



Analysis of the chemical diffusion coefficient of lithium ions in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode material

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ABSTRACT

The chemical diffusion coefficients of lithium ions (D_{Li^+}) in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ between 3.0 and 4.8 V are systematically determined by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic intermittent titration technique (GITT). The D_{Li^+} values are found to be dependent on the voltage state of charge and discharge. Based on the results from all the three techniques, the true diffusion coefficients ($D_{\text{Li}^+}^{\text{true}}$) measured in single-phase region are in the range of 10^{-9} to 10^{-10} $\text{cm}^2 \text{s}^{-1}$. Its apparent diffusion coefficients ($D_{\text{Li}^+}^{\text{app}}$) measured in two-phase regions by CV and GITT range from 10^{-10} to 10^{-11} $\text{cm}^2 \text{s}^{-1}$ and 10^{-8} to 10^{-13} $\text{cm}^2 \text{s}^{-1}$, respectively, depending on the potentials. By the GITT, the D_{Li^+} varies non-linearly in a “W” shape with the charge–discharge voltage, which is ascribed to the strong interactions of Li^+ with surrounding ions. Finally, the chemical diffusion coefficients of lithium ions measured by CV, EIS and GITT are compared to each other.

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1. Introduction

Rechargeable lithium-ion batteries are the most important energy storage systems for a wide application in electronic portable devices, particularly in hybrid electric vehicles. Lithium vanadium phosphate ($\text{Li}_3\text{V}_2(\text{PO}_4)_3$, LVP) with a monoclinic structure has been proposed to be a potential candidate of cathode materials for Li-ion batteries, due to its good ionic mobility, high reversible capacity and relatively high operating voltage [1–6]. The structure of LVP consists of a three-dimensional framework of slightly distorted VO_6 octahedra and PO_4 tetrahedra sharing oxygen vertexes, which house Li^+ ions in relatively large interstitial sites [1,7–9]. Such a framework structure containing corner-shared chains of Li polyhedra and interconnected interstitial space is potentially a fast ionic conductor. All the three Li^+ in the LVP can be removed and reversibly intercalated between 3.0 and 4.8 V, and then high capacity of 197 mAh g^{-1} can be achieved. However, one of the key drawbacks of LVP is its low intrinsic electronic conductivity of about $2.4 \times 10^{-7} \text{ S cm}^{-1}$ at room temperature [9]. Various synthesis and processing approaches have been employed to overcome this problem, such as metal doping [10–12] and carbon coating [1,3,5,6]. It is known that the factors which control the rate capability of Li^+ intercalation/de-intercalation in the LVP mainly depend on the bulk properties including diffusion of Li^+ within the compound and its

electronic conductivity as well as the kinetics of the electrochemical processes at the interface. Because the transport process of Li^+ in the LVP is the key step for the energy storage and output, it is necessary to study the lithium diffusion coefficient and its variation with the lithium content in LVP.

In the literature, much attention has been paid to focus on the kinetic behavior of LiCoO_2 [13–16], LiMn_2O_4 [17–21], $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [22], $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ [23] and LiFePO_4 [24,25], of which the chemical diffusion coefficient of Li ions, D_{Li^+} , is one of the most important kinetic characteristics. In most cases, the solid-state diffusion of Li ions with rather low values of D_{Li^+} may control the rate-determining step of the intercalation process, although there may be particular cases where the rate-determining step is diffusion in the electrolyte solution within the pores of the composite electrodes [26]. Several techniques, such as the cyclic voltammetry (CV) [14,25,27,16–20], electrochemical impedance spectroscopy (EIS) [13,14,25,27,16–22], and galvanostatic intermittent titration technique (GITT) [14,15,18,23,24,27], have been extensively used to measure the chemical diffusion coefficient. The CV can give us quantitative information on the nature of electrode process, and the reversibility, stability and phase transformations during intercalation and de-intercalation reactions [28]. It can also provide effective, or average, values of D_{Li^+} , in the electrode around the potential where a voltammetric peak appears. The EIS is also a powerful technique to determine the D_{Li^+} due to the fact that the low frequency Warburg contribution of the impedance response is directly related to the lithium-ion diffusion process in an electrode material. The GITT is established to be a reliable technique

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to determine the D_{Li^+} with highly resolved data for intercalation compounds of varying lithium content or potential.

