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Characterization and electrochemical properties of high tap-density $LiFePO_4$/C cathode materials by a combination of carbothermal reduction and molten salt methods

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ABSTRACT

Olivine-structured $LiFePO_4$ cathode materials were prepared via a combination of carbothermal reduction (CR) and molten salt (MS) methods. To enhance the powder's tap density, the $LiFePO_4$/C composite was pressed into pellets and then sintered for at least 1 h at 1028 K in the reaction environment of KCl molten salts. The use of molten salt can effectively influence unit cell volume, morphology and tap density of particles, and consequently change the electrochemical performance of $LiFePO_4$/C. The composites were characterized in detail by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), dynamic light scattering (DLS), Raman spectroscopy and tap density testing. The final product with high tap density of 1.50 g cm^{-3} contains 4.58 wt% carbon and exhibits good discharge capacity of 141 mAh g^{-1} at a 0.2 C-rate in the potential range of 2.8–4.0 V.

1. Introduction

$LiFePO_4$ is regarded as a practical and popular cathode material for high power lithium-ion batteries due to its superior safety, low toxicity, high rate capability, low raw material cost, long cycle life, and high theoretical capacity of 170 mAh g^{-1} with a flat charge/discharge potential at 3.5/3.4 V due to the stable Fe^{2+}/Fe^{3+} redox couple versus Li/Li^+ [1].

However, $LiFePO_4$ has intrinsic disadvantages of low tap density, low electronic conductivity, and slow lithium-ion diffusion, which limit its practical application in lithium-ion batteries. To enhance the reversible capacity and rate performance of $LiFePO_4$ cathode materials, several methods have been investigated and reported, such as doping with metal cations [2,3], coating with carbon [4–6], modifying surface morphology [7,8] and minimizing particle size [9–11]. In contrast, there has been little study on increasing the tap density of $LiFePO_4$/C composites. According to the previous studies [5,12,13], higher tap density significantly increased volumetric energy density of $LiFePO_4$/C composites, depending on the carbon content and particle size. Moreover, spherical $LiFePO_4$ materials have higher tap density than irregular particles and greater safety associated with their low interfacial energy [12,13].

Molten salt synthesis is a simple and fast method for preparing highly crystalline inorganic compounds with unusual morphologies. Molten salts as a reaction media could provide a liquid reaction environment for reactants, thereby accelerating the ion diffusion rate and heat transfer rate to change the solubility and reactivity of reactants [14]. Recently, some positive electrode materials for lithium ion batteries were prepared by a molten salt synthesis method, such as $LiCoO_2$ [15], $Li_4Mn_5O_{12}$ [16], $LiFePO_4$ [13], $LiNi_{0.5}Co_{0.5}O_2$ [17] and $Li_4Ti_5O_{12}$ [18]. In 2007, Ni et al. [13] used an expensive divalent iron source ($FeC_2O_4{\cdot}2H_2O$) as the starting material, and successfully synthesized high tap-density $LiFePO_4$/C composites by a KCl molten salt method. The as-synthesized $LiFePO_4$/C had a well-crystallized olivine structure and spherical morphology, and it could deliver an initial discharge capacity of 130 mAh g^{-1} at 0.1 C in the potential range of 2.0–4.0 V. To increase tap density and discharge capacity of $LiFePO_4$/C composites, we combined the advantages of carbothermal reduction and KCl molten salt methods to synthesize and optimize the balance between tap density and specific discharge capacity.

In this work, we prepared $LiFePO_4$/C composites by a carbothermal reduction (CR) method using cheap Fe_2O_3 as the starting material, and then introduced a KCl-assisted molten salt (MS) method to reprocess $LiFePO_4$/C and influence its morphology and particle size. To the best of our knowledge, this combination

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method is an improved technique for preparing inexpensive and high tap-density $LiFePO_4/C$ composites with high discharge capacity.

2. Experimental

2.1. Synthesis of high tap-density $LiFePO_4/C$ composites

$LiFePO_4/C$ composites were synthesized from the carbothermal reduction method and denoted as the CR sample. The industrial starting materials Li_2CO_3, Fe_2O_3, $NH_4H_2PO_4$ and polyethylene glycol (PEG) were weighed in a stoichiometric molar ratio (Li:Fe:P = 1:1:1), then mixed and ground in a planetary ball-mill with a rotation speed of 300 rpm for 3 h in acetone. The mass ratio of the starting materials to zirconia balls was selected to be 1:6. To investigate the relationship between the carbon content of $LiFePO_4/C$ composites and the tap density, various wt% amounts (compared to the $LiFePO_4$ to be coated) of polyethylene glycol were used. After milling, the dark red sticky mixture was dried to remove acetone and ground in motars. The mixture was initially preheated at 573 K for 2 h and then calcined at 973 K for 8 h in a quartz-tube furnace with N_2 flow.

The as-prepared $LiFePO_4/C$ composite was pressed into pellets and covered with KCl (99.5%, Aldrich) in a molar ratio of 1:6, which was placed in an alumina crucible and calcined at 1028 K under flowing N_2 for 0.5–5.0 h. The final products (denoted as the MS samples) were thoroughly washed with de-ionized water and then with ethyl alcohol [13] and filtered and dried at 393 K overnight in vacuum.

