



# Electrochemical characterization for lithium vanadium phosphate with different calcination temperatures prepared by the sol–gel method

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## ABSTRACT

$\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  (LVP/C) composite materials were synthesized via a sol–gel method with oxalic acid as the chelating agent and polyethylene glycol (PEG) as the supplementary carbon source. The oxalic acid and PEG serve as double carbon sources. This study focused on the effect of different calcination temperatures on the electrochemical properties of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ . The diffraction peaks for all of the samples are well indexed to monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  with a  $\text{P}2_1/\text{n}$  space group. The TGA data indicate that the residual carbon content of LVP/C-700 is the highest (i.e., 2.31 wt.%), and as the calcination temperature increased, the residual carbon content of the material gradually decreased. SEM and TEM analyses indicated that the LVP particles that were calcined at 700 °C exhibit a uniform particle size distribution and the carbon coating exhibited a complete and orderly moderate thickness. The LVP/C-700 material exhibits the best electrochemical performance in the voltage range of 3.0 to 4.3 V and 0.1 C where the initial discharge capacity can reach 128.98  $\text{mAh g}^{-1}$ . Even after 200 cycles, the discharge capacity was 119.31  $\text{mAh g}^{-1}$ , and the capacity retention rate was 92.49%.

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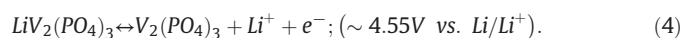
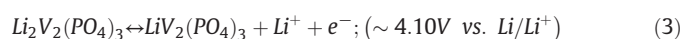
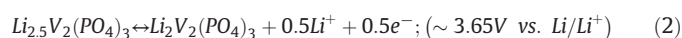
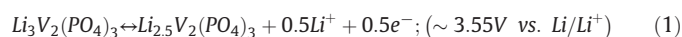
## 1. Introduction

In a lithium ion battery system, the cathode materials play a decisive role in improving the electrochemical performance of the entire cell and occupy a large proportion of the entire cell. Recently, lithium metal phosphates, such as  $\text{LiMPO}_4$  ( $\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Mn}$ ) [1–6] and  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  [7–12], have been proposed as potential cathode materials due to their competitive energy density and excellent thermal stability compared to other spinel-type or layered structured materials.  $\text{LiFePO}_4$  and  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  are two of the most prominent representatives.

In comparison to  $\text{LiFePO}_4$ , monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  has a three-dimensional frame structure that acts as a potential fast ion conductor due to its frame structure with interconnected clearance space [13]. In an open three-dimensional framework, the larger polyanions substitute the smaller  $\text{O}^{2-}$ , which is conducive to maintaining a stable structure and allowing faster ion transport. The lithium ion diffusion coefficient of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  is much higher than that of  $\text{LiFePO}_4$  ( $10^{-14}$ – $10^{-15}$   $\text{cm}^2 \text{s}^{-1}$ ) [14,15]. Therefore, the rapid charging and discharging of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  becomes possible. In addition, the unit cell of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  can accommodate a large quantity of lithium (3 mol Li), which is currently the highest capacity in phosphate ion cathode materials (197  $\text{mAh g}^{-1}$ ) [7,16]. As a NASICON-type compound,  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  has a unique three-dimensional frame

structure, and in the lithium ion embedded process, the formation of  $\text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3$ ,  $\text{Li}_2\text{V}_2(\text{PO}_4)_3$ ,  $\text{LiV}_2(\text{PO}_4)_3$ , and  $\text{V}_2(\text{PO}_4)_3$  can maintain the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  basic structure in the process of lithium ion intercalation and deintercalation, which results in higher thermal stability, safety performance and cycle stability. Its high working potential (~4.0 V) can better satisfy the requirements of lithium ion batteries in electric vehicles (EVs) and hybrid electric vehicles (HEVs). Therefore, the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  cathode material has been developed to replace in lithium ion batteries [9,17–22].

