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Li ion diffusivity and electrochemical properties of $FePO_4$ nanoparticles acted directly as cathode materials in lithium ion rechargeable batteries

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ABSTRACT

$FePO_4$ nanoparticles, acted directly as cathode materials in lithium ion rechargeable batteries, were synthesized by a microemulsion technique. The various grain-sized and crystal-structured $FePO_4$ samples were obtained by sintering at different temperatures (380 °C, 460 °C, 550 °C, 650 °C) for 3 h in air. The structure and morphology were investigated by means of X-ray diffraction (XRD) and field emission-scanning electron microscopy (FE-SEM); the electrochemical properties were characterized by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and galvanostatic charge and discharge tests. Results show that $FePO_4$ sintered at 380 °C and 460 °C for 3 h are amorphous, and with fine sizes in the range of 10–20 nm. Increasing the sintering temperature leads to an increase in grain size and makes the structure change from amorphous to trigonal. The EIS results show that the R_{ct} value of $FePO_4$ sintered at 460 °C is smaller than that sintered at 650 °C. The diffusion coefficients of lithium ion (D_{Li}) of $FePO_4$ sintered at 380 °C, 460 °C, 550 °C and 650 °C measured by EIS are 8.09×10^{-14}, 1.06×10^{-13}, 4.88×10^{-14} and 2.59×10^{-14} cm^2 s^{-1}, respectively. The difference in diffusivity is also confirmed by CV and the D_{Li} values are 6.71×10^{-14}, 8.28×10^{-14}, 4.89×10^{-14} and 1.60×10^{-14} cm^2 s^{-1}, respectively. The correlations between the electrochemical performances of $FePO_4$ and lithium ion diffusion are acquired. The charge and discharge tests show that the initial discharge specific capacity of $FePO_4$ sintered at 460 °C for 3 h reaches 142.3 mAh g^{-1} at 0.1 °C. These results suggest that nanoparticles and amorphous $FePO_4$ facilitates lithium ion diffusion during the charge/discharge cycles.

1. Introduction

Since the pioneering work of Padhi et al. [1], $LiFePO_4$ has become one of the most promising cathode materials for lithium ion batteries with a competitive theoretical capacity of 170 mAh g^{-1}, which is also low-cost, ecologically friendly, and high safety [2,3]. Therefore, extensive efforts on $LiFePO_4$ have been carried out by researchers [4–7].

For $LiFePO_4$, the extraction/insertion mechanism can be described as the two-phase behavior of the $LiFePO_4$–$FePO_4$ system. Lithium iron phosphate can deintercalate 1 molar lithium ion per formula unit, corresponding to the phase transformation from $LiFePO_4$ phase to $FePO_4$ phase, which maintains nearly the same structure. [8] Therefore, $FePO_4$ has also been proposed as suitable cathode material in lithium batteries [9], or anode material in lithium batteries [10].

$FePO_4$ electrode materials in lithium ion batteries also show lots of advantages: firstly, $FePO_4$ is a binary system and Fe (III) compounds are raw materials, the sources of which are easily available. Therefore, the synthesis technology is simple, without any need for a protective atmosphere, saving both equipment and overall cost. Secondly, $FePO_4$ shows a discharge plateau of 3.5 V and a theoretical specific capacity of 178 mAh g^{-1} upon 1 mol of lithium intercalation [11].

However, the application of $FePO_4$ cathode materials is faced with a problem, which is a lack of lithium in the $FePO_4$ compound; this is also the reason why the research has not drawn attention to the study of $FePO_4$ cathode materials. However, there are some ways to solve this issue. Firstly, the compounds containing lithium, such as LiV_3O_8, can be used as anode material; secondly, $FePO_4$ can be transformed to $LiFePO_4$ by way of electrochemically-inserted lithium [12]. $FePO_4$ is emerging as the most promising candidate for cathode materials in secondary lithium ion batteries. Researches on $FePO_4$ electrode materials have been carried out in recent years. Masquelier et al. [13] reported that hydrated amorphous $FePO_4$ showed a superior electrochemical performance. Xu et al. [14] also discovered hydrated amorphous and anhydrous $FePO_4$ demonstrated better electrochemical performance than did pure crystalline $FePO_4$. Y. Yang et al. [15] discovered that amorphous mesoporous $FePO_4$ cathode materials facilitated the diffusion of lithium during the charge/discharge cycles. Croce et al. [16] added RuO_2 to quartz $FePO_4$, thus enhancing the specific capacity with a

