

Short communication

# Synthesis and performance of lithium vanadium phosphate as cathode materials for lithium ion batteries by a sol–gel method

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## Abstract

Monoclinic lithium vanadium phosphate,  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ , was synthesized by a sol–gel method under  $\text{Ar}/\text{H}_2$  (8%  $\text{H}_2$ ) atmosphere. The influence of sintering temperatures on the synthesis of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  has been investigated using X-ray diffraction (XRD), SEM and electrochemical methods. XRD patterns show that the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  crystallinity with monoclinic structure increases with the sintering temperature from 700 to 800 °C and then decreases from 800 to 900 °C. SEM results indicate that the particle size of as-prepared samples increases with the sintering temperature increase and there is minor carbon particles on the surface of the sample particles, which are very useful to enhance the conductivity of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ . Charge–discharge tests show the 800 °C-sample exhibits the highest initial discharge capacity of 131.2 mAh  $\text{g}^{-1}$  at 10 mA  $\text{g}^{-1}$  in the voltage range of 3.0–4.2 V with good capacity retention. CV experiment exhibits that there are three anodic peaks at 3.61, 3.70 and 4.11 V on lithium extraction as well as three cathodic peaks at 3.53, 3.61 and 4.00 V on lithium reinsertion at 0.02 mV  $\text{s}^{-1}$  between 3.0 and 4.3 V. It is suggested that the optimal sintering temperature is 800 °C in order to obtain pure monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  with good electrochemical performance by the sol–gel method, and the monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  can be used as candidate cathode materials for lithium ion batteries.

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**Keywords:** Lithium vanadium phosphate; Cathode materials; Lithium ion batteries; Sol–gel method

## 1. Introduction

In an intensive search for alternative materials, transition metal oxides have been the focus of a wide developing effort as cathode materials [1–4]. Recently, lithium conducting phosphates,  $\text{Li}_3\text{M}_2(\text{PO}_4)_3$ , and materials based on these compounds have emerged as the most promising candidates [5–8]. Of these materials, monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  [9], unlike the rhombohedral one [10], exhibits a complex series of two-phase transitions on Li extraction, followed by a solid solution regime on lithium reinsertion. The reversible cycling of all three lithium from  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  would correspond to a theoretical capacity of 197 mAh  $\text{g}^{-1}$  [11–14], which is the highest for all phosphates reported. Usually, synthesis of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  is mainly performed via hydrogen reduction method [15], which needs high reaction conditions. It is difficult to obtain  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  sample with small particle and homogeneous distribution, which is

critical to its electrochemical performance. Compared with solid state reaction method, sol–gel method can mix the starting ingredients at molecular level. It has enormous advantages such as lower calcination temperature, shorter sintering time and smaller particle size for the resultant powder [16,17]. Thus, sol–gel method is a novel concept for the synthesis of an improved  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ .

In this context, monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  was synthesized by a sol–gel method. Residual carbon left over from the sol–gel method is useful for its electrochemical improvement. It is investigated for the influence of sintering temperatures on the structure, the morphology and the electrochemical properties of monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ .

## 2. Experimental

The samples were prepared by the sol–gel method using  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{NH}_4\text{VO}_3$ ,  $\text{H}_3\text{PO}_4$  and citric acid as raw materials in the molar ratio of 3.05:2.00:3.00:2.00. Citric acid was dissolved in optimal distilled water, and then added aqueous solution of  $\text{NH}_4\text{VO}_3$  and  $\text{LiOH}\cdot\text{H}_2\text{O}$  in sequence under continuously stir-

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ring. The obtained sol darkened after adding  $\text{H}_3\text{PO}_4$ . In order to make metal ions chelated by citric acid thoroughly, adjust the sol PH to about 9 using  $\text{NH}_3 \cdot \text{H}_2\text{O}$  until the solution color gradually turned brown.

