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DURABILITY AND CYCLING STABILITY OF COPPER COATED TITANIA NANOTUBE AS ANODE MATERIALS FOR LI-ION BATTERY

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Abstract

The titania nanotube prepared by using an anodizing was coated with copper by the electrodeposition and its electrochemical properties were investigated as the anode material. The discharge capacity of copper coated titania nanotube composite is higher than that of parent titania nanotube. The initial reversible capacities corresponding to titania nanotube and copper coated titania nanotube composite are 185.35 and 226.54 mAh/g at a high charge/discharge current density of 200 mA/g(1C). After 300 charge/discharge cycles, the discharge capacity reaches 185.64 mAh/g with capacity degradation of only 15.86 % for the copper coated titania nanotube composite while it decreases to 137.2 mAh/g with a capacity loss as high as 25.93 % for the titania nanotube. The results indicated that copper coated titania nanotube shows excellent electrochemical properties as anode materials for lithium-ion batteries.

Introduction

Due to recent advances in mobile devices as well as increasing demands for plug-in electric vehicle and electric vehicle, rechargeable batteries are now considered as promising energy source and energy storage. With various rechargeable batteries exists, lithium-ion batteries have received many attentions to researchers due to relatively high energy density, high working voltage, and lower self-discharge rate [1-3]. Recently, lithium-ion batteries has become essential to providing the electrical power necessary to power and operate portable electronic devices such as cellular phones, laptop computers, digital cameras, etc. And in recent years, they are being used in hybrid-electric vehicle (HEV) and electric vehicle, as well as back-up electricity storage units for renewable energy sources, which must have a large unit. A lithium-ion battery is composed of lithium-metal oxide cathode, carbonate-based organic electrolyte with a Li-containing salt, and a carbonaceous anode. When the discovery of lithium cobalt oxide ($LiCoO_2$) can be utilized as a cathode array, the Lithium ion Rechargeable battery has been commercialized by SONY at 1990 [4]. Since then, many researches about substituting this material has been underway, such as $LiNiO_2$ [5] or $LiMn_2O_4$ [6] for cheaper and having longer life. The electrolyte is usually based on a lithium salt in a solution such as $LiPF_6$ or $LiBF_4$[7-10].

The anode of the lithium-ion rechargeable battery is based on carbon [11-13]. Graphitic carbons have good cycle characteristics and stability because they have excellent reversibility during lithium intercalation / deintercalation between layered lattices of carbon from crystallographical point of view. Also, the carbons have high voltages because reaction potential against lithium-ion is low. However, there is a limit for capacity because only a lithium ion per 6 carbons can intercalate to graphite. Therefore, alternative anode materials have been studied for higher capacity[14].

Due to increased electricity required in portable electronic devices, as well as demands in hybrid electric vehicle and plug-in electric vehicles, the lithium-ion rechargeable battery needs to gain higher specific capacity. Recently, lithium-metal alloys are considered as an alternative anode due to its capacity surpasses the graphite (over 900 mAh/g compared to 372 mAh/g) [15-18]. However, exception of few transition metal oxides, they generally suffer from a large irreversible capacity at the first cycle and poor cycling behavior due to a large volume change during cycling. During cycling, the metals alloying with lithium cause interior volume expansion, and the electrode is cracked. The lithium molecules which do not participate in charge/discharge cycle are also formed which causes poor cycle performances. In this work, we studied the electrochemical performance of copper coated titania nanotube. The titania nanotube fabricated by an anodizing was coated copper as anode materials by the electroplating method for lithium-ion batteries.

Experimental procedure

The titania film was prepared by anodization of the titanium (Ti) sheet. The Ti was cleaned in D.I. water, degreased in acetone and ethanol for 5 min. The anodization was prepared in a two electrode with Ti as working electrode and platinum as counter electrode, with ethylene glycol containing 0.5 wt% NH_4F. The distance between titanium and platinum foil is fixed at 25 mm. The as-anodized sample was cleaned by the ultrasonication in deionized water for 15 min to remove surface debris. Owing to the product of anatase phase, prepared titania nanotube was annealed at 450 ^{o}C for 1hr in Ar gas with heating and cooling rate of 10 K/min.

