# Electrochemical Properties of $Fe_2O_3$ Electrode in Alkaline Solution Containing $K_2S$ Additive

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**Abstract:** To find the suitable materials for Fe/air battery anode, in this study $Fe_2O_3$ electrodes were prepared using $Fe_2O_3$ nanoparticles. The size and morphology of $Fe_2O_3$ material were observed by scanning electron microscope (SEM). The electrochemical properties of the $Fe_2O_3$ electrode in alkaline solution were investigated by using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The effects of $K_2S$ additive in electrolyte solution on the electrochemical characteristics of $Fe_2O_3$ electrodes were also investigated. The obtained results show that the additive strongly affected on the impedance, redox reaction rate and cyclability of $Fe_2O_3$ electrode.

*Keywords:* $Fe_2O_3$ nanoparticles, $Fe_2O_3$ electrode, $K_2S$ additive, Fe-air battery.

## 1. Introduction

Today with the development of science and technology, electric devices and electric vehicles have been also fast growing. To meet the power requirements of these devices and vehicles, researches of batteries have been also constantly evolved. In recent years, iron-air battery have attracted a lot of attentions by scientists because of their high theoretical energy density, long life, environmentally friendly and can be applied in electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1-7]. Although recent researches on this battery has achieved remarkable success, but due to technological challenges the iron electrode still has some shortcomings to overcome such as the passivity caused by the $Fe(OH)_2$ layer formed during the discharge process, hydrogen gas generated simultaneously with the reduction of iron resulting in the low utilization efficiency, actual capacity and efficiency of iron electrode is not high. To overcome the shortcomings of the iron electrode, the electrode additives [8-13], the electrolyte additives [14-17] or both additives [18-19] have been used.

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Our previous works using carbon as an additive for iron electrodes [20] has shown that the cyclability of iron electrode has improved significantly as the $Fe(OH)_2$ layer is distributed on the carbon surface, limiting its passivation and supporting the inner iron layer continue to participate redox reaction thereby enhancing the utilization efficiency of iron electrodes. However, the drawbacks of the iron electrode have not thoroughly resolved, such as its capacity still gradually decreases with increasing number of cycles.Thus $K_2S$ additive to electrolyte has been used and the limitations of iron electrodes have been partially overcome[21]. To meet the actual application requirements, the capacity and cycle performance of the iron electrode still need to be further improved. To find the suitable material for the iron-air battery anode, in this study $Fe_2O_3$ composites were prepared with the different size and morphology of iron oxide particles to enhance the tightly contact between iron particles. The $K_2S$ additive in the electrolyte solution also usedfor further improving the capacity and cycle performance of iron electrode.

## 2. Experimental

In this study, $Fe_2O_3$ nanoparticles (Sigma Aldrich) and $K_2S$ (Wako Pure Chemical Co.) were used as the iron sources and electrolyte additive, respectively. The $Fe_2O_3$ electrode sheets were fabricated by mixing 90 wt.% $Fe_2O_3$ nanoparticles and 10 wt.% polytetrafluoroethylene (PTFE, Daikin Co) followed by rolling. $Fe_2O_3$ electrodes were punched into the form of a pellet with 1 cm in diameter. The thickness of electrodes is about 1 mm.

Two kinds of electrolytes were prepared, without additive (base electrolyte) and with additive. The base electrolyte was an 8 moldm$^{-3}$ aqueous KOH solution, whereas the additive electrolyte was a 7.99 mol dm$^{-3}$ KOH aqueous solution containing 0.01 M $K_2S$.

To determine the electrochemical behavior of $Fe_2O_3$ electrodes in alkaline solution, Cyclic Voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out in a three-electrode glass cell that had a $Fe_2O_3$ as the working electrode, Pt mesh as the counter electrode, and Hg/HgO as the reference electrode. The electrolyte was either a base electrolyte or an additive electrolyte.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. The EIS was performed on a three-electrode glass cell assembly using Auto Lab system. After the cell was cycled and stopped at open circuit potential (OCP) followed by a rest period of 30 minutes, the impedance spectra were recorded. The AC perturbation signal was 10 mV, and the frequency range was from $10^2$ to $2.10^5$ Hz in the EIS.

## 3. Results and discussion

To observe the shape and size of $Fe_2O_3$ particles, the SEM measurement of the $Fe_2O_3$ material were performed and the result is shown in Fig. 1. It can be seen that $Fe_2O_3$ particles are not uniform, few hundred nanometers in size.

