

Preparation of Fe_3O_4 /carbon Composites on the Basis of Cellulose Microspheres and their Application as Anode Material for Lithium-ion Batteries

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Abstract. Fe_3O_4 /carbon microspheres ($\text{Fe}_3\text{O}_4/\text{C}$) were prepared by a facile hydrothermal reaction using cellulose and ferric trichloride as precursors. The resultant composite spheres have been investigated as anode materials for the lithium-ion batteries, and they show high capacity and good cycle stability (830 mAhg^{-1} at a current density of 0.1C up to 70 cycles), as well as enhanced rate capability. The excellent electrochemical performance is attributed to the high structural stability and high rate of ionic/electronic conduction arising from the porous character and the synergetic effect of the carbon coated Fe_3O_4 structure and conductive carbon coating.

1 Introduction

Lithium-ion batteries (LIBs) have generated great interest because of the impact of portable electronic devices. LIBs have been widely used in cellular phone, laptop computer, electric vehicle, and other electronic devices. Transition metal oxides have been considered as promising high-performance anode materials for LIBs due to their lower cost, relative safety, environmental friendliness and high energy density. These metal oxides have distinct interstitial-free structure, which can react with Li via the conversion reaction of $\text{MO}_x + 2\text{xLi} = \text{M} + \text{xLi}_2\text{O}$ ($\text{M}=\text{Fe, Co, Ni, Cu, Mn, etc.}$) [1,2].

Among the above mentioned transition metal oxides, magnetite (Fe_3O_4) has been intensely investigated due to its high theoretical capacity of 926 mAhg^{-1} , low cost, low toxicity and natural abundance. However, The large volume expansion occurring and severe aggregation of active particles during cycling lead to its poor cycling stability, limiting its application in practical batteries. Many approaches have been employed to solve these problems, one is the preparation of nano-sized material, such as nanorings, nanospindles, hollow spheres, nanowires, nanorods, and nanoflowers, The particles with hollow and porous structure can partially alleviate the mechanical stress caused by large volume change, and provide the large surface-to-volume ratio and small lithium ion/electron diffusion distance, which can improve the electrochemical performance of

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Fe_3O_4 anode [3,4]. The other one is fabricating Fe_3O_4 /carbon composites, because carbon materials have been intensively considered as one of the promising matrices to coat or support the metal nanoparticles owing to its chemical stability, flexibility of surface modification, biocompatibility and pore creation, which include Fe_3O_4 nanoparticles embedded in a disordered carbon matrix or graphene nanosheets, and carbon coated Fe_3O_4 particles [5].

In this work, we exploited porous cellulose microspheres, which are prepared by combining spray coagulating with spray drying according to the previously reported methods [6], as carrier to prepare $\text{Fe}_3\text{O}_4/\text{C}$ composite via hydrothermal method used as anode material for LIBs. Cellulose is growing importance in the development and application because it is the abundant renewable natural and cheap materials on earth. The cellulose microspheres have huge specific surface area because they contain a mass of pores. The large specific surface area and the micropores of active carbon can help to fix the Fe_3O_4 particles formed under the solvothermal condition and to accommodate the volume change of Fe_3O_4 particles occurring in the lithium ion insertion/extraction process. The cellulose microspheres can also help to support the Fe_3O_4 nanoparticles under solvothermal condition, preventing the aggregation of Fe_3O_4 nanoparticles as a physical barrier. They can be converted into porous carbon by calcination and coated on the surface of the Fe_3O_4 particles, improving the local conductivity as a conductive network, and providing void to accommodate the volume change of the Fe_3O_4 nanoparticles during the Li ion insertion/extraction process due to its large specific surface area and the micropores. As shown in the results, the prepared $\text{Fe}_3\text{O}_4@\text{C}$ composite exhibits exceptional capacity retention and good cycling stability.

2 Experimental section

2.1 Materials

Ferric trichloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ethylene glycol and sodium acetate anhydrous (Sinopharm Chemical Reagent Co., Ltd. Shanghai, China) were of AR grade and used without further treatment. Cellulose with a viscosity-average molecular weight of 8.5×10^4 was obtained from Hailong Chemical Fibre Co., Ltd. (Weifang, China).

2.2 Preparation of carbon coated Fe_3O_4 composites

The preparation of carbon coated Fe_3O_4 composites can be briefly described as the following process. 1.35 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 40 mL of ethylene glycol and ethyl alcohol mixed solution (3:1) to form a clear yellow solution under a vigorous stirring. Subsequently 3.6 g of sodium acetate anhydrous was added to the solution under continuous stirring for 30 min. Then 0.38 g of cellulose microspheres was dispersed into the mixture solution under ultrasonic for 10 min. After stirring for 3 h, The resultant mixture was transferred to a 100 ml Teflon-lined stainless steel autoclave at 200 °C for 10 h in electronic oven. After the solvothermal treatment, black powders were collected by centrifugation and washed thrice with distilled water and ethanol, then dried in statical oven at 70°C for 4 h. The obtained black powders were calcined at 450°C for 3 h at a rate of 2°C /min in nitrogen environment to carbonize the cellulose. The final samples derived from the cellulose composites with different contents of 0.19 g and 0.38 g, were denoted as $\text{Fe}_3\text{O}_4@\text{C}-1$ and $\text{Fe}_3\text{O}_4@\text{C}-2$, respectively.

