Irreversible Capacity and Lithium-ion Insertion/Extraction Kinetics of a High Potential Negative Electrode $\text{TiO}_2(\text{B})$

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Li^+ ion insertion/extraction properties of $\text{TiO}_2(\text{B})$ powder, which was prepared from a $\text{K}_2\text{Ti}_4\text{O}_9$ precursor by ion-exchange and dehydration, was investigated as a high-potential negative electrode. The irreversible capacity greatly decreased from 124 mAh g^{-1} to *ca.* 40 mAh g^{-1} when the lower potential limit was raised from 1.0 V to $E \geq 1.2$ V, which indicated that the irreversible capacity mainly originated from surface reactions, such as solvent decomposition, at $E \leq 1.2$ V in the first cycle. In galvanostatic intermittent titration tests, large polarization was observed at the beginning and the end of charging. This clearly indicated that a slow process is involved in the insertion reaction at the beginning and the end of charging, which causes solvent decomposition at potentials lower than 1.4 V. The reversible capacity was greatly improved to 246 and 276 mAh g^{-1} at an elevated temperature of 60°C and at a lower rate of C/60, respectively. The $\text{TiO}_2(\text{B})$ sample contained *ca.* 14 wt% of the anatase phase as an impurity, and a reduction of the anatase phase was found to be effective for an increase in reversible capacity at moderate charge/discharge rates.

Key Words : $\text{TiO}_2(\text{B})$, High Potential Negative Electrode, Irreversible Capacity, Cycleability

1 Introduction

Recently, large-size lithium-ion batteries (LIBs) have been intensively developed for use in electric vehicles and energy storage systems. However, there remain serious problems, such as safety, durability, and cost, to be solved before commercialization of large-size LIBs.¹⁾ The use of high potential negative electrodes working at potentials > 1.0 V vs. Li/Li^+ is one of the methods for solving these issues. It has recently reported that nanowires²⁻⁴⁾ and nanotubes⁵⁻⁷⁾ of $\text{TiO}_2(\text{B})$ prepared by hydrothermal treatment have a high capacity of $200\text{--}300 \text{ mAh g}^{-1}$ at about 1.6 V vs. Li/Li^+ with good cycleability.^{2,3)} However, the hydrothermal process is not suitable for mass production, which raises the material cost of $\text{TiO}_2(\text{B})$. From this viewpoint, we have prepared $\text{TiO}_2(\text{B})$ powder from a $\text{K}_2\text{Ti}_4\text{O}_9$ precursor, which was synthesized by a solid-state reaction, and investigated charge/discharge characteristics of the $\text{TiO}_2(\text{B})$ powder as a high potential negative electrode in LIBs.⁸⁾ It had a high discharge capacity of $200\text{--}250 \text{ mAh g}^{-1}$ at around 1.6 V vs. Li/Li^+ , though the capacity was lower than its theoretical capacity (335 mAh g^{-1}). It also showed very good cycleability, and gave a discharge capacity of 171.5 mAh g^{-1} even after 650 cycles (1.0–3.0 V). However, the sample had a high irreversible capacity of 123.0 mAh g^{-1} in the first cycle. It is therefore necessary to reduce the irreversible capacity as well as to further improve the capacity close to the theoretical capacity (335 mAh g^{-1}).

In the present study, Li^+ ion insertion/extraction properties of $\text{TiO}_2(\text{B})$ were investigated in detail to understand the origin of the irreversible capacity and rate-limiting

processes involved in the charge and discharge reactions.

