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Nitrogen-doped carbon coating inside porous TiO_2 using small nitrogen-containing molecules for improving performance of lithium-ion batteries

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ABSTRACT

Alternative anode materials with more positive lithium intercalation potential than that of graphite are desirable for lithium ion batteries with high safety particularly required for electric vehicles and sustainable energy sources. Thermally stable, mesoporous anatase TiO_2 spheres are successfully synthesized, using ethylene diamine as a precursor, *via* a facile solution-phase process incorporating a nanoscopic carbon coating doped with a relatively high nitrogen content which formed a conducting network with mesoporous TiO_2 upon calcination. The structural characterizations demonstrate the crucial function of ethylene diamine in stabilizing and maintaining the well-confined mesoporous structure for TiO_2 during calcination. The porous TiO_2 material with a conducting network exhibits a highly reversible capacity of 182 mA h g^{-1} after 60 cycles at the current density of 0.5 C and an improved rate capability compared to porous TiO_2 without modification, indicating the composite is a promising anode material for Li-ion batteries.

1. Introduction

With increasing concerns over energy shortage and environmental issues from fossil fuels, the demand for green and sustainable energy sources is urgent [1]. Li-ion batteries (LIBs), which have the highest energy density among secondary batteries, are one of the most promising electrochemical power sources to be widely used in portable electronics, electric vehicles, and stationary energy storage systems [2]. However, the safety of LIBs is a key obstacle to their applications in hybrid, plug-in hybrid, and electric vehicles. Some alternative materials with more positive lithium intercalation potential than that of graphite are attracting increased attention from researchers focusing on avoiding formation of lithium dendrites on the graphite anodes after successive cycles [3,4]. Anatase TiO_2, with a relatively high lithiation voltage plateau at around 1.7 V *vs.* Li/Li^+, has been extensively studied as an anode material for LIBs due to its high capability, high safety, and low cost [5]. However, poor electrical conductivity ($\sim 10^{-2}$ to 10^{-7} S cm^{-1}) and a low diffusion coefficient of lithium ions ($\sim 10^{-15}$ to 10^{-9} cm^2 s^{-1}) in the TiO_2 lattice hamper the advancement of TiO_2 as an anode material for LIBs [6,7].

To address this concern, constructing porous structures has been suggested to be an efficient approach to improve the electrochemical performance of TiO_2 materials as the porous structures can enhance diffusion kinetics by reducing the diffusion paths for both electronic and ionic transport [8,9]. Nevertheless, materials with conventional textural porosity created by packing of particles typically exhibit thermal instability, resulting in cracks of the material's interconnecting network during calcination, destroying the material's porous structure and leading to loss of superior lithium storage performance. Additionally, the problem of intrinsic conductivity defects in electrode material cannot be solved effectively through this structural design; so, the rate capability of electrode material remains limited. To overcome these problems, surface modification of materials with conducting layers has been extensively investigated since this strategy can both stabilize the porous structure and enhance the conductivity of the material while retaining electrical contact in the electrode [10]. Recently, instead of using conventional carbon as a conducting layer, the use of N-doped carbon can further improve the electronic conductivity, ion permeability of the carbon layer, and charge transfer at the interface, which brings great advancement in reversible capacity and rate capability of active materials for LIBs [11,12]. Moreover,

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to optimize the electrochemical performance of active material, the conducting layer should be uniform and continuous, so that it can provide rapid, continuous electronic transport and mitigate the formation of the solid electrolyte interface (SEI) layer as well. Fabrication of a uniform and continuous nanoscale N-doped carbon layer around TiO_2 with stable mesophase, thereby, seems to be one of the most effective strategies for applications in LIBs.

Herein, we promote the synthesis of mesoporous TiO_2 spheres coated with N-doped carbon *via* a facile approach, in which, ethylene diamine (EDA) was used as a new precursor to obtain N-doped carbon for the first time. Compared with conventional solid precursors, the EDA species, having small molecular dimension, can penetrate easily into porous materials. Moreover, EDA, which is a strong alkali with two primary amine groups and conventionally used as the structure-directing agent in the synthesis of zeolites to generate and stabilize the porous structures, can have strong interactions with TiO_2 primary particles and readily bind on the surface of TiO_2 [13,14]. As a result, the encircling EDA species can stabilize the network of mesoporous TiO_2 against collapsing at relatively high temperature and maintain a well-confined porous structure [15]. The encircled EDA species will consequently be decomposed into N-doped carbon layer after pyrolysis and the conducting network will be formed with mesoporous TiO_2. Compared with the aforementioned reported work using relative large molecules, such as dopamine, EDTA, and ionic liquids as precursors, the nitrogen content of the carbon coating layer from pyrolysis of the economical EDA species ($C_2H_6N_2$) is relatively high, which may show enhanced improvement of conductivity resulting from a remarkable electron transfer from the surface of the active material to the coating layers [16]. Furthermore, the small molecular size of the EDA species may form a relatively thin coating layer on the surface of the active material avoiding blocking in porous structure and restriction of ion transfer/transport, synonymous with thick coating layers [17]. As expected, the as-obtained mesoporous TiO_2 coated with N-doped carbon, which has a well-confined porous structure and a relative high specific surface area, exhibits great improvement in electrochemical performance as an anode material for LIBs.

