

Amorphous titanium oxide electrode for high-rate discharge and charge

Mitsuhiro Hibino^{a,*}, Keiko Abe^b, Masafumi Mochizuki^b, Masaru Miyayama^c

^a *Energy Electronics Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba central 2, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan*

^b *Department of Industrial Chemistry, Faculty of Engineering, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan*

^c *Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba Meguro-ku, Tokyo 153-8505, Japan*

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Abstract

The composite material of amorphous titanium oxide and acetylene black (AB) was fabricated by hydrolyzing titaniumisopropoxide in the propanol in which acetylene black was dispersed. The composite material was tested electrochemically. Cyclic voltammetry showed that the amount of reversibly reacted lithium was about $x = 0.6$ in terms of Li_xTiO_2 . The composite could be discharged and charged under constant current densities around 2.0 V versus Li/Li^+ . For current densities of 0.1, 1, and 10 A g^{-1} , the specific capacities measured were 185, 145, and 120 mA g^{-1} , respectively. On the basis of the use of the composite material as an anode, the feasibility of energy devices possessing both high-energy and high-power densities in a lithium battery type is discussed.

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1. Introduction

For systems by which the power generation is distributed and for electric vehicles, energy storage devices that can perform high-power operation are required [1–3]. For these uses in particular, high-energy density and small size are also necessary. There are two candidates for such devices: batteries and capacitors. Though a battery system can achieve the required high-energy density quite easily compared to a capacitor system, its power density must exceed the present one by a factor of 10–100. Even so, a battery system seems to have an advantage for such energy storage over the electric double layer capacitor (EDLC), because the EDLC needs to be improved both in terms of the energy density and the power density [4]. In this study we fabricated electrode materials for a lithium ion battery for the purpose of rapid charging and discharging.

Many materials are known as lithium intercalation hosts and have been studied as electrode materials for lithium ion batteries. Though most of these studies have given greater importance to the magnitude of the specific capacity of the materials while discharging or charging, the present study focuses on the rapid intercalation of lithium by means of

raising the electric conductivity of the electrodes and fabricating materials in the form of the smallest particles possible, even if some degree of specific capacity is abandoned. Then we took particular note of titanium oxide considering the following. Vanadium oxide and manganese oxide have been investigated from the viewpoint of high-rate discharge [5–8]. These materials showed a potential of approximately 2.5–3.5 V versus Li/Li^+ and were suitable for use as a cathode. In contrast, titanium oxides that included tetravalent titanium were expected to work well as anode material due to the transition between the tetra and trivalent states induced by the insertion and extraction of lithium. The potential for such electrochemical reaction was expected to be relatively low (below ca. 2.0 V versus Li/Li^+) in anatase, hollandite or an amorphous structure [9–11]. The lithium intercalation properties of anatase TiO_2 have also been studied in terms of an electrochromic material [12,13]. To obtain the material in the form of microparticles, a sol–gel method was adopted in the synthesis [14,15]. Acetylene black (AB) was mixed in as a conducting additive in the synthesis procedure according to the synthesis procedure for vanadium oxide or manganese oxide described above [5,8]. The titanium oxide synthesized was amorphous. The thermal treatment was performed below the crystallization temperature because the crystalline structure sometimes collapsed during the repetition of discharge and charge (lithium intercalation and extraction). To prevent such destruction, the substitution of

* Corresponding author. Tel.: +81-29-861-3421; fax: +81-29-861-5829.
E-mail address: m.hibino@aist.go.jp (M. Hibino).

constituent atoms by other atoms has often been attempted in order to stabilize the structure in various transition metal oxide systems [16,17]. The utilization of amorphous material was another way to prevent the collapse of the crystalline structure and the deterioration of the performance of discharge and charge. The advantage of the use of amorphous material in high-rate discharge and charge has been confirmed by the case of vanadium oxide gel [5].

2. Experimental

Titanium isopropoxide (assay 97%, Aldrich) was diluted in isopropanol. Ammonia water (25 wt.%) was portioned to 0.4M of titanium isopropoxide solution for hydrolysis [18]. To obtain a mixture of titanium oxide and conducting additive, carbon was added to the solution so, that the weight of the carbon should be in equal proportion to that of the produced titanium oxide. The solution thus obtained was stirred for 16 h. The carbon used was acetylene black (DENKA BLACK). As a reference, a specimen to which no carbon was added was also prepared.

Thermal gravimetry (TG) and differential thermal analysis (DTA) were performed to determine the suitable thermal treatment temperature and the amount of carbon. The morphology was observed by scanning electron microscopy (SEM).

