

Short Communication

## Synthesis of $\beta$ -LiVOPO<sub>4</sub>/C by Sol-gel Method and Microwave Sintering as Cathode Material for Lithium Ion Batteries

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The pure phase of  $\beta$ -LiVOPO<sub>4</sub>/C materials was synthesized by sol-gel method and microwave sintering with a starting material of V<sub>2</sub>O<sub>5</sub>, H<sub>3</sub>PO<sub>4</sub>, LiNO<sub>3</sub> and citric acid in microwave oven calcined for 5 min at the power of 900 W. The micro-structure was detected by X-ray diffraction (XRD) and the transmission electron microscopy (TEM) was also conducted to observe morphology of the material. Meanwhile, electrochemical property were also characterized by constant charge/discharge test, AC impedance and Cyclic voltammetry test. The results indicated that the external of LiVOPO<sub>4</sub> was coated on amorphous carbon with a thickness of 1.57 nm, which originated from citric acid, and enhanced the ionic conductivity of the material. Besides, the first discharge capacity is 94.5 mAh·g<sup>-1</sup> between 3 V and 4.5 V at the rate of C/20. The discharge capacity of  $\beta$ -LiVOPO<sub>4</sub>/C maintained at 88.6 mAh·g<sup>-1</sup>, which has 93.8% capacity retention after 30 cycles.

**Keywords:** Sol-gel method; Microwave sintering;  $\beta$ -LiVOPO<sub>4</sub>/C; Electrochemical property;

### 1. INTRODUCTION

At present, the most commonly used commercial lithium-ion batteries are layered oxides. Such as LiCoO<sub>2</sub>[1,2], LiNi<sub>0.33</sub>Mn<sub>0.33</sub>Co<sub>0.33</sub>O<sub>2</sub>[3] and LiMn<sub>2</sub>O<sub>4</sub>[4,5]. However, their high cost, complex preparation processing and inferior structural stability limited their large-scale use. Since Padhi firstly synthesized olivine LiFePO<sub>4</sub>[6,7] and widely reported for this material in 1997. The research of polyanion (PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, SiO<sub>4</sub><sup>4-</sup>, BO<sub>3</sub><sup>3-</sup>) cathode materials became more and more extensively. Compared with Fe, the transition metal V has a lively nature and a variety of valence states. Therefore, there is a large space for the study of the vanadium based on positive electrode materials. So far, the reported types of Vanadium which based on poly anionic cathode materials in the literature are as follows: Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>[8,9], LiVPO<sub>4</sub>F[10], LiVOPO<sub>4</sub>[11-14], VOPO<sub>4</sub>[15], etc.

As to  $\text{LiVOPO}_4$ , its theoretical capacity is  $166 \text{ mAh.g}^{-1}$ , which is as high as the  $\text{LiFePO}_4$  ( $170 \text{ mAh.g}^{-1}$ ), and its charging and discharging voltages up to 4.05 V and 3.90 V.  $\text{LiVOPO}_4$  has two polymorphs including triclinic ( $\alpha\text{-LiVOPO}_4$ ) and orthorhombic ( $\beta\text{-LiVOPO}_4$ ) phases. However, due to lower electrical conductivity, the electrochemical properties of this material are extremely poor. Even in some reports, there is almost no capacity for  $\alpha\text{-LiVOPO}_4$ [12]. Therefore, researchers generally focused on the synthesis of  $\beta\text{-LiVOPO}_4$  material. In 1999, Ganbicher[11]etc, synthesized  $\beta\text{-LiVOPO}_4$  by using electrochemical method. However, it just has the  $80 \text{ mAh.g}^{-1}$  discharge capacity at the rate of C/50. Later, RMM[13]etc, through the sol-gel method with high temperature sintering way to obtain pure phase of  $\beta\text{-LiVOPO}_4$  and coated with nano network conductive material  $\text{RuO}_2$  to improve its electrochemical performance. The initial discharge capacity increased from  $77.7 \text{ mAh.g}^{-1}$  ( $\beta\text{-LiVOPO}_4$ ) to  $118.6 \text{ mAh.g}^{-1}$  ( $\beta\text{-LiVOPO}_4/\text{RuO}_2$ ) at the current density of  $10 \text{ mA.g}^{-1}$ . Meanwhile, Tang AP[14]etc, by ball milling and muffle furnace sintering for  $600^\circ\text{C}$ -8h to get pure  $\beta\text{-LiVOPO}_4$ . The discharge voltage platform was as high as 3.9 V, but its first discharge capacity just remained at  $89.9 \text{ mAh.g}^{-1}$ . These reports showed that the electrochemical properties of  $\beta\text{-LiVOPO}_4$  were also poor, and the results of different investigators were quite different.

