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Mesostructured niobium-doped titanium oxide-carbon (Nb-TiO_2-C) composite as an anode for high-performance lithium-ion batteries

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HIGHLIGHTS

- Mesostructured porous nanocomposites of Nb-doped TiO_2 and carbon are prepared.
- The composites are prepared hydrothermally and used as anodes for Li-ion battery.
- Highly conductive porous carbon and optimized Nb doping (1 wt%) act synergistically.
- ~100% capacity retention (221 mAh/g) after 500 cycles is realized.
- Good rate capability with a high capacity (192 mAh/g) at 5 C is achieved.

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ABSTRACT

Mesostructured niobium (Nb)-doped TiO_2-carbon (Nb-TiO_2-C) composites are synthesized by a hydrothermal process for application as anode materials in Li-ion batteries. The composites have a hierarchical porous structure with the Nb-TiO_2 nanoparticles homogenously distributed throughout the porous carbon matrix. The Nb content is controlled (0–10 wt%) to investigate its effect on the physico-chemical properties and electrochemical performance of the composite. While the crystalline/surface structure varied with the addition of Nb (*d*-spacing of TiO_2: 0.34–0.36 nm), the morphology of the composite remained unaffected. The electrochemical performance (cycle stability and rate capability) of the Nb-TiO_2-C composite anode with 1 wt% Nb doping improved significantly. First, a full cut-off potential (0–2.5 V *vs.* Li/Li^+) of Nb-doped composite anode (1 wt%) provides a higher energy utilization than that of the un-doped TiO_2-C anode. Second, Nb-TiO_2-C composite anode (1 wt%) exhibits an excellent long-term cycle stability (100% capacity retention, 297 mAh/g at 0.5 C after 100 cycles and 221 mAh/g at 2 C after 500 cycles) and improved rate-capability (192 mAh/g at 5 C), respectively (1 C: 150 mA/g). The superior electrochemical performance of Nb-TiO_2-C (1 wt%) could be attributed to the synergistic effect of improved electronic conductivity induced by optimal Nb doping (1 wt%) and lithium-ion penetration (high diffusion kinetics) through unique pore structures.

1. Introduction

Rechargeable Li-ion batteries (LIBs) have attracted considerable attention as suitable electrochemical (EC) energy storage batteries for portable electronic devices and electric vehicles because of their high energy density, long cycling life, and environmental benignness [1,2]. Graphite has been employed as a typical LIB anode material owing to its high reliability and low potentials (below 0.2 V *vs.* Li^+/Li). However, graphite anodes suffer from limited discharge capacity (372 mAh/g), low C-rate capability, low power density, and safety concerns [1,2]. These drawbacks of graphite-based anodes have driven the development of new anode materials [1,2].

In the quest for alternative anode materials, titanium oxide (TiO_2) has been widely recognized as a viable candidate owing to fast Li^+ insertion at low voltages and low volume changes (< 4% for Li_xTiO_2, $0 < x < 1$) during the lithiation/delithiation processes [3,4]. In addition, TiO_2 is well known as a cost-effective material with environmental benignity and high chemical stability (superior safety). However, the application of TiO_2, especially anatase-structured TiO_2, as an LIB anode material has been limited by its poor electronic conductivity

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($\sim 10^{-12}$ to 10^{-7} S/cm), frequently encountered aggregation of TiO_2 nanoparticles, and sluggish Li^+ diffusion rate ($\sim 10^{-15}$ to 10^{-9} cm^2/s) originating from its wide energy band gap (E_g: 3.0–3.4 eV), resulting in drastic capacity fading in the charge/discharge process at a high current density or during long cycling periods [3–5].

To address these problems, there have been considerable efforts to improve the electronic conductivity and ionic transport/kinetics by regulating the conductivity, crystalline structure, and porosity because the Li^+ diffusion pathway and electron transport in the electrode largely depends on these parameters [3–5].

Typically, the electronic conductivity of TiO_2-based anodes has been enhanced by hybridizing them with highly conductive materials (*e.g.,* carbon nanotubes, graphene, and porous carbon) [4,5] or by doping aliovalent elements (B, Nb, Co, and Sn) [6–10]. First, hybridizing TiO_2 with conductive materials is an effective approach to enhance the conductivity of TiO_2 because the electronic transport is facilitated by the assistance of various conductive agents. In this respect, porous carbon-TiO_2 composites are especially attractive owing to their high electrical conductivities as well as large porosities, and specific surface areas [4,5]. In this case, the conformality of the hybrid TiO_2 composite and intrinsic conductivity of the conductive agent determine the electrical properties of TiO_2-composite because of the proximity of the conductivity of the TiO_2 composite and conductive agent [4,5]. Second, doping of TiO_2 with aliovalent ions (B, Nb, Co, and Sn) is considered an efficient approach to enhance the electrical conductivity and internal surface area of TiO_2. This is because of the enhanced Li^+ diffusion kinetics and electronic conductivity by the formation of more open channels and active sites for Li^+ ion transport *via* the interplanar expansion of the TiO_2 lattice and conduction band shift in Ti by the oxygen vacancy, respectively [7,8,11,12]. With respect to EC performance, Nb-doped TiO_2-based electrodes revealed improved capacity because of surface storage enhancement by pseudocapacitive effects [7,8,11,12]. For instance, Usui et al. reported a significantly enhanced electronic conductivity of Nb-doped rutile TiO_2 electrodes resulting in an improved rate capability [7]. Darr et al. presented Nb-doped anatase TiO_2 nanoparticles as the anode for LIBs to achieve improved EC performance owing to a high electronic conductivity, lithium-ion diffusivity, and more active surface sites available for Li-storage [11]. The internal surface area is usually related to the mesoporosity, interplanar spacing, and specific surface area of TiO_2. Nevertheless, the electron and Li^+ ion transports can be improved further by judiciously tailoring the morphologies and particle sizes of TiO_2-based composites [11,12]. Specifically, a high surface/volume ratio can efficiently enhance the lithium storage capability and reaction kinetics owing to a short Li^+ diffusion pathway and effectively accommodate lithiation-induced stresses [2,4].

