Porous Fe$_2$O$_3$ Microspheres as Anode for Lithium-Ion Batteries

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Abstract. In this work, Fe$_2$O$_3$ was successfully synthesized by the hydrothermal process at low temperature. FeCl$_3$.6H$_2$O as precursor and variation of lysine as hydrolyzing agent were used to preparing Fe$_2$O$_3$. SEM images show that the morphology of Fe$_2$O$_3$ is porous microsphere with sizes in the range of (1 to 5) µm in diameter. The as-prepared Fe$_2$O$_3$ with the 2 M of lysine exhibits excellent cycling performance when used as the anode for lithium ion batteries, obtaining reversible discharge capacity of 172.33 mA·h·g$^{-1}$ at 0.5 C after 50 cycles. It is attributed to the unique structure of porous microspheres providing a large surface area which maintains good electronic contact between particles during charge-discharge process. This result demonstrates that Fe$_2$O$_3$ porous microsphere has a high potential as anode material for application of lithium-ion battery.

Keywords. α-Fe$_2$O$_3$, hydrothermal, lithium-ion battery, lysine, and microsphere.

1. Introduction
The lithium-ion battery is the most popular energy storage and energy source today. Lithium-ion batteries are used for various applications such as energy sources in hybrid cars as well as some clean energy storage applications [1]. Research on lithium-ion batteries is still continuously developed. In 2000, the concept of a conversion reaction in the electrochemical-reversible lithium reaction began to be developed on some oxide transition metals, such as FeO, CoO, and NiO [2]. The oxide-transition metal is a good material for the lithium-ion battery anodes because of the metal's ability to deliver a much larger specific capacity than the theoretical capacity of graphite, i.e. 372 mA·h·g$^{-1}$ [3]. From several existing oxide transition metals, Fe$_2$O$_3$ (hematite) is selected for a promising anode material of lithium-ion batteries. This material is selected on the basis of its abundant presence in nature, environmentally friendly, and theoretically specific capacity of 1007 mA·h·g$^{-1}$ [4]. In the application of Fe$_2$O$_3$ as an anode on lithium-ion batteries still have a weakness, such as easy loss of owned capacity and low battery cycling rate [5]. Several previous studies have provided a solution to the problem of synthesizing Fe$_2$O$_3$ in nanostructures with varying morphology, such as nanotubes, nanotubes, nanorods and nano coils [6]. The nanostructure will facilitate the transfer of electrons and Li$^+$ ions by reducing the diffusion paths. In addition, the nanostructures are also capable of improving the kinetic intercalation process by providing larger area contacts [1].
From the results of previous studies, the Fe$_2$O$_3$ material nanostructure shows a significant increase in electrochemical performance. The problem is low volumetric energy density and low conductivity. One effective strategy to overcome the problem is to prepare the material on a nanoscale. One of the methods to synthesize nanostructured materials is by hydrothermal method. The hydrothermal method has high energy efficient and easy to control the size and morphology of the materials [4].

In this work, the Fe$_2$O$_3$ material is prepared and synthesized by hydrothermal method with the addition of lysine. Lysine is used as a hydrolysis agent in Fe$_2$O$_3$ synthesis [6]. Therefore, the effect of lysine on the morphology and electrochemical performance of Fe$_2$O$_3$ will be studied and written systematically to find the optimum concentration of lysine for application Fe$_2$O$_3$ as anode materials for a lithium-ion battery.