2 Experimental

K_2CO_3 (Wako Pure Chemicals, 99.8%) and anatase TiO_2 (Wako Pure Chemicals, 99.9%, average diameter: 20 nm) were mixed in a molar ratio of 1:4, and calcined twice at 1000°C for 24 h to obtain $\text{K}_2\text{Ti}_4\text{O}_9$ powder as a precursor. The $\text{K}_2\text{Ti}_4\text{O}_9$ powder was washed with highly pure water, and was immersed in 1 M HCl for 3 days to exchange the K^+ ions to protons. The resulting protonated powder was dehydrated at 500°C for 30 min to obtain $\text{TiO}_2(\text{B})$. The powder sample was analyzed by X-ray diffraction (XRD, Rigaku, RINT2000) and field-emission scanning electron microscopy (FE-SEM, JEOL, JSM7001FD). The content of the anatase phase in the $\text{TiO}_2(\text{B})$ sample was determined by an internal standard method, in which CaCO_3 and NiO were used as an internal standard substance and as a diluent agent, respectively. The calibration line was obtained from the ratio of the (101) line of the anatase phase and the (104) line of CaCO_3 using the mixtures of anatase TiO_2 (Merck, 99.9%) and CaCO_3 (Wako Pure Chemicals, reagent grade) powder of different compositions.

The $\text{TiO}_2(\text{B})$ powder was mixed with Ketjen Black (KB, Lion Corp., EC600JD) and poly(vinylidene fluoride) (Kureha, KF Polymer) at a weight ratio of 8:1:1, using 1-methyl-2-pyrrolidinone (Wako Pure Chemicals, reagent grade) as a solvent, to make a viscous slurry. The slurry was coated on a copper foil current collector (0.785 cm^2) with a thickness of 100 μm , and then dried overnight at

80 °C under vacuum. The loading of the electrode material was *ca.* 1.5 mg cm⁻². The electrolyte solution was either 1.0 M LiClO₄ dissolved in a 1:1 mixture (by volume) of ethylene carbonate (EC) and diethyl carbonate (DEC) or 1.0 M LiPF₆/EC + DEC (1:1). A coin-type two-electrode half cell was constructed from the TiO₂(B) electrode, a separator (Celgard® 2326) and a lithium-foil counter electrode (Honjo Metal) in argon-filled glove box (Miwa, MDB- 1B + MM3-P60S) with a dew point lower than -60 °C. Charge and discharge characteristics were measured at a C/6 rate between 1.0 V and 3.0 V at 30 °C, unless otherwise noted, using a battery test system (Hokuto Denko, HJ1001SM8). In the present study, lithium-ion insertion into and extraction from TiO₂(B) are denoted as charging and discharging, respectively, considering the role of TiO₂(B) as a negative electrode in LIBs.

The variation of open-circuit potential (OCP) during charging and discharging was measured using the galvanostatic intermittent titration technique (GITT). The electrode was charged or discharged by $x = 0.05$ in Li_xTiO₂(B) at a C/6 rate, and was left for 24 h under open-circuit conditions to measure OCP. This procedure was repeated until the potential reached 1.0 or 3.0 V on charging and discharging, respectively.

3 Results and Discussion

Figure 1 shows the XRD pattern for the synthesized TiO₂(B) powder. The formation of the TiO₂(B) phase (JCPDS 35-0088) was confirmed after the dehydration process. Unfortunately, the TiO₂(B) powder was not a single phase, but contained a considerable amount (14 wt %) of the anatase phase, which was probably formed in the final dehydration process at 500 °C.⁹⁾

SEM images of the TiO₂(B) powder are shown in Fig. 2. The powder has a needle-like structure with a diameter of *ca.* 250 nm and a length of *ca.* 2 μm. The shape, needle-like structure, is characteristic of the K₂Ti₄O₉ precursor, and did not change appreciably after the ion exchange and dehydration processes. Hence the shape of TiO₂(B) is determined in the first calcination process.

Figure 3 shows the charge/discharge curves of the TiO₂(B) powder at 30 °C in 1 M LiClO₄/EC + DEC(1:1). The TiO₂(B) powder gave a high discharge capacity of *ca.* 250 mAh g⁻¹ with a slightly sloping plateau at around 1.6 V on the charge and discharge curves, which are similar to those reported for TiO₂(B) nanowire²⁻⁴⁾ and nanotubes.⁵⁻⁷⁾ The initial discharge capacity of 246 mAh g⁻¹ is higher than that of Li₄Ti₅O₁₂¹⁰⁻¹²⁾ and comparable with those of TiO₂(B) nanowires and nanotubes. On the other hand, a considerably high irreversible capacity (123 mAh g⁻¹) was observed in the first cycle, but disappeared in the second and subsequent cycles. After an initial drop in discharge capacity, high discharge capacities of *ca.* 200 mAh g⁻¹ with Coulombic efficiencies close to 100% were stably obtained in prolonged cycles.⁸⁾ The discharge capacity as high as 170 mAh g⁻¹ was obtained even in the 650th cycle as shown in Fig. 3. The good cycleability indicates a high structural integrity of TiO₂(B), though it is a metastable phase.

