

Electrochemical Behavior of TiO₂ Nanotube/Ti Prepared by Anodizing for Micro-Lithium Ion Batteries

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Abstract : The TiO₂ nanotube/Ti electrode are used as an anode in thin-film lithium microbatteries is known to have high oxidation-reduction potential of 1.8 V (vs. Li/Li⁺). It can prevent from dendrite growth of lithium during charging. The TiO₂ nanotube/Ti electrode was prepared by anodizing at constant voltages for thin-film lithium microbatteries. The capacities of TiO₂ nanotube/Ti anode prepared by anodizing at 10 V, 20 V and 30 V were observed to be 23.9 μAh cm⁻², 43.1 μAh cm⁻² and 74.0 μAh cm⁻². We identified it was found that the capacity of TiO₂ nanotube/Ti increases with increasing anodizing voltage and the anatase structure of TiO₂ nanotube/Ti compared with amorphous structure has better cycle performance than amorphous TiO₂ nanotube/Ti.

Keywords : TiO₂, Nanotube, Micro-batteries, Anodizing

1. Introduction

Lithium ion batteries are an electrochemical power source that is capable to convert chemical energy to electrical energy. In an era of ubiquitous computing, there is brisk demand of lithium ion batteries on chip such as RFID (Radio-Frequency Identification) tag and smart card. The required properties on this lithium ion battery are very thin, low toxicity and good cycle ability, and we call this lithium ion battery thin-film micro-battery. The thin-film micro-batteries can apply to backup supply of computer memory chip, sensor and hazard card. First of all, the most important advantage is application to power supply of small electronic part. Recently, to improve original capacity of thin-film micro-battery which has a limited thickness, three dimensional structure of thin-film micro-battery is suggested. The three dimensional structure causes inter-resistance to decrease and enhances ion conductivity because it diminishes a distance of ion movement between cathode and anode throughout three dimen-

sional structures.¹⁻³⁾ Many researchers pay attention to thin-film for micro-batteries.²⁻⁷⁾ TiO₂ is a potential alternative for the graphite anode, because of its high voltage operation (ca. 1.75 V vs. Li⁺/Li redox couple). The TiO₂ does not have risk of overcharge that may lead to growth of metallic lithium dendrites. The TiO₂ nanotube with a large surface area can improve properties of TiO₂. A method of preparation for the TiO₂ nanotube by electrochemical techniques such as anodizing with low fabrication cost and simple fabrication method has been paying a lot of attention to many researchers.⁸⁻¹¹⁾

In this study, we solved the above problems by using anodizing. We compared with anodizing voltages and crystal structure conditions of TiO₂ nanotube/Ti electrodes. We studied electrochemical properties of TiO₂ nanotube/Ti electrodes from the results of cyclic voltammograms (CV) and galvanostatic cycling.

2. Experimental

Titanium plates (Ga Hee Metal Co. Ltd) were used as an active material for electrode. Ammonium fluoride (NH₄F, Junsei chemical Co., Ltd) and lithium acetate dihydrate (C₂H₃O₂Li₂H₂O, Sigma Aldrich Co., Ltd)

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were used as received. LiBF₄/PC (Cheil Industries Inc.) was used as solvent and organic electrolyte, respectively.

The TiO₂ nanotube/Ti electrodes were obtained by anodizing. The Ti as starting materials was commercially available with purity of 98% and thickness of 300 μm. The experiment of anodizing was carried out by applying constant voltages of 10 V, 20 V, 30 V to a conventional two electrodes during 60 min. The titanium was used as a working electrode and platinum plate was used a counter electrode. A distance of both electrodes were kept in 2 cm. and The solution of ethylene glycol containing 0.3 wt% NH₄F and 2 vol% H₂O was used as the electrolyte.^{9,10)}

Prior to the anodizing, the Ti electrodes were cleaned by sonication in acetone and ethanol during 30 min, and afterwards the Ti electrodes were rinsed with distilled water and dried at 60°C. Annealing treatment was performed at 300°C in air for 2 h.

