



Nanoparticulate Fe₂O₃ and Fe₂O₃/C Composites as Anode Materials for Li-Ion Batteries

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Abstract: Nanoparticulate α -Fe₂O₃ and γ -Fe₂O₃/C composites with different carbon proportions have been prepared by a freeze-drying synthesis procedure. The characterization has been performed by elemental analysis, X-ray powder diffraction (XRD), transmission electron microscopy (TEM), electron paramagnetic resonance (EPR) and magnetic susceptibility measurements. Morphological studies revealed that nanoparticles of γ -Fe₂O₃ in the composites are well-dispersed in the matrix of amorphous carbon. The magnetic and spectroscopic measurements corroborated that described composition and morphology. The electrochemical study showed that composites with carbon have promising electrochemical performances. These samples yielded specific discharge capacities of 1200 mAh/g after operating for 100 cycles at 1C. These excellent results could be explained by the homogeneity of particle size and structure as well as the uniform distribution of γ -Fe₂O₃ nanoparticles in the in situ generated amorphous carbon matrix.

Keywords: Nanoparticle; composite; Li-ion batteries; anode; Fe₂O₃; freeze-drying

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1. Introduction

Lithium ion batteries (LIBs) have attracted extensive attention in various fields such as portable electronic devices or electric/hybrid electric vehicles owing to its high energy density, long cycle life, rapid charge capability, and no memory effect^[1]. For commercial LIBs, the positive electrode material is typically a metal oxide or phosphate while graphite is the most widely used anode material. However, to develop higher energy density systems new materials are required^[2]. In this sense, 3d transition metal oxides (MO_x) are one of the most promising next-generation anode materials under consideration^[3]. In these compounds, contrary to conventional intercalation or alloying mechanisms, the high Li^+ storage capacity is derived from conversion reactions.

Among the metal oxides, Fe_2O_3 has been regarded as a suitable candidate because of its high theoretical capacity (1007 mAh/g), nontoxicity, high corrosion resistance, and low materials and processing costs^[4]. However, further optimization of iron oxides as anode materials is needed due to their poor cycling

2. Results and Discussion

For the nanoparticulate Fe_2O_3 sample calcined in air, hereafter **$\text{Fe}_2\text{O}_3_{\text{air}}$** , the X-ray diffraction peaks could be indexed to hematite $\alpha\text{-Fe}_2\text{O}_3$ structure. XRD patterns of composites prepared with different carbon content are very similar, and all of the diffraction peaks could be indexed to maghemite $\gamma\text{-Fe}_2\text{O}_3$. The calculated size of the crystals from the deconvolution of (311) diffraction maxima is in the range of 10 to 20 nm for samples with a carbon content determined by elemental analysis of 20 to 40 %. Transmission electron micrograph of these samples show that they consist of spherical nanoparticles embedded in the in situ generated carbon matrix. The nanometric particle size can be attributed to the carbon source that prevents the growth of the

performance and limited rate capability. Introducing carbonaceous materials the electronic contact between the iron oxide particles is increased, and the volume and structural changes associated with the transformation of iron oxide particles into metallic iron during the discharge/ charge process are buffered^[5-6]. This improves the cycling stability and rate capability of iron oxides, but a facile synthesis method for large-scale production of these materials for anode materials of LIBs is required. Here, a freeze-drying synthesis procedure, which can be easily implemented as part of an industrial process, has been employed. This synthesis method has already been proven in our group to be useful to obtain nanosized cathodic materials with exceptional electrochemical performance^[7].

In this paper we report on the structural, morphologic, spectroscopic, magnetic and electrochemical characterization of nanoparticulate Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{C}$ composites prepared by the freeze-drying method.

particle. The TEM image of the most homogeneous sample, **$\text{Fe}_2\text{O}_3_{23\%C}$** , is presented in Fig. 1. This sample ($D=15$ nm) was chosen to carry out the comparative electrochemical study.

The EPR spectra of the samples were recorded at X-band (9.4 GHz) at room temperature. A similar pattern was observed in all cases: a very broad and intense signal centered at a g-value close to 2.18–2.20, characteristic of ferri/ ferromagnetic systems. It is also found that composites with higher amount of carbon have a more isotropic EPR signal, probably due to the smaller $\gamma\text{-Fe}_2\text{O}_3$ particle size.

