



Short communication

# Electrochemical behavior of $\text{Li}_{3-x}\text{M}'_x\text{V}_{2-y}\text{M}''_y(\text{PO}_4)_3$ ( $\text{M}' = \text{K}$ , $\text{M}'' = \text{Sc}$ , $\text{Mg} + \text{Ti}$ )/C composite cathode material for lithium-ion batteries

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 $\text{Li}_{3-x}\text{M}'_x\text{V}_{2-y}\text{M}''_y(\text{PO}_4)_3$  ( $\text{M}' = \text{K}$ ,  $\text{M}'' = \text{Sc}$ ,  $\text{Mg} + \text{Ti}$ )

Cathode materials for lithium batteries

## ABSTRACT

Composites of monoclinic  $\text{Li}_{3-x}\text{M}'_x\text{V}_{2-y}\text{M}''_y(\text{PO}_4)_3$  ( $\text{M}' = \text{K}$ ,  $\text{M}'' = \text{Sc}$ ,  $\text{Mg} + \text{Ti}$ ) with carbon were synthesized by solid-state reaction using oxalic acid or 6%  $\text{H}_2/\text{Ar}$  gas mixture as reducing agents at sintering temperature of 850 °C. The samples were characterized by X-ray diffraction (XRD), voltammetry and electrochemical galvanostatic cycling. The capacity of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  synthesized using hydrogen as the reducing agent was 127  $\text{mA h g}^{-1}$  and decreased to 120  $\text{mA h g}^{-1}$  after 20 charge–discharge cycles. The substitution of lithium and vanadium for other ions did not result in the improvement of the electrochemical characteristics of the samples.

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## 1. Introduction

Lithium-ion batteries are regarded as the most advanced energy storage systems. Recently in an intensive search for new cathode materials for lithium-ion batteries, lithium conducting phosphates,  $\text{Li}_3\text{M}_2(\text{PO}_4)_3$ , and systems based on these compounds have been proposed as a new candidates [1–4]. In particular, monoclinic lithium vanadium phosphate,  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  (LVP) is a highly promising material proposed as a cathode for higher voltage lithium-ion batteries because it possesses high reversible capacity and operation voltage [5–9].  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  contains both mobile  $\text{Li}^+$  cations and redox-active metal within a rigid phosphate framework. The reversible extraction of all three lithium ions from  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  would correspond to a theoretical capacity of 197  $\text{mAh g}^{-1}$  [10–12], such capacity is the highest for all phosphates which have been reported. Disadvantage of LVP is non-flat voltage characteristics: there are 3 plateaus at 3.5–3.6, 3.6–3.7 and 4.0–4.1 V corresponding to the same redox process:  $\text{V}^{3+} + \text{e}^- \rightarrow \text{V}^{4+}$ . The possible reasons of such behavior could be polymorphism, concentration phase transitions, change of the symmetry group, formation of defect pairs [ $\text{Li}_i^{\bullet} - \text{V}_{\text{Li}}'$ ] and charge ordering ( $\text{V}^{3+} - \text{V}^{4+}$ ). Monoclinic structure of LVP is very stable and the symmetry does not change on charge–discharge process [5]. Two hypothetical ways to improve the

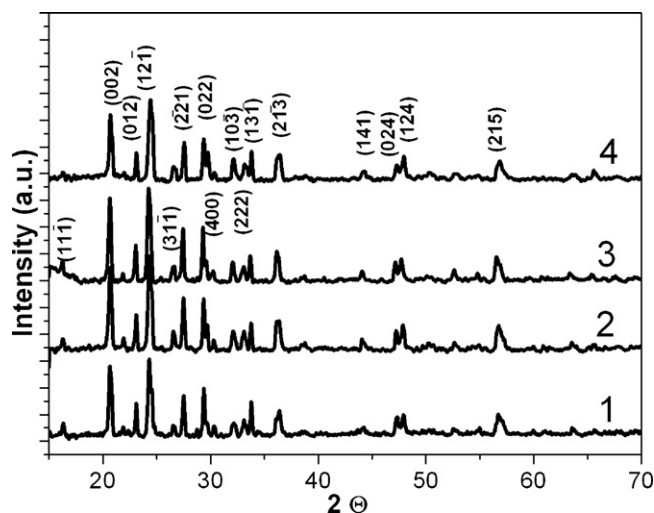
electrochemical properties of LVP (i.e. to make charge–discharge curves more smooth) may be proposed: (a) to stabilize other polymorphs with more symmetric lattice, for example rhombohedral or orthorhombic phases; (b) to diminish ordering effects by the doping of LVP with other cations different in size and charge. It will produce fluctuations in the cationic sublattice. In this article, the influence of cationic substitution in lithium and vanadium sublattices on transport properties and electrochemical performances of monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  as the cathodes materials have been investigated.

