LiMnPO₄•Li₃V₂(PO₄)₃ composite cathode material derived from Mn(VO₃)₂ nanosheet precursor

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Abstract:

The LiMnPO₄•Li₃V₂(PO₄)₃/C composite cathode material was synthesized from Mn(VO₃)₂ nanosheet precursor, which was prepared by a hydrothermal method. The structure and morphology of the composite were systematically investigated by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM) and scanning transmission electron microscopy (STEM), etc. The LiMnPO₄•Li₃V₂(PO₄)₃/C composite material exhibits a low polarization and high specific capacity of 150.7 mAh g⁻¹ at 0.1C in voltage range of 2.5-4.5V, and excellent cycle and rate performance for its stable nanocomposite framework. The composite material dominantly exists in the morphological shape of nanograins and nanorods, which increases the surface area and hence facilitate the electrolyte penetration. The nanoparticle components were even further identified in detail.

Keywords: LiMnPO₄, Li₃V₂(PO₄)₃, Mn(VO₃)₂, cathode material, Lithium ion battery

1. Introduction

Rechargeable lithium ion batteries (LIBs) have been extensively used from portable electronics to emerging electric vehicles (EV) or hybrid electric vehicles (HEV). In the commercial Li-ion cells, layered LiCoO₂ cathode material has advantages of its facile synthesis and excellent cyclability, but the high cost and thermal instability are referred as principal drawbacks. The spinel LiMn₂O₄ is another attractive cathode material, but its cycle stability is quite poor at elevated temperatures. Lithium transition metal phosphates Li_xM_y(PO₄)_z (M = Fe, Mn, Co, Ni, V) have strong P-O bonds and can construct three-dimensional (3D) solid framework [1-7]. Such a crystalline structure guarantees both cyclability and thermal stability to meet the safety demands in EV and HEV. However, the problem associated with such a

structure is its low intrinsic electronic conductivity. Presently, lots of strategies have been reported, including the addition of conductive additives, cation doping, nanoparticle synthesis, and surface modification to minimize the mentioned shortcoming to a maximum possible extent [8-17]. The lithium iron phosphates LiFePO_4 (LFP) has been commercially used owing to its cheap raw materials for synthesis, thermal stability and environmental friendliness. LiMnPO_4 (LMP) has the same theoretical specific capacity of LFP (171 mAh g^{-1}). However, LMP could provide more than 20% energy density than LFP due to its higher redox potential (ca. 4.1 V) than that of LFP (3.5V). The specific capacity and rate capacity of pure LMP are lower than those of LFP, because of its extremely low electric conductivity [8-12]. Therefore, there is a strong incentive in improving the electrochemical performances of LMP. The Monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) has an unique NASICON structure possessing 3D transfer channels which offer a large interstitial space to facilitate the transference of lithium ions [14-17]. LMP and LVP have similar high voltage plateaus (4.1V). Herein, when combining LMP and LVP together, it would be a good choice to strengthen their advantage.

Some efforts have focused on $\text{LiMnPO}_4 \cdot \text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ (LMP•LVP/C) composites recently. Wang et al synthesized a series of $(1-x)\text{LiMnPO}_4 \cdot x\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites by spray drying [18]. Qin and Wang et al had reported a series of $(1-x)\text{LiMnPO}_4 \cdot x\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites prepared by traditional solid-state methods [19-20]. Zhang et al synthesized LMP•LVP/C composite from a rod-like $\text{MnV}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ precursor prepared via aqueous precipitation, following carbon thermal reduction. The initial discharge is 110 mAh g^{-1} and 104.4 mAh g^{-1} at 0.1C and 1C rate, respectively [21]. Zhang et al reported LMP•LVP/C from prickly $\text{MnV}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ precursor [22]. Li et al synthesized $0.5\text{LiMnPO}_4 \cdot 0.5\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite by sol-gel method, showing a capacity of 135.1 mAh g^{-1} at 0.1C [23]. In our work, in order to disperse Mn and V element in atomic level first, $\text{Mn}(\text{VO}_3)_2$ nanosheet was prepared and utilized as precursor to synthesize the LMP•LVP/C composite showing remarkably enhanced electrochemical performances.