The cells for electrochemical measurements were fabricated by using conventional three-electrode configuration. The Ti was used as a current collector. The TiO₂ nanotube/Ti electrodes were used as the working electrode (1 × 1 cm²). A lithium metals were used as both the counter and reference electrode. The 1.5 M LiBF₄ in PC was used as the electrolyte. Cyclic voltammetry (CV) was tested with 1.5 M LiBF₄ in PC electrolytes at potential window of 1 V to 3 V. Scan rate of the CV was 0.5 mV s⁻¹. Galvanostatic intermittent discharge-charge tests were conducted under constant current conditions by using automatic discharge and charge equipment (WBCS 3000, Won-A Tech. Co.). Cut-off voltages of the discharge processes were 1 V and 3 V (vs. Li/Li⁺), respectively. All the cells for electrochemical experiment were fabricated in a argon-filled glove box, and all tests were performed at room temperature.

3. Results and Discussion

SEM pictures of the TiO₂ nanotube/Ti electrodes are shown in Fig. 1(a)~(f). The pore sizes of prepared porous TiO₂ nanotube/Ti electrode is 10~20 nm, 20~30 nm and 30~40 nm at 10 V, 20 V and 30 V, in Fig. 1(a), (c) and (e) respectively. We identified it was found that the pore size of porous TiO₂/Ti electrode increases with increasing anodizing voltage of titanium electrode. Fig. 1(b), (d) and (f). show that the prepared TiO₂ nanotube/Ti electrodes are tube type with length of about

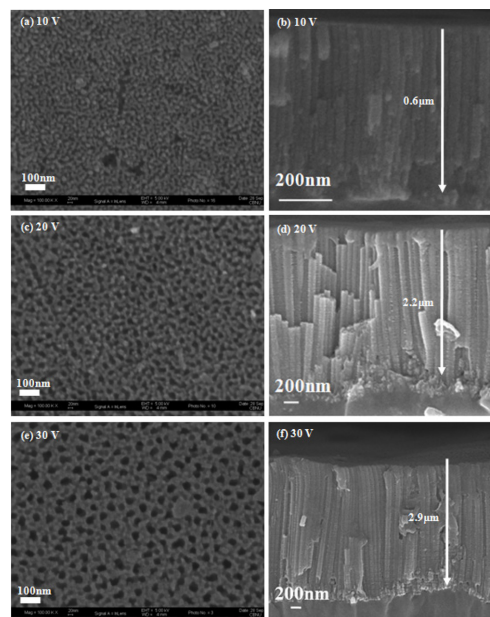


Fig. 1. Surface and cross sectional SEM images of TiO₂ nanotube/Ti electrode prepared at (a) and (b) of 10 V, (c) and (d) of 20 V, (e) and (f) of 30 V.

0.6, 2.1 and 2.8 μm at 10 V, 20 V, 30 V, respectively. These results imply that the pore sizes and tube lengths increase with increasing anodizing voltage.

Figure 2(a) shows XRD patterns of TiO₂ nanotube/Ti electrodes prepared at 10 V, 20 V and 30 V. For all porous TiO₂/Ti electrodes, all the peaks correspond with Titanium (JCPDS file No. 5-682). But the weak peaks turn up at about 76° and 82°; they correspond to (301) and (303) reflections of anatase TiO₂ structure (JCPDS file No. 21-1272).

A thermal treatment (300°C, 2 h, air) of the TiO₂ nanotube/Ti electrodes was prepared at 10, 20 and 30 V. In Fig. 2(b), new intense peaks turn up at about 23.4° it correspond to (101) reflections of anatase TiO₂ structure (JCPDS file No. 21-1272).

Figure 3(a) shows cyclic voltammograms which were performed with different anodizing voltages in the 1.5 M LiBF₄ at PC. For the all samples, intercalation/deintercalation of Li⁺ is observed at different anodizing voltages. Due to the open structure of the amorphous oxide, a distribution of diffusion paths for Li⁺ intercalation looks wide.^{11,12)}

This fact may be interpreted in terms of an extended distribution of intercalation rates provided in a disordered

