



The electrochemical behavior of Cl^- assisted Al^{3+} insertion into titanium dioxide nanotube arrays in aqueous solution for aluminum ion batteries



Yingying Liu^{a,d}, Shangbin Sang^{a,*}, Qiumei Wu^{b,*}, Zhouguang Lu^c,
Kaiyu Liu^a, Hongtao Liu^a

^a College of Chemistry and Chemical Engineering, Central South University, 410083

^b Key State laboratory of powder metallurgy, Central South University, 410083

^c Department of Materials Science & Engineering, South University of Science and Technology of China, 518055

^d Innovation base of energy and chemical materials for graduate students training

ARTICLE INFO

Article history:

Received 3 June 2014

Received in revised form 28 July 2014

Accepted 3 August 2014

Available online 20 August 2014

Keywords:

Titanium dioxide nanotube array

Aluminum ion batteries

Chloride ion

ABSTRACT

The titanium dioxide nanotube array (TiO_2 -NTA) is prepared by a two-step anodic oxidation method and annealed at 450°C subsequently. The Al-inserted TiO_2 -NTA is prepared by polarizing the TiO_2 -NTAs electrode at 0.4 mA for 2 min in 1 mol/L AlCl_3 . The results show that the Al-inserted sample still remains pure anatase TiO_2 phase (by XRD) and keeps intact nanotube array structure (by FE-SEM). The X-ray photoelectron spectroscopy (XPS) analysis indicates that the insertion of Al^{3+} into TiO_2 -NTAs facilitates the reduction of Ti^{4+} to Ti^{3+} . Electrochemical investigation on the Al^{3+} insertion process reveals that presence of Cl^- ions plays vital role for the effective insertion and de-insertion of Al^{3+} into/from the TiO_2 -NTA.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

In recent years, the demand for secondary/rechargeable batteries with higher operating voltages, improved cycling stability, higher power densities, enhanced safety, and lower initial costs has increased to meet new needs for smaller, lighter, more powerful electronic devices [1].

Titanium dioxide nanotube array referred as TiO_2 -NTA hereinafter is one of the most extensively investigated compounds as the electrode material for high performance secondary/rechargeable batteries. The performance using as active materials for dye-sensitized solar cells, photocatalysis, photoelectrochemistry or electrochromic devices has significantly enhanced due to the several advantages such as a high surface area, short solid state diffusion paths of the TiO_2 -NTA [2,3]. Moreover TiO_2 -NTA is considered as excellent electrode candidate for constructing three-dimensional microbatteries that were promising power sources for miniaturized electronics due to large surface area and short

diffusion distance, which favors the electron and Li^+ transfer [4–7]. Nevertheless, the shortage of lithium resources will be further aggravated by the development of the electric vehicle industry with Li-ion batteries as power sources in the near future [8]. Compared with lithium, aluminum is relatively abundant and inexpensive metal in the earth's crust. An aluminium-based redox couple involves three electron transfers during the electrochemical charge/discharge reactions, which provides competitive storage capacity in comparison to the single-electron Li-ion battery. It has higher electrochemical equivalent, namely, 8.04 Ah/cm^3 (5.98 Ah/cm^3 higher than lithium). The obvious advantages of aluminum make it more attractive for future power source development [9].

Furthermore, recent studies showed that TiO_2 -NTA exhibited superior performance as cathode alternative for aluminum ion batteries since Al^{3+} ions can be reversibly inserted and extracted inside the TiO_2 -NTA probably due to the small radius of Al^{3+} (53.5 pm vs 76 pm of Li^+). Preliminary study showed that TiO_2 -NTA has a reversible capacity of about 75 mAh/g at 4 mA/cm^2 in AlCl_3 aqueous electrolyte solution [10]. The feasibility of a safer aluminum ion battery with aqueous electrolyte encourages us to make further investigation to improve the electrochemical performance. A further study of our group showed that it was difficult for Al^{3+} to insert into

* Corresponding authors.

