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Letter

Low temperature synthesis of Fe_3O_4 micro-spheres and its application in lithium ion battery

Shibing Ni[a,*], Deyan He[b], Xuelin Yang[a], Tao Li[a]

[a] *College of Mechanical and Material Engineering, Three Gorges University, 8 Daxue Road, Yichang 443002, PR China*
[b] *Department of Physics, Lanzhou University, Lanzhou 730000, PR China*

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ABSTRACT

Fe_3O_4 micro-spheres with nanoparticles close-packed architectures were synthesized via a simple chemical method using $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$, hexamethylenetetramine, and NaF as reaction materials. This chemical synthesis took place in a vitreous jar under low temperature (90 °C) and atmospheric pressure. The morphology and structure of the as-synthesized products were characterized by field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), and Raman spectrum. Electrochemical properties of the as-synthesized Fe_3O_4 micro-spheres as anode electrode of lithium ion batteries were studied by conventional charge/discharge tests, which exhibit steady charge/discharge platforms at different current densities. The as-prepared Fe_3O_4 electrode shows high initial discharge capacity of 1166 and 1082 mAh g^{-1} at current density of 0.05 and 0.1 mA cm^{-2}, respectively.

1. Introduction

For many years, lithium ion batteries have always been the most utilized batteries in the portable electronic market because they possess of the highest energy density available from existing rechargeable battery techniques. However, their performance still lies behind the demands of the consumer. The exploitation of new types of electrode materials with high specific capacity has played an important role in the development of lithium ion batteries.

Recently, transition metal oxides show high theoretical capacity (500–1000 mAh g^{-1}), based on a novel reaction mechanism ($MxOy + 2ye + 2yLi^+ \leftrightarrow xM + yLi_2O$) [1], making them to be promising anode materials for high performance lithium ion batteries [1–7]. Among them, Fe_3O_4 has attracted special attention due to its compatible advantages of low cost, environmental benignity, as well as high electronic conduction [8,9]. However, Fe_3O_4 anode suffers from the problem of agglomeration and huge volume variation during lithium insertion and extraction, leading to poor cycle performance. Researches on improving the electrochemical properties of Fe_3O_4 anode are mainly focused on two ways. (1) Fe_3O_4/carbon composites [10–13]. (2) Optimizing the architecture of nano-sized Fe_3O_4 [14,15]. Zhang et al. fabricated carbon coated Fe_3O_4 nanospindles, showing improved cycle performance than bare Fe_3O_4 [10]. Wang et al. prepared Fe_3O_4 submicron spheroids, exhibiting high capacity and god cycle performance [14]. It is demonstrated from those reports that Fe_3O_4 has promising application in lithium ion batteries, and its electrochemical performance can be enhanced with designed architecture. In any case, the practical applications of Fe_3O_4 in lithium ion batteries cannot be separated from facile synthesis method. The main objective of this paper is to develop a simple method to synthesize Fe_3O_4 that may have practical application in lithium ion batteries. In this paper, Fe_3O_4 micro-spheres with nanoparticles close-packed architectures are synthesized via a simple chemical method. This method may be adopted for large-scale synthesis due to its low temperature and atmospheric pressure. Furthermore, the charge and discharge behavior of the as-synthesized Fe_3O_4 micro-spheres electrode is studied at different current densities. Steady charge and discharge platforms endow the as-synthesized Fe_3O_4 micro-spheres with potential applications in lithium ion batteries.

2. Experimental details

All the chemicals were analytical grade and purchased from Shanghai Chemical Reagents. In a typical procedure, 10 mmol $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$, 5 mmol hexamethylenetetramine, and 1 g NaF were dissolved in 50 ml distilled water and stirred for 20 min. Then the homogeneous green solution was transferred into a 500 ml vitreous jar, distilled water was subsequently added to 80% of its capacity. The vitreous jar was placed in an oven, heated at 90 °C for 10 h. The suspension was ultrasonically washed with distilled water and ethanol both four times using a magnet as collector. The resulting black precipitate finally was dried in an oven at 80 °C for 24 h [16].

The morphology, composition, and structure of the resulting products were characterized by field-emission scanning electron microscopy (FE-SEM S-4800, Hitachi), X-ray powder diffraction (Rigaku RINT2400 with Cu Kα radiation), and micro-Raman spectrometer (Jobin Yvon LabRAM HR800 UV, YGA 532 nm). For fabricating of Li-ion battery, a mixture of Fe_3O_4 (80 wt%), acetylene black (10 wt%), and polyvinylidene fluoride (PVDF, 10 wt%) electrodes were dried (120 °C, 24 h, vacuum)

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[*] Corresponding author. Fax: +86 717 6397559.
E-mail addresses: shibingni07@gmail.com, nishb05@st.lzu.edu.cn (S. Ni).

