



Effect of Mg doping on electrochemical performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode material for lithium ion batteries

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Abstract: $\text{Li}_3\text{Mg}_{2x}\text{V}_{2-2x}(\text{PO}_4)_3/\text{C}$ ($x=0, 0.05, 0.1, 0.2$) composites were synthesized by carbothermic reduction, using a self-made $\text{MgNH}_4\text{PO}_4/\text{MgHPO}_4$ compound as Mg-doping agent. X-ray diffraction (XRD), scanning electron microscope (SEM), electrochemical performance tests were employed to investigate the effect of Mg doping on $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ samples. The results showed that a proper quantity of Mg doping was beneficial to the reduction of charge transfer resistance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ compound without changing the lattice structure, which led to larger charge/discharge capacity and better cycle performance especially at high current density. $\text{Li}_3\text{Mg}_{2x}\text{V}_{2-2x}(\text{PO}_4)_3/\text{C}$ sample with $x=0.05$ exhibited a better performance with initial charge/discharge capacity of 146/128 mA·h/g and discharge capacity of 115 mA·h/g at 5C, while these two figures were 142/118 mA·h/g and 90 mA·h/g respectively for samples without Mg doping, indicating that a proper amount of doped Mg can improve the electrochemical performance of LVP sample. All of these proved that, as a trial Mg dopant, the synthesized $\text{MgNH}_4\text{PO}_4/\text{MgHPO}_4$ compound exhibited well doping effect.

Key words: lithium vanadium phosphate; Mg-doping; cathode materials; carbothermic reduction

1 Introduction

Lithium-ion rechargeable batteries have seized the most share in electronics consumption market due to their relatively high energy density and capacity [1,2]. The cathode is particularly critical in determining the capacity and cyclability of lithium-ion batteries [3,4]. In recent years, framework materials based on the phosphate polyanion have been identified as highly competitive cathode materials for lithium ion battery [5,6]. Without exception, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) has also attracted extensive attention [7–9]. In LVP structure, two lithium ions can be extracted between 3.0 and 4.3 V (vs Li/Li^+) based on the $\text{V}^{3+}/\text{V}^{3-}$ redox couple, which correspond to a theoretical capacity of 133 mA·h/g [10]. However, the low electrical conductivity of this material, which is about 1×10^{-8} S/cm, deteriorates the electrochemical performance seriously [11]. Therefore, hot spots about research of LVP concentrate on the improvement of conductivity. To achieve this, plenty of work has been done such as optimizing synthesis process [12–17], surface coating [18–20] and doping [4,21–29].

It has been proved that Mg can effectively enhance

the capacity and rate performance of LiFePO_4 , without any change to its olivine structure [30]. In this work, Mg^{2+} is used to take the place of V^{3+} in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, which is expected to create electron hole in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ lattice and enhance ionic conductivity. Many kinds of Mg sources have been used as doping agent such as MgO , $\text{Mg}(\text{OH})_2$, $\text{Mg}(\text{Ac})_2$, $\text{Mg}(\text{NO}_3)_2$ and $\text{Mg}(\text{OH})_2 \cdot 4\text{MgCO}_3 \cdot 6\text{H}_2\text{O}$ [31–35], but here we considered to synthesize a relatively complicated Mg dopant, trying to improve the doping effect of Mg dopant. So, in this work, we worked out a more active Mg dopant, and synthesized a series of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples with different Mg doping amounts using the self-made Mg dopant by carbothermic reduction method. A series of tests were carried out to made comparison of these samples and proved that a proper amount of Mg doping can improve the electrochemical capacity of LVP as well as the cycle performance, especially at a high current density.

2 Experimental

2.1 Synthesis of Mg dopant

A solution of 0.5 mol/L $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was dropped

into a solution of 0.5 mol/L PO_4^{3-} with intense stirring, adjusting the pH values at 9–10 by adding ammonia solution. The mixed liquor was filtered before repeatedly washed with de-ionized water. The filter cake was dried in an oven followed by grinding to powders in a mortar for later use.

