



Synthesis and electrochemical performance of $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ composite cathode materials for lithium-ion batteries

Wu-mei YIN¹, Ting-ting ZHANG¹, Qing ZHU², Quan-qi CHEN^{1,2}, Gu-cai LI³, Ling-zhi ZHANG²

1. School of Chemistry, Xiangtan University, Xiangtan 411105, China;

2. College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, China;

3. College of Chemistry and Chemical Engineering, Hunan Institute of Engineering, Xiangtan 411104, China

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Abstract: The $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ ($x=0, 0.01, 0.03$ and 0.05) composites were prepared by a sol–gel method and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemical measurements. The XRD results reveal that a small amount of Mg^{2+} doping into Li sites does not significantly change the monoclinic structure of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, but Mg-doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ has larger cell volume than the pristine $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. All Mg-doped composites display better electrochemical performance than the pristine one, and $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ composite exhibits the highest capacity and the best cycle performance among all above-mentioned composites. The analysis of Li^+ diffusion coefficients in $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ and $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ indicates that rapid Li^+ diffusion results from the doping of Mg^{2+} and the rapid Li^+ diffusion is responsible for the better electrochemical performance of Mg-doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite cathode materials.

Key words: lithium-ion batteries; lithium vanadium phosphate; diffusion coefficient; sol–gel method

1 Introduction

The lithium-ion battery has been recognized as one of the most promising energy systems because of its high efficiency of energy conversion, high energy density and long cycle life, and its electrochemical performance is mainly dependent on cathode and anode materials. Recently, monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode material has received extensive attention due to its high theoretical capacity, high operating voltage and excellent thermostability [1–3]. However, the low electronic conductivity ($2 \times 10^{-8} \text{ S/cm}$) [2] of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ degrades its electrochemical performance and limits its large-scale applications, especially in electric vehicles (EVs) and hybrid electric vehicles (HEVs). Numerous reports have confirmed that the addition of conductive carbon materials to $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ can greatly enhance the electronic conductivity of the composite and hence to improve the electrochemical performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [3–6]. However, the addition of conductive carbon

materials cannot improve the intrinsic electronic conductivity of the electroactive materials and plays adverse roles in the enhancement of the density of the electrode materials due to the low density of the conductive carbon materials, which is unfavorable for the improvement of energy density. Compared with the addition of conductive carbon, the improvement of intrinsic conductivity of the electroactive materials is a more effective way to improve the electrochemical performance and energy density. It was reported that the intrinsic electronic conductivity of LiFePO_4 , which was much lower than that of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, was increased by 8 orders magnitude by partial substitution of Li^+ with high-valent cations such as Zr^{4+} [7], Nb^{5+} [7], Mg^{2+} [7] and Cr^{3+} [8], and those doped LiFePO_4 samples exhibited excellent electrochemical performance. However, to our knowledge, the doping of high valent cations except Ca^{2+} [9] in Li sites of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ has not been explored. Based on the consideration that the cations in lattice are easily replaced by other cations with similar radii and Mg^{2+} has a radius of 0.066 nm, similar to that

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Corresponding author: Quan-qi CHEN; Tel: +86-773-5898551; E-mail: quanqi.chen@glut.edu.cn; quanqi.chen@yahoo.com

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of Li^+ ($r=0.068$ nm), the monoclinic Mg-doped $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3$ samples may be readily synthesized and the samples potentially exhibit better electrochemical performance than the pristine $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. In this work, $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ composites were prepared by a sol-gel method and the effects of Mg^{2+} content on the physical and electrochemical properties of $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ ($x=0, 0.01, 0.03$ and 0.05) composites were investigated.

2 Experimental

All the $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ ($x=0, 0.01, 0.03$ and 0.05) composites were prepared by a sol-gel method, which is similar to the previous reports [10,11]. The typical procedure of preparation of $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ is as follows: a certain amount of V_2O_5 powder was dissolved in 10% (volume fraction) hydrogen peroxide solution to form a clear brown solution, then citric acid with equivalent mole to V_2O_5 and stoichiometric amounts of $\text{NH}_4\text{H}_2\text{PO}_4$, $\text{CH}_3\text{COOLi}\cdot 2\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ were added to the above brown solution with vigorous stirring. The mixture solution was aged with continuous stirring at 80°C for 10 h in thermostatic bath to obtain a dark green gel. The obtained gel was dried in a vacuum oven at 120°C , pelletized and calcined at 300°C for 4 h in a tubular furnace with the following argon gas to get a fluffy black product. The resulted product was reground and pelletized again, and sintered at 800°C for 8 h in argon atmosphere at a ramp rate of $2^\circ\text{C}/\text{min}$, and then cooled to room temperature to yield a black $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ composite.