After evaporated water at  $80^\circ\text{C}$ , the as-prepared brown sol became gel. The gel was put into vacuum drying oven at  $120^\circ\text{C}$  for 8 h to become dry gel. The dry gel was initially heated to  $300^\circ\text{C}$  in air for 3 h to expel  $\text{H}_2\text{O}$  and  $\text{NH}_3$  as well as  $\text{CO}_2$  due to organic partly decomposing. The resulting product was then sintered for 8 h at the temperatures ranging from 700 to  $900^\circ\text{C}$  under a reducing atmosphere (92% Ar + 8%  $\text{H}_2$ ).

The completion of the reaction and the phase purity of the samples were confirmed by XRD using an X'pert powder diffractometer (Philip, Holland).

Thermal analysis of the raw material mixture was performed between room temperature and  $1000^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$  under Ar flow ( $20 \text{ ml min}^{-1}$ ).

The morphology and particle size of the samples were observed with field emission scanning electron microscope (JEOL, JSM-6700F).

The charge–discharge tests were performed using CR2016 coin-type cell by an automatic battery tester system (Land<sup>®</sup>, China). The test cell consisted of the positive electrode and lithium foil negative electrode separated by Celgard 2300 separator, and 1 M  $\text{LiPF}_6$  in EC, EMC and DMC (1:1:1 by volume) as the electrolyte. For the positive electrode, it was composed of the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  powder, acetylene black and PTFE in weight ratio of 80:15:5. Charge–discharge measurements were performed in the voltage range of 3.0–4.2 V at the current density of  $10 \text{ mA g}^{-1}$ . Cyclic voltammograms were tested using CHI650A electrochemical analyzer (Shanghai, China) at a scan rate of  $0.02 \text{ mV s}^{-1}$  in the voltage range of 3.0–4.3 V.

### 3. Results and discussion

In order to determine preheating and calcining temperature of the dry gel mixture, TG and DTA were performed. TG/DTA spectra for the gel precursor obtained are shown in Fig. 1.

The thermogram (TG) shows that weigh loss took place in several main steps. The first step occurred between room tem-

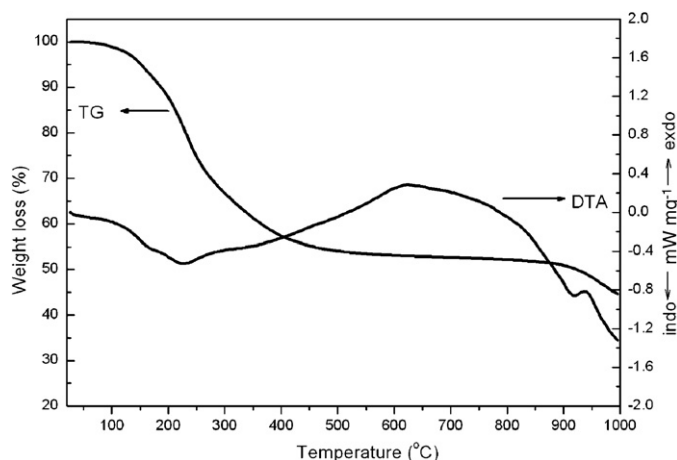


Fig. 1. TG/DTA patterns for the gel precursor in Ar atmosphere.

perature and  $120^\circ\text{C}$  with  $\sim 4\%$  weight loss, which was mainly attributed to the removal of water from the gel. The following step of around 40% weight loss between 120 and  $500^\circ\text{C}$  was the decomposition of lithium and vanadium citric compounds to form oxides and excess carbon, corresponding to a bump endothermic peak at  $200^\circ\text{C}$  in the DTA curve.

From 500 to  $900^\circ\text{C}$ , there was no obvious weight loss in TG curve, but there was a bump exothermic peak around  $620^\circ\text{C}$  in DTA curve. During this process, lithium oxide, vanadium oxide, phosphate and excess carbon reacted further to form well-crystallized  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ . After  $900^\circ\text{C}$ , the weight loss turns distinct again, about 9% weight loss can be seen, which may be caused by some side reaction due to  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  decomposition. In order to obtain complete crystallization of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  with monoclinic structure, the gel mixture must be sintered between 700 and  $900^\circ\text{C}$  as evidenced by the following X-ray diffraction (XRD) studies.

