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Orthorhombic Lithium Titanium Phosphate as an Anode Material for Li-ion Rechargeable Battery

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ABSTRACT

Rhombohedral lithium titanium phosphate, $LiTi_2(PO_4)_3$, has been considered a suitable anode material for aqueous lithium-ion batteries. However, the electrochemical behaviors of pure lithium-rich polymorphs have not been described yet even Li-rich phase may show better electrochemical properties than conventional $LiTi_2(PO_4)_3$ at the expense of somewhat lowered capacity. We have synthesized orthorhombic $Li_{1.5}Ti_2(PO_4)_3$ (OLTP) and rhombohedral $LiTi_2(PO_4)_3$ (RLTP) via sol-gel reactions and studied their fundamental electrochemical properties using galvanostatic charge/discharge and cyclic voltammetry (CV). Their feasibility as anode materials in $LiFePO_4//Li_xTi_2(PO_4)_3$ configurations using aqueous electrolytes were also considered. The faster kinetics of the orthorhombic lithium titanium phosphate in this study were attributed to higher Li^+ diffusivity and electrical conductivity, making this material an attractive alternative for conventional rhombohedral $LiTi_2(PO_4)_3$.

1. Introduction

The wide voltage window and the reasonable ionic conductivity of the organic electrolytes presently adopted in the Li-ion secondary batteries allow high power output and energy density. However, the thermal instability and comparatively high production costs of these organic electrolytes have become a major hindrance to the significant scale-up of Li-ion batteries. Aqueous electrolytes could considerably reduce the production cost of the lithium-ion batteries and completely eliminate the fire hazard at the expense of reduced energy density.

On the other hand, the restricted voltage window of the aqueous electrolytes allows only non-conventional sets of anode and cathode electrode materials to meet the proper working voltage of ~1.2 V in the full-cell configuration [1]. This requirement is met by using a non-carbonaceous host such as rhombohedral $LiTi_2(PO_4)_3$ (RLTP) as an anode material with a redox potential of 2.5 V for the Ti^{4+}/Ti^{3+} couple against Li. A number of studies on aqueous rechargeable Li-ion batteries using RLTP as an anode have been published along with the development of RLTP. For example, an $LiMn_2O_4//LiTi_2(PO_4)_3$ cell with 1 M Li_2SO_4 as an aqueous electrolyte showed an initial capacity of 40 mAh g^{-1}, and $LiMn_{0.05}Ni_{0.05}Fe_{0.9}PO_4//LiTi_2(PO_4)_3$ with saturated Li_2SO_4 as an aqueous electrolyte showed an initial capacity of 87 mAh g^{-1} [2,3]. However, regardless of the nature of the cathode materials, the large initial irreversibility and the gradual capacity fade of RLTP have hindered its application as an anode for aqueous Li-ion batteries. Attempts to improve the electrochemical properties of RLTP by nano-sizing [4] and controlling the oxygen vacancy [5] have recently been reported. Meanwhile, the use of Li-rich lithium titanium phosphate phases instead of current RLTP has not been described yet. We consider that the use of Li-rich phases of $Li_{1+x}Ti_2(PO_4)_3$ could be expected to improve the cycle life at the expense of somewhat lowered capacity.

On the other hand, our preliminary attempts to synthesize Li-rich single-phases of $Li_{1+x}Ti_2(PO_4)_3$ ($0 \leq x \leq 2$) revealed that the well-known rhombohedral $LiTi_2(PO_4)_3$ could be easily formed as a product with other stable phases as impurities in the compositional space Li-Ti-P-O, such as $LiTiPO_5$, $Li_4Ti_5O_{12}$, and TiO_2, depending on the synthesis temperature and the stoichiometry of the starting materials, which showed a similar tendency with previous works done by N. V. Kosova et al. [6]. Therefore, our primary goal was to synthesize a single lithium-rich phase, which exists in a space group system different from that of RLTP (R-3c).

A systematic approach to stabilize isotypic mixed-valent structures was previously pioneered by M. Catti. In that work, it was suggested that mixed-valent superstructures of $Li_{1+x}In_xTi_{2-x}(PO_4)_3$ could exist when $x < 0.5$ or $x > 1.0$ [7], which

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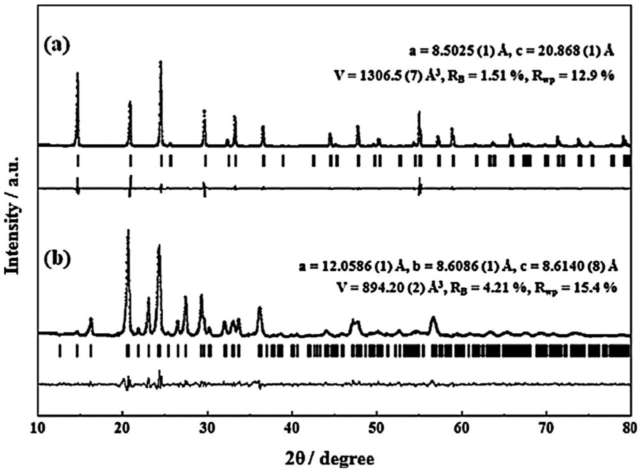

Fig. 1. Powder diffraction patterns of rhombohedral $LiTi_2(PO_4)_3$ (a) and orthorhombic $Li_{1.5}Ti_2(PO_4)_3$ (b).

is in good agreement with our preliminary data. Therefore, the smallest amount of lithium, x=0.5, was chosen to isolate the single phase of mixed-valent orthorhombic $Li_{1.5}Ti_2(PO_4)_3$.

