cycleability of Fe₂O₃/AB composite electrode.

Keywords: Fe₂O₃ nanoparticles, carbon additive, Fe₂O₃/AB composite electrode, Fe/air battery anode.

Classification numbers: 2.8.2; 3.4.1.

1. INTRODUCTION

In recent years, rechargeable lithium-ion batteries have attracted much attention and are considered as the most promising power sources for electric vehicles (EVs) and hybrid electric vehicles (HEVs) due to their unique features. However, the present carbonaceous negative electrode, has not satisfied the requirements of high energy and high power application for EVs and HEVs due to their relatively low specific capacity (e.g. 372 mAh/g for graphite). Thus, lithium ion batteries have been applied in portable electronics for decades [1].

Rechargeable metal/air batteries are of special interest to battery researchers because they have much higher theoretical capacity than other sorts of batteries [2]. Metal/air batteries using several different metals have been investigated [3–6]. Among them, Fe/air batteries have

received considerable attention due to their high theoretical capacity, long cycle life, high electrochemical stability, low cost, and environmental safety [7]. Fe is cheap, non-toxic and highly safety, a Fe/air rechargeable battery is expected as the promising battery for EVs and HEVs. Alkaline liquid electrolyte has been used for electrolyte of the conventional Fe/air battery, however, because of the change in the shape of Fe electrode during discharge, Fe/air battery has poor cycle stability and low efficiency of charge and discharge [8].

The practical application of Fe/air batteries has been limited by the thermodynamic instability of iron in alkaline environments and the low hydrogen overpotential of porous iron electrodes [9]. The hydrogen evolution reaction competes with the electrode charge reaction and results in low battery cycling efficiency [10]

Using iron oxide instead of iron for Fe/air battery anode showed many advantages, including environmental compatibility, low cost, and good safety [11], limiting the changes the shape of the iron electrodes being discharged [12].

To improve the electrochemical characteristics of Fe/air batteries, various kinds of metal sulfide additives have been applied to iron electrodes [9, 13 - 15] and/or associated electrolytes [13, 14, 16]. Our previous work demonstrated that the addition of carbon species into iron electrodes improved the conductivity and redox current [17]. Moreover, by loading Fe₂O₃ nanoparticles onto carbon nanotubes, the electrochemical characteristics of Fe/C electrodes were improved further [14, 18, 19]. The positive effects of K₂S additive to electrolyte on the cycleability of Fe/C electrodes were demonstrated [13, 14].

In this report, the effects of the carbon additives and binders to the cycleability of Fe-air battery negative electrode are investigated by electrochemical measurements in the alkaline aqueous electrolyte.

2. EXPERIMENTAL

Fe₂O₃ nanoparticles (Wako Pure Chemical Co.) and acetylene black (AB, Denki Kagaku Co. Ltd.) were used as the iron sources and carbon additives, respectively to prepare the Fe₂O₃/AB materials by a ball milling method. The weight ratio of Fe₂O₃:AB = 1:1 in the Fe₂O₃/AB materials. Two types of electrode, with and without AB additive, were prepared. The Fe₂O₃ electrode sheet free AB additive was fabricated by mixing of 90 wt.% Fe₂O₃ and 10 wt.% polytetrafluoroethylene (PTFE; Daikin Co.) followed by rolling. Each electrode was made into a 1 cm-dia. pellet. The Fe₂O₃/AB composite electrodes were prepared by the same procedure. In Fe₂O₃/AB composite electrodes, PTFE binders were present at two levels 10, 15 wt.% and Fe₂O₃/AB were 90, 85 wt.%, respectively. The weight ratio of Fe₂O₃:AB = 1:1, thus Fe₂O₃ and AB components were 45, 42.5 wt.% respectively.

To investigate the effect of AB additive as well as the PTFE binder contents on the electrochemical properties of the Fe₂O₃/AB electrodes, cyclic voltammetry was carried out in three-electrode glass cells with Fe₂O₃ or Fe₂O₃/AB composite electrode as the working electrode, Pt mesh as the counter electrode, and Hg/HgO as the reference electrode. The electrolyte was 8 mol dm⁻³ KOH aqueous solution. CV measurements were taken at a scan rate of 1 mV s⁻¹ and within a range of -1.3 V to -0.1 V. In all electrochemical measurements, we used fresh electrodes without pre-cycling.

