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Improved rate and cycle performance of nano-sized $5LiFePO_4 \cdot Li_3V_2(PO_4)_3/C$ via high-energy ball milling assisted carbothermal reduction

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ABSTRACT

Nano-sized $5LiFePO_4 \cdot Li_3V_2(PO_4)_3/C$ composite was synthesized via improved carbothermal reduction combined high-energy ball milling. XRD results reveal that the composite is composed of olivine $LiFePO_4$ and monoclinic $Li_3V_2(PO_4)_3$ phases. Meanwhile small amounts of V^{3+} and Fe^{2+} as dopants entered into the lattices of $LiFePO_4$ and $Li_3V_2(PO_4)_3$, respectively. Trace amounts of Fe_2O_3 in $LiFePO_4/C$ and Fe_2P in $5LiFePO_4 \cdot Li_3V_2(PO_4)_3/C$ were identified and quantified by magnetic tests. And magnetic parameters of $5LiFePO_4 \cdot Li_3V_2(PO_4)_3/C$ are significantly different from $LiFePO_4/C$. The $5LiFePO_4 \cdot Li_3V_2(PO_4)_3/C$ presents initial discharge specific capacities of 145.2 mAh g^{-1} and 133.9 mAh g^{-1} and no capacity attenuations after 50 cycles can be observed at 2C and 5C respectively. Compared with $LiFePO_4/C$, its rate capability and cyclic stability are both enhanced greatly. The mutual doping, synergistical effect of $LiFePO_4$ and $Li_3V_2(PO_4)_3$ and contribution of Fe_2P are mainly responsible for the excellent electrochemical performances.

1. Introduction

Polyanion phosphate materials have attracted great attention as promising cathode materials for lithium ion battery, since olivine $LiFePO_4$ (LFP) was firstly reported in 1997 [1]. LFP has achieved success because of excellent electrochemical properties, as well as low cost and environment friendliness [2]. Nevertheless, LFP does suffer from poor intrinsic electronic and ionic conductivity, which lead it difficult to satisfy with the higher request of electric vehicles and hybrid electric vehicles on capacity, cycle life and safety [3,4].

Carbon coating and particle size controlling are common methods used to mitigate these drawbacks. Well-coated carbon insures high electrical contact between particles and reduces particle size at the same time. Many studies showed that carbon coated nano $LiFePO_4/C$ (LFP/C) exhibits much better rate capability and cyclic stability [5–8]. Nevertheless, it should not be ignored simultaneously that all these improvements are at cost of the decrease in volumetric energy density. Moreover, carbon coating has no good effect on lithium ion mobility and electronic conductivity in the bulk phase of particles. Therefore, there is a pressing need for more effective ways to further improve rate and cycle properties of LFP/C.

Chemical doping with multivalent cations could improve the internal electronic and ionic conductivity due to induced lattice distortion, reduced particle size or enhanced structural stability [9–11]. Beneficial effects of V substitution for Fe-site in LFP/C have been proved so far. For example, Chen et al. [12] synthesized $LiFe_{0.97}V_{0.03}PO_4/C$ with high rate discharge capacity of 105.8 mAh g^{-1} at 20C through a quasi-sol-gel method. $LiFe_{0.95}V_{0.05}PO_4/C$ also achieved specific capacity of 119 mAh g^{-1} at 1500 mA g^{-1} via pilot-scale continuous synthesis [13]. Interestingly, the mixed phases of LFP and $Li_3V_2(PO_4)_3$ (LVP) were observed in high-level V-doped LFP/C [14,15]. Compared with LFP, LVP possesses high operating voltage, large ion diffusion coefficient and good thermal stability [16,17], which has been supposed to improve the electrochemical performance of LFP/C.

