Formation of TiO$_2$(B) Prepared from Lepidocrocite Type Precursor Containing Potassium

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ABSTRACT

A new synthetic route for TiO$_2$(B) via lepidocrocite type K$_x$LiyTi$_2$O$_{4+x}$ (KLTO) was established. Pure layered titanate acids were obtained by proton exchange of KLTO in 3 mol dm$^{-3}$ HNO$_3$ and HCl solution. The obtained titanate acid transformed into TiO$_2$(B) phase at 350°C and it was stable up to 450°C. Plate-like morphology particles was formed during proton exchange and transformation process to TiO$_2$(B). TiO$_2$(B) samples with high tapping density (0.9–1.1 g cm$^{-3}$) was prepared and they delivered discharge capacities of more than 100 mAh g$^{-1}$ even at 2 C.

Keywords: Lepidocrocite, Plate-Like TiO$_2$(B), High Potential Anode Material, Lithium Ion Battery

1. Introduction

Carbon anode is widely used in Lithium-Ion Batteries since it was first commercialized by Sony Company in 1990. Although the relatively high specific capacity of carbon has made it a successful anode material for lithium ion battery, the lower working voltage of carbon still hinders its further application in large size batteries. Recently, some alternative anode materials for carbon have been studied extensively. Among them Sn based alloy$^1$ anode with higher capacity and spinel Li$_2$Ti$_3$O$_7$$^{2,3}$ anode with better safety have been commercialized recently.

So far, various titanium oxides have been proposed as high potential anode material for lithium-ion batteries. Massive materials, such as Li$_2$Ti$_3$O$_7$, Li$_4$Ti$_5$O$_12$, and TiO$_2$(B)$^8$ as well as nano-materials, such as anatase TiO$_2$, rutile TiO$_2$, TiO$_2$(B)$^{11,12}$ and amorphous TiO$_2$, have been intensively evaluated as anode materials for lithium ion batteries. From the practical viewpoint, massive material is suitable to withdraw higher volumetric capacity. Furthermore, Inaba et al. have clarified that the degradation of anode caused by carbon can be avoided in TiO$_2$(B)$^8$ which would be an advantage as anode materials in lithium ion battery.

Since massive and nano-size TiO$_2$(B) gives highest gravimetric capacity among TiO$_2$ polymorphs, it becomes a strong candidate for high voltage anode material in lithium-ion batteries. The aforementioned TiO$_2$(B) was prepared by the heat-treatment of titanate acid, which were prepared either by proton exchange of K$_2$Ti$_4$O$_9$ (massive)$^5$ or sodium titanate through hydrothermal method (nano-size).$^{13}$ The shapes of both TiO$_2$(B) were needle, wire or rods which were similar to the shape of the parent materials. Such morphology and smaller particle size gave lower tapping density, around 0.3 g cm$^{-3}$. Therefore, isotropic morphology and large particle size would be suitable as a precursor for preparing dense electrode.

Herein, we developed a new route for the synthesis of TiO$_2$(B) in which the KLTO compounds were prepared from titanate K$_x$LiyTi$_2$O$_{4+x}$ with γ-FeOOH (lepidocrocite) type structure,$^3,6$ and amorphous TiO$_2$, were used to prepare dense TiO$_2$(B). KLTO compounds have relatively isotropic particle shapes and the resulting TiO$_2$(B) with plate-like shape have higher tapping density, which leads to dense electrode for the evolution of high energy density in lithium ion batteries.

2. Experimental

Precursor KLTO was prepared from K$_2$CO$_3$, LiCH$_3$COO 2H$_2$O and anatase TiO$_2$ or amorphous TiO$_2$ (ca. 50 nm). All reagents were obtained from Wako Pure Chemicals. The chemical composition was calculated from the weight of the above starting materials. After adding the starting materials with water, the mixture was heated up to 500°C to remove organic component. Finally, the mixture was heated at 900°C for 10 h. The resulting precursor was then immersed into 0.5–5 mol dm$^{-3}$ HNO$_3$ or HCl solution during one night and the precipitated titanate acid was filtrated. The obtained titanate acid was transformed to TiO$_2$(B) by heating at higher temperature than 250°C. The powder samples were analyzed by X-Ray Diffraction (XRD, Rigaku, RINT1000), Thermo-Gravimetric/Differential Thermal Analysis (TG/DTA, Rigaku, TG-8110), Scanning Electron Microscope (SEM, JOEL, JSM-5200), and N$_2$ gas adsorption with Floworb II (SHIMADZU, FlowPrep-060). TG-DTA measurement was performed under air atmosphere at a heating rate of 5°C/min.

