



Determination of the chemical diffusion coefficient of Li^+ in intercalation-type $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ anode material

X.H. Rui, N. Yesibolati, S.R. Li, C.C. Yuan, C.H. Chen*

CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, Anhui Hefei 230026, China

ARTICLE INFO

Article history:

Received 25 November 2010
Received in revised form 15 February 2011
Accepted 16 February 2011
Available online 10 March 2011

Keywords:

Lithium vanadium phosphate
Lithium ion battery
Anode
Chemical diffusion coefficient

ABSTRACT

The chemical diffusion coefficients of lithium ion (D_{Li^+}) in intercalation-type $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) anode material as a function of cell voltage between 3.0 and 0.0 V are systematically determined by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic intermittent titration technique (GITT). The true chemical diffusion coefficients ($D_{\text{Li}^+}^{\text{true}}$) obtained from EIS and GITT for the single-phase region (1.6–0.0 V vs. Li^+/Li) are in the range of 10^{-10} to 10^{-9} cm^2s^{-1} and 10^{-11} to 10^{-10} cm^2s^{-1} , respectively, and exhibit a decreasing trend of the change of $D_{\text{Li}^+}^{\text{true}}$ vs. voltage as the discharge and charge proceeded. The apparent chemical diffusion coefficients ($D_{\text{Li}^+}^{\text{app}}$) measured from CV and GITT for the two-phase regions (around 2.5–1.6 V) are in the range of 10^{-10} cm^2s^{-1} and 10^{-12} to 10^{-10} cm^2s^{-1} , respectively. For GITT, $D_{\text{Li}^+}^{\text{app}}$ vs. voltage plots display a characteristic of “W” shape due to the strong interactions of Li^+ with surrounding ions. Finally, the D_{Li^+} values of LVP anode are compared with other anode materials, illustrating that LVP can also be used as a potential anode material to achieve high rate capability.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The monoclinic lithium vanadium phosphate, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP), has been employed as a promising cathode material in rechargeable lithium ion batteries, due to its good ionic mobility, high reversible capacity and relatively high operating voltage [1–3]. The 3D framework structure of LVP is built from slightly distorted VO_6 octahedra and PO_4^{3-} tetrahedral anions [4]. Each VO_6 octahedron is surrounded by six PO_4 tetrahedra, whereas each PO_4 tetrahedron is surrounded by four VO_6 octahedra. This configuration containing relatively large interconnected interstitial space is potentially a fast ionic conductor. One of the major problems limiting the application of LVP cathode in high power density batteries is its low intrinsic electronic conductivity (about 10^{-8} Scm^{-1} [5]). As a result, many investigations have been focused on its synthesis and improvement of electrochemical capacities in non-aqueous electrolytes [6–8]. In the past few years, conductivity is usually enhanced appreciably by coating LVP particles with electrically conductive carbon materials [6–8].

Interestingly, in our recent work, we have successfully confirmed that the carbon coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP/C) can also be used as an intercalation-type anode material with superior electrochemical performance [9]. It exhibits a stable reversible capacity of 203 mAh g^{-1} in the voltage range of 3.0–0.0 V vs. Li^+/Li , and the Coulombic efficiency is close to 100% after the third cycle. In addition, the monoclinic LVP

structure can be still retained during the lithium ions insertion/extraction process. In the discharge process, there are initially a sequence of two-phase transition processes taking place at 1.95 V ($\text{Li}_3\text{V}_2(\text{PO}_4)_3 \rightarrow \text{Li}_{3.5}\text{V}_2(\text{PO}_4)_3$), 1.86 V ($\text{Li}_{3.5}\text{V}_2(\text{PO}_4)_3 \rightarrow \text{Li}_4\text{V}_2(\text{PO}_4)_3$), 1.74 V ($\text{Li}_4\text{V}_2(\text{PO}_4)_3 \rightarrow \text{Li}_{4.5}\text{V}_2(\text{PO}_4)_3$) and 1.66 V ($\text{Li}_{4.5}\text{V}_2(\text{PO}_4)_3 \rightarrow \text{Li}_5\text{V}_2(\text{PO}_4)_3$), respectively. Subsequently, a single-phase region between 1.6 V and 0.0 V is occurred, corresponding to 2 Li^+ insertion ($\text{Li}_5\text{V}_2(\text{PO}_4)_3 \rightarrow \text{Li}_7\text{V}_2(\text{PO}_4)_3$) associated with the V^{2+}/V^+ redox couple. And the lithium ions extraction is a reversible process. Furthermore, with increasing interest in high power density of Li-ion batteries, kinetics of lithium ions transfer in LVP anode material is also necessary to be evaluated and understood since they govern the intercalation/deintercalation rate.

