Evolution of electrochemical performance in Li₃V₂(PO₄)₃/C composites caused by cation incorporation

Lu-Lu Zhang, Gan Liang, Gang Peng, Yan Jiang, Hui Fang, Yun-Hui Huang, Mark C. Croft, Alexander Ignatov

1. Introduction

Monoclinic Li₃V₂(PO₄)₃ (LVP) has been proposed as one of the most promising cathode materials for lithium-ion batteries due to its large theoretical capacity (197 mAh g⁻¹), high operating voltage (up to 4.0 V), and fast lithium-ion migration [1–7]. However, similar to other lithium transition metal phosphates, poor intrinsic electronic transport of LVP limits its application [1,2]. Carbon coating [1,6–9], oxide modification [5,20], and cation doping [21–33] have been proved to be effective to enhance the intrinsic electronic conductivity. Compared to other modification methods, metallic ion doping has been paid more attention. Hitherto, there is still some controversy about the mechanism and the doping effect. Actually, cation doping is an efficient way to improve the intrinsic electronic conductivity and chemical diffusion coefficient of lithium ions within the crystals. Due to the electrochemical activity, Fe, Co, Ni and Mn are commonly used as doping elements in Li₃V₂(PO₄)₃, LiFePO₄ and other cathode materials [21,33–41]. For Li₃V₂(PO₄)₃, Ren et al. [21] synthesized LiₓFeₓV₂₋ₓ(PO₄)₃ (0 ≤ x ≤ 0.06) by solid-state reaction, and found that LVP with optimal Fe-doping content (x = 0.02 – 0.04) could achieve high discharge capacity and good cyclic stability. They also reported that the oxidation state of Fe in LiₓFe₀.₀₂V₁.₉₈(PO₄)₃ was +3, which is somewhat different from our previous work [42]. Kuang et al. [43] prepared Co-doped LiₓV₂₋ₓCoₓ(PO₄)₃/C (0 ≤ x ≤ 0.15) via solid-state reaction, and found that V⁴⁺ and V⁵⁺ ions coexisted in the Co²⁺-doped LVP samples; Li₁ₓV₁.₉₅Co₀.₁₅(PO₄)₃/C exhibited the best electrochemical performance due to enhanced structural stability and alleviated volume change (expansion/contraction). Bini et al. [30] investigated the Mn substitution in LVP on a series of samples obtained by different synthesis methods, and found that the sol-gel-derived samples showed slightly enhanced capacity due to the Mn substitution within a solubility limit (x = 0.124), whereas the solid-state synthesized samples showed significantly enhanced capacity due to the microstructure of the crystallites and the phase formation of LiMnPO₄. Zhang et al. [33] prepared a series of Ni-doped LVP samples by microwave-assisted
subsequently, Mn) monochromator

2.2. \( \text{LVCoP/C, (M}\) the diffractometer investigated LVCoP/C, \( \text{Ni}\) investigated X-ray absorption spectroscopy (XAS), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and electrochemical measurements.