Therefore, $xLiFePO_4 \cdot yLi_3V_2(PO_4)_3/C$ composites have drawn growing interests recently. For instance, $9LiFePO_4 \cdot Li_3V_2(PO_4)_3/C$

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(sol-gel synthesis) [18], $xLiFePO_4 \cdot yLi_3V_2(PO_4)_3/C$ (polyol process) [19], $0.7LiFePO_4 \cdot 0.3Li_3V_2(PO_4)_3/C$ (spray-drying technique) [20], $2LiFePO_4 \cdot Li_3V_2(PO_4)_3/C$ (spray drying method) [21] and $8LiFePO_4 \cdot Li_3V_2(PO_4)_3/C$ (solid-state reaction in molten hydrocarbon) [22] etc, have been researched and the results showed that these composites displayed better electrochemical performances than pristine LFP/C. It was ascribed to the mutual doping of V and Fe, favorable crystal structure, uniform size distribution and so on. In brief, this kind of composite is expected to synergistically provide a diversity of complex effects and complementary advantages. Among $xLiFePO_4 \cdot yLi_3V_2(PO_4)_3/C$ composites, $5LiFePO_4 \cdot Li_3V_2(PO_4)_3/C$ (5LFP·LVP/C) have also been researched by several authors [23–25], while there still are large room for improving electrochemical performances and the microstructures need to be clarified in detail. Furthermore, the structural complexity of 5LFP·LVP/C presents a characterization challenge. As far as we know, the qualitative and quantitative research on trace impurities and changed microstructures of this composite is very lacking, which really play important roles on the electrochemical property. In addition, the reasons for enhanced electrochemical property of 5LFP·LVP/C are worth highlighting further.

With the aim to be easily industrialized, an improved carbothermal reduction combined with high-energy ball milling method was adopted to synthesize nano-scale 5LFP·LVP/C in this study. Then its structure, morphology, magnetic and electrochemical properties were investigated in detail. And the reasons of excellent electrochemical property for this composite were analyzed further. Magnetic analyses (combination of M (H) and H/M (T) datum) were newly introduced in 5LFP·LVP/C, because they are highly sensitive to impurities and structural defects beyond that of X-ray diffraction.

2. Experimental

2.1. Materials synthesis

5LFP·LVP/C composite was prepared by a carbothermal reduction method. $LiOH \cdot H_2O$, $FePO_4 \cdot 2H_2O$, NH_4VO_3, $NH_4H_2PO_4$ and $C_6H_{12}O_6$ with molar ratio of 8:5:2:8:5 were used as raw materials and dispersed in ethanol. After a homogenously dispersed mixture was formed by high-energy ball milling, it was dried at 100 °C overnight to obtain precursor powders. As-prepared powders were ground and calcined at 300 °C for 5 h in argon atmosphere. Then they were cooled to room temperature. The resulted products were ground and sintered again at 750 °C for 10 h in flowing argon followed by one more high-energy ball milling to yield black 5LFP·LVP/C. At last, another heat treatment (700 °C, 1 h) was applied to eliminate crystal defect and reduce surface energy. For comparison, the LFP/C and $Li_3V_2(PO_4)_3/C$ (LVP/C) were prepared via the same process without addition of NH_4VO_3 or $FePO_4 \cdot 2H_2O$.

2.2. Materials characterization

The crystallinity and structure were characterized by X-ray diffraction (XRD, Rigaku D/max-RB, Japan) using Co Kα radiation with scan speed of 2°/min. The carbon content was tested using a CS-8810C high-frequency infrared Carbon and sulfur analyzer (Wuxi, China). The X-ray photoelectron spectroscopy (XPS) was obtained by using VG ESCALab250 spectrometer with monochromatic Al Kα radiation. The Raman spectra were recorded on a HORIBA LabRAM HR with 633 nm He-Ne laser excitation. The surface morphology and particle information were observed with a scanning electron microscopy (SEM, Hitachi, S-4800, Japan). The microstructures of 5LFP·LVP/C were examined, and selected area electron diffraction (SAED) patterns were collected through scanning transmission electron microscopy (STEM and high-resolution TEM (HRTEM), ARM-200F, 200 kV, with energy-dispersive X-ray spectroscopy (EDX) detector). Magnetic measurements (magnetization and susceptibility) were performed on a fully automated magnetometer (MPMS-5S from Quantum Design) equipped with an ultra-sensitive SQUID within the temperature range of 4–300 K.