The crystal structure of the resulted composites was analyzed by a Rigaku 2500 X-ray diffractometer (XRD) with $\text{Cu K}\alpha$ radiation ($\lambda=0.15418$ nm). The carbon content of the samples was determined by a carbon-sulfur analyzer (Mlti EA2000). The surface morphology of the samples was observed by a JSM-5600LV scanning electron microscope (SEM).

The electrochemical tests of $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ composites were carried out using 2032 coin cells. The cathodes were prepared by pasting the mixture of 80% $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ composite, 10% acetylene black and 10% polyvinylidene fluoride (PVDF) (mass fraction) onto an aluminum foil current collector. The coin cell was assembled in an argon-filled glove box using Li foil as the anode, 1 mol/L LiPF_6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, volume ratio) as the electrolyte, and Celgard 2400 as the separator. The coin cells were galvanostatically cycled at different current densities ($1\text{C}=133$ mA/g) in the voltage range of 3.0–4.3 V at 25°C using a NEWARE battery testing system. The specific capacity and current density

were calculated based on the mass of the active materials. The measurements of electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were conducted on an IM6ex electrochemistry workstation (Zahner Elektrick, German).

3 Results and discussion

All the final products are black and contain about 3.6% carbon (mass fraction), which was determined by a carbon-sulfur analyzer. The XRD patterns of the final products are presented in Fig. 1. All diffraction peaks of the samples can be indexed by a well-defined monoclinic phase, which is consistent with monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (PDF: 01-074-3236). The absence of diffraction peaks of impurity suggests that the final products are composites of a monoclinic phase and amorphous carbon, implying that a small amount of Mg^{2+} dopant does not significantly affect the monoclinic structure of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. The composites are denoted as $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$, $\text{Li}_{2.98}\text{Mg}_{0.01}\text{V}_2(\text{PO}_4)_3/\text{C}$, $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ and $\text{Li}_{2.90}\text{Mg}_{0.05}\text{V}_2(\text{PO}_4)_3/\text{C}$, respectively, and the cell parameters of the corresponding compounds are listed in Table 1.

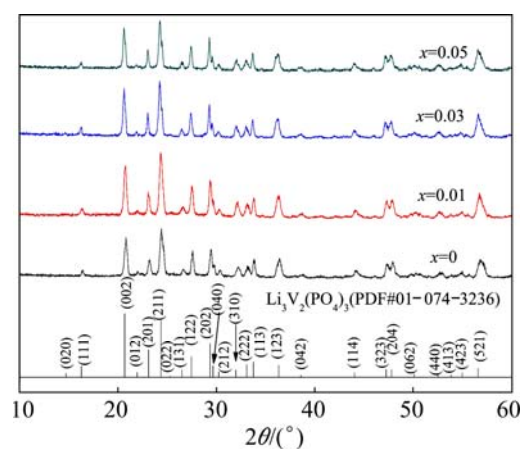


Fig. 1 XRD patterns of $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ composites

Table 1 Lattice parameters of $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3$ compounds

Compound	a/nm	b/nm	c/nm	$\beta/(^\circ)$	Cell
					volume/ nm^3
$\text{Li}_3\text{V}_2(\text{PO}_4)_3$	0.8588	1.2040	0.8599	90.2	0.8891
$\text{Li}_{2.98}\text{Mg}_{0.01}\text{V}_2(\text{PO}_4)_3$	0.8602	1.2064	0.8595	90.1	0.8919
$\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3$	0.8623	1.2107	0.8612	90.1	0.8991
$\text{Li}_{2.90}\text{Mg}_{0.05}\text{V}_2(\text{PO}_4)_3$	0.8617	1.2098	0.8613	90.1	0.8979

The results reveal that the cell parameters slightly increase with the addition of Mg. The cell volumes of Mg-doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ compounds are somewhat larger than that of the pristine one and similar to the variation

trends of that of Na-doped, K-doped and Ca-doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples [9,12–14], and the partial substitution of monovalent Li^+ ($r=0.068$ nm) by bivalent Mg^{2+} ($r=0.066$ nm) with approximate radius is responsible for the variation. The larger cell volume could provide larger channel for Li^+ transport and facilitate rapid diffusion of Li^+ in the active materials, which is beneficial to improving the electrochemical performance of $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ composites. Furthermore, the partial replacement of monovalent Li^+ by bivalent Mg^{2+} produces vacancies in Li sites [7,15], which may be favorable to facilitating the transport of electrons and Li^+ , possibly resulting in much better electrochemical performance of the electroactive material.

The SEM images of $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ composites are shown in Fig. 2. It can be clearly seen that the composites display similar morphologies, indicating that the introduction of small amounts of Mg^{2+} into Li sites does not affect the morphologies of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites.

