



Electrochemical reactions of layered niobate material as novel anode for sodium ion batteries



Hideki Nakayama^{*}, Masafumi Nose, Shinji Nakanishi, Hideki Iba

Toyota Motor Corporation, Battery Research Division, 1200 Mishuku, Susono, Shizuoka 410-1193, Japan

HIGHLIGHTS

- The layered niobate of KNb_3O_8 was first introduced as an anode for the sodium-ion battery.
- KNb_3O_8 reversibly reacts with Na^+ at the potential around 1 V vs. Na/Na^+ via the $\text{Nb}^{5+/4+}$ redox reaction.
- The reversible capacity of KNb_3O_8 reached 104 mAh/g corresponding to 1.7 Na^+ .
- The KNb_3O_8 has an excellent cycling stability and rate capability.

ARTICLE INFO

Article history:
Received 30 January 2015
Received in revised form
23 March 2015
Accepted 9 April 2015
Available online

Keywords:
Sodium-ion battery
Anode material
Layered niobate
 KNb_3O_8

ABSTRACT

The electrochemical performances of layered niobium oxide materials were investigated for the first time as novel anode active materials for the sodium-ion battery. The layered niobate with the formula KNb_3O_8 was synthesized by a solid-state reaction and has been evaluated as an anode electrode by a cyclic voltammetry technique and galvanostatic charge/discharge tests. The crystal structure of KNb_3O_8 contains the NbO_6 octahedral units and potassium alkali-metal ions interlayer to form the layered structure. KNb_3O_8 has a redox reaction around 1 V vs. Na/Na^+ and has a reversible capacity of 104 mAh/g corresponding to the 1.7 Na^+ insertion/extraction in the KNb_3O_8 structure. The Nb K-edge X-ray absorption near edge structure (XANES) shows that the Nb oxidation state is converted from Nb^{5+} to Nb^{4+} during the Na^+ insertion stage, and reversibly recovered to Nb^{5+} during the Na^+ extraction stage. This is the first report that the layered niobate of KNb_3O_8 reversibly reacts with Na^+ at the potential around 1 V vs. Na/Na^+ via the $\text{Nb}^{5+/4+}$ redox reaction.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Rechargeable Li-ion batteries have been widely used in large scale electric storage devices such as hybrid vehicles (HVs), plug-in hybrid vehicles (PHVs) and electric vehicles (EVs), because of their advantages of high energy density, high power, light weight, long cycle stability, etc. In order to improve the energy and power densities of rechargeable batteries, much effort has been currently devoted to new types of batteries such as other alkali-ion batteries [1–5], all solid-state batteries [6,7] and lithium-air batteries [8,9], etc. One of these, an interesting alternative to the lithium technology is the sodium-ion battery. In fact, many kinds of cathode materials for the sodium-ion batteries have recently been developed [10–18]. However, quite a few anode materials for the

sodium-ion batteries have been reported so far. One of the candidate anode materials is hard carbon [19] which shows the large reversible capacity and good cycle performance. However, the Na^+ insertion potential is very close to the potential of Na/Na^+ . The low Na^+ insertion potential indicates the problems of sodium metal deposition and sodium dendrite formation which can cause safety concerns for practical applications. Recently, several groups have reported titanium-based oxide compounds, such as $\text{Na}_2\text{Ti}_3\text{O}_7$ [20], $\text{Na}_2\text{Ti}_6\text{O}_{13}$ [21], $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [22], $\text{NaTi}_3\text{O}_6(\text{OH}) \cdot 2\text{H}_2\text{O}$ [23] and anatase- TiO_2 [24] as anode materials for the sodium-ion batteries. These titanium-based oxide materials react with Na^+ at an elevated potential compared to the reaction potential of hard carbon. Among these titanium-based materials, there are very few anode materials which are compatible with the reversible capacity, appropriate reaction potential, cycle life and rate performance. In order to develop the anode active materials, the niobates should be considered as well as the titanates because the redox of $\text{Nb}^{5+}/\text{Nb}^{4+}$

^{*} Corresponding author.

E-mail address: hideki_nakayama@mail.toyota.co.jp (H. Nakayama).

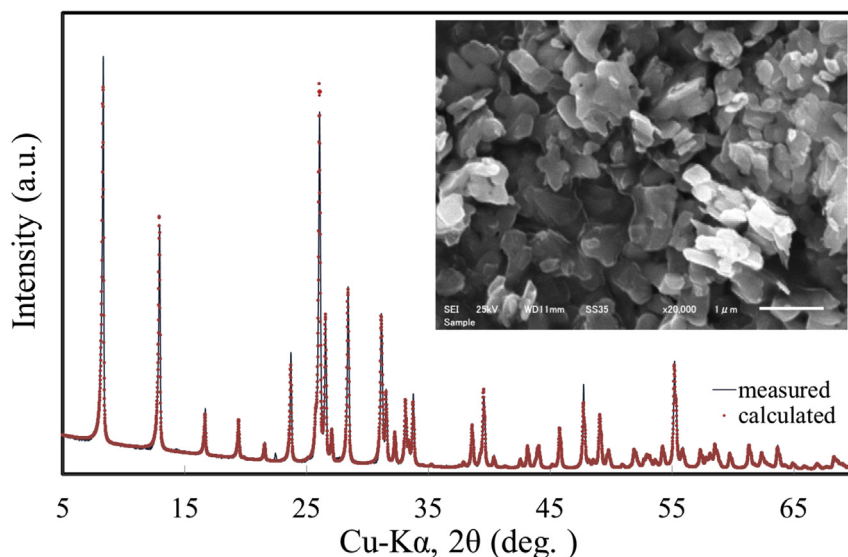


Fig. 1. Experimental XRD pattern and SEM image of synthesized KNb_3O_8 powder.