2.2 Synthesis of $\text{Li}_3\text{Mg}_{2x}\text{V}_{2-2x}(\text{PO}_4)_3/\text{C}$

$\text{Li}_3\text{Mg}_{2x}\text{V}_{2-2x}(\text{PO}_4)_3/\text{C}$ samples were synthesized by the chemical pure materials of Li_2CO_3 , NH_4VO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$ and self-made Mg dopant with carbothermic reduction. Their stoichiometric amount was determined according to the chemical formula $\text{Li}_3\text{Mg}_{2x}\text{V}_{2-2x}(\text{PO}_4)_3$, and a calculated sucrose amount to get 3% carbon residue of the synthesized samples was added. All the reagents were firstly ball-milled together for 4 h with pure ethanol as a dispersant. The mixture was dried at 80 °C for 10 h, and then heated at 350 °C in nitrogen for 2 h to expel NH_3 and H_2O . After that, the mixture was ground and heated at 800 °C under nitrogen atmosphere for 10 h. The product was ground in an agate mortar for later use.

2.3 Physical characterization and cell assembly

Power X-ray diffraction employing $\text{Cu K}\alpha$ radiation was used to identify the crystalline phase of the Mg dopant and the synthesized materials. The surface morphologies were observed with a scanning electron microscope (JSM-6360LV).

Electrochemical tests were carried out on a coin-type cell based on the synthesized material. The cathode was prepared by mixing 80% active material, 10% acetylene carbon black and 10% polyvinylidene fluoride (PVDF) dissolved in N-methylpyrrolidone (NMP). The slurry was coated on an Al foil and dried at 130 °C for 10 h. A lithium foil was used as anode. The electrolyte used was LiPF_6 . The cells were assembled in an argon-filled glove box with H_2O and O_2 concentration below 1×10^{-6} .

2.4 Electrochemical measurements

The electrochemical properties of the constructed cells were measured by employing land testing system (CT2001A) at various currents with a voltage range from 3.0 V to 4.3 V. Electrochemical impedance measurements were performed with a Princeton electrochemistry workstation (VNC-4), and the applied frequency range is between 100 kHz and 0.1 Hz.

3 Results and discussion

3.1 Structure and morphology characteristics

Figure 1 shows the XRD patterns and SEM image of the Mg dopant synthesized at room temperature. The

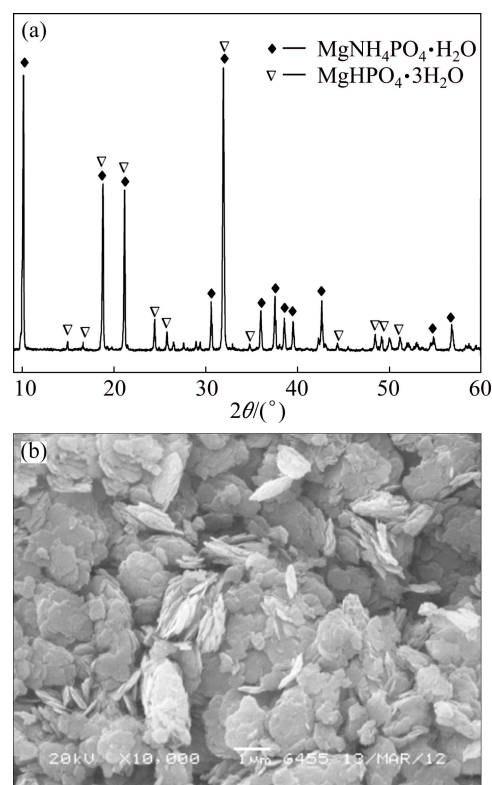


Fig. 1 XRD patterns (a) and SEM image (b) of prepared Mg dopant

XRD diffraction peak shows that the resultant is a mixture of $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ and $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$. Both of them belong to orthorhombic system, which is the same as the raw materials NH_4VO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$, and the similar structure may benefit polymerization and promote the doping process. As shown in the SEM image (Fig. 1(b)), the compound features sheet morphology and its size is about 100 nm in thickness and 1 μm in diameter. This kind of morphology could be beneficial to the completed reaction with other reactant and promote the doping process with respect to broad contact surface.