One of the drawbacks of TiO₂(B) is the high irreversible capacity in the first cycle as described above. To understand the origin of the irreversible capacity, we investigate the effect of the lower potential limit in charge and discharge tests. Figure 4 shows charge/discharge curves of the TiO₂(B) in various potential ranges of (a) 1.6-3.0, (b) 1.4-3.0, (c) 1.2-3.0, and (d) 0.8-3.0 V vs. Li/Li⁺ in 1.0 M LiClO₄/EC + DEC (1:1). In all cases, the irreversible capacity was observed only in the first cycle, but disappeared in the second and subsequent cycles. The irreversible capacity in the first cycle was high (> 100 mAh g⁻¹) when the lower potential limit was set at 1.0 V (see Fig. 3) or lower, but was greatly reduced to *ca.* 40 mAh g⁻¹ when the lower potential limit was set at 1.2 V or higher. Lower discharge rates did not appreciably reduce the irreversible capacity (not shown), and hence the high irreversible capacity is not due to slow kinetics in the extraction of Li⁺ ions. It is therefore considered that the high irreversible capacity mainly originated from surface reactions, such as solvent decomposition at potentials ≤ 1.2 V. As shown in Fig. 4, the cycleability was also improved when the lower potential limit was set at potentials ≥ 1.2 V, which may be due to suppression of solvent decomposition. From standpoints of irreversible capacity and cycleability, the lower potential limit should be set at 1.2 V or higher; however, raising

Fig. 1 XRD patterns of the synthesized TiO₂(B) powder.

Fig. 2 SEM images of TiO₂(B) particles.

the lower potential limit from 1.0 V to 1.2-1.4 V resulted in a reduced capacity of *ca.* 170 mAh g⁻¹.

The rate-limiting processes in the charge and discharge reactions of TiO₂(B) were investigated using GITT. Figure 5 shows the variations of open-circuit potential (OCP) during intermittent charging and discharging at C/6 in the second cycle. On the galvanostatic intermittent titration curves, large polarization was observed at the beginning and the end of charging. It is widely known that Ti(IV)O₂ is an insulator, but introduction of Ti³⁺ ions by Li⁺ insertion greatly improves the electronic conductivity of lithiated Li_xTiO₂. However, when the average valence of Ti ions falls down below 3.5, the electronic conductivity would drop sharply as was reported for the Magneli phase Ti_nO_{2n-1}.¹³⁾ Hence the large polarization was attributed to low electronic conductivity of Ti(IV)O₂(B) and LiTi(III)O₂, which appear at the beginning and the end of charging, respectively.

Fig. 3 Charge and discharge curves of TiO₂(B) in 1 M LiClO₄/EC + DEC(1:1). Potential range: 1.0-3.0 V vs. Li/Li⁺.

Another plausible reason for the large polarization is a lack of available sites for Li⁺ ions in the lattice to move, especially at the end of charging. It should be noted that the OCP was never lower than 1.4 V even at the end of charging. This clearly indicates that the large polarization at the end of charging causes irreversible surface reactions, such as solvent decomposition, which led to the high irreversible capacity when the lower potential limit was set at 1.0 V or lower shown in Figs. 3 and 4.

