

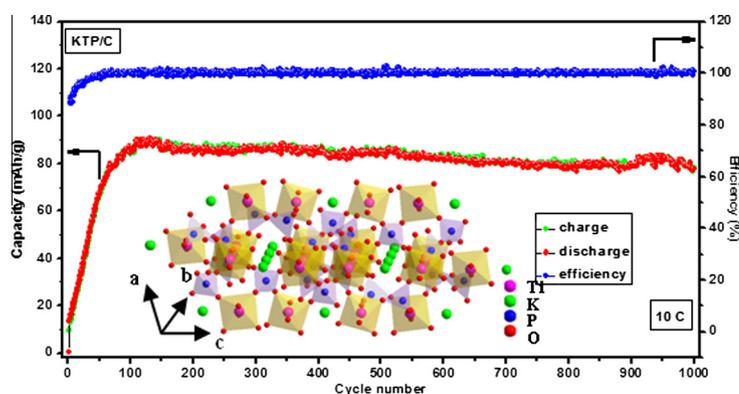
Cubic $\text{KTi}_2(\text{PO}_4)_3$ as electrode materials for sodium-ion batteries

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GRAPHICAL ABSTRACT



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ABSTRACT

A novel cubic $\text{KTi}_2(\text{PO}_4)_3$ is successfully synthesized via a facile hydrothermal method combined with a subsequent annealing treatment and further used as electrode material for sodium-ion batteries for the first time. For comparison, carbon-coated $\text{KTi}_2(\text{PO}_4)_3$ obtained by a normal cane sugar-assisted method reveals superior electrochemical performances in sodium-ion battery. Besides of the high coulombic efficiency of nearly 100% after 100 cycles, a stable capacity of 112 mA h g^{-1} can be achieved at 0.5 C after 100 cycles, and still maintains to 105 mA h g^{-1} after 500 cycles with capacity retention of approximately 90%.

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1. Introduction

When it comes to environmental protection, developing renewable energy sources such as solar and wind have been a hot topic. However, it is still a challenge of integrating renewable energy sources into the grid [1]. Thus, developing large-scale energy storage systems (EES) that possess superior properties, high safety, and

low cost for grid utilization is an urgent demand [2,3]. Battery is a promising candidate for storing electricity owing to its dexterity, convenience, and high-energy conversion efficiency [4–6]. Lithium-ion batteries (LIBs) possessing high energy density has expanded its application from portable electronics to electric vehicles (EV) and hybrid electric vehicles (HEV) [7,8]. However, lithium is not an abundant element and the increasing cost has limited its widespread large-scale application [9]. Therefore, alternative energy storage devices based on earth-abundant elements are urgently called for [10,11]. From this point, sodium, occupying 2.3 wt.% in comparison with 0.0017 wt.% occupation of lithium in

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Earth crust and sharing similar physical/chemical properties with lithium in many aspects, is a promising candidate for replacing lithium in energy storage systems [12,13]. It becomes incentive and significant to explore and develop effective and novel sodium-ion batteries (SIBs) systems.

Recently, several potassium containing compounds have been investigated in SIBs. Liu et al. found that the potassium ion intercalated manganese oxide ($K_{0.27}MnO_2$) with large ion diffusion channels showed superior cycling stability and rate capability for sodium storage [14]. Xu et al. reported that $K_{0.23}V_2O_5$ with multi-layered structure presented high capability and fine cycling stability [15]. Besides, a novel potassium containing phosphate material found by Wang et al., $K_3V_2(PO_4)_3$, obtained remarkable electrochemical performance with ultrahigh cycling stability for sodium storage [9]. These inspiring works indicate that the potassium-containing compounds have much possibility in energy storage.

Herein, a novel cubic $KTi_2(PO_4)_3$ is designed and explored in energy storage as sodium-ion battery electrode for the first time. The cubic $KTi_2(PO_4)_3$ was synthesized by a facile hydrothermal method and coated by carbon using a normal cane sugar-assisted method. When evaluated as electrode material for SIBs, carbon-coated $KTi_2(PO_4)_3$ ($KTi_2(PO_4)_3/C$) delivered an excellent electrochemistry performance.

2. Experimental

2.1. Synthesis of materials

The cubic $KTi_2(PO_4)_3$ was prepared by a facile hydrothermal reaction combined with a subsequent annealing treatment. All chemicals were of analytical grade and are used as received without further purification. In a typical procedure, 0.5 g anatase TiO_2 (Aladdin Ltd, the average diameter of 25 nm), 0.5 g $KH_2PO_4 \cdot 2H_2O$ (Aladdin Ltd), 0.5 mL 85% H_3PO_4 (Aladdin Ltd) and 0.5 mL deionized water were thoroughly mixed and creamed well in a mortar. Then the mixture was transferred to a stainless steel cylinder with a Teflon liner and heated in an oven at 180 °C for 48 h. After natural cooling to room temperature, the obtained white precipitate was washed three times with deionized water and ethanol, respectively. Immediately, the precursor were dried at 60 °C overnight. Finally, the desired product was obtained after being calcined at 500 °C in Ar flow for 4 h. For preparation of $KTi_2(PO_4)_3/C$, a traditional process was chosen, cane sugar was added into the as-prepared $KTi_2(PO_4)_3$ with an amount of 8% C to the composite precursor. After grounded for 1 h, and ball-milled for 4 h, the mixture was treated at 450 °C in Ar flow for 4 h. Finally, the $KTi_2(PO_4)_3/C$ was obtained after cooling down to room temperature.

