



Li-storage of Fe₃O₄/C composite prepared by one-step carbothermal reduction method



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ABSTRACT

The Fe₃O₄/C is prepared by novel and cost effective carbothermal reduction method from commercial Fe₂O₃ and characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM) and high resolution-transmission electron microscopy (HR-TEM). Li-storage behaviour of Fe₃O₄/C has been evaluated by galvanostatic discharge-charge cycling and cyclic voltammetry (CV) in cells with Li-metal as counter electrode in the range of 0.005–3.0 V at ambient temperature. Results show that a high initial first cycle reversible capacity of 910 (±10) mA h g⁻¹ (~7.9 mol of Li per mole of Fe₃O₄) is achieved when cycled at 60 mA g⁻¹ and remained as 740 (±10) mA h g⁻¹ (~6.43 mol of Li) at the end of 60 cycles. In this material, conductive carbon introduced during synthesis not only adds to the conductivity to the composite, but also alleviate the volume change during cycling. The Coulombic efficiency is found to be >96% in the range of 10–60 cycles. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) are carried out to complement the galvanostatic cycling data. The experimental results suggest that composite Fe₃O₄/C has the potential to provide large and almost stable capacity for practical applications, and good opportunity for large scale synthesis using Fe₂O₃, which is commercially available.

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1. Introduction

Lithium ion batteries (LIBs) are considered as the promising secondary power sources for modern portable electronic devices. However, its low energy density restricted its potential use in case of electric vehicle/hybrid electric vehicles (EVs/HEVs). High capacity, long cycle life and good rate capability have become the essential requirements for the development of electrode materials in next-generation LIBs [1–4]. In 2000, Poizot et al. reported the Li-storage and cyclability of transitional metal oxides, MO, where M = Co, Cu, Ni and Fe with rock salt crystal structures. They reported that MO (M = Co) showed a high capacity of ~700 mA h g⁻¹, with good capacity-retention up to 100 cycles at a high C-rate [5]. The reaction mechanism involved during Li-cycling is different from that of intercalation/de-intercalation and alloying/de-alloying, and involves the formation and decomposition of Li₂O, along with the reduction to, and oxidation of, metal nanoparticles, the so called ‘conversion/displacement reaction’ by the following equation:



Fe₃O₄ is another binary oxide, which adopts an inverse spinel structure, where Fe³⁺ ions occupy tetrahedral (8a) sites and the Fe²⁺ and Fe³⁺ ions occupy the octahedral (16d) sites in the crystal

structure [6]. It has been extensively studied as anode material due to its high theoretical capacity values (~926 mA h g⁻¹), low cost and environmental friendliness [7,8]. However, the poor cycling performance is delaying its practical application. In order to improve the cyclability of Fe₃O₄, many approaches have been adopted in the literature, such as carbon-coating, nanocomposites and nanostructures [9–12]. Wang et al. reported the hydrothermal preparation of Fe₃O₄/graphene composite, which showed a high reversible capacity of 771 mA h g⁻¹ at the end of 50th cycle [13]. Zhang et al. synthesized carbon coated Fe₃O₄ nanospindles by partial reduction of mono-dispersed Fe₂O₃. The Fe₃O₄/C showed a high reversible capacity of 745 mA h g⁻¹ at 0.2 C and 600 mA h g⁻¹ at 0.5 C [14]. Liu et al. reported the preparation of Fe₃O₄ core-shell nanorods by hydrothermal method using Fe₂O₃ nanorods as precursor, which showed an initial Li-storage capacity of 1120 mA h g⁻¹ and a reversible capacity of 394 mA h g⁻¹ after 100 cycles [15]. He et al. reported the preparation of Fe₃O₄/CNT composite by chemical precipitation and showed a high discharge capacity of 656 mA h g⁻¹ at the end of 145th cycle [16]. Lee et al. prepared the core-shell nanostructure of Fe/Fe₃O₄, which showed a reversible capacity of ~600 mA h g⁻¹ after 50 cycles [17].

