The effect of synthesis temperature on the properties of TiO$_2$ (B) nanorods and its precursors as anode materials for lithium-ion batteries

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Abstract
In this work, we carried out a detailed research on the effect of synthesis temperature on the properties of TiO$_2$ (B) nanorods and its hydrogen titanate precursors. At the initial stage, hydrogen titanates (HTOs) were synthesised at different temperatures (140 °C–180 °C). The HTO materials were then annealed at 400 °C for 2 h in the second-stage to produce TiO$_2$ (B) nanorods. It is interesting to note that the pure anatase phase of TiO$_2$ nanorods (TO140) was achieved from the HTO material (HTO140) prepared at 140 °C, while the TiO$_2$ (B) nanorods were only formed from those synthesised at 160 °C (HTO160) and 180 °C (HTO180). In the evaluation of these materials as anodes for lithium ion batteries (LIBs), HTO140 showed better rate performance at higher current rates (500–1000 mAg$^{-1}$). However, HTO160 and HTO180 displayed lower initial discharge capacities than that of their precursor (the commercial TO) at 200 mAg$^{-1}$. Additionally, HTO160 exhibited the best stability with 71.5% retention after 100 cycles at 200 mAg$^{-1}$. Moreover, the annealed product of TO140 from HTO140 demonstrated the highest initial discharge capacity with a value of 164.3 mAhg$^{-1}$ at a current of 200 mAg$^{-1}$, which is corresponding to its low charge transfer resistance. However, TO160 showed a superior stability with 92.3% retained capacity after 100 cycles at 200 mAg$^{-1}$. Overall, 160 °C is the optimum temperature to synthesise TiO$_2$ (B) nanorods, regarding to its good cycling stability and mild capacity as anode materials. The investigation showed that the synthesis temperature is a determining factor to producing either TiO$_2$ (B) or anatase TiO$_2$ nanorods, has an influence on the properties of the precursor as well as the TiO$_2$ (B) as anode materials for LIBs.

1. Introduction

Many efforts have been made over the years to find alternative anode materials for applications in lithium-ion batteries (LIBs) with high energy and power. The anode materials, such as Si [1–3], Sn [4, 5], Sb [6, 7], Al [8], CuO [9, 10], MoO$_3$ [11], Co$_3$O$_4$ [12], MnO$_2$ [13] and WO$_3$ [14] have been investigated and were found to be attractive with high capacities ranging from 200–4200 mAh g$^{-1}$ [1, 8, 11, 14–21]. However, most of these high capacity materials, including graphite suffers from large volume expansion (300%–400%) due to low operating voltages (0–0.05 V), which causes pulverization of the materials and results in rapid capacity decay [8, 22, 23]. This effect promotes the decomposition of most organic electrolytes, which leads to pressure build due to release of gases and highly endangers the safety of the battery. Alternatively, Titanium-based oxides mainly referred to as lithium titanate Li$_x$Ti$_2$O$_3$ (LTO) and titanium dioxide (TiO$_2$), have been considered as the next-generation potential graphite substitutes anode materials. In fact, LTO is commercially available as an alternative or possible replacement of graphite for lithium-ion batteries. However, the LTO has a low theoretical capacity of 175 mAh g$^{-1}$, a poor electronic and lithium ionic conductivities which limit its high-rate capability [24–27]. Alternatively, the theoretical capacity of TiO$_2$ is 335 mAh g$^{-1}$ that is gravimetrically comparable with the commercialized graphite (372 mAh g$^{-1}$) [28]. In addition, it operates at a relatively high voltage (1.5–1.8 V versus Li/Li$^+$) where most organic electrolytes are thermally stable [21]. TiO$_2$ affords LIBs safety with a volume...
change of \(<3\%\) during insertion of Li-ions, which makes this material of exceptional value [29]. The latter is considered the most important requirement for LIBs, especially for stationary energy storage purposes [23]. It is also an abundant resource with relatively low costs, environmentally friendly and chemically stable [23, 29–31]. Unfortunately, TiO\(_2\) is associated with conductivity and ion transport limitations during cycling, which makes it a poor electrical conductor with low diffusion coefficient of the Li-ions [32]. Moreover, TiO\(_2\) has low specific capacity of 160 mAh g \(^{-1}\). Some approaches were explored to increase specific capacity of TiO\(_2\) to reach theoretical capacity, including restructure, composited with other materials, carbon coating and ion doping [13, 33, 34]. Among these, the nanostructured materials, including nanowires, nanotubes, nanosheets, nanorods and nanofibres have afforded some advantages, improving the capacity, cycle life and rate capability. Although, the larger surface area of the nanostructured materials reduces the diffusion length, the many active sites allow uncontrollable external reactions to occur, which would result in biased overall performance of the material [34, 35]. Besides three natural polymorphs of tetragonal anatase, tetragonal rutile, and orthorhombic brookite phases, TiO\(_2\)-bronce (B) phase has attracted great attention due to its unique monoclinic structure with fibrous morphology. It possesses a relatively lower density/higher volume than that of the three popular phases of the anatase, rutile, or brookite [36].