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higher material interparticle electronic conductivity. Shi et al. [17] obtained amorphous mesoporous $FePO_4$ by a template method, which was then used as cathode material. X. Yang et al. [18] found that the Cr^{3+} ion-doped $FePO_4$ ($Fe_{1-x}Cr_xPO_4$) could effectively improve electrochemical performance overall.

Although extensive efforts on $FePO_4$ have been expended to improve electronic conductivity and the diffusion of lithium ions, there have not yet been significant improvements. Not unlike $LiFePO_4$, $FePO_4$ cathode materials also suffer from not only the low electronic conductivity, but also difficulties related to diffusing lithium ions into the structure [19–22].

The diffusion coefficient of lithium ion batteries is one of the most important parameters used to value electrode materials. Various mechanisms have been proposed to explain the processes of diffusion; almost all of them are based on the vibrational energy of atoms in a solid. Common diffusion mechanisms include direct-interchange, cyclic, interstitial, and vacancies; however, the most probable mechanism of diffusion is that in which the magnitude of the energy barrier (activation energy) to be overcome by moving atoms is the lowest. The diffusion coefficient of lithium ions, D_{Li} can be written as $D_{Li} = D_0 \exp^{-\Delta G/KT}$, where D_0 is the pre-exponential factor, ΔG is activation energy for diffusion, and k is the Boltzmann constant. D_0 is known to be related to location vacancy concentration [23]. Activation energy depends on the forces of interatomic bonds, crystal lattice defects, and the size of the atom, which facilitate diffusion transfer (the activation energy at grain boundaries is only one half of that in the bulk of a grain). The activation energy required is high for large-sized atoms and strongly bonded material.

Amorphous solids are considered to be disordered crystalline solids [24]. In the field of geometric crystallography, a disordered crystalline structure implies the presence of defects which are defined relative to the perfectly ordered structure [25]. Therefore, disordered materials are crystalline materials that can be, in principle, restored to the perfect crystalline state by the removal of defects [26]. The amorphous structure is promising for the diffusion of the lithium ion. The main reasons are listed as follows: Firstly, the disorder structure provides more diffusion pathways for lithium ions, unlike the crystalline structure having the local diffusion pathway for lithium ions, during the intercalation and de-intercalation of lithium ions in the electrode material. Secondly, the presence of defects in an amorphous structure can decrease the energy barrier.

Several electrochemical techniques have been developed to determine the diffusion coefficient of the lithium ion according to the Fick's second law, such as the potential intermittent titration technique (PITT) [27], current pulse relaxation (CPR) [28], potential step chronoamperometry (PSCA) [29], electrochemical impedance spectrum (EIS) [30], and cyclic voltammetry (CV) [31].

The EIS technique can analyze the rate-controlling step of the electrochemical process according to the parameters of different frequencies. Prosini et al. [32] measured D_{Li} using electrochemical impedance spectroscopy (EIS) and reported the D_{Li} value of carbon coated $LiFePO_4$/C ranging from 10^{-17} to 10^{-14} $cm^2\,s^{-1}$. On the other hand, Yu et al. [33] obtained the D_{Li} value of $LiFePO_4$/C using cyclic voltammetry (CV) and reported it to be 5×10^{-15} to 2.2×10^{-14} $cm^2\,s^{-1}$. However, little work reported the D_{Li} value of $FePO_4$.

In this work, we synthesized the nano-sized $FePO_4$ cathode materials via the microemulsion method in an H_2O/cyclohexane/Triton X-100/n-butyl alcohol system, and then sintered at different temperatures to get the different crystal structure and grain size $FePO_4$. The diffusion coefficients of lithium ions (D_{Li}) were measured by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), thus acquiring the correlation between the electrochemical performances of $FePO_4$ and lithium ion diffusion.