To evaluate the effects of partial substitution of Li^+ by Mg^{2+} on the electrochemical mechanism of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, the cyclic voltammetry tests at a scan rate of 0.05 mV/s in the potential range of 3.0–4.3 V were carried out on the Mg-doped and pristine composites,

and the cyclic voltammograms (CVs) are presented in Fig. 3. All the $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ composites exhibit similar shape of the CV curves including three anodic peaks (denoted as a_1 , a_2 and a_3) and three cathodic peaks (labeled as c_1 , c_2 and c_3), suggesting that the dopant of Mg^{2+} in Li sites does not alter the mechanism of the insertion/extraction of Li^+ into/from $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ during the discharge–charge processes. However, compared with the pristine $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ sample, the Mg-doped samples display lower anodic peak potentials and higher cathodic peak potentials, which implies that the doped samples exhibit smaller polarization than the pristine one during the charge–discharge processes. The detailed peak potentials of the samples are listed in Table 2. The potential differences between the anodic peaks and the corresponding cathodic peaks of doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples are lower than those of pristine $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, and the potential difference of $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ is the smallest among all the samples, suggesting that $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ may have the best electrochemical performance.

Figure 4 shows the impedance behavior of $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ composites which are initially charged to 4.3 V, and all the composites display typical Nyquist characteristics. It can be seen that all the Nyquist plots are comprised of an intercept in the high frequency

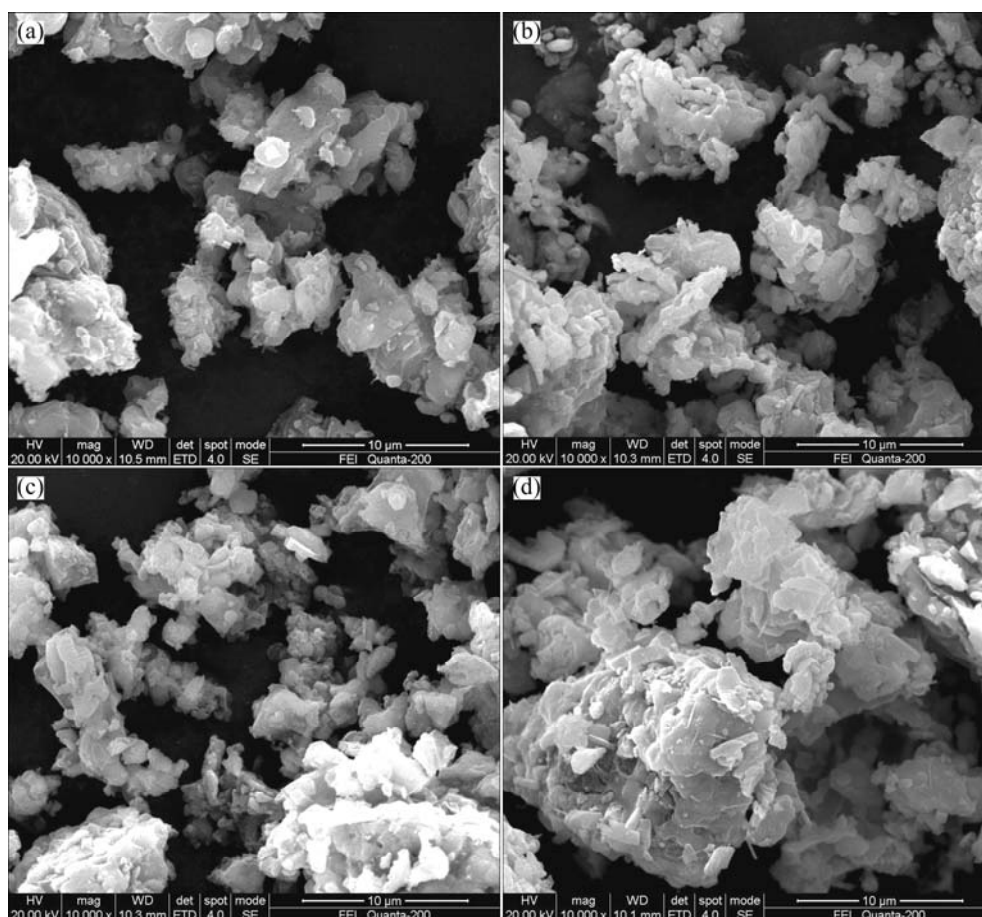


Fig. 2 SEM images of $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$: (a) $x=0$; (b) $x=0.01$; (c) $x=0.03$; (d) $x=0.05$