2.3. Electrochemical measurement

The electrochemical characteristics were investigated using CR2032 coin cells assembled in an argon-filled glove box. The cathode consisted of as-synthesized materials, acetylene black and polyvinylidene fluoride (PVDF) binder in a weight ratio of 85:10:5. A metallic lithium foil served as the counter and reference electrode. The electrolyte was 1 M $LiPF_6$ dissolved in ethylene carbonate (EC)-dimethyl carbonate (DMC) (1:1 in volume). Galvanostatic charge-discharge tests were conducted with a LAND-2001A battery testing system (Wuhan, China) in a potential range of 2.5–4.2 V (vs Li^+/Li). The measurements of electrochemical impedance spectroscopy (EIS) and cyclic voltammograms (CV) were carried out on a CHI660E electrochemical workstation (Chenhua, China). EIS experiments were performed within frequency range from 1 to 10^5 Hz. CV curves were recorded in a potential window of 2.5–4.2 V (vs Li^+/Li) at scan rates of 0.1–0.5 mV s^{-1}.

3. Results and discussion

The Rietveld refinement XRD results of LFP/C, 5LFP·LVP/C and LVP/C are illustrated in Fig. 1. As Fig. 1 shows, all diffraction peaks of LFP/C and LVP/C are indexed as olivine phase LFP (PDF no. 81-1173) and monoclinic phase LVP (PDF no. 78-1106) with well ordered structures, respectively. While 5LFP·LVP/C composite consists of both LFP and LVP phases without any other impurities detected. The weight ratio of LFP is 65.8% and LVP is 34.2% in 5LFP·LVP/C, in good accordance with theoretical values of 65.9% and 34.1%, respectively. The refined lattice parameters and corresponding crystallite sizes for these samples are summarized in Table 1. From Table 1, it can be seen that the lattices of LFP in 5LFP·LVP/C were expanded in all dimensions compared with pristine LFP/C, yet they are smaller for LVP in 5LFP·LVP/C than those of pristine LVP/C (except b). The slight expansion/contraction in cell parameters is attributed to the mutual doping, i. e., some vanadium occupied the crystal sites of Fe^{2+} and meanwhile some iron occupied the crystal sites of V^{3+}. The calculated crystallite size of these samples is in range of 60–75 nm. Additionally, there is no evidence of carbon related peaks in XRD patterns. However, the contents of residual carbon in LFP/C, 5LFP·LVP/C and LVP/C are separately about 5.18 wt %, 4.52 wt% and 4.49 wt% by C-S analysis. And the existence of carbon can also be confirmed by XPS and Raman results in Fig. 2. The peak at 284.84 eV in high-resolution XPS spectra (Fig. 2b) is C1s emission which confirms the presence of residual carbon on surface of this composite [26,27]. From Raman spectra (inset of Fig. 2b), D-band (disorder band) in the range of 1270–1480 cm^{-1}, G-band (graphite band) between 1550 and 1640 cm^{-1} and the presence of 2D-band and (D + G)-band can be clearly seen. The peak intensity ratio ($I_D/I_G = 0.62$) is much lower than those in Ref. [6]. All these indicate that the composite possesses a uniform distribution of highly ordering carbon on particle surface. The coated carbon can inhibit the grain growth and form a conductive network among particles to improve electronic conductivity.

Fig. 3a, b compare SEM images of LFP/C and 5LFP·LVP/C. Obviously, the particle sizes of LFP/C are about 100–200 nm with uniform distribution and partial agglomeration. In contrast, 5LFP·LVP/C is consisted of agglomerated second particles with dominant diameters ranging from 1 to 1.5 μm combined numerous pores (inset of Fig. 3b) and the primary particles are about 100 nm. These