The decoration of copper coated titania nanotube was based on the electrodeposition. To fabricate copper solution based ethylene glycol, copper nitrate was used. The copper nitrate powder (0.5 wt%) was placed in the beaker, then 10 wt.% deionized water was added in the beaker under stirring. And ethylene glycol solution was introduced. The sample was immerged in copper nitrate solution. The electrodeposition was performed in a two-electrode configuration with titania nanotube on Ti foil as the anode and Ti metal foil as cathode. The electrodepositing voltage was maintained as 15 V, and electrodepositing time was fixed at 20 min. After the electrodeposition, copper coated titania nanotube was cleaned in deionised water, and then calcined at 300 ^{o}C for 1 hr under Ar gas.

The X-ray diffraction was measured on X-ray diffractometer (XRD, Rigaku, Japan). The morphologies were characterized using scanning electron microscopy (SEM, Hitachi, Japan). The electrochemical performance of titania array film was evaluated using a half cell. The half cell was assembled in the Ar filled glove box with less than 1.0 ppm each of O_2 and H_2O. The charge-discharge cycle test was measured using a battery cycler with cut-off voltage of 2.7 V to 1.0 V. The impedance of electrochemical was measured by electrochemical workstation.

Results and discussion

The figure 1 shows the SEM image of top and tilted titania nanotube fabricated by anodizing with the 40 V for 7 hrs. The anodized titania nanotube was covered with the debris, which can remove by ultrasonic in the deionized water. From the figure 1(a) of titania nanotube, the titania nanotube with 15 nm wall thickness and 90 nm diameter was distributed, and each nanotube was 18 μm in the figure 1(b).

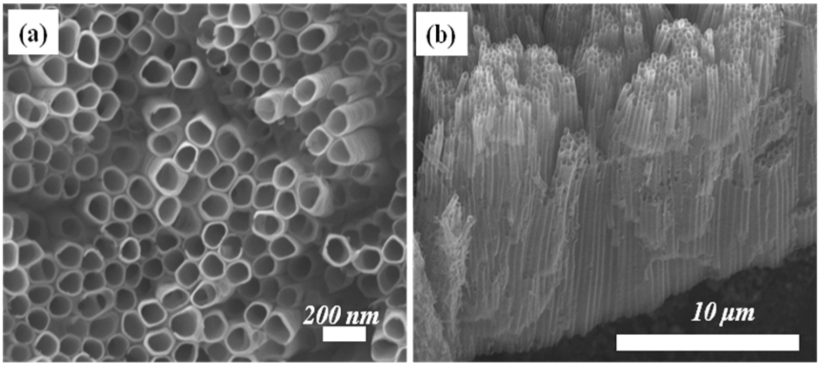

Figure 1. SEM image of top (a) and tilted (b) titania nanotube at 40 V for 7 hrs.

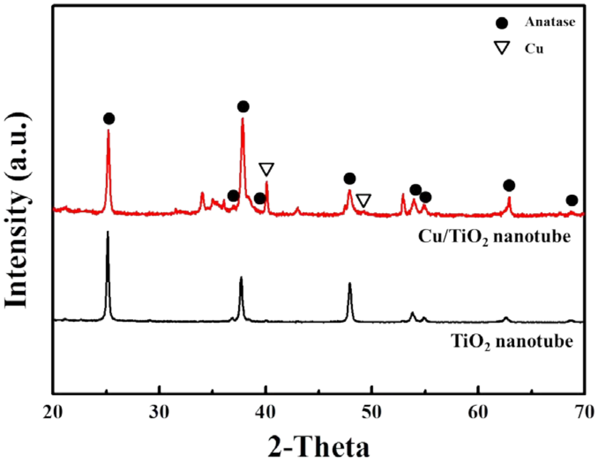

Figure 2. The XRD of titania nanotube and copper coted titania nanotube.

