



Towards a high-rate and long-life LiVPO₄F/C cathode material for lithium ion batteries by potassium and zirconium co-doping

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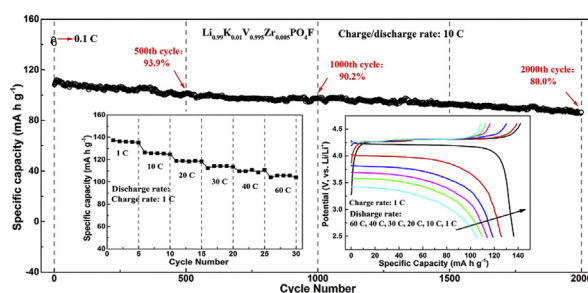
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HIGHLIGHTS

- K⁺ and Zr⁴⁺ co-doped LiVPO₄F/C has superior high-rate and long-life performance.
- Zr⁴⁺ substituting V³⁺ is confirmed as a donor doping by Hall effect.
- K⁺ assisted by Zr⁴⁺ expands Li⁺ migration pathway.

GRAPHICAL ABSTRACT



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ABSTRACT

As a high-potential and high-stability cathode material, LiVPO₄F/C is modified by K⁺ and Zr⁴⁺ co-doping to significantly improve its high-rate and long-life performance. K⁺ assisted by Zr⁴⁺ slightly enlarges the unit cell volume to expand Li⁺ migration pathway. K⁺ substituting Li⁺ can also achieve pillar effect to increase the structural stability. Hall effect reveals that Zr⁴⁺ substituting V³⁺ is a donor doping, leading to the transformation of conductive type from p-type to n-type and a great increase of carrier density by 10⁶ times. Therefore, the electronic conductivity ($1.1 \times 10^{-2} \text{ S cm}^{-1}$) increases by a factor of $\sim 10^4$. The charge transfer resistance decreases to 82.81 Ω and the Li⁺ diffusion coefficient ($9.83 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$) increases to 7 times that of undoped LiVPO₄F/C. The discharge capacities of Li_{0.99}K_{0.01}V_{0.995}Zr_{0.005}PO₄F/C at 0.1C and 1C are 143.3 mA h g⁻¹ and 135.5 mA h g⁻¹, respectively. The capacity retention at the charge/discharge rate of 10C is as high as 80.0% after 2000 cycles with an initial capacity of 108.1 mA h g⁻¹. Even at the discharge rate of 60C (charging at 1C), the capacity reaches 105.7 mA h g⁻¹.

1. Introduction

As the popularization of electric vehicles (EVs) and hybrid electric vehicles (HEVs), new demand for high energy density and high safety lithium ion batteries (LIBs) has attracted widespread attention [1]. For the anode materials, silicon [2] and its derivatives (silicon oxycarbide [3,4], silicon suboxides [5] and so on) have been regarded as an

alternative to graphitic carbon due to its large gravimetric capacity, and their behaviors of lithiation and delithiation are investigated in detail by first-principles. As the cathode materials, polyanionic compounds [6] exhibit long cycle life and superior structural stability due to the stable XO₄ⁿ⁻ (X = P, Si, S, W, Mo, ...) [7] tetrahedra connected by strong covalent bonds, leading to a promising application. Polyanionic compound LiFePO₄ is widely commercialized especially in the public

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bus for its merits of safety, stability and low cost, greatly making up for its shortcoming of potential (3.4 V vs. Li/Li⁺) [8] and theoretical energy density (578 Wh kg⁻¹).

