Journal of Power Sources 324 (2016) 378–387

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Towards environmentally friendly Na-ion batteries: Moisture and water stability of $Na_2Ti_3O_7$

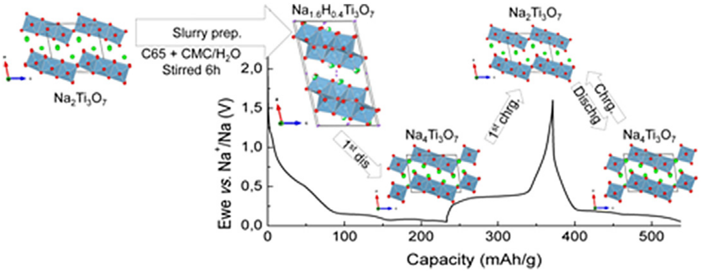
M. Zarrabeitia [a], E. Castillo-Martínez [a], J.M. López Del Amo [a], A. Eguía-Barrio [b], M.A. Muñoz-Márquez [a], T. Rojo [a, b], M. Casas-Cabanas [a, *]

[a] CIC Energigune, C/Albert Einstein 48, 01510, Parque Tecnológico de Álava, Miñano, Spain
[b] Departamento de Química Inorgánica, Universidad del País Vasco, UPV/EHU, P.O. Box 664, 48080, Leioa, Spain

HIGHLIGHTS

- Transformation of $Na_2Ti_3O_7$ into $Na_{2-x}H_xTi_3O_7$ ($2 < x < 0$) in contact with air or H_2O.
- First structural resolution of $Na_{2-x}H_xTi_3O_7$ ($x = 1.4$, $x = 0.7$) by neutron diffraction.
- $Na_{2-x}H_xTi_3O_7$ ($2 < x \leq 0$) transforms into $Na_2Ti_3O_7$ after the first cycle in a Na half-cell.
- CMC binder improves the electrochemical performance of $Na_2Ti_3O_7$.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 January 2016
Received in revised form
18 May 2016
Accepted 23 May 2016

Keywords:
Na-ion battery
$Na_2Ti_3O_7$
Aqueous electrode processing
Ion exchange
Carboxymethyl cellulose

ABSTRACT

We report here on the moisture and water stability of the promising Na-ion anode material $Na_2Ti_3O_7$. Spontaneous Na^+/H^+ exchange is detected by PXRD after air exposure, forming solid solution compounds of the form $Na_{2-x}H_xTi_3O_7$ ($0 < x < 2$). By controlled ion exchange in aqueous solution two mixed compositions are prepared and their composition and structure are characterized with a panel of techniques. Both mixed compositions crystallize in $C2/m$ space group like $H_2Ti_3O_7$, and therefore Na^+/H^+ exchange is found to involve a structural transition from AA stacking of $[TiO_6]$ layers to AB stacking sequence. The electrochemical behaviour of the mixed compositions *vs.* Na^+/Na is studied as well as that of an electrode of pure $Na_2Ti_3O_7$ prepared in water media. The water-processed electrode is shown to exhibit a superior cycling stability and therefore the results obtained highlight the potential of $Na_2Ti_3O_7$ as a green, low cost anode material for NIBs.

1. Introduction

Na-ion batteries (NIBs) are being investigated as a potential solution to store the excess energy produced by renewable sources because of their comparable energy density and lower cost with respect to Li-ion batteries (LIBs) [1]. Moreover, Na is one of the most abundant elements, easier to extract, and evenly distributed [2]. NIBs are thus potentially green devices with a low ecological footprint provided that environmentally friendly constituents and processing techniques are used. One of the most significant challenges in the NIBs field is to find suitable and safe anode materials able to deliver a stable capacity without the risks of operating at low voltages [3]. Indeed, graphite, which is the most common Li-ion anode material, is able to insert a very limited amount of Na^+ [4], and hard carbons [5,6] or phosphorous/carbon composites [7]

---

[*] Corresponding author.
E-mail address: mcasas@cicenergigune.com (M. Casas-Cabanas).

