



# The multiple effects of potassium doping on LiVPO<sub>4</sub>F/C composite cathode material for lithium ion batteries



Jiebing Wu<sup>a,b</sup>, Youlong Xu<sup>a,b,\*</sup>, Xiaofei Sun<sup>a,b</sup>, Chao Wang<sup>a</sup>, Baofeng Zhang<sup>b</sup>, Jing Zhao<sup>a</sup>

<sup>a</sup> Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an, China

<sup>b</sup> Shaanxi Engineering Research Center of Advanced Energy Materials & Devices, Xi'an Jiaotong University, Xi'an, China

## HIGHLIGHTS

- Potassium-doped LiVPO<sub>4</sub>F was first synthesized by two-step reaction route.
- K<sup>+</sup> dopant suppresses Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and reduces particle agglomeration.
- K<sup>+</sup> doping greatly improves the electrochemical performance.
- K<sup>+</sup> doping expands the Li<sup>+</sup> migration and diffusion pathway.

## ARTICLE INFO

### Keywords:

Lithium ion batteries  
Cathode material  
Lithium vanadium fluorophosphate  
Potassium doping

## ABSTRACT

The intermediate product VPO<sub>4</sub>/C is synthesized via sol-gel method, then it is mixed with other raw materials and calcined to prepare Li<sub>1-x</sub>K<sub>x</sub>VPO<sub>4</sub>F/C ( $x = 0, 0.005, 0.01, 0.02$ ). Potassium with large ionic radius partially substitutes the lithium site and slightly increases the unit cell volume. The potassium dopant suppresses the formation of Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and reduces the particle agglomeration. The doped samples possess lower polarization and higher discharge plateau than the pristine LiVPO<sub>4</sub>F/C, and Li<sub>0.99</sub>K<sub>0.01</sub>VPO<sub>4</sub>F/C exhibits the best electrochemical performance. With 2.9 wt% amorphous carbon uniformly wrapping the surface, Li<sub>0.99</sub>K<sub>0.01</sub>VPO<sub>4</sub>F/C delivers a reversible capacity of 140.9 mA h g<sup>-1</sup> at 0.12 C and maintains 98.3 mA h g<sup>-1</sup> at the charge/discharge rate of 10 C. Its specific discharge capacity with a retention of 96.13% decreases from 131.9 to 126.8 mA h g<sup>-1</sup> after 125 cycles at the charge/discharge rate of 1 C. The improvement of rate and cycling performance is ascribed to the decrease of charge transfer resistance (88.47 Ω) and the increase of Li<sup>+</sup> diffusion coefficient ( $6.75 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ ), indicating that potassium doping facilitates the migration and diffusion of Li<sup>+</sup> due to the expansion of Li<sup>+</sup> pathway.

## 1. Introduction

As the conversion device of clean energy, lithium ion batteries (LIBs) are in line with the sustainable development of our society and widely used in various fields [1,2]. Meanwhile, stable polyanionic compounds [3] are becoming popular with the popularization of electric vehicles. Polyanionic compounds have XO (X = P, Si, S, etc.) tetrahedra with strong covalent bonds, which can efficiently improve their structural and thermal stabilities [4]. However, the most widely commercialized polyanionic compound LiFePO<sub>4</sub> has a low discharge potential (3.4 V vs. Li/Li<sup>+</sup>) [5,6], which leads to great internal resistance consumption for connecting more battery packs in series to meet the requirement of high operating voltage and thus limits its further practical application.

As a new polyanionic cathode material, LiVPO<sub>4</sub>F possesses stable structure, high potential (4.2 V vs. Li/Li<sup>+</sup>) as well as high energy density (655 Wh kg<sup>-1</sup>). LiVPO<sub>4</sub>F with the same structure as tavorite (LiFePO<sub>4</sub>·OH) was first synthesized by J. Barker [7] through a two-step carbothermal reduction (CTR) method in 2003. Its theoretical capacity is as high as 156 mA h g<sup>-1</sup>. The common induction effect of F<sup>-</sup> and PO<sub>4</sub><sup>3+</sup> increases the energy level of the V<sup>4+</sup>/V<sup>3+</sup> redox couple [7,8], leading to a higher potential.

However, LiVPO<sub>4</sub>F can be unintentionally synthesized with by-product Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> due to the loss of fluoride [9,10], which limits its further study. Rapid calcination and rapid quenching are usually adopted in the previous work to avoid the formation of impurity. However, LiVOPO<sub>4</sub> is easily formed on the surface or in the bulk [11]

\* Corresponding author. Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an, China.