In this context, it is essential to combine the above approaches (conductive agent compositing, substitutive ion doping and tailored morphology) to further boost the EC performance of TiO_2-based LIB anodes because of the facilitation of electron transport along the porous carbon and doped TiO_2 [3–5]. This goal may be achieved through the formation of mesostructured, doped TiO_2-conductive carbon composites with enhanced conductivities and facilitated lithium ion transport [3–5]. Despite elaborate efforts, to our best knowledge, there are only few reports describing such composites for application in lithium ion batteries. Moreover, despite improved EC performances of TiO_2-based composites, most of the reported synthetic methods are complicated and are not viable for practical applications [5,8,11,12]. Therefore, developing a simple synthetic route for developing a mesostructured composite of Nb-doped TiO_2 and conductive porous carbon with a homogeneous distribution of the Nb-doped TiO_2 nanocrystals in the carbon matrix remains a challenge.

Herein, we present a mesostructured Nb-doped TiO_2-carbon (Nb-TiO_2-C) composite for high-performance lithium-ion battery applications. Mesostructured Nb-TiO_2-C composites were prepared by a simple and scalable hydrothermal synthetic approach using $NbCl_2$ and Ti-isopropoxide as precursors for Nb-TiO_2 nanoparticles and dextrose for porous carbon. In contrast to conventional syntheses of carbon composites, the simplicity and scalability of the hydrothermal approach renders our process suitable for practical applications [4].

We characterized the as-formed Nb-TiO_2-C composites by various microscopic, analytical, and spectroscopic methods. Our Nb-TiO_2-C composite exhibits a homogeneous distribution of the Nb-TiO_2 nanoparticles (*ca.* 18 nm) and a unique composite structure because the conformal structure formed between the nanoparticles and carbon could efficiently inhibit the growth of Nb-TiO_2 nanocrystals. Further, using the composite as an anode material in LIBs, we investigated its EC performance. The incorporated Nb^{5+} not only affects the band structure of TiO_2, but also improves the electrical conductivity and Li^+ diffusion kinetics of the composite by promoting carbon graphitization and reducing crystallization of TiO_2. The synergistic effect of porous carbon and Nb doping in the Nb-TiO_2-C composites leads to good EC performance (long-time cycle stability and high-rate capability).

2. Experimental

2.1. Material synthesis

All materials were purchased from Sigma-Aldrich and used without further purification.

Mesostructured Nb-TiO_2-carbon composite: The Nb-TiO_2-C composite was prepared by a simple and scalable hydrothermal synthesis method followed by a sintering process (900 °C under N_2 atmosphere), as illustrated in Scheme 1. In the hydrothermal synthesis, tetrabutyl titanate, niobium chloride, and glucose were used as Ti, Nb, and carbon precursors, respectively. In a typical synthesis, 8.4 g of dextrose, 8.4 g of titanium isopropoxide, known amounts of niobium chloride (0–10 wt %), and 0.5 g of HCl were dissolved in 40 ml of water under magnetic stirring until complete homogenization. The mixture was transferred to a hydrothermal bomb reactor and maintained undisturbed at 180 °C for 18 h. Subsequently, the as-prepared hydrothermal product was carbonized at 900 °C for 2 h under nitrogen atmosphere at a heating rate of 5 °C min^{-1}. The TiO_2-C composite (TiO_2-C) without Nb was also prepared by a similar process, to serve as a control sample.

2.2. Material characterization

The size and morphology of the samples were analyzed by transmission electron microscopy (TEM, CM120, FEI) at a 100 kV accelerating voltage, high-resolution transmission electron microscopy (HR-TEM, JEM-2100F) at a 200 kV accelerating voltage, and scanning electron microscopy (SEM, NanoSEM 630, NOVA) at a 1.5 kV accelerating voltage. The elemental composition and distribution (elemental maps) of the samples were also analyzed by electron microscopes (SEM and TEM) equipped with energy-dispersive spectroscopy (EDS) and high-angle annular dark field (HAADF) mode of scanning-TEM (S-TEM). The crystalline structure of the samples was characterized by powder X-ray diffraction (XRD, RAD-3C, Rigaku) using Cu-$K\alpha$ radiation (λ: 1.541 Å) at room temperature in the 2θ range of 10–90°. In addition, the chemical bonds and surface elemental composition of the samples were analyzed *via* X-ray photoelectron spectroscopy (XPS, Escalab 250, Thermo Fisher Scientific) with an Al-$K\alpha$ (h_m: 1486.6 eV) source. The composition of the samples was further examined by thermogravimetric analysis (TGA, Thermo Fisher Scientific) under air to determine the accurate carbon content of the composite (temperature range (25–900 °C), ramping rate (2 °C min^{-1})). The Raman spectra of the samples were obtained with a Raman spectrometer (Renishaw) in the backscattering geometry. Spectra were averaged over 20 accumulations and the laser power was maintained at 2.5 mW. Nitrogen sorption isotherms for the samples were obtained with a porosity analyzer (ASAP 2000, Micromeritics). The adsorption and desorption isotherms for the samples were analyzed using the Brunauer-Emmett-Teller (BET)