http://dx.doi.org/10.1016/j.jpowsour.2016.05.103
0378-7753/

which have been proposed as alternative, might represent a safety hazard. Conversely, titanium-based oxides represent a promising family of negative electrode materials because of their low cost, low toxicity and easiness of preparation [8]. There is a wide variety of reported titanate compounds with general formula $A_xTi_nO_{2n+1}$ or $A_xTi_nO_{2n+2}$ that crystallize in layered or tunnel structures which can reversibly insert Na^+. These include $H_2Ti_3O_7$ [9], $Na_2Ti_6O_{13}$ [10], monoclinic $Na_4Ti_5O_{12}$ [11], $Na_2Ti_7O_{15}$ nanotubes [12], $Na_4Ti_9O_{20}\cdot nH_2O$, $NaTi_3O_6(OH)\cdot 2H_2O$ [8] and $Na_2Ti_3O_7$ [13]. The latter is the oxide electrode with the lowest voltage ever reported (at 0.3 V *vs.* Na^+/Na) [13]. Its structure consists of zigzag layers of edge-sharing $[TiO_6]$ octahedra (Fig. S1a), stacked along the *a* cell axis resulting in AA $[TiO_6]$ layer stacking sequence and $P2_1/m$ monoclinic space group [14]. Two types of Na^+ (Na1 and Na2) are located in the interlayer space at 2*e* Wyckoff sites [14] and two additional Na^+ can be inserted at additional 2*e* Wyckoff sites [15], leading to a specific capacity close to 178 mA h/g [13].

$Na_2Ti_3O_7$ and $H_2Ti_3O_7$ form a complete solid solution of the form $Na_{2-x}H_xTi_3O_7$ ($0 \leq x \leq 2$) [16–18]. The structure of $H_2Ti_3O_7$ is slightly different and is indexed with the monoclinic $C2/m$ space group. In this compound the layers are displaced by *b*/2 due to the formation of H bonds, which leads to a doubling of the unit cell and AB $[TiO_6]$ layer stacking sequence (Fig. S1b) [17]. Two types of H^+ at 4*i* Wyckoff positions were reported by Kataoka *et al.* from neutron diffraction data [19]. However, Eguía-Barrio *et al.* recently reported an extra type of H^+ at 2*a* Wyckoff position for $H_2Ti_3O_7$, and therefore three types of H^+ can be found in the structure which explains that the relative population of the two ^{1}H-NMR signals is 3:1 and not 1:1 [9]. Although the structure of $H_2Ti_3O_7$ is similar to that of $Na_2Ti_3O_7$, it can only reversibly insert one Na^+ at 1.3 V *vs.* Na^+/Na and H^+ are thought to be irreversibly extracted upon oxidation [9]. The structural characterization of the mixed $Na_{2-x}H_xTi_3O_7$ ($0 < x < 2$) compositions is still controversial because $Na_2Ti_3O_7$ and $H_2Ti_3O_7$ crystallize in a slightly different crystal structure. Izawa *et al.* used a primitive unit cell and the same space group as $Na_2Ti_3O_7$ ($P2_1/m$) to index a compound described as $Na_{1.43}H_{0.57}Ti_3O_7$ (Fig. S1a) [16]. On the other hand, Feist *et al.* described the structure of $Na_{0.8}H_{1.2}Ti_3O_7$ with the same layer stacking as $H_2Ti_3O_7$, and therefore a $C2/m$ unit cell [17]. They proposed H bond formation as the reason for this (Fig. S1b). Mori *et al.* investigated the structure of the whole $Na_{2-x}H_xTi_3O_7$ ($0 \leq x \leq 2$) series by first-principle calculations [18], concluding that compositions between $0 \leq x \leq 0.75$ would present an AA stacking like $Na_2Ti_3O_7$, while the phases in the range $1 \leq x \leq 2$ would crystallize in AB stacking sequence as $H_2Ti_3O_7$. However, the theoretical results of Mori *et al.* have not been experimentally validated and the exact positions of Na^+ and H^+ in $Na_{2-x}H_xTi_3O_7$ are not known yet.

In this work, motivated by the technological interest of $Na_2Ti_3O_7$ as anode for NIBs, we revisit this system and put the focus on the moisture and water stability of this compound. Both aspects are extremely relevant since they determine the storage and electrode preparation conditions, which are going to have an impact in both the environmental footprint and final cost of NIBs. Indeed, the use of aqueous solutions instead of organic solvents to prepare slurries of electroactive materials is preferred for environmental and handling reasons. Additionally, low cost environmental friendly binders like carboxymethyl cellulose (CMC) which is soluble in water could replace polyvinylidene fluoride (PVdF), shown to form a non-stable SEI layer in $Na_2Ti_3O_7$ [20].

