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Preparation of Brookite-Type TiO_2/Carbon Nanocomposite Electrodes for Application to Li Ion Batteries

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The increasing demand for portable energy has generated significant research interest in nanostructured electrode materials, because of their large interfacial contact area with the electrolyte and short path lengths for Li ion transport. To date, titanium dioxide (TiO_2) has been widely investigated as an electroactive, Li-insertion host. However, the lithium reactivity of brookite-type TiO_2 has rarely been addressed compared to the common polymorphs, anatase and rutile, because of the difficulties encountered in obtaining a phase-pure brookite structure. Herein, we report on the simple synthesis of nanocrystalline brookite-type TiO_2 using titanium trichloride ($TiCl_3$) and urea [$(NH_2)_2CO$]. The average size of the particles precipitated at 100 °C was ca. 10 nm. The brookite structure was stable up to 500 °C and was completely transformed to the rutile structure at 900 °C in an O_2 atmosphere. We evaluated the electrochemical properties of each TiO_2 powder heat-treated sample at a preset temperature. Hybrid carbon/TiO_2 nanocomposites with high conductivity were also fabricated using a stable suspension of multi-walled carbon nanotubes (MWCNTs) in aqueous suspension with an appropriate surfactant and subsequent precipitation of TiO_2. The carbon incorporation clearly improved the capacity retention of TiO_2 upon cycling.

Introduction

Titanium dioxide (TiO_2) commonly exists in three polymorphs: rutile (tetragonal, space group $P4_2/mnm$), anatase (tetragonal, $I4_1/amd$), and brookite (orthorhombic, *Pcab*).[1,2] It is well documented that the metastable anatase phase can be fully stabilized into a nanoscale regime at ambient conditions and irreversibly transformed to the rutile phase at high temperature, which is the thermodynamically most stable modification of TiO_2. On the other hand, only a few studies have examined the synthesis of the other metastable phase: brookite.[3,4] In most cases of TiO_2 synthesis, brookite occurs as a minority phase in concentrations that depend on the synthetic conditions. However, it has recently been reported that the pure brookite phase can be prepared by the thermolysis and precipitation of titanium chloride in an aqueous medium.[5,6]

Nano-sized TiO_2 has been widely emphasized as a key component in technological applications such as nanoelectronics, gas sensors, environmental photocatalysis, and solar-energy conversion.[7–10] Additionally, various anatase nanostructures (nanoparticles, nanowires, nanorods, and nanotubes) have been shown to be good candidates as the electrode for lithium ion batteries because of their ready availability, low cost, and safety.[11–13] TiO_2 (B), which is a metastable monoclinic modification of TiO_2, has been studied as an excellent intercalation host for Li by Bruce et al.[14,15] In contrast to anatase and TiO_2 (B), the Li insertion into the rutile and brookite polymorphs is mostly reported to be negligible. More recently, the high Li electroactivity of the nanocrystalline rutile and brookite TiO_2 polymorphs was reported for the first time.[16,17]

Herein, we report the high yield formation of high-purity brookite nanoparticles by urea precipitation in an aqueous solution process.[5] The electrochemical activity of brookite is evaluated in detail. Furthermore, we demonstrate that the preparation of the hybrid multi-walled carbon nanotube (MWCNT)/brookite improves the specific capacity and capacity retention on cycling.

Results and Discussion

The XRD pattern taken from the powders dried at 100 °C indicated phase-pure brookite, as shown in Figure 1. We deduced the lattice parameters from the Rietveld refinement of the XRD pattern. The reported (JCPDS, No. 29–1360) and calculated lattice parameters (a = 5.46127 ± 0.00600 Å, b = 9.18005 ± 0.01419 Å, and c = 5.15043 ± 0.00577 Å) of brookite show good agreement. The TEM image (Figure 1, inset) confirms that the powders are com-

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posed of spherical nanocrystallites that are 10–20 nm in size. However, the nanoparticles were largely overlapping and formed rather large aggregates. The assumed reaction processes are shown in Equations (1), (2), and (3).

