



Expansion of titanate nanotubes by the use of a surfactant and its improved performance as an anode in Li-ion batteries



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ABSTRACT

The tubular and layered structure of titanate nanotubes facilitate ion movement and provide a high rate capability. Moreover, expansion of the material can enhance its performance. In this study, regular titanate nanotubes and expanded titanate nanotubes were synthesized. To expand the nanotubes, dodecylamine were used under hydrothermal conditions. SEM, TEM, BET, and XRD were utilized to characterize these materials. In addition to that, electrochemical characterizations like cyclic voltammetry, rate capability, and cycle stability tests were made to understand the effect of titanate expansion on Li-ion electrode performance. After the expansion, the d-spacing increased from 8.1 Å to 9.5 Å and parallel to that, the specific surface area reached to 297 m² g⁻¹ from 204 m² g⁻¹. Cyclic voltammograms had broad peaks and suggested a pseudocapacitive character; which is common for titanate nanotubes. Sloping potential-capacity profiles also supported this character. The first discharge capacity of regular nanotubes was 823 mAh g⁻¹. However, after the expansion, it increased to 1017 mAh g⁻¹. Above all, both of the nanotubes had superior rate capabilities and stabilities due to their high aspect ratios. Moreover, dodecylamine created a protective layer on the titanate surface and enhanced the stability. Finally, it was realized that the expansion of the structure is crucial and enhances the electrode performance.

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1. Introduction

Portable electronics like mobile phones and notebook computers have become a part of our daily life, and even electric cars and grid storage systems are in that trend [1–5]. As their usage increases, the demand for high capacity and better performing Li-ion batteries also increases. Especially batteries with high rate capability and stable cycling are important parameters to consider. For that purpose, materials with improved electron transport and high Li-ion mobility should be developed [6]. Likewise, the material's structure should be durable enough to withstand long-cycle conditions [7].

In Li-ion batteries, the mostly utilized anode material is graphite for its cost and good electrochemical performance. However, safety is another significant factor and graphite anodes suffer from dendrite formation because of its low charging potential [8]. Another limiting issue is their poor cyclability caused by the solid electrolyte interphase (SEI) materialized after

the decomposition of the electrolyte [9]. Various methods like metal or metal oxide deposition [10], coating [11] and mild expansion [12] have been utilized to enhance graphite's performance as an anode. Performance improvement with mild expansion is especially important since it also enhances the Li-ion mobility in the material. With the mild expansion, at the first cycle, about 70 mAh/g of capacity increase was obtained. Additionally, rate capability performance was improved notably at high current rates [12].

Titania and its derivatives have a higher lithiation/delithiation potential that inhibits dendrite formation and prevents solid electrolyte interphase (SEI) formation [13]. From that perspective, titania-based materials have the potential to please the energy and safety requirements. Especially hydrogen titanate (H₂Ti₃O₇) nanotubes show exceptional Li-ion mobility in the electrode [14]. This high mobility between the titanate layers is due to the pseudocapacitive nature of the nanotubes. Therefore titanate nanotubes, in comparison with typical anode materials, show much better high current performance [15,16]. Titanates can be produced in high amounts without any difficulty; consequently, these materials can be easily implemented to grid storage, hybrid electric vehicle, and electric vehicle applications [17,18].

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Titanate nanotubes have titanate layers that rolled on itself which creates a multi-layered nanotube structure [19]. The spacing between these layers is wider than a standard intercalation anode material, thus, the ions can move between the layers with less resistance. For titanate nanotube Li-ion anodes, the interlayer distance is very crucial because lithiation and delithiation take place by a surface redox mechanism [20]. Modification at the micropore and mesopore region causes a substantial improvement in the battery performance. In a study with lithium zinc titanate, the structure was expanded with Na doping and the material showed an improved performance thanks to improved mobility of Li ions [21]. In our previous study, we showed that introducing some amount of Na to elongated titanate nanotubes expands the structure and enhances not only the capacity but also the rate capability of the material [14].

The aim of this work is to increase the interlayer distance of elongated titanate nanotubes with the help of surfactants. When compared with ion doping, the introduction of surfactants is certainly better for obtaining expanded structures. Here we synthesized expanded and elongated titanate nanotubes using dodecyl amine as a surfactant, hence, better structures for Li-ion transfer was achieved. The structural and electrochemical performance was studied in detail. To the best of our knowledge, introduction of surfactants and their effects on Li-ion battery performance have not been reported until this study. The results show a significant improvement in the battery performance and this study presents a novel concept for electrochemically active material development, particularly in high current applications.

2. Experimental

2.1. Materials

For titanate nanotube synthesis, anatase (TiO_2) powder was utilized (Aldrich). The hydrothermal treatment of anatase under basic condition was performed using sodium hydroxide (NaOH) pellets (Sigma-Aldrich). In addition to that, the pH adjustment was done using an HCl solution (Sigma-Aldrich). Surfactant utilized for titanate expansion was dodecylamine (Sigma-Aldrich). All of the chemicals were utilized without any additional purification and the solutions were prepared with deionized water. The hydrothermal synthesis reactions were carried out in stainless steel autoclaves with Teflon lining.