Electrochemical measurements were carried out by using the CR2320 coin cell. Typically, the working electrode was fabricated by compressing a mixture of 20 mg active material and 10 mg conducting binder. Lithium metal was used as a counter electrode. The cells were assembled in the argon conducting binder. Lithium metal was used as a counter electrode. The cells were assembled in the argon filled glove box. The electrolyte was 1 mol dm$^{-3}$ LiPF$_6$ EC-DMC (1:1 in volume). The cell was cycled between 2.5 and 1.0 V (vs. Li/Li$^+$) at current density of 0.2 or 0.4 mA cm$^{-2}$.

3. Results and Discussions

3.1 Chemical composition of lepidocrocite phase

Figure 1 shows XRD profiles of K-Li-Ti-O compounds prepared from anatase TiO$_2$ by heating the mixture of various Li content (K/Ti = 1/2, Li/Ti = 0–0.15 in atomic ratio) at 900°C. It was found that new peaks are developed at Li/Ti = 0.15. New peaks coincided with those of lepidocrocite type structure, which would be written as $K_x$Ti$_{2-\alpha/3}$Li$_{\alpha/3}$O$_4$ (0.7 ≤ $\alpha$ ≤ 0.8).$^{15}$ Chemical composition of prepared lepidocrocite type compound was described as $K_{0.69}$Ti$_{1.77}$Li$_{0.23}$O$_{4.04}$, which is slightly different from the reported values, $K_{0.60}$Ti$_{1.77}$Li$_{0.23}$O$_{4.04}$ (x = 0.69). Orthorhombic lattice parameters of $K_{0.69}$Ti$_{1.77}$Li$_{0.23}$O$_{4.04}$ were...
calculated to be a = 0.38 nm, b = 1.55 nm, and c = 0.30 nm, respectively. Those values are closed to reported values of K0.8Ti1.73Li0.27O4 (x = 0.8) (a = 0.382 nm, b = 1.553 nm, and c = 0.30 nm). Amorphous TiO2 gives similar products with anatase TiO2. The formation of lepidocrocite phase was examined in detail at 900°C. Eleven samples were found to be pure lepidocrocite phase and both atomic ratios of metal ions in starting material as well as chemical composition expressed by KA(Ti2Liy)O4 were summarized in Table 1. Additional impurity phases are Li2TiO3 and K2Ti4O9 for higher and lower Li content, respectively. The mixtures for higher and lower K content are K2Ti6O13, K2Ti2O5 and Li2TiO3 and that of K2Ti6O13 and Li0.88Ti2.2O4, respectively.

The authors postulated chemical formula of the lepidocrocite phase as KxTi2(y+x/4)LiyO4 and determined by the values of x, y, and m, respectively. Plots of (x + y)/m against x + y and those of x against y are illustrated in Figs. 2(a) and 2(b), respectively. Excellent linear relationship is observed in Fig. 2(a) and m value is exactly determined to be 4.0. On the other hand, weak correlation between x and y was observed. The ratio of x/y are scattered between the range of 3.0 to 3.6. Then empirical chemical formula of the lepidocrocite phase is expressed as KxTi2(y+x/4)LiyO4 (0.96 < x + y < 1.22, 3.0 < x/y < 3.6). This chemical formula is similar to that of Cs containing lepidocrocite phase, Cs6Ti2x-yLiyO4.18

3.2 Formation of titanic acid from lepidocrocite phase

Four kinds of mineral acids, such as HNO3, HCl, H2SO4, and HClO4, were used for proton exchange of KLTO. Among them H2SO4 and HClO4 were not suitable, because it was difficult to remove SO4<sup>2-</sup> and ClO4<sup>-</sup> even by careful washing. Sample 1, K0.860Ti1.720Li0.258O4, was used to examine the proton exchange reaction of KLTO precursor. Effect of proton exchange condition with HNO3 for the formation of titanic acid was examined by using XRD and the results are shown in Figs. 3 and 4. KLTO precursor phases were found to remain in the case of 0.5 and 1 mol dm<sup>-3</sup> of HNO3. At higher concentration more than 3 mol dm<sup>-3</sup> of HNO3, it could completely convert KLTO to titanic acid. The obtained titanic acid had various interlayer distances, which could be easily calculated from the XRD peaks at around 10°. The interlayer distances of titanic acids were 0.70 nm by the proton exchange in 3 mol dm<sup>-3</sup> HNO3 as well as 0.75 and 0.88 nm in 5 mol dm<sup>-3</sup> HNO3, respectively. Similar results were obtained in HCl treated samples. Besides this, the interlayer distances were found to be different from

![Figure 1](image1.png)  
Figure 1. XRD profiles of KLTO prepared at 900°C.

![Figure 2](image2.png)  
Figure 2. Relation between (x + y)/m and x + y (a) and between x and y (b) in KxTi2-xLiyO4.