$$(NH_2)_2CO + 3\,H_2O \rightarrow CO_2 + 2\,NH_3{\cdot}H_2O \rightarrow CO_2 + 2\,NH_4^+ + 2\,OH^- \quad (1)$$

$$TiCl_3 + 3\,OH^- \rightarrow Ti(OH)_3 + 3\,Cl^- \quad (2)$$

$$n\,Ti(OH)_3 + O_2 \rightarrow n\,TiO_2 + (2n - 2)\,H_2O + (4 - n)\,OH^-(aq.)\ (n = 1, 2, \text{or } 3) \quad (3)$$

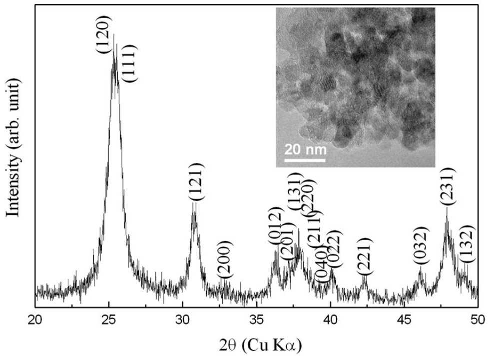

Figure 1. XRD pattern and typical TEM image of brookite nanopowders dried at 100 °C.

The solution was maintained under an acidic condition ($pH < 1$) up to 70 °C because of the dissociation of HCl in the $TiCl_3$ source. However, on the basis of Equations (1) and (2), urea decomposes to gradually release free OH^- ions into the solutions and titanium hydroxide is subsequently formed from an ion exchange reaction at ca. 70 °C.[18,19] These suggested reactions were clearly evidenced in the present results by the systematic color change from violet at room temperature to a dark purple at ca. 70 °C.[5] Additionally, low solution pH and Cl^- ion concentration were previously reported as a possible reaction pathway for brookite formation from the intermediate complex.[4] Later, we observed the precipitation of white titanium oxide particles at 100 °C, which originated from the oxidation reaction [Equation (3)] by the introduction of atmospheric oxygen. The sudden increase in pH from ca. 1 to ca. 7 indicates the generation of OH^- during the oxidation reaction. Therefore, it was believed that the ion-exchange reaction under low solution pH and Cl^- ion concentration [Equations (1) and (2)], along with the oxidation reaction [Equation (3)], should favor the formation of brookite nanoparticles during our synthetic process.

The crystal structure of brookite comprises TiO_6 octahedra that share both edges and corners. It has been suggested that the channels, which are apparently free of atoms, observed in brookite along the [001] direction are good candidates for allowing lithium mobility.[2] We evaluated the electrochemical activity of brookite by means of cyclic voltammetry (CV), using a brookite/Li half cell, operating at 0.2 mV/s (Figure 2). The current was normalized with respect to the brookite mass. The CV profiles of brookite were almost identical to those of anatase.[13,20] A major pair of cathodic/anodic peaks for Li intercalation/deintercalation was observed at 1.70 and 2.02 V, respectively, in accordance with the pair of peaks at 1.64 and 2.10 V in anatase. This result confirms the electrochemical activity of the brookite nanomaterials. Another pair of peaks (at 1.58 and 1.86 V) associated with differing site occupations might be attributed to the formation of the discrete phase or imperfection of the TiO_2 lattice, which facilitate the transport of Li through surface defects and in bulk materials.[21,22] Indeed, the shape of the CV profiles remained stable after the second cycle, indicating that the Li intercalation/deintercalation occurs reversibly in brookite.

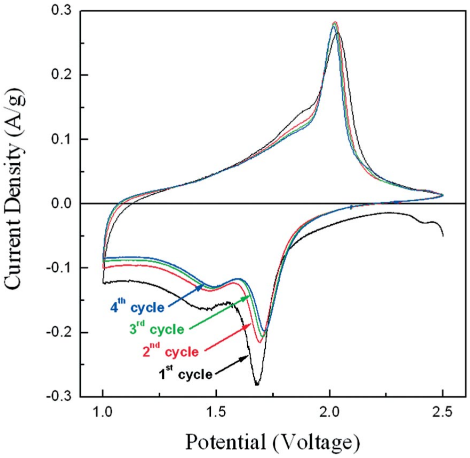

Figure 2. Cyclic voltammetry of the brookite nanopowders dried at 100 °C at a scanning rate of 0.2 mV/s.