2. Experimental

2.1. Synthesis of \( \text{Li}_x\text{V}_{1.9}\text{M}_{0.1}\text{(PO}_4\text{)}_3/C \) \( \text{(M}\) Fe, Co, Ni, Mn)

To prepare \( \text{Li}_x\text{V}_{1.9}\text{M}_{0.1}\text{(PO}_4\text{)}_3/C \) \( \text{(M}\) Fe, Co, Ni, Mn) composites, stoichiometric \( \text{Li}_2\text{CO}_3, \text{NH}_4\text{VO}_3 \) and \( \text{NH}_4\text{H}_2\text{PO}_4 \) were mixed with \( \text{FeC}_2\text{O}_4, \text{Co(CH}_3\text{CO}_2\text{)}_2\cdot\text{H}_2\text{O, Ni(CH}_3\text{CO}_2\text{)}_2\cdot\text{H}_2\text{O, and Mn(CH}_3\text{CO}_2\text{)}_2\cdot\text{H}_2\text{O} \), respectively, and then ball-milled for 10 h in ethanol. The mixture was dried in air at 60 °C for 12 h, followed by calcining at 350 °C for 6 h in nitrogen atmosphere and then cooling down to room temperature. Glucose (15 wt.%), which acts as not only carbon source but also reductive agent, was added into the resulting precursor and further ball-milled for 6 h in ethanol. Subsequently, the mixture was dried and sintered at 700 °C for 10 h with a heating rate of 3 °C min\(^{-1}\) in nitrogen atmosphere to achieve the final products. Here, the M-incorporated \( \text{Li}_x\text{V}_{1.9}\text{M}_{0.1}\text{(PO}_4\text{)}_3/C \) \( \text{(M}\) Fe, Co, Ni, Mn) composites are denoted as \( \text{LiFeP/C, LiCoP/C, LiNP/C, and LiNiP/C, respectively. For comparison, pristine LVP/C composite was also prepared via the same process.} \)

2.2. Sample characterization

X-ray diffraction patterns were obtained using a XPert Pro diffractometer with Cu-Kα radiation (λ = 1.5406 Å) (XRD, XPert Pro, PANalytical B.V.). Morphology and structure of the samples were observed with scanning electron microscope (SEM, Sirion 200, Holland) and high-resolution transmission electron microscopy (HRTEM, JEM-2100, JEOL). Carbon content was determined by carbon-sulfur analyzer (CS600, LECO, US), and electrical conductivity was measured with standard four-probe method on resistivity measurement system (RTS-8, China). Oxidation state of V and Mn \( \text{(M}\) Fe, Co, Ni, Mn) in pristine LVP/C and LVP/C-Fe samples was investigated by X-ray photoelectron spectroscopy (XPS, PHI Quan- terall, Japan) and X-ray absorption spectroscopy (XAS). The V, Fe, Co, Ni, and Mn K-edge XAS data were taken in fluorescence and transmission mode at beam line X-19A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. A standard \( \text{Sr}_3\text{V}_2\text{O}_9, \text{FeO, CoO, NiO, and MnO for V, Fe, Co, Ni, and Mn K-edge, respectively} \) was run in transmission mode simultaneously with the samples for energy calibration. A double-crystal Si(1 1 1) monochromator was used for energy selection and was detuned by reducing the incident photon flux 20% from its maximum value to suppress contamination from harmonics. The energy resolution (ΔE/ΔE) of the X-19A beam line was 2 × 10\(^{-4}\), corresponding to about 1.1 eV at V K-edge, 1.4 eV at Fe K-edge, 1.5 eV at Co K-edge, 1.7 eV at Ni K-edge, and 1.3 eV at Mn K-edge. The XAS spectra presented in this paper were background subtracted and normalized to unity in the continuum region about 100 eV above the edge.

2.3. Electrochemical measurements

The working electrodes were prepared by roll milling a mixture of 75 wt.% active materials, 20 wt.% carbon black and 5 wt.% PFPE with N-methyl pyrrolidinone. Electrodes were punched into discs (q8 mm) and transferred into argon-filled glove box (Super 1220/750, Mikrouna) shortly after drying at 80 °C for 24 h in vacuum. 2032 coin cells were assembled with Celgard 2300 as the separator, lithium foil as counter and reference electrodes, and 1 mol L\(^{-1}\) LiPF\(_6\) in EC: DMC (LB-3711, China) as electrolyte. To avoid the influence of electrolyte decomposition under high voltage on the electrochemical behavior of LVP, a low charge voltage of 4.3 V was chosen here. The specific capacities of samples were measured by constant current charge/discharge testing between 2.5 and 4.3 V (vs. Li\(^+\)/Li\(^-\)) (LAND CT2001A, China). Cyclic voltammetry (CV) measurements were performed on an electrochemical workstation (PARSTAT 2273, Princeton Applied Research, US) at progressive scanning rates from 0.05 to 0.3 mV s\(^{-1}\) within a voltage range of 3.3 – 4.3 V.