In this work, we report on the hydrothermally synthesized TiO\(_2\) (B) under different temperatures. Additionally, the effects of thermal treatment on the morphology and electrochemical performance of the materials are explored. Moreover, a comparison study of the battery performances are carried out between the precursors (hydrogen titanates) and TiO\(_2\) (B) nanorods through thermal treatment.

2. Experimental section

2.1. Synthesis of TiO\(_2\) nanorods

TiO\(_2\) (P25, Degussa, Germany) powder was washed with deionised water to remove impurities prior to the synthesis. A two-step synthesis procedure was followed to produce TiO\(_2\) nanorods from the preliminary product, hydrogen titanate (HTO) materials using the hydrothermal method [37]. In the first step, TiO\(_2\) powder was mixed with 150 ml of 10 M NaOH aqueous solution. After stirring for 2 h the suspensions were transferred into a Teflon-lined autoclave and heated at different temperatures (140, 160 and 180 °C) for 48 h with continuous stirring. The products were filtered, acid-washed with 0.1 M HCl, filtered again and finally washed with distilled water to a neutral pH and dried at 110 °C overnight. The products were marked as HTO140, HTO160 and HTO180, respectively. The samples were then annealed in the second-step using a tube furnace at 400 °C for 2 h under air to obtain TiO\(_2\) (B) nanorods labelled as TO140, TO160 and TO180, respectively.

2.2. Materials characterization

The resultant powders were characterized by an x-ray diffractometer (Rigaku, Japan) using a CuK\(_\alpha\) radiation with \(\lambda = 0.1545 \text{ nm}\) at 45 kV and 40 mA. The morphology of the materials was determined by the field emission scanning microscope (FE-SEM, Joel JSM-7500F, Tokyo, Japan). An ink was made from the active material, carbon black and binder with ratio of 80:10:10, respectively in N-methyl-pyrrolidone (NMP). The ink was uniformly spread on a copper foil using a doctor blade and dried in a vacuum oven at 110 °C overnight. The electrochemical coin cells (CR 2032) were assembled in an argon filled glove box with oxygen (O\(_2\)) and moisture (H\(_2\)O) contents less than 10 ppm. The HTO and TO as the working electrodes, while Li metal was used as both the reference and counter electrodes. Celgard porous propylene film as the separator and 1 M LiPF\(_6\) dissolved in a 1:1:1 ratio mixture of ethylene carbonate (EC)/diethyl carbonate (DEC)/dimethyl carbonate (DMC) was used as the electrolyte. The assembled coin cells were aged for 24 h prior to the electrochemical measurements. The MACCOR battery tester (series 4000, Tusla, USA) was used for testing battery performance. The mass of the active material was used to calculate the current density and the specific capacity. The electrochemical impedance spectrometry (EIS) and cycle voltammetry (CV) experiments were carried out using a Bio-Logic science VMP3-based instrument.