To investigate the effect of KCl molten salt on the structure, morphology and particle size of $LiFePO_4/C$ composites, a comparison of products synthesized using and not using the MS method was conducted. The $LiFePO_4/C$ composites were prepared first by the CR method, and then sintered for 1 h at 1028 K both with and without assistance of KCl molten salts. The former product using the MS method is denoted as the MS sample, whereas the latter product without using the MS method as the NR sample.

2.2. Material characterization

Powder samples were identified for structural analysis using an X-ray diffractometer (XRD), Siemens D-5000, Mac Science MXP18, equipped with a nickel-filtered Cu Kα radiation source ($\lambda = 1.5405$ Å). The diffraction patterns were recorded between scattering angles of 15° and 75° in steps of 0.02°. Crystal structure refinements were carried out by the Rietveld method using the General Structure Analysis System (GSAS) software suite. Field-emission scanning electron microscope (FE-SEM, Hitachi S-3500V) was used to observe particle morphology. The microstructure and morphology of the samples were observed using a high resolution transmission electron microscope (HRTEM, Hitachi HF 2000) equipped with a field emission gun. Electron diffraction patterns were obtained through selected area electron diffraction (SAED). The elemental composition of the separated phases was determined by nanobeam energy dispersive spectroscopy (EDS). For these experiments, samples were previously dispersed in acetone and deposited on a holey copper grid coated with a silicon monoxide film. The surface carbon structure in the $LiFePO_4/C$ composite was investigated by Raman spectroscopy (ISA T64000) in the range of 800–1750 cm^{-1}. The excitation wavelength was supplied by an internal 10 mW Ar-ion laser.

The particle size distribution was measured by a dynamic light-scattering particle size analyzer (DLS, Malvern Zetasizer Nano). The resistivity of samples was measured by four-point conductivity measurements with a Keithley Model 2400S source meter. Each sample weighed about 0.2 g, and was pressed into pellets under 10 tons cm^{-2} pressure. According to the Ven der Pauw method: $\sigma = \ln 2 \times \pi^{-1} \times t^{-1} \times R^{-1}$ [19], the resistivity, R, and thickness, t, of samples were used to evaluate the electronic conductivity, σ. The carbon content in $LiFePO_4/C$ composites was determined by total organic carbon (TOC) analysis. TOC measurements were conducted using an OIA Model Solids module, which was based on the detection of CO_2 resulting from the combustion of organics measured by an infrared gas analysis method. The absorbance or concentration of CO_2 was calibrated by a standard solution determined with a non-dispersive infrared (NDIR) gas analyzer. The tap density of $LiFePO_4/C$ composites was determined by a tapping tester (Shin Kwang Machinery Industry Co. Ltd.). After measuring the weight of the powder, the cylinder filled with the powder was fixed on the desk. The vibration desk vibrated vertically at a tapping rate of 85 times per minute with an amplitude of 2 cm, and the cylinder tapped approximately 1000 times. The tap density of $LiFePO_4/C$ composite materials was calculated using the weight and volume of the powder.

2.3. Electrochemical characterization

The cathodes were prepared by mixing 85 wt% active materials with 10 wt% conductive carbon black and 5 wt% poly(vinylidene fluoride) in a N-methyl-2-pyrrolidone (NMP) solvent, which was then applied onto an etched aluminum foil current collector and dried at 393 K for 12 h in an oven. The thickness of the coating electrodes was about 80 μm with the active material loading per geometric area of 3.73 ± 0.22 mg cm^{-2}. Lithium metal (Foote Mineral) was used as the anode and 1 M solution of $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1, v/v) (Tomiyama Chemicals) was used as the electrolyte with a Celgard membrane as the separator. Finally, the CR2032 coin cells were assembled in a glove box filled with argon gas. The cells were galvanostatically cycled at a current of 0.2 C with cut-off voltages of 2.8 and 4.0 V (versus Li/Li^+) at 298 K in a multi-channel battery tester (Maccor 4000).

Cyclic voltammetric measurements were performed on the Li-ion coin cell to identify the characteristics of the redox reactions using a Solartron 1287 Electrochemical Interface with a scan rate of 0.05–1.0 mV s^{-1} between 2.8 and 4.6 V. The cells were assembled inside a glove box with lithium metal foil as the counter and the reference electrode. The working electrode was the $LiFePO_4$ cathode electrode prepared by the above slurry coating procedure with a dimension of 1.33 cm^2, and the electrolyte was the same as that for the coin cell.

3. Results and discussion

3.1. X-ray diffraction

Powder X-ray diffraction was carried out to study the effect of KCl molten salts on the lattice structure of $LiFePO_4/C$ composites after the re-sintering process. Fig. 1 shows the diffraction peaks of all the samples are identified as the orthorhombic phase with the space group Pnma, which indicates that the olivine structure did not change during the reprocessing of KCl molten salt containing $LiFePO_4/C$ composites sintered in the KCl molten phase and the final products were washed with de-ionized water to remove residual KCl salts. The R factors and the lattice parameters based on the Rietveld refinement of all four samples are summarized in Table 1, and the fitting results of observed and calculated patterns of MS samples sintered for 1.0 h are presented in Fig. 2. Satisfactory and acceptable statistical fit values (R_{wp} and R_p) were obtained. It was found that lattice parameters of the as-prepared $LiFePO_4/C$ composites were influenced by the reprocessing of KCl molten