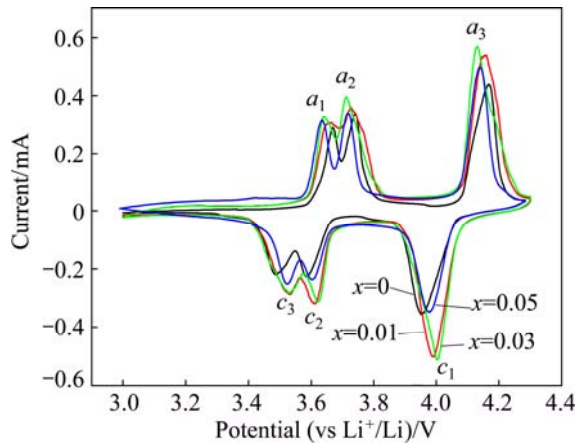


Fig. 3 Cyclic voltammograms of $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ composites at scan rate of 0.05 mV/s in potential range of 3.0–4.3 V at 25 °C

Table 2 Potentials for CV peaks of $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ composites

Sample	Potential/V					
	a_1	a_2	a_3	c_1	c_2	c_3
$\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$	3.669	3.741	4.167	3.952	3.584	3.487
$\text{Li}_{2.98}\text{Mg}_{0.01}\text{V}_2(\text{PO}_4)_3/\text{C}$	3.664	3.727	4.154	3.991	3.612	3.553
$\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$	3.640	3.712	4.130	4.003	3.623	3.535
$\text{Li}_{2.90}\text{Mg}_{0.05}\text{V}_2(\text{PO}_4)_3/\text{C}$	3.635	3.718	4.139	3.977	3.603	3.524

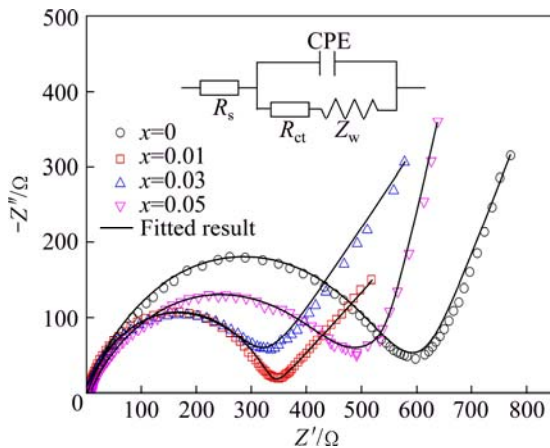


Fig. 4 Nyquist plots of $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ composites initially charged to 4.3 V (Equivalent circuit used for curve fitting is shown in inset)

region, a depressed semicircle in the high-middle frequency region, and an inclined line in the low frequency region. The intercept impedance on the Z' real axis represents ohmic resistance (R_s), which is the total resistance of the electrolyte, electrodes and contacts of the cell. The semicircle indicates the charge transfer process on the electrode interface, demonstrating the lithium transfer rate parameters as well as the

capacitance of the electrolyte/SEI (solid electrolyte interface) double-layer. The inclined line depicts the Warburg impedance (Z_W), which relates with the diffusion of Li^+ in $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3$ active particles. The constant phase element (CPE) stands for the double-layer capacitance.

The equivalent circuit shown in the inset of Fig. 4 was used to fit the plots, and the fitted results are listed in Table 3. The charge transfer resistance (R_{ct}) of all Mg-doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites is lower than that of pristine $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$. The smaller R_{ct} is favorable for rapid electrochemical reaction and may result in better electrochemical performance, and the smallest R_{ct} for $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ indicates that $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ has the best electrochemical performance among the four composites.

Table 3 Fitting results for Nyquist plots of $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ composites

x	R_s/Ω	R_{ct}/Ω
0	3.4	570.8
0.01	2.8	331.6
0.03	2.3	310.6
0.05	3.2	467.7

Figure 5 shows the initial charge–discharge profiles and the cycle performance of $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ composites ($x=0, 0.01, 0.03$ and 0.05) at 0.1C (13.3 mA/g) in the voltage range of 3.0–4.3 V at 25 °C. Figure 5(a) demonstrates that all the $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ composites exhibit three charge voltage plateaus and three discharge ones, which implies that there exist three two-phase reactions in the electrochemical intercalation/extraction of lithium in all the composites during the charge–discharge processes, which is in accordance with the results of CVs in Fig. 3.