In this present work, a cost effective and novel carbothermal reduction method was employed to prepare submicron size Fe₃O₄ and Fe₃O₄/C at 750 °C in Ar-atmosphere for 8 h. Carbon was used as reducing agent for the preparation of Fe₃O₄ from commercial Fe₂O₃. Extra amount of carbon was added during the preparation for Fe₃O₄/C, which showed better cycling performance

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compared to Fe_3O_4 due to the increase in electronic conductivity. When used as electrode material, the $\text{Fe}_3\text{O}_4/\text{C}$ showed a high initial reversible capacity of $\sim 910 \text{ mA h g}^{-1}$ ($\sim 7.9 \text{ mol of Li}$) and remained as $\sim 740 \text{ mA h g}^{-1}$ ($\sim 6.43 \text{ mol of Li}$) after 60 cycles. The cyclic voltammetry and electrochemical impedance spectroscopy were also carried out to support the galvanostatic data. The $\text{Fe}_3\text{O}_4/\text{C}$ showed improved performance which is comparable to the Fe_3O_4 results reported in literatures [13–17]. The cost effective, large scale method of preparation and high capacity make $\text{Fe}_3\text{O}_4/\text{C}$ composite as potential anode material for LIBs.

2. Experimental details

The compound, Fe_3O_4 was prepared by using the mixture of commercial Fe_2O_3 (99.9%; Sigma Aldrich) and Carbon (C) (MMM carbon) in a molar ratio of 3:1 by carbothermal reduction method. The mixture were ground in a mechanical grinder for 15 min and pressed in to pellet. The pellet was kept in a carbon crucible (size, $10 \times 2.5 \text{ cm}$) and heated at 750°C for 8 h in flowing Ar gas in a tubular furnace (Carbolite, UK) and cooled to ambient temperature. The compound, $\text{Fe}_3\text{O}_4/\text{C}$ was prepared by using equi-molar mixture of Fe_2O_3 and Carbon (Extra carbon was added in order to prepare $\text{Fe}_3\text{O}_4/\text{C}$ composite during synthesis). The formation of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{C}$ from commercial Fe_2O_3 and carbon (C) can be explained by the following equations;



The Gibb's free energy for above reactions are calculated to be negative at 750°C ($\Delta G < 0$), thus carbon can reduce Fe_2O_3 to form Fe_3O_4 [18].

Powder X-ray diffraction (XRD) data were collected using Philips X'PERT MPD instrument (Cu $K\alpha$ -radiation) and the unit cell lattice parameters were obtained by using Rietveld refinement of the XRD data (TOPAS R software) (2000 Bruker AXS, Germany). The morphology of the powder was characterised by scanning electron microscopy (SEM) using JEOL JSM 6700F. The high resolution-transmission microscopy (HR-TEM) and selective area electron diffraction (SAED) images were taken using JEOL JEM 3010 operating at 300 kV. Fabrication of the electrodes was carried out using the active material, super P carbon black and binder (Kynar 2801) in the weight ratio 70:15:15 using N-methyl-pyrrolidinone (NMP) as the solvent for the binder. An etched Cu-foil was used as current collector. Li-metal was

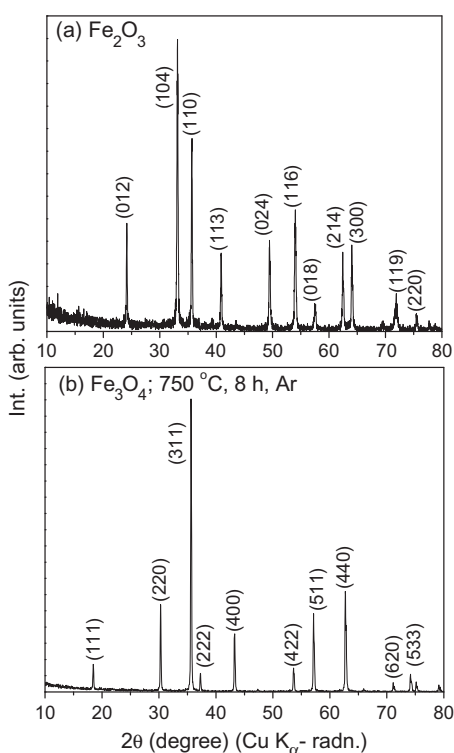


Fig. 1. The XRD pattern of (a) Fe_2O_3 commercial powder and (b) Fe_3O_4 prepared at 750°C , 8 h, Ar atm.

