



Synthesis, characterization and electrochemical performances of MoO₂ and carbon co-coated LiFePO₄ cathode materials

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Abstract

The MoO₂ and carbon co-coated LiFePO₄ cathode materials were synthesized by a combined technique of solid state synthesis and the sol–gel method. Phase compositions and microstructures of the products were characterized by X-ray powder diffraction (XRD), Raman, SEM and TEM. Results indicate that MoO₂ can sufficiently coat on the LiFePO₄ surface and does not alter LiFePO₄ crystal structure, and the existence of MoO₂ increases the graphitization degree of carbon. SEM and TEM images reveal that MoO₂ presence has little impact on LiFePO₄ particle size. The electrochemical behavior of cathode materials was analyzed using galvanostatic measurement and cyclic voltammetry (CV). The results show that the existence of MoO₂ improves electrochemical performance of LiFePO₄ cathode material in specific capability and low-temperature behavior. The apparent lithium ion diffusion coefficient increases with MoO₂ content and maximizes around the MoO₂ content of $x=5$ wt%. It has been had further proved that the higher electronic conductivity of MoO₂ and carbon enhances the lithium ion transport to improve the electrochemical performance of LiFePO₄ cathode materials.

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1. Introduction

Lithium-ion batteries are regarded as the most advanced energy storage systems, which have been widely used in electric vehicles (EVs), hybrid electric vehicles (HEVs), dispersed energy storage systems, and so on. Since the olivine-type lithium iron phosphate (LiFePO₄) was reported by Padhi et al. in 1997 [1], it has received much attention as a promising storage compound for cathodes in lithium-ion batteries due to LiFePO₄ has high theoretical specific capacity (about 170 mAh g⁻¹), low costs, environmental friendliness and safety [2–4]. In addition, LiFePO₄ presents good cycle stability owing to its structural similarity in the charged and discharged states [5].

However, LiFePO₄ shows poor electronic conductivity and low lithium ion diffusivity, which are an obstacle when applied in high power batteries [1,6]. In order to overcome these problems, all kinds of methods have been proposed including carbon-coating on LiFePO₄ surface [7–10], cation doping [11–15] and particle size minimization [16–18]. Wherein, the carbon-coating and particles size minimization can improve the electrochemical performances of LiFePO₄ due to the increasing electronic conductivity and shortening diffusion length of lithium ions, respectively, however, the carbon addition and small particles size will reduce tap density and energy density [19]. Recently, some new methods have been explored to enhance electrochemical performances of LiFePO₄, such as oxide coated or modified LiFePO₄/C composites. Li et al. [20] proposed that SiO₂ coated LiFePO₄/C effectively enhanced the cycling capacity and reduced capacity fading at high temperature and alleviated the cell impedance. Liu et al. reported that the electrochemical lithium-ion deintercalation–intercalation processes of CeO₂ modified LiFePO₄ electrodes were improved compared to the pristine

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LiFePO₄ electrode [21]. CuO and carbon co-coated LiFePO₄ was reported by Cui et al. [22], the study found that the co-coating reduced the capacity fading and the interfacial resistances and the polarization of the cathode. Jin et al. reported that V₂O₃ modified LiFePO₄/C materials exhibited improved electrochemical performance both in rate capability and low-temperature behavior, and the presence of V₂O₃ improved the apparent lithium ion diffusion coefficient of LiFePO₄/C [23].

After review on the existing literatures, it can be found that oxide coating or modifying can improve the electrochemical performances of LiFePO₄ in cycling capacity, capacity fading, cell impedance, polarization and apparent lithium ion diffusion coefficient, and so on. But, most of oxides are electrochemical inactive metal oxide or semiconductor oxide with lower electronic conductivities in these literatures. In this paper, we have attempted to synthesize MoO₂ and carbon co-coated LiFePO₄ cathode materials by a combined technique of solid state synthesis and the sol–gel method. MoO₂ possesses high electrical conductivity [24], therefore, it is interesting to investigate the influence of MoO₂ and carbon co-coating on the electrochemical performance of LiFePO₄ cathode materials.