In the past studies, high temperature solid method[16] was used frequently. However, it lasted up to dozens of hours and accompanied by a large amount of energy consumption. For microwave sintering method, this heat treatment method has the advantages of energy saving, high efficiency, environmental protection, simple operation and the like. In this paper, the excellent electrochemical performance of pure  $\beta\text{-LiVOPO}_4/\text{C}$  can be obtained by using household microwave oven within a few minutes, which is also the first report that the  $\beta\text{-LiVOPO}_4/\text{C}$  can be synthesized in such a fast, convenient, and clean way as well as energy conservation.

## 2. EXPERIMENTAL

In this research all reagents were used directly without further depuration.

### 2.1 Synthesis

The precursor of  $\beta\text{-LiVOPO}_4/\text{C}$  was prepared by taking  $\text{V}_2\text{O}_5$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{LiNO}_3$  and citric acid according to the stoichiometric ratio.  $\text{V}_2\text{O}_5$  was firstly dissolved in  $\text{H}_2\text{O}_2$  with a small amount of water and vigorous agitation. Next, after the solution became orange, drop  $\text{H}_3\text{PO}_4$ ,  $\text{LiNO}_3$  and citric acid aqueous solution in sequence. After 4 h of intense agitation, the obtained solution was put into  $80^\circ\text{C}$  drying oven for 12 h to remove the solvent and make it get precursor. After that, the as-prepared precursor was made into pills. Then, put the pills into a 10 ml crucible. Next, the crucible was sent into a volume of 80 ml big crucible and buried with graphite powder. Finally, the big crucible was sent into the household microwave oven and sintering for 5 min (heating power: 900 W). The pure  $\beta\text{-LiVOPO}_4/\text{C}$  can easily be synthesized.

## 2.2 Characterization

The phase identification of  $\beta$ -LiVOPO<sub>4</sub>/C was implemented by X-Ray diffraction (Bruker D2,) which was equipped with Cu K $\alpha$  radiation in the 2 $\theta$  range 10–70 °. The morphology of  $\beta$ -LiVOPO<sub>4</sub>/C was characterized by transmission electron microscopy (TEM, H-600, Hitachi).

## 2.3 Electrochemical test

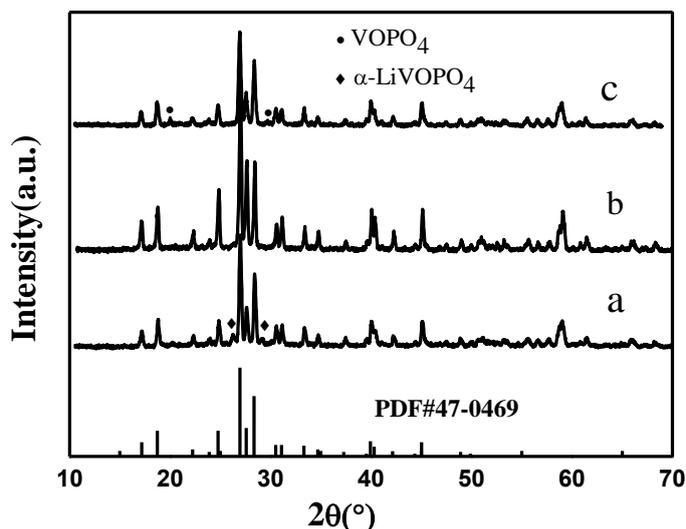
The  $\beta$ -LiVOPO<sub>4</sub>/C was made into coin-type half cells (LIR 2025) to test its electrochemical property, which was installed in a vacuum glove box. The  $\beta$ -LiVOPO<sub>4</sub>/C was mixed with acetylene black and polyvinylidene difluoride according to the proportion of 80:10:10 to form the mash. The mash was smeared on an aluminum foil with the cut into disks of 10 mm in diameter, then, put the disks into a 110 °C vacuum oven for 12 h to release moisture. The electrolyte was made by dissolved 1M LiPF<sub>6</sub> into a compound of ethylene carbonate, ethyl methyl carbonate and dimethyl carbonate according to the proportion of 1: 1: 1. Counter reference electrodes used lithium metal, and the separator was Celgard 2400.