Electrochemical measurements were performed using a three-electrode beaker cell assembled in an inert gas system. The working electrode was prepared as follows. Porous nickel (foamed nickel) was soaked in the 16h solution, dried for 3 h in an ambient atmosphere, and heated at 150 °C for 2 h. For counter and reference electrodes, lithium metals were pressed on nickel mesh. We used 1M LiPF₆/(EC + DEC, 1:1 volume ratio) as an electrolyte. Cyclic voltammogram was recorded between 1.2 and 3.6 V versus Li/Li⁺ at 100 and 5 mV s⁻¹. The discharge-charge test was performed between 1.2 and 3.6 V under 1 and 10 A g⁻¹. Here, the weight was based on the active material, titanium oxide. After each discharge and after each charge, the circuit was opened and rest periods of 30 min for the cells using 10 A g⁻¹ and 1 h for 1 A g⁻¹ were given.

3. Results and discussion

The results of TG–DTA in air are shown in Fig. 1. The weight of the composite decreased gradually while being heated to 500 °C. An abrupt weight change due to the oxidation of AB started near 500 °C. The exothermic reaction near 190 °C together with a trace weight loss was thought to be combustion of some organic residues. From XRD, the exothermic peak around 420 °C was attributed to crystallization into an anatase structure. Fig. 2 shows XRD profiles for the sample after a 120 °C thermal treatment and AB. The sample had no peaks other than the ones attributed to AB,

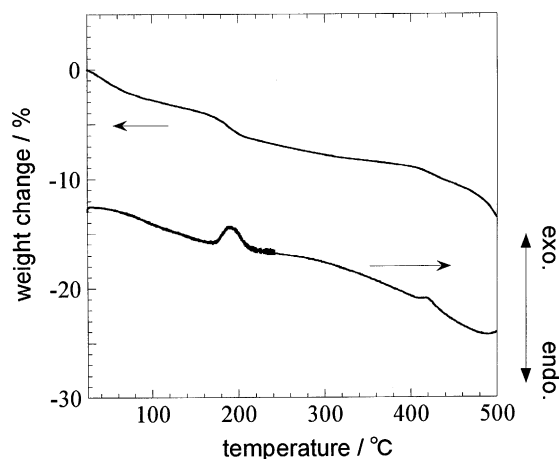


Fig. 1. TG–DTA profiles for the composite of TiO₂ and acetylene black (AB).

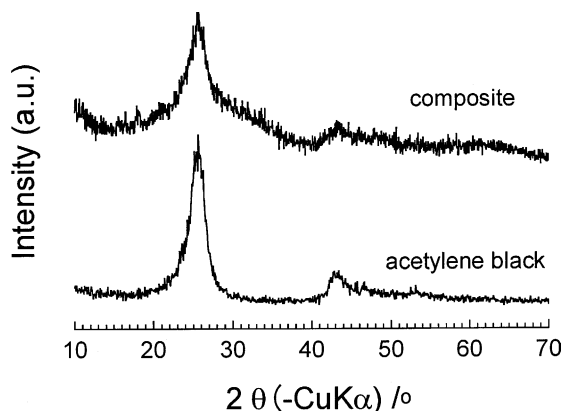


Fig. 2. XRD patterns of (a) the composite of TiO₂ and AB, and (b) AB.

indicating that the titanium oxide took on an amorphous structure.

SEM photographs of the composite of titanium oxide and carbon are shown in Fig. 3. The particles observed (ca. 50 nm in diameter) were AB because they had the same size and

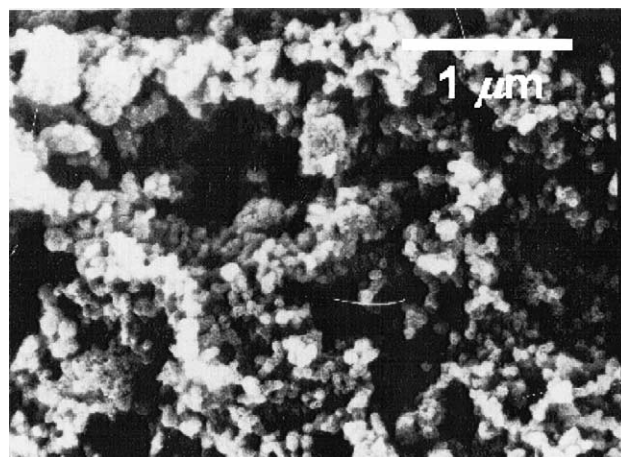


Fig. 3. SEM image of the composite of TiO₂ and AB.

shape as the originally added AB, and the aggregates were thought to be titanium oxide. However, considering that the content of titanium oxide was ca. 50 wt.% of the composite, the small titanium oxide particles may be dispersed and attached to the surface of AB particles. We did not, however, perform other forms of observation such as TEM to clarify the fine structure, because in the present study we focused on the electrochemical properties of the composite.