## 2. Experimental

The monoclinic  $\text{Li}_{3-x}\text{M}'_x\text{V}_{2-y}\text{M}''_y(\text{PO}_4)_3$  ( $\text{M}' = \text{K}$ ,  $\text{M}'' = \text{Sc}$ ,  $\text{Mg} + \text{Ti}$ ) samples were obtained using a standard solid-state reaction by mixing stoichiometric amounts of  $\text{LiOH} \cdot \text{H}_2\text{O}$ ,  $\text{V}_2\text{O}_5$ ,  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{KOH}$ ,  $\text{Sc}_2\text{O}_3$ ,  $(\text{MgOH})_2\text{CO}_3$ ,  $\text{TiO}_2$  and 5 mass percent of oxalic acid  $\text{H}_2\text{C}_2\text{O}_4$  excess of over the stoichiometric reaction. The mixtures were initially heated at 300 °C in drying oven for 3 h for complete removal of gaseous products, pelletized, and then heated at 850 °C for 5 h under a flow of ( $\text{Ar} + 6\%\text{H}_2$ ) gas mixture. The crystal structure of the reaction products was determined from powder diffraction data obtained using a Bruker D8 Diffractometer with  $\text{Cu K}\alpha$  radiation. Electrical conductivity was measured on the pellets by two-terminal technique with Ag-paste electrodes in vacuum ( $10^{-2}$  Torr) with a Hewlett Packard 4284A Precision LCR Meter within the frequency range of 20 Hz to 1 MHz. Pellets were compacted at 500 MPa and sintered at the temperature 850 °C for 4 h. The  $\text{Li}_{3-x}\text{M}'_x\text{V}_{2-y}\text{M}''_y(\text{PO}_4)_3$  ( $\text{M}' = \text{K}$ ,  $\text{M}'' = \text{Sc}$ ,  $\text{Ti} + \text{Mg}$ )/C composite cathode electrodes were prepared by mixing of 10% acetylene black

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**Fig. 1.** XRD pattern for the samples:  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  (1);  $\text{Li}_3\text{Mg}_{0.1}\text{Ti}_{0.1}\text{V}_{1.8}(\text{PO}_4)_3$  (2);  $\text{Li}_3\text{Sc}_{0.2}\text{V}_{1.8}(\text{PO}_4)_3$  (3) and  $\text{Li}_{2.85}\text{K}_{0.15}\text{V}_2(\text{PO}_4)_3$  (4).

and 90% active material, dried in vacuum furnace at  $90^\circ\text{C}$  for 24 h and put as a powder on the stainless steel plunger of the measuring cell. Estimated thickness of the cathode layer was  $10\text{--}20\ \mu\text{m}$ . The electrolyte consisted of 1 M  $\text{LiPF}_6$  solution in a mixture of ethylene carbonate and dimethyl carbonate with the volumetric ratio of 1:1. Two-electrode electrochemical cells were assembled in glove box filled with high-purity argon, where the lithium metal foil was used as anode and Celgard<sup>®</sup> 2320 as a separator. The electrochemical cycling measurements were performed in the voltage range between 3.0 and 4.8 V; the electrochemical capacity of samples was evaluated on the active materials. The charge–discharge curves were measured using a Maccor-32 battery tester. Cyclic voltammetry (CV) was performed with an electrochemical instrument Autolab at scan rate of  $0.05\ \text{mV s}^{-1}$  in the range of 3.0–5 V.