E-mail addresses: shangbinsang@yahoo.com (S. Sang), wuqiumei20073@126.com, sangsb@126.com (Q. Wu).

TiO₂-NTA in Al₂(SO₄)₃ aqueous solution. The same phenomenon was also observed in an aprotic electrolyte system by N. Jayaprakash et al. [1], by using two different electrolytes of 1:1 v/v of Al triflate in PC/THF and 1.1:1 molar ratio of AlCl₃ in [EMIm]Cl at room temperature. No redox anodic and cathodic peaks was observed in the CV curves for the Al-ion battery using V₂O₅ nano-wire cathode and Al triflate in PC/THF as the electrolyte in the measured voltage range of -0.75–4.2 V, however, a pair of obvious reversible redox peaks were detected for the Al-ion battery with AlCl₃ in [EMIm]Cl electrolyte. It is anticipated that chloride ion (Cl⁻) plays a vital role in the insertion process of Al³⁺. The presence of Cl⁻ promotes the reversible and effective insertion and de-insertion of Al³⁺ into and from perhaps which would be an important theory basis in the research of aluminum storage behavior of transitional metal nanomaterials (such as anatase TiO₂ nanotube arrays and V₂O₅ nano-wire), which might be the fundamentals governing the improved electrochemical performance of in aqueous solution for aluminum ion batteries in the future [10]. In this paper, cyclic voltammetry (CV), electrochemical impedance spectra (EIS) and galvanostatic electrochemical charge-discharge method are performed to investigate the effect of Cl⁻ on Al³⁺ insertion/extraction process into the TiO₂-NTA in a series of aqueous solution. Virtually perfect hexagonally ordered arrays of TiO₂ were synthesized by a two-step anodic oxidation method followed by calcinations at 450 °C [11,12]. The effect on Al³⁺ insertion/extraction process into the TiO₂-NTA of Cl⁻ is discussed.

2. Experimental

2.1. Preparation of the TiO₂ nanotube arrays

All chemical agents used were purchased from Changsha Shenghua Chemical Agents Corporation limitd, China). Anatase TiO₂-NTA were prepared by a two-step anodic oxidation method. Prior to the anodization, the titanium foils (99.7% purity, thickness of 0.1mm, Baoji Queen Titanium Corporation limited, Shanxi Province, China) with dimensions of 1.5 × 2.5 cm² were polished with 800 mesh abrasive paper, then ultrasonically cleaned in distilled water, acetone (99.5% AR.), alcohol (99.7% AR.) and the mixture of 15 wt% hydrogen peroxide (30% AR.) and 0.06 mol/L sodium hydroxide (96.0% AR.) respectively for 15 min. Finally, a chemical polish was carried out in 4 wt% HF (40.0% AR.) for 10 min. This was the key step in our pre-experiments, which determined the surface status of the titanium foils, and all foils were dried in a N₂ stream. During anodization process, a two-electrode system (a Pt electrode as cathode electrode, titanium foils as anode electrode) was performed, and temperature-controlled water bath (DF-101S) was used to control temperature. A stirring apparatus was used to make sure that the reaction occurred in a uniform electrolyte. A regulated DC power supply (DAZHENG PS-6050) was used to ensure a uniform voltage. Anodization was carried out in ethylene glycol (99.7% AR.)/deionized water (24:1) electrolyte containing 0.3 wt% ammonium fluoride (99.6% AR.) at 60 V for 4 h to form a TiO₂ nanotube layer at ambient temperatures [13,14]. After the anodization, the oxide layer would be ultrasonically peeled off the titanium foils. Next, we used the remaining titanium foils as a new anode electrode. The following anodization operation was the same as before, however, the second anodization was performed for 1 h. Highly ordered TiO₂-NTAs were fabricated through this two-step anodizing electrochemical procedure. After two-step oxidation the samples were washed with distilled water and dried in an N₂ stream. Thermal annealing was performed with muffle (SK-5-12 K) at 450 °C for 2 h at a ramping rate of 1 °C/min to obtain an anatase structure.