Figures 6(a) and (b) show the charge/discharge curves of TiO₂(B) at an elevated temperature and at a slower rate, respectively, between 1.4 and 3.0 V in 1.0 M LiPF₆ dissolved in EC + DEC (1:1). As shown in Fig. 4(b), the discharge capacity was 167 mAh g⁻¹ at C/6 and 30 °C. In contrast, it increased greatly at an elevated temperature (246 mAh g⁻¹ at 60 °C) and at a lower rate (267 mAh g⁻¹

Fig. 5 Variation of open-circuit voltage of TiO₂(B) as a function of x in Li _{x} TiO₂(B) in the 2nd cycle in 1 M LiPF₆/EC + DEC(1:1) at C/6. Each intermittence time was 24 h.

Fig. 4 Charge and discharge curves of TiO₂(B) in various potential ranges in 1 M LiClO₄/EC + DEC(1:1). Potential range: (a) 1.6-3.0 V, (b) 1.4-3.0 V, (c) 1.2-3.0 V and (d) 0.8-3.0 V vs. Li/Li⁺.

at C/60). These facts show that the reversible capacity is limited by a slow process at the end of charging as mentioned above. Hence accelerating the Li^+ insertion rate at the end of charging is important to improve the reversible capacity close to the theoretical capacity (335 mAh g^{-1}). In addition, an obscure potential plateau appeared at *ca.* 1.8 V vs. Li/Li^+ on the charge and discharge curves in Fig. 6(b). The potential plateau is attributed to the Li^+ insertion into and extraction from the anatase phase, in which the Li^+ diffusion rate is much slower than that in $\text{TiO}_2(\text{B})$.¹⁴ As shown in Fig. 1, our $\text{TiO}_2(\text{B})$ sample contains a considerable amount (14%) of the anatase phase. It is therefore considered that the reversible capacity also can be improved by decreasing the amount of the anatase phase.

It should be noted that the irreversible capacity increased to *ca.* 100 mAh g^{-1} at an elevated temperature (60°C) in Fig. 6(a). This fact implies that solvent decomposed even at potential higher than 1.4 V, which was enhanced by raising the temperature. Further investigation on solvent decomposition and the resulting surface film formation is necessary for minimizing the irreversible capacity and improving cycleability at elevated temperatures.

4 Conclusions

A $\text{TiO}_2(\text{B})$ powder sample was prepared from a

Fig. 6 Charge/discharge curves of $\text{TiO}_2(\text{B})$ at different rates and temperatures in 1 M $\text{LiPF}_6/\text{EC} + \text{DEC}(1:1)$. Potential range: 1.4–3.0 V vs. Li/Li^+ . (a) C/6, 60°C ; (b) C/60, 30°C .

$\text{K}_2\text{Ti}_4\text{O}_9$ precursor by ion-exchange and dehydration. Li^+ ion insertion/extraction properties of the $\text{TiO}_2(\text{B})$ sample as a high-potential negative electrode were investigated, aiming at reducing the irreversible capacity and improving the reversible capacity. The irreversible capacity greatly decreased to *ca.* 40 mAh g^{-1} when the lower potential limit was set at $E \geq 1.2 \text{ V}$. This indicated that the irreversible capacity mainly originated from surface reactions, such as solvent decomposition, at $E \leq 1.2 \text{ V}$ in the first cycle. Raising the lower potential limit to 1.2–1.4 V also improved the cycleability of $\text{TiO}_2(\text{B})$, but brought about a trade-off of a reduction in reversible capacity (to *ca.* 170 mAh g^{-1}).

In galvanostatic intermittent titration tests, large polarization was observed at the beginning and the end of charging. This clearly indicated that a slow process is involved in the insertion reaction at the beginning and the end of charging, which causes solvent decomposition at potentials lower than 1.4 V at the end of charging. It is therefore important to improve the reaction rate, in particular, at the end of charging. In fact, the reversible capacity was greatly improved to 246 and 276 mAh g^{-1} at an elevated temperature of 60°C and at a lower rate of C/60, respectively. In addition, an obscure potential plateau, which is assigned to the anatase phase, appeared on the charge and discharge profile at a low rate of C/60. The $\text{TiO}_2(\text{B})$ sample contained *ca.* 14% of the anatase phase as an impurity, and a reduction of the anatase phase was found to be effective for an increase in reversible capacity at moderate charge/discharge rates.

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