Electrochemical Lithium Storage of Titanate and Titania Nanotubes and Nanorods

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Layered protonated titanate nanotubes, synthesized via a hydrothermal reaction in alkaline solution, were calcined at different temperatures (200–500 °C) in air to achieve the products of various morphologies and crystal-phase compositions. The microstructure of obtained products was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and N2 adsorption. The electrochemical lithium storage of these samples was studied by galvanostatic method and cyclic voltammetry. It is found that the protonated titanate nanotubes maintain layered structure below 300 °C and undergo phase transition to a mixture of anatase and TiO2(B) with anatase as the main phase between 300 and 500 °C. In addition, the hollow nanotube morphology still remains below 400 °C, but the tubes convert to solid nanorods during the calcination at 500 °C. It is found the nanotubes calcined at 300 and 400 °C have larger surface areas and exhibit relatively large reversible capacity and good reversibility (remain about 200 mA h/g after 80 cycles). Moreover, the electrochemical lithium storage is controlled by the pseudocapacitive effect, the mixed process of both the pseudocapacitive effect, and diffusion-limited reaction, and the diffusion-limited reaction depends on different microstructures of the resulting samples. The relationship among their phase composition, morphology, porous structure, and electrochemical properties is also discussed.

I. Introduction

Nanostructured titania have been found to be very attractive materials because of their superior physicochemical properties as active materials for photocatalysis,1 lithium ion batteries,2–4 electrochemical capacitors,5 and dye-sensitive solar cells.6,7 Recently, the protonated titanate and titania nanotubes are of particular significance for electrochemical lithium storage due to their large specific surface area and numerous surface defects.8–13 These solids could maintain high capacity and good cycle stability under a high charge and discharge rate. Actually, it was demonstrated that the electrochemical pseudocapacitance was involved during the electrochemical lithium storage of protonated titanate nanowires, TiO2(B) single crystalline nanowires, and anatase/TiO2(B) polycrystalline nanotubes,14–17 which was beneficial to the large reversible capacity and excellent rate capability of the electrochemical lithium insertion and extraction. The microstructure of protonated titanate and titanotubos or nanowires seems to be dominant on electrochemical lithium insertion and extraction due to their freely accessible parallel channels for lithium ion transport into one-dimensional (1D) nanostructure. Three titania polymorphs of interest, i.e., TiO2-(B), anatase, and rutile nanotubes, are extensively studied recently.8,11–13,18,19 The hydrothermal reaction in alkaline solution is a simple method to synthesize protonated titanate nanotubes using titania as raw materials. We believe that the calcination of the titanate nanotubes at different temperatures could yield products with different crystal-phase compositions, morphologies, and pore structures, and it will be of great interest to understand how the electrochemical performance of the products for lithium storage varies with the structure changes.

In this work, protonated titanate nanotubes with outer diameters of 10–15 nm were prepared via a hydrothermal reaction of rutile with NaOH solution and converted gradually into titanate nanotubes or nanorods with a diameter between 10 and 15 nm by the calcination at a temperature from 200 to 500 °C. The electrochemical properties of the calcined samples for electrochemical lithium storage were investigated by galvanostatic method and cyclic voltammetry. The results suggest that the electrochemical lithium intercalation and extraction process is determined by the microstructure change during the calcinations.

II. Experimental Section

A. Sample Preparation and Characterization. The samples were prepared via a hydrothermal reaction of titania with NaOH solution using the synthesis procedure similar to those in the previous reports.8,20 Rutile powders (analytical grade) were mixed with 10 M NaOH solution, sonicated in an ultrasonic bath for 0.5 h, and then transferred to a Teflon-lined autoclave. After being maintained at 150 °C for 48 h, the precipitates were recovered and rinsed with distilled water, HCl solution (0.1 M), and distilled water until pH 7 was reached. After being dried at 60 °C for at least 2 days, the as-prepared sample was calcined in an oven at 200, 300, 400, and 500 °C for 6 h in air, respectively. The microstructure and morphology of the resultant samples were examined using X-ray diffractometer (XRD, Rigaku D/max-2500) and transmission electron microscopy (TEM, FEI Tecnai 20). N2 adsorption data were measured using a NOVA 2000e (Quantachrome) instrument at −196 °C after degassing the samples for 10 h under vacuum at 200 °C, and the specific surface area was calculated by the Brunauer–
Emmett–Teller (BET) equation, using the data in a $P/P_0$ range between 0.05 and 0.25. The thermogravimetric analysis (TGA) was performed on a NETZSCH TG 209 in a N$_2$ flow and at a heating rate of 10 °C/min.

