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Study of improved electrochemical performance of LiFePO_4/C electrode for LIB

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Abstract: Lithium iron phosphate is a most promising cathode material for Li-ion batteries (LIB). But the key barrier limiting its application is extremely low electronic conductivity. Meanwhile the low electron conductivity can be improved by preparing LiFePO_4 with carbon modified. LiFePO_4/C was synthesized by high temperature solid-state reaction using iron (II) oxalate, ammonium dihydrogen phosphate and lithium carbonate with a kind of organic compound (CR) that can be dissolved in the dispersant (ethanol) as carbon sources added to the synthetic precursor in this paper. The samples were characterized by X-ray diffraction, scanning electron microscope observations, charge/discharge test, cyclic voltammetry and carbon analysis. It was believed that the synthesized LiFePO_4/C with perfect olivine structure by X-ray diffraction. The carbon brought about two advantages: (i) an optimized particle size of LiFePO_4 , and (ii) increasing the electronic conductivity and Li^+ diffusivity. The cathode material could demonstrate a charge/discharge flat voltage of 3.4V (Vs Li^+/Li). Especially the active material with 20% organic added according to the final product of LiFePO_4 showed very good electrochemical performance reaching about initial 162.0 mAh/g specific capacity at 0.1C rate and could also keep excellent discharge capacity even at 3C rate (510 mA/g) current and good cycle performance. The carbon content in the final production was only 5.29% (mass fraction).

Key words: Li-ion battery; cathode materials; LiFePO_4/C

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1 Introduction

The ever-growing demand for portable batteries with high energy density is exerting pressure for the development of advanced Li-ion batteries. The remaining challenges are cost, abuse tolerance, and low-temperature performance. One critical challenge is the thermal stability of the battery components. Presently LiFePO_4 with a structure of olivine-type, first published by Goodenough^[1], has become more concerned because of its high energy density, low raw materials cost, environmental friendliness and safety^[2-8]. So the material is particularly suitable for the production of electrochemical accumulators with high power. But the extremely low electronic conductivity and low Li^+ diffusivity made the capacity of the LiFePO_4 electrode decreased dramatically when working at large current density^[1]. So the LiFePO_4 electrode must be modified so as to improve the electron conductivity and lithium diffusivity.

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2 Experimental

2.1 Synthesis of cathode materials

The cathode materials were prepared by solid-state reaction of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Aldrich), $\text{NH}_4\text{H}_2\text{PO}_4$ (Aldrich), Li_2CO_3 (Aldrich) and CR (Aldrich). The stoichiometric mixtures of the raw materials were mixed by ball-milling (500 r/min) for 12 h with agate balls in alcohol, followed by drying. Then these mixture were ground with a mortar and pestle and calcined at 350°C for 8 h in flowing Ar_2 . Final firing for crystallization of the olivine phase was made at 750°C for 24 h in Ar_2 flowing ambience. The samples of (a), (b), (c), (d) and (e) correspond to the LiFePO_4 with 0 (uncoated), 10%, 15%, 20% and 25% organic compound mixed respectively according to the product of LiFePO_4 .

2.2 Characteristic of cathode materials

2.2.1 Phase identify and particle size analysis

The phase analysis and particle size of all samples were determined by using X-ray diffraction (XRD, D/max-r A type Cu-K α 1, 40 kV, 300 mA, 10° – 70° , Japan).

2.2.2 Microstructures of the cathode material

Scanning electron microscope (SEM) was used to examine the microstructures of the cathode material (SEM, KYKY 2800, Japan).

2.2.3 Electrochemical measurements

The electrochemical cycling performances of the cathode powders were evaluated at room temperature (20°C) with laboratory-scale Li/cathode button cells including a lithium metal foil as counter electrode, a composite of 80% (mass fraction) cathode powder, 10% (mass fraction) acetylene black (AB), and 10% (mass fraction) polytetrafluoroethylene (PTFE) binder as a cathode. A micro-porous polypropylene film (Celgard 2400) was used as a separator and 1 M LiPF_6 solution with the 1 : 1 volumetric (EC+DEC). All cells were assembled inside a glove box filled with ultra-pure argon. Charge/discharge characteristics of the active material were recorded in the potential range 2.5 V and 4.1 V using a LAND CT2001A computer-controlled galvanostat.

2.2.4 Cyclic voltammetry test and electrochemical impedance spectroscopy (EIS) measurements

The samples d and a, b, c, d, e are applied to study the cyclic voltammetry of power micro-electrode and electrochemical impedance spectroscopy respectively by using Model 273A Potentiostat/Galvanostat and Model 5210 Dual Phase Lock-in Amplifier, USA.

2.2.5 Carbon concentration

The carbon concentration of the composite was analyzed using CS-444 carbon/sulfur determinator (LECO Co. USA).