![Figure 3](image3.png)  
Figure 3. XRD profiles of titanic acids prepared from K0.860Ti1.720Li0.258O4 and HNO3(0.5–5 mol dm<sup>-3</sup>) at room temperature.

![Figure 4](image4.png)  
Figure 4. XRD profiles of proton exchange products from K0.860Ti1.720Li0.258O4 and 3 mol dm<sup>-3</sup> HNO3 at various temperature.

<table>
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<tr>
<th>No.</th>
<th>Metal ratio</th>
<th>Chemical composition</th>
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<tr>
<td>1</td>
<td>2 4 0.6</td>
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</tr>
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<td>2.24 4 0.64</td>
<td>K0.940Ti1.645LiyO4</td>
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Table 1. Chemical composition of pure lepidocrocite phase.
Figure 5. TG/DTA curves of titanic acid prepared from K$_{0.860}$Ti$_{1.720}$Li$_{0.258}$O$_4$ and 3 mol dm$^{-3}$ HNO$_3$ at room temperature.

Figure 6. XRD profiles of heat-treated titanic acids at 250–500°C.

Figure 7. Relation between 2 V plateau capacities and Ti/K ratio in lepidocrocite type KLTO.

that of HNO$_3$ treated samples and the values were 0.70 and 0.79 nm for 3 and 5 mol dm$^{-3}$ HCl, respectively.

XRD profiles of proton exchange products in 3 mol dm$^{-3}$ HNO$_3$ solution at various temperatures are shown in Fig. 4. Trace amount of KLT$_O$ was suggested to be remain at 10°C, because the peak at 2θ = 29° could be assigned to KLT$_O$ precursor. Titanic acids with various interlayer spacing (0.74–0.91 nm) were formed in the reaction at 30–70°C, where the higher reaction temperature caused the decrease of interlayer distance due to the lower content of water in titanic acid at the time of treating at higher temperature. However, reaction temperature higher than 80°C was not appropriate because of the undesirable side reactions, such as the formation of rutile phase. Slightly different behavior was observed in HCl solution. In this case, interlayer spacing at 30°C was 0.7 nm and that at 40–70°C were calculated to be 0.91 nm. Finally, from the above results, we can conclude that the interlayer spacing of titanic acid strongly depended on the proton exchange conditions and the value changed from 0.7 to 0.91 nm.

3.3 Formation of TiO$_2$(B) by heating titanic acid

Since TiO$_2$(B) is generally prepared by the heat-treatment of titanics, it is very important to clarify the thermal property of titanic acid. The results of TG/DTA analysis of titanic acid prepared by HNO$_3$ treatment for precursor sample 1 at RT are shown in Fig. 5. Weight losses were observed in three temperature regions which were less than 200, 200–320, and 320–500°C. Initial two regions accompanied with endothermic peaks and the value of weight loss was approximately 3.6 wt%, which was slightly larger than that of the latter region. Ideal proton exchange product of sample 1 was described as H$_{1.118}$Ti$_{1.72}$O$_4$ (TiO$_2$ 0.325H$_2$O). On the other hand, chemical formula of titanic acid could be calculated by the total weight loss, 6.1 wt%, which means the chemical formula of obtained titanic acid is expressed as TiO$_2$ 0.5H$_2$O. Therefore, above formula could be expressed as H$_{1.118}$Ti$_{1.72}$O$_4$ 0.3H$_2$O. If excess water intercalated into interlayer of titanic acid and changed the water content, weight loss of titanic acid became high. In practice, weight loss of titanic acid with wider interlayer distances reached ca. 8–20 wt% and main increase in weight loss was observed at lower temperature than 200°C.

XRD profiles of several heat-treated products of titanic acid obtained from sample 1 are shown in Fig. 6. XRD profile of the product at 250°C was constructed by two types of peaks. Sharp peaks appeared at 2θ = 12, 25, 45, and 48° could be assigned to original titanic acid. On the other hand, new broad peaks at ca. 15 and 30° were due to TiO$_2$(B). Heat-treatment at 350°C caused complete transformation of layered titanic acid to TiO$_2$(B). Similar XRD pattern was observed for the product at 450°C. However heat-treatment at 500°C caused the formation of anatase phase which was confirmed by the appearance of peak at 2θ = 26°. Since the formation of anatase phase from titanic acids prepared from K$_2$Ti$_4$O$_9$ and Cs$_2$Ti$_5$O$_{11}$ starts at 500°C,14,19 there are no remarkable differences in thermal stability of TiO$_2$(B) prepared from various precursors.