**B. Electrochemical Performance.** The working electrode was prepared by compressing a mixture of active materials, acetylene black, and binder (poly(tetrafluoroethylene) (PTFE)) in a weight ratio of 80:15:5. Lithium metal was used as the counter and reference electrodes. The electrolyte was LiPF$_6$ (1 M) in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) in a weight ratio of 1:1:1. The galvanostatic method at the discharge–charge current density of 50 mA/g was used to measure the electrochemical capacity of the electrodes at room temperature using a LAND-CT2001A instrument. The cutoff potentials for charge and discharge were set at 2.5 and 1.0 V vs Li$^+$/Li, respectively. The CV experiment was conducted using a CHI 600A potentiostat at room temperature.

**III. Results and Discussion**

The as-prepared nanotubes are several hundred nanometers in length with the outer diameter of about 10–15 nm, as shown in Figure 1a. Such hollow tubular morphology could be converted to the solid nanorod morphology when calcined at 500 °C in air (Figure 1e), which is different from the nanotube morphology calcined at 500 °C in argon atmosphere. Moreover, the nanorods are shortened or broken to some extent during the calcination. The interference fringe spacing of the nanorods is derived from the high-resolution transmission electron microscopy (HRTEM) image of the sample (the insert in Figure 1e), being about 0.35 nm, which is consistent with the interplanar distance of the (101) plane in anatase phase. Thus, the calcination in air is more favorable for forming solid anatase nanorods. When the calcination is conducted between 200 and 400 °C, most of the products still remain with the tubular morphology with the inner diameter of about 4–6 nm. The nanotubes calcined at 400 °C are curved or collapsed to some extent as compared to the parent uncalcined nanotubes.

![Figure 1](Image) **Figure 1.** TEM images of original protonated titanate nanotubes (a) and the samples calcined at 200 (b), 300 (c), 400 (d), and 500 °C (e). Some HRTEM images are inserted.

![Figure 2](Image) **Figure 2.** Pore size distribution of original protonated titanate nanotubes and the samples calcined at 200, 300, 400, and 500 °C. The insert shows the specific surface area of all the samples.

![Figure 3](Image) **Figure 3.** XRD patterns of original protonated titanate nanotubes and the samples calcined at different temperatures.

The pore size distribution (PSD) curves calculated from N$_2$ adsorption data of the obtained samples, using the tangents of comparison plots reported previously, are displayed in Figure 2. A sharp peak around 3–6 nm on the PSD plots is generally observed for the nanotubes, while the peak is greatly depressed for the solid nanorods calcined at 500 °C. This is in good agreement with the results of TEM observation in most cases. The relationship between the specific surface area of all samples and calcined temperature (insert in Figure 2) also confirms the TEM observation. The specific surface area is over 231 m$^2$/g for the samples calcined between 200 and 400 °C, implying the retention of tubular morphology. The largest specific surface area of 323 m$^2$/g is obtained for the sample calcined at 200 °C, as was also found previously, due to the appearance of small particles attached outside or inside the nanotubes (Figure 1b). It should be noted that the attached small particles are unstable under a strong radiation in HRTEM observation (insert in Figure 1b) and almost disappear when the calcination temperature rises to 300 °C or above. The specific surface area of the sample calcined at 500 °C decreases dramatically to 97 m$^2$/g because of the morphological transformation from hollow nanotubes to solid nanorods.

XRD patterns of as-prepared and calcined samples are given in Figure 3. It is found that the pattern of the as-prepared sample with a relatively low intensity should be assigned to layered
protonated titanate (JCPDS, Card 47-0124) with poor crystallinity.\textsuperscript{23-24} It is also shown that the interlayer distance of nanotubes is reduced, but with a layered structure retained, when the calcination temperature is below 300 °C. After the calcination at 400 °C, the anatase phase seems to coexist with the metastable monoclinic TiO\textsubscript{2} (B) (JCPDS 35-0088), which is usually formed during the dehydration of layered titanate nanotubes or nanowires at low temperature.\textsuperscript{11,12,14,25,26} The pure anatase nanorods with a tetragonal structure are formed when the titanate nanotubes are calcined at 500 °C in air, which is also confirmed by HRTEM observation.