In literatures, several techniques including cyclic voltammetry (CV) [10,11], electrochemical impedance spectroscopy (EIS) [12,13] and galvanostatic intermittent titration technique (GITT) [14,15], have been extensively used to study the diffusion kinetics of Li^+ intercalation/deintercalation and to estimate the chemical diffusion coefficients of Li^+ in solid electrodes. Here, it should be noted that, for the diffusion coefficient with a physical meaning (named true diffusion coefficient, $D_{\text{Li}^+}^{\text{true}}$), the Li^+ concentration of electrodes must be changed monotonically as intercalation proceeds [16], which is valid only for topotactic solid-state intercalation reactions. When the intercalation of lithium ions is accompanied by strong electron-ion interactions, the intercalation proceeds following one or several reaction fronts, and leads to the coexistence of two phases [15]. Thus, the physical meaning of the chemical diffusion coefficient, D_{Li^+} , as a function of lithium composition becomes obscure. However, the obtained D_{Li^+} can be taken

* Corresponding author: Tel.: +86 551 3606971; fax: +86 551 3601592.
E-mail address: cchchen@ustc.edu.cn (C.H. Chen).

as an effective measurement to reflect the intensity of long- and short-range interactions of lithium ions. At this condition, the D_{Li^+} is called as apparent diffusion coefficient, $D_{\text{Li}^+}^{\text{app}}$. We have reported the diffusion coefficients ($D_{\text{Li}^+}^{\text{true}}$ and $D_{\text{Li}^+}^{\text{app}}$) of LVP cathode in the voltage window of 3.0–4.8 V through CV, GITT and EIS methods [17]. $D_{\text{Li}^+}^{\text{true}}$ measured in the single-phase region is in the range of 10^{-10} to 10^{-9} $\text{cm}^2 \text{s}^{-1}$, and $D_{\text{Li}^+}^{\text{app}}$ derived from two-phase regions by the CV and GITT is in the range of 10^{-11} to 10^{-10} $\text{cm}^2 \text{s}^{-1}$ and 10^{-13} to 10^{-8} $\text{cm}^2 \text{s}^{-1}$, respectively. In the present paper, a systematic measurement and discussion of the $D_{\text{Li}^+}^{\text{true}}$ and $D_{\text{Li}^+}^{\text{app}}$ of LVP anode was conducted, using three different techniques, CV, EIS and GITT.

2. Experimental

The monoclinic LVP/C sample was synthesized by the carbothermal reduction method. The detailed sample preparation, structural and morphological characterization have been described elsewhere [9].

The electrochemical tests of LVP/C composites were carried out in coin-type cells. The working electrodes were prepared by mixing 80 wt.% LVP/C composites, 10 wt.% acetylene black and 10 wt.% poly(vinylidene fluoride) in N-methyl pyrrolidone to ensure homogeneity, and then followed by coating the slurry onto Cu foil current collector and drying at 70 °C. The electrolyte was a solution of 1 M LiPF₆ dissolved in EC/DMC (1:1 w/w), and lithium metal was chosen as the counter electrode. 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 3.0–0.0 V at a constant current of 0.1 mA. The cyclic voltammetry (CV, scan rate: 0.05, 0.1 and 0.2 mV s^{-1}) and electrochemical impedance spectroscopy (EIS, frequency range: 0.001– 10^5 Hz) at different charge–discharge states were performed on a CHI 604B electrochemical workstation. In order to realize an equilibrium state, all cells for EIS were kept at open circuit condition for 30 min before measurement. The galvanostatic intermittent titration technique (GITT) measurement was programmed to supply a constant current flux of 0.1 mA for 10 min followed by an open circuit stand for 40 min. The sequence was continued for the composition (x in $\text{Li}_{3+x}\text{V}_2(\text{PO}_4)_3$ or voltage) of interest.

3. Results and discussion

The X-ray diffraction (XRD), scanning electron microscope (SEM) and high-resolution transmission electron microscope (HRTEM) results have been discussed in our previous work [9].

Galvanostatic charge–discharge curves of the LVP anode at a constant current density of 0.013 mA cm^{-2} between 3.0 and 0.0 V during the 1st and 2nd cycles are shown in Fig. 1. From inset of Fig. 1, as described in the Introduction part, in the first discharge process (Li^+ insertion), four plateaus located at around 1.95, 1.86, 1.74 and 1.66 V correspond to a sequence of phase transition processes. Subsequently, a solid solution behavior (i.e. single-phase region) is displayed as indicated by a smoothly sloped curve down to 0.0 V with a capacity of about 310 mAh g^{-1} . Then, the Li^+ extraction is a reversible process. In addition, a large irreversible capacity originated from the single-phase region can be observed on the initial cycle, which is mainly attributed to the formation of the solid electrolyte interphase (SEI) film [18,19]. On the subsequent cycles, there is about 2 Li^+ insertion/extraction ($\text{Li}_5\text{V}_2(\text{PO}_4)_3 \leftrightarrow \text{Li}_7\text{V}_2(\text{PO}_4)_3$) in the single-phase region associated with the V^{2+}/V^+ redox couple.