It was reported that XRD peaks of TiO$_2$(B) obtained from lepidocrocite type precursor are broader than those prepared from the other precursors.14,19 Such poor crystallinity might be due to the presence of cation vacancy in titanic acids as reported in H$_{1.118}$Ti$_{1.72}$O$_4$ obtained from lepidocrocite type C$_{0.8}$Ti$_2$O$_4$.18 It is well known that the contamination of anatase phase in TiO$_2$(B) causes the degradation of anode property in lithium ion battery, however it is difficult to judge the presence of anatase phase from their XRD profiles. Since anatase TiO$_2$(B) shows characteristic discharge plateau at ca. 2 V,14 we propose that contamination of anatase phase in TiO$_2$(B) can be evaluated by using capacity of 2 V plateau at 0.1 mA cm$^{-2}$. Various TiO$_2$(B) samples heated at 450°C were prepared from the variety of lepidocrocite precursors with different Ti/K ratio. Figure 7 shows relation between capacities of 2 V discharge plateau and Ti/K ratio in precursor. Since the lowest capacity was observed at Ti/K = 2.0, we conclude that K$_{0.860}$Ti$_{1.720}$Li$_{0.258}$O$_4$ is the best precursor to prepare TiO$_2$(B) via titanic acid.

The SEM images of original KLTO (prepared from anatase TiO$_2$ at 900°C), titanic acid, and TiO$_2$(B) are shown in Fig. 8. The shapes of KLTO were cubic or rectangular with particle size around 3–20 μm and it was different from needle like K$_2$Ti$_4$O$_9$ or nanowire sodium containing titanic.31 Clear cleavage or exfoliation of the particles was observed for titanic acid. Such cleavage would occur along (010) plane based on the character of lepidocrocite and gives plate-like titanic acid with the thickness of ca. 0.5 μm. The cleavage may be accelerated during the transformation of TiO$_2$(B) accompanying the release of H$_2$O. Thickness of plate became 1/3 to 1/10 during phase transformation and isolated thin sheets could also
be observed. Similar behaviors were observed when amorphous TiO₂ was used as the starting materials. The BET surface area of TiO₂(B) prepared from anatase TiO₂ is 3.2 m²/g, which is ca. 1/3 of TiO₂(B) prepared from amorphous TiO₂ (9.8 m²/g). Tapping densities prepared from anatase and amorphous TiO₂ was ca. 1.1 and 0.9 g dm⁻³, respectively. Those values were much higher than that of prepared by Cs₂Ti₅O₁₁ with needle-like shape, 0.3 g dm⁻³. 

3.4 Electrochemical property of TiO₂(B)

The rate performances for 2 kinds of TiO₂(B) prepared from anatase TiO₂ and amorphous TiO₂ are shown in Fig. 9. That samples were prepared by heat-treatment at 350°C and typical S type curves were observed for both samples as reported in the literatures. In addition of that TiO₂(B) sample obtained from amorphous TiO₂ gave 2.2V discharge plateau at a lower discharge rate of 0.4 mA cm⁻², even though the optimized composition was used. That plateau was considered to be due to existence of anatase TiO₂. Charge capacities of both TiO₂(B) were ca. 200 mAh g⁻¹, however, their discharge capacities were 140 and 153 mAh g⁻¹ at 0.4 mA cm⁻². In spite of the presence of anatase phase, TiO₂(B) prepared from amorphous TiO₂ showed higher capacity than that from anatase TiO₂. The variation of the capacities were explained by the difference in their surface area. On the other hand, both samples delivered discharge capacity more than 100 mAh g⁻¹ at 5 mA cm⁻² (ca. 2C). Such performance is much poorer than the reported values. Lithium ion diffusion in TiO₂(B) proceeds one dimensionally and its direction is parallel to plate surface. Consequently, new morphology of TiO₂(B) would not be suitable for lithium ion diffusion.

4. Conclusion

Formation process of TiO₂(B) from lepidocrocite type K-Li-Ti-O compound was examined in details. Chemical composition of lepidocrocite type precursor was determined to be KₓTi₂₋ₓ(4−3x)/₂Li₂O (0.96 < x < 1.22, 3.0 < x+y < 3.6). Layered titanic acid formed by immersion in 3 mol dm⁻³ HNO₃ and HCl during one night. In this case, temperature was an important factor and it was found that the temperature range from room temperature to 70°C was favorable. Water content in titanic acid was also influenced by proton exchange condition and titanic acid with high water content shows large amount of weight loss at lower temperature than 200°C and higher interlayer distance. The cleavage of particle initially occurred during the transformation of titanic acid and it was accelerated in the formation process of TiO₂(B). Although the electrochemical properties of the as-prepared TiO₂(B) were far from perfect, we could successfully synthesize plate-like TiO₂(B) with higher tapping density around 0.9–1.1 g cm⁻³. Further study is necessary to optimize the synthetic route to improve the electrochemical properties of plate-like TiO₂(B).

References