



Influence of the Preparation Methods on $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ Hybrid Material

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The "lithium iron(II) phosphate"- "lithium vanadium phosphate" hybrid composites (LFVP) were synthesized by two different methods, chemical blending and physical blending. The materials obtained from the experiment were samples of chemical LFVP (C-LFVP) and physical LFVP (P-LFVP). Comparing with the lithium iron(II) phosphate (LFP) and lithium vanadium phosphate (LVP), both hybrid samples showed improvements in electrochemical performance. The new substances yielding in the blending process were largely accountable for the improvements. Compared to P-LFVP sample synthesized by physical blending, the C-LFVP sample synthesized by chemical blending had demonstrated uniform shape, smooth surface and superior electrochemical performance. Thus, preparation methods had substantial influences on the hybrid materials. In the physical blending process (ball milling), the mechanical energy (high-speed ball running) undermined the crystallinity and grain morphology of the P-LFVP. The electrochemical performance of the chemical C-LFVP was much better than that of P-LFVP. The discharge capacity of C-LFVP is 192 mA h g^{-1} at $0.1 \text{ }^\circ\text{C}$, which was significantly higher than that of P-LFVP at the same rate. So chemical blending was a preferred method to prepare LFVP hybrid materials.

Key Words: Lithium iron phosphate, Lithium vanadium phosphate, Lithium ion battery, Cathode, Hybrid materials, Blending.

INTRODUCTION

In recent years, environmental pollution and energy crisis have made it a high time to develop green automobiles. A reliable and highly-functional battery is essential to guarantee a successful development. Lithium ion battery has attracted increasing attention for its consistent performance. While cathode is the key element of lithium ion battery, lithium metal oxides is known as the most popular material for lithium ion battery cathode¹. However, the low thermal stability of lithium metal oxides hinders its large-scale application in electric vehicles. In contrast, poly-anionic phosphate materials such as lithium iron(II) phosphate (LiFePO_4) and lithium vanadium phosphate [$\text{Li}_3\text{V}_2(\text{PO}_4)_3$] enjoy good thermal stability and high voltage, making them the most promising cathode candidates. However, LiFePO_4 and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ have their own advantages and drawbacks. LiFePO_4 has stable voltage platform and its cyclic attenuation rate is almost negligible. But the relatively low capacity and low voltage limit its energy density, which hinders LiFePO_4 to be used widely. Although $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ has high voltage and capacity, it invariably suffers from severe attenuation^{2,3}.

In order to integrate the technical advantages from different materials, scientists proposed hybrid materials long ago. For example, the ternary material ($\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$) exemplified advantages of LiNiO_2 , LiCoO_2 and $\text{LiMnO}_2/\text{LiMn}_2\text{O}_4$ ⁴⁻¹⁰. There

are some questions arise in present study: Whether LiFePO_4 and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ be compatible to each other and eventually create an effective hybrid when mixed. As of the preparation method, whether it will affect the hybrid cathode materials. This paper reports these queries.

EXPERIMENTAL

Using acetone as dispersant, mixed stoichiometric LiH_2PO_4 , $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ with glucose and ball milled for 10 h to obtain precursor; heated the precursor at $800 \text{ }^\circ\text{C}$ under nitrogen protection for 20 h to get LiFePO_4 sample (marked as LFP). Only replacing $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ with V_2O_5 , the same method and ingredients were utilized to obtain $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ sample (marked as LVP). The "lithium iron(II) phosphate"- "lithium vanadium phosphate" hybrid composites (LFVP) were synthesized by two different methods, chemical blending and physical blending. Specific instructions are as follows. Chemical method: employed stoichiometric LiH_2PO_4 , $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, V_2O_5 , glucose as raw materials and applied the same procedures to obtain $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ (marked as C-LFVP); Physical method: prepared LiFePO_4 and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ according to the previous instructions, mixed stoichiometric LiFePO_4 and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ in ball mill for 6 h to get physically procured $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ sample (marked as P-LFVP).

X-Ray diffraction (D/max-rB, Rigaku, CuK_α radiation) was used to analyze the crystalline structure of each cathode

sample and its matching software Jade5.0 was adopted to process relevant data. Scanning electron microscope (SEM, SPA400 Seiko Instruments) was employed to observe the carbon distribution on the sample surface. Conductivity was tested by D41-11C/ZM four-probe resistivity tester. EA3000 elemental analyzer was utilized to determine the carbon content. CV curves were obtained from PARSTAT2273 electrochemical workstation.