It should be noted that the classical application of the EIS and GITT techniques is related to systems in which the concentration of the intercalant changes monotonically as intercalation proceeds [24,29]. Such a situation is valid only for topotactic solid-state intercalation reactions which lead to the formation of solid solution phases. When the intercalation/de-intercalation of Li^+ is accompanied by strong electron-ion interactions, the intercalation proceeds following one or several reaction fronts, and leads to the coexistence of two phases [24]. Thus, the physical meaning of the chemical diffusion coefficient D_{Li^+} as a function of the composition in the situation of two-phase coexistence becomes obscure. However, in the literature, we can easily find D_{Li^+} for intercalation systems with two-phase reactions [18,24,25,30]. In these cases, the obtained diffusion coefficients from EIS and GITT measurement, may be taken as an effective measure which reflects the intensity of long- and short-range interactions between the intercalated species. Hence, the derived D_{Li^+} may be named as apparent diffusion coefficient ($D_{\text{Li}^+}^{\text{app}}$).

Though the structural aspects and electrochemical performance of LVP compound have been elucidated in many papers [1–12], there are few reports on the diffusion coefficient which especially controls the rate performance of a cell with LVP as the cathode. According to the charge-discharge mechanisms of LVP in the voltage range of 3.0–4.8 V reported by Yin et al. [7–9], a sequence of two-phase transitions take place at 3.60 V ($\text{Li}_3\text{V}_2(\text{PO}_4)_3 \rightarrow \text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3$), 3.70 V ($\text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3 \rightarrow \text{Li}_2\text{V}_2(\text{PO}_4)_3$), 4.10 V ($\text{Li}_2\text{V}_2(\text{PO}_4)_3 \rightarrow \text{LiV}_2(\text{PO}_4)_3$) and 4.55 V ($\text{LiV}_2(\text{PO}_4)_3 \rightarrow \text{V}_2(\text{PO}_4)_3$), respectively, in the charge process. On the other hand, in the discharge process, it shows initially a solid solution behavior in the voltage range from 4.70 to 3.68 V ($\text{V}_2(\text{PO}_4)_3 \rightarrow \text{Li}_2\text{V}_2(\text{PO}_4)_3$), and then two-phase behavior at about 3.65 V ($\text{Li}_2\text{V}_2(\text{PO}_4)_3 \rightarrow \text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3$) and 3.55 V ($\text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3 \rightarrow \text{Li}_3\text{V}_2(\text{PO}_4)_3$). Therefore, it is significant to investigate the diffusion coefficient data for LVP between 3.0 and 4.8 V related to the formation of solid solution (true diffusion coefficient, $D_{\text{Li}^+}^{\text{true}}$) with a physical meaning as well as the two-phase reaction pathway (apparent diffusion coefficient, $D_{\text{Li}^+}^{\text{app}}$), which was treated as an insertion process with a Frumkin-type sorption isotherm [24,29].

In this paper, a carbon coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP/C) composite synthesized by a maltose-based sol-gel route is used as the active material. We focus on the systematic measurements and discussion of the diffusion coefficients of lithium ions, including both $D_{\text{Li}^+}^{\text{true}}$ and $D_{\text{Li}^+}^{\text{app}}$, in LVP by means of three different techniques, namely, CV, GITT and EIS.

