



Synthesis and improved electrochemical performances of porous $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ spheres as cathode material for lithium-ion batteries

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ABSTRACT

Spherical $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites are synthesized by a soft chemistry route using hydrazine hydrate as the spheroidizing medium. The electrochemical properties of the materials are investigated by galvanostatic charge–discharge tests, cyclic voltammograms and electrochemical impedance spectrum. The porous $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ spheres exhibit better electrochemical performances than the solid ones. The spherical porous $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ electrode shows a high discharge capacity of 129.1 and 125.6 mAh g^{-1} between 3.0 and 4.3 V, and 183.8 and 160.9 mAh g^{-1} between 3.0 and 4.8 V at 0.2 and 1 C, respectively. Even at a charge–discharge rate of 15 C, this material can still deliver a discharge capacity of 100.5 and 121.5 mAh g^{-1} in the potential regions of 3.0–4.3 V and 3.0–4.8 V, respectively. The excellent electrochemical performance can be attributed to the porous structure, which can make the lithium ion diffusion and electron transfer more easily across the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{electrolyte}$ interfaces, thus resulting in enhanced electrode reaction kinetics and improved electrochemical performance.

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1. Introduction

Monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ has attracted extensive interest as a potential cathode material for lithium-ion batteries due to its good ion mobility, high theoretical capacity (197 mAh g^{-1}) and high operating voltage [1,2]. $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ possesses a NASICON-type structure consisting of slightly distorted VO_6 octahedra and PO_4 tetrahedra that share oxygen vertices with mobile Li^+ ions housed within the framework [1,3,4]. This NASICON-type structure with relatively larger interstitial space created by the PO_4^{3-} units is in favor of the fast ionic conductivity [5–8]. However, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ as well as LiFePO_4 have a problem of low intrinsic electronic conductivity ($2.4 \times 10^{-7} \text{ S cm}^{-1}$) [9], which greatly impedes their practical application. To solve this problem, various methods have been employed to overcome this disadvantage, such as doping with foreign atoms [10–14], decreasing the particle size [5,15] and carbon coating [16–27].

As has been reported in previous publication [15], nanosized $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ favors excellent electrochemical performance due to the enhanced specific surface area and reduced diffusion length of the ions and electrons in the electrode. However, the nanosized particles are unfavorable for electrode preparation because they have very high specific surface area and high

surface energy [28–30]. Further, nanosized particles have the drawback of electrochemical agglomeration during electrochemical cycling [28]. It has been reported [28–36] that the spherical morphology has many advantages in comparison with irregular aggregation such as higher volumetric energy density, lower interfacial energy, higher tap density and better fluidity characteristics. Traditionally, spray drying method is one of the most widely used techniques for preparation of spherical materials such as in the case of LiMn_2O_4 [37] and LiFePO_4 [29,30,38,39]. Recently, Wang et al. [40] successfully synthesized spherical $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ by using N_2H_4 as reducer and the material exhibited initial discharge capacities of 123 mAh g^{-1} (0.2 C) and 132 mAh g^{-1} (0.5 C) in the potential ranges of 3.0–4.3 V and 3.0–4.8 V, respectively.

In the present work, we present a soft chemistry route to obtain spherical $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ by using hydrazine hydrate as the spheroidizing medium. Hydrazine hydrate was also acting as a reducer to reduce partially V^{5+} to lower valence at room temperature and then carbothermal reduction method was performed at high temperature to obtain the spherical $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$. Herein, porous $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ spheres can be obtained by adjusting the pH value of the solution. Porous spherical particles show great advantages such as good contact with electrolyte, high specific surface area, quick Li^+ permeation and easier to bind than isolated nanosized particles [29,30,38,39]. Therefore, we prepared two types of spherical $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites with porous and solid structures and their electrochemical performances were investigated.

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2. Experimental

The spherical $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites were synthesized using a soft chemistry route followed by a carbothermal reduction synthesis. Here, hydrazine hydrate was used as the spheroidizing medium and 1,4-dihydroxy-2-butyne was employed as the carbon source. First, NH_4VO_3 (5 g) was added to 20 mL of deionized water under magnetic stirring to obtain a white turbid liquid. Then stoichiometric of 30 mL $\text{LiOH}\cdot\text{H}_2\text{O}$ (2.83 g) solution was added to the above white turbid liquid under magnetic stirring at room temperature until a transparent solution was formed. An appropriate quantity of hydrazine hydrate was added dropwise to this transparent solution under magnetic stirring until the solution was become to straw yellow. Afterward, 30 mL of $(\text{NH}_4)_2\text{HPO}_4$ (8.465 g) solution and 30 mL of 1,4-dihydroxy-2-butyne (2 g) solution were added to the straw yellow solution gradually. The resulting solution with a pH value of 9.0–10.0 was transferred into a polytetrafluoroethylene (PTFE) container and sealed at 200°C for 12 h, and then cooled to room temperature. Finally, the resulting precursor was washed with deionized water, separated by centrifugation for several times and dried at 60°C (denoted as precursor-1). The processing conditions of the precursor of porous $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ spheres (denoted as precursor-2) were the same as those of the precursor-1 except the pH value of the solution was adjusted at 13.0–14.0 by adding appropriate of ammonia before transferred into the PTFE container. The two precursors were sintered at 750°C for 10 h under Ar flow in a tube furnace to obtain the spherical $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders. The final product obtained from precursor-1 was solid sphere (denoted as SS-LVP/C), while the product obtained from precursor-2 was porous sphere (denoted as PS-LVP/C).