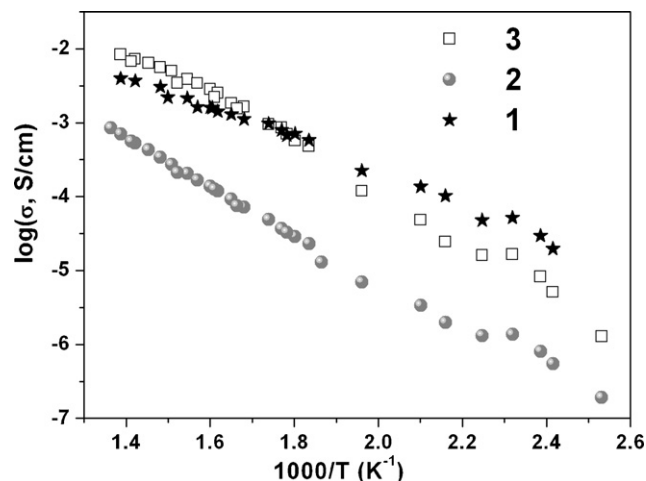
### 3. Results and discussion

#### 3.1. Crystal structure and cationic distribution

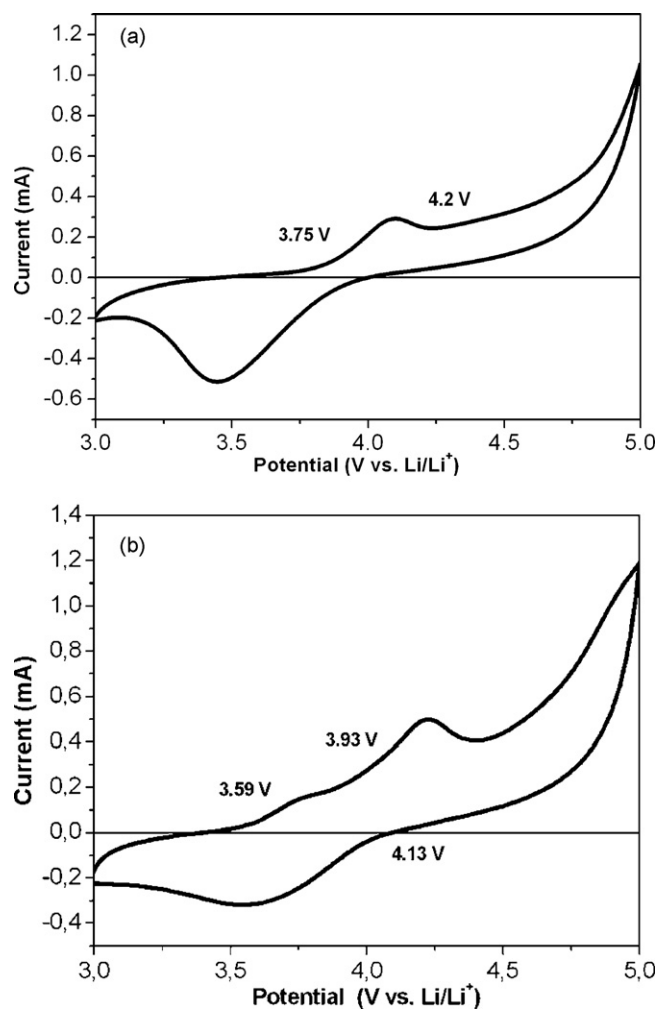
**Fig. 1** shows the XRD pattern for the  $\text{Li}_{3-x}\text{M}'_x\text{V}_{2-y}\text{M}''_y(\text{PO}_4)_3$  ( $\text{M}' = \text{K}, \text{M}'' = \text{Sc}, \text{Mg} + \text{Ti}$ )/C composite. All the X-ray diffraction peaks correspond to single-phase materials and are indexed with monoclinic structure (space group  $\text{P}21/\text{n}$ ) [10,11]. Lattice parameters were calculated using a U-Fit program with R-factor of less than 5%. The numerous data are shown in **Table 1**. The cell parameters are consistent with those in previous reports [13,14]. As seen from the data, the substitution of  $\text{V}^{3+}$  (the ionic radius,  $r = 0.065\ \text{nm}$ ) for larger cations  $\text{Mg}^{2+}$  ( $r = 0.078\ \text{nm}$ ),  $\text{Sc}^{3+}$  ( $r = 0.083\ \text{nm}$ ) as well as  $\text{Li}^+$  ( $r = 0.078\ \text{nm}$ ) for  $\text{K}^+$  ( $r = 0.133\ \text{nm}$ ), is accompanied by the increase in the crystal lattice volume.

#### 3.2. Electrical properties

Conductivity of lithium phosphates under study was investigated by a complex impedance technique. Analysis of the conductivity data (**Fig. 2**) shows that electrical conductivity of sam-



**Fig. 2.** Arrhenius dependences of conductivity for the samples  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ ,  $\text{Li}_3\text{Mg}_{0.1}\text{Ti}_{0.1}\text{V}_{1.8}(\text{PO}_4)_3$  and  $\text{Li}_3\text{Sc}_{0.2}\text{V}_{1.8}(\text{PO}_4)_3$ , points 1, 2 and 3, respectively.



