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Characterization and electrochemical performances of MoO_2 modified $LiFePO_4/C$ cathode materials synthesized by in situ synthesis method

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ABSTRACT

The MoO_2 modified $LiFePO_4/C$ cathode materials were synthesized by in situ synthesis method. Phase compositions and microstructures of the products were characterized by X-ray powder diffraction (XRD), SEM, TEM and EDS. Results indicate that MoO_2 can sufficiently coat on the $LiFePO_4$ surface and does not alter $LiFePO_4$ crystal structure, the existence of MoO_2 decreases the particles size and increases the tap density of cathode materials. The electrochemical behavior of cathode materials was analyzed using galvanostatic measurement, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The results show that the existence of MoO_2 improves electrochemical performance of $LiFePO_4$ cathode materials in specific capability and lithium ion diffusion and charge transfer resistance. The initial charge–discharge specific capacity and apparent lithium ion diffusion coefficient increase, the charge transfer resistance decreases with MoO_2 content and maximizes around the MoO_2 content is 5 wt%. It has been had further proved that the MoO_2 adding enhances the electronic conductivity and lithium ion transport to improve the electrochemical performance of $LiFePO_4$ cathode materials.

1. Introduction

Since the olivine-type lithium iron phosphate ($LiFePO_4$) was reported by Padhi et al. in 1997 [1], it has received widespread attention as a promising cathode material for high power applications, such as power tools or hybrid electric vehicles. It is because that $LiFePO_4$ possess high theoretical capacity (170 mA h g^{-1}), low cost, low toxicity, environmental friendliness, thermal stability and excellent cycle stability [2–4]. Unfortunately, the major problems of $LiFePO_4$ are low electronic conductivity ($\sim 10^{-9}$ S cm^{-1}), low ionic diffusion coefficient ($\sim 1.8 \times 10^{-14}$ cm^2 s^{-1}) [5] and poor tap density [6].

The problems of conductivity and lithium ion diffusion can be solved by some methods and technologies including coating with conducting polymers [7] and carbon [8] or silver [9], cation doping [10–14] and particle size minimization [15–17]. The carbon coating and particles size minimization can improve the electrochemical performances of $LiFePO_4$ due to the increase electronic conductivity and the short diffusion length of lithium ions, respectively. Cation doping will work particularly well when combined with carbon coating. But carbon addition and small particles size will reduce tap density and energy density [6]. Recently, some studies showed that the surface coating or modification of $LiFePO_4$ with metal or nonmetal oxide significantly improved the electrochemical performance of $LiFePO_4$ cathode materials, such as SiO_2 [18], CuO [19], V_2O_3 [20] and CeO_2 [21] coated or modified $LiFePO_4/C$ composites. However, most of oxides reported are electrochemical inactive oxides or semiconductor oxides, which electronic conductivity are lower. In this study, we attempt to introduce a conducting metal oxide (MoO_2) as the third phase to modify carbon-coated $LiFePO_4$ ($LiFePO_4/C$) particles in order to enhance their electrochemical performance. MoO_2 possesses metallic conductivity [22] (the electronic conductivity is about 1.14×10^3 S cm^{-1} [23,24]), Therefore, it is interesting to investigate the influence of MoO_2 modification on the electrochemical performance of $LiFePO_4/C$ cathode materials.

2. Experimental

2.1. Synthesis

The MoO_2 modified $LiFePO_4/C$ cathode materials were prepared by in situ synthesis method. The starting materials were ammonium dihydrogen phosphate ($NH_4H_2PO_4$, A.R.), iron oxalate dehydrate ($FeC_2O_4 \cdot 2H_2O$, A.R.), lithium carbonate (Li_2CO_3, A.R.), ammonium molybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, A.R.) and glucose ($C_6H_{12}O_6$, AR, 5 wt% of starting materials). Firstly, all the starting materials were dispersed into ethanol and then ball milled for 4 h. The mixture was initially dried