The cyclic voltammograms at different sweep rates are shown in Fig. 4(a) and (b), and the amount of the reduction or oxidation charge calculated from the integration of the induced cathodic and anodic current in Fig. 5. The cathodic current started to rise at about 2.2 V versus Li/Li⁺, which

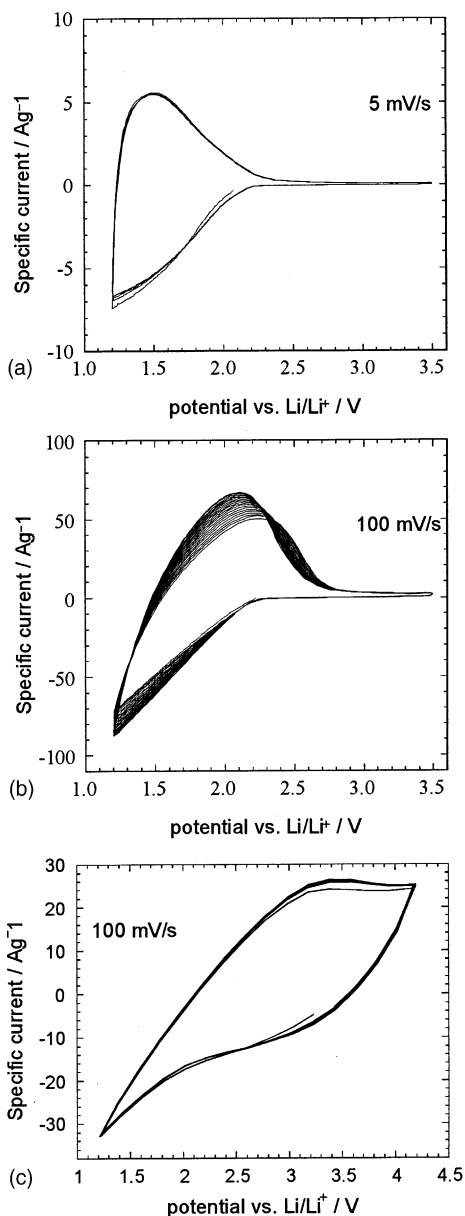


Fig. 4. Cyclic voltammograms of the composite of TiO₂ and AB at scan rate of (a) 5 and (b) 100 mV s⁻¹, and (c) the composite to which AB was added, not during sol–gel synthesis but during fabrication of the electrode.

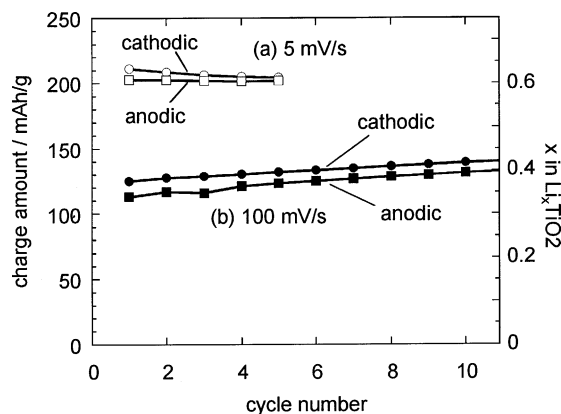


Fig. 5. The charge amount of oxidation and reduction against the cycle number of cyclic voltammetry at scan rate of (a) 5 and (b) 100 mV s⁻¹.

was higher than that of anatase or many other TiO₂s [9–11]. Considering that in ramsdellite it was shown that lithium intercalation started at ca. 2.3 V [19], the lithium intercalation sites in the sample may be more similar to those in ramsdellite than in anatase or hollandite [9,10]. The composite material showed 120–150 mA h g⁻¹ of charge amount at a sweep rate of 100 mV s⁻¹, which was too high a rate for the evaluation of the electrode of a normal lithium battery. This value corresponded to about $x = 0.4$ in terms of Li_xTiO₂. At a sweep rate of 5 mV s⁻¹, the charge amount was higher and measured about $x = 0.6$. In Fig. 5, the fact that the amount of cathodic charge was larger than that of the anodic charge implied poor reversibility and that the lithium present could not be extracted entirely from the specimen. The gradual increase in the charge amount with cycle repetition may be a result of the suppression of polarity due to poor electric conductivity. The reduction of titanium oxide due to the residual lithium could cause the growth of electric conductivity. The amount of cathodic and anodic charges at a sweep rate of 5 mV s⁻¹ matched each other better than they did at 100 mV s⁻¹ and remained constant at about 205 mA h g⁻¹, corresponding to $x = 0.6$ in terms of Li_xTiO₂, as the cycles increased. Thus, the slow sweep rate tended to result in a preferable, reversibility.

