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Fabrication and characterization of $Li_{0.5}Fe_{2.5}O_4$ octahedrons via a TEA-assisted route

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Abstract Octahedral-like $Li_{0.5}Fe_{2.5}O_4$ crystallites have been fabricated using a TEA-assisted route under mild conditions. The as-prepared powders were characterized in detail by conventional techniques such as XRD, TEM, and FESEM. The saturation magnetization (*M*s), remnant magnetization (*M*r), and coercivity (*H*c) have been determined to be 84, 6 emu/g, and 85 Oe, respectively. Meanwhile, the electrochemical properties of $Li_{0.5}Fe_{2.5}O_4$ demonstrate that it delivers a large discharge capacity, which might find possible application as an electrode material in lithium cells.

Introduction

The study of electrode materials for rechargeable lithium ion batteries remains a major topic in the area of energy storage. Transition metal oxides are promising candidates as cathode materials for lithium secondary batteries [1–3]. Because of the low cost and environmentally benign, iron-based oxides have attracted the attention of scientists for a long time, showing a big advantage compared to $LiCoO_2$ and $LiNiO_2$ for practical use [4–12]. As an important transition metal spinel oxide, Li–ferrite, $Li_{0.5}Fe_{2.5}O_4$, is an inverse spinel with the Li^{1+} and three-fifths of the Fe^{3+} ions occupying the octahedral B sites of the cubic spinel structure of the general formula AB_2O_4. Because of the peculiar 1:3 ratio of the Li^{1+} and Fe^{3+} ions in the octahedral sites, there exists two different crystalline forms of lithium ferrite [13]. The α-phase is an ordered phase wherein the Li^{+1} and Fe^{3+} ions are ordered in the 1:3 ratio in the octahedral sites of the cubic spinel structure, whereas the β-phase is a disordered phase where the Li^{1+} and Fe^{3+} ions are randomly distributed in the octahedral sites [14]. During the usual ceramic method of synthesis of the bulk ferrite, a slow cooling process from above 755 °C yields the ordered phase, whereas the disordered phase can be obtained by quenching from high temperatures. An order–disorder phase transition takes place in the temperature range 735–755 °C [15]. Traditional preparation methods of lithium ferrite have involved high temperature [16–20]. Recently, Tabuchi [21] reported a new form of metastable lithium iron oxides ($Li_{1+x}Fe_{5+x}O_8$), which was synthesized using α-$NaFeO_2$ and LiCl in ethanol by the solvothermal reaction at a low temperature (220 °C). In other studies, Kim and Manthiram prepared amorphous lithium iron oxide ($Li_xFe_yO_z$) nanoparticles, delivering a high discharge capacity of about 140 mA h/g with a fairly good cycleability in the range of 1.5–4.5 V [22, 23].

Here we report a simple hydrothermal route without a preformed template for the preparation of $Li_{0.5}Fe_{2.5}O_4$ octahedrons. The hydrothermal process is one of the more successful ways for crystals growing from various materials, owing to its low expense and highly controllable composition. [24] In addition, the hydrothermal synthesis requires neither extremely high processing temperature nor sophisticated processing. For example, ferrites can be prepared via the hydrothermal method at a temperature of about 150 °C,

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whereas the solid state method requires a temperature of 800 °C [25]. Hydrothermal synthesis of several ferrites has been reported [26, 27]. Moreover, there is no report on the synthesis of single-crystalline $Li_{0.5}Fe_{2.5}O_4$ octahedrons. Our aim was to develop a low-temperature hydrothermal process for the preparation of $Li_{0.5}Fe_{2.5}O_4$ octahedrons that might find applications in perpendicular recording media and electrode materials.

Experimental

All chemicals were analytical grade and used without purification. A typical experiment was as following: 10 mL triethanolamine (TEA) was added dropwise into 20 mL aqueous solution of Fe^{2+} salts under stirring. Then 10 mL solution of 0.8 g LiOH was added. The whole mixture was stirred for another 5 min to obtain a homogeneous solution and subsequently transferred into a 50 mL autoclave, sealed, and maintained at 150 °C for 12 h, then cooled to room temperature naturally. The products were filtered and washed several times with distilled water and absolute ethanol, and finally dried in a vacuum oven at 50 °C for 12 h.