2.2. Morphological characterization

For surface morphological characterization of the TiO₂-NTAs layers, top view and cross-sectional were analyzed by field-emission scanning electron microscopy (Nova NanoSEM 230). The crystal structure of sample was determined by X-ray diffraction (XRD, Phillips Xpert-MPD PW3040 diffractometer) using Cu K α radiation ($\lambda=1.5406 \text{ \AA}$). The chemical composition of the layers was characterized by X-ray photoelectron spectroscopy (XPS, K-Alpha 1063) using Al K α radiation of 1468.6 eV.

2.3. Electrochemical performance measurement

All electrochemical experiments were carried out by three-electrode system. The self-standing TiO₂-NTA film was used as the working electrode, silver-silver chloride electrode as the reference electrode, and a platinum foil with dimensions of 2 cm × 2 cm as the counter electrode. Cyclic voltammetry (CHI 660D) was performed with a series of electrolyte, namely, 0.50 mol/L Al₂(SO₄)₃ (99.0% AR.), 1.00 mol/L AlCl₃ (97.0% AR.) and two groups of mixed solution (0.25 mol/L Al₂(SO₄)₃ mixed with different concentrations of NaCl solution; 1.50 mol/L NaCl mixed with different concentrations of Al₂(SO₄)₃ solution). CVs at different scan rates were conducted in the mixed solution (0.25 mol/L Al₂(SO₄)₃ and 1.50 mol/L NaCl). Electrochemical impedance spectra (PARSTAT2273 Advanced Electrochemical System) were carried out in a frequency range from 0.1 Hz to 100 kHz. The apparent area of the TiO₂ working electrode for CV and EIS tests were about 0.25 cm² after coating epoxy resin on the edge and back of the metallic titanium foil. In the galvanostatic electrochemical charge-discharge test, the working electrode (TiO₂-NTAs) with total area of 1 cm² was charged for 1 min and discharged to -0.7 V (vs. Ag/AgCl) at a current density of 4 mA/cm² in the mixed solution 0.25 mol/L Al₂(SO₄)₃ and 1.5 mol/L NaCl. The Al-inserted sample used for XRD, SEM and XPS spectra analysis were prepared by polarizing the TiO₂-NTAs electrode at 0.4 mA for 2 min in 1 mol/L AlCl₃, followed by washing with deionized water and drying in vacuum at ambient temperature. All the electrochemical tests were performed at ambient temperature.

3. Results and discussion

3.1. Morphology and Crystal structure

Fig. 1a and Fig. 1b show the top-view and side-view FE-SEM image of the as-prepared TiO₂-NTAs, respectively. As we can see from the images, the nanotubes with smooth walls and uniform dimensions are formed on the Ti substrate. The average outside and inside diameters of the nanotubes are about 160 nm and 130 nm, respectively, and the obtained thickness is approximately 3 μm as shown in Fig. 1b. The highly ordered vertically oriented tube-like nanostructures with the short ion diffusion path through walls of nanotubes and large surfare area between active materials and electrolyte are in favor of the transfer of electron and Al³⁺. The top-view and side-view FE-SEM images of Al-inserted TiO₂-NTA are shown in Fig. 1c and Fig. 1d, as shown in the figure, the nanotube array structure remains relatively intact with Al³⁺ inserted into lattice, which adequately proves that the TiO₂-NTA film is potential electrode material in the aluminum-ion battery due to the special structure and stability.

X-ray diffraction analysis was conducted to investigate the crystal structure of the TiO₂-NTAs, and the results are shown in Fig. 2, a set of reflection centered at 2 θ degree of 25.3°, 37.8°, 48.0°, 53.9°, and 55.1° can be indexed to the (101), (004), (200), (105), and (211) peaks, respectively, of tetragonal anatase TiO₂ (JCPDS no. 84-1285), coexisting with the metallic Ti peak form the titanium foil substrate.

Download English Version:

<https://daneshyari.com/en/article/185171>

Download Persian Version:

<https://daneshyari.com/article/185171>

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