3 Results and discussion

The phases of all the samples were shown in Fig. 1 a, b, c, d and e from the powder X-ray diffraction (XRD). It was identified that the synthetic LiFePO_4 phase with ordered olivine structure. We can also know from the Table 1 that the diffraction intensity of 311 peak of LiFePO_4 compound declines with the more carbon coated in the LiFePO_4/C composites and the particle size of LiFePO_4 turns finer and finer. This means that with the increasing amount of carbon coated the amorphous phases in the composite are increasing too. But their peaks are in the same positions indicating that carbon coating doesn't affect the inner

crystal structure of LiFePO₄.

Table 1 Relative intensity of 311 peak and grain size of (a), (b), (c), (d), and (e) samples

Samples	$I_{311}/(\text{CPS})$	XS/nm
a	28250	69.3
b	18013	59.4
c	15643	50.5
d	14253	43.6
e	12853	38.3

From the SEM photographs of the Fig. 2 it can also be known that the adding of carbon has an evident effect on controlling the growing particles of cathode power, and the grain size of LiFePO₄/C (d) is more well-proportioned than that of the pure LiFePO₄ (a). A wide size distribution ranging from a few to 5 μm for the LiFePO₄ particles could be recognized in Fig. 2(a). The refined LiFePO₄ grain coated by carbon can help to increase the diffusivity of lithium ion and electron transfers during the electrode process.

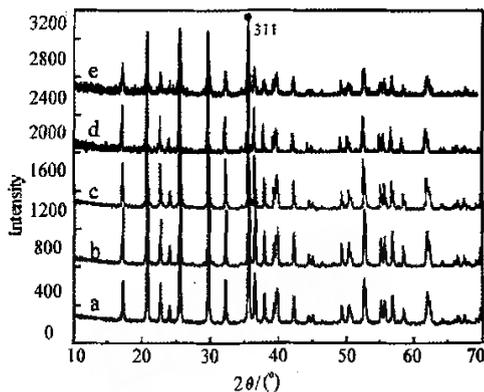


Fig. 1 XRD patterns of a, b, c, d, and e samples

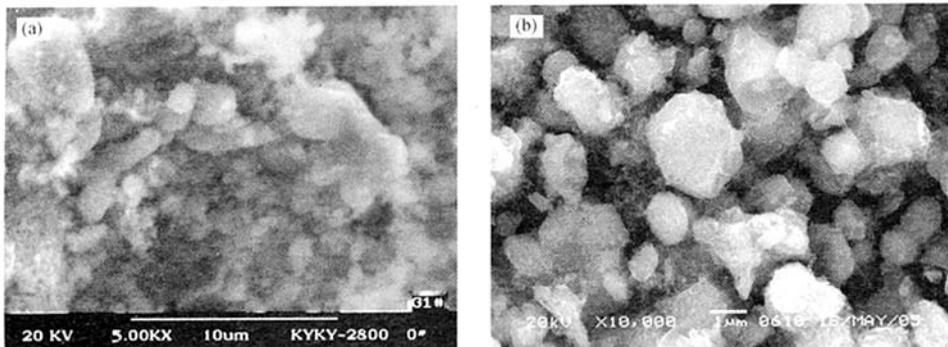


Fig. 2 SEM micrographs of sample (a) and sample (b)

The electrochemical insertion/deinsertion of lithium ions into LiFePO₄ can be described as following formulas (1):



This reaction occurs on a flat plateau at 3.4 V vs. Li⁺/Li as a two-phase process of FePO₄/LiFePO₄, and the complete extraction of lithium (x=1) corresponds to a theoretical specific capacity of 170 mAh/g.

From the Fig. 4 above we can clearly know that initial specific capacity of the pure LiFePO₄ can only get 120.4 mAh/g owing to the low electric conductivity^[1]. While the LiFePO₄/C composites showed excellent electrochemical performance. The sampled can retain 156.90 mAh/g after 20 cycles with the initial capacity of 162.0 mAh/g and the carbon weight amount is only 5.29% and can keep relative high specific capacity even at 3C rate. The capacity loss is very small. The reason is that carbon coated can improve the active material conductivity and the Li⁺ diffusivity.

We investigated the electrochemical performance of sample (d) by using cycle voltammetry. Fig. 4 shows a cyclic voltammogram of sample (d) measured at 20°C. The pair of peaks, consisting of an anodic and a cathodic peak, observed around 3.4 V vs. Li/Li⁺ corresponded to the two-phase charge/discharge re-

action of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple. This voltammogram indicated that only one electrochemical reaction, corresponding to the peak pair shown around 3.4 V vs. Li/Li^+ , occurred during the charge and discharge of the LiFePO_4 .