2. Experimental

2.1. Materials synthesis

$\text{Mn}(\text{VO}_3)_2$ was synthesized via a hydrothermal method. Stoichiometric ratio of NH_4VO_3 and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in deionized water separately, mixed under vigorous stirring about half an hour at $\sim 55^\circ\text{C}$. A yellowish brown suspension formed slowly. Then the suspension was transferred into Teflon-lined stainless steel autoclaves, sealed and heated to 180°C for 15h. After cooling to room temperature, centrifuged and washed with deionized water and alcohol for three times, then dried in vacuum for 3h at 80°C . A blackish-brown powder of $\text{Mn}(\text{VO}_3)_2$ was collected.

Second, stoichiometric $\text{Mn}(\text{VO}_3)_2$, Li_2CO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$ were mixed with oxalic acid and glucose in small amount of ethanol. Both oxalic acid and glucose were used as reduce agent and carbon source. The slurry was ground by high energy ball-milling for 4 h at 400 rpm (Fritsch). After that, the mixture was dried and calcined at 350°C for 3h, 700°C for 12h in H_2/Ar atmosphere ($v/v = 5:95$) with a heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$. Finally, the black product of LMP•LVP/C composite was collected.

2.2. Structure and morphology characterization

All samples were ground into a fine powder before structural analyses. Product crystallinity and phase purity were characterized by powder X-ray diffraction analysis (XRD, Bruker D8 Advance) using $\text{Cu K}\alpha$ radiation with scanning rate of $6^\circ\cdot\text{min}^{-1}$. Material morphologies were observed using a field emission scanning electron microscope (SEM, FEI Nova Nano SEM 450), transmission electron microscope (TEM, JEOL 2100F) and scanning transmission electron microscope (STEM, probe-aberration corrected FEI Titan STEM and image-corrected FEI ETEM), etc. The carbon content was measured by equipment of high frequency infrared ray carbon sulfur analyzer (CS-206 Shanghai Baoying). The carbon content was found to be 6.35 wt%. The electrical conductivity was tested by 4-point probe resistivity measurement system (RTS-8 type 4-probes TECH, Guangzhou). The electronic conductivity of LMP•LVP/C composite material was measured with the value of $2 \times 10^{-4} \text{ S cm}^{-1}$.

2.3. Electrochemical measurements

LMP•LVP/C active material, Timcal Super P, polyvinylidene fluoride (PVDF) were mixed in the gravimetric ratio of 8:1:1. PVDF was dissolved in N-methyl-2-pyrrolidone (NMP) as the binder. The slurry was coated onto aluminum foil and dried under vacuum at 120 °C for 12h. The electrode sheet was pressed and punched into Φ12 mm diameter discs as cathode. Lithium foil was used as anode, 1M LiPF₆ dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (v/v = 1:1) was used as the electrolyte, and Entek ET20-26 as the separator. Additionally, the cells were assembled in an argon-filled dry glove box where humidity and oxygen were controlled less than 1 ppm.

The CR2016 coin-type cells were tested within a voltage range of 2.5-4.5 V using a constant current-constant voltage (CC-CV) protocol at various discharge rates with potentiostatic steps at the cutoff potential on Lanhe CT2001A battery test systems. The capacity was calculated based on the pure composite material excluding carbon. The cyclic voltammetry (CV) was measured on a Chenhua cell test system. The electrochemical impedance spectroscopy (EIS) was measured by an electrochemical workstation (Autolab PGSTAT 302N). All tests were conducted at constant room temperature (25°C).

3. Results and Discussion

3.1. Material characterization

The XRD pattern of precursor is shown in Fig. 1a. All peaks are indexed and attributed to Monoclinic Mn(VO₃)₂ (JCPDS No. 35-0139). No impurities are found in the sample. The SEM images of Mn(VO₃)₂ exhibit nanosheets stack together forming clusters with thickness of 30-80 nm (Fig. 1b, c), which is different from previous reports [21, 22, 24-30]. Interestingly, Mn(VO₃)₂ exhibits brannerite structure which has ion transfer channel as an anode material for lithium ion battery [24-30].