The Cyclic voltammetry and AC impedance of  $\beta$ -LiVOPO<sub>4</sub>/C were detected by CHI 660D electrochemical analyzer (Chenhua, Shanghai, China). The CV curve was tested at the scan rate of 0.1 mV.s<sup>-1</sup>. The EIS was conducted at the frequent range from 10 Hz to 100 Hz. The charge/discharge test was conducted by using Land battery tester (LAND 2001A, Shanghai), and the voltage range was 3.0–4.5 V.

## 3. RESULTS AND DISCUSSION

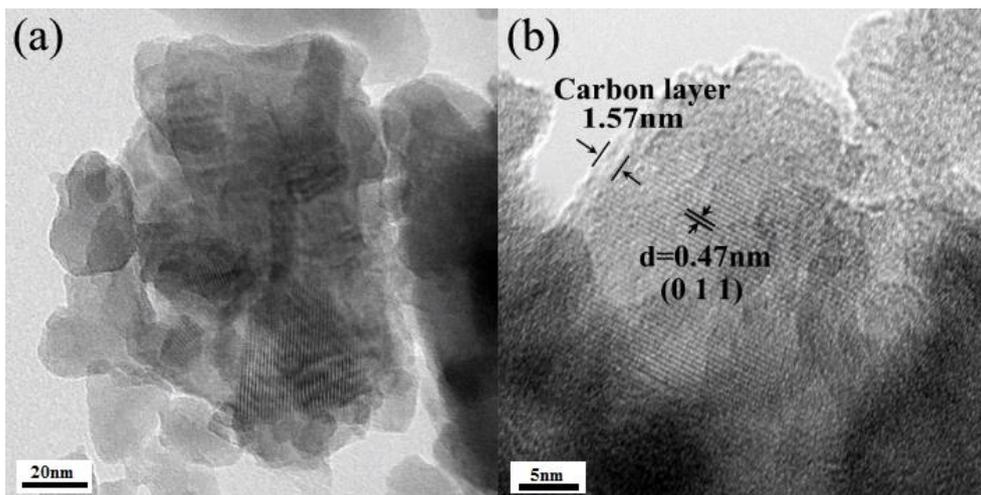
### 3.1 Structure and morphology

The XRD patterns of  $\beta$ -LiVOPO<sub>4</sub>/C powders are shown in Fig. 1. As is shown in the XRD patterns in Fig. 1a, there are two impurity peaks, which correspond to  $\alpha$ -LiVOPO<sub>4</sub> (JCPDS: 72-2253) at 26.38 ° and 29.34 ° for the reason that  $\alpha$ -LiVOPO<sub>4</sub> [17, 18] can be synthesized at low temperature. From fig. 1c, two weak peaks originate from  $\alpha$ -VOPO<sub>4</sub> (PDF#34-1247) at 19.98 °(2 $\theta$ ) and 29.69 °(2 $\theta$ ). It is due to the fly of lithium ion at high temperature, so it causes the existence of a little  $\alpha$ -VOPO<sub>4</sub> [19] phase. Besides, there's any impurity peaks can be found. From fig. 1b, the incisive diffraction peaks showed the integrity of crystallinity. Furthermore, all the characteristic diffraction peaks appear to be exactly the same as the standard card (PDF#47-0469). It can be proved that the obtained material is pure phase. Although, citric acid is used as carbon coating [20] and electronating agent in this experiment, in  $\beta$ -LiVOPO<sub>4</sub>/C composites, no carbon diffraction peaks were detected. It can be concluded that the crystal structure of  $\beta$ -LiVOPO<sub>4</sub>/C is not influenced by the amorphous carbon.



**Figure 1.** XRD patterns of  $\text{LiVOPO}_4/\text{C}$  by microwave sintering at different time: (a) 4min (b) 5min (c) 6min and the microwave power is 900 W

Fig. 2 shows the TEM images of  $\beta\text{-LiVOPO}_4/\text{C}$  composites. As is shown in Fig. 2a. The as-prepared materials are polygonal granular. Notably, in Fig. 2b. The lattice fringe of  $\beta\text{-LiVOPO}_4/\text{C}$  with an inter planar spacing of 0.47 nm is conformity to the (0 1 1) lattice planes. Meanwhile, it can be observed that the amorphous carbon [21] is cladded on  $\beta\text{-LiVOPO}_4/\text{C}$  with a thickness of 1.57 nm, which prevents the growth of the grain and enhances the conductivity of the material.