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at 85 °C, then treated at 350 °C for 6 h, finally calcined at 700 °C for 24 h in a tube furnace under flow purified N_2 atmosphere with the heating rate of 5 °C min^{-1}. After the tube furnace is cooled to room temperature, The MoO_2 modified $LiFePO_4$/C cathode materials (MoO_2 content is 0 wt%, 1 wt%, 3 wt%, 5 wt%, 7 wt% and 10 wt%, respectively) were obtained. The obtained products were defined as sample A, B, C, D, E and F, respectively. The carbon content of samples is about 0.5 wt%.

2.2. Characterization and electrochemical measurements

Structural analysis was carried out using X-ray diffraction (XRD, X'Pert PRO, Cu Kα radiation). The morphology and microstructure of MoO_2 modified $LiFePO_4$/C cathode materials were observed with a scanning electron microscope (SEM, FEI Quanta 200F) and a transmission electron microscope (TEM, JEM-2100). The element distribution of particles surface were analyzed by energy-dispersive spectrometry (EDS). The density of samples was measured on tap density instrument (PF-200B).

Coin cells of the 2430 configuration were assembled in an argon–filled glove box. The cathode was prepared by mixing 80 wt% MoO_2 modified $LiFePO_4$/C 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 $LiPF_6$ in EC: DEC (1: 1, v/v) was used as the electrolyte with a microporous polypropylene sheet (Celgard 2320) as the separator. The charge–discharge test was conducted on a battery test system (Land, C2001A) with cut-off voltages of 2.5 V and 4.2 V, the cyclic voltammetry (CV) was conducted on a CHI660E electrochemical workstation in the voltage range of 2.5–4.2 V, and the electrochemical impedance spectroscopy (EIS) was employed using a CHI660E electrochemical workstation over the frequency range from 0.01 to 100 kHz with amplitude of 5 mV at room temperature.

3. Results and discussion

3.1. Phase composition and morphology

Fig. 1 shows the X–ray diffraction patterns (XRD) of MoO_2 modified $LiFePO_4$/C cathode materials. It can be seen that the main phase of these samples can be identified as $LiFePO_4$ with an ordered olivine structure indexed to orthorhombic *Pnma* (PDF card number: 81-1173), and there is no evidence of diffraction peaks for MoO_2 and carbon due to their amorphous structure and/or low content in samples A, B, C, D and E (Fig. 1a). With the content of MoO_2 increasing, the diffraction peaks of MoO_2 are detected in sample F (Fig. 1b). The formation of MoO_2 must be from the decomposition of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ and the carbothermal reduction from Mo^{6+} to Mo^{4+}, the possible reaction mechanism is $H_{24}N_6O_{24}Mo_7{\cdot}4H_2O \rightarrow 7MoO_3 + 6NH_3\uparrow + 7H_2O\uparrow$, $2MoO_3 + C \rightarrow 2MoO_2 + CO_2\uparrow$ and $Fe_2C_2O_4{\cdot}2H_2O \rightarrow 2FeO + 2CO\uparrow + 2H_2O\uparrow$, $MoO_3 + CO \rightarrow MoO_2 + CO_2$. Because the sensitivity of XRD analysis is finite, MoO_2 is likely present in samples B, C, D and E. In addition, no impurities such as MoO_3, Li_3PO_4 and others are observed. All diffraction peaks are narrow, indicating that the $LiFePO_4$ grains are high crystallinity.