Figure 2 shows XRD patterns of $\text{Li}_3\text{Mg}_{2x}\text{V}_{2-2x}(\text{PO}_4)_3$ ($x=0, 0.05, 0.1, 0.2$) samples

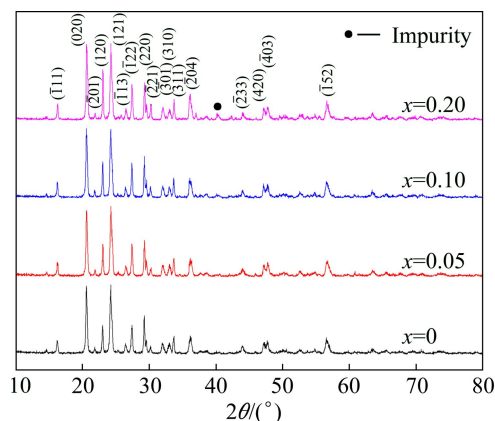


Fig. 2 XRD patterns of prepared $\text{Li}_3\text{Mg}_{2x}\text{V}_{2-2x}(\text{PO}_4)_3$ ($x=0, 0.05, 0.1, 0.2$) samples

(PO₄)₃/C samples with various Mg contents. The samples with $x=0, 0.05, 0.1$ are identified to be monoclinic Li₃V₂(PO₄)₃ phase with a $p2_1/n$ space group containing no unwanted impurities, which means that a small quantity of doped Mg would take the place of V in the lattice without altering the structure. The electron holes in the structure caused by this replacement can cause p-type conductivity [36], and this improves the electronic conductivity in the lithium vanadium phosphate material. However, trace impurity was found in sample with $x=0.2$, which indicated that the upper limit for Mg doping is about $x=0.2$.

Figure 3 shows the morphology of the synthesized samples. It can be seen from the images that the synthesized Li₃Mg_{2x}V_{2-2x}(PO₄)₃ ($x=0, 0.05, 0.1, 0.2$) samples are composed of irregular particles with an initial particle size distribution of 0.5–3 μm , and the particles aggregate to form meso porous dusters. With x increasing, the particle size decreased slightly, which may be attributed to that the doped Mg formed more crystallization center. The decrease of particle size can shorten the diffusion path of the lithium ion as well as increase the area for electrode reaction, which is in favor of the electrochemical performance improvement.

3.2 Electrochemical performance

The initial charge/discharge curves of Li₃Mg_{2x}V_{2-2x}(PO₄)₃ ($x=0, 0.05, 0.1, 0.2$) composites with different Mg-doping amounts under 0.1C rate in the potential from 3.0 V to 4.3 V (vs Li⁺/Li) are shown in

Fig. 4. It demonstrated that the initial discharge specific capacities of Li₃Mg_{2x}V_{2-2x}(PO₄)₃ ($x=0, 0.05, 0.1, 0.2$) depended on the Mg doping amounts significantly. The first charge/discharge specific capacities of Li₃V₂(PO₄)₃, Li₃Mg_{0.1}V_{1.9}(PO₄)₃, Li₃Mg_{0.2}V_{1.8}(PO₄)₃ and Li₃Mg_{0.4}V_{1.6}(PO₄)₃ are about 142/118, 146/128, 143/119 and 131/110 mA·h/g, respectively. The corresponding coulombic efficiencies are 83.0%, 87.7%, 83.2% and 84.0%, respectively. It is clear that the discharge specific capacity as well as the coulombic efficiency is enhanced considerably when $x=0.05$. That may be attributed to the moderate amount of Mg dopant which enhanced the conductivity of the sample compared with the undoped one.

3.3 Rate and cycle performance

All Li₃Mg_{2x}V_{2-2x}(PO₄)₃ ($x=0, 0.05, 0.1, 0.2$) samples were cycled at various current densities (0.1C, 0.2C, 0.5C, 1C, 2C, 5C) between 3.0 and 4.3 V and the results are shown in Fig. 5. Each current density was applied for 10 cycles. It was found that the composite material with a Mg doping amount of $x=0.05$ exhibited the highest capacity under all the tested current density owing to the improvement of the Li⁺ insertion/de-insertion kinetics situation caused by Mg doping. When tested under current densities from 0.1C to 2C, Li₃V₂(PO₄)₃ and Li₃Mg_{0.2}V_{1.8}(PO₄)₃ samples exhibited a discharge capacity with little difference. However, when the current density was increased to 5C, the discharge capacity of Li₃V₂(PO₄)₃ rapidly decreased to ~90 mA·h/g