3. RESULT AND DISCUSSION

Acetylene black (AB, Denki Kagaku Co.) with average diameters of 100 nm was used as the additive in the present work. SEM image of AB material is shown in Fig. 1. The shape of AB is relative uniform and they also look like balls. It is used as an additive to electrode to enhance the conductivity of $\text{Fe}_2\text{O}_3/\text{C}$ electrode.

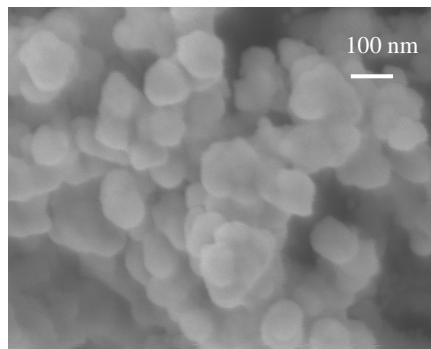


Figure 1. SEM image of AB.

Figure 2 shows the SEM image of Fe_2O_3 powder (Wako Pure Chemical, Co.). It can be seen that Fe_2O_3 particles have similar shape and morphology and they look like the balls. The size of Fe_2O_3 particles is less than 100 nm.

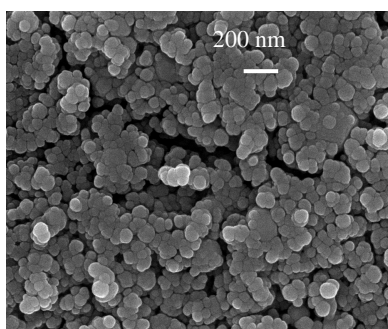


Figure 2. SEM image of Fe_2O_3 powder.

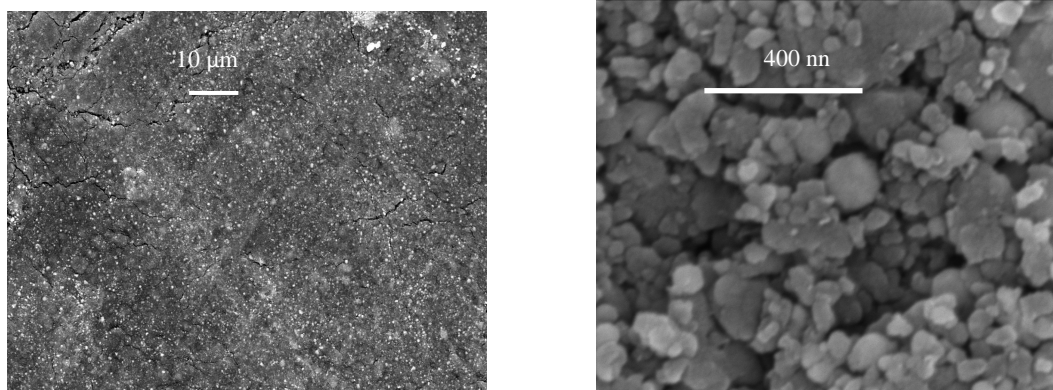


Figure 3. SEM image of the $\text{Fe}_2\text{O}_3/\text{AB}$ nanocomposite at various magnifications.

Fe₂O₃ is nonconductor, when Fe₂O₃ is mixed with AB (Fig. 3), the conductivity of Fe₂O₃/AB electrode will be increased. The white pots on Fig. 3 are Fe₂O₃. It is clear that the distribution of Fe₂O₃ on AB is relative uniform. Both the AB and Fe₂O₃ have size of nano-scale, therefore Fe₂O₃/AB nanocomposite is expected to provide better cyclability and the high capacity for Fe-air battery anode.