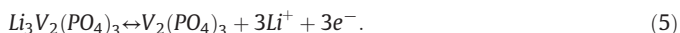
In addition, as a NASICON-type compound,  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  is attracting much more attention than other polyanion framework materials due to the multiple oxidation states of the vanadium transition metal [23,24]. As an anode material, the  $\text{V}^{3+}/\text{V}^{4+}$  redox couple can be exploited at approximately ~4 V vs.  $\text{Li}/\text{Li}^+$  by two phase reaction and subsequent partial oxidation of  $\text{V}^{4+}$  to  $\text{V}^{5+}$  at ~4.6 V vs.  $\text{Li}/\text{Li}^+$  with a theoretical capacity of 197  $\text{mAh g}^{-1}$  for complete removal of 3 mol of lithium. In general, the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  chemical reactions during the charging and discharging process are as follows:



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Total reaction equation:



$\text{Li}_3\text{V}_2(\text{PO}_4)_3$  exhibits a low electronic conductivity (i.e., approximately  $2.3 \times 10^{-8} \text{ S cm}^{-1}$  at 300 K) due to the polarization of the V–O bond [25], which substantially restricts its practical application in lithium ion batteries. Therefore, to overcome this disadvantage, several methods have been developed, such as coating with carbon or metal [7,26–31], doping with metal cations [32–34], and decreasing the particle size [35]. Carbon coating is a simple and effective method for improving the electronic conductivity of the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  materials. Carbon coating can substantially improve the electronic conductivity of the LVP and prevent direct contact between the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  particles and the electrolyte, which is helpful in alleviating the dissolution of vanadium ions in the electrolyte [36]. Several studies have demonstrated that the preparation method of the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  material strongly influences its electrochemical properties including its discharge capacity, rate capacity and cycle performances. In particular, carbon-coated  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  particles were synthesized by various methods, such as solid-state reaction [26,37], sol–gel process [38], and hydrothermal method [28,39], and these particles exhibited better electrochemical performances than the bare  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  powders. Rui et al. synthesized a  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  composite material and studied the effect of the different carbon sources (i.e., citric acid, glucose, PVDF and starch) on its electrochemical properties [40]. Finally, the residual carbon content of the synthetic materials was 1.3, 13.3, 12.7, and 10.5 wt.%, respectively. SEM analysis indicates that the use of PVDF as a carbon source for the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  material with a relatively uniform nanoscale carbon coating layer in the four types of materials exhibited the best electrochemical performance in the voltage range of 3.0 to 4.3 V and 5 C, and the discharge capacity can reach  $95 \text{ mAh g}^{-1}$ . In comparison to the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  pure phase material, although the electrochemical properties of the synthesized  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  were substantially improved, the residual carbon content of the synthesized material was relatively high (12.7 wt.%), which affects the active  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  and the proportion of the total electrode and limits further promotion of the capacity of the material. In addition, different preparation methods typically lead to the formation of final products with different microstructures, morphologies, size distributions, specific surface areas, crystallinity and phase purity, which ultimately affect the electrochemical performance of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ . However, most of the preparative methods typically require long preparation times, expensive starting materials, and complicated processes. Therefore, a simple and convenient method for the preparation of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  cathode materials with high electrochemical performances is required.

$\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  composite materials have been successfully synthesized via a sol–gel method with oxalic acid as the chelating agent and polyethylene glycol (PEG) as the supplementary carbon source, where the oxalic acid and PEG serve as double carbon sources [41]. It is important to note that PEG is simultaneously used as a supplementary carbon source and a surface active agent for the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  composites, which is prepared using the sol–gel method and ensures the quality of the carbon coating layer. It is important to note that PEG is not only a supplement carbon source but also a surface active agent, which results in a complete, orderly, moderate thickness of the carbon coating on the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  composite prepared using the sol–gel method. The results indicate that the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  composite material with the addition of 10 wt.% PEG exhibits the best electrochemical performance.