The magnetization of the $\text{Fe}_2\text{O}_3_{\text{air}}$ sample is close to saturation under relatively small applied

fields (<5 kOe). However, there is also quasi-linear contribution that is almost independent of temperature. This feature is compatible with the presence of an antiferromagnetic phase of high ordering temperature as it is α -Fe₂O₃. After subtraction of this antiferromagnetic component, a relative content for the γ -Fe₂O₃ ferromagnetic phase of at least 13% in weight is estimated. In contrast, the magnetization of Fe₂O₃_23%C perfectly saturates at 80 emu/g, which is very close to the value of pure maghemite in bulk. The coercive field is ~250 Oe, smaller than in Fe₂O₃_air (450 Oe), in agreement with values reported in the literature for maghemite nanoparticles of similar sizes^[8]. In composites with higher carbon content, the lack of saturation at high fields (>20 kOe) can be explained as originating from very small and isolated magnetic nanoparticles, whose magnetization does not saturate at 5 K and consequently also reduces the average magnetization of the sample^[9]. Magnetization versus temperature measurements for these samples showed the presence of para- and superparamagnetic contributions ascribed to very small superparamagnetic γ -Fe₂O₃ nanoparticles.

The theoretical capacity of Fe₂O₃ for complete reduction of Fe³⁺ to Fe⁰ is 1007 mAh/g, corresponding to a maximum lithium uptake of 6 Li⁺ per Fe₂O₃ formula unit. However, our samples exhibit higher initial values (1216 and 1451 mAh/g for Fe₂O₃_air and Fe₂O₃_23%C, respectively) due to the partial decomposition of the electrolyte^[10] and the extra capacity provided by the carbon in the composite^[11].

The cycling stability of the electrodes based on Fe₂O₃_air and Fe₂O₃_23%C, was investigated at a current rate of 1C. As shown in Figure 2, the capacity retention was better for the carbon composite. This fact could be attributed to the heterogeneity of the Fe₂O₃_air sample as well as to the lack of an in situ generated carbon matrix in this compound. The carbon matrix enhances the cycling performance of the samples since it improves the electrical connection between the nanoparticles and facilitates the accommodation of the structure change associated with successive charge and discharge cycles. Figure 2 also shows the Coulombic efficiencies at C/10 (defined as the ratio between charge and discharge capacity) of the cells for the first 20 cycles. The Coulombic efficiencies in the first cycles were only 70% and 53% for the Fe₂O₃_air and Fe₂O₃_23%C cells, respectively. However, in the successive cycles these values increased noticeably. The highest Coulombic efficiency after the first cycle was that of the cell containing the Fe₂O₃_23%C composite, probably in large part resulting from the homogeneous particle size distribution of the γ -Fe₂O₃.

Thus, composite materials show a promising electrochemical performance providing a specific discharge capacity of around 1200 mAh/g after operating for 100 cycles at 1C. These excellent results could be explained by considering the structural and particle size homogeneity as well as the uniform distribution of the NPs in the in situ generated amorphous carbon matrix.

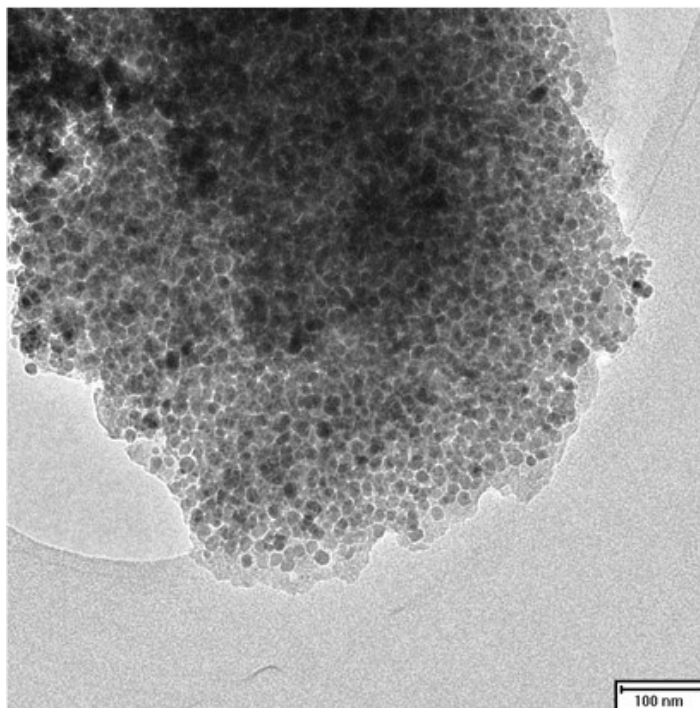


Figure 1. TEM image of Fe₂O₃_23%C.