The dehydration process of the original protonated titanate nanotube was monitored by thermogravimetric analysis, and the TGA plot is depicted in Figure 4. The protonated titanate nanotubes show a weight loss of about 18% after heating up to 800 °C, depending on the temperature and time for drying or different washing times,\textsuperscript{27} due to the strong water-absorbent capability by the capillarity in the nanotubes. The steep weight loss is found before 200 °C, which is usually attributed to the adsorbed water and interlayer water.\textsuperscript{20,23} The weight loss above 200 °C is thought to be the dehydration of structural water. Such a dehydration process did not finish until 500 °C, where the transition of crystal form from titanate to anatase could occur as demonstrated previously by differential scanning calorimetry (DSC).\textsuperscript{28} Combining the above analysis with XRD and TEM, it is suggested that the layered titanate, which loses some structural water at the first step, reconstructs slowly to anatase phase from about 400 °C. During this process, some metastable phase such as TiO\textsubscript{2} (B) appears simultaneously. Because all the structural water is lost at elevated temperature, such a phase transition process is completed at about 500 °C, accompanied by a morphology change from nanotubes to nanorods. Usually, titanate nanotubes are thermodynamically less stable as compared with anatase nanorods. The transformation of the phase and morphology during the calcination is somewhat analogous to the tube-to-rod transformation in hydrothermal treatment in acidic condition by preferential elongation due to the specific feature of the nanotubes.\textsuperscript{29} The oriented attachment and the Ostwald ripening process may be involved in this transformation.\textsuperscript{30} The diameter of anatase nanorods with the polycrystalline structure is very close to the external diameter of titanate nanotubes from the above TEM observation. The solid polycrystalline anatase nanorods can be formed by the local shrinkage of titanate nanotubes during the dehydration, in combination with the expense of some unstable nanotubes being dissolved and the subsequent oriented attachment inside tubes. Therefore, the calcination at low-temperature could be beneficial to the formation of inner hollow nanotubes with the large specific surface area and TiO\textsubscript{2} (B) structure, while solid anatase nanorods with the reduced specific surface area are formed after the calcination at high temperature.

The first discharge—charge curves of all samples are displayed in Figure 5. A high initial discharge capacity over 330 mA h/g is observed for the as-prepared titanate nanotubes and the samples calcined at 200 and 300 °C. However, the discharge (or charge) curves decay (or rise) gradually without any potential plateau, similar to the titanate nanotubes and TiO\textsubscript{2} (B) nanotubes reported previously.\textsuperscript{10,11} Moreover, the irreversible capacities of the three samples in the first cycle are 142, 113, and 88 mA h/g, respectively, and are obviously larger than those of ordinary nanocrystalline titania.\textsuperscript{31} The loss of the binding water in the layered titanate nanotubes, which could react irreversibly with lithium to form Li\textsubscript{2}O on the surface and inside the layer, is the major reason for the larger capacity loss in the first cycle. It is noted that the irreversible capacities of the samples calcined at 400 and 500 °C decrease dramatically, although the initial discharge capacity is only slightly lower than that of the samples calcined below 300 °C. Usually, lithium intercalation in TiO\textsubscript{2} anatase causes an increase in the fraction of Li-rich titanate and a decrease in the fraction of the Li-poor anatase fraction.\textsuperscript{32} The two coexisting phases are responsible for the appearance of the
potential plateau. Therefore, the discharge and charge potential plateaus are presented at about 1.76 and 1.90 V (vs Li+/Li) for lithium insertion and extraction, respectively, which is related to the fraction of the anatase phase in the solid nanorods. The formation of the solid solution lithium titanate within hollow nanotubes contributes to the slopping discharge curves for the nanotubes as-prepared and calcined at 200 and 300 °C. At the ending stage of discharging of the anatase nanorods the potential declines gradually, being similar to that of amorphous titania, nanocrystalline, nanotextured anatase, or mesoporous anatase spheres.8,33–37 There are some extra site occupations of the anatase nanorods for lithium insertion, related to the surface imperfection and the formation of solid solution lithium titanate on the surface.

The cycle performance of all samples is illustrated in Figure 6. It is shown that the electrochemical cycle stability of layered titanate nanotubes and anatase nanorods is relatively poor. However, the electrochemical discharge capacities of the nanotubes obtained after the calcination at 300 and 400 °C decrease gradually to 206 and 200 mA h/g after 80 cycles, respectively, exhibiting a good electrochemical cycle stability for lithium insertion and extraction processes. The improved cycle stability is mainly attributed to the large accommodation of the structure strain inside hollow nanotubes produced during lithium storage. The poor electrochemical cycle stability of the solid anatase nanorods formed after the calcination at 500 °C is usually attributed to the relatively large structure strain during repeated lithium insertion and extraction processes. After 80 cycles at 1 C rate, the nanotube morphology still remains for the sample after the calcination at 300 °C as shown in the TEM image (Figure S1 of the Supporting Information), demonstrating that the Li ions can move in and out of the interior of the nanotubes. Therefore, the electrochemical lithium storage is
determined by the water content, crystal structure, and morphology of the samples.

