



Fabrication of Cu-coated TiO₂ nanotubes and enhanced electrochemical performance of lithium ion batteries



Seong-Hwan Kim, Se-Young Choi *

Department of Materials Science and Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, Republic of Korea

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ABSTRACT

Parent TiO₂ nanotubes were synthesized through an anodizing process and Cu coating was applied on these nanotubes by electroplating to take advantage of their improved Li ion intercalation properties. The field emission scanning electron microscope (FESEM), transmission electron microscope (TEM), energy dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD) results demonstrated that the products consisted of impurity-free, anatase-phase TiO₂ nanotubes uniformly coated with a Cu layer. The charge-transfer resistance of the Cu-coated TiO₂ nanotubes decreased by more than 39% compared to that of the parent TiO₂ nanotubes. The first reversible capacity of the Cu-coated TiO₂ nanotubes was 226.5 mA h g⁻¹ at a high current density of 200 mA g⁻¹. After the 300th cycle, the discharge capacity of the Cu-coated TiO₂ nanotubes decreased by 18.1%, compared to the initial discharge capacity, to 185.6 mA h g⁻¹. These results represent 23.6% and 35.3% improvements, respectively, over the parent TiO₂ nanotubes. The enhanced electrical performances of the Cu-coated TiO₂ nanotubes, ascribed to the increase in electrical conductivity, led to improvements in the reversible capacity and cycle stability of the anode materials. It is speculated that Cu-coated TiO₂ nanotubes are a promising anode material for Li ion batteries.

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1. Introduction

TiO₂ has many applications as anticorrosive materials, self-cleaning coatings, solar cells, and photocatalysts. These applications are a result of its numerous advantages including its chemical stability, low cost, and non-toxicity. Recently, TiO₂ has also been reliably used as an electrode in Li ion batteries [1,2]. Generally, TiO₂ can exist as eight polymorphs: rutile (space group *P4₂/mnm*), anatase (*I4₁/amd*), brookite (*Pbca*), TiO₂ B (bronze, *C2/m*), TiO₂ R (ramsdellite, *Pbnm*), TiO₂ H (hollandite, *I4/m*), TiO₂ II (columbite, α -PbO₂, *Pbcn*), and TiO₂ III (baddeleyite, *P2₁/c*) [3]. Many methods have been reported to easily control these TiO₂ particle morphologies [3–5].

The electrochemical reaction of TiO₂ is typically written as $\text{TiO}_2 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{TiO}_2$, where x is the Li insertion coefficient. The maximum Li ion insertion in TiO₂ (anatase phase) was originally thought to be $x = 0.5$ in Li_xTiO_2 [6]. However, through the formation of nanostructures, it was proven that $x > 0.9$ was possible because of the shorter Li ion diffusion length between intercalation and deintercalation [7]. Many studies have been

conducted to synthesize TiO₂ nanostructures, such as nanoparticles, nanotubes, nanorods, and mesoporous particles, because of their high capacity and rate capability [1,5,8,9]. TiO₂ nanostructures have large surface areas and many electrolyte–electrode contacts. Therefore, such nanostructures are easily fabricated and can increase Li ion intercalation [7]. Among the TiO₂ nanostructures, nanotubes are the best electrode material candidate. This is because the surface areas of TiO₂ nanotubes are larger than those of nanowires, which are in turn larger than those of nanorods. Moreover, the rate capacity when employing nanotube structures increased by approximately 60% compared to the corresponding nanorod structures at 50 mA g⁻¹ [5,10].

The demand for Li ion batteries as power sources for electric vehicles and portable devices is increasing owing to changes in social and environmental attitudes. Therefore, electrode materials require high rate performance when Li ions are transported during intercalation-deintercalation [11]. However, the rate performance of TiO₂ is hindered by low electrical conductivity (10^{-7} – 10^{-9} S cm⁻¹) [12]. This means that large amounts of conductive materials, such as carbon black, are required [13]. Additionally, many studies involving metal coatings on nanocomposite or nanoparticle surfaces have been carried out to solve these physical problems. For example, mesoporous TiO₂ with RuO₂ nanocomposite additives can increase the rate capability by 50%, compared to the parent

* Corresponding author.

E-mail address: sychoi@yonsei.ac.kr (S.-Y. Choi).

mesoporous TiO₂, to 672 mA g⁻¹ [14]. Moreover, Ag, Sn, and V₂O₅ coatings on an anatase TiO₂ nanostructure have been reported to increase the rate capability [15–17].

In contrast to TiO₂, Cu has excellent electrical conductivity and is less expensive than noble metals such as Ag; consequently, it is used in many applications [18]. Moreover, Cu is well suited to be the current collector of the Li ion battery anode because it is stable during the repetition of charge–discharge cycles. It also shows no response to Li ions during the electrochemical reactions. Furthermore, Suzuki et al. reported that Li ions could be transported through a Cu layer deposited on carbon fiber during the intercalation-deintercalation process [19]. Therefore, Cu is a suitable candidate for improving the electrical conductivity of TiO₂ nanotubes.

There are several reports on fabricating TiO₂ nanotubes using an anodizing process, but none on Cu-coated TiO₂ nanotubes via an electroplating process. In this study, in order to confirm the effect of Cu layer formation on electrochemical performance, uniform Cu layers are coated onto parent TiO₂ nanotubes that are fabricated using an anodizing process. The electrochemical performances, such as electrical conductivity, high-rate discharge capacity, and cycling stability, were evaluated and compared to those of parent TiO₂ nanotubes.