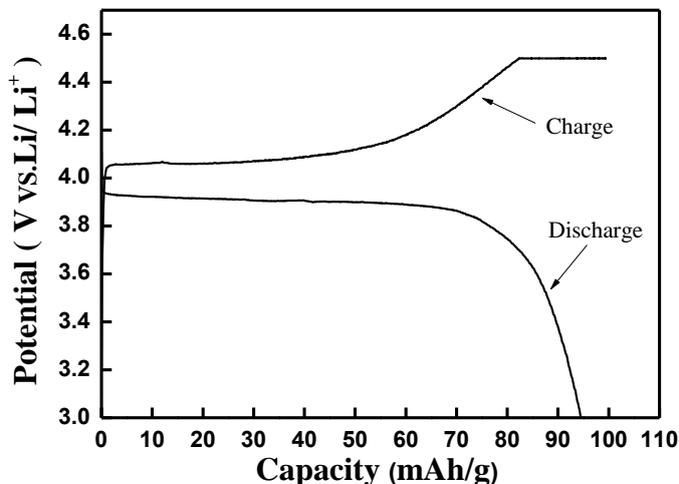


**Figure 2.** TEM images of  $\beta\text{-LiVOPO}_4/\text{C}$  samples (a) and (b)

### 3.2 Electrochemical performance

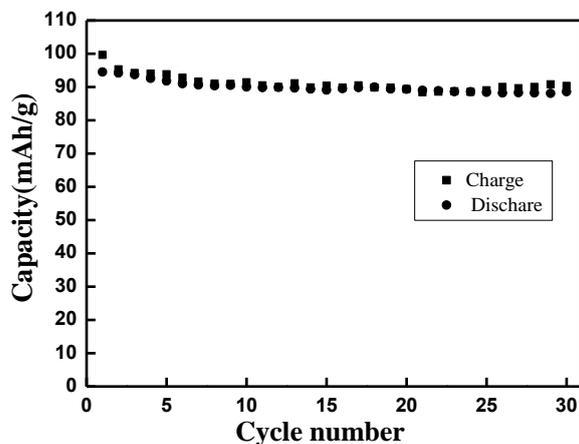
Fig. 3 shows the charge/discharge curves of  $\beta\text{-LiVOPO}_4/\text{C}$  materials between 3 V and 4.5 V, and the rate is 0.05 C. As can be seen from Figure 3. The pure  $\beta\text{-LiVOPO}_4/\text{C}$  expresses  $94.5 \text{ mAh}\cdot\text{g}^{-1}$  first discharge capacity. Besides, the material shows a charge platform around 4.05 V and a

corresponding discharge platform around 3.90 V. Obviously, the charge/discharge plateau is almost consistent with the report of literatures[13,14,17] and the discharge capacitance is slightly higher than the reported of Tang et al. [14] and Bustam et al. [17]. However, there is also a big gap between the discharge capacity and theoretical capacity ( $166 \text{ mAh.g}^{-1}$ ). According to the above research results, the electrochemical performance of  $\beta\text{-LiVOPO}_4$  still has great space for research.



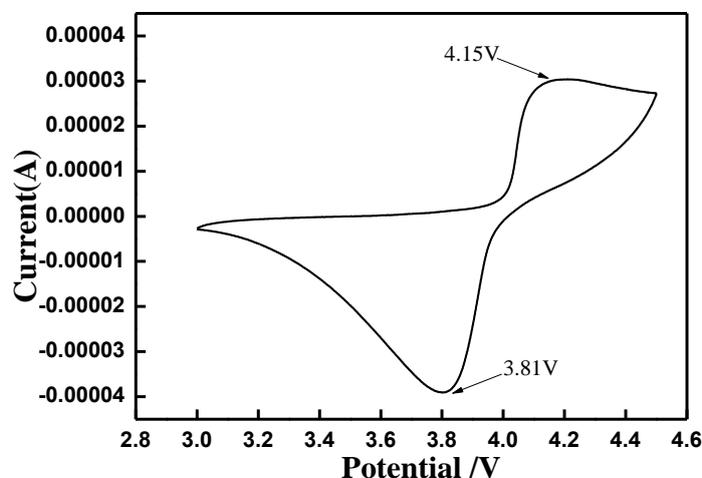
**Figure 3.** The initial charge/discharge curves of the  $\beta\text{-LiVOPO}_4/\text{C}$  materials between 3-4.5V at 0.05 C

Fig. 4 shows the cycling stability between 3 V and 4.5 V at 0.05 C after 30 cycles. It can be broadly observed that the  $\beta\text{-LiVOPO}_4/\text{C}$  discharge capacity maintained at  $88.6 \text{ mAh.g}^{-1}$  after 30 cycles, which accounts for 93.8% of the initial discharge capacity, and the average loss per cycle is only 0.21%. Besides, it shows excellent cycle stability than the reported of Tang et al. [14]. For  $\beta\text{-LiVOPO}_4/\text{C}$ , a small amount of amorphous carbon is coated on the surface and makes the conductivity of the material enhanced. Meanwhile, it is also restrained the growth of crystalline grain. Smaller particle size cut down the diffusion length of lithium ion and enhance conductivity and surface area of materials, which improves the electrochemical performance [22] of  $\beta\text{-LiVOPO}_4/\text{C}$ .