**Fig. 3.** Cyclic voltammograms at scanning rate of  $0.05\ \text{mV s}^{-1}$  for  $\text{Li}_3\text{Mg}_{0.1}\text{Ti}_{0.1}\text{V}_{1.8}(\text{PO}_4)_3/\text{C}$  (a) and  $\text{Li}_3\text{Sc}_{0.1}\text{V}_{1.8}(\text{PO}_4)_3/\text{C}$  (b).

**Table 1**

Lattice parameters and the cell volume for the samples under study.

Samples	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$ ( $^\circ$ )	Cell volume (Å <sup>3</sup> )
$\text{Li}_3\text{V}_2(\text{PO}_4)_3$	11.98(15)	8.59(4)	8.57(3)	90.19(1)	882.9(7)
$\text{Li}_3\text{Mg}_{0.1}\text{Ti}_{0.1}\text{V}_{1.8}(\text{PO}_4)_3$	12.03(12)	8.58(6)	8.58(6)	90.23(3)	887.0(5)
$\text{Li}_3\text{Sc}_{0.2}\text{V}_{1.8}(\text{PO}_4)_3$	12.05(15)	8.60(7)	8.60(5)	90.20(4)	892.0(8)
$\text{Li}_{2.85}\text{K}_{0.15}\text{V}_2(\text{PO}_4)_3$	12.01(12)	8.57(7)	8.58(5)	90.23(3)	884.3(6)

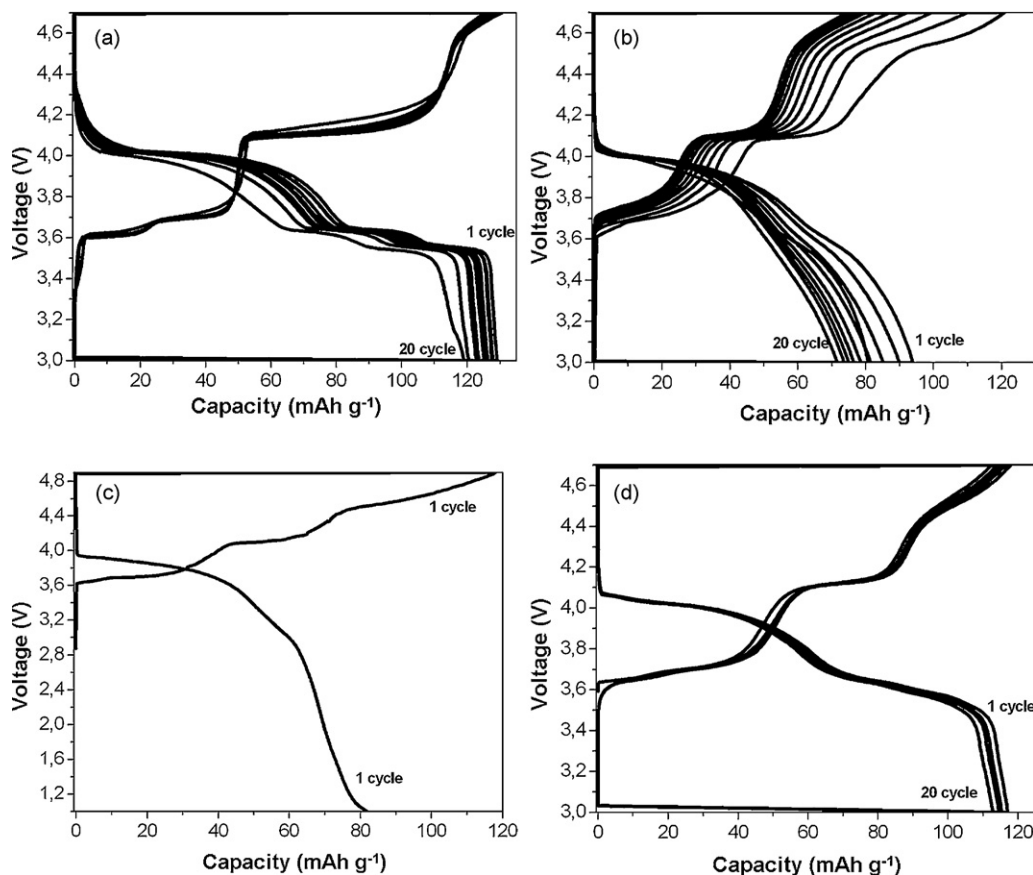


Fig. 4. Charge–discharge curves for electrochemical cell with cathode:  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  (a);  $\text{Li}_{2.85}\text{K}_{0.15}\text{V}_2(\text{PO}_4)_3/\text{C}$  (b);  $\text{Li}_3\text{Mg}_{0.1}\text{Ti}_{0.1}\text{V}_{1.8}(\text{PO}_4)_3/\text{C}$  (c);  $\text{Li}_3\text{Sc}_{0.2}\text{V}_{1.8}(\text{PO}_4)_3/\text{C}$  (d).