X-ray powder diffraction (XRD) patterns were determined using a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite-monochromatized Cu Ka radiation ($\lambda = 1.5418$ Å). The X-ray photoelectron spectra (XPS) were collected on an ESCALab MKII X-ray photoelectron spectrometer, using nonmonochromatized Mg KR X-ray as the excitation source. Transmission electron microscopic (TEM) images were characterized by Hitachi H-800 transmission electron microscope with a tungsten filament and an accelerating voltage of 200 kV. Field emission scanning electron microscopic (FESEM) images were taken with a JEOL JSM6700F scanning electron microscope. The magnetic measurement was carried out at room temperature by a VSM (vibrating sample magnetometer, BHV-55) technique with a maximum magnetic field of 15 kOe.

The positive electrodes were fabricated by pasting slurries of the as-prepared $Li_{0.5}Fe_{2.5}O_4$ crystallites (85 wt%), carbon black (Super P, 10 wt %), and polyvinylidene (PVDF, 5 wt%) dissolved in *N*-methylpyrrolidinone (NMP) on Al foil strips by the doctor blade technique. Then the strips were dried at 160 °C for 24 h in an air oven, pressed under 20 MPa pressure, and kept at 120 °C for 12 h in vacuum. The electrolyte was 1 M LiPF6 in a 1:1 mixture of ethylene carbonate (EC)/diethyl carbonate (DEC); the separator was Celgard 2500. The cells were assembled in the glovebox filled with highly pure argon gas. The cyclic voltammetry (CV) test was carried out on an automated LK98BII electrochemical measurement system with metal lithium anode. The cells were galvanostatically cycled in the 1.5–4.5 V range at different current densities.

Results and discussion

Figure 1 exhibits the XRD pattern of the product hydrothermally synthesized at 150 °C for 12 h. All diffraction peaks can be easily indexed to a pure cubic phase (space group *Fd*3 *m* [227]) of *β*-$Li_{0.5}Fe_{2.5}O_4$, which matches well with the reported value (JCPDS 74–1911) and is close to that reported in the previous literature [28–30]. The products obtained are further examined by X-ray photoelectron spectra (XPS). The spectra of the products corresponding to the binding energies of Li 1s and Fe 2p are shown in Fig. 2a and b. The figures show that the binding energies relating to Li 1s, Fe $2p_{3/2}$, and Fe $2p_{1/2}$ are about 55.72, 710.4, and 724.2 eV, respectively. The data are consistent with the values reported for lithium ferrite in the literature [31]. Therefore, XPS results also prove the composition of the products.

Figure 3a and b shows the FESEM images of $Li_{0.5}Fe_{2.5}O_4$ crystallites with different magnifications. It is shown that there exists a large number of octahedral $Li_{0.5}Fe_{2.5}O_4$ crystallites with the average diameter of one micrometer. For an octahedral crystal, every facet is close to an equilateral triangle. All the surfaces are smooth, and there are no obvious defects. The representative TEM image of the sample is shown in Fig. 2c, consistent with those of a sample observed by FESEM. The SAED pattern taken from a single octahedron can be exactly indexed to a $Li_{0.5}Fe_{2.5}O_4$ single crystal recorded from the [111] zone axis (Fig. 2d). Because all the manipulations were conducted in air, oxygen was inevitably involved in the