Here, we compared the manner in which AB was added to the sol solution with the manner in which AB was added during the electrode fabrication after titanium oxide was precipitated and dried. The former led to a large amount of reacted lithium and raised the rate performance to a high level. Fig. 4(c) shows that the shape of the cyclic voltammogram of the sample prepared in the latter manner was depressed more than that prepared in the former one (Fig. 4(b)), and implies that electrochemical reactions such as lithium intercalation would occur more slowly in the latter sample than in the former one. The composite prepared in the latter manner was liable to have a poorer mixture condition, and should therefore contain some areas that are electrically conductive and some areas that are poorly conductive [8]. In this situation, the electric current is concentrated on the electrically

conductive area in the discharge and charge processes. Such current-intensive areas would deteriorate quickly and have a tendency to undergo side reactions. This may be one of the reasons for the poor reversibility that occurs at high sweep rates. The irreversibility observed might also be interpreted on the basis of the structure of the cell we used in our experiment, that is, on the basis of the distance between the sample surface and the tip of the capillary connecting reference electrode described later.

Next, the profiles of discharge and charge performed under various current densities are shown in Fig. 6(a)–(c). The specific capacity is given in Fig. 7. Although, in general the discharge and charge capacities tend to decrease with an increasing applied current, the opposite phenomenon occurred for the case of the discharge capacity. The specific discharge capacities were found to rise when the current density increased. This result was probably caused by the following: the current density per area for 10 A g^{-1} was about 40 mA cm^{-2} in the case of 1 mg of sample and 0.25 cm^2 of electrode area in our experiment. The three-electrode cell we used had a capillary in which, the electrolyte solution was connected in the vicinity of the surface of the specimen with the reference lithium. Assuming that the distance between the tip of the capillary and the surface of the sample was about 1 mm , and that the resistivity of the electrolyte was roughly $10^2 \Omega \text{ cm}$ [20], the difference in potential between the sample surface and the tip would reach about 0.4 V and would not be negligible. As a result, when the potential in the vicinity of the tip reached the cut-off potential of the discharge test, the sample was forced to a still lower potential, which could be the cause of some sort of side reaction. Thus the large capacity that was measured was probably attributable to such reactions, instead of to the reversible lithium intercalation. This finding was supported by the fact that the electrolyte of the cell for 10 A g^{-1} tests turned dark yellow after the cycles, though 0.1 A g^{-1} tests did not change the color. The electrolyte was undoubtedly related to some side reactions, though the details have not yet been clarified. There was a possibility of lithium intercalation in carbon, because for 10 A g^{-1} tests, the potential of the sample surface might decrease to about 1.0 V (versus Li/Li^+), a level at which lithium could intercalate in carbon. However, even if so, the potential was thought to be higher than that at which large amounts of lithium would started to be inserted and the time available for lithium insertion was probably very limited because the period when the potential was near 1 V was only a small part of the total discharge time that was about 1 min for 10 A g^{-1} discharge. As a result, the contribution of lithium intercalation in carbon was thought to be small. In the charge process, the actual potential applied to the sample would become larger than the cut-off potential for the same reason as for discharge. The charge capacity, however, showed a decrease with an increase in current density as initially expected. This was probably because a higher potential induced much fewer side reactions than a lower potential did. Consequently, these charging capaci-