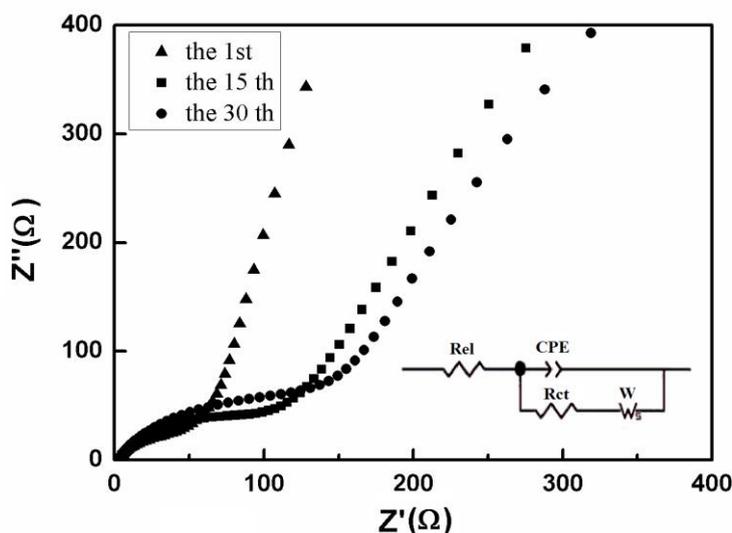


**Figure 4.** The cycling stability between 3-4.5 V at 0.05 C

The cyclic voltammetry curves of  $\beta$ -LiVOPO<sub>4</sub>/C materials shows in Fig. 5. It can be distinctly seen from the graph that the CV curve is corresponding to a couple of oxygen reduction peaks [23], which is corresponding to the free ionization of lithium ions into LiVOPO<sub>4</sub> crystal structure. In addition, the oxidation peak corresponds to 4.15 V and the reduction peak corresponds to 3.81 V. This pair of redox peaks also represent the presence of only one redox process in the electrode [24].



**Figure 5.** Cyclic voltammetry curves of  $\beta$ -LiVOPO<sub>4</sub>/C materials at the voltage range of 3.0–4.5 V and the scan rate of 0.1 mV.s<sup>-1</sup>.



**Figure 6.** AC impedance spectra and equivalent circuit diagram of  $\beta$ -LiVOPO<sub>4</sub>/C at the microwave power of 900 W: 5 min

The EIS was carried out to investigate the electrochemical process of the electrode and electrolyte interface. As it was shown in Fig. 6. The high frequency region is a semicircle, and the low frequency region is a quasi-straight line. The intersection point value of the semicircle in the high frequency region shows the impedance caused by the migration of Li<sup>+</sup> ions on the external of the

electrode and electrolyte, which was attributed to the charge transfer resistance [25]. The “Warburg impedance” [26] corresponding to the quasi-straight line in the low frequency region has a bearing on lithium ion diffusion through the oxide. Besides, the semicircle corresponding to the high frequency region increases with the cycle times, which depends on the formation of the solid SEI film [27, 28]. The SEI film adds the difficulty of diffusion of lithium ions between electrolytes and consumes part of the active material. Thus, it leads to capacity decay of the material during cycling. In general, the EIS result is consistent with the conclusion of cycle performance of materials. In addition, the equivalent circuit diagram also shows in the figure [29].

#### 4. CONCLUSIONS

The pure phase of  $\beta$ -LiVOPO<sub>4</sub>/C was synthesized by Sol-gel method and Microwave sintering at the power of 900 W for 5 min. The first discharge capacity was 94.5 mAh·g<sup>-1</sup> at the rate of 0.05 C. After 30 cycles charge/discharge performance test, the capacity was retained at 88.6 mAh·g<sup>-1</sup>, which account for 93.8% of initial discharge capacity. TEM indicated that the surface of pure  $\beta$ -LiVOPO<sub>4</sub> materials were coated with amorphous carbon, with the layer of 1.57 nm thick, which enhanced the conductivity of the material and made electrochemical performance of the pure  $\beta$ -LiVOPO<sub>4</sub> more excellent.

#### ACKNOWLEDGEMENTS

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