E-mail address: [yixu@mail.xjtu.edu.cn](mailto:yixu@mail.xjtu.edu.cn) (Y. Xu).

<https://doi.org/10.1016/j.jpowsour.2018.06.020>

Received 6 April 2018; Received in revised form 22 May 2018; Accepted 3 June 2018  
0378-7753/ © 2018 Elsevier B.V. All rights reserved.

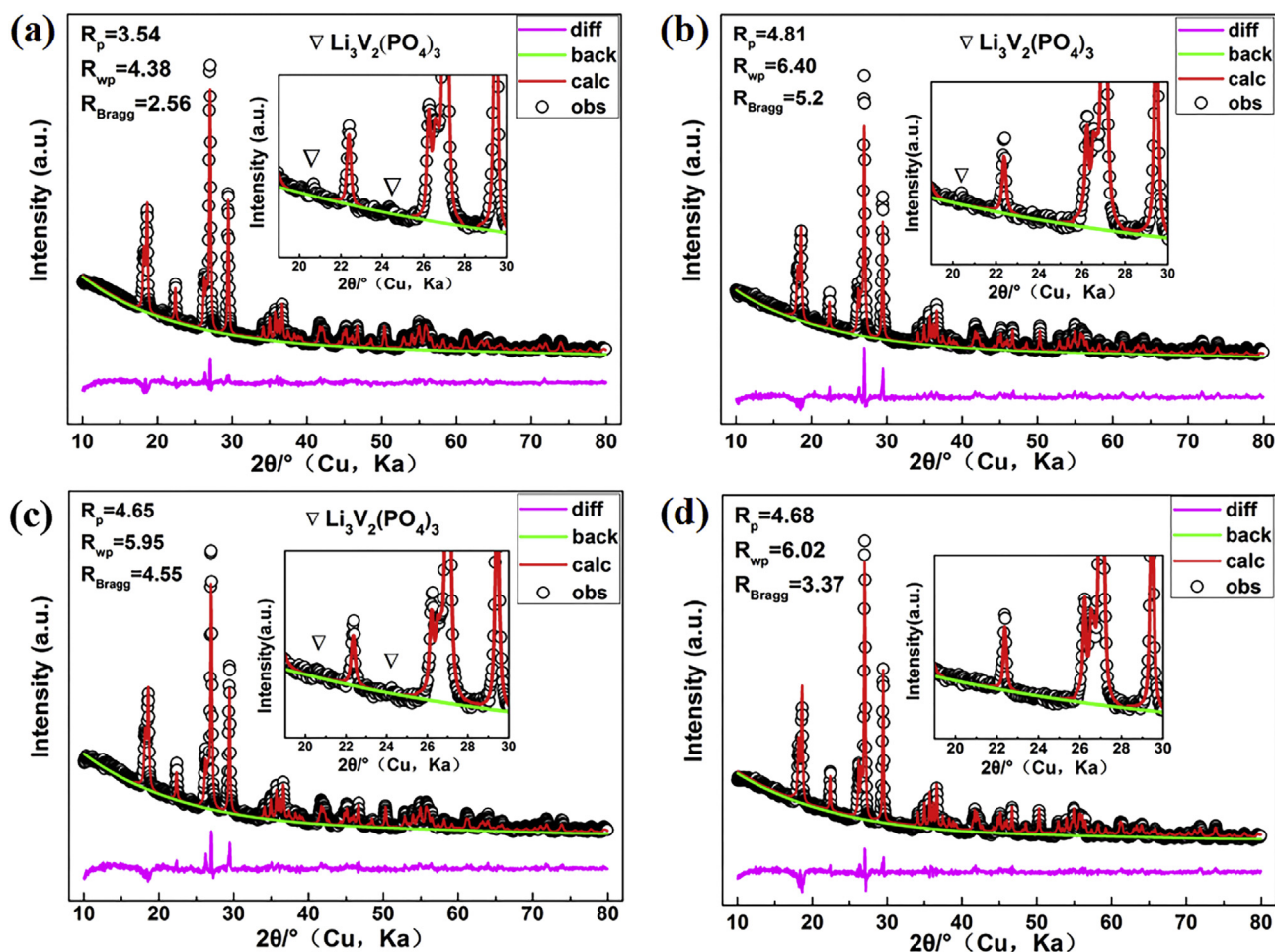


Fig. 1. The XRD patterns of (a) K0, (b) K0.5, (c) K1 and (d) K2 fitted by Rietveld refinement.