Compared with the pristine $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite, the doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites display lower charge voltage plateaus and higher discharge ones, suggesting that the Mg^{2+} doping in Li sites favors decreasing the polarization during the charge and discharge processes. Among the above-mentioned doped samples, $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ shows the lowest charge voltage plateaus and the highest discharge ones with the highest charge and discharge capacities. By comparison with the initial discharge capacity of 125 mA·h/g for pristine $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$, the doped composites exhibit higher initial discharge capacity. As shown in Fig. 5(b), the initial discharge capacities for $\text{Li}_{2.98}\text{Mg}_{0.01}\text{V}_2(\text{PO}_4)_3/\text{C}$, $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ and $\text{Li}_{2.90}\text{Mg}_{0.05}\text{V}_2(\text{PO}_4)_3/\text{C}$ are 129, 131 and 127 mA·h/g, respectively. After 30 cycles, the corresponding discharge capacities are 122, 125 and 119 mA·h/g, with the capacity retention rates of 94.6%,

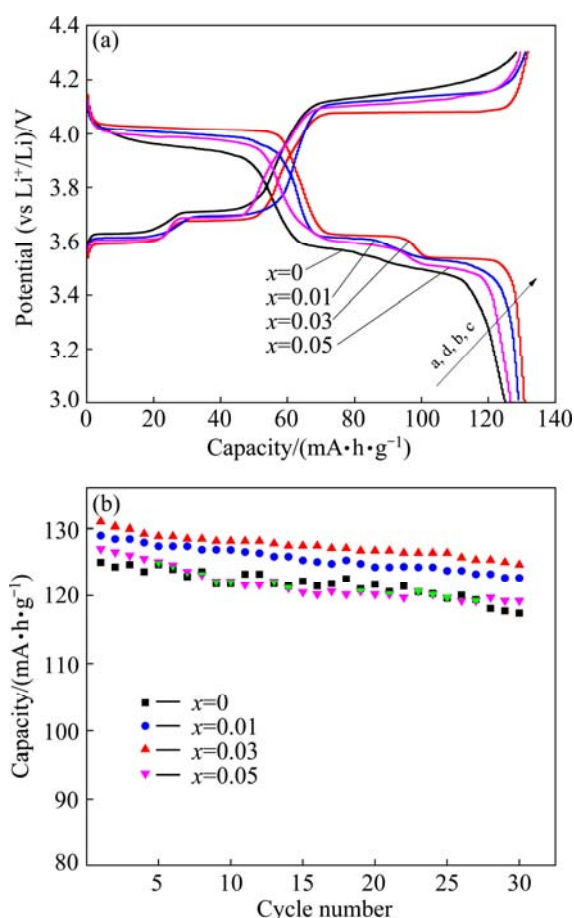


Fig. 5 Initial charge/discharge profiles (a) and cycle performance (b) of $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ composites at 0.1C in voltage range of 3.0–4.3 V at 25 °C

95.4% and 93.7%, respectively, which are somewhat higher than that of 93.5% for the pristine $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$. The capacity of the Mg-doped $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ is much higher than that of Ca-doped $\text{Li}_{2.96}\text{Ca}_{0.02}\text{V}_2(\text{PO}_4)_3/\text{C}$ (93 mA·h/g) [9] and K-doped $\text{Li}_{2.85}\text{K}_{0.15}\text{V}_2(\text{PO}_4)_3/\text{C}$ (95 mA·h/g) [14], and the cyclability of $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ is also higher than those of Ca-doped and K-doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ samples, indicating that Mg^{2+} may be more suitable than Ca^{2+} and K^+ to substitute Li^+ of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ to improve the electrochemical performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.

Figure 6 depicts the initial charge–discharge profiles and the cycle performance of $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ composites ($x=0, 0.01, 0.03$ and 0.05) at 1C (133 mA/g) in the voltage range of 3.0–4.3 V at 25 °C. As observed in Fig. 6(a), the initial discharge capacities of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$, $\text{Li}_{2.98}\text{Mg}_{0.01}\text{V}_2(\text{PO}_4)_3/\text{C}$, $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ and $\text{Li}_{2.90}\text{Mg}_{0.05}\text{V}_2(\text{PO}_4)_3/\text{C}$ are 117, 124, 127 and 121 mA·h/g, respectively, which are smaller than those of the corresponding composites at 0.1C, resulting from higher polarization at higher current density.

Among all the composites, $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ delivers the highest discharge capacity and the smallest