For comparison, brookite and rutile powders with a larger crystallite size were also prepared by calcining at 500 and 900 °C, respectively. Figure 3 shows the XRD patterns of brookite calcined at various temperatures for 2 h in an O_2 atmosphere. The brookite phase was stable up to ca. 500 °C, but was transformed to rutile over the temperature range of 600 to 900 °C.

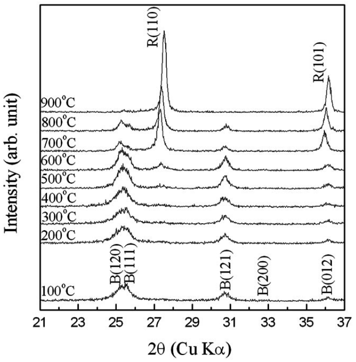

Figure 3. XRD patterns of the TiO_2 nanopowders calcined at various temperatures for 2 h in an O_2 atmosphere showing the brookite-to-rutile phase transformation (B: brookite phase, R: rutile phase).

We confirmed the size-dependency of the capacity of our TiO_2 particles calcined at 500 and 900 °C under the same electrochemical test conditions. The voltage/specific capacity curves were obtained for each sample/Li half-cell and are presented in Figure 4. The cells were cycled at a rate of C/5 (here, C was defined as 0.5 Li ions per hour per formula unit of TiO_2 on the basis of the reaction, $TiO_2 + 0.5Li \rightarrow Li_{0.5}TiO_2$).[23] The brookite particles dried at 100 °C exhibited a first discharge capacity of 284 mAh/g and a reversible capacity of ca. 100 mAh/g after 10 cycles. However, the capacity of the particles calcined at 500 and 900 °C faded rapidly to ca. 80 and ca. 49 mAh/g, respectively. It is difficult to explain their poor electrochemical performance in terms of different crystal structures. As well as taking into account the crystallite size of each particle, it has been suggested that the Li ion dynamics in electrode materials including anatase TiO_2 are greatly influenced by the size of the nanoparticles.[24] The brookite nanoparticles dried at 100 °C had a large surface area of 103.2 m^2/g as measured by the Brunauer–Emmett–Teller (BET) method (Figure 4 inset). However, this surface area decreased to 79.7 and 32.8 m^2/g by calcining at 500 and 900 °C, respectively, which suggests a rapid crystallite growth. These results confirm the dependence of the Li electroactivity of TiO_2 on the crystallite sizes.

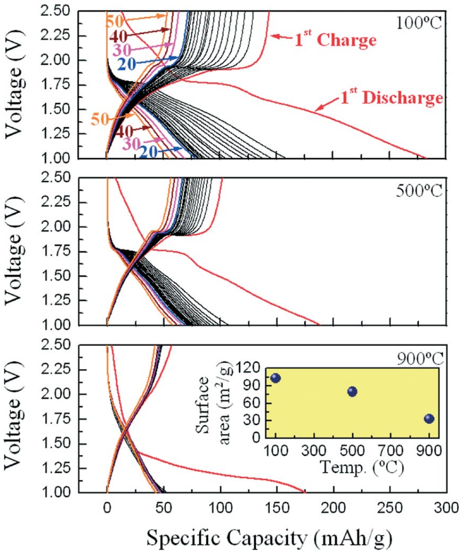

Figure 4. Charging–discharging curves of the TiO_2/Li half cells cycled between 2.5 and 1.0 V at a rate of C/5. The inset shows the BET surface areas of each powder.

Despite the relatively small crystallite size of 10–20 nm (the mean crystallite size of ca. 9 nm from Scherrer's equation) for the brookite sample dried at 100 °C, part of the problem associated with using brookite nanoparticles as an electrode material remains the considerable capacity fading upon cycling, as shown in Figure 4. Oxide hosts for Li intercalation generally have a low electronic conductivity, which necessitates the presence of electronic conduction paths in the host materials to decrease the charge-transfer resistance.[25,26] Although conducting additives such as carbon black can be mechanically mixed with the host material in conventional Li battery electrodes, it is difficult to mix such conducting additives with nanomaterials that are easily aggregated. Thus, Moriguchi et al. recently reported that the incorporation of cut single-walled carbon nanotubes (c-SWCNTs) inside or beside an anatase TiO_2 nanophase by means of the bicontinuous microemulsion-aided process effectively improves the charging–discharging property of anatase TiO_2.[27]