2. Materials and methods

The Fe$_2$O$_3$ microsphere is synthesized by hydrothermal method with FeCl$_3$.6H$_2$O as precursor and variations of lysine concentration. Lysine variation of 0.5 M, 1 M and 2 M are mixed with 1 M FeCl$_3$.6H$_2$O in 30 mL of di-water and stirred with magnetic stirring for 30 min. The solution then is transferred to 120 mL Teflon-autoclave and heated in a muffle furnace with a temperature of 180 °C for 12 h. The precipitate is separated by centrifuge for approximately 45 min. Then it is obtained a thin deposit at the bottom of the centrifuge tube and washed with di-water for several times. The remaining sediment is dried in the oven at temperature 90 °C for 24 h. To prepare the electrode, the prepared Fe$_2$O$_3$ microsphere is mixed with carbon black, and polyvinylidene fluoride (PVDF) according to mass ratio of 80:15:5. After the mixing process is complete, then N-Methyl-2-Pyrolidone is added to obtain a paste and coated with Cu foil with area 1 cm$^2$ using doctor blade method. The electrodes are heated into an oven at a temperature of 100 °C for 12 h. Fe$_2$O$_3$ microsphere was analyzed with XRD (PANalytical, Cu Kα radiation) to identify the phase and crystal structure. Morphology was carried out using SEM (FEI Inspect 250). Electrochemical performance was tested with CR2032 coin cells between voltage ranges (0.1 to 3.0) V. The coin cells were fabricated with Fe$_2$O$_3$ microsphere as working electrode, metallic lithium as counter electrode, 1 M LiPF$_6$ in mixed diethyl carbonate/ethylene carbonate (1:1 in volume) solution as the electrolyte, and Celgard polypropylene as the separator inside glove box system (Vigor) under Ar flow with adjustable rate. Cyclic voltammetry was measured by an electrochemistry workstation (WonATech WBCS 2000) with sweep scan rate 0.1 mV.s$^{-1}$ and potential range between (0.1 to 3.0) V. The coin cells were tested galvanostatic charged – discharged on a recycler battery system (WonATech WBCS 2000) with various C – rates from 0.3 C to 3 C with 5 cycles for each various rates and then back to rate 0.3 C. The impedance of coin cells was tested with electrochemical impedance measurement (AutoLab) using (0.1 to 20000) Hz and potential 3 V.

3. Results and discussion

Figure 1 shows XRD patterns of Fe$_2$O$_3$ microsphere at various concentration of lysine. It shows that the all of samples is successfully indexed as hematite (JCPDS No. 33-0664) with no impurity peaks detected.

It is clearly observed that the intensity peak of Fe$_2$O$_3$ 2 M lysine has the highest intensity compare to other samples. It could be at the highest concentration of lysine enhancing the crystallinity of Fe$_2$O$_3$. The higher crystallinity and smaller particle size are due to the role of lysine as an inhibitor in the nucleation process by decreasing the rate of crystallization. The addition of lysine concentration plays a significant role in decreasing the size of the crystal by surface adsorption mechanism [7]. The smaller crystal size will decrease the diffusion path, increase the kinetic intercalation and enlarge the contact area of the lithium ion which will improve the electrochemical performance of the material [6].

Figure 2 shows that the all samples of Fe$_2$O$_3$ have the morphology microsphere with the size of (0.15 to 1.5) μm. In the three samples show that the increased concentration of lysine reduces the size of the microsphere. The mechanism of microsphere formation starts with the occurrence of nucleation or nucleation, then there is aggregation where the interconnected particle formed to bind each other
towards the center [6]. Fe$_2$O$_3$ material with 2 M of lysine has microsphere size smaller than the other two samples. This is due to the addition of lysine concentration triggering less aggregation during hydrothermal process.

![Figure 1. XRD patterns of Fe$_2$O$_3$ microsphere with various concentration of lysine (a) JCPDS 33-0664 of hematite (b) 0.5 M (c) 1 M (d) 2 M of lysine](image)

![Figure 2. SEM images of Fe$_2$O$_3$ with variation (a) 0.5 M (b) 1 M (c) 2 M of lysine](image)

Figure 3 shows the cyclic voltammetry curve of three first cycles of all Fe$_2$O$_3$ samples with two reduction peaks and single oxidation peak. The reduction peak is occurred below 1.0 V indicating the reaction process with electrolyte and carbon contained in the anode sample. In this peak, a solid electrolyte interface (SEI) is formed between the surface of the Fe$_2$O$_3$ anode and the LiPF$_6$ electrolyte [2]. The absence of the reduction peak below 1.0 V in the second cycle and the third cycle, it could be the SEI film formed is too thick. During the charging process in the half-cell, oxidation reactions occur in Fe$_2$O$_3$ that satisfy the reaction Equation (1).