The XRD of titania nanotube and copper coated titania nanotube were shown in figure 2. From figure 2, after calcinations (450 °C, 1 hr) besides the peaks for the substrate Ti, the peaks can be indexed as anatase phase. The peak about 25.3° was typical for the crystal face (101) reflection of the anatase phase. The diffraction peak of the copper coated titania nanotube can be readily indexed to the monoclinic-phase copper and titania with anatase phase.

Both anatase and rutile phase have tetragonal structures. In such a structure, a Ti-ion was surrounded by a distorted oxygen octahedron, and numerous vacant octahedral and tetrahedral sites exist between these octahedrons. Li-ions can be accommodated in these vacant sites. It should also be noted that Li-ion insertion can lead to a phase transition from a Li-poor (tetragonal) phase to a Li-rich (orthorhombic, cubic spinel, cubic rocksalt, etc.) phase [19,20].

Figure 3 shows the cycle capacities of the copper coated titania nanotube and parent titania nanotube electrodes at the current density of 50 and 200 mA/g (0.25C, 1C). The initial capacities corresponding to the parent titania nanotube and copper coated titania nanotube were 185.35 and 226.54 mAh/g at a current density of 200 mA/g. The discharge capacity of copper coated titania nanotube composite with less capacity loss was higher than that of titania nanotube. The discharge capacity reaches 185.35 mAh/g after 300 cycles with capacity degradation of 15.86 % for the copper coated titania nanotube while it decreases to 132.2 mAh/g with a capacity loss as high as 25.93 % for the titania nanotube at the current density of 200 mA/g. The 300th discharge capacity of 200 mA/g is 88.9 % of that discharge at the current density of 50 mA/g (208.81 mAh/g) for copper coated titania nanotube composite, but for titania nanotube, it is only 84.97 % of the capacity at the current density of 50 mA/g (161.45 mAh/g). It was that copper additive improved the reversible capacity and the cycling stability of the titania nanotube. The discharge capacities and cycling stability of the copper coated titania nanotube was higher than parent titania nanotube.

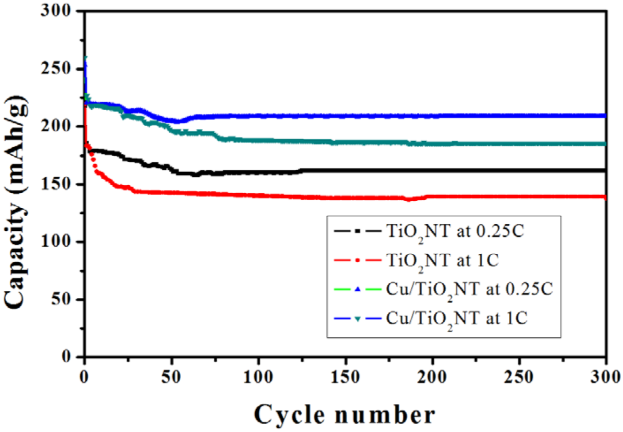

Figure 3. Discharge capacity and cycle number for the copper coated titania nanotube and the bare titania nanotube at various current.

Conclusion

The copper nanotube and copper coated titania nanotube were prepared by electro-deposition method. The copper additive nanotube was improved the cycling stability and reversible capacity of titania nanotube. The copper coated titania nanotube was showed excellent electrochemical properties as anode materials for lithium-ion batteries. The copper coated titania nanotube as anode material for lithium-ion battery showed higher reversible capacity, better durability and high rate performance than the parent titania nanotube. The higher electrochemical performance can be attributed to the effect of copper coated titania nanotube. Due to the higher electrical conductivity of copper coated titania nanotube, the lithium extraction reversibility was improved.

The copper coated titania nanotube shows excellent electrochemical properties as anode materials for lithium-ion batteries.

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