3. Results and discussion

Fig. 1 shows the XRD patterns of pristine LVP/C and LVP/C \( \text{(M}\) Fe, Co, Ni, Mn) samples. For pristine LVP/C and the \( \text{M}\) Fe, Co, and Ni samples, the XRD patterns can be indexed as monoclinic structure of LVP with a space group of \( \text{P2}_1\)/\( \text{n}\) and no any impurity phases were detected. For the \( \text{M}\) Mn sample, some weak lines of \( \text{LiMnP/O}_4\) impurity phase are observed in the XRD pattern. These results indicate that a small incorporation level (i.e., about 5 at.% doping level) of alien electrochemically-active metal ions does not change the monoclinic structure of LVP. The enlarged patterns shown on the right side of Fig. 1 reveal that all patterns for the LVMnP/C \( \text{(M}\) Fe, Co, Ni, Mn) samples display a slight shift of the (−1 2 1), (0 1 2), (2 0 1) and (−2 1 1) reflection lines to higher 2θ degree, suggesting that the lattice parameters of the LVP lattice are reduced by the doping of the M atoms into the lattice structure [43–45]. To confirm this conclusion, a full Rietveld refinement was carried out on all these five samples and the results are listed in
Table 1. The refinement model was chosen from a P2₁/n space group. It can be clearly seen that the unit cell volume decreases after incorporation of M (M = Fe, Co, Ni, Mn) amounting at least part of these transition metal ions are doped into the lattice structure of LVP. The excessive part beyond solubility limit may form minor impurity phases that are difficult to be detected by XRD measurement. It is noticed that the cell volume change with the M incorporation cannot be fully explained by the size difference between the V ion and doped M ions due to the lack of information regarding vacancies in the lattice and whether the doped M ions primarily occupy the M1 or M2 sites in the lattice structure. The lack of the diffraction lines from the XRD patterns shown in Fig. 1 may indicate that the carbon concentration from pyrolysis of glucose was too low to detect or the produced carbon is in amorphous form.

To investigate the oxidation state of V and M (M = Fe, Co, Ni, Mn) and to find whether M atoms are doped into the LVP lattice, V 2p and M 2p XPS data were taken for the pristine LVP/C and LVP/C samples at both the surface and in the interior (at ∼60 nm depth). The XPS spectra are shown in Fig. 2. The binding energy (BE) obtained from the XPS data analysis was calibrated using 284.5 eV as the BE of C 1s line. Figs. 2a–c, e show a V 2p 3/2 main peak at ∼517 eV, which is the value reported by Ren et al. [21] for the BE of V⁵⁺ in LVP. Thus, our XPS results indicate that the oxidation state of V in all the five samples is close to +3, and the incorporation of Fe, Co, Ni, and Mn in LVP does not change the valence state of the V ions in the M-doped LVP/C samples. In addition, as shown in Fig. 2b–c, e, the Fe 2p 3/2, Co 2p 3/2, Ni 2p 3/2, and Mn 2p 3/2 main peaks are clearly observed not only at the surface but also in the interior (∼60 nm in depth) of the LVP/C particles. This result clearly demonstrates that M atoms are doped into the bulk of the LVP particles. Since the M 2p 3/2 XPS spectra shown in Fig. 2 are quite noisy due to the low concentration level of the doped M atoms, it is difficult to draw a definite conclusion regarding the valence state (or oxidation state) of the M ions in the M-doped LVP/C samples and thus XAS will be used below for determining the valence state of these doped M ions.

