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Synthesis and electrochemical sodium and lithium insertion properties of sodium titanium oxide with the tunnel type structure

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HIGHLIGHTS

- Polycrystalline sample of $Na_2Ti_4O_9$ was synthesized by solid state reaction.
- The new anode material for the sodium-ion and lithium-ion batteries.
- The Na insertion-extraction revealed the reversible capacity of approximately 45 mAh g^{-1}.
- The Li insertion-extraction revealed the reversible capacity of approximately 104 mAh g^{-1}.

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ABSTRACT

Polycrystalline sample of sodium titanium oxide $Na_2Ti_4O_9$ with the tunnel-type structure was prepared by topotactic sodium extraction in air atmosphere from the as prepared $Na_3Ti_4O_9$ sample. The starting $Na_3Ti_4O_9$ compound was synthesized by solid state reaction at 1273 K in Ar atmosphere. The completeness of oxidation reaction from $Na_3Ti_4O_9$ to $Na_2Ti_4O_9$ was monitored by the change in color from dark blue to white, and was also confirmed by the Rietveld refinement using the powder X-ray diffraction data. The sodium deficient $Na_2Ti_4O_9$ maintained the original $Na_{2.08}Ti_4O_9$-type tunnel structure and had the monoclinic crystal system, space group $C2/m$, and the lattice parameters of $a = 23.1698(3)$ Å, $b = 2.9406(1)$ Å, $c = 10.6038(2)$ Å, $\beta = 102.422(3)^\circ$, and $V = 705.57(2)$ Å^3. The electrochemical measurements of thus obtained $Na_2Ti_4O_9$ sample showed the reversible sodium insertion and extraction reactions at 1.1 V, 1.5 V, and 1.8 V vs. Na/Na^+, and reversible lithium insertion and extraction reactions at around 1.4 V, 1.8 V, and 2.0 V vs. Li/Li^+. The reversible capacity for the lithium cell was achieved to be 104 mAh g^{-1} at the 100th cycle.

1. Introduction

Sodium titanium oxides in Na_2O–TiO_2 system shows interesting electrochemical sodium and/or lithium insertion properties. Especially, the stepped layered structure-type $Na_2Ti_3O_7$ is very attractive as one of the oxide negative electrode materials for sodium-ion batteries, since this material exhibits the reversible Na insertion and extraction reactions at 0.3–0.5 V (vs. Na/Na^+) with a reversible capacity approaching 200 mAh g^{-1} [1–3]. In addition, the reversible Na and Li insertion properties for $Na_2Ti_6O_{13}$ with the tunnel-type structure were recently reported [4–6].

In the Na–Ti^{3+}–Ti^{4+}–O system, various compounds have been reported in the literature; e.g., $Na_4Ti_5O_{12}$ [7,8], $Na_{2.08}Ti_4O_9$ [9,10], $NaTi_2O_4$ [11–13], $Na_xTi_2O_4$ ($0.50 < x < 0.57$) [14], $Na_{1.7}Ti_6O_{11}$ [15], and $NaTi_8O_{13}$ [16]. However, most of them were only demonstrated on the synthesis and crystal structure, and the chemical and electrochemical properties for these compounds have not been clarified yet. Very recently, the sodium insertion properties of two kinds of $Na_4Ti_5O_{12}$ were reported [17,18].

In the present study, we focused on the tunnel-type crystal structure of $Na_{2.08}Ti_4O_9$. Previously, small single crystal specimens of $Na_{2.08}Ti_4O_9$ were synthesized by a reaction of Na_2O and Ti_2O_3 at 1273 K [9], and the crystal structure was determined by single-crystal X-ray diffraction technique [9,10]. The framework structure was constructed from single, double, and triple rutile-type chains of edge-sharing TiO_6 octahedra along the *c*-axis direction, and produces a large tunnel space where three types of sodium atoms located. These sodium sites were partly occupied by sodium atoms in the case of $Na_{2.08}Ti_4O_9$ [9]. However, if these sites are fully

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occupied by sodium atoms, the postulated chemical formula $Na_3Ti_4O_9$, which can be also represented as $Na_3Ti^{3+}Ti_3^{4+}O_9$, would be achieved, although the $Na_3Ti_4O_9$ sample has not been synthesized yet, to our knowledge.