used as the counter electrode. LiPF_6 in ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as the electrolyte and glass microfiber filter (GF/F) (Whatman Int. Ltd., Maidstone, England) as the separator. The coin type cells (2016) were fabricated inside the glove box (MBraun, Germany), where H_2O and O_2 level was maintained at $<1 \text{ ppm}$. More details on the cell fabrication are described elsewhere [19,20]. The fabricated cells were aged for 12 h before measurement to ensure penetration of electrolyte into the active material. The galvanostatic cycling and cyclic voltammetry were carried out in the voltage range of $0.005\text{--}3.0 \text{ V}$ at room temperature using multichannel battery tester (model SCN, Bitrode, USA) and Macpile II system (Biologic, France), respectively. Impedance measurements were carried out with the computer controlled Solartron Impedance/gain-phase analyser (model SI 1255) coupled with a computer controlled battery test unit (model 1470) at room temperature (RT). The frequency range was varied from 0.18 MHz to 3 MHz with ac signal amplitude of 10 mV . The collected data were analysed using Z plot and Z view software (Version 2.2, Scribner associates Inc., USA) to obtain the Nyquist plots (Z' vs. $-Z''$).

3. Results and discussion

3.1. Structure and morphology

The XRD pattern of Fe_3O_4 prepared by carbothermal reduction method is shown in Fig. 1. This shows the line characteristics of pure phase Fe_3O_4 with high crystallinity. The lines characteristic show cubic crystal structure with $Fd\bar{3}m$ space group. The lattice parameter was obtained from Rietveld refinement and is, $a = 8.391 (\pm 0.002) \text{ \AA}$ [JCPDS card No. 85-1436]. The SEM photographs of $\text{Fe}_3\text{O}_4/\text{C}$ are shown in Fig. 2. The sub-micron size particles with agglomerated morphology are seen, due to the high temperature

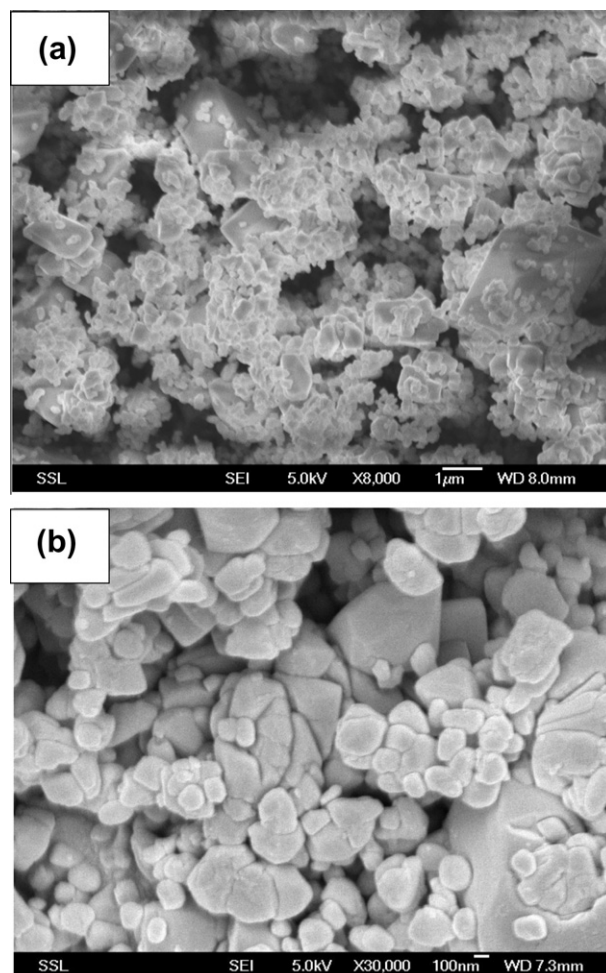


Fig. 2. SEM images of $\text{Fe}_3\text{O}_4/\text{C}$ composite prepared at 750°C , 8 h, Ar atm. Scale bars are shown.

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