2.2. Materials characterization

The crystal structures of the materials were recorded with a Philips X-ray diffractometer (XRD) and Cu K-alpha radiation ($\lambda = 1.5406$ nm) with a scan rate of 2° min^{-1} over the 2θ range 10–70°. Morphology and microstructure of the as-prepared products were examined by scanning electron microscopy (SEM, JSM-6700F, Japan) and transmission electron microscopy (TEM, JEM-2100, Japan). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a spectrometer (Escalab 250xi, Thermo Scientific). The calcination process in air was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DTA) using a heating rate of $10^\circ \text{ C min}^{-1}$. Cyclic voltammetry (CV) was measured in a Zivelab electrochemical workstation. Galvanostatic charge/discharge tests were conducted using a LAND battery testing system.

2.3. Electrochemical measurements

The composite cathodes were prepared by mixing active material ($KTi_2(PO_4)_3$ and $KTi_2(PO_4)_3/C$), super-P carbon black (C), and polyvinylidene fluoride (PVdF) binder in the weight ratio of 70:20:10, with N-Methyl-2-pyrrolidone (NMP), to form slurry. The well-mixed, homogenous mixture was coated on an etched aluminum foil using a doctor blade and then dried at 120 °C under vacuum for 12 h to remove the solvent. After drying the electrodes were assembled in half-cell configuration in 2032 coin cells, using sodium metal pieces as the anode, separated by Celgard 2400 with sodium ion-conducting electrolyte. The electrolyte consisted of 1 M $NaClO_4$ in ethylene carbonate-dimethyl carbonate (EC-DEC, 1:1 (v/v)) (Sigma). The cells were constructed in an Ar-filled MBraun glove box and then cycled galvanostatically between 1.2 and 2.8 V (versus Na^+/Na) at a desired current density on a Land battery testing system at room temperature.

3. Results and discussion

The phase composition and crystallinity of the as-synthesized product is characterised by XRD. As shown in Fig. 1(a), the positions and relative intensities of all diffraction peaks can be perfectly indexed as rhombohedral structured $KTi_2(PO_4)_3$ (JCPDS No. 79-1880) with a space group of $R\bar{3}_c$ (no. 167), indicating its high purity. In the projections of the KTP structure (inset in Fig. 1), the basic unit of the $[Ti_2(PO_4)_3]$ framework is constructed by two TiO_6 octahedra and three PO_4 tetrahedra via corner sharing and potassium ions fully occupy the interstitial sites. The 3D framework of $KTi_2(PO_4)_3$ crystal not only provides the large interstitial spaces, but also offers open channels for ion transport.

Fig. 2 shows the SEM and TEM images of the cubic $KTi_2(PO_4)_3$ and $KTi_2(PO_4)_3/C$ composite at different magnifications. Fig. 2(a) is typical SEM image of novel cubic $KTi_2(PO_4)_3$ at relatively low magnification. The standard cubes in Fig. 2(b) presents uniform cubes with a diameter of 200–300 nm. In addition, the energy dispersive spectrometer (EDS) element distribution mapping images of the $KTi_2(PO_4)_3$ are shown in Fig. S1, indicating the homogeneous distribution of the four elements. $KTi_2(PO_4)_3/C$ at a low magnification is shown in Fig. 2(c), which presents that cubic $KTi_2(PO_4)_3$ is adequately coated by carbon. The TEM image of as-prepared $KTi_2(PO_4)_3/C$ in Fig. 2(d) shows the covered amorphous carbon on the cube with the thickness of ~ 10 nm, and the lattice fringes having an interlayer distance of 0.367 nm agree well with the lattice

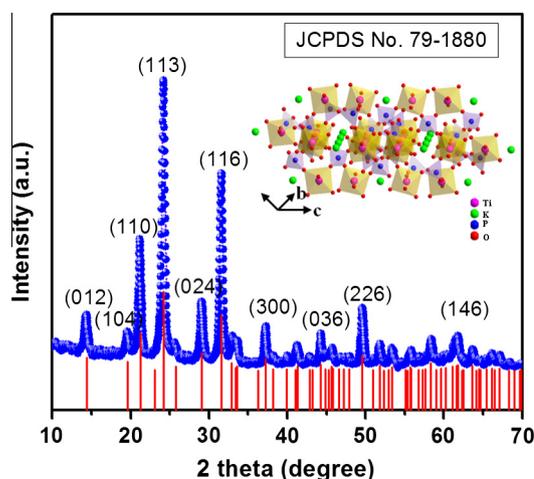


Fig. 1. XRD pattern of the $KTi_2(PO_4)_3$ material (inset shows the projections of the KTP structure).

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