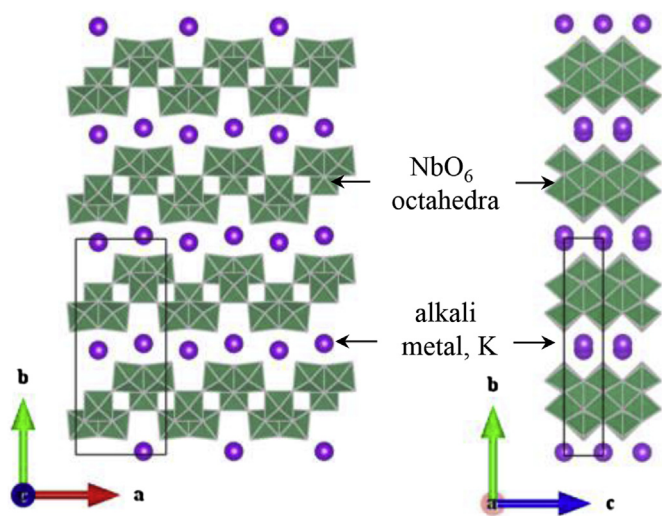


Fig. 2. Crystal structure of KNb_3O_8 with orthorhombic structure in the $A_{m\bar{m}m}$ space group.

has the possibility to realize the reversible reaction with sodium at an elevated potential as anode. However, the anode active materials containing the niobium transition-metal for the sodium-ion batteries have not yet been reported.

We now introduce, for the first time, a novel anode material of layered niobate KNb_3O_8 for use in the sodium-ion batteries. The crystal structure of KNb_3O_8 contains the NbO_6 octahedral unit and alkali-metal (potassium) interlayer to form the layered structure [25]. We have succeeded in discovering, for the first time, that KNb_3O_8 reversibly operated at a reaction potential around 1 V vs. Na/Na^+ as the anode active material in the sodium-ion batteries. The reversibility of the Nb redox and crystal structure change during the Na^+ insertion/extraction process were estimated by the Nb K-edge X-ray absorption near edge structure (XANES) and in-situ XRD analyze, respectively.

2. Experimental sections

The layered niobate of KNb_3O_8 was synthesized by a traditional

solid-state reaction from potassium carbonate (K_2CO_3 , Sigma Aldrich) and niobium pentoxide (Nb_2O_5 , Sigma Aldrich) and used directly without further purification. The starting materials were mixed in the molar ratio of $\text{K}_2\text{CO}_3 : \text{Nb}_2\text{O}_5 = 1 : 3$ and pressed into a pellet, then annealed at 800°C for 40hr in air to obtain the final KNb_3O_8 powder.

The crystal structure and particle morphology of KNb_3O_8 was investigated by X-ray diffraction using $\text{Cu-K}\alpha$ radiation (XRD, Rigaku UltimaIV, $\lambda = 1.5418 \text{ \AA}$) and scanning electron microscopy (SEM, JEOL JSM-6610LA), respectively.

For the electrochemical characterization, the working electrodes consisting of a mixture of KNb_3O_8 , conductive carbon and PVdF binder were coated on Cu foil. Pure sodium metal (Sigma Aldrich) was used as the counter electrodes and 1.0 mol/cm^3 NaPF_6 (Kishida Chem.) dissolved in ethylene carbonate (EC)/diethylene carbonate (DEC) (1:1 in volume, Kishida Chem.) was employed as the electrolyte. The electrodes of KNb_3O_8 were assembled into CR2032 coin cells to evaluate their electrochemical properties. The process of cell assembly was done in an Ar-filled glove box. Cyclic voltammetry and galvanostatic charge/discharge tests were carried out using a VMP potentiostat and battery tester, respectively. All the electrochemical tests were performed at 25°C .

For analysis of the Nb oxidation states, Nb K-edge X-ray absorption fine-structure spectroscopy (XAFS) measurements were performed at the beamline BL12C of the Photon Factory (Ibaragi, Japan). Incident X-ray energy was selected using a $\text{Si}(111)$ double-crystal monochromator and the XAFS data were measured in the transmission mode.

In order to investigate the crystal structure changes in KNb_3O_8 during the Na^+ insertion/extraction process, in-situ XRD studies were carried out by X-ray diffraction using $\text{Cu-K}\alpha$ radiation (XRD, Rigaku SmartLab, $\lambda = 1.5418 \text{ \AA}$, $\phi 100 \mu\text{m}$) and a battery tester. In order for the X-rays to penetrate through the cell during the charge/discharge process, the CR2032 cell with a $\phi 2 \text{ mm}$ pin-hole was prepared for the in-situ XRD analysis.

3. Results and discussion

The XRD pattern and SEM image of the synthesized powder are shown in Fig. 1. The diffraction peaks were successfully indexed as KNb_3O_8 , the purity of synthesized raw material was 98.6% and 1.4%

Download English Version:

<https://daneshyari.com/en/article/7732505>

Download Persian Version:

<https://daneshyari.com/article/7732505>

[Daneshyari.com](https://daneshyari.com)