In Fig. 3a, the V K-edge XAS spectra of the pristine LVP/C and the M-doped LVP/C (M = Fe, Co, Ni, and Mn) samples are shown in comparison with the spectra of some reference compounds. For the reference compounds, the formal valence values for V are +3 for LaVO₄ and Eu₂V₂O₇; +4 for La₂NiVO₄ and Sr₃V₂O₇; and +5 for Sr₃V₂O₈. It is well known that the primary indicator of the valence variation is the chemical shift in the main portion of the edge to higher energy with increasing valence. The edge energy here is defined as the energy at inflection point of the rising part of the edge. It can be seen from Fig. 3a that the edge energy increases from about 5480 eV to 5482 eV and then to 5484 eV with the increase of valence of V from +3 to +4 and then to +5. The values of the edge energy for the pristine LVP/C and LVP/C with M = Fe, Co, Ni, and Mn samples are 5480.2 eV, 5480.3 eV, 5480.3 eV, 5479.8 eV, and 5479.8 eV, respectively. These values are almost the same as those for the trivalent V reference compounds (see the largest rectangular box in the Fig. 3a). This result indicates that the valence of V in LVP/C and LVP/C samples should be very close to +3 and it shows that the M-incorporation into LVP/C does not change the valence state of the V ions.

To find the valence values of the doped M (M = Fe, Co, Ni, and Mn) in LVP/C, we show in Fig. 3b–e the M K-edge spectra for the LVP/C samples and some corresponding reference samples. In Fig. 3b, the Fe K-edge spectra for the LVFeP/C sample are shown along with the spectra of five reference compounds. The formal valence values for Fe are: +2 for FeO and LiFePO₄; +2.67 for Fe₂O₃; and +3 for γ-Fe₂O₃ and Fe₃O₄. Fig. 3b shows that the edge energies are about 7120 eV for the two Fe²⁺ compounds, but are shifted about 6 eV to the higher energy side for the Fe³⁺ compounds γ-Fe₂O₃ and Fe₃O₄. The edge energy for the LVFeP/C sample is between that for Fe₂O₃ and the two Fe³⁺ compounds γ-Fe₂O₃ and Fe₃O₄, indicating that the valence of Fe in this LVFeP/C sample is between +2.67 and +3. This result means that there are both Fe²⁺ and Fe³⁺ in the LVFeP/C sample. This result is in consistent with our previous study [42] on the Fe-doped LVP cathode materials for which Fe in the interior of the sample particles is found to exist mainly in the lower valence state (i.e., Fe₂⁺), while Fe at the surface exists largely in the higher valence state (i.e., Fe³⁺).

In Fig. 3c, the Co K-edge spectra for the LVCoP/C sample and some Co reference compounds: CoO₂O, La₃Co₂O₆, Sr₂Co₂+MoO₄, and LaCoO₃, can be seen from Fig. 3c that with increasing the Co formal valence from +2 to +3, there is a big chemical shift to higher energy from the edge energies of the three divalent Co reference compounds to that of the trivalent Co compound LaCoO₃. The main edge portion of the spectrum for the LVCoP/C sample is situated between that for the divalent Co standard CoO₂O and the other two divalent compounds La₃Co₂⁺O₆ and Sr₂Co₂⁺MoO₄, indicating clearly the Co valence in the LVCoP/C sample is +2, which is in consistent with the result reported by Kuang et al. [24]. Similar to the Co K-edge analysis, the main edge portion of the Ni K-edge spectrum for LVNiP/C displayed in Fig. 3d is positioned between the spectra for the divalent Ni reference compounds NiO₂, O and Sr₂Ni²⁺MoO₄ but much lower in energy than that for the trivalent Ni compound LaNiNiO₄, indicating that the valence of Ni in the LVNiP/C sample is +2. In Fig. 3e, it can be seen that the edge energy of the Mn K-edge for LVMMnP/C sample is very close to that for the Mn standard MnO but far below the edge energies of the Mn reference compounds MnO₂, MnO₂⁻O, and KMnO₄, which has higher Mn formal valence +3, +4, and +7, respectively. This result demonstrates that the valence of Mn in LVMMnP/C sample is also +2.

Fig. 4 shows the SEM images of pristine LVP/C and LVP/C (M = Fe, Co, Ni, Mn) powders. All the five samples exhibit irregular granular shapes, but M incorporation slightly affects particle size and morphology. Especially, the LVFeP/C particles present less agglomeration with a relatively narrow size distribution ranging from ~100 to 500 nm (Fig. 4b), which is advantageous to shorten the diffusion distance for lithium-ion transport during the intercalation/deintercalation reaction.