In the present study, we synthesized the polycrystalline samples of $Na_3Ti_4O_9$ by solid state reaction at 1273 K in Ar atmosphere, and characterized the sodium deficient $Na_2Ti_4O_9$ sample by powder X-ray diffraction. Furthermore, the electrochemical sodium and lithium insertion properties of $Na_2Ti_4O_9$ were clarified for the first time.

2. Experimental procedure

In the present study, the sample preparation was performed by three synthetic steps. The starting $Na_4Ti_5O_{12}$ precursor was first prepared by firing Na_2CO_3 (99.9%, Kojundo Chemical Lab. Co., Ltd.) and TiO_2 (99.9%, Kojundo Chemical Lab. Co., Ltd.) in the correct proportion at 923 K for 60 h in air. Next, $Na_3Ti_4O_9$ was synthesized by solid–state reaction as a following reaction: $3\ Na_4Ti_5O_{12} + Ti \rightarrow 4\ Na_3Ti_4O_9$. A mixture of the $Na_4Ti_5O_{12}$ precursor and Ti metal powder (99.9%, Kojundo Chemical Lab. Co., Ltd.) in a molar ratio of 3: 1 was pressed into a pellet, placed in an iron crucible, and heated in a resistance furnace at 1273 K in an argon gas flow for 25 h.

Finally, the sodium deficient $Na_2Ti_4O_9$ sample was prepared from as-prepared $Na_3Ti_4O_9$ using topotactic oxidation method at room temperature, because the as-prepared $Na_3Ti_4O_9$ sample was unstable in air atmosphere. The resultant sample was washed by distilled water for 30 min at room temperature so as to extract the precipitated sodium hydroxide or sodium carbonate, and was dried for a day at 353 K in air. The completeness of oxidation reaction was monitored by changing in the color from dark blue to white, and examined by the following chemical and structural analyses.

Chemical compositions of the products were analyzed by SEM–EDX (JEOL JSM-5400) at an acceleration voltage of 20 kV using powder specimens. The particle morphology was observed using SEM (JEOL JCM-6000) at an acceleration voltage of 15 kV.

The phase purity and crystal structure of the obtained samples were characterized by powder X-ray diffraction (XRD) profiles measured at room temperature with Cu $K\alpha_1$ radiation using a Rigaku SmartLab diffractometer (operating conditions: 40 kV, 30 mA) equipped with a curved crystal of a Johansson type monochromator. The XRD intensity data were collected for 1 s at each 0.01° step over a 2θ range from 5.005° to 149.995° for the Rietveld refinement. In the case of $Na_3Ti_4O_9$, the sample was handled in Ar-filled grove box, and non-air exposure holder was used for XRD measurement. The Rietveld refinement for $Na_2Ti_4O_9$ was performed using the computer program Jana2006 [19].

Electrochemical sodium and lithium insertion-extraction experiments for $Na_2Ti_4O_9$ were performed using coin-type cells. The working electrode was prepared by mixing 62% active material, 31% acetylene black, and 7% polytetrafluoroethylene (PTFE) powder in weight, and by pressing the mixture on to a Ti mesh having a diameter of 15 mm under a pressure of 20 MPa. The counter electrode was a Li foil having a diameter of 20 mm for the Li cell, and a Na metal on Ti mesh having a diameter of 20 mm for the Na cell. The separator was a microporous polypropylene sheet. A solution of 1 M $LiPF_6$ in a 50:50 mixture of ethylene carbonate (EC) and diethylcarbonate (DEC) by volume (Kishida Chemical Co., Ltd.) was used as the electrolyte for the Li cell. On the other hand, for the Na cell, a solution of 1 M sodium perchlorate in propylene carbonate (PC) (Kishida Chemical Co., Ltd.) was used as the electrolyte. Cells were constructed in an argon-filled glove box. Electrochemical lithium insertion (charge) and extraction (discharge) experiments were performed between 1.0 and 3.0 V at 25 °C by the reference voltage range that is frequently reported in the electrochemical measurement of $Li_4Ti_5O_{12}$ after standing 6 h under an open circuit condition. The cell was first charged to 1.0 V at a constant current density of per unit of mass of the active material, 12 mA g^{-1}, then kept at 1.0 V for 2 h, so-called CC–CV charging mode, and then discharged to 3.0 V at the same current density, so-called CC discharging mode. Electrochemical sodium insertion and extraction experiment was performed between 0.1 and 2.5 V at 25 °C by reference to Ref. [1] after standing 6 h under an open circuit condition using a similar charge–discharge mode to the Li cell.