The electrochemical properties of samples were evaluated with a gas-tight coin cell assembled in an argon-filled anhydrous glove-box. The working cathode slurries comprised 80 % active material, 15 % acetylene black, 5 % polyvinylidene fluoride (PVDF) binder and N-methyl-2-pyrrolidinon anhydrous (NMP) solvent. The electrode slurry was coated onto the aluminum current collector. The electrode was then dried for 12 h under vacuum at 90 °C. The electrodes were tested in a CR2032 coin cell with 1M LiPF₆ (EC-PC-DEC to 1:1:1 volume %) electrolyte in 1:1:1 (v/v/v) ethylene carbonate/polycarbonate/diethyl carbonate (EC:PC:DEC), a Teflon Celgard separator (#2400, 16 mm diameter) and lithium ribbon as the counter and reference electrode. The cells were tested galvanostatically on a multichannel battery test system (Neware BTS-610, Shenzhen, China) at 0.1 °C in room temperature between 2.5-4.8 V *versus* Li/Li⁺.

RESULTS AND DISCUSSION

To judge cathode material, one of the major benchmarks is its electrochemical performance. Furthermore, possible causes for the different performances will be explored based on sufficient laboratory results.

Fig. 1 illustrates the specific discharge capacity and charge-discharge voltage platform of LFP, LVP, C-LFVP and P-LFVP. It is noted that C-LFVP has much the best electrochemical performances, the highest discharge capacity and the lowest attenuation. In the voltage range of 2.5-4.8 V, the initial discharge capacity of LFP is 159 mA h g⁻¹ and LVP's is 167 mA h g⁻¹; while the C-LFVP's initial discharge capacity can reach as high as 192 mA h g⁻¹; yet P-LFVP's capacity is 168 mA h g⁻¹, which has little significant improvements. After 15 cycles, their capacities remain 155, 152, 184 and 161 mA h g⁻¹, respectively, accordingly the capacity retention is 97.5, 91.0, 95.8 and 95.8 %. So it is concluded that the hybrid materials can not only increase the discharge capacity (for LFP), but also improve the cycle stability (for LVP) and C-LFVP has more outstanding electrochemical performance than P-LFVP.

The voltage plateaus of C-LFVP are very similar to that of P-LFVP. On the charge curves they both have four plateaus, the two in the high voltage range are clear, but the two in the low voltage range are confused. However there is only one slash on the discharge curves, which is similar to the discharge curve of LVP. All these can be attributed to the plateaus of LFP and LVP. LFP has one charge voltage plateau at about 3.5 V and the lowest charge voltage plateau of LVP is also at about 3.5 V, so the two plateaus of the hybrid in the low are actually at about 3.5 V. The tilt discharge curve of the LVP leads to the slash voltage curve of the hybrid materials. In a word, the voltage plateaus of the hybrid materials are overlapping lines of that of LFP and LVP. Fig. 2 shows the CV curves of the C-LFVP and P-LFVP, Li metal was used as