2. Experimental

2.1. Material fabrication

TiO₂ nanotube arrays were prepared via potentiostatic anodization of a titanium sheet (99.6%, thickness of 0.3 mm). The titanium sheet was cleaned prior to anodizing with deionized water and then degreased by sonication in acetone and ethanol for 10 min. The anodization was conducted in a two-electrode system composed of a working electrode (Ti sheet) and a counter electrode (Pt sheet) in an ethylene glycol (99.5%, Duksan, Korea) solution containing 0.5 wt% ammonium fluoride (practical grade, Duksan, Korea) as the electrolyte. The distance between the Ti and Pt sheets was fixed at 2.5 cm. The anodization voltage and time were 40 V and 7 h, respectively. The as-anodized samples were ultrasonically cleaned in deionized water for 15 min to remove surface debris. In order to produce a defined anatase structure, the as-prepared TiO₂ nanotubes were annealed at 450 °C for 1 h under an argon atmosphere, with a heating and cooling rate of 10 K min⁻¹.

The surface coating of the TiO₂ nanotubes with Cu was based on the electroplating method. The copper solution for electroplating was prepared as follows. First, 0.5 wt% copper nitrate powder (99.5%, Yakuri, Japan) was placed in a 50 mL beaker, and then 10 wt% deionized water was added dropwise while stirring until the powder was fully dissolved. Next, the ethylene glycol mixture was introduced. The sample was then submerged in the copper solution at room temperature. The electroplating was performed in a two-electrode configuration with TiO₂ nanotubes on the Ti sheet as the anode and another Ti sheet as the cathode. The distance between the TiO₂ nanotubes and Ti sheet was fixed at 2.5 cm. The electroplating voltage was maintained at 15 V and the electroplating time ranged from 10 to 40 min. After electroplating, the Cu-coated TiO₂ nanotubes were cleaned with deionized water and then calcined at 300 °C for 1 h under an argon atmosphere.

2.2. Material characterization

The X-ray diffraction patterns were measured using an X-ray diffractometer (XRD, Rigaku DMAX-III A, Japan) using Cu K α radiation. The morphologies were characterized using field emission

scanning electron microscopy (FESEM, S-4200, Hitachi, Japan). The transmission electron microscope (TEM) images were obtained with a JEOL JEM-1011; the samples were coated on a copper micro grid coated with holey carbon. The elemental analysis of the parent and Cu-coated TiO₂ nanotubes was performed using an energy dispersive X-ray spectrometer (EDS, Inca Energy 250, Oxford Instruments, UK).

2.3. Electrochemical measurements

The electrochemical performance of the as-prepared parent and Cu-coated TiO₂ nanotube arrays was evaluated using the vial-type half-cell design. The two-electrode electrochemical cell was composed of a TiO₂ nanotube array on a Ti sheet (without any binder and electrical conducting carbon) as the working electrode and Li metal as the counter electrode. The electrolyte used was 1.0 M LiPF₆ (battery grade) dissolved in a mixture of 1:1 (wt%) ethylene carbonate (EC, battery grade) and dimethyl carbonate (DMC, battery grade). The galvanostatic charge–discharge cycling was performed using a battery cycler (WonATech, WBCS 3000, Korea) with current densities ranging from 50 to 2000 mA g⁻¹ and cut-off voltages ranging from 2.7 to 1.0 V vs. Li/Li⁺. The electrochemical impedance was measured using an electrochemical workstation (BioLogic, VMP3, France). The electrochemical impedance spectra measurements were carried out under frequencies ranging from 1 MHz to 0.001 Hz at an oscillation amplitude of 10 mV. In the experiments, the cell was discharged to the designated potential and then was maintained at the open-circuit conditions for 1 h to ensure equilibrium of the cells before performing the impedance tests.

3. Results and discussion

Fig. 1 shows the FESEM and TEM images of the parent and Cu-coated TiO₂ nanotube arrays. Fig. 1a and b show the top and side views, respectively, of the highly ordered TiO₂ nanotube array produced by anodizing with a voltage of 40 V for 7 h. From the SEM and TEM (inset in upper right corner) images of the TiO₂ nanotube array shown in Fig. 1a, it can be seen that the nanotubes have inner diameters of approximately 100 nm and wall thicknesses of approximately 15 nm. The TiO₂ nanotube array shown in Fig. 1a is uniformly distributed on the surface. Fig. 1b shows that the lengths of the TiO₂ nanotubes are approximately 18 μ m (aspect ratio, $L/D = 180$). In order to fabricate the TiO₂ nanotube array, the anodizing conditions, including the applied voltage and time, were controlled. The maximum outer and inner diameters of the TiO₂ nanotube array were obtained at an applied voltage of 40 V and an anodizing time of 7 h. These results can be expected to maximize the thickness of the metallic Cu layer on the TiO₂ nanotubes. Fig. 1d–f show SEM and TEM images of the Cu-coated TiO₂ nanotube array after 20 min of electroplating, and Fig. 1c shows a schematic illustration. Compared to the parent TiO₂ nanotubes (Fig. 1a), the inner diameter of the nanotubes ranged from 40 to 50 nm and the inner wall thickness is approximately 30 nm; the outer wall thickness is approximately 10 nm. The inner diameter of the Cu-coated TiO₂ nanotubes decreased compared to the parent TiO₂ nanotubes owing to the uniformly coated Cu on the surface of the TiO₂ nanotubes. According to the SEM and TEM images in Fig. 1, Cu is uniformly deposited on the surface of the TiO₂ nanotubes.

Table 1 presents the energy dispersive X-ray spectroscopy (EDS) elemental analysis of the parent and Cu-coated TiO₂ nanotubes. The parent TiO₂ nanotubes consisted of O and Ti. On the other hand, the Cu-coated TiO₂ nanotubes consisted of O, Ti, and Cu.

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