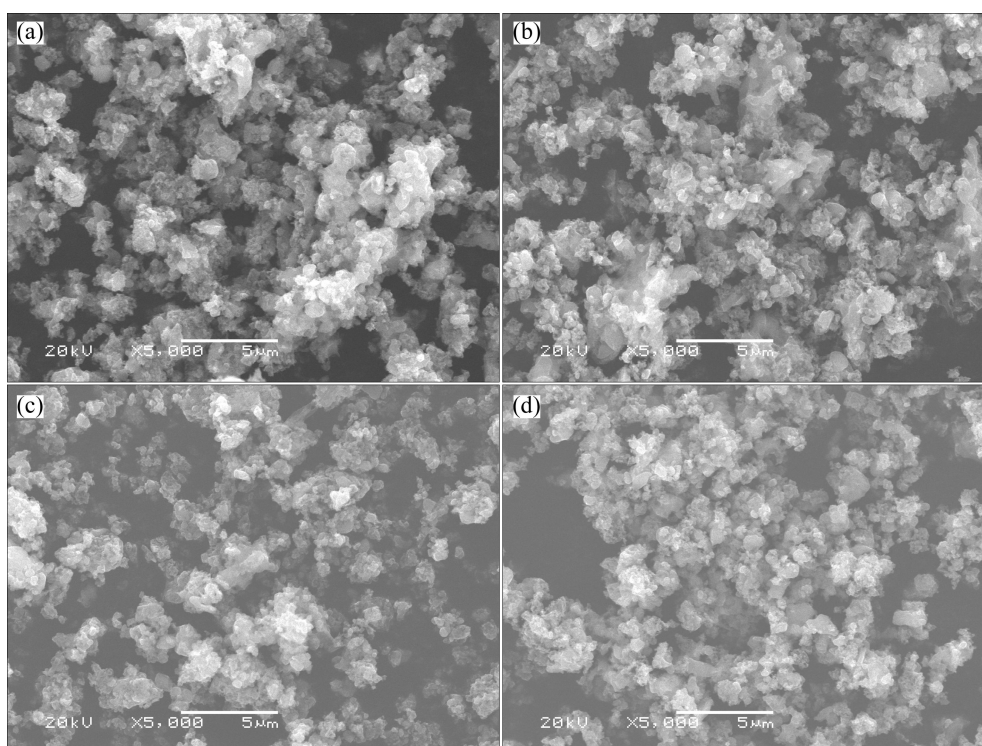


Fig. 3 SEM images of Li₃Mg_{2x}V_{2-2x}(PO₄)₃ samples: (a) $x=0$; (b) $x=0.05$; (c) $x=0.1$; (d) $x=0.2$

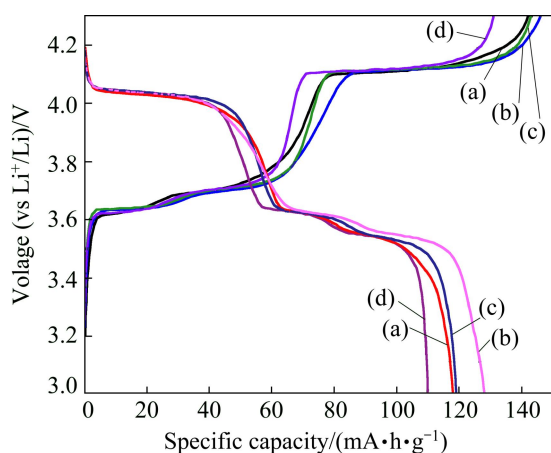


Fig. 4 Initial charge/discharge curves of $\text{Li}_3\text{Mg}_{2x}\text{V}_{2-2x}(\text{PO}_4)_3$ samples at 0.1C rate in voltage of 3.0–4.3 V: (a) $x=0$; (b) 0.05; (c) 0.1; (d) 0.2

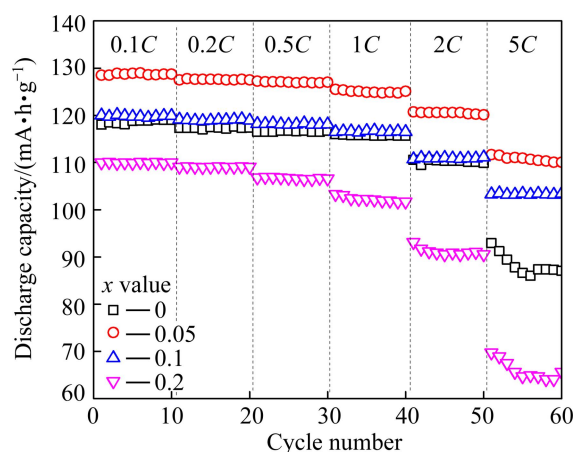


Fig. 5 Discharge capacities of $\text{Li}_3\text{Mg}_{2x}\text{V}_{2-2x}(\text{PO}_4)_3$ ($x=0, 0.05, 0.1, 0.2$) samples at current densities of 0.1C, 0.2C, 0.5C, 1C, 2C and 5C in voltage range of 3.0–4.3 V