Fig. 2 shows the XRD patterns of the samples synthesized by the sol–gel method at different temperatures. As shown in Fig. 2a and b,  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  phase cannot be observed for the gel mixture at room temperature and for the sample at the pre-heating temperature of  $300^\circ\text{C}$ , which were mainly composed of lithium, vanadium and phosphorus oxides as well as extra carbon by prolysis of organic chelant citric acid. When the sintering temperature comes to  $700^\circ\text{C}$  (Fig. 2c), monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  becomes the dominant phase. Further increasing the sintering temperature to 800 and  $900^\circ\text{C}$ , respectively, the intensities of characteristic peaks of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  increase. As seen from Fig. 2c–e, the  $2\theta$  angle of diffraction peaks increases from 700 to  $800^\circ\text{C}$  and then decreases slightly from 800 to  $900^\circ\text{C}$ . Lattice parameters were calculated by Retveld Refinement. The result is shown in Table 1. It indicates that the cell volume of  $800^\circ\text{C}$ -sample ( $V = 889.47(2) \text{ \AA}^3$ ) is the smallest. The unit cell volume increase may be the possibility of creation of oxygen vacancies due to incomplete monoclinic crystalline of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ . All these results show that the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  crystallinity with monoclinic structure increases with the sintering temperature from 700 to  $800^\circ\text{C}$  and then decreases from 800 to  $900^\circ\text{C}$ .

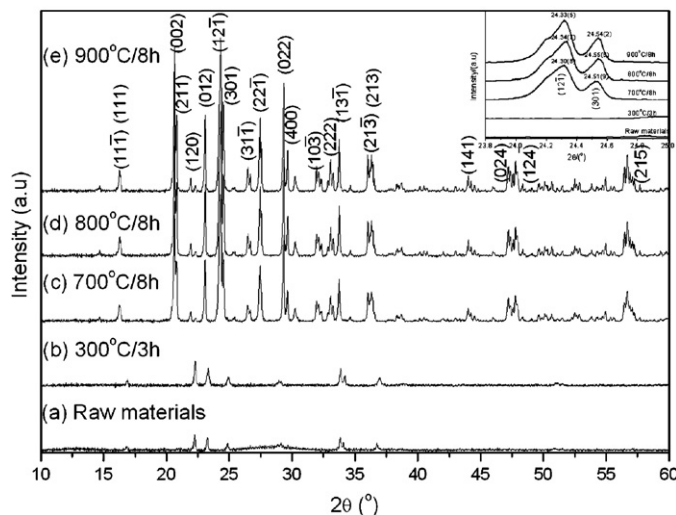


Fig. 2. XRD patterns of the samples sintered at different temperatures.

Table 1  
Lattice parameters of the samples

Samples (°C)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)	Cell volume (Å <sup>3</sup> )
700	12.056(0)	8.587(0)	8.613(2)	90.60(3)	891.62(7)
800	12.043(3)	8.580(0)	8.608(4)	90.61(0)	889.47(2)
900	12.049(9)	8.584(6)	8.609(5)	90.58(0)	890.54(7)

The morphology of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  samples sintered at three different temperatures is shown in Fig. 3. As seen from Fig. 3a, the particle of the sample sintered at 700 °C has a poly edged shape with an average size of  $\sim 0.2 \mu\text{m}$  in diameter. This sinter-