Fig. 2 shows SEM images of sample A (Fig. 2a), sample B (Fig. 2b), sample C (Fig. 2c), sample D (Fig. 2d), and sample E (Fig. 2e). The SEM images show that the samples are uniform in particle size and no agglomeration, the particles size of cathode materials decreases gradually with increase of MoO_2 content, sample A without MoO_2 is about 700 nm, sample C with 3 wt% MoO_2 is about 500 nm, and sample E with 7 wt% MoO_2 is about 300 nm. The decomposition process of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ and the existence of MoO_2 inhibit grain growth of $LiFePO_4$ effectively and improve the particles dispersion. The existence of MoO_2 would be good for improving the electrochemical performances of cathode materials because: (1) MoO_2 possesses high electronic conductivity; (2) The decreased particles size can shorten diffusion length of lithium ions to improve the lithium ions diffusion coefficient of cathode materials. Fig. 3 shows TEM images of sample A (Fig. 3a) and sample D (Fig. 3b), we can find that the surface of sample D is rougher than sample A due to MoO_2 coating on the surface of $LiFePO_4$ particles, and it can be seen that MoO_2 and carbon coat on the surface of $LiFePO_4$ particles and fill the interspaces between $LiFePO_4$ particles. Table 1 shows the relationship between MoO_2 content and tap density of cathode materials. It can be found that the sample A without MoO_2 has the minimum tap density and sample B has the maximum tap density. The tap density decrease gradually with MoO_2 content because that the particles size decreases with MoO_2 content, and the particles size decreasing can reduce the tap density of materials, but the MoO_2 modified $LiFePO_4$/C cathode materials still show higher tap density. The analysis of element distribution mapping by Energy Dispersive Spectroscopy (EDS) (Fig. 4) displays rather uniform distribution of Fe, P, O and Mo in sample D, indicating that molybdenum (MoO_2) is everywhere on the particle surface.

3.2. Electrochemical performance

Fig. 5 shows the initial charge–discharge curves at 0.1 °C at room temperature for all samples. The initial charge–discharge specific capacity of sample A without MoO_2 is very low (about 28.5 mA h g^{-1}), and the voltage platform is very poor, indicating that the electron conductivity of sample A is very low and the electrode polarization is serious during the charge–discharge process. The voltage platform becomes better, electrode polarization decreases and the initial charge–discharge specific capacity increases with the MoO_2 content. When the MoO_2 content is 5 wt%, the sample D has the highest initial discharge specific capacity of 142.6 mAh g^{-1}, the flat voltage platform around 3.5 V corresponding to the two–phase reaction of lithium ions extraction and insertion between $LiFePO_4$ and $FePO_4$ [25,26]. In the synthesis process,

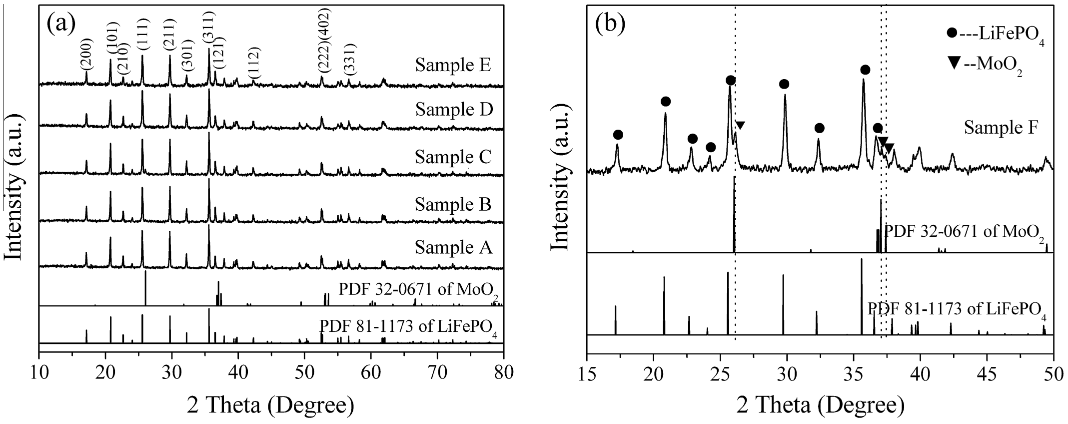

Fig. 1. XRD patterns of the MoO_2 modified $LiFePO_4$/C cathode materials.