To investigate the electrochemical properties of $Fe_2O_3$ nanoparticles, the cyclic voltammograms (CV) of the $Fe_2O_3$ electrode with $Fe_2O_3$:PTFE = 90:10 wt% in base electrolyte KOH 8M  during the initial five cycles (marked1, 2, 3, 4 and 5) are carried out and the results are shown in Fig. 2.
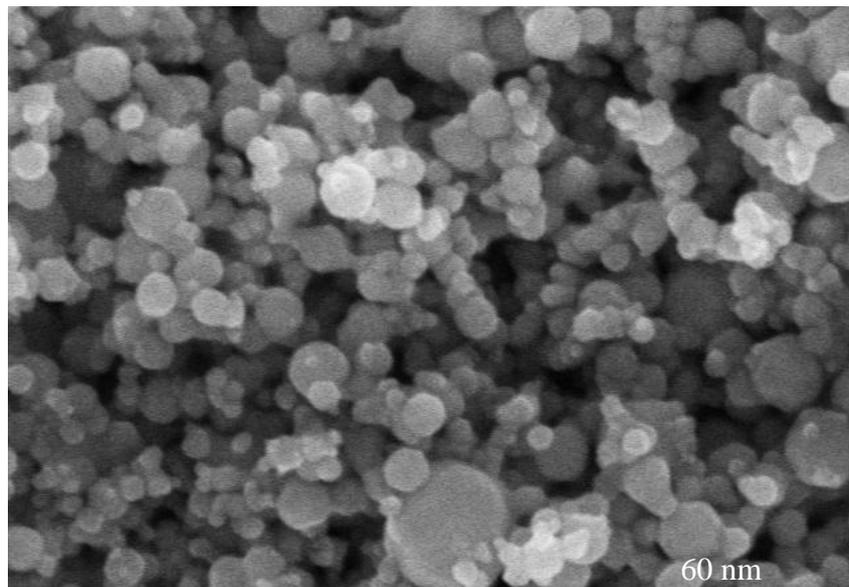
Figure 1. SEM image of $Fe_2O_3$ powder
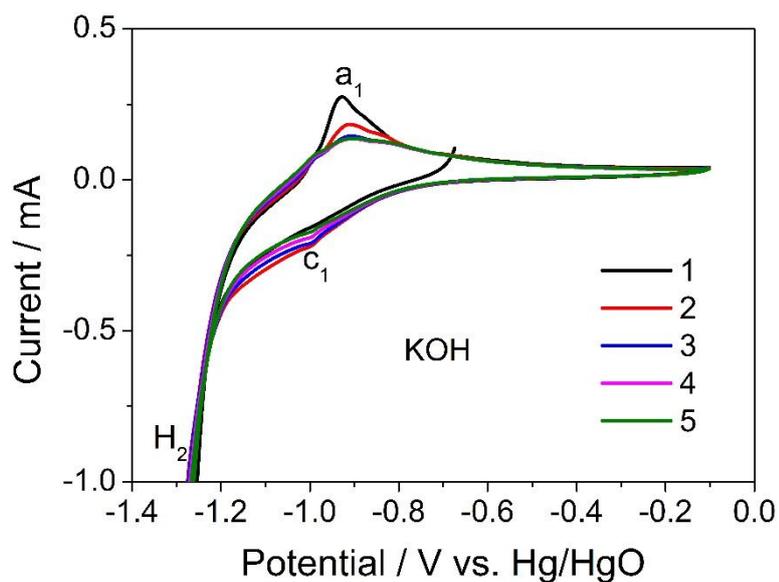


Figure 2. CV profiles of $Fe_2O_3$ electrode in KOH electrolyte solution.

On forward scan from −1.3 V to −0.1 V, only one oxidation peak $a_1$ occurs at about −0.8V and the corresponding reduction peak $c_1$ at about −0.9 V along with the hydrogen evolution at around −1.2V on backward scan. This $a_1/c_1$ couple peak corresponds to the redox couple Fe/Fe (II). The couple peak corresponds to the redox couple of Fe (II)/Fe (III) ($a_2/c_2$) was not observed. When repeated cycling the redox currents are decreased. It may be due to the insulating of $Fe(OH)_2$ layer formed during the oxidation inhibits the dissolution of the underlying iron oxide leading to un-observable of (II)/Fe (III)