The morphologies and structures of the as-synthesized powders were characterized using field emission scanning electron microscopy (FESEM, FEI SIRION) and X-ray diffraction (XRD, Philips PC-APD with Cu $K\alpha$ radiation). The residual carbon contents of the powders were determined by means of an automatic elemental analyzer (EA, Flash EA1112). Raman scattering spectroscopy (LABRAM HR-800) was recorded at room temperature with the wave number shift among $4000\text{--}100\text{ cm}^{-1}$ in ultraviolet laser excitation line of 325 nm .

Electrochemical performances of the spherical $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites were investigated using CR2025 coin-type cell. A metallic lithium foil served as the anode electrode. The cathode consisted of 85 wt.% active material, 10 wt.% acetylene black and 5 wt.% polyvinylidene fluoride (PVDF) on aluminum foil. 1 M LiPF_6 in ethylene carbonate (EC)–dimethyl carbonate (DMC) (1:1 in volume) as the electrolyte, and a polypropylene micro-porous film (Cellgard 2300) as the separator. The cells were assembled in a glove box filled with high-purity argon. The charge–discharge tests were conducted on LAND battery program-control test system (Wuhan, China) between 3.0 and 4.3 V, 3.0 and 4.8 V by applying from 0.1 to 15 C current densities at room temperature, respectively. For electrochemical impedance spectroscopy (EIS) measurements, the test cells were with the metallic lithium foil as both the reference and counter electrodes. EIS measurements were performed on CHI660C electrochemical workstation over a frequency range of 100 kHz to 10 mHz at a stage of discharge (3.0 V) by applying an AC signal of 5 mV. Cyclic voltammetry (CV) was performed on this electrochemical workstation in the potential ranges of 3.0–4.3 V and 3.0–4.8 V (vs. Li/Li^+) at a scan rate of 0.1 mV s^{-1} , respectively.

3. Results and discussion

Fig. 1 shows the XRD patterns of SS-LVP/C and PS-LVP/C composites. The diffraction peaks of both samples can be attributed to monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ with the space group of $P2_1/n$ (ICSD

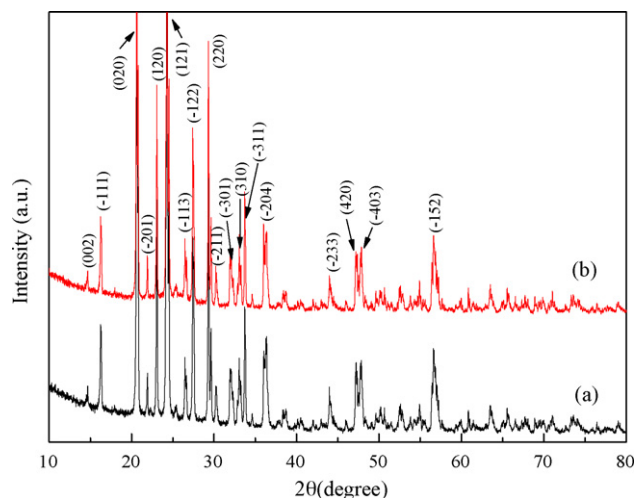


Fig. 1. XRD patterns of (a) SS-LVP/C and (b) PS-LVP/C composites.

#96962). Although about 11 wt.% 1,4-dihydroxy-2-butyne (carbon source) of total weight of the raw materials is used for the preparation of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites, the residual carbon is not detected in the XRD patterns since the state of the carbon is amorphous, or the amount of carbon is too small to be detected. However, according to elemental analysis, the carbon content in the final products is 2.87 and 2.62 wt.% for the SS-LVP/C and PS-LVP/C samples, respectively. Raman scattering results also indicate the presence of residual carbon in the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites, as shown in Fig. 2. In the two Raman spectra, two intense broad bands at 1590 cm^{-1} and 1353 cm^{-1} are attributed to the graphite band (G-band) and the disorder-induced phonon mode (D-band), respectively. According to the fitting results, the I_D/I_G value of the SS-LVP/C and PS-LVP/C composite is 0.88 and 0.87, respectively. This suggests that the graphite-like carbon in the residual carbon is about 50%, which is similar to the previous reports [7,18]. It is believed that low ratio value (I_D/I_G) of carbon coating is helpful for improving the electronic conductivity and electrochemical performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [7,18]. In addition, there are three broad Raman bands at 1136, 1050 and 970 cm^{-1} , which can be assigned to the vibrations of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [41].

Fig. 3 shows the SEM images of precursors and spherical $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders. As seen in Fig. 3a, precursor-1 has a spherical morphology but with a non-uniform size distribution. The

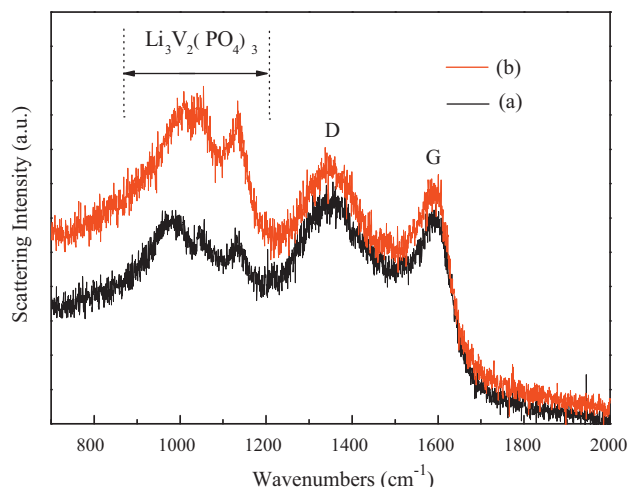


Fig. 2. Raman scattering spectra of (a) SS-LVP/C and (b) PS-LVP/C composites.

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