(~115 $\text{mA}\cdot\text{h}/\text{g}$ at 2C) while $\text{Li}_3\text{Mg}_{0.2}\text{V}_{1.8}(\text{PO}_4)_3$ sample just decreased to ~110 $\text{mA}\cdot\text{h}/\text{g}$. This phenomenon proved that a certain amount of doped Mg can improve the discharge performance of LVP materials at high current density. It can be concluded that a low amount of Mg doping can increase both the cycle stability and discharge capacity for LVP materials, especially at a high current density.

3.4 EIS measurement

Electrochemical impedance spectroscopy (EIS) measurements were carried out to study the effect of Mg doping on the impedance response. Figure 6 shows the Nyquist plots of the $\text{Li}_3\text{Mg}_{2x}\text{V}_{2-2x}(\text{PO}_4)_3$ ($x=0, 0.05, 0.1, 0.2$) samples. All the electrodes were prepared in the same way and activated at a current of 0.1C before EIS measurement. All the Nyquist plots have a semicircle and a sloping line. The semicircle can be attributed to the charge transfer reaction, and the sloping line can be

attributed to the lithium diffusion in the solid phase. The equivalent circuit for the Nyquist plots fitted by Zview is shown in Fig. 7(a), where R_e is the electrolyte resistance; R_{ct} is the charge transfer resistance; Q denotes the constant-phase element and Z_w is the Warburg impedance.

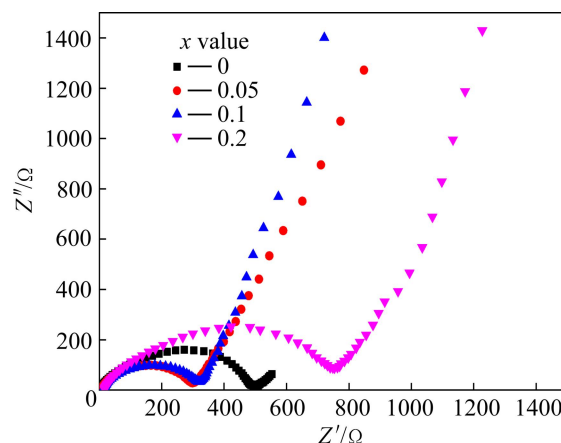


Fig. 6 Nyquist plots of $\text{Li}_3\text{Mg}_{2x}\text{V}_{2-2x}(\text{PO}_4)_3$ ($x=0, 0.05, 0.1, 0.2$) samples

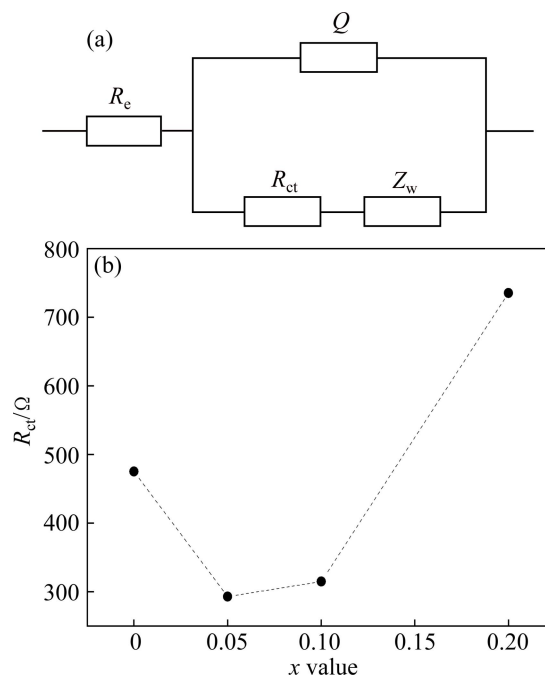


Fig. 7 Equivalent circuit for Nyquist plots (a) and charge transfer resistances (b) of $\text{Li}_3\text{Mg}_{2x}\text{V}_{2-2x}(\text{PO}_4)_3$ ($x=0, 0.05, 0.1, 0.2$) samples