3. Results and discussion

3.1. SEM images

The SEM images in figure 1 depict the morphology of the as-synthesised materials, HTO140, HTO160, HTO180, and TO160 and the commercial TO. The commercial TO shows nanoparticles in the range 40–60 nm and were converted to HTO nanorods (figures 1(b)–(d)) after the hydrothermal treatment. With increasing temperature, more HTO layers were formed and became longer, as shown in figures 1(b)–(d). For comparison, the SEM image of TO160 in figure 1(e) shows rods through edging differences compared with the layered HTO160 (figure 1(c)), although both materials have similar sizes and shapes.
3.2. XRD analysis

The XRD patterns of the as prepared HTO, TO materials and the commercial TO are depicted in figure 2. All the observed diffraction patterns of the commercial TO in figure 2(a) were consistent with the crystal structure of anatase (ICPDS-21–1272) with impurity traits of rutile marked R [38]. The HTO140, HTO160 and HTO180 powders (figure 2(a)), can be identified as mixtures of H$_2$Ti$_3$O$_7$ and H$_x$Ti$_{2-4x/2}$O$_4$ ($x = 0.75$) with typical plane of (200) located in $\sim$10° [39]. With increasing temperature, the peak of the (200) plane increased also, indicating the improved crystallinity of HTO. Figure 2(b) shows the XRD of TO nanorods from HTO materials and commercial TO. It is interesting that HTO140 converted to the pure anatase phase (TO140) without rutile impurities. TO160 and TO180 materials were corresponding to the monoclinic TiO$_2$ (B) phase with typical planes of [110], [101], [003], [020] and [022] [40, 41]. The formation of the phases can be explained from the following mechanism during the synthesis process on mixing TO powder with NaOH solution at high temperatures, the Ti–O–Ti bond might cleave to form a mixture of layered sodium titanate (Ti–O–Na). The lamellar sheets will then form due to the electrostatic repulsion of the charge on the Na. Acid wash with HCl causes an ion exchange between the Na$^+$ and H$^+$ to obtain the HTO [40, 41]. Therefore, it is only after calcination of HTO that the loss of water gives TO as the resultant product. However, it is evident that only TO140 was able to convert to pure anatase TO phase, while TO160 and TO180 exhibited the monoclinic TiO$_2$ (B) structure. This is suspected to be due to hindrances within the crystal structure for proper roll up of the lamellar sheets into rods influenced by the effects of temperature during the synthesis [40]. Previous studies reported that temperatures greater than 150 °C during the synthesis are prone to destruct the roll up of the lamellar sheets due to granular particles from agglomerations and this decreases the surface area and pore size [40, 41].
3.3. Battery performance

The battery behaviours of the HTO before and after annealing as well as the commercial TO materials are shown in figure 3 and table 1. The discharge/charge profiles in figures 3(a), (b) displays similar behaviours with the HTO nanosheets without platform [42].

The HTO materials delivered capacities in the range of 122.9–140.2 mAh g⁻¹ at 200 mAg⁻¹ as illustrated in figure 3(a) and table 1, which are lower than that of 161.3 mAh g⁻¹ of the commercial TO nanoparticles. The order of capacity decrease was the commercial TO (160 mAh g⁻¹) > HTO180 (140.2 mAh g⁻¹) > HTO140 (126.5 mAh g⁻¹) > HTO160 (122.9 mAh g⁻¹). After annealing, TO140 showed an improved capacity and better reversibility compared to HTO140 in figure 3(b). TO160 maintained a similar capacity with HTO160. However, the capacity of TO180 worsened compared to it precursor of the HTO180.