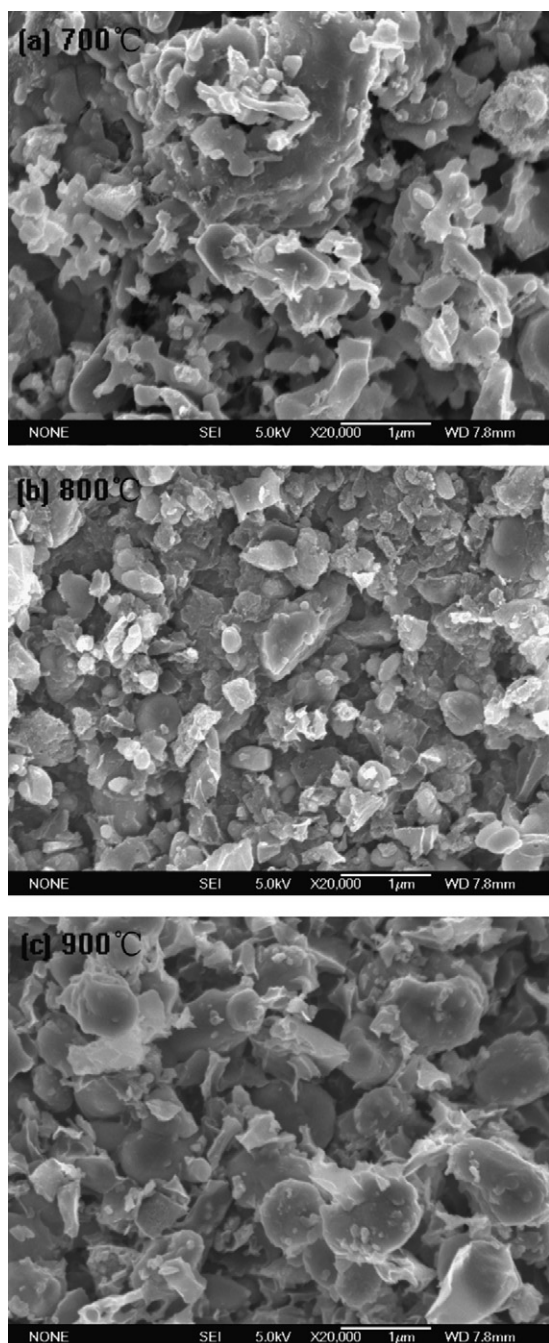


Fig. 3. SEM images of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  samples at different sintering temperatures.

ing temperature of 700 °C cannot be high enough to synthesize the pure phase of monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  sample as indicated by XRD. When the sample sintered at 800 °C (Fig. 3b), the particle with an average size of about  $0.4 \mu\text{m}$  are observed, which are larger than that of 700 °C-particles, The SEM images shown in Fig. 3 suggest that the particles of all the samples sintered at different temperatures are covered with a slice of carbon which are attributed to the residual carbon particles left over from the sol–gel method. The residual carbon particles can favor stabilization of  $\text{V}^{3+}$  and facilitate the diffusion of  $\text{Li}^+$ . This is to say, it is the result as a consequence of citric acid decomposition during preheating and sintering process and produces a composite powder with superior conductivity [14]. However, higher temperature (900 °C) preparation causes the abrupt growth of particles with a smooth surface particle of  $\sim 1 \mu\text{m}$ . It has been reported that the morphology and surface area of obtained particles have a notable effect on the electrochemical performance of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  and optimizing particle size or introducing conductive additives can improve the performance [18]. As nanometer size carbon particles can be dispersed uniformly between  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  particles, it has played a beneficial role in obtaining samples with small and uniform particle size and enhancing overall conductivity. Furthermore, the sol–gel method can prevent particles from agglomeration. Therefore, the sol–gel method can reduce particle size and optimize conductivity so as to improve the electrochemical performance of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ . For  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  synthesized by solid state reaction method [19], it requires high synthesizing temperature and long sintering time, and its particle size is about  $2 \mu\text{m}$  in diameter. Compared with  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  by solid state reaction method, it shows that the sample by sol–gel method has small particles and relatively lower synthesizing temperature.