A lower charge transfer resistance leads to larger exchange current density [31]. Figure 7(b) shows the charge transfer resistance (R_{ct}) of all the samples. When x increased from 0 to 0.05, R_{ct} decreased from 475 to 293 Ω , and then slightly increased to 314 Ω at $x=0.1$, then a quick increase to 735 Ω at $x=0.2$. This change of R_{ct} can be attributed to two factors. A small amount of doped Mg contributes to improving the conductivity of the material

as well as increasing the area for electrode reaction by refining crystal grain (Fig. 3). This factor can decrease charge transfer resistance. However, Mg doping leads to a smaller amount of V, thus lessen the active spot for charge transfer of lithium ion, and the cation mixing between Mg and Li will also impede the transition of Li^+ . This factor leads to the increase of the value of R_{ct} . When x is less than 0.05, the former is the main influencing factor. While x increases from this point, the latter factor gradually takes over and is much more obvious than the former one when x goes to 0.2. Therefore, $\text{Li}_3\text{Mg}_{0.1}\text{V}_{1.99}(\text{PO}_4)_3$ with a minimum R_{ct} value presents the best high rate discharge capability among all the samples in Fig. 7(b).

In the research of DAI et al [37], the study of Mg doped LVP samples with $\text{Mg}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ as dopant was reported. They found that $\text{Li}_3\text{Mg}_{2x}\text{V}_{2-2x}(\text{PO}_4)_3$ sample with $x=0.1$ as cathodic material exhibited the best performance with a capacity of about 112 mA·h/g at a rate of 0.5C and 109 mA·h/g at 1C. However, in our research, samples achieved the best performance when $x=0.05$, less than DAI's result, but with a larger capacity of about 127 mA·h/g at 0.5C and 125 mA·h/g at 1C. This indicates that the self-made Mg dopant involved in the doping process was more efficient than that of $\text{Mg}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$.

4 Conclusions

1) The $\text{Li}_3\text{Mg}_{2x}\text{V}_{2-2x}(\text{PO}_4)_3$ ($x=0, 0.05, 0.1, 0.2$) samples were successfully prepared by a carbothermic reduction method with self-made $\text{MgNH}_4\text{PO}_4/\text{MgHPO}_4$ compounds as Mg dopant.

2) The influence of Mg doping amount on the electrochemical performance was remarkable. It was found that $\text{Li}_3\text{Mg}_{0.1}\text{V}_{1.9}(\text{PO}_4)_3$ exhibited the best electrochemical performance among all the compounds with different doping ratios, batteries consisted of this sample exhibited a initial discharge capacity of 128 mA·h/g at 0.1C and a discharge capacity of 115 mA·h/g at 5C rate. Results also showed that batteries consisted of Mg doped compound exhibit improved cycle performance under large current density condition.

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Mg 掺杂对锂离子电池正极材料 Li₃V₂(PO₄)₃/C 电化学性能的影响

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摘 要: 使用自制的 MgNH₄PO₄/MgHPO₄ 混合物为掺杂剂, 利用碳热还原法制备 Li₃Mg_{2x}V_{2-2x}(PO₄)₃/C ($x=0, 0.05, 0.1, 0.2$) 材料。运用 XRD、SEM、电化学性能测试等方法研究 Mg 掺杂对 Li₃V₂(PO₄)₃/C 的影响。结果表明, 适量的 Mg 掺杂不会改变 Li₃V₂(PO₄)₃/C 的结构, 且有助于减小电荷迁移阻力, 由此提高材料的容量, 改善循环和倍率性能。当 $x=0.05$ 时, Li₃Mg_{2x}V_{2-2x}(PO₄)₃/C 表现出更好的性能, 首次充放电容量为 146/128 mA·h/g, 在 5C 电流强度下放电容量约为 115 mA·h/g; 而当 $x=0$ 时, 两者分别为 142/118 mA·h/g 和 90 mA·h/g。表明适量的 Mg 掺杂能提高磷酸钒锂的电化学性能。合成的 MgNH₄PO₄/MgHPO₄ 作为一种尝试性镁掺杂剂, 能起到良好的掺杂效果。

关键词: 磷酸钒锂; Mg 掺杂; 正极材料; 碳热还原

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