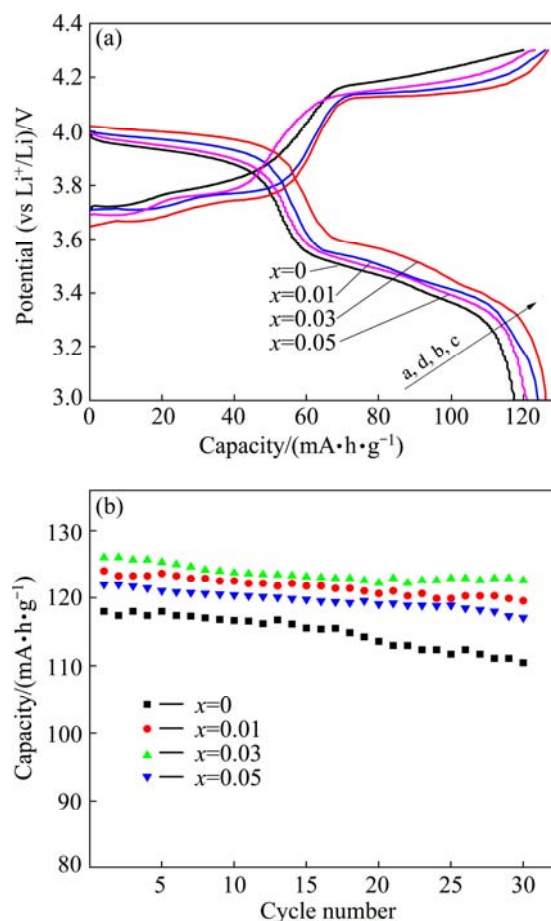


Fig. 6 Initial charge/discharge profiles (a) and cycle performance (b) of $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ composites at 1C in voltage range of 3.0–4.3 V at 25 °C

voltage difference between charge and discharge voltage plateaus, suggesting that $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ has the lowest electrochemical polarization and results in better reversibility during the charge–discharge processes. The discharge capacity of $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ at 1C is much higher than those of $\text{Li}_{2.96}\text{Ca}_{0.02}\text{V}_2(\text{PO}_4)_3/\text{C}$ (80 mA·h/g) [9], $\text{Li}_{2.9}\text{Na}_{0.1}\text{V}_2(\text{PO}_4)_3/\text{C}$ (120.57 mA·h/g at 0.5C) [13] and $\text{Li}_3(\text{V}_{0.9}\text{Mg}_{0.1})_2(\text{PO}_4)_3/\text{C}$ (121 mA·h/g at 0.5C) [16], suggesting that $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ exhibits higher capacity and better rate capability than $\text{Li}_{2.96}\text{Ca}_{0.02}\text{V}_2(\text{PO}_4)_3/\text{C}$, and Mg^{2+} doping in Li sites is more favorable than doping in V sites to improve the electrochemical performance, which might be caused by different amount of vacancies in Li sites for $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ and $\text{Li}_3(\text{V}_{0.9}\text{Mg}_{0.1})_2(\text{PO}_4)_3/\text{C}$ composites. Figure 6(b) illustrates that the four composites still keep good cycle performance at higher current density of 1C, which may be attributed to the excellent structural stability of the pristine and Mg-doped monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, further revealing that the doping of Mg^{2+} in Li sites does not affect the stable monoclinic structure of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ displays the highest discharge capacity and the

best cyclability among the four composites, and exhibits capacity retention of 96.8% and still remains a capacity of 123 mA·h/g at 1C after 30 cycles, while the capacity retention rates of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$, $\text{Li}_{2.98}\text{Mg}_{0.01}\text{V}_2(\text{PO}_4)_3/\text{C}$ and $\text{Li}_{2.90}\text{Mg}_{0.05}\text{V}_2(\text{PO}_4)_3/\text{C}$ are 95.9%, 95.6% and 93.2%, respectively. The above results indicate that the doping of Mg^{2+} in Li sites favors improving the capacity and cycle performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.

In order to investigate the effect of Mg^{2+} doping on the diffusion of Li^+ in the electroactive $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3$ particles, the comparison of Li^+ diffusion coefficient, D_{Li} , in $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ and $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ was carried out. The diffusion coefficient of Li^+ was determined by a CV method and D_{Li} was calculated according to the classical Randles–Sevcik equation [17–20]:

$$I_p = 2.69 \times 10^5 n^{3/2} A D_{\text{Li}}^{1/2} C_{\text{Li}}^* \nu^{1/2} \quad (1)$$

where I_p , n , A , C_{Li}^* and ν are the peak current (mA), the charge-transfer number, the electrode area (cm^2), the bulk concentration of Li^+ in the electrode (mol/cm^3), and the potential scan rate (mV/s), respectively.

Figures 7(a) and (b) show the CVs of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ and $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ at different scan rates. It is