2. Experimental

2.1. Synthesis of $Na_{2-x}H_xTi_3O_7$ ($0 \leq x \leq 2$)

$Na_2Ti_3O_7$ (NTO7), was synthesized by mixing anatase TiO_2 (Alfa Aesar) with a 5% excess of $Na_2CO_3\cdot H_2O$ (Sigma Aldrich) and annealing at 800 °C for 24 h [21]. To monitor the evolution of ion exchange in $Na_2Ti_3O_7$ when exposed to moisture, a powder sample of NTO7 was stored in a desiccator at room temperature with a beaker full of water to accelerate the process in a saturated moisture environment and PXRD patterns were collected every week for a total of eight weeks. Additionally two $Na_{2-x}H_xTi_3O_7$ ($0 < x < 2$) samples were prepared by ionic exchange. The first was prepared by soaking $Na_2Ti_3O_7$ in distilled water and refluxing at 60 °C for 1 day (NHTO7-H_2O), while for the second $Na_2Ti_3O_7$ was soaked in a 0.1 M HCl (Panreac) solution at room temperature (RT) for 1 h (NHTO7-HCl). $H_2Ti_3O_7$ (HTO7) was also prepared by ion exchange by soaking $Na_2Ti_3O_7$ in excess HCl 0.1 M and refluxing at 60 °C for 3 days. After the ion exchange reaction the samples were filtered and washed with distilled water and dried under vacuum overnight at 60 °C.

2.2. Material characterization

Powder X-ray diffraction data (PXRD) were recorded on a Bruker Advance D8 instrument with copper radiation (λ (Cu K$\alpha_{1,2}$) = 1.5418 Å). A FEI Tecnai G2 transmission electron microscopy (TEM) was used to gather electron diffraction (ED) data of the prepared samples, previously dispersed in acetone and placed onto a holey-carbon film. Fourier transform infrared spectroscopy (FTIR) data were collected in a FTIR Spectrum 400 DTGS (Perkin Elmer) after diluting the sample in KBr.

Magic angle spinning nuclear magnetic resonance (MAS-NMR) spectra were recorded with a WB Bruker Advance III 500 spectrometer working at a frequency $\nu_o = 132.29$ MHz for ^{23}Na. The experiments were performed on powdered samples spun at the magic angle with a 2.5 mm standard probe. The MAS frequency was set to 20 kHz in all cases. ^{23}Na spectra were referenced to a 0.1 M NaCl solution resonating at 0 ppm. The one dimensional ^{23}Na-NMR spectra were recorded using a non-selective $\pi/2$ pulse with the duration adjusted to 1.3 μs and a recycling delay of 5 s. The ^{1}H-NMR spectra were recorded using rotor synchronized echo experiments with a $\pi/2$ pulse of 3 μs and the recycling delay was set to 100 s. The ^{23}Na multiple quantum magic angle spectra (MQMAS) were recorded using a 3 pulse basic sequence with z-filter [22]. The first two hard pulses were set to 4.6 and 1.4 μs respectively, and the final soft pulse to 19 μs.

Thermogravimetric analysis (STA 449 F3 system-Netzch) and inductively coupled plasma optical emission spectroscopy (ICP-OES Horiba-Ultima 2 Sequential) were used to quantify the amount of H^+ and Na^+ in the studied samples. Additionally, a more accurate and full analysis of the composition of the samples was performed by ion beam analysis (IBA) techniques at the Centro Nacional de Aceleradores (CNA) in Seville (Spain) where a 3 MV Tandem accelerator is available to deliver H^+ or He^{2+} high energy beams. For this analysis, two pellets of NHTO7-H_2O and NHTO7-HCl were prepared. The Na, Ti and O content was determined by means of Rutherford backscattering spectrometry (RBS); a beam of 1.5 MeV alpha particles was projected on the samples and the backscattered particles were collected with a Si solid state detector placed at a scattering angle of 165°. The intensity of backscattered particles was calibrated using a Pt standard (18×10^{15} at/cm^2) so the exact concentrations could be determined. Although RBS can provide very accurate concentration determination, it is not suited for the determination of H^+ concentration, in this case elastic recoil detection analysis (ERDA) was performed with 3.0 MeV He^{2+} particles at a scattering angle of 34°. With this forward scattering configuration the He^{2+} incident ions drag H^+ from the sample, an Al coated Mylar filter is placed between the sample and the detector in such a way that the scattered He^{2+} particles are stopped and only