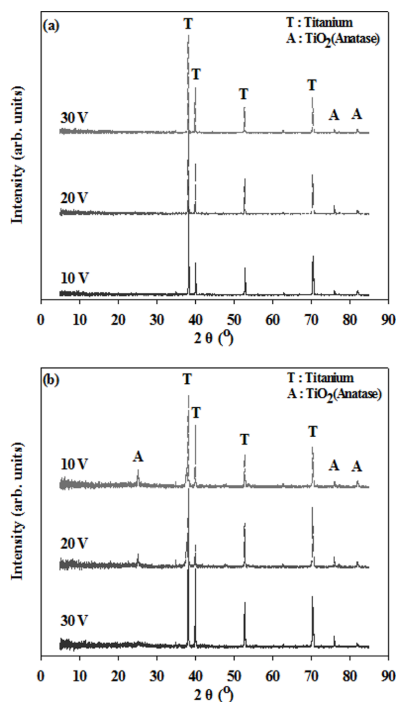


Fig. 2. X-ray diffraction patterns of porous TiO_2 nanotube/Ti electrode prepared at 10 V, 20 V, 30 V before (a) and after (b) annealing 300°C .

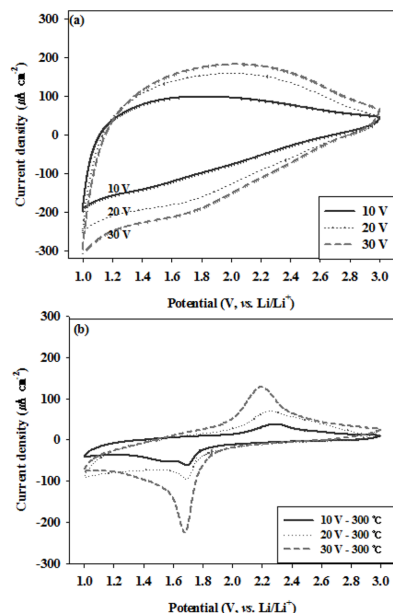


Fig. 3. Cyclic voltammograms of 10 V, 20 V and 30 V TiO_2 nanotube/Ti electrode before (a) and after (b) annealing 300°C , scan rate 0.5 mV s^{-1} at 3rd cycle in electrolyte, $1.5 \text{ M LiBF}_4/\text{PC}$.

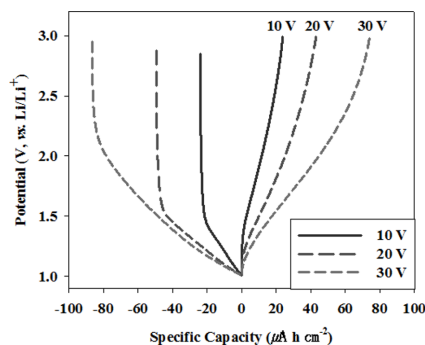


Fig. 4. Charge/discharge curves for prepared TiO_2 nanotube/Ti electrodes at 10 V, 20 V and 30 V, the potential range between 3 V and 1 V (vs. Li/Li^+) at current density, $10 \mu\text{A cm}^{-2}$ at 2nd cycle in electrolyte, $1.5 \text{ M LiBF}_4/\text{PC}$.

oxide structure. Fig. 3(b) shows cyclic voltammograms of TiO_2 nanotube/Ti electrodes after annealing 300°C . The reductive/oxidative peaks of TiO_2 nanotube/Ti electrodes (anatase structure) is well-defined at 1.7/2.2 V.^{13,14}

From literature, the anodic peak corresponds to the Li^+ release while the cathodic peak is generally ascribed to Ti^{4+} reduction combined with Li^+ intercalation.¹⁵ We observed that the TiO_2 nanotube/Ti electrodes prepared at 30 V have the highest anodic peak. This result clearly shows that the TiO_2 nanotube/Ti electrodes prepared at 30 V present a much better capacity of Li-loading than other anodizing voltages such as 10 V and 20 V in a storage device application. It's because the high anodizing voltage makes surface area of TiO_2 nanotube/Ti increase.

