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New hydrogen titanium phosphate sulfate electrodes for Li-ion and Na-ion batteries

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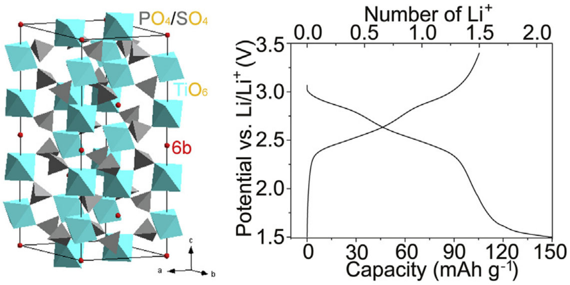
HIGHLIGHTS

- A new NASICON compound $H_{0.4}Ti_2(PO_4)_{2.4}(SO_4)_{0.6}$ (HTPS) is prepared.
- HTPS has nanocrystalline microstructure with meso- and micropores.
- Electrodes of as-prepared, ball-milled, and HTPS in carbon composites are studied.
- Lithiation and sodiation mechanisms are revealed using XRD and XPS.
- Capacities of 148 mAh g^{-1} for Li and 103 mAh g^{-1} for Na are obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

NASICON-type materials with general formula $A_xM_2(PO_4)_3$ (A = Li or Na, M = Ti, V, and Fe) are promising candidates for Li- and Na-ion batteries due to their open three-dimensional framework structure. Here we report the electrochemical properties of hydrogen titanium phosphate sulfate, $H_{0.4}Ti_2(PO_4)_{2.4}(SO_4)_{0.6}$ (HTPS), a new mixed polyanion material with NASICON structure. Micron-sized HTPS aggregates with crystallite grain size of ca. 23 nm are synthesized using a sol-gel synthesis in an acidic medium. The properties of the as-synthesized HTPS, ball-milled HTPS, and samples prepared as carbon composites using an *in-situ* glucose decomposition reaction are investigated. A capacity of 148 mAh g^{-1} corresponding to insertion of 2 Li^+ per formula unit is observed in the ball-milled HTPS over the potential window of 1.5–3.4 V vs. Li/Li^+. Lithiation at ca. 2.8 and 2.5 V is determined to occur through filling of the M1 and M2 sites, respectively. Powder X-ray diffraction (PXRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) are used characterize the HTPS before and after cycling. Evaluation of the HTPS in a Na-ion cell is also performed. A discharge capacity of 93 mAh g^{-1} with sodiation at ca. 2.9 and 2.2 V vs. Na/Na^+ is observed.

1. Introduction

Since Na^+ ion transport through the sodium superionic conductor $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$ (NASICON) was first observed [1,2], compounds with similar rhombohedral structures have been widely studied for applications in fuel cells, gas sensors, and

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batteries [3–5]. In particular, NASICON-type phosphates with general chemical formula $A_xM_2(PO_4)_3$ (A = Li or Na, M = Ti, V, and Fe) have been investigated as solid electrolytes [6–8], cathodes for Li-ion and Na-ion batteries [9–13] and anodes for aqueous based batteries [14,15]. These compounds contain a three-dimensional (3D) framework of PO_4 tetrahedra that are corner-shared with MO_6 octahedra. Substitutions are possible at various lattice sites and the open 3D crystal structure enables easy diffusion of alkali cations within the channels.

The physicochemical and electrochemical properties of NASICON-type compounds can be tuned through mixing of the tetrahedral oxoanions. For instance, previous reports have shown that the Li^+ conductivity in titanium phosphates could be improved by doping the materials with silicate [16,17], vanadate [18–20], and niobate [18–20] anions. The lithium/delithiation potential can furthermore be tuned using the induction effect, whereby the redox energies of the transition metal ions are affected by the electronegativity and bond strength with the oxoanions [21–23]. For example, insertion of Li^+ into rhombohedral forms of $Fe_2(SO_4)_3$ and $Li_3Fe_2(PO_4)_3$ showed that the position of the Fe^{3+}/Fe^{2+} redox couple was at 3.6 and 2.8 V vs. Li^+/Li, respectively; when phosphate was substituted with sulfate, the Fe^{3+}/Fe^{2+} redox couple for rhombohedral $LiFe_2(SO_4)_2(PO_4)$ was observed at 3.3–3.4 V vs. Li^+/Li [22].

Recently, new hydrogen titanium phosphate sulfate (HTPS) compounds were synthesized using a peroxide-based sol-gel method [24] with composition $H_{1-x}Ti_2(PO_4)_{3-x}(SO_4)_x$ ($x = 0.5–1$) and structure resembling that of $LiTi_2(PO_4)_3$ (LTP) (Fig. 1). In LTP (space group$R\bar{3}c$), two Li^+ ions may be intercalated through a two-phase reaction mechanism at 2.5 V vs. Li/Li^+ to form $Li_3Ti_2(PO_4)_3$ (space group$R\bar{3}$). There are two types of cavities in the NASICON-type structure, with the M1 site located between two TiO_6 octahedra along the *c*-axis, and the M2 cavities found surrounding the M1 sites [25] (Fig. 1B). The Li^+ ions in LTP reside solely within the M1 cavities, while in $Li_3Ti_2(PO_4)_3$ the M1 sites are empty and the Li^+ ions fully occupy the M2 sites [13]. The flat voltage plateau observed during lithiation of LTP is attributed to the filling of the M2 cavity through a mechanism that involves cooperative migration of Li^+ from the M1 to M2 sites [10].

