

Synthesis, characterization and electrochemical performance of mesoporous FePO₄ as cathode material for rechargeable lithium batteries

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Abstract

Mesoporous FePO₄ could deliver enhanced specific capacity of 160 mAh g⁻¹ at first discharge process, 90% of theoretical capacity of pure FePO₄, and 135 mAh g⁻¹ in the following cycles at 0.1 C rate. At 1 and 3 C rates, the capacities are 110 and 85 mAh g⁻¹, respectively, which is much higher than that of previously reported for modified FePO₄ materials. Electrochemical impedance spectroscopy (EIS) tests proved that mesoporous structure in FePO₄ materials enhanced the lithium ion intercalation/deintercalation kinetics as indicated by smaller charge transfer resistance (R_{ct}) of these materials. These results revealed that this mesoporous electrode material can be a potential candidate for high-power energy conversion devices.

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1. Introduction

In recent years, nanostructured electrode materials, such as mesoporous materials, have shown promising applications in energy conversion devices [1–5]. Fe-based cathode materials, such as Fe(III)PO₄ and LiFe(II)PO₄, are attractive lithium intercalation electrode materials for their low cost, environmentally friendly and high theoretical specific capacity [6–12]. FePO₄ shows a discharge process from 3.5 V down to 2.5 V and a theoretical specific capacity of 178 mAh g⁻¹ upon 1 mol of lithium intercalation [6]. However, the practical specific capacity of FePO₄ is quite low due to the poor kinetics of lithium intercalation/deintercalation process. To improve the electrochemical performance of FePO₄, Croce et al. added RuO₂ to quartz FePO₄ to enhance its specific capacity with a higher material interparticle electronic conductivity [8]. Both amorphous hydrated and

anhydrous FePO₄ were also found to have better electrochemical performance than that of pure crystalline FePO₄ [9–11]. The specific capacity of FePO₄ is still incomparable to its reported theoretical one.

We first reported that importing mesoporous structure into FePO₄, by a surfactant (EO₂₀-PO₇₀-EO₂₀, Pluronic P123) self-assembly method resulted in enhancement of the electrochemical performance of FePO₄ [2]. The preparation conditions and electrochemical performance of the mesoporous FePO₄ were also primarily optimized. Afterwards, mesoporous FePO₄ with smaller pore diameter acted as a good storage material especially as lithium ion intercalation cathode material [13]. By using cetyltrimethyl ammonium bromide (CTAB) as template, this mesoporous FePO₄ had a mesostructure with a pore diameter of 3–4 nm as confirmed by small angle X-ray diffraction compared with the results of Guo et al. [14], where the pore diameters were not large enough for the fast transport of electrolyte and failed to improve the kinetics of lithium ion intercalation with a result of relative low capacity.

In this work, systematic studies on synthesis, characterization and electrochemical performance of mesoporous FePO₄ were conducted, aimed at improving FePO₄ electrochemical performance.

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2. Experimental

2.1. Samples preparation

FePO₄ samples were synthesized by a surfactant (EO₂₀-PO₇₀-EO₂₀, Pluronic P123) self-assembly method similar to that reported in our previous work [2]. After solvent evaporation, precursor gels were firstly dried at 80 °C for at least 10 h, and then calcinated in a muffle furnace in air for 10 h. We synthesized FePO₄ samples with different P123/(Fe + P) molar ratio of 0.013, 0.026, 0.039, and 0.052 (named as 1P, 2P, 3P, and 4P) at different calcination temperatures of 400, 450, 500, 600, and 700 °C. Therefore, we got three series of FePO₄ samples named as follows—(1) 1P-FPO samples: 1P-400, 1P-450, 1P-500, 1P-600, and 1P-700; (2) 3P-FPO samples: 3P-400, 3P-450, 3P-500, 3P-600, and 3P-700; (3) 450 °C-FPO samples: 1P-450, 2P-450, 3P-450, and 4P-450.