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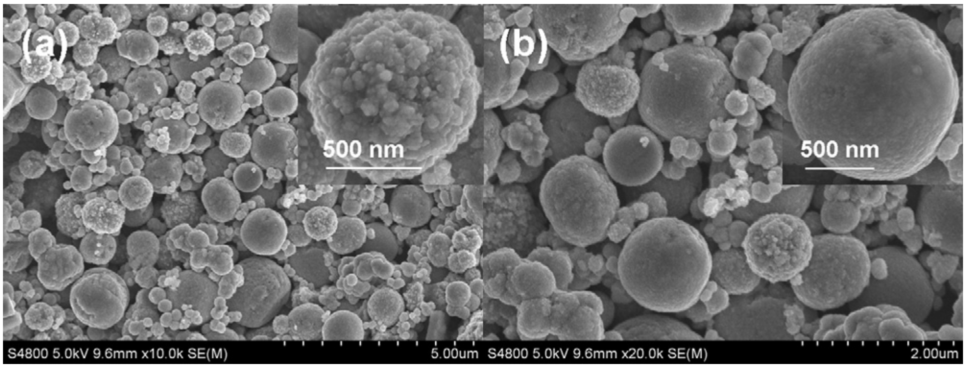

Fig. 1. SEM images of the as-synthesized products with low (a) and high (b) magnification. The insert of (a) is a SEM image of a single sphere with coarse surface. The insert of (b) is a SEM image of a single sphere with lubricous surface.

and compressed on copper foil. Coin-type cells (2032) of Li/1 M $LiPF_6$ in ethylene carbonate, dimethyl carbonate and ethylmethyl carbonate (EC/DMC/EMC, 1:1:1, v/v/v)/Fe_3O_4 were assembled in an argon-filled dry box (Lab star mbraun). A Celgard 2320 microporous polypropylene was used as the separator membrane. The cells were tested in the voltage range between 0.02 and 3 V with a multichannel battery test system (NewareBTS-610).

3. Results and discussion

Fig. 1(a) is a low magnification SEM image of the products, which shows the coexisting of a large number of big-sized micro-spheres together with a small quantity of small-sized particles. The mean size of those micro-spheres and particles is about 800 nm and 200 nm, respectively. It can be seen from a high magnification SEM image of the products (Fig. 1(b)) that those micro-spheres are of two kinds of surface morphology including coarse and lubricous. For further elucidation the surface morphology and size of the as-synthesized micro-spheres, magnified SEM images of single spheres are shown in inserts of Fig. 1(a) and (b). The insert of Fig. 1(a) is a SEM image of a sphere with coarse surface. The diameter of the sphere is about 750 nm, consisting of close-packed nanoparticles with mean size about 30 nm. The insert of Fig. 1(b) is a SEM image of a sphere with lubricous surface. The diameter of the sphere is about 1 μm, being composed of close-packed nanoparticles with mean size less than 10 nm. This process of crystal growth and morphology evolution can be described as Ostwald ripening which involves the growth of large particles at the expense of the smaller ones driven by the tendency of the solid phase in the systems to adjust itself to achieve a minimum total surface free energy [17].

Typical XRD pattern of the as-synthesized micro-spheres is shown in Fig. 2. All diffraction peaks can be indexed as face centered cubic Fe_3O_4 with lattice constant $a = 8.391$ Å, which are in good agreement with JCPDS, No. 19-0629. No diffraction peaks other than those from Fe_3O_4 are observed, indicating high purity of the as-synthesized Fe_3O_4 micro-spheres. Strong and sharp peaks suggest that the as-synthesized Fe_3O_4 micro-spheres are well crystallized.

As shown in Fig. 3, Raman spectrum of the as-synthesized Fe_3O_4 micro-spheres in the wavelength region of 150–1200 cm^{-1} is dominated by three peaks locate at 298, 532 and 671 cm^{-1}, respectively. Those peaks are typical Raman peaks of Fe_3O_4, which can be assigned to Eg, T2g, and A1g mode of Fe_3O_4 [18].

Fig. 4 is the first discharge and charge curves of Fe_3O_4 micro-spheres electrode at current density of 0.05 and 0.1 mA cm^{-2}. It shows a high initial discharge capacity of 1166 mAh g^{-1} at a current density of 0.05 mA cm^{-2}, being much bigger than that of the theoretical capacity of 928 mAh g^{-1} based on the reaction $8Li^+ + 8e + Fe_3O_4 \leftrightarrow 3Fe + 4Li_2O$. The first discharge capacity of the as-prepared electrode at a current density of 0.1 mA cm^{-2} also arrived at 1082 mAh g^{-1}, being bigger than that of the theoretical value of Fe_3O_4. The charge capacity of Fe_3O_4 micro-spheres electrode at current density of 0.05 and 0.1 mA cm^{-2} are 881 and 813 mAh g^{-1}, respectively, being little smaller than the values of discharge capacity. This may be ascribed to irreversible Li^+ con-