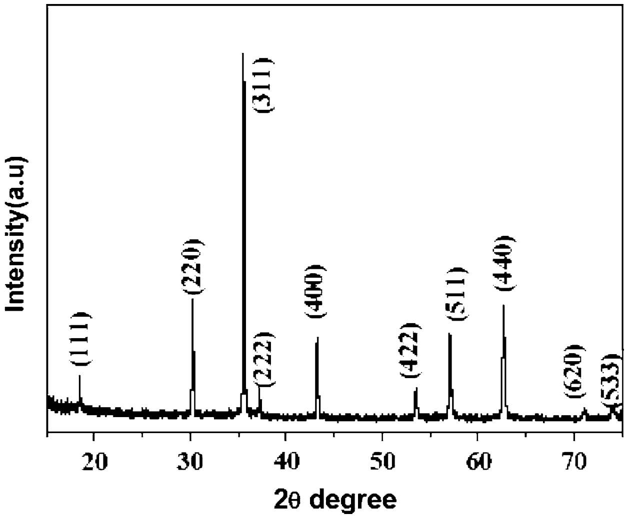

Fig. 1 XRD patterns of the samples hydrothermally synthesized at 150 °C

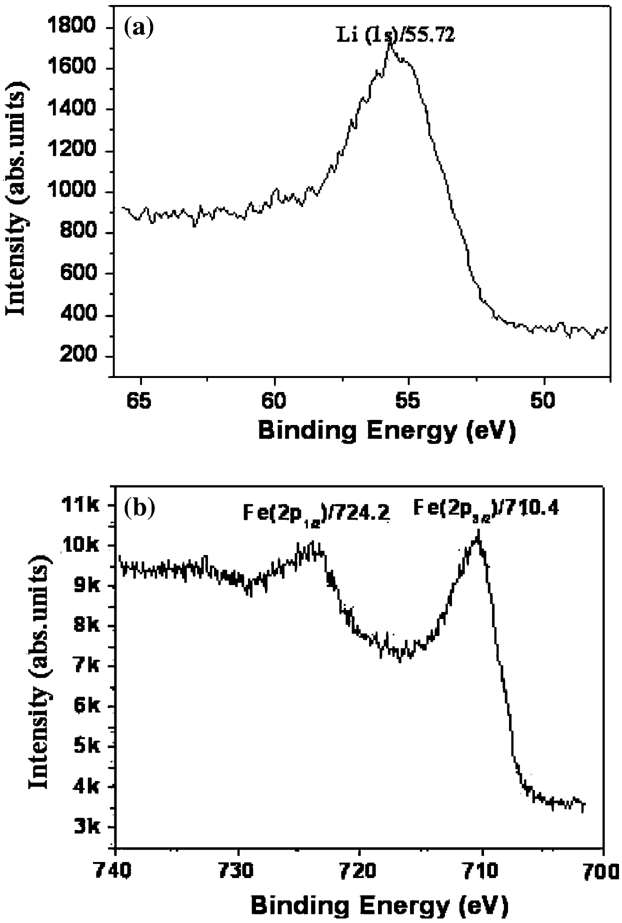

Fig. 2 XPS analysis of the samples (**a**) Li 1s; (**b**) Fe 2p

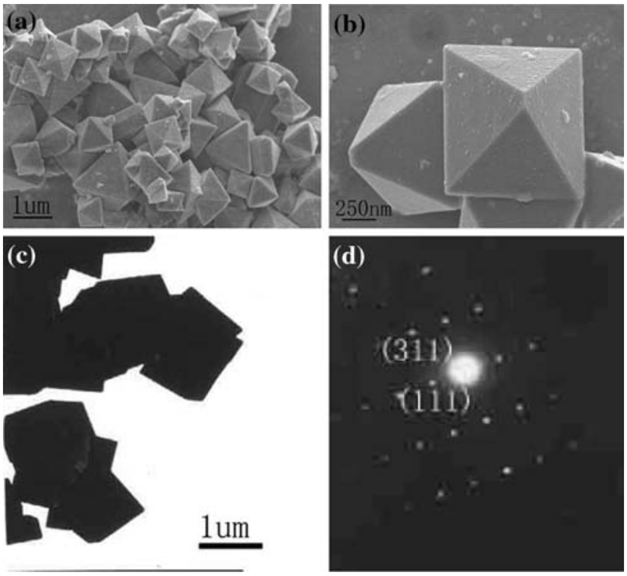

Fig. 3 FESEM (**a**, **b**) and TEM (**c**) images and SAED (**d**) of octahedral $Li_{0.5}Fe_{2.5}O_4$ crystallites

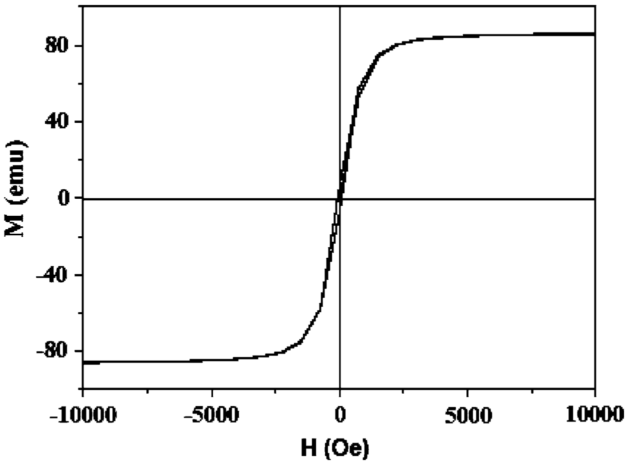

Fig. 4 Hysteresis loop for $Li_{0.5}Fe_{2.5}O_4$ octahedrons measured at room temperature