LiVPO₄F with high potential (4.2 V vs. Li/Li⁺) and high theoretical energy density (655 Wh kg⁻¹) can be the best candidate for the replacement of LiFePO₄. LiVPO₄F first proposed by J. Barker [9] in 2003 inherits stable structure of phosphate. The triclinic LiVPO₄F constructed by PO₄ tetrahedron and VO₄F₂ octahedron [10] is isostructural with tavorite [9,11] (LiFePO₄OH). Lithium ions locate in the above three-dimensional framework, while LiVPO₄F is a one-dimensional-ion conductor with the lowest activation energy along [0.012–0.17 0.572] direction [12]. The charged LiVPO₄F also possesses higher thermal stability than oxide-based cathode materials by differential scanning calorimeter (DSC) test [13]. In addition, the strong electronegativity of F⁻ and the inductive effect of PO₄³⁻ greatly raises the redox potential of V³⁺/V⁴⁺ [9,14].

Carbon coating and cation doping are typically adopted to efficiently modify LiVPO₄F due to its low intrinsic electronic conductivity (~10⁻¹¹ S cm⁻¹) and ionic conductivity (~8 × 10⁻⁷ S cm⁻¹) [15]. Carbon coating not only constructs a conductive frame to increase the surface electronic conductivity of particles but also reduces particle size, which can shorten Li⁺ migration pathway to facilitate the insertion/extraction of Li⁺ [16]. In our previous work, the multiple effects of K⁺ doping in the Li site of LiVPO₄F achieve enhanced electrochemical performance, resulting from the expansion of Li⁺ migration pathway as well as the reduction of particle agglomeration [17]. Manganese partially substituting vanadium to obtain LiV_{0.96}Mn_{0.04}PO₄F/C successfully improves the cycle stability, and the capacity retention is 90% after 1000 cycles at 1C [18]. Briefly speaking, cation doping not limited to LiVPO₄F can also achieve the slight altering of lattice parameters, the stability of structure [19,20], the reduction of band gap [12] and the change of particle morphology [17,21,22]. Although many doped cations (such as Co²⁺/Co³⁺ [21], Cr³⁺ [23], Al³⁺ [12,24], Ti⁴⁺ [25] and Na⁺ [26].) have been applied to LiVPO₄F, the detailed mechanism of electronic conductivity increased by cation doping needs to be further studied.

In this work, the Zr⁴⁺ with strong Zr-O and Zr-F ionic bonds was doped in the V site of LiVPO₄F on the basis of K⁺ doping in the Li site through a two-step reaction route. The supervalent Zr⁴⁺ is expected to be a donor doping and enhance the bulk electronic conductivity of LiVPO₄F. The optimum doping amount was explored in single doping systems for both K⁺ (1 at% of Li⁺ [17]) and Zr⁴⁺ (0.5 at% of V³⁺, Fig S2 of supplementary material), and then we used the optimum doping amount of these two cations to prepare co-doped LiVPO₄F.

2. Experimental

2.1. Materials preparation

A two-step reaction route with the assistance of sol-gel method was adopted to prepare K⁺ and Zr⁴⁺ co-doped LiVPO₄F. NH₄VO₃ (2.328 g, 99%), chelating agent C₂H₂O₄·2H₂O (3.782 g, 99%) and ZrO₂ (0.0123 g, 99%) were added into water with continuously stirring at 80 °C for an hour. Then NH₄H₂PO₄ (2.301 g, 99%) and sucrose (0.146 g, 99%) were dissolved in the dark green solution. Keep heating until the water was evaporated to obtain a gel. The dried gel was sintered at 750 °C for 4 h in Ar to synthesize the intermediate V_{0.995}Zr_{0.005}PO₄/C. The intermediate was ball milled with LiF and potassium hydrogen phthalate (C₈H₅O₄K) at a molar ratio of 1: 0.99: 0.01. In addition, polytetrafluoroethylene (PTFE, 10 wt% of V_{0.995}Zr_{0.005}PO₄/C and LiF) was also added into the mixture to compensate the loss of fluoride and reduce the formation of Li₃V₂(PO₄)₃ [27]. Finally, the mixture was sintered at 700 °C for a short holding time to prepare Li_{0.99}K_{0.01}V_{0.995}Zr_{0.005}PO₄F/C labeled as K1Zr0.5.