The cyclic voltammetry (CV) is widely used to study the oxidation/reduction characteristics in electrochemical reactions and to obtain the apparent chemical diffusion coefficient of lithium ions. Fig. 2 shows CV curves of the LVP anode during the third cycle at different

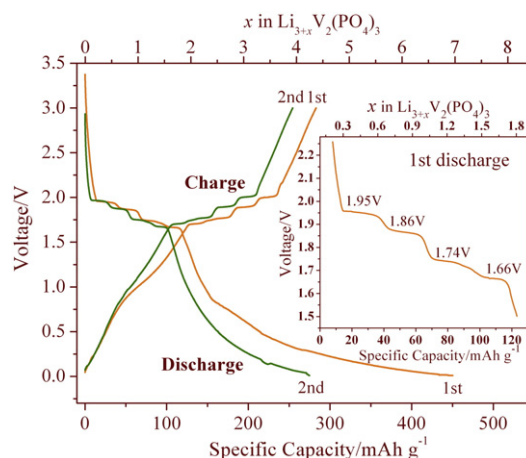


Fig. 1. Galvanostatic charge–discharge curves of the LVP anode at a constant current density of 0.013 mA cm^{-2} between 3.0 and 0.0 V during the 1st and 2nd cycles. Inset is the amplification of four plateaus in the first discharge process.

scan rates of 0.05, 0.1 and 0.2 mV s^{-1} between 3.0 and 0.0 V. At a slow scan rate of 0.05 mV s^{-1} , it can be clearly seen that, on the Li^+ insertion, there are four cathodic peaks at around 1.91 V (C1), 1.83 V (C2), 1.70 V (C3) and 1.62 V (C4) as well as a sloping curve down to 0.0 V, which are indicative of the coexistence of two intercalated phases and a solid solution behavior. On the Li^+ extraction, the sloping curve is up to about 1.6 V and three anodic peaks are located at around 1.82 V (A1), 1.94 V (A2) and 2.04 V (A3). The cyclic voltammetry peaks coincide well with the voltage plateaus in the galvanostatic charge–discharge curves (Fig. 1). The anodic peak A1 corresponds to two discharge plateaus around 1.70 and 1.77 V in Fig. 1. In CV scan, the heights of the anodic and cathodic peaks increase with increasing of the potential sweep rate. It is because of the peak area divided by the scan rate yields the capacity of the electrode which is a constant. Noting that, at a high scan rate (>0.2 mV s^{-1}), the redox peaks have a trend of combination and become difficult to distinguish, thus, we only conducted the CV curves at three low scan rates. As shown in Fig. 3, each redox peak current (i_p) shows a linear relationship with the square root of scan rate ($v^{1/2}$), which is expected for the diffusion-limited intercalation/deintercalation processes of Li^+ . Herein, the classical Randles–Sevcik equation for a semi-infinite diffusion of Li^+ into LVP anode can be applied. This equation is derived from the similar adsorption process theory at the metal/solution interface [12,20] as shown below:

$$i_p = (2.69 \times 10^5) n^{3/2} S D_{\text{Li}^+}^{1/2} C_{\text{Li}^+}^* v^{1/2} \quad (1)$$

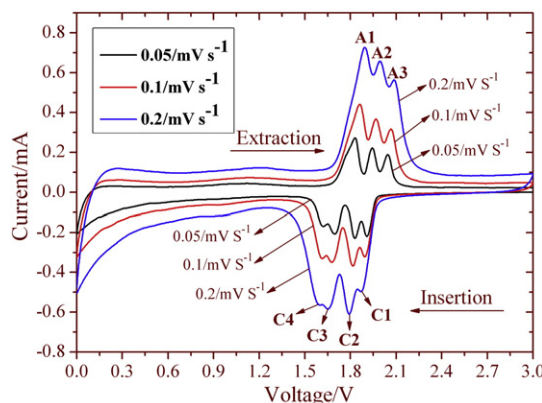


Fig. 2. Cyclic voltammetry curves of the LVP anode during the third cycle at different scan rates of 0.05, 0.1 and 0.2 mV s^{-1} between 3.0 and 0.0 V.

Download English Version:

<https://daneshyari.com/en/article/1298260>

Download Persian Version:

<https://daneshyari.com/article/1298260>

[Daneshyari.com](https://daneshyari.com)