The residual carbon in FePO₄ samples was analyzed by elemental analysis using an EA1110 (ThermoQuest Italia S.P.A., Italy) instrument, the precision of the measurements was ±0.3%. X-ray diffraction (XRD) experiments were carried out by a Panalytical X-pert diffractometer (PANalytical, The Netherlands), using Cu K α radiation ($\lambda = 1.54059 \text{ \AA}$). Fourier transform infrared (FTIR) spectra were recorded on an Avatar 360 spectrophotometer (Nicolet, USA) and the resolution of spectra collected at 2 cm⁻¹ interval over the range measured of wavenumber. The mesoporous structure information (specific surface area and pore diameter distributions) of FePO₄ samples were obtained from N₂ sorption isotherm plot on TriStar3000 (Micromeritics, USA) based on Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) equations, the error in determination of BET surface area and porosity was in the range of ±10%. The structure and morphology of FePO₄ samples were further characterized by high resolution transmission electron microscopy (HRTEM) technique by using Tecnai F30 (Philips-FEI, Netherlands) where

the samples were suspended in ethanol solution by the help of ultrasonic bath, then mounted on a carbon holder, and left to dry before examination.

2.2. Cell fabrication and testing

The electrochemical performance of FePO₄ samples were assessed using CR2025 coin cells. The preparation of the electrodes and the assembly of coin cells are the same as that reported in Ref. [2], in which the electrolyte was 1 M LiPF₆ dissolved in EC + DMC (1:1, v/v) and all potentials mentioned in this work were recorded versus Li/Li⁺ electrode. Charge–discharge experiments were performed between 1.5 and 4.0 V at various current densities (0.1, 1, 3 and 0.1 C) consecutively using a LAND CT2001A Battery Cycler (Wuhan, China). Electrochemical impedance spectroscopy (EIS) experiments of these cycled coin cells were done using an impedance/gain-phase analyzer (Solartron SI 1260) combined with an electrochemical interface (Solartron SI 1287) at an equilibrium charge/discharge state. The impedance spectra were obtained by applying a 10 mV potential amplitude excitation over a frequency range from 10⁶ to 10⁻³ Hz. Impedance data acquisition and analysis were performed by using the electrochemical impedance software ZPlot and Zview (version 2.90, Scribner Associates Inc., USA).

3. Results and discussion

3.1. Samples synthesis and phase analysis

Table 1 shows the residual carbon in all synthesized samples and surface properties of the samples. Table 1 shows that the residual carbon is inversely proportional to the temperature used for calcination of samples, i.e., by increasing the temperature from 400 to 500 °C, the amount of residual carbon decreased from 1.48 to 0.94 wt.% in 1P samples, and similarly for 3P samples, the residual carbon decreased upon increasing the tem-

Table 1
Residual carbon and surface properties of FePO₄ samples

Properties	P123/(Fe + P) molar ratio	400 °C	450 °C	500 °C	600 °C	700 °C
Residual carbon content (wt.%) in FePO ₄ samples	1P	1.48	1.30	0.94	0.09	0.06
	2P	N/A	1.67	N/A	N/A	N/A
	3P	1.79	1.74	1.38	0.09	0.06
	4P	N/A	1.72	N/A	N/A	N/A
Specific surfaces area (m ² g ⁻¹) of FePO ₄ samples	1P	101	87	61	2.7	1.4
	2P	N/A	108	N/A	N/A	N/A
	3P	108	113	99	1.9	1.7
	4P	N/A	127	N/A	N/A	N/A
Pore volume (cm ³ g ⁻¹) of FePO ₄ samples	1P	0.28	0.26	0.20	0.02	0.01
	2P	N/A	0.27	N/A	N/A	N/A
	3P	0.38	0.40	0.37	0.01	0.01
	4P	N/A	0.50	N/A	N/A	N/A
Pore diameter (nm) of FePO ₄ samples	1P	4.8	5.0	7.0	N/A	N/A
	2P	N/A	6.2	N/A	N/A	N/A
	3P	7.5	9.0	11.0	N/A	N/A
	4P	N/A	10.0	N/A	N/A	N/A

N/A signifies that these samples were not tested.

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