In this study we satisfied this need to provide a sufficient electronically conducting network by forming hybrid MWCNT/brookite nanocomposite materials. The high MWCNT stability in the aqueous suspension with an appropriate amount of cetyltrimethylammonium bromide (CTAB) was maintained among the various surfactants investigated.[28] After suspending the MWCNTs, brookite was synthesized via urea-mediated homogeneous precipitation resulting in hybrid MWCNT/brookite nanocomposites. The presence of brookite was also confirmed by XRD results. A thermogravimetric (TG) analysis indicated that ca. 17 wt.-% of the MWCNTs was associated with brookite. The weight percentages of the MWCNT and brookite in the composites were also exactly determined after the composite powders were heat treated at 1200 °C for 2 h in an O_2 atmosphere to eliminate the MWCNT.

Parts (a) and (b) of Figure 5 show the typical FESEM images of the MWCNT/brookite composite particles. Individual MWCNTs were spatially dispersed in the composites. Furthermore, lots of brookite nanoparticles were directly deposited onto the MWCNT surface, as was also observed in the TEM micrographs [Figure 5, (c) and (d)]. These observations supported the greater likelihood that MWCNT facilitates a suitable electron-transport path upon cycling of the brookite. The incorporation of MWCNT clearly increased the reaction rate upon lithiation of the brookite, as indicated by the enhanced first cathodic peak in part (a) of Figure 6 (measured on the samples of similar mass at the same voltage sweep rate). It is believed that MWCNT improved the Li electroactivity of brookite nanomaterials because of its effect on the conductivity and catalytic efficiency.[29] The first and tenth discharge capacities of MWCNT/brookite were 321 and 183 mAh/g, respectively. The existence of an exceptionally high first discharge capacity could be attributed to the irreversible formation of a solid-electrolyte interface (SEI). However, it was reported that the low-voltage cut-off of brookite used here is 1 V and this should minimize electrolyte reduction and hence any SEI layer formation.[30] Another possible reason for a large irreversible capacity in the first cycle might be the decomposition of water molecules, as observed in anatase TiO_2 nanotubes.[31] On the basis of the thermogravimetric (TG) analysis of brookite, the final weight loss of our brookite TiO_2 was ca. 8.3%, corresponding to a composition of $TiO_2 \cdot 0.4H_2O$. The complete dehydration of our powders by washing with other solvents or long-time thermal treatment is under investigation. As noted above, brookite nanoparticles have poor capacity retention upon cycling. However, we obtained a reversible capacity of ca. 160 mAh/g even after 50 cycles (theoretical capacity of TiO_2: 165 mAh/g) in the hybrid MWCNT/brookite nanocomposites, equating to a much smaller capacity fading of only 0.28% per cycle after 10 cycles. In summary, these results confirm the potential for this approach to offer an effective improvement in electrochemical performance of nanomaterials for Li ion battery electrodes.

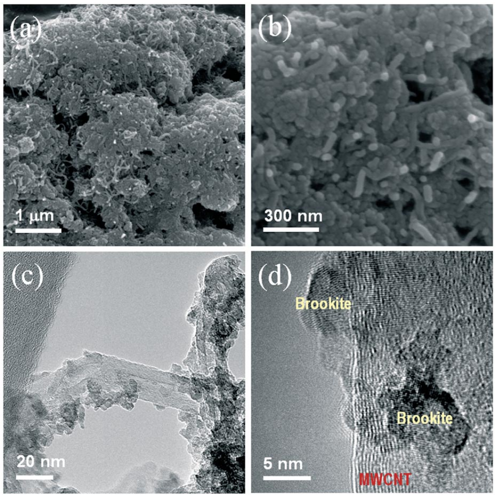

Figure 5. (a, b) Typical FESEM images and (c,d) TEM images of the MWCNT/brookite nanocomposites.