The cyclic voltammograms of the Fe₂O₃ free AB additive electrode are shown in Figure 4. An oxidation peak was observed around -0.85 V (a₁) while a respective reduction peak occurred below -1.0 V (c₂). The reduction peak c₂ was overlapped by hydrogen evolution observed around -1.1 V (c₃). The hydrogen evolution reaction competes with the electrode charge reaction and results in low cycling efficiency of Fe₂O₃ electrode. The previous investigation [17] indicated that the clear surface of iron was never exposed to the electrolyte, and over a partially oxidized surface, adsorption of hydroxyl ion takes place. The dissolution of the oxide or underlying metal by the ion transport through the oxide can also take place. The anodic peak a₁ can be attributed to oxidation of Fe to Fe(II) while cathodic peak c₁ correspond to the reduction of Fe(II) to Fe, respectively. At the first scan, the Fe₂O₃ was converted to Fe(II) (c₁) at low potential around -1.05 V and the reduction peak of Fe(II)/Fe (c₂) was not observable due to the hydrogen evolution. With further cycling, the anodic and cathodic peaks moved to a more negative potential and the current under these peaks maintained.

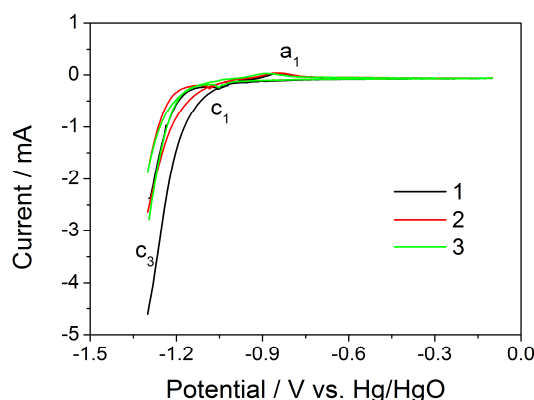


Figure 4. Voltammograms of Fe₂O₃ composite electrode with Fe₂O₃:PTFE = 90:10 wt.% in KOH electrolyte.

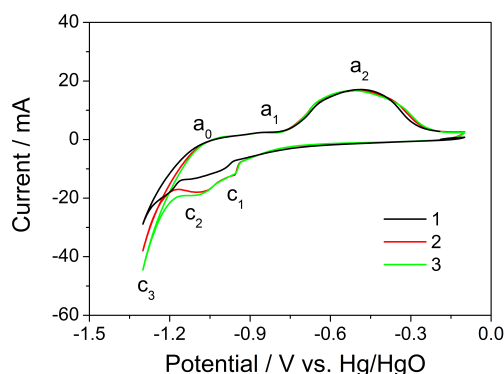


Figure 5. Voltammograms of Fe₂O₃/AB composite electrode with Fe₂O₃:AB:PTFE = 45 : 45 : 10 wt.% in KOH electrolyte.

The cyclic voltammograms of the $\text{Fe}_2\text{O}_3/\text{AB}$ composite electrode in KOH aqueous solution are showed in Fig. 5. Compared with the CV results of Fe_2O_3 free AB additive electrode (Fig. 4), we can see that CV curves of $\text{Fe}_2\text{O}_3/\text{AB}$ composite electrode are quite different. On the forward scan, two oxidation peaks of Fe/Fe(II) (a_1) and Fe(II)/Fe(III) (a_2) were observed around -0.85 V and -0.5 V while two small reduction peaks of Fe(III)/Fe(II) (c_1) and Fe(II)/Fe (c_2) occurred around -0.9 V and -1.1 V, respectively on the reversed scan. Along with the appearance of four peaks a_1 , a_2 and c_1 , c_2 , a small anodic peak a_0 was occurred around -1.0 V on the forward scan due to oxidation of iron to $[\text{Fe}(\text{OH})]_{\text{ads}}$ with the adsorption of OH^- ion. Thus, in this case, the appearance of peak a_1 is due to the oxidation of the both Fe to Fe(II) and Fe(I) to Fe(II). Different with the CV profile of Fe_2O_3 electrode (Fig. 4), the reduction peaks of iron deposition (c_2) and hydrogen evolution (c_3) of the $\text{Fe}_2\text{O}_3/\text{AB}$ electrode were observed separately. However, the cathodic peaks c_1 , c_2 are relative small compared with anodic peaks. In addition, the anodic peak a_2 is broader and much higher than a_1 . Thus all redox peaks of $\text{Fe}_2\text{O}_3/\text{AB}$ electrode (Fig.5) appear clearly and distinctly, and the redox currents under these peaks are larger than those of Fe_2O_3 electrode (Fig. 4). With further cycling the redox currents under all the peaks of the $\text{Fe}_2\text{O}_3/\text{AB}$ electrode were increased in initial cycles and then decreased. This could be ascribed to the insulating nature of the $\text{Fe}(\text{OH})_2$ active material forming during cycling. From these CV profiles it is clear that the carbon component shows the positive effects the redox behavior of Fe_2O_3 electrode. Using AB as additive, the cycleability of $\text{Fe}_2\text{O}_3/\text{AB}$ was improved. This behavior is acceptable from the view point that AB additive has small particle size, large surface area, on the one hand increases the electrical conductivity of $\text{Fe}_2\text{O}_3/\text{AB}$ electrode, on the other hand supports for the more distribution of iron pieces formed during cycling leading to increase the iron active surface area. The positive effects of AB additive to $\text{Fe}_2\text{O}_3/\text{AB}$ electrode is expected to improve the cycle performance of Fe/air battery anode.