($a_2/c_2$) couple and decrease in current. Further cycling there is a fall in redox current, thus the utilization of $Fe_2O_3$ electrode in base electrolyte is gradually decreased with repeated cycling.
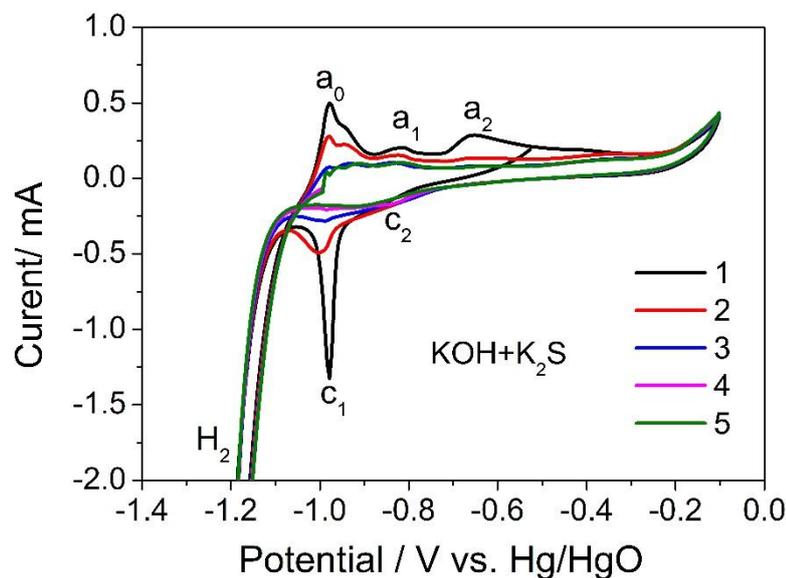


Figure 3. CV profiles of $Fe_2O_3$ composite electrode in KOH+$K_2S$ electrolyte solution

Voltammograms of the $Fe_2O_3$ electrodes in electrolyte containing 0.01 M $K_2S$ additive during the initial five cycles(marked1, 2, 3, 4 and 5) are presented in Fig. 3. From these profiles it is clear that the $K_2S$ additive strongly affect the redox behaviors of iron oxide. It can be seen on CV curves that both couple peaks $a_1/c_1$ and $a_2/c_2$ are observable. Besides that, the oxidation peak $a_0$ and the hydrogen evolution peak also occurs. The $a_0$ peak was ascribed to the oxidation of Fe to $Fe(OH)_{ad}$ before forming $Fe(OH)_2$. Peak $a_0$ appears only with the addition of $S^{2-}$ ion into electrolyte, thus the presence of $K_2S$ additive in electrolyte increases the reaction rate of Fe/Fe(I). It is noteworthy that the redox peaks of $Fe_2O_3$ electrode in the additive electrolyte are sharper and larger than those in base KOH solution (Fig.2). This proves that $K_2S$ additive improves the oxidation of Fe to Fe(I), Fe(II) and Fe(II) to Fe(III) leading to improves the cyclability of iron oxide electrode. In other words, the reaction rate of Fe/Fe(II) and Fe(II)/Fe(III) was increased 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 to promote the dissolution of iron and enhance the bulk conductivity of the electrode, thereby improving cycleability [22-23].

With further cycling, the current under these peaks decreased. This suggests that the inner resistance of the electrode was increased due to the insulating of $Fe(OH)_2$ formed 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, $Fe(OH)_2$ film formed is thicker, the passivation overwhelms the increase in the redox reaction rate supported by $K_2S$ thereby reduced the redox current. Consequently, $K_2S$ additive proved the positive effects on the electetrochemicalbehaviors of $Fe_2O_3$ composite electrode.

To determine the electrode resistance, the electrochemical impedance measurements were carried out on the $Fe_2O_3$ electrodes in base electrolyte and additive electrolyte, before and after five initial

cycles at open circuit potential (OCP) and the results are displayed in Figs. 4 and 5, respectively. In general, each spectrum consisted 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. Since the limitation of the apparatus with lowest frequency of 100 Hz, straight line at lower frequencies isshort or not obtained. In the case of KOH electrolyte free additive, before cycling, the semicircle was observed but not completely. After cycling, the semicircle was observable without a straight line in the lower frequency region, and semicircle diameter of the electrode after cycling is larger than that before cycle.This suggested that the resistance of electrodes was increased after cycling and increased with an increase of cycle number. This result consists with CV result (Fig.2), redox current decreased with repeated cycling. This result also confirmed the supposition mentioned above in the CV measurements.
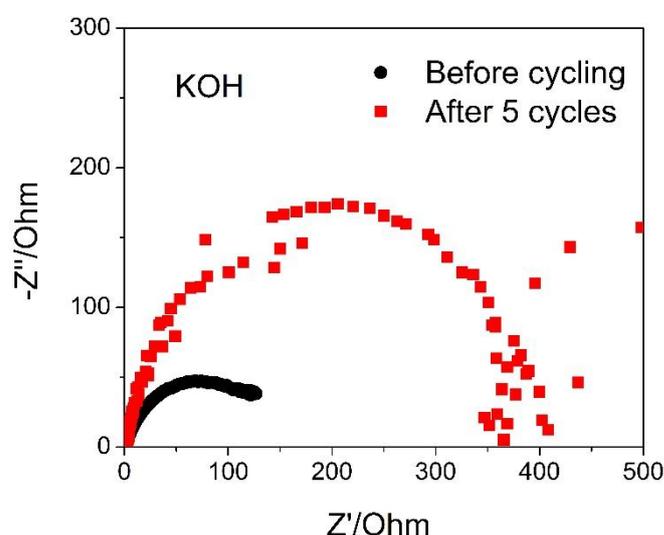