The structure and morphology of LVMP/C (M = Fe, Co, Ni, Mn) samples were further studied by HRTEM. It is clearly seen in Fig. 5 that amorphous carbon is either connecting the LVMP particles or coated on the surface of the LVMP particles, which is favorable for improving conductivity and alleviating vanadium dissolution in the electrolyte [46]. In addition, the HRTEM and the corresponding fast Fourier transform (FFT) patterns confirm the formation of crystalline LiMPO₄ associated with the corresponding LVMP/C samples, which agrees well with the valence of M (+2) obtained from XPS and XAS analysis. However, Fe³⁺ should also exist in the LVFeP/C sample though no Fe³⁺-containing composites are detected. It is speculated that the content level of any FePO₄ is too low or is amorphous [42].
Fig. 2. XPS spectra of (a) pristine LVP/C, (b) LVFeP/C, (c) LVCoP/C, (d) LVNiP/C, and (e) LV MnP/C.
Fig. 3. XAS K-edge spectra for pristine LVP/C, LVMP/C (M = Fe, Co, Ni, and Mn), and some reference compounds: (a) V K-edge, (b) Fe K-edge, (c) Co K-edge, (d) Ni K-edge, and (e) Mn K-edge.

Fig. 6 shows the initial charge/discharge profiles, cycle performance and rate capability of pristine and LVMP/C (M = Fe, Co, Ni, Mn) cathode samples. In the first cycle, as shown in Fig. 6a, there are three charge/discharge plateaus around 3.60/3.57 V, 3.69/3.66 V and 4.09/4.06 V for all the five electrode samples, corresponding to a sequence of phase transitions: Li3V2(PO4)3 ↔ Li2.5V2(PO4)3, Li2.5V2(PO4)3 ↔ Li2V2(PO4)3, and Li2V2(PO4)3 ↔ LiV2(PO4)3, respectively, associated with V3+/V4+ redox couple [4]. Surprisingly, for LVFeP/C electrode, another charge/discharge plateau around 3.49/3.40 V appears in the initial charge/discharge profiles (Fig. 6a, marked in orange circles), which is exactly the characteristics of the electrochemical reaction of LiFePO4, associated with Fe2+/Fe3+ redox couple. However, no other extra charge/discharge plateaus related to Co, Ni and Mn-containing composites are detected, which may attribute to the low charge voltage (4.3 V). It is also found in Fig. 6 that the electrochemically active metal ions (Fe, Co, Ni, Mn) do not have the same effect on the electrochemical performance of LVP, LVFeP/C, LVCoP/C, and LVMMn/C electrodes show better electrochemical performance than LVNiP/C electrode. Particularly, the LVFeP/C delivers the highest initial discharge capacity of 131.4 mAh g⁻¹ at 0.1 C, which is close to the theoretical capacity (132 mAh g⁻¹). In addition, LVFeP/C exhibits a significantly enhanced rate capability with an average capacity of 122.4 mAh g⁻¹ at 1 C and 93.5 mAh g⁻¹ at 5 C (Fig. 6c). Whereas, LVNiP/C delivers the lowest initial discharge capacity of 117.1 mAh g⁻¹ at 0.1 C (Fig. 6a and b) and also shows the decreased rate capability with 102.3 mAh g⁻¹ at 1 C and 35.4 mAh g⁻¹ at 5 C (Fig. 6c).
Fig. 4. SEM images of the as-prepared samples: (a) pristine LVP/C, (b) LVFeP/C, (c) LVCoP/C, (d) LVNiP/C, and (e) LVMnP/C.

