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Carbon-coated titanium dioxide micro-bowls as an anode material for Li-ion batteries

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ABSTRACT

A series of micro-sized TiO_2 materials with different morphologies were synthesized via pyrolysis of spray-dried precursors, which were obtained via tetrabutyl titanate (TBT) hydrolysis reaction. The pH value of the precursor sol and its TBT content significantly influenced the morphology of the synthesized TiO_2 materials but showed little effect on the improvement of lithiation-delithiation capacity. The carbon coating effect on the electrochemical performance improvement depended on the morphology of the synthesized TiO_2 particles. Carbon-coated TiO_2 bowls with a large thickness (1.18 μm) provide an initial Li^+ insertion capacity of 310 mAh g^{-1} at a cut-off voltage of 1 V vs. Li^+/Li, which is much higher than the carbon-coated TiO_2 bowls with a small thickness (0.62 μm, capacity: 22 mAh g^{-1}). Carbon-coated TiO_2 bowls with a small thickness can be activated via lithiation-delithiation cycling between 0 and 3 V.

1. Introduction

Titanium dioxide (TiO_2) is a versatile material used as photocatalysts for photocatalytic hydrogen production and wastewater remediation [1], anode materials for photovoltaic cells [2], and electrode materials for Li-ion batteries [3]. The theoretical lithiation capacity of TiO_2 is 334 mAh g^{-1}, which is a little lower than that of graphite (372 mAh g^{-1}). At room temperature, TiO_2 usually provides a lithiation capacity of about 168 mAh g^{-1}, which is the equivalent of $x = 0.5$ in Li_xTiO_2 at bulk [4]. The high lithiation potential of TiO_2 results in a low energy density compared with graphite. However, the volume change in TiO_2 after lithiation is less than 4% [5], thereby providing TiO_2 with outstanding structure stability during lithiation and delithiation cycling.

The electrochemical performances of TiO_2 depend on its crystal structure and morphology, which are significantly influenced by synthesis methods and conditions [6–10]. Anatase TiO_2 shows a higher lithiation-delithiation capacity than its other polymorphs, such as rutile and brookite. For anatase TiO_2, the size of the particles [5] or wall thickness of the nanotube [6] is a critical factor in determining the lithiation capacity. $LiTiO_2$ can be obtained through the chemical insertion of nano-TiO_2 powders (7 nm) with *n*-butyllithium [11]. However, electrochemical Li-ion insertion in Li_xTiO_2 is difficult because of the strong repulsive force between Li ions when the insertion ratio is larger than 0.5 ($x > 0.5$ in Li_xTiO_2) [12–14] and the poor ionic conductivity of the $LiTiO_2$ phase [15,16]. Blending carbon materials, such as graphene [17] and single-wall carbon nanohorns [18], to fabricate TiO_2-C nanocomposite is an effective way to improve the lithiation-delithiation performance of TiO_2.

Tetrabutyl titanate (TBT) hydrolysis is an effective method for obtaining nano-TiO_2 materials [19,20] because TBT hydrolysis reaction is a bimolecular nucleophilic substitution reaction (SN2 reaction):

$$Ti(OR)_4 + xH_2O \rightarrow Ti(OH)_x(OR)_{4-x} + xROH \quad (1)$$

H_2O (nucleophile) attacks titanium (electron deficient electrophilic center) in TBT, which results in OH bonding to Ti and the expulsion of OR (leaving group) to form a sol. The pH value of the sol significantly influences the TBT hydrolysis and $Ti(OH)_4$ polycondensation [21]. The protonated OR group induced by H_3O^+ enhances the expulsion between Ti and OR to catalyze the TBT hydrolysis reaction. Moreover, the expulsion among protonated OR groups or between Ti and the protonated OR group hinders the polycondensation of $Ti(OH)_x(OR)_{4-x}$ and $Ti(OH)_4$ with $Ti(OH)_x(OR)_{4-x}$ ($x < 4$). Thus, polycondensation reaction occurs mainly among $Ti(OH)_4$ molecules and proceeds slowly to form a stable sol [22]. The particulate size and specific pore volume of the synthesized TiO_2 powders depend on the sol aging conditions [9].

The present study explores a synthesis method for preparing micro-sized TiO_2 as anode materials for Li-ion batteries. The spray drying technology is used for the preparation of micro-sized

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TiO_2 bowls (secondary particle) composed of nano-TiO_2 particles (primary particle) via TBT hydrolysis. The effects of pH value and TBT content in the precursor sol on the morphology and lithiation-delithiation capacity of the synthesized TiO_2 materials are investigated. The formation mechanism of the synthesized TiO_2 materials with special morphologies such as TiO_2 bowls is discussed. Carbon is coated to the surfaces of the TiO_2 bowls to improve their electric conductivity to enhance the lithiation and delithiation of the synthesized micro-sized TiO_2 materials. The effect of the coating layer on the rate performance and performance durability of the TiO_2 bowls with different thicknesses is studied via material characterizations and electrochemical analyses.

2. Materials and methods

2.1. Preparation of anatase TiO_2 and carbon-coated TiO_2

$Ti(OBu)_4$ (varied from 12 mL to 44 mL) was added dropwise into a dilute nitric acid solution (200 mL) with pH values of 0.5, 1.0, 1.5, and 2.0 to obtain sols after stirring for 15 min, which were then subjected to spray drying to prepare the TiO_2 precursor. Spray drying was conducted using a high-pressure swirl nozzle to disperse the precursor sol into a controlled drop size spray. Anatase TiO_2 for Li-ion battery was then obtained via the pyrolysis of the spray-dried materials at 300 °C for 2 h and then at 450 °C for 2 h in a muffle furnace.