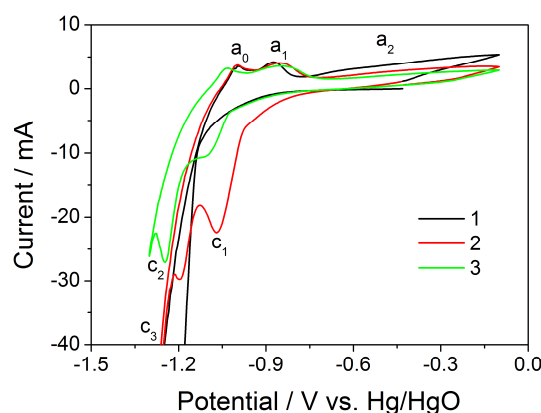


Figure 6. Voltammograms of $\text{Fe}_2\text{O}_3/\text{AB}$ composite electrode with $\text{Fe}_2\text{O}_3:\text{AB}:\text{PTFE}=42.5:42.5:15$ wt.% in KOH electrolyte.

To investigate of the impact of the binder in electrode to electrochemical behavior of $\text{Fe}_2\text{O}_3/\text{AB}$, the cyclic voltammetry of $\text{Fe}_2\text{O}_3/\text{AB}$ with 15 wt% PTFE binder is presented in Fig. 6. The oxidation peaks a_1 , a_2 and reduction peaks c_1 , c_2 occurred at around -1.0 V, -0.85 V and -1.05 V, -1.2 V, respectively, however, the current under these peaks was relative small. Otherwise redox peaks appeared at more negative potentials than those of electrode containing 10 wt% PTFE binder. A small oxidation peak a_0 was observed around -1.0 V on the forward scan. In comparison with the correspond results of electrode 10 wt% PTFE binder (Fig. 5), it is

clear that increasing the binder content (Fig. 6) caused negative effect on the cycleability of Fe₂O₃/AB composite electrode by the evidences that lower redox peaks, the cathodic peaks c_1 , c_2 were not separated from hydrogen evolution peak c_3 . With repeated cycling, the currents under the redox peaks were a little decreased. These results revealed that the Fe₂O₃/AB electrode containing higher binder content had larger internal resistance than that of lower binder content electrode. Increasing PTFE content can make better binding in electrode but it also causes the larger internal resistance because PTFE is non-conductivity material.

With further investigation of ratio between active material, additive and binder, Fe₂O₃/AB composite electrode is expected to be a potential candidate for use in Fe/air battery anode.

4. CONCLUSION

In this study, the role of AB additive and binder in Fe₂O₃/AB composite electrode was investigated in detail. The results of electrochemical measurements showed that both the AB additive and binder content significantly affected on the electrochemical behaviors of Fe₂O₃/AB electrodes. The AB carbon additive showed the positive effects on the cycleability of Fe₂O₃/AB electrode in alkaline solution. Increasing binder content caused the negative effects on the electrochemical behaviors of Fe₂O₃/AB electrode such as lower redox currents, reduction peaks emerged in hydrogen evolution.

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