The XRD pattern of LMP•LVP/C composite is shown in Fig. 2. The diffraction peaks are assigned to the composition of Orthorhombic structure LMP (Space group Pmnb (62), JCPDS No. 74-0375) and Monoclinic LVP (Space group P21/n (14), JCPDS No. 47-0107) [31]. The weak peak at 28.9° is attributed to the impurity of Li₃PO₄ (shown in inset image of Fig. 2). Li₃PO₄ is a fast solid lithium ion conductor

which may improve the ionic conductivity within the composite [32-36]. The coating carbon isn't detected by XRD due to its amorphous state. The main chemical reactions are listed as below:

The SEM images of LMP•LVP/C composite show the coexistence of nanograins and nanorods (Fig. 3). Nanograins agglomerate to similar irregular particles showing a length up to 50-200 nm. The thickness of nanorods is between 50-100 nm and length up to ~ 1 μm . The coexistence of non-uniform particles is primarily because of different crystalline structures of LMP and LVP. When the microcrystal is forming and growing, LMP and LVP have individually preferred growing orientations. The nanorods are identified as Li_3PO_4 impurity conformed by HRTEM and STEM discussed below. The composite material has not uniform particles shape which is different from the reports [18-23]. Although two distinct shapes of nanograins and nanorods accumulate, the composite can provide higher value of specific surface area which is beneficial for electrolyte penetration.

The TEM, SAED, HRTEM images of nanograins are shown in Fig. 4. Three stochastic nanograins were chosen for analysis. For particle a, blue cycle labelled one in Fig. a1, the LMP phase was annotated in SAED pattern (a2) with (101) and (120) crystal plane along $[-212]$ zone axis. The HRTEM image (a3) taken from the edge of the marked nanograin displays a clear crystal lattice. The d-spacing values of 3.970, 3.526 and 2.313 Å correspond to (120), (111) and (012) plane of Orthorhombic phase of LMP, respectively. The d-spacing of 2.698 Å corresponds to (141) plane of Monoclinic LVP.

Particle b shows an analogous cubic morphology (b1). The corresponding SAED pattern is similar with that of particle a. The HRTEM image (b3) of cubic edge shows an interplanar spacing value of 3.745 Å, belonging to (101) plane of LMP. In SAED patterns of a2 and b2, some diffraction points distribute out of parallelogram, which would be unannotated LVP component. So, it demonstrates a heterogeneous phase system, i.e. LMP and LVP. For particle c (blue labelled), the corresponding SAED

pattern (c2) displays the (020) and (002) reciprocal lattice vectors of LVP along the [-100] zone axis. The HRTEM image (c3) taken from a nanograin shows the fringe spacing value of 3.352 Å, which is in agreement with the (13 $\bar{1}$) crystalline plane of LVP. Furthermore, an amorphous carbon layer covers the surface of nanoparticles with a thickness of 5-10 nm. Finally, it can be concluded that some nanograins consist of LMP and LVP phase and some of them are main LVP.

The d-spacing of nanorods in Fig. 5 is 2.463 Å, corresponding to (200) plane of Li₃PO₄. Notably, the nanorods are sensitive under strong electronic beam stimulating, leading to the formation of some holes.

All the above mentioned analysis is further confirmed by STEM-EDX characterization shown in Fig. 6. Some nanoparticles consist of LiMnPO₄ and Li₃V₂(PO₄)₃, where LMP is the main component with a molar ratio of Mn : V = 8.19:7.73 (Fig.6a). Some nanoparticles are main LVP, where LMP hardly exists, showing a molar ratio of V : Mn = 11.34 : 0.05 (Fig. 6b). The nanorod is confirmed as Li₃PO₄ compound, in which neither V nor Mn element is detected (Fig. 6c). The conclusion is well accorded with SAED and HRTEM analysis.