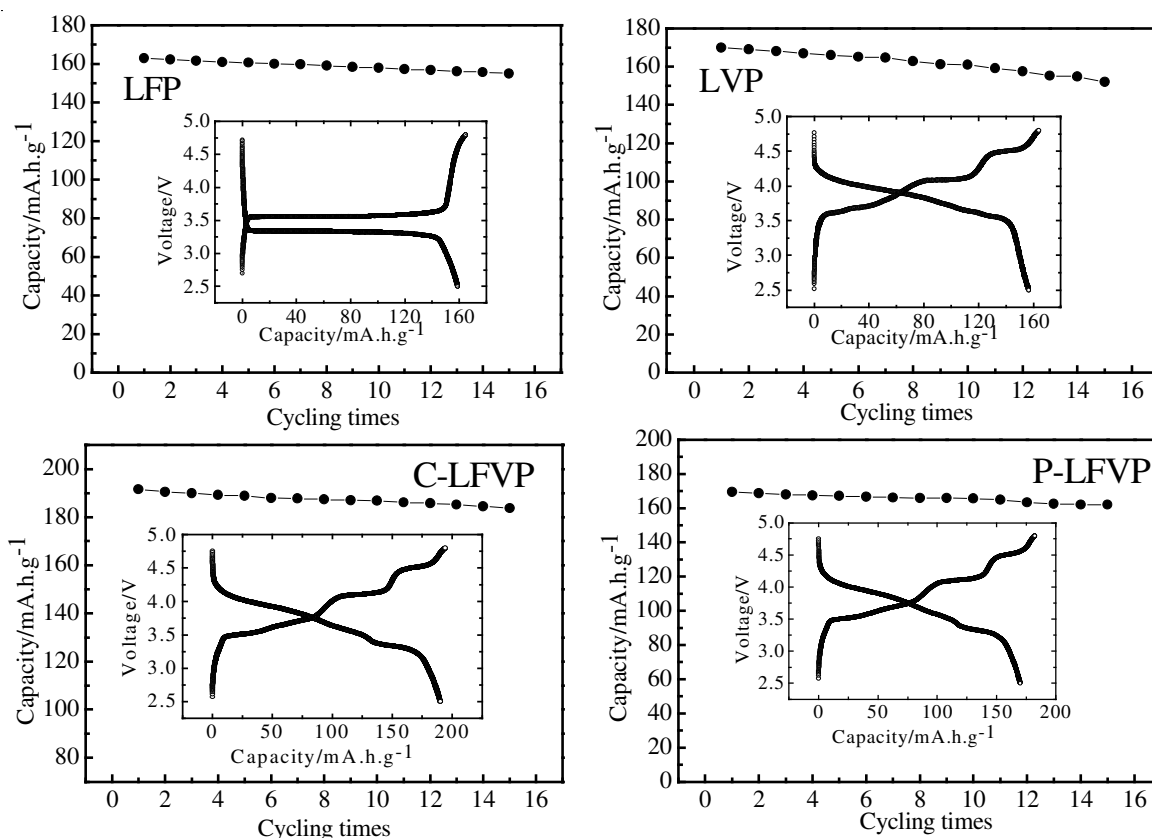


Fig. 1. Discharge capacities and voltage plateaus of LFP, LVP, C-LFVP and P-LFVP

counter electrode in button battery. There are four oxidation peaks (at 3.53, 3.63, 3.72 and 4.13 V, respectively) and four reduction peaks (at 3.35, 3.54, 3.62 and 3.99 V, respectively) in both of the two hybrid materials. All these peaks coincide basically with the peaks of LFP and LVP respectively. So we can infer that the LFP and LVP exist independently in both of the two hybrid materials.

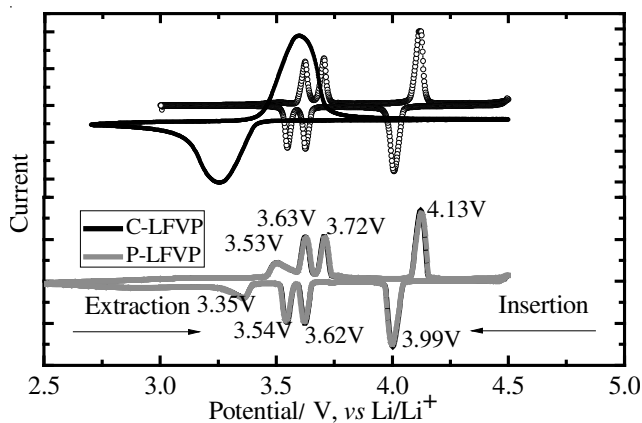


Fig. 2. CV curves of LFP, LVP, C-LFVP and P-LFVP

The X-ray diffraction patterns of LFP, LVP, C-LFVP and P-LFVP samples are shown in Fig. 3. C-LFVP's flat line basement and sharp diffraction peaks indicate good crystallinity. Meanwhile it can be seen clearly that its diffraction peaks are overlay by that of LFP and LVP, implying that LVP and LFP exist in hybrid materials independently, which is consistent with the conclusion of CV. In contrast, for the XRD of P-LFVP, its basement is rough, diffraction peaks intensity is not enough and the contrast between each peak is not clear-cut, all these can demonstrate fully bad crystallinity of P-LFVP, which is also a good proof that the electrochemical performance of C-LFVP is better than that of P-LFVP.