Carbon-coated TiO_2 was prepared via the pyrolysis of polyethylene glycol (PEG)-coated TiO_2 at 450 °C for 2 h in a muffle furnace at N_2 atmosphere. PEG-coated TiO_2 was obtained via the evaporation of a mixture containing TiO_2 (0.5 g), PEG (2 g, molecular weight: 10000 g mol^{-1}), and deionized water (40 mL) at 100 °C after stirring for 30 min. The carbon content in the carbon-coated TiO_2 was determined to be 15 ± 1 wt.% based on the mass loss after the pyrolysis of the samples in air.

2.2. Physical characterization

The material structure was identified via X-ray diffraction (XRD) by using a Rigaku D/MAX-2550-PC X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54059$ Å, operated at 40 kV, 250 mA). The synthesized materials were observed via scanning electron microscopy (SEM) by using ZEISS ULTRA 55. The TiO_2-bowls were mounted into a resin by hot-pressing the mixture of TiO_2-bowls and resin powders and then polished with diamond oil slurry (0.1 μm) to observe the cross-section profile and to evaluate the thickness of the synthesized TiO_2-bowls via SEM before Au-coating [23].

The specific surface area was determined via the Brunnauer-Emmett-Teller (BET) method based on the N_2 adsorption–desorption isotherms of the synthesized TiO_2 samples by using an Autosorb-1-C automatic surface area analyzer (Quatachrome Corp.) at -196 °C. The samples were degassed to 10^{-5} Pa for 2 h at 200 °C before testing.

2.3. Electrode and electrochemical evaluation

The working electrode was prepared by coating the electrode slurry on a copper foil. The slurry was composed of the electrode material (80 wt.%), an acetylene black (10 wt.%) as the conducting agent, and a polyvinylidene fluoride (PVDF) (10 wt.%) as the binder in methyl-2-pyrrolidinone. The working electrode contains 2.4 mg of synthesized TiO_2, 0.3 mg of acetylene black, and 0.3 mg of PVDF. Coin cells (CR2025) were assembled in an Ar-filled glove box by using a metallic lithium foil as the counter electrode. The electrolyte was composed of 1 M $LiPF_6$ in an ethylene carbonate-dimethyl carbonate solution (1:1 ratio in volume). The working and counter electrodes were separated by a micro porous polypropylene membrane.

The lithiation and delithiation of the synthesized TiO_2 were performed at a constant current of 34 mA g^{-1} (0.1 C) between 1 and 3 V vs. lithium. The rate lithiation capability was measured after 10 h of galvanostatic delithiation (34 mA g^{-1} of TiO_2) and 1 h of potentiostatic delithiation at 3 V. The rest time for all these measurements was 5 min. Carbon-coated TiO_2 was activated through lithiation and delithiation between 0 and 3 V at a constant current of 28 mA g^{-1} (equivalent to 34 mA g^{-1} of TiO_2), with 1 h potentiostatic delithiation at 3 V after galvanostatic delithiation. Electrochemical impedance spectrum analyses were carried out using a Zahner IM6e analyzer in a two-electrode system. The AC frequency varied from 100 kHz to 1 mHz, with an amplitude of 5 mV. All measurements were conducted at 25 °C.

3. Results and discussion

3.1. Morphological effect on lithiation and delithiation

When the sols were atomized into micro-sized droplets at a high driving pressure during spray drying, $Ti(OH)_4$ polycondensation occurred, depending on the pH value and water content in the sol droplets. Low water content and high pH value promote $Ti(OH)_4$ polycondensation. The pH value of the precursor sol is higher when the same amount of TBT is added into the HNO_3 solutions with higher pH values. Fig. 1 shows the XRD patterns of TiO_2 prepared via the pyrolysis of spray-dried materials from precursor sols containing 20 mL of TBT in 200 mL of dilute HNO_3 solutions with different pH values and different TBT contents in 200 mL of dilute HNO_3 solution (pH = 1). The phase structure and morphology (secondary particles) are significantly affected by the pH value of the precursor sol, as shown in Figs. 1 and 2. The synthesized TiO_2 samples are composed of anatase and rutile phases. The anatase and rutile peaks are labeled as A(xxx) and R(xxx), respectively. TiO_2 from the precursor sols with lower pH value contains more rutile phase with regard to the relative diffraction intensities of the anatase and rutile phases. However, the TBT content in the precursor sol has little influence on the crystal structure of the synthesized TiO_2, but affects its morphology, as shown in Figs. 1 and 3.

At the beginning of spray drying, $Ti(OH)_4$ polycondensates rapidly on the sol droplet surface because of rapid water evaporation. When the pH value of sols is high (pH > 1.5), $Ti(OH)_4$ polycondensation rapidly occurs to form particles. The chemical stability of the sol increases with the decrease in the pH value of the sols (more H_3O^+). Water evaporation is hindered when a shell is formed during spray drying. $Ti(OH)_4$ then polycondensates slowly to form a hollow structure in the subsequent drying process. The hollow structure depends on the strength of the formed shell. When the shell is too weak (thin shell) to support its shape, the hollow structure collapses to form bowls, as shown in Fig. 2 (c). The shell is composed of nano-sized particles, as shown in the insert of Fig. 2 (c). Further decrease in the pH value of sols leads to further retardation of $Ti(OH)_4$ polycondensation, which results in the formation of an extremely weak shell. This weak shell cannot support the hollow structure, thereby collapsing to form a curled structure, as shown in Fig. 2 (d).

Fig. 4 shows the lithiation and delithiation of TiO_2 prepared via the pyrolysis of spray-dried materials from precursor sols with different pH values. Based on the first-principles statistical mechanical study of the thermodynamic and kinetic properties of lithiated anatase Li_xTiO_2 [24], TiO_2 undergoes the following steps to accomplish a lithiation-delithiation loop, as shown in Fig. 3(d):