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Preparation and electrochemical evaluation of manganese ferrite spheres as anode materials for half and full lithium-ion batteries

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ABSTRACT

A simple hydrothermal method combined with a post annealing treatment is developed to produce high crystallinity manganese ferrite ($MnFe_2O_4$) spheres. The lithium storage properties of the material as an anode in both half and full lithium-ion batteries are investigated. And the electrochemical behaviors of the electrode during lithiation and delithiation process are clarified. Benefited from its sphere-like morphology, the $MnFe_2O_4$ electrode exhibits better lithium storage exhibitions than commercial $MnFe_2O_4$ particles in half cell system. When assembled with $LiCoO_2$ to construct a full lithium-ion battery ($LiCoO_2$//$MnFe_2O_4$), the spheres could deliver a reversible capacity of higher than 600 mA h g^{-1} at a current density of 0.1 A g^{-1} in the potential range of 1.2–3.8 V. This work clearly demonstrates the possibility of using $LiCoO_2$//$MnFe_2O_4$ configuration for practical high-performance lithium-ion batteries in the near future.

1. Introduction

With the increasing demand of the world energy consumption, rechargeable lithium-ion batteries with high storage capacity and cycling stability are considered to be the versatile, clean, and promising power source [1]. Although graphite has served as a reliable anode material for commercial lithium-ion batteries with good reversibility, its high sensitivity to electrolyte, and low theoretical capacity (372 mA h g^{-1}) could not meet the requirements of next generation lithium-ion batteries [2]. Due to the fact that the practical applications of lithium-ion batteries mainly depend on the properties of electrodes, how to design and obtain high-performance and low-cost electrode materials thus becomes a challenge in the field of energy storage. Over the past decade, a worldwide effort has been made to search for alternative anode materials with excellent lithium storage properties [3–6]. Among the explored systems, transition metal oxides with monometal or bimetal have been considered as potential substitutes because of their higher reversible capacity (about two or three times larger than that of graphite) [7–15].

As a spinel-ferrite type bimetal oxide material, manganese ferrite ($MnFe_2O_4$) has been familiar with us mainly because of its attractive magnetic and electromagnetic properties, which made it a promising candidate for applications in microwave devices and magnetic storage instruments [16–20]. Besides the existing properties, recently, investigations on its electrochemical properties have attracted increasing interests due to its ability to realize reversible lithium storage when applied as an electrode for lithium-ion batteries. However, current studies on $MnFe_2O_4$ electrodes are relatively infrequent compared with other transition metal oxide electrodes. Only several research teams have focused their interests on the synthesis and electrochemical investigation of the materials. And surprisingly, their research results all indicated that the $MnFe_2O_4$ materials could only exhibit limited lithium storage properties and the actual specific capacity of the materials were even lower than graphite after certain cycles [21,22]. Thus the main information obtained from these literatures is that the reversible lithium storage process could be occurred on $MnFe_2O_4$ electrode but the actual electrochemical performance of $MnFe_2O_4$ materials was unsatisfactory. The dissatisfied electrochemical performance of the reported $MnFe_2O_4$ electrodes implied that drastic changes have been occurred during repeated lithiation–delithiation process, which lead to the structure collapse of the materials and the pulverization of the electrodes. Such phenomena will definitely prohibit the usage of $MnFe_2O_4$ for practical lithium-ion battery systems in the near future. Additionally, when used as anode materials for lithium-ion batteries, the reported electrochemical data for $MnFe_2O_4$ electrodes were mainly measured from

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half lithium-ion batteries with lithium foil as counter electrode. That is to say, the research results usually ended up in half cell systems. And there were no extensive reports available on the electrochemical performance of the electrodes in full lithium-ion battery systems with any of the commercial cathodes to evaluate its compatibility toward an intercalation host. In order to estimate the feasibility for a practical use of $MnFe_2O_4$ anodes, measurements based on a full cell system with commercial electrode like lithium cobalt oxides ($LiCoO_2$) as cathodes is extremely necessary.

In the present work, we demonstrate the synthesis of sphere-like $MnFe_2O_4$ particles with high crystallinity through a two-step route, which including a hydrothermal approach using $FeCl_3$ and $MnCl_2$ as the starting materials and a subsequent calcination process. The electrochemical performance of the spheres as anode materials for half and full lithium-ion batteries was investigated and evaluated. Due to the dispersed sphere-like morphology, it is found that the synthesized material exhibited better electrochemical performance than commercial $MnFe_2O_4$ particles. Also the material showed favorable operation in full lithium-ion battery system comprising $LiCoO_2$ cathode.

2. Experimental section

2.1. Synthesis of $MnFe_2O_4$ spheres

In a typical synthesis, 5 mmol $FeCl_3 \cdot 6H_2O$, 2.5 mmol $MnCl_2 \cdot 6H_2O$, and 0.05 mmol NH_4Ac were firstly dissolved in 30 ml ethylene glycol. The mixture, after being magnetically stirred for 10 min in air at room temperature, was transferred into a 50 ml Teflon-lined stainless autoclave. The autoclave was then tightly sealed and left in an oven at 200 °C for 12 h, the resulting product was centrifuged, rinsed with ethanol, and then dried in a vacuum oven at 60 °C for 10 h. The final product was obtained after annealing at 350 °C in air for 2 h.