Fig. 5. HRTEM images of samples: (a) LVFeP/C, (b) LVCoP/C, (c) LVNiP/C, and (d) LVMnP/C.
To investigate the effect of the doped M atoms (M = Fe, Co, Ni, Mn) on the electrochemical performance of LVP/C, carbon content, electronic conductivity and CV profiles for all as-obtained samples were measured. Carbon content and electronic conductivity of all samples are listed in Table 2. The carbon contents for the four M-incorporated LVP/C samples are all lower than that for pristine LVP/C. This may result from the consumption of pyrolytic carbon to maintain the reductive state of Fe, Co and Ni during the synthesis process. Pristine LVP/C shows the highest electronic conductivity value of $3.17 \times 10^{-2}$ S cm$^{-1}$ due to its highest carbon content. The electronic conductivity is in the following order from higher to lower values for the LVMP/C samples: LVFeP/C > LVMnP/C > LVCoP/C > LVNiP/C. The LVNiP/C shows the lowest electronic conductivity with $4.52 \times 10^{-3}$ S cm$^{-1}$, which could be mainly responsible for the observed poorest electrochemical performance. However, in spite of lower electronic conductivity caused by lower-level carbon, the electrochemical performance of LVFeP/C is actually better than that of pristine LVP/C (see Fig. 6).

Fig. 7 displays the CV curves for the pristine and M-doped LVP/C samples. All the electrodes present three pairs of oxidation and reduction peaks, which are labeled as A1/C1, A2/C2, and A3/C3, corresponding to a sequence of phase transition processes for Li$_x$V$_2$(PO$_4$)$_2$ at $x = 3.0, 2.5, 2.0$ and $1.0$ [4]. This CV result is in good agreement with the positions of the charge/discharge plateaus observed in Fig. 6a. For LVFeP/C, another pair of redox potential peaks around 3.5/3.4 V are also seen in Fig. 7b (marked by red arrows). These peaks are associated with Fe$^{2+}$/Fe$^{3+}$ redox couple for LiFePO$_4$ and are consistent with the observed charge/discharge plateaus in Fig. 6a. However, such extra redox peaks related to Co, Ni and Mn are not observed and this may due to the low charge voltage (4.3 V). Thus, combined with our results from XRD, TEM and charge/discharge profiles, it is reasonable to believe that LiMPO$_4$ (M = Fe, Co, Ni and Mn) coexists as an impurity phase with the primary M-doped LVP phase in LVMP/C samples though it is not detected in the XRD patterns (see Fig. 1). For LVFeP/C, the theoretical capacity of LiFePO$_4$ (170 mAh g$^{-1}$) impurity is higher than that of LVP (132 mAh g$^{-1}$) when charged to 4.3 V. So, the existence of LiFePO$_4$ in the LVFeP/C sample can make additional contribution to the total capacity, whereas LiCoPO$_4$, LiNiPO$_4$ and LiMnPPO$_4$ are electrochemically inactive between 2.5 and 4.3 V. Furthermore, the CV peak current ($I_p$) increases with scanning rate, indicative of a diffusion control. The relationship between the peak current and square root of the scan rate can be expressed by the classical Randles Sevick equation [47]:

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} v^{1/2},$$

where $I_p$ is the CV peak current (A), $n$ is the number of electrons involved in the redox process, $A$ is the electrode area (cm$^2$), $D$ is the Li$^+$ diffusion coefficient (cm$^2$ s$^{-1}$), $v$ is the potential scan rate (V s$^{-1}$), and $C$ is the concentration of lithium ions in the cathode (mol cm$^{-3}$). Therefore, the lower CV peak current, the lower the Li ion diffusion coefficient is. In the insets of Figs. 7a–d, the CV peak current $I_p$ for the peak A3 is plotted against the potential scan rate $v$. Using the equation above and the values of the slope of $I_p$ vs. $v^{1/2}$ plots shown in the insets of Figs. 7a–e, the values of the lithium ion diffusion coefficient D are calculated to be $2.63 \times 10^{-9}, 8.59 \times 10^{-9}, 4.48 \times 10^{-9}, 1.79 \times 10^{-9}$, and $4.96 \times 10^{-9}$ cm$^2$ s$^{-1}$, respectively (Table 2), for LVP/C, LVFeP/C, LVCoP/C, LVNiP/C, and LVnP/C samples. Obviously, compared with LVP/C, LVFeP/C has the fastest lithium ion diffusion and LVNiP/C has the slowest lithium ion diffusion. This result agrees well with the conclusion made in Fig. 6 that LVFeP/C and LVNiP/C show the best and worst electrochemical performance, respectively, among the four LMVP/C cathode samples.