ples obeys Arrhenius dependences. Complete absence of electrode contribution to the complex impedance suggests that conductivity of all samples under study is due to electronic (polaron-type) charge carriers. Conductivity is thermally activated, the activation energy increases as a result of the cationic substitution from 0.47 eV for pure  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  to  $\sim 0.70$  eV for the substituted forms  $\text{Li}_3\text{Mg}_{0.1}\text{Ti}_{0.1}\text{V}_{1.8}(\text{PO}_4)_3$  and  $\text{Li}_3\text{Sc}_{0.2}\text{V}_{1.8}(\text{PO}_4)_3$ . At room temperature the pure LVP has the highest conductivity.

### 3.3. Electrochemical modification

The monoclinic LVP contains three different lithium sites within a rigid three-dimensional framework, which consists of metal octahedral and phosphorous tetrahedral [15]. All three  $\text{Li}^+$  ions may be reversibly extracted from LVP and hence high capacity can be expected in this system [5]. Two  $\text{Li}^+$  ions can be easily extracted/inserted reversibly between 3.0 and 4.3 V based on the  $\text{V}^{3+}/\text{V}^{4+}$  redox couple [16]. When charged to 4.8 V, three  $\text{Li}^+$  ions can be completely extracted [11], associated with the  $\text{V}^{4+}/\text{V}^{5+}$  redox couple [10]. Fig. 3 shows the cyclic voltammograms (CV) of the  $\text{Li}_3\text{V}_{2-y}\text{M}''_y(\text{PO}_4)_3/\text{C}$  ( $\text{M}'' = \text{Sc}, \text{Mg} + \text{Ti}$ ) material recorded between 3.0 and 5.0 V at a scanning rate of  $0.05 \text{ mV s}^{-1}$ . The peak potentials in intercalation processes are located at 3.75 and 4.2 V for  $\text{Li}_3\text{Mg}_{0.1}\text{Ti}_{0.1}\text{V}_{1.8}(\text{PO}_4)_3$  and 3.59 and 3.95 V for  $\text{Li}_3\text{Sc}_{0.1}\text{V}_{1.8}(\text{PO}_4)_3$  in fair agreement with the results of the galvanostatic charge/discharge curves. During reverse scans, there are single cathodic peaks at 4.0 (for  $\text{Li}_3\text{Mg}_{0.1}\text{Ti}_{0.1}\text{V}_{1.8}(\text{PO}_4)_3/\text{C}$ ) and 4.13 V ( $\text{Li}_3\text{Sc}_{0.1}\text{V}_{1.8}(\text{PO}_4)_3/\text{C}$ ) due to lithium insertion. Fig. 4 shows charge–discharge curves for electrochemical cell  $\text{Li}_{3-x}\text{M}'_x\text{V}_{2-y}\text{M}''_y(\text{PO}_4)_3/\text{C}$  ( $\text{M}' = \text{K}, \text{M}'' = \text{Sc}, \text{Mg} + \text{Ti}$ )/ $\text{LiPF}_6 + \text{EC}:\text{DMC}/\text{Li}$ , obtained at 0.1 C rate. There are three charge plateaus around 3.60, 3.68 and 4.08 V, which correspond to

a sequence of phase transitions between the phases  $\text{Li}_{3-x}\text{V}_2(\text{PO}_4)_3$  (Fig. 4a):  $x = 3.0, 2.5, 2.0$  and  $1.0$ , respectively. On the reduction curve, there are three discharge plateaus around 3.56, 3.64 and 4 V. As seen from Fig. 4a, initial charge and discharge capacities of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  are 125 and  $124 \text{ mAh g}^{-1}$ , respectively. The discharge capacity decreases from  $124 \text{ mAh g}^{-1}$  on the first cycle to  $118 \text{ mAh g}^{-1}$  on the 20th cycle that is 95% of initial discharge capacity. For  $\text{Li}_{2.85}\text{K}_{0.15}\text{V}_2(\text{PO}_4)_3/\text{C}$  the charge curve contains 2 plateaus around 3.72 and 4.05 V; the discharge curve has a smooth plateau around 3.95 V (Fig. 4b). The first charge and discharge capacities