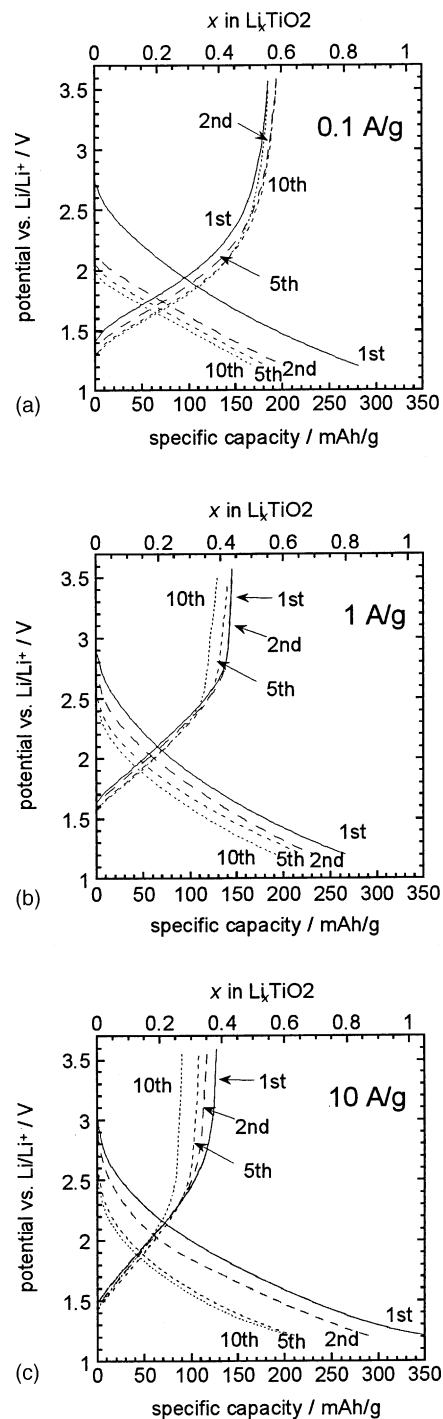


Fig. 6. Discharge and charge profiles of the composite of TiO_2 and AB under (a) 0.1 , (b) 1 , and (c) 10 A g^{-1} of current density.

ties could be considered to be a contribution of reversible lithium intercalation. Based on this finding, the specific capacity under a large current of 10 A g^{-1} was expected to be about 120 mA h g^{-1} .

Here, let us assume that this composite material will be used as one electrode with vanadium oxide as the other electrode (ca. 3.0 V versus Li/Li^+ , 200 mA h g^{-1} for 10 A g^{-1} as has been developed in 5). Considering that both electrode

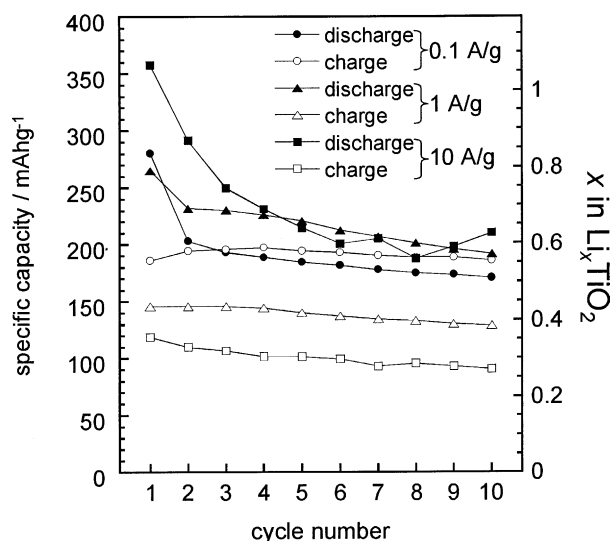


Fig. 7. Specific capacities of discharge and charge under 0.1, 1, and 10 A g⁻¹ against the cycle number.

materials include AB in equal weight to the active material and assuming an operating voltage of 1.2 V and a current of 2.5 A g⁻¹ (both electrodes), a power density of 3 kW/kg and an energy density of 30 Wh/kg will be expected on the basis of the sum of the weight of both electrode materials. Assuming that the factor of weight increase due to the other parts of battery, such as the current collector, electrolyte, or chassis, was five, which, depends on the envisioned scale of the device [4], energy devices possessing 0.6 kW/kg and 5 Wh/kg could be expected to be fabricated. These calculations are about one order of magnitude larger in power density and lower by a factor of 1/2 in energy density than those of commercially available lithium batteries [21]. Compared to a commercially available ultracapacitor, about comparable or double the power and energy densities can be expected [21]. This suggests that the titanium oxide prepared above can be expected as a negative electrode material of energy devices with high-power density and that lithium intercalation may be available for device with both high-energy and high-power densities beyond normal batteries.

4. Conclusions

Amorphous titanium oxide was synthesized by the sol-gel method. The composite of titanium oxide and AB was fabricated by adding AB during hydrolysis of titaniumisopropoxide. The composite material could be discharged and charged under a high current density, such as 10 A g⁻¹, and could hold 120 mA h g⁻¹ of specific capacity under 10 A g⁻¹ operation. The potential for electrochemical reaction was around 2.0 V versus Li/Li⁺, suggesting that amorphous titanium oxide is a potential material for the anode of high-rate dischargeable and chargeable lithium ion batteries.

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