2. Experimental Section

2.1. Materials synthesis

In a typical procedure for synthesis of titanium ethylene glycolate (TEG), 3.0 mL of tetrabutoxy titanium (TBT) was added to 50 mL of ethylene glycol (EG) and the mixed solution was stirred for 8 h at room temperature. Then the mixture was poured into 200 mL acetone containing 0.5 mL deionized water with stirring at room temperature for 1 h. The white precipitate was harvested by centrifugation, then washed three times with ethanol and finally dried in an oven at 333 K for 12 h.

Synthesis of dense TiO_2 spheres (d-TiO_2): The TEG precursor was calcinated in air at 723 K for 4 h with a heating rate of 1 K min^{-1}, followed by natural cooling in ambient conditions.

Synthesis of porous TiO_2 sphere (p-TiO_2): A measured amount (2.0 g) of TEG precursor was dispersed into 100 mL of distilled water under stirring and then refluxed at 373 K for 1 h. The white precipitate was harvested by centrifugation and then washed with distilled water several times, followed by drying at 333 K in an oven. The dried powder was calcinated in air at 723 K for 4 h with a heating rate of 1 K min^{-1} and finally cooled to room temperature.

Synthesis of porous TiO_2 coated with N-doped carbon (p-TiO_2@NC): For synthesis, 2.0 g of porous TiO_2 spheres were dispersed in 100 mL of EDA solution under stirring and then refluxed at 368 K for 48 h. The light yellow precipitate was harvested by centrifugation and then washed with ethanol several times. After drying at 333 K in an oven, the obtained powder was calcinated in an Ar atmosphere at 723 K for 4 h with a heating rate of 1 K min^{-1}, followed by natural cooling to room temperature.

2.2. Structural characterization

The crystallinity of the samples was examined by X-ray power diffraction (XRD) using X Pert-ProMPd (Holand) D/max-A X-ray diffractometer with Cu Kα radiation (λ= 0.1514178 nm), operated at 40 kV and 40 mA. Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectrometry (EDS) were taken on a FEI-quanta 200F scanning electron microscope with an acceleration voltage of 30 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded with a FEI-Tecnai F20 (200 kV) transmission electron microscope. X-ray Photoelectron Spectroscopy (XPS) data was obtained by using a KRATOS Axis ultra-DLD X-ray photoelectron spectrometer with a monochromatic Mg Kα X-ray ($h\nu = 1283.3$ eV) and XPS samples were prepared by drying a dispersion of micro-crystals onto a piece of silicon wafer. The N_2 adsorption/desorption isotherms were obtained via a Quadrasorb 2MP (Micromeritics Industrument Corp.) surface area & porosity analyzer at 77 K. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The pore size distribution was calculated by the Barret-Joyner-Halenda (BJH) method. The Fourier transform infrared spectra (FT-IR) of samples were measured by the KBr pellet method using Bruker Vertex 70 spectrometer.

2.3. Electrochemical characterization

Electrochemical characterization was performed using coin cells. The working electrodes were prepared by mixing 80 wt% of active anode material, 10 wt% of conducting additive (Super-P carbon black), and 10 wt% of polyvinylidene fluoride (PVDF) binder in N-methylpyrrolidone (NMP) to form a homogenous slurry. The slurry was applied to a copper foil current collector and dried at 393 K for more than 12 h before cutting into a circular sheet. The cut sheet was dried at 393 K in a vacuum oven for another 12 h. A pure lithium metal foil was used as the counter electrode and a 1 M $LiPF_6$ solution in a 50: 50 v/v mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) was used as the electrolyte. Battery assembly of CR2016 coin cells was carried out in a glove box recirculating with Ar in which both oxygen and moisture contents were kept below 1 ppm. Cyclic voltammetry (CV) tests were performed between 0.01 and 3.0 V at a scan rate of 0.1 mV s^{-1} on a CHI600B electrochemical workstation system (Shanghai, China). The coin cells were cycled at different current densities between 1.0 and 3.0 V on a LAND CT2001A cell test instrument (Wuhan, China) at room temperature ($\sim$ 398 K). The electrochemical impedance spectroscopy (EIS) measurements were performed via PARSTAT 2273 electrochemical workstation system (Princeton Applied Research, AMETEK, America) over frequency range 100 kHz - 10 mHz with amplitude of 10 mV.

3. Results and discussion

As depicted by the XRD patterns in Fig. 1, the d-TiO_2 spheres were consisted of only anatase phase; while, both p-TiO_2 and p-TiO_2@NC spheres were composed of the anatase phase with a trace of brookite, in accordance with previous reports [18,19]. The peaks at 25.3°, 37.8°, 48.0°, 53.9°, 55.1°, 62.7°, 68.8°, 70.3°,and 75.0° can be indexed to (101), (004), (200), (105), (211), (204), (116), (220), and (215) crystal planes of anatase (JCPDS 21-1272), while the peak at 30.8° corresponds to the (121) plane of brookite (JCPDS 75-1582).