But why does the crystal structure of C-LFVP differ from P-LFVP? The reason lies in intense ball-milling. It is known that external forces can't change materials' internal crystalline structure, but long-hour ball-milling is an exception. During the ball milling process, the great energy generated by the collision damages part of crystalline structure of LFP and LVP, this is the main reason that causes the difference of micro-structure of P-LFVP and C-LFVP. Secondly, to prepare P-LFVP with crystalline LVP and LFP by ball milling, may also lead to oxidation of iron(II) and vanadium (III).

Table-1 listed the samples' crystallite lattice parameters. It is properly inferred from their space group, crystalline axis and lattice parameters that chemical changes occurred when mixing LFP and LVP together (yet we must recognize that due to different level of energy supply, the chemical changes of physical blending and chemical blending differ in scale). It is worth to noted that new miscellaneous substances like LiFeO_2 , Fe_2P , FePO_4 , Li_2O are found in both C-LFVP and P-LFVP. Theoretically, these substances may cause crystalline defects, which are responsible for the conductivity coefficient improvement of lithium ion, herein improve the hybrid material's electrochemical performance. It is surprising, P-LFVP's electrochemical performance gets little improvement. Since

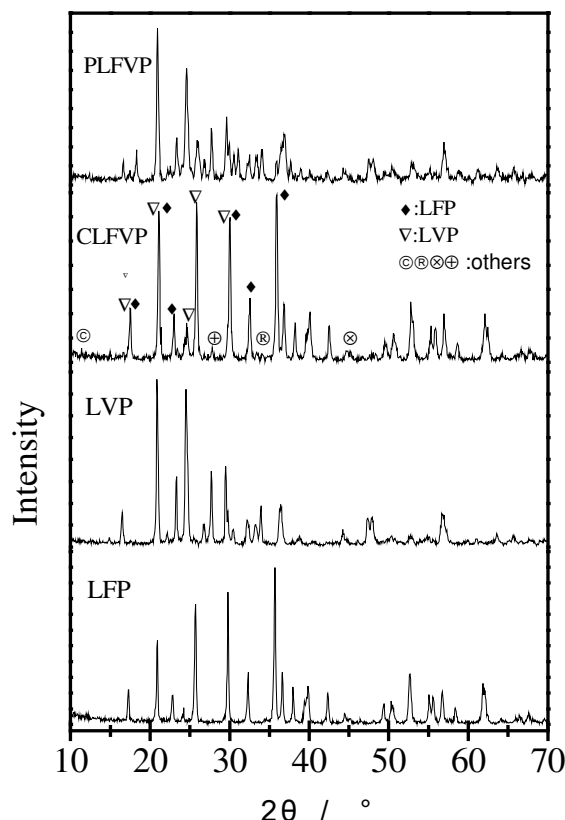


Fig. 3. XRD images of LFP, LVP, C-LFVP and P-LFVP

TABLE-1
CRYSTAL PARAMETERS OF THE SAMPLES

	LFP	LVP	C-LFVP	P-LFVP
a (nm)	1.0322	0.4016	0.8193	0.7052
b (nm)	0.5982	1.2047	0.7698	0.9234
c (nm)	0.4658	0.6322	0.6358	0.6431
Angle (°)	90.00	108.27	90.00	90.00
V (nm ³)	0.2877	0.2904	0.401	0.4187
Crystallite (A)	450	350	350	550

the mechanical method doesn't suffice evenly-distributed energy, LFP and LVP diminished in part during the ball milling and no sufficient energy was ready to produce new crystallized materials.

On the other hand, intense mechanical ball milling have the surface structure, especially the carbon-coated layer on top of P-LFVP. Fig. 4 showed that A is the SEM image of P-LFVP, B is the SEM image of C-LFVP, C is the SEM image of LFP and D is the SEM image of LVP. Comparing to the LFP and LVP (samples before ball milling), P-LFVP has a very rough surface and tiny carbon particles are scattered around the P-LFVP grains. SEM image of C-LFVP shows its particle diameter is unanimously within 100-200 nm and the grain surface is very neat and smooth. While the heating processed, the evenly-distributed glucose at the material surface (lithium, iron, vanadium, phosphorus) can effectively prevent the particles agglomeration of finished product. The decomposed glucose forms a smooth and uniform carbon layer, which would effectively improve the conductivity of the C-LFVP. Thus, whereas C-LFVP and P-LFVP are of about the same carbon content (C-LFVP:4.2 %, P-LFVP:4.5 %), their electrical