Figure 4. Electrochemical impedance spectroscopy (EIS) of $Fe_2O_3$ electrode in base electrolyte solution

In the case of electrolyte solution containing $K_2S$ additive (Fig. 5), the semicircle diameter of the electrode after cycling is also larger than that of the electrode before cycle like in the KOH solution. This means the electrode resistance increases during the charge-discharge process. In addition, the semicircle diameters of electrode before and after cycling in the electrolyte containing $K_2S$ (Fig. 4) are larger than those in the base electrolyte (Figure 4). This result demonstrates that the resistance of the $Fe_2O_3$ electrode in the KOH + $K_2S$ solution is larger than that in the KOH solution. The reason of this phenomenon is the $S^{2-}$ ion in the electrolyte solution adsorbed on the surface of the $Fe_2O_3$ electrode causesing an increase in the contact resistance between the electrode surface and the electrolyte solution. However, the presence of the $K_2S$ additive in the electrolyte enhances the redox current (Fig. 3), meaning that increase the redox reaction rate of the $Fe_2O_3$ electrode. Thus the presence of $K_2S$ in the electrolyte solution increases the resistance of the $Fe_2O_3$ electrode, but on the other hand it also enhances the oxidation-reduction rate of the $Fe_2O_3$ electrode. After several cycles, the current intensity of iron electrode decreases gradually as the passive layer $Fe(OH)_2$ formed during the discharge. Adding $K_2S$ into the electrolyte solution, initially the reaction rate of the Fe/Fe(II) couple increases, but the $Fe(OH)_2$ layer becomes thicker when repeated cycling, passivation overwhelms the increase in the reaction rate leading to reducing redox current.
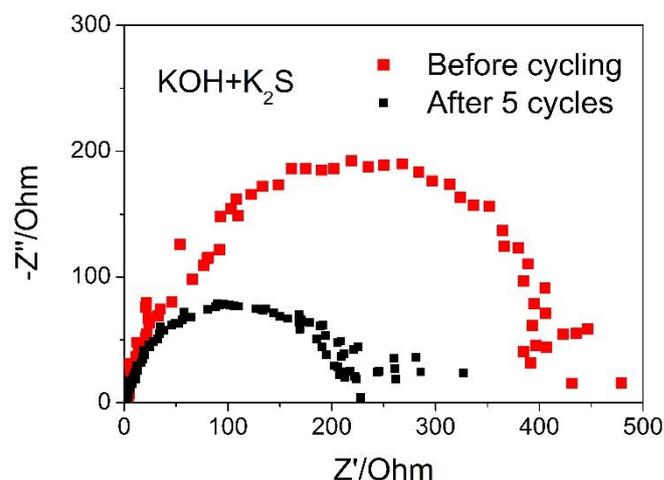
Figure 5. Electrochemical impedance spectroscopy (EIS) of $Fe_2O_3$ electrode in KOH +$K_2$Selectrolyte solution

## 4. Conclusion

$Fe_2O_3$ electrode was prepared using $Fe_2O_3$ nanoparticles. The electrochemical behaviors of the $Fe_2O_3$ electrode in KOH electrolyte were investigated. The effect of $K_2S$ additive in electrolyte solution on electrochemical properties of $Fe_2O_3$ electrode was also measured. The results showed that the $K_2S$ additive affected the electrochemical impedance, redox reaction rate and the cyclability of $Fe_2O_3$. In the presence of $K_2S$ additive in electrolyte, the redox reaction rate of Fe/Fe(II) and Fe(II)/Fe(III) couples was increased resulting in cyclability of $Fe_2O_3$ electrode was improved. The resistance of the $Fe_2O_3$ electrode after cycling is higher than that of before cycling in both electrolytes containing $K_2S$ additive and free additive. The electrochemical impedance of the $Fe_2O_3$ electrode in the electrolyte containing $K_2S$ additive a little increased with respect to that in the basic KOH electrolyte.

## Acknowledgments

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