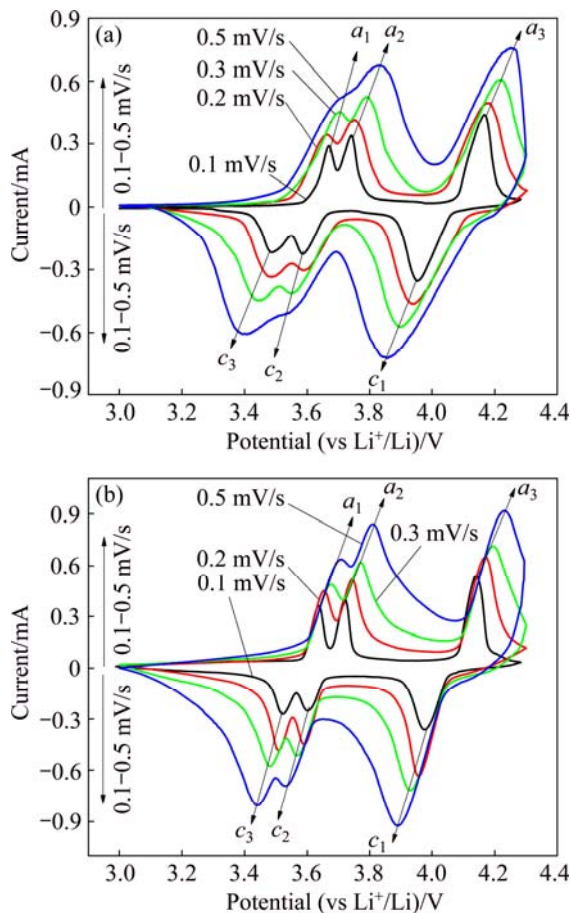


Fig. 7 Cyclic voltammograms of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ (a) and $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ (b) composites at different scan rates in potential range of 3.0–4.3 V

obvious that the height and area of redox peaks increase with increasing the potential scan rates. The peak area divided by the scan rate should be equal to the total charge and discharge capacity of the same electrode based on the assumption of no polarization. Additionally, the anodic peaks shift to higher potentials and the corresponding cathodic peaks shift to lower potentials when the potential scan rate increases, implying that polarization becomes stronger due to the increase of scan rates. Although the polarization increases with increasing the potential scan rates, the shapes of CVs of $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ keep almost unchanged even at high scan rate of 0.5 mV/s, while two anodic peaks (a_1 and a_2) and two cathodic peaks (c_2 and c_3) of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ emerge into one anodic peak and one cathodic peak, respectively, indicating that $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ displays smaller polarization and better reversibility than $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$.

As shown in Figs. 8(a) and (b), the peak current (I_p) has a linear relationship with the square root of scan rate ($\nu^{1/2}$), revealing that it is reasonable to calculate the diffusion coefficient of Li^+ , D_{Li} , by Eq. (1). Based on the slope of I_p versus $\nu^{1/2}$ and Eq. (1), the diffusion coefficients of Li^+ for $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ resulting from a_2 ,

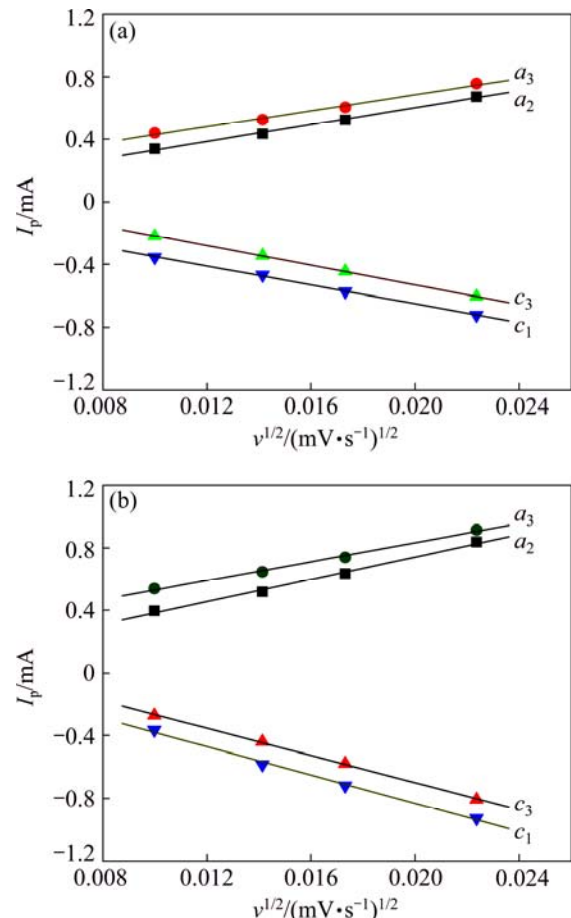


Fig. 8 Relationship between peak current (I_p) and square root of scan rate ($\nu^{1/2}$) for CVs of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ (a) and $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ (b)