Fig. 5 represents the Nyquist plots of samples (a, b, c, d and e) at 3.52 V measured at ambient temperature. From the plots we can know that with the increasing of carbon amount the Rct decreased from several hundred ohm to about 50 Ω . That because the carbon coated on the surface of particles of LiFePO_4 can improve the electron conductivity of the electrode. Here we can know from the Fig. 6(a) and (b)^[8].

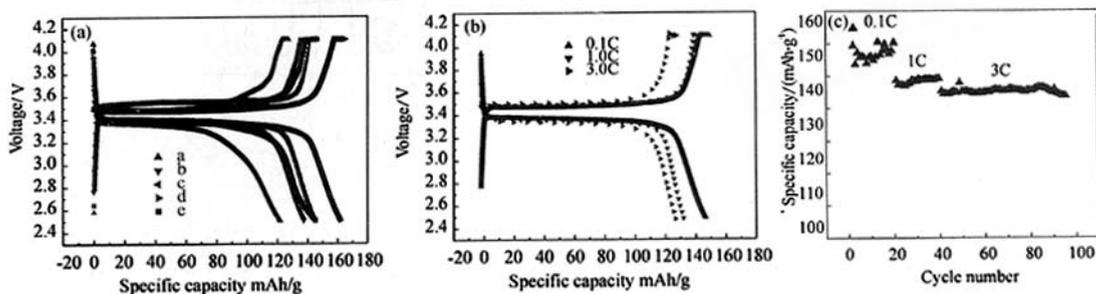


Fig. 3 (a) Initial charge-discharge profiles of samples a, b, c, d, and e; (b) Initial charge-discharge curves of sample (d) at 0.1C, 1C and 3C rate; (c) Cycling behaviors of the sample (d)

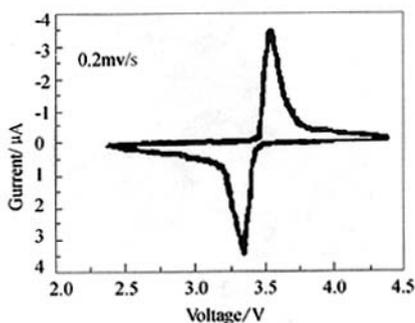


Fig. 4 The cyclic voltammograms curve of sample d at 0.2 mV/s, measure at 20°C

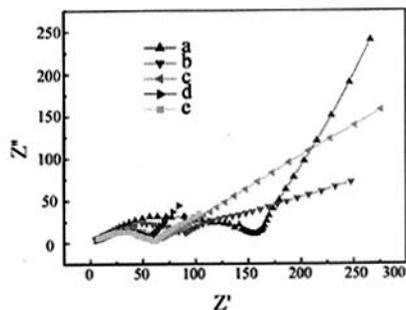


Fig. 5 The EIS curves of samples (a, b, c, d and e), charged to 3.52 V, measure at 20°C

4 Conclusions

The adding CR to the synthetic precursor can help to improve the electrical conductivity of LiFePO_4 and prevent growth of the particle. The most important thing is that the production of LiFePO_4 will be covered by refined carbon uniformity after the precursor has been sintered. It contributes to the transfer of electron and Li^+ during the electrode process. Meanwhile the carbon existing can prevent the production of Fe^{3+} phase to some extent. The sample (d) showed high specific capacity and cycle capability exhibiting $\sim 95\%$ theoretic capacity, 162.0 mAh/g, at room temperature. This indicates that LiFePO_4/C composite will be an attractive candidate as cathode material for Li-ion battery.

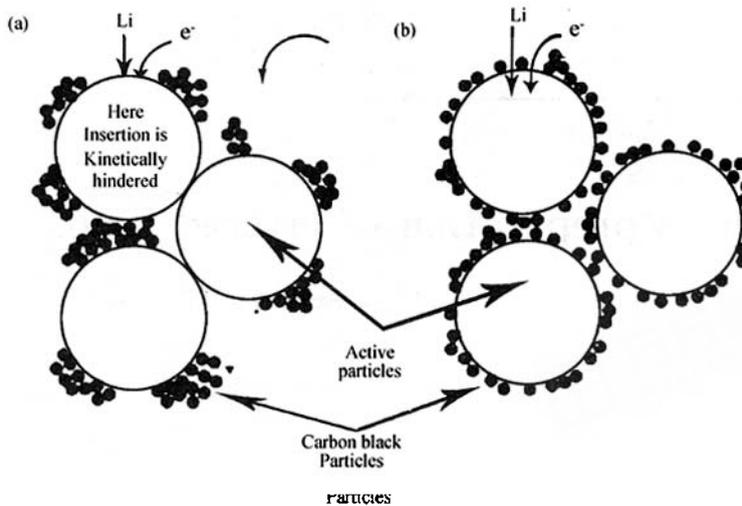


Fig. 6 The kinetics of Li ions and electron in LiFePO_4 cathodes, carbon distribute ununiformly (a) and uniformly (b)

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