Split test cells, lithium chips with 15.6 mm diameter and 0.45 mm thickness, copper foil with 9 μm thickness, poly(vinylidene fluoride) (PVdF) and carbon black (MTI Corporation) were used for the battery testing part. For the paste preparation, N-methyl-2-pyrrolidone was utilized. The battery separator was Celgard 2400 film. The electrolyte used in the battery was 1.0 M lithium hexafluorophosphate (LiPF_6) solution in ethylene carbonate and dimethyl carbonate (50% mixture by volume).

2.2. Preparation of elongated and expanded titanate nanotubes

The regular (RN) and elongated-expanded (EN) titanate nanotubes were synthesized by a reaction of anatase with NaOH solution under hydrothermal conditions. For RN, 1.5 g of TiO_2 were mixed with 100 mL 10 M NaOH solution and placed in an autoclave. Similar to RN, for EN, 1.5 g of TiO_2 were mixed with 100 mL 10 M NaOH solution. After that, 0.17 g of dodecylamine were added to the mixture (to investigate the effect of dodecylamine loading, 1.50, 0.75, and 0.35 g of dodecylamine were also tried. However, only 0.17 g of dodecylamine loading gave satisfactory morphologies. The results of different loadings were given in the supplementary information part). The temperature of the autoclave was increased to 130 °C. After that, the mixture was kept at

that temperature for 48 h. At the end of hydrothermal treatment, the obtained titanate was filtered and dried for the following step. After drying, for the ion-exchange of Na^+ and H^+ , the titanate powder was put in deionized water. While stirring the mixture for 48 h, the pH was adjusted to 4 with 0.1 M HCl solution. Titanate nanotubes, below certain pH values, lose their structure and transforms back to anatase. In literature, it was shown that transformation starts below pH 4 [22]. So during titanate nanotube synthesis, the solution pH should not go below 4. Also, it was shown that at pH 4 all of the sodium ions between the titanate layers are replaced with hydronium ions [23]. According to these results, to obtain pure titanate nanotubes the synthesis should be made at pH 4. The critical situation to get elongated structures is to stir the mixture continuously all through the pH adjustment stage. With this method, micron-long titanate nanotubes can be obtained much more easily as to the methods utilize autoclaves with sophisticated structures. At the end of acid washing, the titanate powder was dried at 100 °C to obtain the active materials.

2.3. Morphological properties of expanded titanate nanotubes

For the XRD characterization, the analyses were performed between 2θ values of 5–90°, with Cu K α radiation with Bruker AXS-D8 diffractometer. For the specific surface area and pore size distribution data of titanate nanotubes, a Quantachrome NOVA 2200e analyzer was used. Before the analyses, the samples were dried at 110 °C for 12 h. The calculation of BET surface areas was done between the relative pressures of 0.05–0.3, the pore size distribution data was evaluated with the Barrett–Joyner–Halenda (BJH) technique using the desorption branch. To determine the morphological structure of titanate nanotubes, a scanning electron microscope (Leo-G34 SEM) was utilized at 5 kV. The transmission electron microscopy (TEM) characterizations were performed on JEOL JEM 2100 HRTEM at 200 kV.

2.4. Electrochemical characterization of titanate nanotubes

The electrochemical characterizations of the materials were performed in a split cell by galvanostatically charging and discharging the cell. For the electrode slurry, first, RN and EN samples were added to carbon black and PVdF (active material: carbon black:PVdF = 80:15:5), after that, a slurry was obtained by pouring NMP. That slurry was coated onto copper foil then dried for 24 h at 110 °C (For RN the average material loading was 0.95 mg/cm² and for EN the average loading was 0.86 mg/cm²). Following the drying step, electrodes were placed in a Jacomex GP glove box (argon atmosphere: $\text{C}_{\text{O}_2} < 0.1$ ppm, $\text{C}_{\text{H}_2\text{O}} < 0.1$ ppm). The cell components were put together in a test cell (MTI) and the counter electrode was a lithium chip. The electrochemical characterizations were performed in a PARSTAT MC system. The cyclic voltammograms (CV) data were obtained in the voltage range of 1 and 3 V (scan rate: 0.01 mV s⁻¹). Galvanostatic charging and discharging was performed at various current rates like 0.1C, 0.5C, 1C, and 5C for 40 cycles between 1–3 V (versus Li/Li⁺) (theoretical capacity of titanate nanotubes were calculated as 199 mAh/g according to their discharge formula of $\text{Li}_2\text{Ti}_3\text{O}_7$). In addition to that, the rate capability tests were carried out by changing the current rate in the order of 0.1C (10 cycles), 0.5C (10 cycles), 1C (10 cycles), 5C (10 cycles), again 0.1C (10 cycles).

3. Results and discussion

3.1. XRD characterization of the titanate nanotubes

For the titanate nanotube synthesis, anatase was treated hydrothermally for 48 h in a 10 M NaOH solution. The crystal

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