2. Experimental

$FePO_4$ samples were synthesized by a microemulsion route. Two H_2O (deionized water)/cyclohexane(AR)/Triton X-100 (aMResco,AR)/n-butylalcohol (AR) microemulsion systems in a volume ratio of 35:25:15:5, A and B, differing only in the aqueous phase, were prepared. The aqueous phase of microemulsion A was the reactant solution, which is the 0.1 mol L^{-1} $Fe(NO_3)_3{\cdot}9H_2O$ (AR) solution. The aqueous phase of microemulsion B was the precipitant solution, which is the 0.1 mol L^{-1} $NH_4H_2PO_4$ (AR) solution. Microemulsion B was added dropwise to microemulsion A under constant stirring of 350 rpm for 30 min at room temperature, and then continued with stirring at 45 °C under pH 2.6 for 3 h. Finally, the powders were obtained by centrifugal separation and washed with ethanol three times to remove the solvents. The obtained precipitates were dried at 100 °C for 12 h, and then sintered under an air atmosphere at different temperatures (380 °C, 460 °C, 550 °C and 650 °C) for 3 h.

The crystal phases were identified using X-ray diffraction (D8 Advance, Bruker Germany) with Cu K_α radiation with 2θ in ranging from 20° to 90° at a scan rate of 2° min^{-1} at room temperature. The surface morphology of powder particles was characterized using field emission-scanning electron microscopy (SU70, Japan). The characterization of electrochemical properties of the synthesized $FePO_4$ was accomplished by assembling CR2016 coin cells. The composite positive electrodes were prepared by ball-milling a mixture of the active materials, conductive material (acetylene black), and binder (polytetra-fluoroethylene, PTFE) in a weight ratio of 75:17:8. The average mass of composite loading to electrode is 15 mg; the electrode sheet was then dried in vacuum oven at 120 °C for 24 h. Finally, coin-type cells were assembled in a glove box (RH < 0.1%, at 20 °C), which used lithium foil as the anode, Celgard 2400 microporous polypropylene film as the separator, and 1 M $LiPF_6$ in PC/DEM (1:1) as the electrolyte. Charge-discharge tests were performed between 2.0 V and 4.0 V using the Land Battery test system (Wuhan LAND, China). The AC perturbation signal was 5 mV, and the frequency range was from 0.01 Hz to 100 kHz. All tests were performed at room temperature (25 °C). A cyclic voltammetry test was performed on a CHI660B electrochemical workstation (Chenhua, Shanghai, China) at a scan rate of 0.05 mV s^{-1}, 0.08 mV s^{-1}, 0.1 mV s^{-1}, and 0.12 mV s^{-1}, respectively, on the potential interval 2.5–4.2 V (vs. Li/Li^+).

3. Results and discussion

Fig. 1 shows the XRD patterns of $FePO_4$ samples sintered at different temperatures (380 °C, 460 °C, 550 °C, 650 °C) for 3 h in air. The results reveal that the samples sintered at 380 °C and 460 °C are amorphous. In the case of the sample sintered at 550 °C, the pattern shows several weak peaks of an unidentified phase and several peaks of trigonal $FePO_4$. The peaks become stronger at 650 °C, which corresponds well with the trigonal $FePO_4$ (JCPDS 50-1635). The standard lattice parameters are: $a = b = 5.048$, $c = 11.215$, $\alpha = \beta = 90°$, $\gamma = 120°$. The phase composition of the samples and the lattice parameters of the $FePO_4$ calculated by the Rietveld refinement method are listed in Table 1. The fact that the lattice parameters of $FePO_4$ sintered at 550 °C differ with the standard may be due to the poor crystallinity. The lattice parameters of $FePO_4$ sintered at 650 °C show little change, which indicate that $FePO_4$ has acceptable crystallinity.

The typical morphologies of $FePO_4$ samples sintered at different temperatures (380 °C, 460 °C, 550 °C, 650 °C) for 3 h in air are displayed in Fig. 2. The samples sintered at 380 °C and 460 °C consists mainly of spherical nanoparticles with an average diameter of ca.20 nm, which are also homogeneously distributed. The