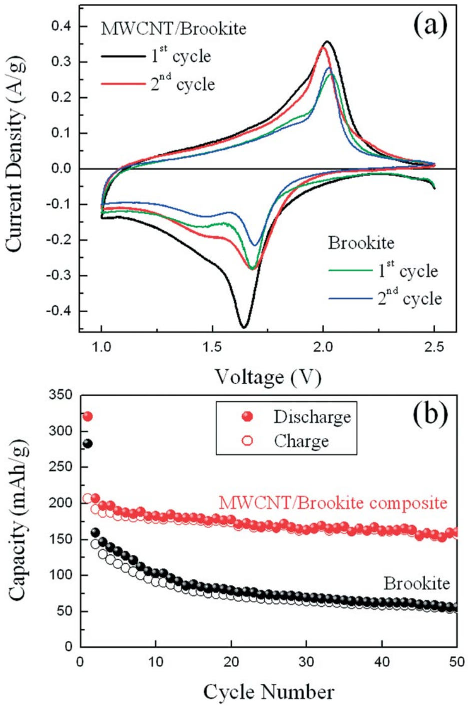

Figure 6. (a) Cyclic voltammetries of the brookite and MWCNT/brookite at a scanning rate of 0.2 mV/s. (b) Variation of the discharge–charge specific capacity versus the cycle number for the brookite and MWCNT/brookite.

Conclusions

Possible ion exchange and a subsequent oxidation reaction were suggested during the formation of phase-pure brookite by a urea-mediated precipitation process. Homogeneous hydrolysis of urea leads to the effective precipitation of nano-sized brookite (10–20 nm). Attention has been paid not only to the crystal structure, but also to particle size with regard to the Li reactivity of brookite. We also prepared hybrid MWCNT/brookite nanocomposites, which demonstrated a stable capacity of ca. 160 mAh/g over 50 cycles. The improved reversible capacity and cycling performance of this nanocomposite electrode were explained by the formation of an electronically conducting network.

Experimental Section

Urea [$(NH_2)_2CO$, 0.5 M, Alfa Aesar, 99.3%] was dissolved in an aqueous solution containing titanium trichloride ($TiCl_3$, 0.015 M, Alfa Aesar, 20% in 3% hydrochloric acid). The solution was refluxed at 100 °C for 7 h whilst stirring, followed by centrifuging and washing repeatedly (four times with deionized water and once with anhydrous ethanol). The precipitated powders were then dried at 100 °C for 2 d in a vacuum oven. For the preparation of hybrid carbon/TiO_2 composites, a calculated amount (200 mg/L) of synthetic multi-walled carbon nanotube (MWCNT, CNT Co., Ltd., Incheon, Korea) was first dispersed in deionized water in the presence of cetyltrimethylammonium bromide (CTAB, 2 mg/L, Aldrich). The solution was sonicated for 3 h before the addition of $TiCl_3$ and urea. The preparation of the MWCNT/TiO_2 composite precipitates followed the same steps as those for the TiO_2 particles. The resultant powders were calcined at 200–1000 °C for 2 h in an O_2 atmosphere, in order to study the TiO_2 phase transformation.

For the electrochemical evaluation of pure TiO_2 powders, positive electrodes were prepared by mixing 1–3 mg of powder, Kynar 2801 (PVdF-HFP) binder, and Super P (MMM Carbon, Brussels, Belgium) carbon black as a conducting additive at a mass ratio of 68:12:20. However, the MWCNT/TiO_2 composite electrodes were prepared without the addition of Super P carbon black. Swagelok-type cells using Li metal foil as the negative electrode and a separator film of Celgard 2400 were assembled and saturated with the liquid electrolyte $LiPF_6$ (1 M) in ethylene carbonate and dimethyl carbonate (1:1 by volume). The assembled cells were galvanostatically cycled between 2.5 and 1.0 V using a Toyo system automated tester (TOSCAT-3100, Toyo System Co., LTD., Fukushima, Japan). The powders were characterized by using X-ray powder diffraction (XRD: M18XHF, Macscience Instruments, Japan), high resolution transmission electron microscopy (HRTEM: JEM-3000F, JEOL, Japan), and field emission scanning microscopy (FESEM: JSM-6330F, JEOL, Japan).

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