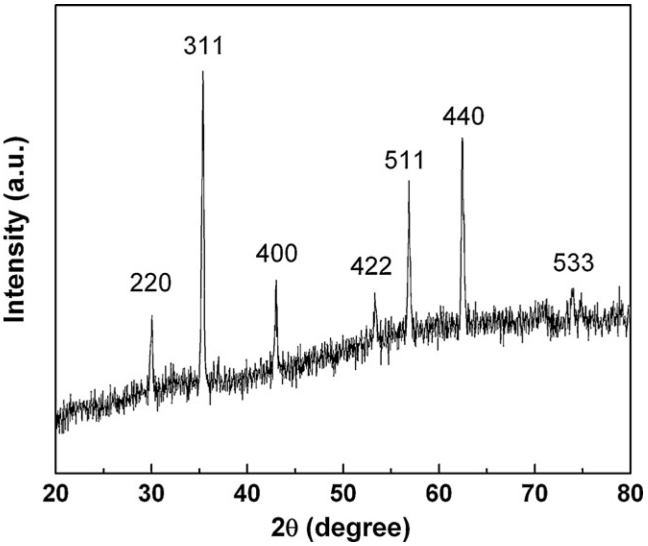

Fig. 2. XRD pattern of the as-synthesized micro-spheres.

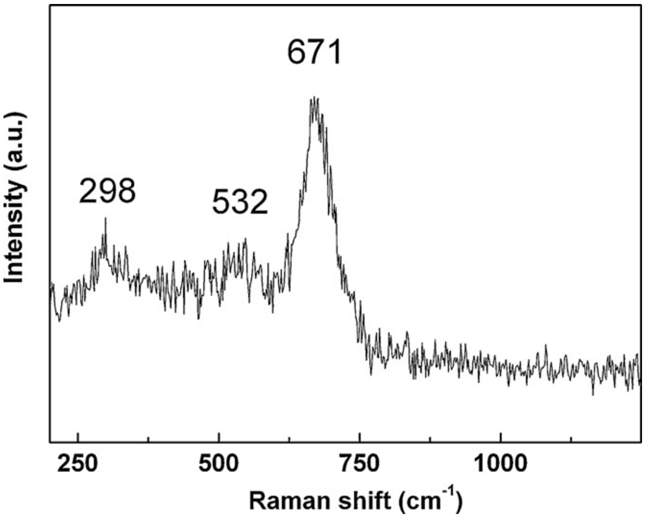

Fig. 3. Raman spectrum of the as-synthesized Fe_3O_4 micro-spheres.

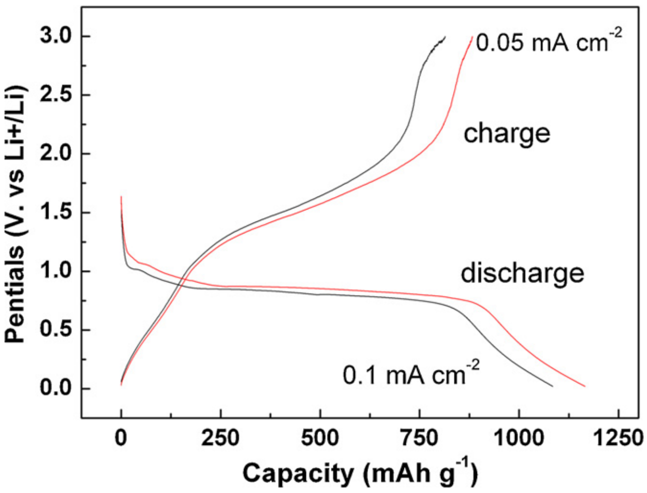

Fig. 4. First discharge and charge curves of Fe_3O_4 micro-spheres electrode at different current densities.

sumptions while the electrolyte being reduced to form a solid electrolyte interphase (SEI) layer, the reduction of the adsorbed impurities on Fe_3O_4 surfaces, the initial formation of lithium oxide due to the presence of some residual OH groups in the surface of active Fe_3O_4, and possible interfacial lithium storage [19,20]. The discharge capacity value of Fe_3O_4 micro-spheres is smaller than that of Fe_3O_4 nanoparticles [21], which is relevant to their surface-volume-ratios. Fe_3O_4 micro-spheres with nanoparticles close-packed architectures have smaller surface-volume-ratio than that of Fe_3O_4 nanoparticles. Small surface-volume-ratio will prevent excessive contact between electrode and electrolyte, facilitating mild reactions between Fe_3O_4 micro-spheres electrode and Li^+. As a result, on the one hand, it shows little discharge capacity than that of Fe_3O_4 nanoparticles. On the other hand, it exhibits steady voltage plateaus.

4. Conclusions

In summary, Fe_3O_4 micro-spheres with nanoparticles close-packed architectures were synthesized by a simple chemical method. This method is hopeful to be adopted for large scale synthesis of Fe_3O_4 micro-spheres due to its low temperature and atmospheric pressure. The as-synthesized Fe_3O_4 micro-spheres electrode shows steady charge/discharge platforms at different current densities, indicating mild chemical reactions between Fe_3O_4 and Li^+. The first discharge capacity of Fe_3O_4 electrode at current density of 0.05 and 0.1 $mA\,cm^{-2}$ arrives at 1166 and 1082 $mAh\,g^{-1}$, while the charge capacity maintains at 881 and 813 $mAh\,g^{-1}$, respectively. This endows Fe_3O_4 micro-spheres with potential applications in lithium ion batteries. In addition, low temperature and atmospheric pressure synthesis has important utility significance.

Acknowledgements

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