Fig. 4 shows the first charge–discharge curves and cycling performance of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  samples synthesized at 700, 800 and 900 °C at the current density of  $10 \text{mAh g}^{-1}$  between 3.0 and 4.2 V. All the samples exhibit three charge flat plateaus around 3.61, 3.68 and 4.09 V and three discharge flat plateaus around 3.56, 3.65 and 4.03 V, which have been identified as the two-phase transitions during charge and discharge process [10]. It can also be seen that the sintering temperature has an enormous effect on the capacity. As shown in Fig. 4a, the initial charge and discharge capacity of 700 °C-sample are  $130.3$  and  $119.3 \text{mAh g}^{-1}$ , respectively, so the first Columbic efficiency is 91.6%. Fig. 4b shows its discharge capacity decreases from  $119.3 \text{mAh g}^{-1}$  of the first cycle to  $116.8 \text{mAh g}^{-1}$  of the 15th cycle, indicating that its capacity retention is 97.9% of the first discharge capacity. Compared with other two samples, this relating bad electrochemical performance is attributed to the incomplete  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  crystalline with low intensities of diffraction peaks as indicated by XRD. For 800 °C-sample, the first charge and discharge capacity are  $136.6$  and  $131.2 \text{mAh g}^{-1}$ , respectively, and the Columbic efficiency is as high as 96.0%. After 15 cycles, 99.2% capacity retention can be held. For 900 °C-sample, the first charge and discharge capacities are  $120.7$  and  $107.6 \text{mAh g}^{-1}$ , respectively, so its initial Columbic efficiency is 89.1 with 96.0% capacity retention up to 15



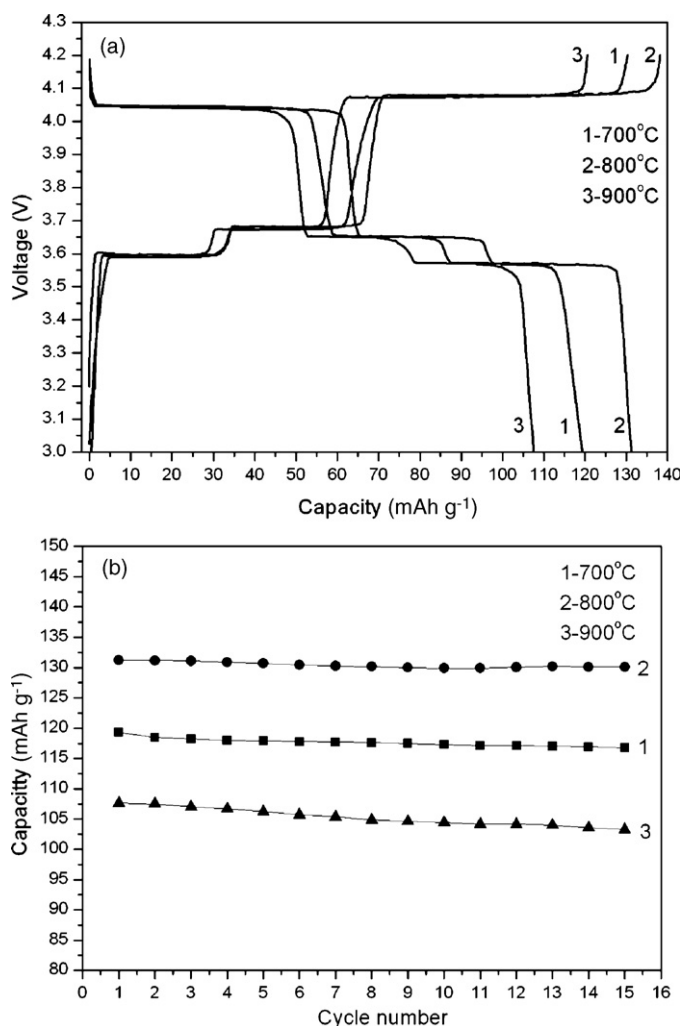


Fig. 4. The first charge–discharge curves (a) and cycling performance (b) of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  sintered at different temperatures.