3.2. Electrochemical performances

The first charge-discharge curves at different rates from 0.1C to 5C are shown in Fig. 7a. Three charging plateaus under 0.1C appear at ca. 3.6V, 3.7V, 4.1V obviously that are associated with lithium ion extraction of Li₃V₂(PO₄)₃ to Li_{2.5}V₂(PO₄)₃, Li_{2.5}V₂(PO₄)₃ to Li₂V₂(PO₄)₃ and Li₂V₂(PO₄)₃ to LiV₂(PO₄)₃ for LVP. The lithium ion extraction of LiMnPO₄ to MnPO₄ also occurs at the plateau of 4.1V.

Based on the two Li⁺ ions intercalation, the theoretical capacity of LMP•LVP is 143 mAh g⁻¹ where the theoretical capacities of LMP and LVP are 171 and 133 mAh g⁻¹, respectively. The initial discharge capacity of LMP•LVP/C is 150.7 mAh g⁻¹ at 0.1C which exceeds the theoretical value due to the fact that the partial third Li⁺ ions of LVP take part in the reaction. After 150 cycle, the discharge capacity is 112.5 mAh g⁻¹ with ca. 75 % retention (Fig. 7b). And the composite cathode has excellent rate performance, showing the discharge capacities of ca. 108 mAh g⁻¹ and 100 mAh g⁻¹ at

2C and 5C, respectively (Fig. 7c). The unstable capacity data especially for 0.1C could be explained by the structure degradation at the early cycling stage, especially for LVP phase. The electrode can be long-cycled at high rate (Fig.7d). The 1st discharge capacities at rate of 1C and 5C are 117.6, 104.0 mAh g⁻¹(charged at 0.2C). After the 300th cycle, the discharge capacities are 87.4 and 77.7 mAh g⁻¹, respectively. They exhibit a similar capacity retention of 75%. The electrolyte decomposition could be induced for the long-term cycling at a high potential, which will, in turn, influence the interfacial property, while the inner crystalline structure could be changed with the repeated Li⁺ ions insertion and extraction. All these phenomena could cause capacity fading.

The LMP•LVP/C composite would be a potential cathode candidate used in practical industry. The outstanding high-rate performance and long cycle life are speculated by the following reasons: First of all, the excellent cyclability and rate capability are attributed to the splendid structure stability of Lithium transition metal phosphates. Secondly, Mn and V co-doping could occur in LMP•LVP/C composite material. Doping would generate some local defects in the crystal structure, which improves the electrical conductivity. The mutual doping in both the phases has been confirmed by ref. [20, 22, 23, 37]. Thirdly, the coexistence of nanograins and nanorods increases the specific surface area which would provide convenience for electrolyte penetration and Li⁺ ions diffusion.

The cyclic voltammogram (CV) test was carried out at 0.1 mV s⁻¹ between 2.5 and 4.5V (versus Li/Li⁺) (Fig. 8a). The LMP•LVP/C composite exhibits three oxidation peaks at 4.13, 3.71, 3.63 V and the corresponding reduction response at 4.03, 3.64, 3.55 V. The separation potentials are 0.10, 0.07, 0.08 V, which are lower than reported ref. [21]. The more symmetric and spiculate peak profile for LMP•LVP/C composite indicates a better reversible electrochemical reaction during Li⁺ ions insertion and extraction. The peaks at 3.63, 3.71 V correspond to the extraction of one Li⁺ ion from LVP, in accordance with the discharging plateaus in Fig. 7a. The peak located at 4.13 V is related to the second Li⁺ ion extraction from Li₂V₂(PO₄)₃. The reduction peaks at 3.55, 3.64, 4.03 V are associated with the reversible insertion of extracted Li⁺ ions in

$\text{Li}_3\text{V}_2(\text{PO}_4)_3$. The redox peaks at 4.03, 4.13V are also related to the reduction and oxidation of the $\text{Mn}^{2+}/\text{Mn}^{3+}$ redox couple of LMP, which are overlapped with those of LVP [37-40].