3. Results and discussion

3.1. Synthesis and chemical characterization

The powder X-ray diffraction data of sodium deficient $Na_2Ti_4O_9$ sample was identified to be a single phase of the $Na_{2.08}Ti_4O_9$ type structure [9,10], monoclinic crystal system, and space group $C2/m$. As mentioned above, the sodium deficient $Na_2Ti_4O_9$ sample was easily prepared from as-prepared $Na_3Ti_4O_9$ sample at room temperature, because the as-prepared $Na_3Ti_4O_9$ sample was unstable in air atmosphere. The resultant sample was washed by distilled water 30 min at room temperature so as to extract the precipitated sodium hydroxide or sodium carbonate, and was dried for a day at 353 K in air. The completeness of oxidation reaction was confirmed by the EDX analysis. The atomic ratio was determined to be Na/Ti = 1.0/2 for the $Na_2Ti_4O_9$ sample. Fig. 1 shows a typical SEM image of the polycrystalline sample of sodium-deficient $Na_2Ti_4O_9$. The particle morphology was needle-like and the length was estimated to be about 10–50 μm.

Fig. 2 presents observed, calculated and difference patterns for Rietveld refinement from the XRD data. An initial structure model used in the calculations was atomic coordinates of $Na_{2.08}Ti_4O_9$ [10]. The resultant R-values reached $R_{wp} = 20.75\%$ and $R_p = 13.87\%$ for $Na_2Ti_4O_9$. Good agreement between the observed and calculated XRD patterns has been clearly visible in Fig. 2. The lattice parameters for the $Na_2Ti_4O_9$ sample were refined to be $a = 23.1698(3)$ Å, $b = 2.9406(1)$ Å, $c = 10.6038(2)$ Å, $\beta = 102.422(3)$ °, and $V = 705.57(2)$ Å^3. These values were in good agreement with those for the previous single-crystal data of $Na_{2.08}Ti_4O_9$ [9]. The atomic coordinates thus refined by the present Rietveld analysis (Table 1) were basically identical to those in the previous report [10].

The crystal structure of $Na_2Ti_4O_9$ are shown in Fig. 3. The basic framework structure in $Na_2Ti_4O_9$ is maintained nearly unchanged from those in the previous report for $Na_{2.08}Ti_4O_9$. All of the TiO_6 octahedra were strongly distorted, and the Ti–O distances were in

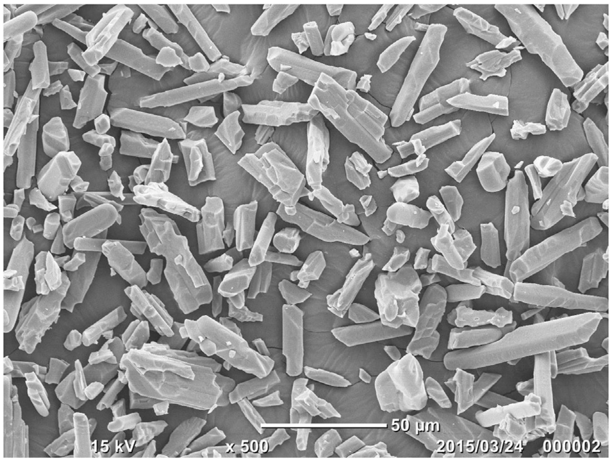

Fig. 1. SEM photograph of the polycrystalline $Na_2Ti_4O_9$ sample.