Figure 4 shows the charge/discharge curves of TiO_2 nanotube/Ti electrodes prepared at 10 V, 20 V and 30 V at the potential range of 1~3 V (vs. Li/Li^+). The discharge capacities of 10 V, 20 V and 30 V are 23.9, 43.1 and $74.0 \mu\text{A h cm}^{-2}$, respectively. The capacity of 30 V of TiO_2 nanotube/Ti electrodes is the best due to the surface area of it is the highest than others. The potential plateau of it is also invisible. It corresponds to result of cyclic voltammogram in Fig. 3(a).

After annealing at 300°C , we observed potential plateau at 1.7 V, 2.2 V during charging and discharging in Fig. 5. The TiO_2 nanotube/Ti electrode prepared at 30 V also has the highest capacity because the high pore size and tube length of TiO_2 nanotube/Ti electrode make Li ion diffusion coefficient increase.

The discharge capacity of amorphous structure is higher than that of anatase structure. Therefore, the Li ion diffusion

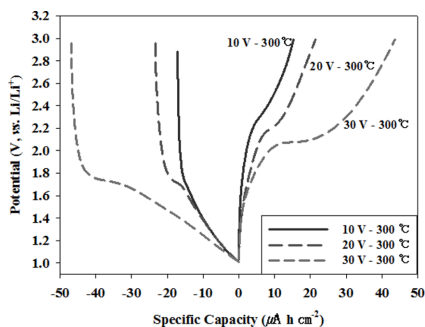


Fig. 5. Charge/discharge curves for prepared TiO_2 nanotube/Ti electrodes at 10 V, 20 V and 30 V after annealing 300°C , the potential range between 3 V and 1 V (vs. Li/Li^+) at current density, $50 \mu\text{A cm}^{-2}$ at 2nd cycle in electrolyte, 1.5 M LiBF_4/PC .

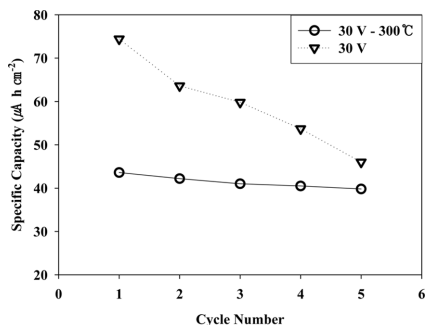


Fig. 6. Cycling performance for prepared TiO_2 nanotube/Ti electrode at 30 V after annealing at 300°C , the potential range between 3 V and 1 V (vs. Li/Li^+) at current density, $10 \mu\text{A cm}^{-2}$ at 1.5 M LiBF_4/PC .

coefficient of amorphous TiO_2 nanotube/Ti electrode is also higher than that of anatase TiO_2 nanotube/Ti electrode.

Figure 6 shows results of cycle performance at two different kinetics. The capacity of amorphous TiO_2 nanotube/Ti electrode is $74 \mu\text{Ah cm}^{-2}$ and after 5 cycles, efficiency of the capacity is about 62%. The TiO_2 nanotube/Ti electrode annealed at 300°C presents a maximum capacity of $44 \mu\text{Ah cm}^{-2}$, and after 5 cycles, the capacity decreases to $40 \mu\text{Ah cm}^{-2}$, and efficiency of the capacity is about 91%. These results suggest that amorphous TiO_2 nanotube/Ti electrode can accommodate extra Li onto its structure as compared with annealed TiO_2 nanotube/Ti electrode. It also facilitates an extra lithium insertion. But from Fig. 6 the energy storage mechanism for intercalation reaction of anatase structure has better cycle performance than that of redox reaction of amorphous structure.

4. Conclusion

The TiO_2 nanotube/Ti electrodes were prepared successfully by anodizing. We identified that the capacities of TiO_2 nanotube/Ti electrodes improve by high pore size and tube length with increasing anodizing voltage. We also identified that the capacity of TiO_2 nanotube/Ti electrode prepared at 30 V is $74 \mu\text{Ah cm}^{-2}$ with current density of $10 \mu\text{A cm}^{-2}$. The Li ion diffusion coefficients for amorphous structure are higher than that of anatase structure. But the cycle performance of amorphous structure is lower than that of anatase structure. These results suggest that the TiO_2 nanotube/Ti electrode with anodizing voltage of 30 V and anatase structure can be used as an alternative electrode for rechargeable Li-ion micro-batteries.

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