For comparison, LiV_{1-x}Zr_xPO₄F/C (x = 0.005, 0.01, 0.02) labeled as Zr0.5, Zr1 and Zr2 was synthesized with the only dopant ZrO₂ by the

similar method. Undoped LiVPO₄F/C labeled as LVPF was synthesized without any dopant.

2.2. Characterization

X-ray diffraction (XRD) measured on an X'pert Pro (PANalytical) was carried out to characterize the crystal structure at a scan range of 10°–80°. Scanning electron microscopy (SEM, FEI Quanta FEG 250) and transmission electron microscopy (TEM, JEM 2100 Plus) were used to observe particle morphology. The distribution of particle size was analyzed by zeta potential particle size analyzer (Nano-ZS90, Malvern). X-ray photoelectron spectroscopy (XPS, AXIS ultra DLD) was collected to detect the binding energy of different elements and their corresponding intensities.

2.3. Electrochemical performance

The electrochemical performance of the prepared materials was tested on LAND CT2001A battery test system through the fabrication of CR2016 coin cells. A uniform slurry including active materials, conductive agents and binders at a mass ratio of 80: 10: 10 was evenly distributed on an aluminum foil to make the working electrode. The typical loading density of each working electrode was ~2.0 mg cm⁻¹. 1 M LiPF₆ dissolved in the solvent (EC: DMC = 1: 1) was acted as the electrolyte. The fabrication process was carried out in a glove box filled with Ar. Cyclic voltammetry (CV) was measured at a scan rate of 0.1 mV s⁻¹ from 3.0 V to 4.6 V, while electrochemical impedance spectroscopy (EIS) using an AC amplitude of 5 mV was tested in a frequency range from 0.01 Hz to 100 kHz. Both CV and EIS were tested by Versatile Multichannel Galvanostat 2/Z (VMP2, Princeton Applied Research). The powders of LVPF, K1, Zr0.5 and K1Zr0.5 were pressed by a pressure of 20 MPa to become disks with ~1 cm diameter, which have thicknesses of 1.05 mm, 1.96 mm, 1.14 mm and 1.61 mm, respectively. Then the disks were measured by Hall effect and four-point conductivity measurement using van der Pauw method.

3. Results and discussion

The XRD pattern of K1Zr0.5 in Fig. 1 is refined by Rietveld method according to the LiVPO₄F model built by J. M. A. Mba et al. [28]. The red lines corresponding to fitting results well match the raw data (circles), and the sharp peaks with high intensity reveal the great crystallinity of K1Zr0.5. No significant effect on the intrinsic structure of LiVPO₄F is observed after K⁺ and Zr⁴⁺ co-doping. The XRD patterns shown in Fig S1 (Supplementary Material) also indicates the great crystallinity of Zr0.5, Zr1 and Zr2. The by-product Li₃V₂(PO₄)₃, which can be unintentionally synthesized for the loss of fluoride VF₃ [28,29], is efficiently suppressed in all the materials due to the additional PTFE.

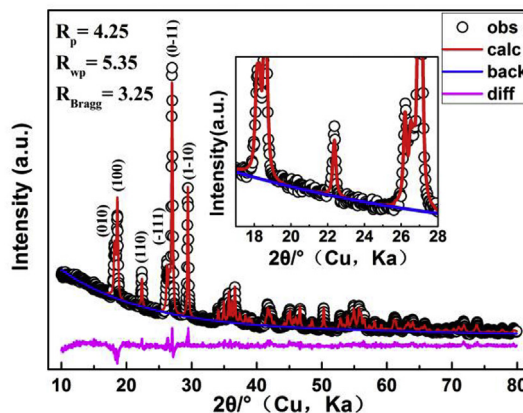


Fig. 1. The XRD pattern of K1Zr0.5 fitted by Rietveld refinement.

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