In this preliminary study, we tried to clarify how electrochemical properties could vary in the seemingly similar compounds $LiTi_2(PO_4)_3$ and $Li_{1.5}Ti_2(PO_4)_3$. The electrochemical properties of these materials were evaluated versus Li metal to measure Li-ionic diffusivity of these structures. In addition, their feasibilities as anodes for aqueous lithium-ion cells were tested in $LiFePO_4//Li_xTi_2(PO_4)_3$ full-cell configurations using 1 M Li_2SO_4 electrolytes.

2. Experimental

RLTP and OLTP were synthesized via sol-gel synthesis. A stoichiometric combination of the starting materials, $LiOH{\cdot}H_2O$ (Sigma-Aldrich), $Ti[OCH(CH_3)_2]_4$ (Sigma-Aldrich), $NH_4H_2PO_4$ (Nacalai Tesque), and citric acid (10% by weight) was dissolved in 100 mL water and stirred at 80°C for 12 h. The mixture was preheated at 300 °C for 5 h, and then further sintered at 700 °C for 12 h under Ar flow. Commercial $LiFePO_4$ (Hohsen Corp.) was used as the cathode in full-cells.

X-ray diffraction patterns of the as-synthesized materials were obtained by an X-ray diffractometer (XRD, Rigaku; Cu-Kα, 50 kV, 300 mA) in 2θ range of 10–80° at a scan rate of 0.1°/min with a step size of 0.02° and refined by the Fullprof Suite refinement program. The atomic coordinates and atomic displacement parameters for OLTP were obtained from previously reported $Li_2Ti_2(PO_4)_3$ single crystal data [8] and used for further refinement. The background of the XRD profile was fitted with linear interpolation between a set of 55 points with refinable heights, and the peak shape was refined with the convolution of a pseudo-Voigt function.

The electrical conductivity of the samples was evaluated using a powder resistivity measuring system (Mitsubishi Chemical Analytech). The resistivity measuring system is equipped with a high precision pressure gauge directly attached to a Teflon-coated cylindrical holder (model MCP-PD522), allowing measurements under various pressures while accounting for the thickness, volume, and density of the sample under that pressure.

The working electrodes were prepared by ball-milling a mixture of 70 wt.% electrode active materials and 25 wt.% acetylene black. Then, 5 wt.% PTFE binder was added to the mixture, and approximately 5 mg of pellets were prepared manually using a mortar and pestle. The electrode pellets were vacuum-dried at 100 °C overnight and then assembled in 2032 coin cells with 1 M $LiPF_6$ in EC:DMC (1:1 in volume). To balance the full aqueous cells, a comparably low current rate of 15 mA g^{-1} was applied for $LiFePO_4$, RLTP, and OLTP versus Li metal to obtain the initial specific capacities. The cyclic voltammograms (CV) were measured in a range of scan rates to obtain the precise peak current, which was then treated by the Randles-Sevcik equation to estimate the Li^+ diffusion coefficient in both the OLTP and RLTP

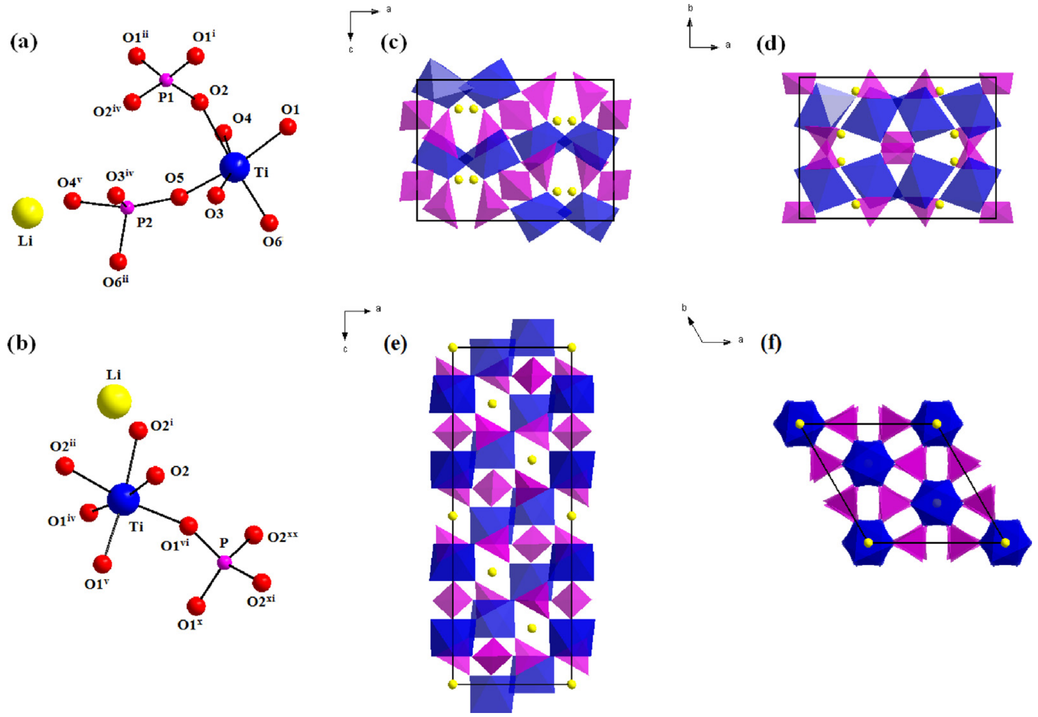

Fig. 2. Local coordination environments of the Ti and P atoms with the atom labeling scheme and the schematic views for orthorhombic $Li_{1.5}Ti_2(PO_4)_3$ (a, c, d) and rhombohedral $LiTi_2(PO_4)_3$ (b, e, f) along the b- and c-axes. Blue octahedra and purple tetrahedra represent TiO_6 and PO_4, respectively.