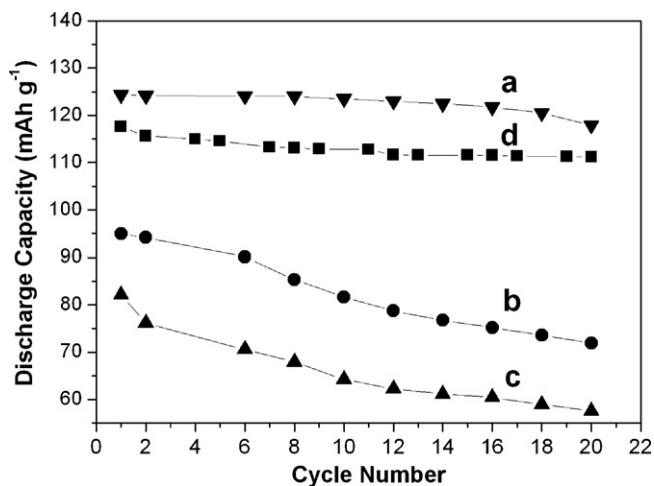


Fig. 5. Change of the discharge capacity of the composite cathodes:  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  (a);  $\text{Li}_{2.85}\text{K}_{0.15}\text{V}_2(\text{PO}_4)_3/\text{C}$  (b);  $\text{Li}_3\text{Mg}_{0.1}\text{Ti}_{0.1}\text{V}_{1.8}(\text{PO}_4)_3/\text{C}$  (c) and  $\text{Li}_3\text{Sc}_{0.2}\text{V}_{1.8}(\text{PO}_4)_3/\text{C}$  (d) with the number of cycles. The data obtained at 0.1 C rate between 3.0 and 4.7 V.

are 120 and 95 mAh g<sup>-1</sup>, respectively. After 20 cycles, the capacity falls down to 75.8% of the initial value. For Li<sub>3</sub>Mg<sub>0.1</sub>Ti<sub>0.1</sub>V<sub>1.8</sub>(PO<sub>4</sub>)<sub>3</sub> charge curve has 3 electrochemical plateaus at 3.68, 4.1 and 4.55 V, the discharge curve contains 1 plateau at 3.86 V. Charge and discharge capacities on the first cycle are 120 and 82 mAh g<sup>-1</sup>, respectively (Fig. 4c). After 20 cycles charge and discharge capacities are 58 mAh g<sup>-1</sup>. The discharge curve of Li<sub>3</sub>Sc<sub>0.2</sub>V<sub>1.8</sub>(PO<sub>4</sub>)<sub>3</sub>/C contains 2 plateaus at 3.65 and 4.03 V. For Sc-doped sample (Li<sub>3</sub>Sc<sub>0.2</sub>V<sub>1.8</sub>(PO<sub>4</sub>)<sub>3</sub>/C) the initial charge capacity is 118 mAh g<sup>-1</sup>, and initial discharge capacity is 117 mAh g<sup>-1</sup>. After 20 cycles the discharge capacity is 111 mAh g<sup>-1</sup> corresponding to 94% of the initial value (Fig. 5). Thus, the substitution of lithium and vanadium for other ions did not result in the improvement of the electrochemical characteristics of the samples.

#### 4. Conclusions

In summary, the monoclinic Li<sub>3-x</sub>M'<sub>x</sub>V<sub>2-y</sub>M''<sub>y</sub>(PO<sub>4</sub>)<sub>3</sub> (M' = K, M'' = Sc, Mg + Ti)/C material can be synthesized by a solid-state reaction route using oxalic acid as the reduction agent and carbon source. Conductivity of Li<sub>3-x</sub>M'<sub>x</sub>V<sub>2-y</sub>M''<sub>y</sub>(PO<sub>4</sub>)<sub>3</sub> (M' = K, M'' = Sc, Mg + Ti)/C is electronic and depends on the dopant type. Pure LVP has the highest discharge capacity and the best cycleability in the voltage range of 3.0–4.8 V. The samples doped with K exhibit flat charge/discharge curves but worse cycleability. Among the substituted samples, ones doped with Sc have superior characteristics and might be regarded as promising cathode materials.

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