$$3\text{Li}_2\text{O} + 2\text{Fe} \leftrightarrow \text{Fe}_2\text{O}_3 + 6\text{Li}^+ + 6\text{e}^- \quad (1)$$

The discharge occurs the reduction reaction with Equation (2).

$$\text{Fe}_2\text{O}_3 + 6\text{Li}^+ + 6\text{e}^- \leftrightarrow 3\text{Li}_2\text{O} + 2\text{Fe} \quad (2)$$
Figure 3. Cyclic voltammetry curves of Fe$_2$O$_3$ with variation (a) 0.5 M (b) 1 M (c) 2 M lysine.

In the sample with a concentration of a 2-mole lysine has the highest intensity of the reduction peak indicating the amount of Li$^+$ which is capable of being inserted. Figure 3 (c) also shows that the distance polarization of reduction and oxidation peak is smaller than other samples. It is demonstrated that Fe$_2$O$_3$ with a 2-mole lysine has faster intercalation and de-intercalation Li$^+$ ions. It appears that the greater the addition of lysine, the greater the intensity current. The greater intensity will affect the transfer rate of electrons in the Fe$_2$O$_3$ material. Thus, from the CV test, it is found that Fe$_2$O$_3$ of a 2-mole lysine has better electron transfer capability than other variations.

It could be the smallest size of particle that it is clearly observed in SEM images of Fe$_2$O$_3$ of a 2-mole lysine. The Fe$_2$O$_3$ material of a 2-mole lysine has the smallest range of particle sizes, which increases the kinetic intercalation of lithium ions to give a better ion transfer efficiency compared to other samples.

Figure 4. Charge-discharge curves of the Fe$_2$O$_3$ (a) 0.5 mole (b) 1 mole (c) 2 mole of lysine for selected cycles.

In Figure 4 shows that the Fe$_2$O$_3$ of a 2-mole lysine has the largest discharge capacity of 172.33 mA·h·g$^{-1}$ and capacity fading of 41.8 % after 50 cycles. The Fe$_2$O$_3$ of a 2-mole lysine has the greatest initial discharge capacity when associated with the CV results due to the highest intensity of reduction peak and smaller polarization peak. SEM images in Figure 3 also show that the Fe$_2$O$_3$ of a 2-mole lysine has smaller particle size indicating greatly affords the Li$^+$ ions to intercalate and de-intercalate [6].
Figure 5 shows the Nyquist plots of all samples. The Rs value determines the electron transfer capability of the electrolyte of a sample. Here, it is seen that Fe₂O₃ of 2-mole lysine has the lower Rs than other samples indicating that the electrolyte of a 2-mole lysine sample has the highest electron transfer capability. The Act value indicates the impedance of the sample where the smaller impedance will enhance the insertion and extraction of Li⁺ ion. It can be seen that the smallest Rct value is owned by a sample with a variation of a 2-mole lysine facilitating fast ion exchange in this sample. It is attributing to the higher crystallinity, and smaller size of Fe₂O₃ of a 2-mole lysine compare to other samples.

4. Conclusions
In this work shows that the Fe₂O₃ of a 2-mole lysine has the best electrochemical performance. Where the sample produces a sharp diffraction peak with the highest intensity indicates more crystalline phase. The Fe₂O₃ of a 2-mole lysine shows the morphological form of the microsphere with the smallest diameter. The Fe₂O₃ of a 2-mole lysine has the highest specific discharge capacity of 172.33 mA h g⁻¹ and capacity fading of 41.8 % indicating that the anode material can withstand a redox reaction for 50 cycles. The charge transfer resistance of the Fe₂O₃ 2-mole lysine is lower than other samples. Therefore, the Fe₂O₃ of 2-mole lysine has great potential as anode material for a lithium-ion battery.

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