2. Experimental

2.1. Synthesis

LiFePO₄ cathode materials were prepared by solid phase synthesis process. The starting materials were ammonium dihydrogen phosphate (NH₄H₂PO₄, A.R.), iron oxalate dehydrate (FeC₂O₄·2H₂O, A.R.), and lithium carbonate (Li₂CO₃, A.R.). Firstly, all the starting materials were dispersed into ethanol and then ball milled for 4 h. The mixture was initially dried at 80 °C, hand ground with an agate mortar, and treated at 350 °C for 6 h, then calcined at 700 °C for 24 h in a tube furnace under flow purified N₂ atmosphere with the heating rate of 5 °C min⁻¹. After the tube furnace is cooled to room temperature, LiFePO₄ was obtained and was defined as sample F, it was used as a raw material for MoO₂ and carbon co-coated LiFePO₄ cathode materials. The MoO₂ and carbon co-coated LiFePO₄ cathode materials were synthesized by a sol–gel method. Firstly, ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O, A.R.) and citric acid (C₆H₈O₇·H₂O, A.R., 10 wt% of sample F mass) were dissolved into distilled water, then added LiFePO₄ (sample F). Then the slurry was stirred for 1 h and dried at 80 °C. Finally, the dried precursors were treated at 350 °C for 3 h then was heated to 600 °C for 6 h in a purified N₂ gas flow and the MoO₂ and carbon co-coated LiFePO₄ cathode materials (MoO₂ content is 0 wt%, 1 wt%, 3 wt%, 5 wt% and 10 wt%) were obtained. The obtained products were defined as sample A, B, C, D and E, respectively.

2.2. Characterization and electrochemical measurements

Structural analysis was carried out using X-ray diffraction (XRD, X'Pert PRO, CuKα radiation) and Raman spectroscopy (Raman, InVia, wavelength is 514.5 nm). The morphology and

microstructure of the MoO₂ and carbon co-coated LiFePO₄ cathode materials were observed with a scanning electron microscope (SEM, FEI Quanta 200F) and a transmission electron microscope (TEM, JEM-2100).

Coin cells of the 2430 configuration were assembled in an argon-filled glove box. The cathode was prepared by mixing 80 wt% MoO₂ and carbon co-coated LiFePO₄ powder with 10 wt% conductive carbon black and 10 wt% polyvinylidene fluoride (PVDF) in a n-methyl-2-pyrrolidone (NMP) solution, which was then coated onto aluminum foil current collector and dried at 115 °C for 12 h in a vacuum drying oven. Lithium metal was used as the anode and a 1 M solution of LiPF₆ in EC: DEC (1:1, v/v) was used as the electrolyte with a microporous polypropylene sheet (Celgard 2320) as the separator. The cells were charged and discharged galvanostatically between 2.5 V and 4.2 V (vs. Li/Li⁺) using a battery test system (LAND CT2001A). The cyclic voltammetry (CV) curves were obtained between the ranges of 2.5–4.2 V on an electrochemical work station (CHI 660E).

3. Results and discussion

3.1. Phase composition and morphology

Fig. 1 shows the X-ray diffraction patterns (XRD) of MoO₂ and carbon co-coated LiFePO₄ cathode materials. It can be seen that the main phase in these samples is orthorhombic LiFePO₄ with a space group of Pmna, and there is no evidence of diffraction peaks for MoO₂ and carbon due to their amorphous structure and/or low content in samples A, B, C and D. With the content of MoO₂ increasing, the diffraction peaks of MoO₂ are detected in sample E. The formation of MoO₂ must be from the decomposition of (NH₄)₆Mo₇O₂₄·4H₂O and the carbothermal reduction from Mo⁶⁺ to Mo⁴⁺. Because the sensitivity of XRD analysis is finite, MoO₂ is likely present in samples B, C and D. In addition, no impurities such as Fe₂P, Li₃PO₄ and others are

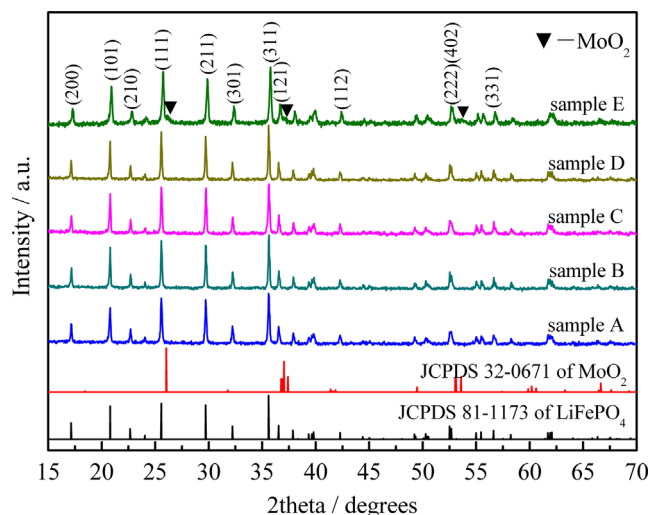


Fig. 1. XRD patterns of the MoO₂ and carbon co-coated LiFePO₄ cathode materials.

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