Figure 7 shows the cyclic voltammograms (CVs) of the samples at a scan rate of 0.1 mV/s. In the first cycle, there is only a pair of broad redox peaks for the nanotubes as-prepared and calcined at 200 °C in agreement with the gradually declining potential curves during the galvanostatic discharge/charge process as mentioned above, which was also observed in amorphous titania and titane nanotubes. In the case of the nanotubes calcined at 300 °C, a pair of shoulder redox peaks near the larger broad redox peaks appears at 1.76 and 1.95 V (vs Li+/Li, depending on the scan rate), which is characteristic for lithium insertion into anatase lattice, revealing the possible phase transition from titinate to anatase. The notable change of the cathodic process between the first and second cycles displays the larger irreversible electrochemical discharge capacities for the nanotubes as-prepared and calcined below 300 °C. Obviously, the pair of shoulder redox peaks related to lithium insertion/extraction in anatase becomes larger with increasing calcination temperature, accompanied by a decrease of the broad redox peaks and a structure transformation from titinate to TiO2(B). It was also reported that two pairs of redox peaks at relative potential, denoted as S1 and S2, were assigned to TiO2(B) with the large parallel channel for Li+ ions accommodation and without any significant distortion of the structure. Therefore, two pairs of redox peaks for the nanotubes calcined at 400 °C appearing at 1.5 and 1.6 V (vs Li+/Li) can further confirm the formation of TiO2(B) in XRD patterns. Finally, after the calcination at 500 °C, the pair of sharp redox peaks related to the anatase is dominant for the anatase nanorods; the redox peaks related to TiO2(B) almost disappear in the meantime. This observation is in accordance with the XRD result.

It is well-known that the relation between peak currents and scan rates indicates the different electrochemical reaction characteristics, including diffusion-controlled or surface-confined charge-transfer processes. It was reported recently that the faradaic pseudocapacitance was involved in the electrochemical lithium storage of TiO2(B), where the peak current of S-peaks was found to scale with the first power of the scan rate. Therefore, two pairs of redox peaks for the nanotubes calcined at 400 °C appearing at 1.5 and 1.6 V (vs Li+/Li) can further confirm the formation of TiO2(B) in XRD patterns. Finally, after the calcination at 500 °C, the pair of sharp redox peaks related to the anatase is dominant for the anatase nanorods; the redox peaks related to TiO2(B) almost disappear in the meantime. This observation is in accordance with the XRD result.

In summary, the phase composition, morphology, and nanoporous structure of protonated titanate nanotubes synthesized via hydrothermal reaction in alkaline solution can be changed considerably by the calcinations at different temperatures in air. The calcination at low temperature leads to the formation of inner hollow nanotubes with the large specific surface area and TiO2(B) structure. The solid anatase nanorods with the reduced specific surface area can be obtained by the calcination at 500 °C. It is demonstrated that the notable changes in the structure storage mechanism is closely related to different phases, morphologies, and nanoporous structures of the resulting products.

IV. Conclusion

In summary, the phase composition, morphology, and nanoporous structure of protonated titanate nanotubes synthesized via hydrothermal reaction in alkaline solution can be changed considerably by the calcinations at different temperatures in air. The calcination at low temperature leads to the formation of inner hollow nanotubes with the large specific surface area and TiO2(B) structure. The solid anatase nanorods with the reduced specific surface area can be obtained by the calcination at 500 °C. It is demonstrated that the notable changes in the structure
and morphology have profound influence on the electrochemical lithium storage of the resulting products, as well as the reversible capacity, potential plateau, cycle stability, and lithium intercalation mechanism. By comparison, the nanotubes calcined at 400 °C deliver the optimal electrochemical lithium storage performance, where the mixed process of the faradaic pseudocapacitance and diffusion-limited reaction is observed due to the coexistence of TiO2(B) and anatase phases. Therefore, the fabrication of new materials with the delicate 1D nanostructure is important for electrochemical lithium storage, and this study acquires useful knowledge for developing new lithium electrode materials.

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Supporting Information Available: TEM image of the sample after the calcination at 300 °C after 80 cycles at 1 C rate (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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