2.2. Material characterization

Powder X-ray diffraction (XRD) patterns of samples were recorded by a Bruker D8 ADVANCE X-ray powder diffractometer using Cu Kα radiation ($\lambda = 0.15418$ nm) at a scanning rate of 0.02° s^{-1} in the 2θ range from 20° to 70°. X-ray photoelectron spectrum (XPS) measurements were performed on a PHI-5400 electron spectrometer. Scanning electron microscopy (SEM) images of samples were measured by a FEI Quanta 400 ESEM-FEG (environmental scanning electron microscope-field emission gun) instrument with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and fast Fourier transform (FFT) results of the samples were obtained on a FEI Tecnai G2 F20 S-TWIN instrument.

2.3. Electrochemical measurements

Electrochemical measurements of half cells were performed at 25 °C using coin cells (CR2025) with pure lithium foil as the counter electrode. The working electrodes were prepared by casting and pressing a mixture of 80 wt% of the $MnFe_2O_4$ material, 10 wt% of acetylene black and 10 wt% of polytetrafluoroethylene (PTFE) in N-methyl pyrrolidinone solvent on Cu foil followed by drying for 12 h at 80 °C. The cells were constructed in a glove box in argon atmosphere under a dew point below −65°. The electrolyte was 1 M $LiPF_6$ dissolved in a mixture of dimethyl carbonate, diethyl carbonate and ethylene carbonate (1:1:1 by volume), and the separator was mesoporous polypropylene film. The charge–discharge tests were carried out on a LAND battery program-control test system in a cut-off potential window of 0–3.0 V. For comparison, another commercial $MnFe_2O_4$ sample (Sinopharm Chemical Reagent Co., Ltd., China, Fig. 1) with irregular and aggregated morphology was also prepared with acetylene black and PTFE in a weight ratio of 80:10:10 as electrode and tested at a current density of 0.1 A g^{-1}. Cyclic voltammetry (CV) measurements were carried out on a CHI 660D electrochemical workstation at a scan rate of 0.1 mV s^{-1} in the potential range of 0–3.0 V vs. Li/Li^+. Electrochemical impedance spectroscopy (EIS) was measured by using the same electrochemical workstation with the frequency range from 0.01 to 100 kHz. The electrochemical measurements of full lithium-ion batteries were performed and fabricated by using the same type coin cells with $MnFe_2O_4$ as anode and commercial $LiCoO_2$ cathode as the counter electrode. The electrolyte, separator and the package technology used were similar to the fabrication process for half cell system. The full cell system is defined as $LiCoO_2//MnFe_2O_4$, which has a capacity ratio of $LiCoO_2$ to $MnFe_2O_4$ of 1.2 ($MnFe_2O_4$ is a limiting electrode). The cathode material was located in excess to balance the irreversible capacity of the anode. The electrochemical performance tests for full

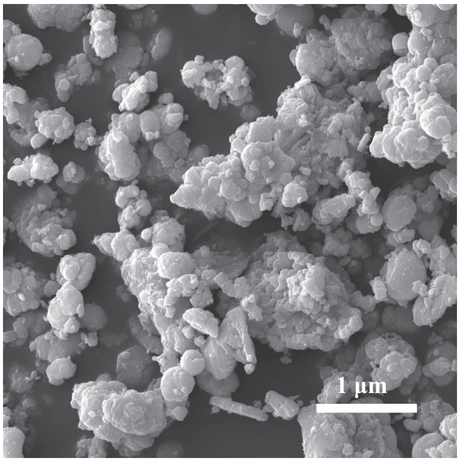

Fig. 1. SEM image of the commercial $MnFe_2O_4$ particles.

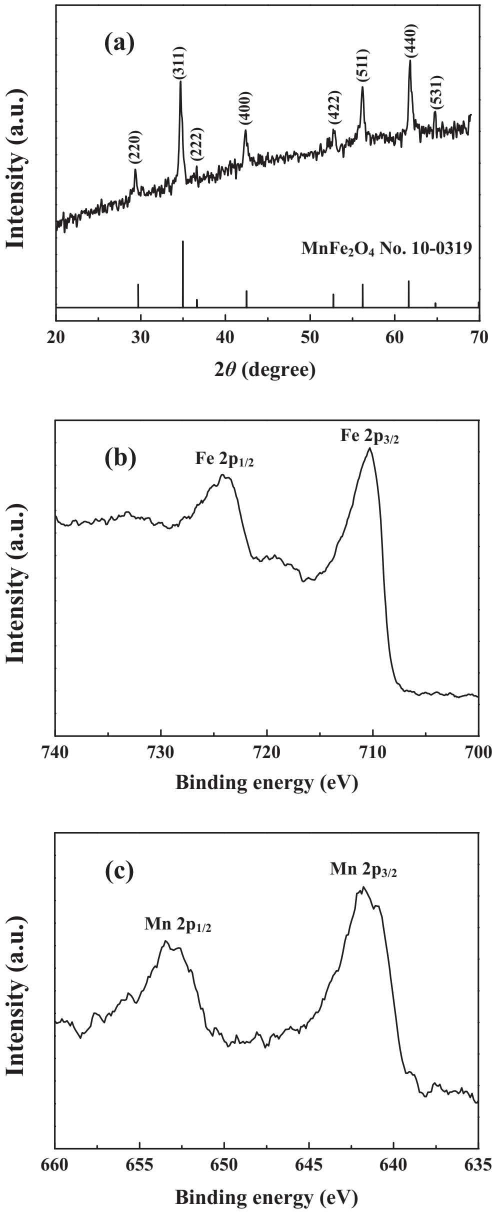

Fig. 2. (a) XRD pattern of the $MnFe_2O_4$ spheres and the XPS spectra of (b) Fe 2p and (c) Mn 2p of the $MnFe_2O_4$ sample.