In HTPS, the alkali-free NASICON-type phase is proposed to be stabilized through incorporation of sulfate ions (present from the $TiOSO_4$ precursor used in the synthesis) to create the mixed polyanion compound [24]. Unlike other reported NASICON-type compounds that contain only phosphate anions, in HTPS the 6*b* sites may be occupied by protons to maintain charge neutrality due to the presence of the two differently charged tetrahedral oxoanions. Both sulfate and phosphate anions are found in the 18*e* sites with P/S ~2.57 (Fig. 1A).

Here we report, for the first time, the electrochemical properties of HTPS with chemical formula $H_{0.39}Ti_2(PO_4)_{2.39}(SO_4)_{0.61}$, including a detailed study comparing the lithiation and sodiation reaction mechanisms with those found in other NASICON-type compounds. Four different types of HTPS samples, namely the as-prepared, ball-milled (BM-HTPS), heat treated (500-HTPS), and carbon composite (C-HTPS) materials, were studied and evaluated in Li-ion cells. We find that different from lithiation in LTP, the lithiation mechanism of HTPS is a two-step process, whereby the Li^+ first insert into the M1 sites at ca. 2.8 V vs. Li/Li^+ followed by insertion into the M2 sites at ca. 2.5 V. This makes HTPS more similar to Mn-NASICON compounds such as $Mn_{0.5}Ti_2(PO_4)_3$ than to LTP. The reaction of ambient H_2O with H^+ to form H_3O^+ within the HTPS structure can block Li^+ insertion, but the H_2O can be removed by heating the electrode prior to electrochemical testing. We find that HTPS also can be used as a sodium battery cathode in a similar two-step sodiation process at ca. 2.9 and 2.2 V vs. Na/Na^+, with a discharge capacity of about 90 mAh g^{-1} remaining after 50 cycles.

2. Experimental section

2.1. Synthesis of HTPS

2.1.1. HTPS

5.8 g $TiOSO_4 \cdot 0.18H_2SO_4 \cdot 3.11H_2O$ (Sigma-Aldrich) was dissolved in 11.3 g of deionized water into which 3.3 g of a 27 wt% H_2O_2 solution (Alfa Aesar) was subsequently added. The solution was stirred until it became homogeneous. To this solution, 3.6 g of 85 wt% H_3PO_4 solution (Alfa Aesar) was added and dissolved with stirring until the solution became homogeneous. This solution was left

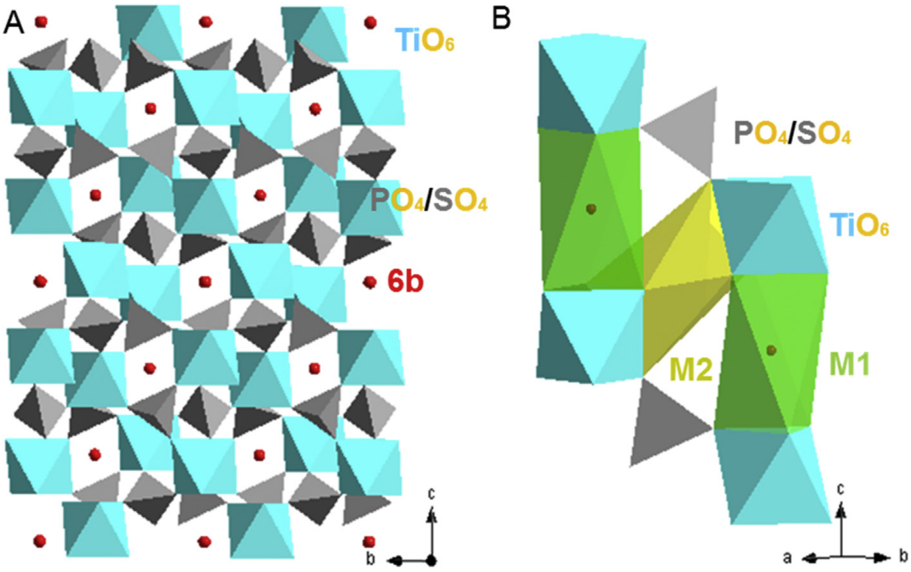

Fig. 1. HTPS crystal structure (A) HTPS structure viewed along the *a*-axis to illustrate the ion channels. (B) M1 and M2 sites in the HTPS structure. The PO_4/SO_4 tetrahedra are shown in grey, the TiO_6 octahedra are shown in blue, M1 sites are in green, M2 sites are in yellow, and the 6*b* sites are in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)