The resulting EIS during cycling were collected in the frequency range of 100 kHz to 0.01Hz with the amplitude of 10 mV (in discharged state)(Fig. 8b). The Nyquist plots show a depressed semicircle in the high-medium frequency range, which can be divided by two arcs according to EIS simulation (Fig. 8c), and a slanted line in the low frequency region. The arc centered at high frequency can be attributed to the resistance of solid-electrolyte interphase (SEI) layer (R_f) and the corresponding constant phase element (CPE_f) with the double-layer capacitance caused by the conductive substrate and electrolyte, while the latter arc indicates the charge-transfer resistance (R_{ct}) combined with double-layer capacitance (CPE_{ct}) between the active material and electrolyte [37]. The slanted line in the low-frequency region represents the Warburg impedance (W), which denotes the Li^+ diffusion resistance through the active material. Table 1 shows the calculated electrochemical parameters of LMP•LVP/C. The decreased resistance during cycling, which has been also observed by other group [37], is probably due to the electrode activation at the early cycling stage for improved ion transfer within the electrode and active material.

4. Conclusions

$\text{Mn}(\text{VO}_3)_2$ nanosheets with brannerite structure were prepared and utilized as a precursor to synthesize a LMP•LVP/C composite material via the carbon thermal reduction process. It is found that LMP•LVP/C composite nanograins and Li_3PO_4 nanorods coexist in the material. The coexistence of two shapes could facilitate the electrolyte penetration and Li_3PO_4 component could act as a fast ion conductor. LMP•LVP/C composite exhibits a low polarization and a high initial specific capacity of 150.7 mAh g^{-1} at 0.1C in voltage range of 2.5-4.5V. Furthermore, it demonstrates the outstanding high-rate capability up to 5C and good cycling performance. In this material, the stable olivine structure of LMP is integrated with NASSICON structure of LVP. And the Mn/V co-doping would occur in two phases of LMP and LVP. All of

these distinguishing features can improve the lithium ion diffusion and electrical conductivity, leading to the good electrochemical performance.

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Fig. 1. The XRD pattern (a) and SEM images of $\text{Mn}(\text{VO}_3)_2$ (b, c), (b) overall morphology of the products, (c) high-magnification SEM image of circular area.

Fig. 2. The XRD pattern of LMP•LVP/C composite. Inset image show the Li₃PO₄ impurity peaks at 28.9° .

Fig. 3. The SEM images of LMP•LVP/C composite material.

Fig. 4. The TEM (a1), SAED (a2), HRTEM (a3) pattern of nanograins. The following patterns are the same as the nanograin found in b and c.

Fig. 5. The STEM (a, b), HRSTEM (c) images of nanorods are also shown. Under the electrical beam stimulating, the nanorods are very sensitive (b).

Fig. 6. The EDX spectrum and analysis of LMP•LVP/C composite: nanograins (a1, b1), nanorod (c1). And inserts show corresponding STEM images (a2), (b2) and (c2).

Fig. 7. The first charge / discharge curves of LMP•LVP/C at different rates (a). Cycling performance at 0.1C (b). Rate performance (c). Long-term cycling at discharge rates of 1C and 5C and charge rate of 0.2C (d).

Fig. 8. Cycling voltammogram for LMP•LVP/C composite at a scan rate of 0.1 mV s⁻¹ between 2.5 and 4.5 V (a). Nyquist plots of the LMP•LVP/C (b). Equivalent circuit used for simulating the experimental impedance data (c).

Table 1 Calculated electrochemical parameters from ac impedance spectra of the LMP•LVP/C sample using ZView 2 software.

Cycle No.	$R_f (\Omega)$	CPE_f ($\times 10^{-5} F$)	$R_{ct} (\Omega)$	CPE_{ct} ($\times 10^{-5} F$)	$W_o (\Omega)$
1 st	29.75	1.1313	579.7	1.9745	626.8
10 th	47.42	0.6107	296.8	1.9223	687
51 st	71.25	6.8423	90.42	9.3193	213.4