Table 1

The calculated lattice parameters of K0, K0.5, K1 and K2.

Sample	a/Å	b/Å	c/Å	$\alpha^\circ$	$\beta^\circ$	$\gamma^\circ$	V/Å <sup>3</sup>
K0	5.1775	5.3065	7.2592	107.595	107.972	98.389	174.434
K0.5	5.1771	5.3069	7.2615	107.610	107.999	98.366	174.451
K1	5.1816	5.3071	7.2621	107.607	107.975	98.389	174.639
K2	5.1752	5.3068	7.2649	107.596	108.012	98.326	174.504

when contacting with oxygen in the quenching process. Recently, Minkyung Kim [11] proposed that polytetrafluoroethylene (PTFE) can compensate the loss of fluoride and effectively suppress the formation of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ .

To improve the electrochemical performance of  $\text{LiVPO}_4\text{F}$ , surface coating and cationic doping are usually applied to modify it. The residual carbon wrapping the material can decrease the particle size and improve the electronic conductivity. Other coating materials including graphene [12–16],  $\text{Li}_3\text{PO}_4$  [17],  $\text{MoS}_2$  [18,19] and polyaniline [20] can also improve electronic or ionic conductivity, and some may form a physical barrier [17]. The doped cations partially substitute lithium ions (such as  $\text{Na}^+$  [21],  $\text{Cr}^{3+}$  [22]) or vanadium ions (such as  $\text{Mn}^{3+}/\text{Mn}^{4+}$  [23],  $\text{Al}^{3+}$  [24,25],  $\text{Co}^{3+}/\text{Co}^{2+}$  [26],  $\text{Ti}^{4+}$  [27]), and some of them may change the electronic cloud structure of the 3d spin orbit in different degrees, consequently narrowing the band gap and increasing the electronic conductivity [28]. Meanwhile, some inactive doped cations may facilitate the  $\text{Li}^+$  diffusion and stabilize the structure [29] to improve the rate and cycling performance, which has been confirmed in  $\text{LiFePO}_4$ .

In this paper,  $\text{LiVPO}_4\text{F}$  was synthesized by a novel two-step reaction route and PTFE was added to compensate the loss of fluoride. At the same time, potassium partially substitutes lithium to explore its influence on the crystal structure, particle morphology, kinetic parameters and electrochemical performance of  $\text{LiVPO}_4\text{F}$ .

## 2. Experimental

### 2.1. Materials preparation

Firstly, the intermediate product  $\text{VPO}_4/\text{C}$  was synthesized by sol-gel method. A stoichiometric ratio of  $\text{NH}_4\text{VO}_3$  and chelating agent oxalic acid were dissolved in water with magnetic stirring at  $80^\circ\text{C}$  for 1 h. Then  $\text{NH}_4\text{H}_2\text{PO}_4$  and sucrose were added into the solution with continuously heating to obtain a gel. The obtained gel was dried in a vacuum oven and calcined in argon at  $750^\circ\text{C}$  for 4 h to prepare  $\text{VPO}_4/\text{C}$ . Finally, the  $\text{VPO}_4/\text{C}$  was mixed with LiF, PTFE and sucrose by the ball mill and calcined at  $700^\circ\text{C}$  for 10 min to prepare  $\text{LiVPO}_4\text{F}/\text{C}$  named as K0. Since the PTFE is insoluble in water, it is difficult to synthesize  $\text{LiVPO}_4\text{F}/\text{C}$  by a single sol-gel method. Rapid calcination can increase the antisite defects to improve the electrochemical performance of the material [11].

$\text{Li}_{1-x}\text{K}_x\text{VPO}_4\text{F}/\text{C}$  ( $x = 0.005, 0.01, 0.02$ ) were synthesized in the same way. In addition, a stoichiometric ratio of potassium hydrogen phthalate ( $\text{C}_8\text{H}_5\text{O}_4\text{K}$ ) was mixed with  $\text{VPO}_4/\text{C}$ , LiF, PTFE and sucrose to prepare  $\text{Li}_{1-x}\text{K}_x\text{VPO}_4\text{F}/\text{C}$  ( $x = 0.005, 0.01, 0.02$ ) named as K0.5, K1 and K2, respectively.

Download English Version:

<https://daneshyari.com/en/article/7724795>

Download Persian Version:

<https://daneshyari.com/article/7724795>

[Daneshyari.com](https://daneshyari.com)