3 Result and Discussion

3.1 XRD

Figure 1 shows the typical XRD pattern of these $\text{Fe}_3\text{O}_4/\text{C}$ composites deduced by carbonizing the cellulose microspheres at 450°C for 3h in nitrogen. A series of characteristic peaks at $2\theta = 30.2, 35.5, 43.1, 53.4, 57.0$, and 62.6 were observed. These diffraction peaks match well in position and intensity with the standard XRD date of Fe_3O_4 with a cubic inverse spinel structure (JCPDS No. 19-0629) [7]. The main peaks are similar to that of the pristine Fe_3O_4 powders but they showed wide FWHM (full width at half maximum), which is mainly resulted from the smaller particle size of Fe_3O_4 in $\text{Fe}_3\text{O}_4/\text{C}$ composite. No obvious diffraction peaks of carbon can be observed, indicating that the stacking of carbon is amorphous or disordered in these composites.

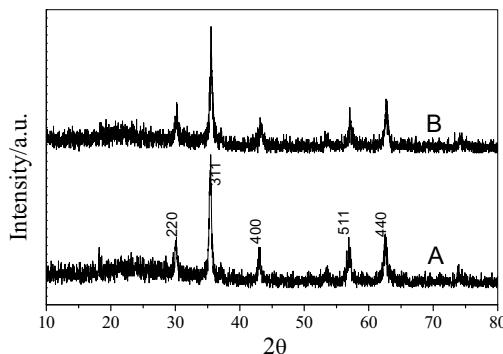


Fig. 1. Typical XRD patterns $\text{Fe}_3\text{O}_4/\text{C}-1$ (A) and $\text{Fe}_3\text{O}_4/\text{C}-2$ (B).

3.2 Nitrogen adsorption–desorption measurements

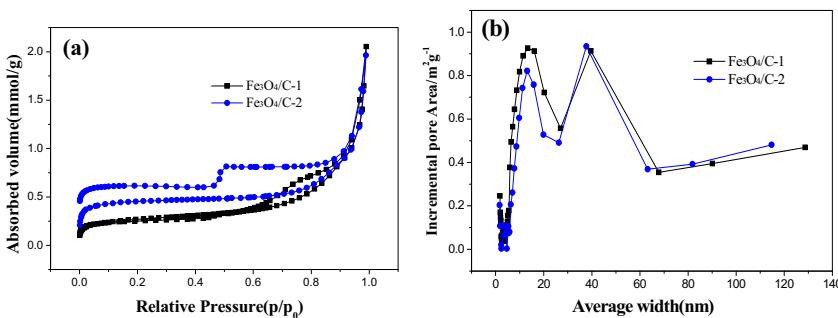


Fig. 2. Nitrogen adsorption–desorption isotherms and corresponding BJH desorption pore size distributions (inset) of $\text{Fe}_3\text{O}_4/\text{C}-1$ and $\text{Fe}_3\text{O}_4/\text{C}-2$.

The nitrogen adsorption–desorption isotherms and corresponding BJH desorption pore size distributions of three samples are displayed in Figure 2. It can be seen that the obvious isotherms feature hysteresis between the desorption and adsorption branches, indicating the presence of interspace [8]. The pore size distribution of sample $\text{Fe}_3\text{O}_4/\text{C}-1$ in the range 10–50 nm and a BET surface area of about $16.8 \text{ m}^2 \text{ g}^{-1}$ have been calculated. With the improvement of the cellulose content, an evident increase in the surface area ($25.2 \text{ m}^2 \text{ g}^{-1}$) was observed. It is resonable for that the porosity originating mainly from the porous

carbon moiety in the composites, and a higher carbon content will result in a large specific surface area.

3.3 SEM and TEM measurements

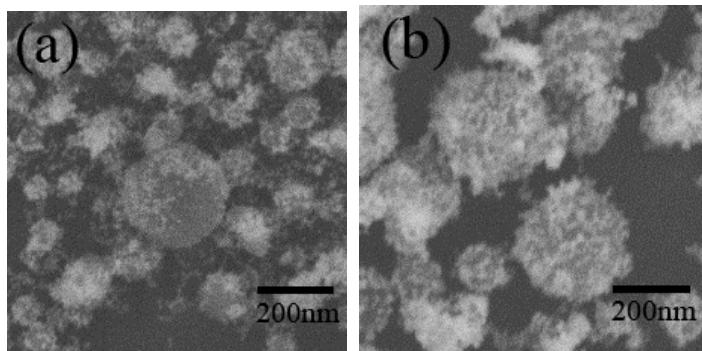


Fig. 3. The SEM images of sample Fe₃O₄/C-1 (a) and sample Fe₃O₄/C-2 (b).