cycles. Of all the three samples, the first and the 15th discharge capacity retention of 800 °C-sample are the highest, which is attributed to the pure monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  and relatively high-specific surface area of carbon-coated  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  particles. For  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  synthesized by solid state reaction method [19], it has 119.3  $\text{mAh g}^{-1}$  of the first discharge capacity and 94.8% retention of its initial discharge capacity after 15 cycles. In comparison with the sample by solid state method, the 800 °C-sample by sol–gel has higher initial-specific capacity and good capacity retention. This is related to the morphology and specific surface area of obtained samples. Considering the conductivity of active materials  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ , the sample with a larger particle size has a relative lower-specific area, and the lithium ions have to diffuse over longer distance between the surface and center during lithium insertion or extraction, resulting in the active material near the center of particle contributing very little to the lithium insertion/desertion reaction. The sample with smaller particles, which has relative higher-specific surface area and shorter distance from the center to the surface of the particles, will have better electrochemical performance. To our experimental results, it is suggest that the better performance of

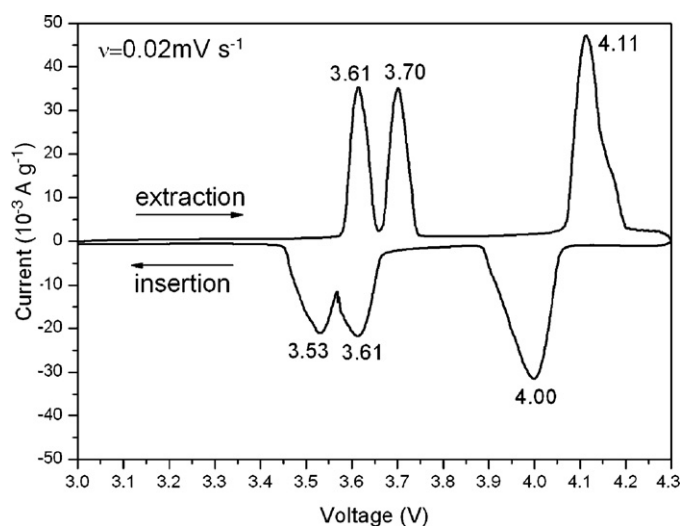


Fig. 5. CV curves of 800 °C- $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  at a scan rate of 0.02  $\text{mV s}^{-1}$  in the voltage range of 3.0–4.3 V.

monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  by sol–gel method can be obtained at a moderate sintering temperature of 800 °C for 8 h.

Fig. 5 shows the cyclic voltammetry (CV) for 800 °C-sample at a scanning rate of 0.02  $\text{mV s}^{-1}$  between 3.0 and 4.3 V. As known, CV indicates the oxidation/reduction potential at which lithium ions were extracted from the lattice or inserted into the lattice as well as phase transitions. As shown in Fig. 5, during the positive scan, there are three anodic peaks at 3.61, 3.70 and 4.11 V, which was corresponded to the lithium extraction as the following stoichiometric ranges:  $x=0.0$ –0.50, 0.50–1.0, and 1.0–2.0 in  $\text{Li}_{3-x}\text{V}_2(\text{PO}_4)_3$ , respectively. During the negative scan, there are correspondingly three cathodic peaks at 3.53, 3.61 and 4.00 V due to lithium insertion. It is well known that each anodic or cathodic peak in CV curve stands for two-phase transitions. This results are in good agreement with the first charge–discharge study (Fig. 4a).

#### 4. Conclusions

Monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  has been successfully synthesized by a sol–gel method under  $\text{Ar}/\text{H}_2$  (8%  $\text{H}_2$ ) atmosphere. The influence of sintering temperatures between 700 and 900 °C on the synthesis of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  has been investigated. Charge–discharge tests show that the 800 °C-sample exhibits the highest initial discharge capacity of 131.2  $\text{mAh g}^{-1}$  and good capacity retention between 3.0 and 4.2 V at the current density of 10  $\text{mA g}^{-1}$ . It is suggested that the optimal sintering temperature is 800 °C in order to obtain pure monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  with good electrochemical performance by the sol–gel method, and the monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  can be used as candidate cathode materials for lithium ion batteries.

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