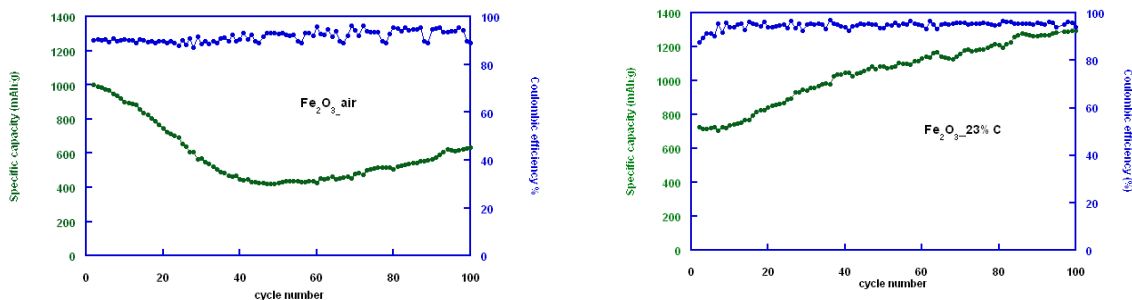


Figure 2. Cyclability at 1C rate and Coulombic efficiencies at C/10 for Fe₂O₃_air and Fe₂O₃_23%C.

3. Materials and Methods

Citric acid monohydrate (99.5 %) and iron(III) citrate (98%) were purchased from Sigma-Aldrich and used as received without further purification. C₆H₈O₇·H₂O and C₆H₅FeO₇ reagents were dissolved in water in required molar ratios. The resulting solutions were subsequently frozen in a round-bottom flask that contained liquid nitrogen. Afterward, the round-bottom flasks were connected to the freeze-dryer for 48 h at a pressure of 3×10^{-1} mbar and a

temperature of -80 °C to sublime the solvent. The as-obtained precursors were subjected to a single heat treatment at 400 °C for 6 h in air or nitrogen atmosphere and ball-milled for 30 min.

Structural characterization of the samples was carried out using X-ray powder diffraction with a Bruker D8 Advance Vario diffractometer. The morphologies of the materials were studied by transmission electron microscopy (TEM) using a FEI TECNAI F30. A Bruker ELEXSYS 500

spectrometer operating at the X-band was used to record the EPR polycrystalline spectra. Magnetic susceptibility measurements were carried out between 5 and 300 K with a Quantum Design SQUID magnetometer. CR2032 coin cells were assembled to evaluate the electrochemical performances of the samples. All the

electrochemical measurements were carried out on a Bio-Logic VMP3 potentiostat/galvanostat at room temperature. The galvanostatic charge/discharge experiments were performed between 0.1 and 3 V at 0.1C and 1C current rates.

4. Conclusions

Fe₂O₃/C composites with different carbon content were successfully prepared by a freeze-drying method, crystallizing in the γ -Fe₂O₃ maghemite structure. TEM micrographs have shown that the Fe₂O₃ particles are well dispersed in the matrix of amorphous carbon that was generated in situ during the synthesis procedure. Electron paramagnetic resonance spectra are in good agreement with the composition and morphology of each sample. The magnetic measurements showed a lack of saturation of the magnetization at high magnetic fields (>20 kOe) due to the presence of very small isolated maghemite nanoparticles. The galvanostatic experiments revealed that composite materials show a promising electrochemical performance. This could be attributed to several factors, such as the suitable morphology of the samples and the good connection that provides the in situ generated carbon matrix without blocking the lithium ion diffusion pathways..

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Author Contributions

All authors contributed equally to this work.

Conflicts of Interest

The authors declare no conflict of interest

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