2. Experimental

The monoclinic LVP/C composite was synthesized by a sol-gel route. Firstly, NH_4VO_3 powder was dissolved in distilled water with continued stirring at 60 °C until a clear yellow solution was formed, and then stoichiometric amounts of $\text{CH}_3\text{COOLi}\cdot 2\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ were added in sequence. Secondly, to above solution, oxalic acid and maltose with a molar ratio of LVP:oxalic acid:maltose = 1:2.4:0.35 were added. The mixture was heated at 60 °C with continuous stirring for about 12 h to remove the excess water, and then a light green gel was obtained. Here the oxalic acid was employed as a chelating reagent, which made the mixing of cations at the molecular level in a sol-gel process. The maltose acted as a carbon source, which could reduce vanadium from pentavalent to trivalent state and also form a network structure of carbon for electron conduction. Finally, the obtained gel was dried at 70 °C in an oven.

Afterward, the as-prepared gel precursor was ground and initially heated to 350 °C in a tubular furnace with a flowing N_2 atmosphere and kept for 5 h to remove H_2O , NH_3 and CO_2 out of the decomposition of organic components. After cooling to room temperature, the resulted powder was then reground and sintered for 8 h at the temperature of 750 °C in N_2 atmosphere to yield the LVP/C composite.

The structural analysis of the samples was performed by the X-ray diffraction (XRD) using a diffractometer (Philips X'Pert Pro Super, Cu K_α radiation). The diffraction patterns were recorded at room temperature in the 2θ range from 10° to 60°. The morphology of the powders was observed under a scanning electron microscope (SEM, JSM-6390LA).

The cathode was prepared by mixing 80 wt% LVP/C, 10 wt% carbon black and 10 wt% PVDF. The electrolyte was a solution of 1 M LiPF_6 dissolved in EC/DMC (1:1, w/w), and lithium metal was chosen as the anode. The coin-cells (CR2032 size) were fabricated in an argon-filled glove box (MBraun Labmaster 130) with a porous polypropylene membrane (Celgard 2400) as the separator.

The cells were tested on a multi-channel battery test system (NEWARE BTS-610) with galvanostatic charge and discharge in the voltage range of 3.0–4.8 V at a constant current of 0.1 mA. The CV and EIS of the cells were measured on a CHI 604B electrochemical workstation. The GITT was employed at a pulse of 0.1 mA for 10 min and with 40 min interruption between each pulse.

3. Results and discussion

The X-ray diffraction pattern of LVP/C composite is shown in Fig. 1. It can be clearly seen that all the peaks correspond to a single phase of LVP and can be indexed as a monoclinic structure with the space group $P2_1/n$. Based on XRD analysis, there is no evidence of diffraction peaks from carbon, which indicates that the residual carbon is with an amorphous structure and/or the thickness of the residual carbon layer on the LVP/C particles is too thin to be detected by the powder XRD [27]. The carbon content in the LVP/C composite is calculated as about 11.6 wt% based on the weight variation of LVP/C after its oxidation in air at 600 °C. The methodology of this residual carbon measurement will be given elsewhere.

Fig. 2 shows the morphology of LVP/C composite powder. From the SEM observations, there are a lot of fine irregular particles with an average size of about 500 nm except for a few large agglomerated abnormal particles. The residual carbon is not very homogeneously dispersed, where some LVP particles are deeply embedded and

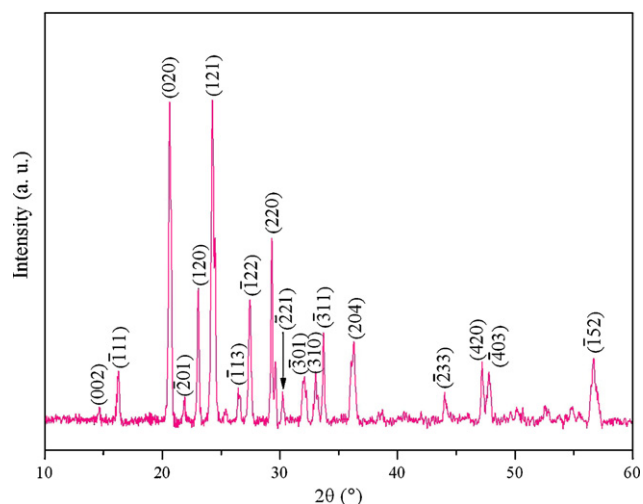


Fig. 1. The XRD pattern of LVP/C composite.

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