The SEM images of the Fe₃O₄/C composites were prepared with different ratios of Fe₃O₄ and cellulose at same temperatures were presented in Figure 3. It is clear that the Fe₃O₄/C composite microspheres (samples Fe₃O₄/C-1 and Fe₃O₄/C-2) showed similar spherical morphology and a size of the microspheres is about 50-200 nm in diameter. Moreover, in comparison with that of sample Fe₃O₄/C-1 (panel a), the average diameter of sample Fe₃O₄/C-2 (panel b) are increased a little bit, which can be ascribed to the increase of the cellulose content.

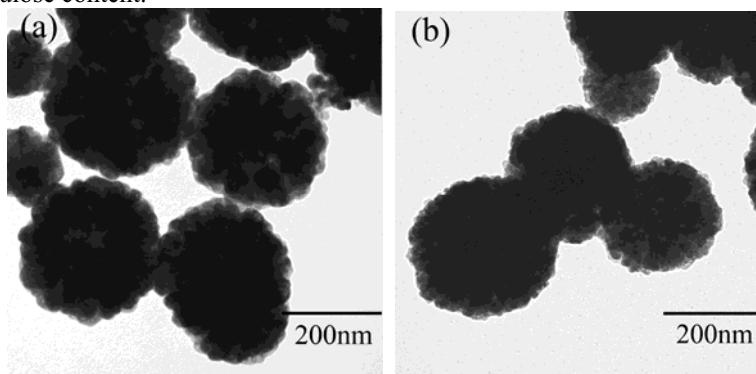


Fig. 4. The TEM images of sample Fe₃O₄/C-1 (a) and sample Fe₃O₄/C-2 (b).

Figure 4 displays the TEM images of the sample Fe₃O₄/C-1 (a) and sample Fe₃O₄/C-2 (b). It is obvious that both the samples show similar spherical morphologies with size diameters in the range of 50-200 nm. Moreover, it can be seen that the particle size of the Fe₃O₄ particles in the composite spheres of Fe₃O₄/C-1 is larger than those in the composite sample of Fe₃O₄/C-2. The variation of the particle size of the Fe₃O₄ in the two different composite microspheres can be explained as due to the separation effect of the cellulose wire, which hinders the aggregation of the Fe₃O₄ nanoparticles during the calcination process.

3.4 Electrochemical Properties

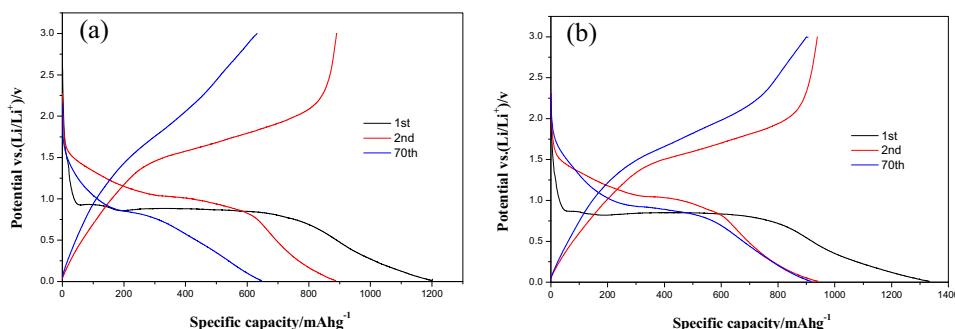


Fig. 5. The charge/discharge profiles of the sample $\text{Fe}_3\text{O}_4/\text{C}-1$ (a) and sample $\text{Fe}_3\text{O}_4/\text{C}-2$ (b) in the voltage range of 0.01–3.0V at a current rate of 0.1C.

The charge/discharge curves of the sample $\text{Fe}_3\text{O}_4/\text{C}-1$ (panel a) and sample $\text{Fe}_3\text{O}_4/\text{C}-2$ (panel b) for the 1st, 2nd and 70th cycles obtained at a rate of 0.1C in the voltage window of 0.01–3.0V (vs. Li/Li^+) are shown in Figure 5. For the two different samples, the first charge capacities are 1200 mAhg^{-1} and 1325 mAhg^{-1} , respectively. After 70 cycles, the charge capacities of the sample $\text{Fe}_3\text{O}_4/\text{C}-1$ retained at about 652 mAhg^{-1} , in contrast the $\text{Fe}_3\text{O}_4/\text{C}-2$ sample could still deliver a charge capacity of about 916 mAhg^{-1} . The high cycle stability of $\text{Fe}_3\text{O}_4/\text{C}-2$ sample might be due to its high porosity[9,10].

4 Summary

In summary, we have developed a simple hydrothermal method to prepare $\text{Fe}_3\text{O}_4/\text{carbon}$ microsphere based on cellulose as carbon source and using FeCl_3 as precursor. The obtained $\text{Fe}_3\text{O}_4/\text{carbon}$ microspheres show high capacity, good cycle stability as anode material in lithium-ion battery, which is attribute to its high structural stability and high rate of ionic/electronic conduction arising from the high specific surface area and conductive carbon coating. In a word, the $\text{Fe}_3\text{O}_4/\text{carbon}$ composite microspheres produced by hydrothermal method with good electrochemical performance will be a promising anode material for high-performance lithium ion batteries.

5 Acknowledgements

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