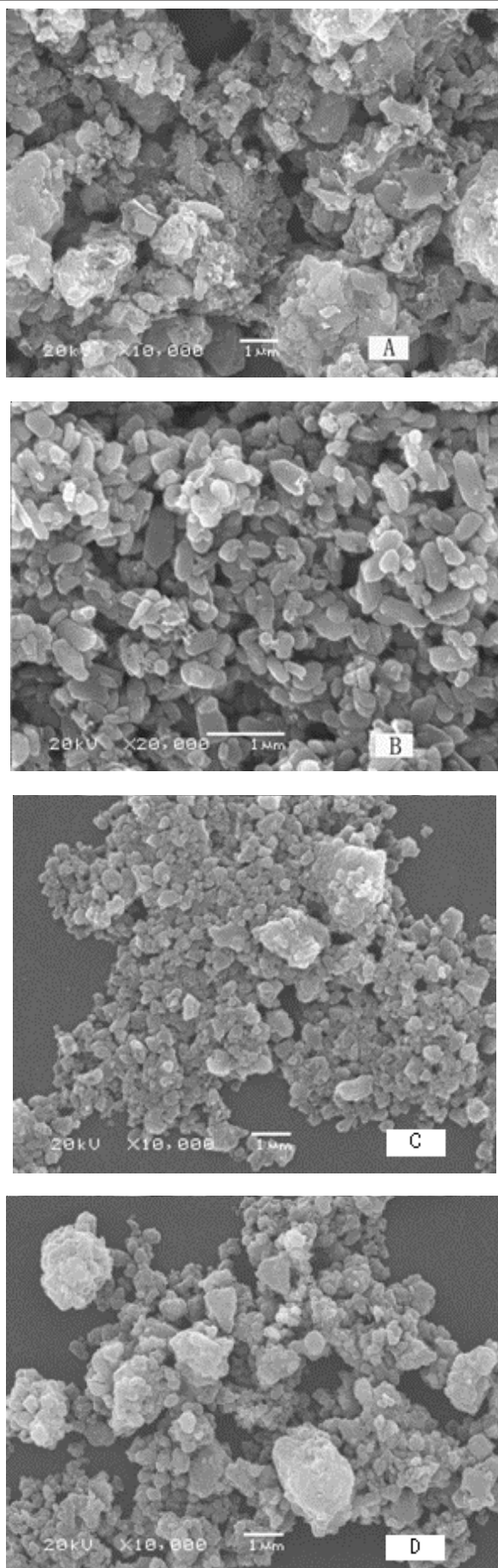


Fig. 4. SEM images of LFP, LVP, C-LFVP and P-LFVP

conductivity varies greatly (C-LFVP: $3.5 \times 10^{-2} \text{ s cm}^{-1}$, P-LFVP: $2.3 \times 10^{-4} \text{ s cm}^{-1}$). Similar conclusion was drawn by Guo *et al.*¹¹. This is another reason why C-LFVP surpasses P-LFVP in electrochemical performance.

Conclusion

This paper compares influences of two preparation methods (chemical blending and physical blending) on $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ hybrid materials, mixing of LFP and LVP can greatly improve the performances of the hybrid materials, achieving the complement of each other's advantages. The chemical binding proved to be an effective way of integrating advantages of different materials. The new miscellaneous substances yielding in the blending process improved invariably the material's electrochemical performance. The hybrid material synthesized by chemical blending enjoyed complete crystalline structure, regular grain shape and uniform particle size. On the other hand, physical blending did damage to micro-crystalline structure and particle morphology of the materials, which greatly reduced the electrochemical performances of materials. Therefore chemical blending is an arguably better way to prepare $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$.

$\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ hybrid is by no means a one case scenario, the chemical blending-over-physical blending may be extended to other materials. For example, lithium iron silicate cathode material has many advantages: easily accessible, cheap in cost and environmental friendly, but its poor conductivity and relatively low capacity limit its popular use. We can apply the $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ chemical blending to it, by blending lithium iron silicate with other materials. Given meticulous thought and further investigation, it would be very worth engaging to apply the findings in this paper to other related fields and hopefully this paper will serve the basis for future scientific research.

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