Table 2: Carbon content, electronic conductivity and lithium-ion coefficient of pristine LVP/C and LVMP/C (Fe, Co, Ni, Mn) samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon content (wt.%)</th>
<th>Electronic conductivity (S cm$^{-1}$)</th>
<th>Lithium-ion coefficient (cm$^{-2}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LVP/C</td>
<td>3.66</td>
<td>3.17 × 10$^{-2}$</td>
<td>2.63 × 10$^{-9}$</td>
</tr>
<tr>
<td>LVFeP/C</td>
<td>3.00</td>
<td>1.75 × 10$^{-2}$</td>
<td>8.59 × 10$^{-9}$</td>
</tr>
<tr>
<td>LVCoP/C</td>
<td>2.94</td>
<td>6.38 × 10$^{-3}$</td>
<td>4.48 × 10$^{-9}$</td>
</tr>
<tr>
<td>LVNiP/C</td>
<td>3.01</td>
<td>4.52 × 10$^{-3}$</td>
<td>1.79 × 10$^{-9}$</td>
</tr>
<tr>
<td>LVnP/C</td>
<td>3.13</td>
<td>1.49 × 10$^{-2}$</td>
<td>4.96 × 10$^{-9}$</td>
</tr>
</tbody>
</table>

Fig. 6. (a, b) Initial charge/discharge profiles and cyclic performances of pristine LVP/C and M-modified LVP/C electrodes at 0.1 C, respectively; and (c) Cyclic performances of pristine LVP/C and M-modified LVP/C electrodes at different C-rate, ranging from 0.5 to 5.0 C for ten cycles at each rate.
4. Conclusions

Li$_3$V$_2$(PO$_4$)$_3$/C was incorporated by four electrochemically active metal atoms (Fe, Co, Ni, Mn) by a two-step solid-state sintering method. The experiment shows that M-incorporation does not change the monoclinic structure of Li$_3$V$_2$(PO$_4$)$_3$, but forms some solid solutions. Minor LiMPO$_4$ (M = Fe, Co, Ni, Mn) impurity phase could be formed in the LVMP/C samples. Moreover, FePO$_4$ also exists as impurity in the LVFeP/C sample. Compared with pristine LVP/C, LVNiP/C electrode exhibits the lowest capacity, resulting from the decreased electronic conductivity and the lowest Li-ion diffusion coefficient, whereas LVFeP/C shows the best electrochemical performance which is indicated by the highest initial discharge capacity of 131.4 mAh g$^{-1}$ at 0.1 C and an excellent rate capability with average capacity of 122.4 mAh g$^{-1}$ at 1 C and 93.5 mAh g$^{-1}$ at 5 C. The enhancement in electrochemical performance of LVFeP/C is attributed to the reduced particle size, the improved electronic conductivity, the highest Li-ion diffusion coefficient, and the contribution of LiFePO$_4$ to the capacity. Our results have specified the influence of electrochemically active metal ions (Fe, Co, Ni, Mn) on the electrochemical performance of Li$_3$V$_2$(PO$_4$)$_3$, which is helpful to understand the modified mechanism of some cathode materials for lithium-ion batteries.

Acknowledgements

This work was supported by the NSFC (No. 21175050, 51272128) and the MOST of China (Nos. 2011AA11290, 2011DFB70020); the key project of Hubei Provincial Department of Education (No. D20131303); US National Science Foundation.
References

[38] D.W. Han, Y.M. Kang, R.Z. Yin, M.S. Song, H.S. Kwon, Electrochemical Communications 11 (2009) 137.