process. The Fe^{2+} would be oxidized to the oxidation state of +3 due to the low value of standard electromotive force of Fe^{3+} ions ($Fe^{3+} + e = Fe^{2+}$, $E^0 = 0.770$ V). As well known, TEA could coordinate with Fe^{3+}, forming a very stable complex, which avoid the formation of $Fe(OH)_3$ after lithium alkaline was added into the solution. Moreover, the formation of the complexes can reduce the formation rate of free Fe^{3+} in the solution. At low concentration of free Fe^{2+} and Li^+, the supersaturation is low, and therefore, ions can combine to form nuclei. Later slowly generated ions have sufficient time to adsorb on those nuclei to form $Li_{0.5}Fe_{2.5}O_4$ octahedrons. In the absence of TEA, only dispersed particles were obtained in the final product.

Figure 4 shows magnetic hysteresis curves for the samples investigated at room temperature. The hysteresis loop of the products shows ferromagnetic behavior with saturation magnetization (Ms), remnant magnetization (Mr), and coercivity (Hc) values of about 84, 6 emu/g, and 85 Oe, respectively. The coercive force is much smaller than that of the nanocrystallites (162 Oe) with 40 nm prepared by the autocombustion method [14]. This may be due to the low shape anisotropy and multiple domains of $Li_{0.5}Fe_{2.5}O_4$ octahedrons, which let them magnetizing easily in directions along their magnetic axes.

Electrochemical performances of $Li_{0.5}Fe_{2.5}O_4$ in the cell configuration $Li_{0.5}Fe_{2.5}O_4$/Li have been evaluated. Figure 5 shows the voltage versus capacity for the cells between 1.5 and 4.5 V at a current density of 0.1 mA cm^{-2}. During the first discharge process, the potential rapidly drops to 3.5 V, then gradually reaches a plateau of 1.8 V, and finally decreases down to 1.5 V. The first discharge/charge capacity is about 155 and 126 mA h/g, respectively, which is different from that of synthetic $LiFe_5O_8$ nanoparticles (162 and 120 mA h/g) reported by Wang et al [23] and

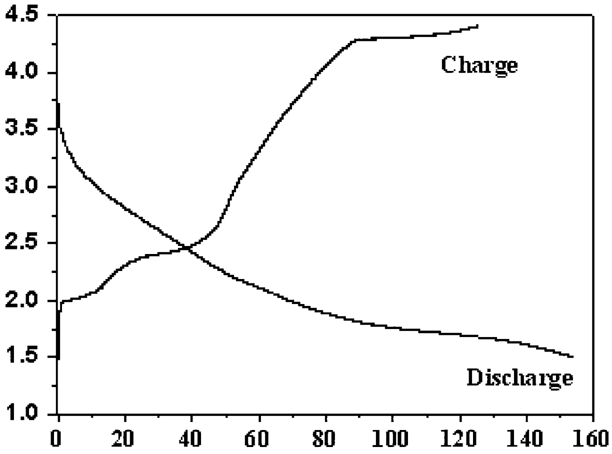

Fig. 5 Voltage versus capacity curves for the β-$Li_{0.5}Fe_{2.5}O_4$/Li cell between 1.5 and 4.5 V at a current density of 0.1 mA cm^{-2}

other known lithium ferrites [32–35], may be ascribed to the unique microstructure.

Conclusions

In summary, we have synthesized octahedral $Li_{0.5}Fe_{2.5}O_4$ crystallites using a TEA-assisted route under mild conditions. The as-prepared products are composed of a large number of octahedral $Li_{0.5}Fe_{2.5}O_4$ crystallites with the average diameter of 1 um. The magnetic properties of *M*s, *M*r, and *H*c are different from those reported for $Li_{0.5}Fe_{2.5}O_4$ nanorods and nanoparticles. The electrochemical properties of $Li_{0.5}Fe_{2.5}O_4$ demonstrate that it delivers a large discharge capacity. The experimental results show TAE plays important roles in the formation of the products in the process. This method can be easily controlled and is expected to be applicable for the preparation of other metal oxides with special morphologies.

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