Some studies have used two or two more carbon sources to synthesize  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  composite materials. However, based on these limited studies, the synthesis conditions can affect the microstructures, morphologies, particle size distributions, specific surface areas, crystallinity, and carbon-coated layer of the final composite materials, which ultimately affect the electrochemical performance of these materials. In particular, due to the effects of the calcination temperature on the synthesis process, the obtained  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  possess different residual

carbon contents depending on the calcination temperatures, and the surface of the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  particles can coated with a complete and orderly medium thickness of carbon during the synthesis process to provide a good conductive network to improve the inherent conductivity of the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  material. Simultaneously, the different carbon coatings obtained under different calcination temperatures, which affect the grain growth and crystallinity, lead  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  materials with different morphologies and particle sizes. In addition, the path and direction of the channels are different in the lithium ion intercalation and deintercalation processes, which affects the lithium ion diffusion efficiency of the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  materials.

Therefore, the calcination temperature has an important influence on the lithium ion battery electrode material. Therefore, in this study, we studied the effects of different calcination temperatures on the electrochemical properties of the material. Using oxalic acid,  $\text{V}_2\text{O}_5$ ,  $\text{LiOH} \cdot \text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  as raw materials, we synthesized five  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  cathode materials under five different calcination temperatures using a sol–gel method. In addition, we added 10% wt PEG prior to calcination. Then, physical characterization, such as XRD, TGA, SEM, TEM and electrochemical performance testing, was employed to gain insight into how different calcination temperatures change the morphologies, residual carbon contents, crystallinity and carbon coating layers of the final materials and ultimately affect the electrochemical properties of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ .

## 2. Experimental

### 2.1. Synthesis of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite cathode materials

The  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  composites were synthesized via a sol–gel route. All of the reagents were analytical grade. In the first step,  $\text{V}_2\text{O}_5$  and oxalic acid in a stoichiometric molar ratio of 1:3 were dissolved with stirring in deionized water at  $80^\circ\text{C}$  to form a clear blue solution. Second, a stoichiometric mixture of  $\text{LiOH} \cdot \text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  were sequentially added to the solution. The mixture was heated to  $80^\circ\text{C}$  until a green gel formed. Finally, the gel was dried at  $80^\circ\text{C}$  overnight under vacuum to obtain the dry gel. The dry gel was preheated at  $350^\circ\text{C}$  for 6 h in a  $\text{N}_2$  atmosphere and then cooled to room temperature to obtain the precursor powder. PEG (10 wt.% of the precursor powder) was added and milled with the precursor powder in ethanol for 30 min followed by drying at  $65^\circ\text{C}$  for 8 h in an oven. This mixture was sintered under different calcination temperatures (i.e.,  $700^\circ\text{C}$ ,  $750^\circ\text{C}$ ,  $800^\circ\text{C}$ ,  $850^\circ\text{C}$  and  $900^\circ\text{C}$ ) for 10 h in a  $\text{N}_2$  atmosphere to prepare the LVP/C composite materials. The samples prepared under different calcination temperatures are referred to as LVP/C-700, LVP/C-750, LVP/C-800, LVP/C-850 and LVP/C-900, respectively.

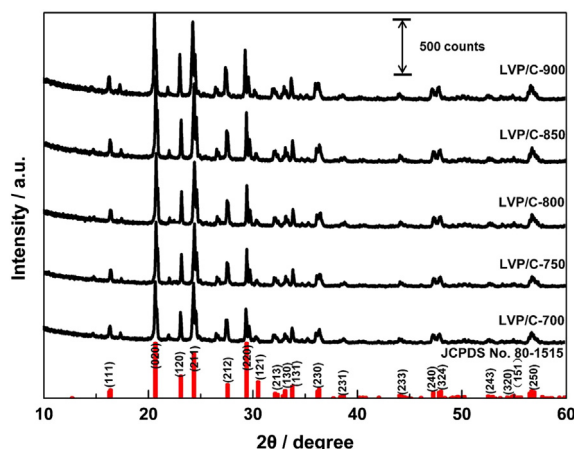


Fig. 1. X-Ray diffraction patterns for the as-prepared  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  samples.

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