a_3 , c_1 and c_3 are 3.7×10^{-11} , 3.4×10^{-11} , 4.9×10^{-11} and 4.4×10^{-11} cm²/s, respectively, while the corresponding diffusion coefficients of Li⁺ for Li_{2.94}Mg_{0.03}V₂(PO₄)₃/C are 6.6×10^{-11} , 5.2×10^{-11} , 9.0×10^{-11} and 1.0×10^{-10} cm²/s, respectively. It is obvious that the Li⁺ diffusion coefficients of Li_{2.94}Mg_{0.03}V₂(PO₄)₃/C are at least 1.5 times of the corresponding D_{Li} of Li₃V₂(PO₄)₃/C, suggesting that Li_{2.94}Mg_{0.03}V₂(PO₄)₃/C is more favorable to rapid diffusion of Li⁺ and the rapid diffusion of Li⁺ may result in better electrochemical performance of the electroactive materials. The difference of Li₃V₂(PO₄)₃/C and Li_{2.94}Mg_{0.03}V₂(PO₄)₃/C in Li⁺ diffusion coefficients results from Mg²⁺ doping into Li sites. The Mg²⁺ doping plays key roles in improving Li⁺ diffusion coefficients. On one hand, the substitution of monovalent Li⁺ by bivalent Mg²⁺ produces vacancies in Li sites, which is beneficial to facilitating the transport of electrons and Li⁺, resulting in the improved rapid Li⁺ diffusion. On the other hand, Mg²⁺ doping enlarges the cell volume of the pristine Li₃V₂(PO₄)₃ and provides larger channel for Li⁺ transport in the electroactive materials, leading to the improved rapid Li⁺ diffusion.

4 Conclusions

1) Li_{3-2x}Mg_xV₂(PO₄)₃/C ($x=0, 0.01, 0.03$ and 0.05) composites were prepared by a sol-gel method and the composites are comprised of a single monoclinic phase of pristine Li₃V₂(PO₄)₃ or Mg-doped Li₃V₂(PO₄)₃ and amorphous carbon.

2) The cell volume of Mg-doped Li₃V₂(PO₄)₃ is somewhat larger than that of pristine Li₃V₂(PO₄)₃.

3) The electrochemical performances of all Mg-doped Li₃V₂(PO₄)₃/C are better than those of pristine Li₃V₂(PO₄)₃/C. Li_{2.94}Mg_{0.03}V₂(PO₄)₃/C exhibits the best electrochemical performance among the four composites, and the capacities of Li_{2.94}Mg_{0.03}V₂(PO₄)₃/C at 0.1C and 1C are 131 and 127 mA·h/g, respectively, which are higher than those of 125 mA·h/g (at 0.1C) and 117 mA·h/g (at 1C) for Li₃V₂(PO₄)₃/C. Furthermore, Li_{2.94}Mg_{0.03}V₂(PO₄)₃/C displays better cycle performance at both 0.1C and 1C than Li₃V₂(PO₄)₃/C.

4) The comparative investigation on Li⁺ diffusion coefficients of Li₃V₂(PO₄)₃/C and Li_{2.94}Mg_{0.03}V₂(PO₄)₃/C indicates that the partial substitution of monovalent Li⁺ by a suitable amount of bivalent Mg²⁺ is favorable to improving the diffusion rate of Li⁺ and results in high capacity and better cycle performance.

5) The results suggest that the partial substitution of Li⁺ by high valence of ions with similar radius may be an effective way to improve the electrochemical performance of other cathode and anode electrode materials for lithium-ion batteries.

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锂离子电池复合正极材料 $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ 的合成及其电化学性能

尹武梅¹, 张婷婷¹, 朱庆², 陈权启^{1,2}, 李谷才³, 张灵志²

1. 湘潭大学 化学学院, 湘潭 411105;

2. 桂林理工大学 化学与生物工程学院, 桂林 541004;

3. 湖南工程学院 化学化工学院, 湘潭 411104

摘要: 采用溶胶-凝胶法制备 $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ ($x=0, 0.01, 0.03, 0.05$) 复合材料, 并通过 X 射线衍射(XRD)、扫描电镜(SEM)和电化学测试等测试手段对合成材料进行表征。XRD 结果表明: 在 $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ 的锂位掺杂少量 Mg^{2+} , 并没有明显改变 $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ 晶体的单斜结构, 但镁掺杂 $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ 的晶胞体积大于未掺杂 $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ 的晶胞体积。所有镁掺杂复合材料 $\text{Li}_{3-2x}\text{Mg}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ ($x=0.01, 0.03, 0.05$) 的电化学性能均优于 $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ 复合材料, 其中, $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ 在上述所有材料中具有最高的容量和最好的循环性能。对 $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ 和 $\text{Li}_{2.94}\text{Mg}_{0.03}\text{V}_2(\text{PO}_4)_3/\text{C}$ 的锂离子扩散系数及电化学性能进行对比分析, 结果表明: Li^+ 在镁掺杂 $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ 材料中的快速扩散是由 Mg^{2+} 在锂位的掺杂造成, Li^+ 在活性材料中的快速扩散使镁掺杂 $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ 材料具有优良的电化学性能。

关键词: 锂离子电池; 磷酸钒锂; 扩散系数; 溶胶-凝胶法

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