To further evaluate the battery performance, the rate performances were plotted in figures 3(c), (f) at various current densities (100–1000 mA g⁻¹) for HTO, TO and commercial TO materials. Generally, the rate performance shows the relation between capacity and increasing current density. In addition, the retained capacity corresponds to the stability of the material. It can be seen in figure 3(e) that the discharge capacity of the commercial TO material is highest in the lower current density (100–200 mA g⁻¹) among the other materials. However, the HTO140 shows the best capacity in the current range of 500–1000 mA g⁻¹. The HTO180 capacity
decreased drastically when the current increased. After annealing, TO160 shows the best performance in the full range of current, followed by TO140 and TO180 as depicted in figure 3. The cycling performances of the commercial TO and the HTO materials were also tested before and after annealing at 200 mAg\(^{-1}\) for 100 cycles as displayed in figures 3(e), (f). Before annealing, HTO160 had the best stability with 71.5% retained capacity after 100 cycles, followed by HTO140 (65.0%), HTO180 (53.9%) and TO (44.4%), which is in agreement with the rate performances of figure 3(c). After annealing, the TO materials displayed the same order with the HTO materials, TO160 had the best stability with 92.3% retention, which matches with the rate performance displayed in figure 3(d). The coulombic efficiency of the materials were compared in figures 3(e), (f). It is observed that all the materials show low initial efficiency and after few cycles remain above 99% through 100 cycles.

### 3.4. Electrochemical behaviour

Figure 4 displays cycle voltammetry (CV) and electrochemical impedance spectrometry (EIS). To understand the ionic diffusion process and phase transformation during the electrode reactions, the CV curves were conducted in the potential range of 1.0 ~ 3.0 V at a scan rate of 0.1 mV s\(^{-1}\) as shown in figure 4(a), (b). The anodic peaks of the HTO materials in figure 4(a) were more negative and wide compared with the commercial TO material. The pair of peaks on the HTO materials are ascribed to the pseudocapacitive lithium storage behaviour, while the pair of the commercial TO at 1.5(1.7)/2.1 V are assigned to the solid-state lithium diffusion.
into TiO₂, which are consistent with previously reported data [43–45]. The TO electrode has two cathodic peaks due to impurities. By comparing the CV curves of the TO electrode with that of the HTO, the gap between the redox peaks of the latter are smaller, indicating a lower electrode polarization and a higher lithium-ion diffusivity.

The CV curves of the HTO materials after annealing are shown in figure 4(b). Compared with the TO160 and TO180, it was observed that the shapes of redox peak on the TO140 electrode at 1.5/2.2 V are sharper and intense, which is similar to the commercial TO due to the pure anatase phase of the TO140. It is notable that the TO160 shows two pairs of peaks at 1.3/1.7 V and 1.7/2.1 V, which are a match with the pseudocapacitive process and lithium intercalation of TiO₂ (B). The gap between the redox peaks of the TO160 and TO180 are smaller than that of the TO140. The phenomenon confirms that the HTO with/without annealing are beneficial to intercalation/deintercalation of lithium.

Figures 4(c), (d) shows the Nyquist plot for both the HTO and TO electrodes. All the Nyquist plots are defined by a semicircle at high frequencies and a straight line at low frequencies, corresponding to the charge transfer (Rct) and diffusion of Li ions, respectively [46]. The Rct values of the HTO140, HTO160 and HTO180 are 383.4, 422.3 and 1412.5 Ω, respectively, which are lower than the 1470.3 Ω of the TO. After annealing, the increasing order of Rct value is TO140 (362.5 Ω) < TO160 (520.3 Ω) < TO180 (832.1 Ω). Overall, the prepared HTO materials before/after annealing have shown better charge transfer than the commercial TO.

4. Conclusions

A series of hydrogen titanates (HTOs) were synthesised at 140, 160, and 180 °C using the hydrothermal method. TiO₂ nanorods were obtained after annealing of the HTO at 400 °C for 2 h. HTO140 converted to the pure anatase TiO₂ nanorods (TO140). While HTO160 and HTO180, synthesised above 140 °C formed TiO₂ (B) nanorods. The HTO and the TO materials battery performances were explored as promising anode materials. The HTO materials displayed lower initial discharge capacity (~123–~140 mAh g⁻¹) than that of their precursor (~160 mAh g⁻¹) at a current of 200 mAg⁻¹. However, the HTO140 showed better rate performance than that of the precursor in the higher rates. Moreover, the HTO160 exhibited best stability with 71.5% retention after 100 cycles at 200 mAg⁻¹. After annealing of the HTO materials, the TO140 material demonstrated the highest initial discharge capacity. However, TO160 showed superior stability with 92.3% retained capacity after 100 cycles at 200 mAg⁻¹.

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