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Controlled synthesis of dual-phase carbon-coated $Nb_2O_5/TiNb_2O_7$ porous spheres and their Li-ion storage properties

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ABSTRACT

Dual-phase $Nb_2O_5/TiNb_2O_7$ and carbon-coated $Nb_2O_5/TiNb_2O_7$ porous spheres were synthesized using a simple solvothermal method followed by post-heat treatment. The $Nb_2O_5/TiNb_2O_7$ materials comprised porous spheres with 3-dimensional interconnected microsphere architectures, with a homogeneous dispersion of carbon coating the $Nb_2O_5/TiNb_2O_7$ spheres. As the anode for a Li-ion battery, the dual-phase carbon-coated $Nb_2O_5/TiNb_2O_7$ porous spheres delivered a high gravimetric capacity of >247 mA h g^{-1} with good cycling performance, as well as a high rate capability. The unique and advantageous characteristics of the dual-phase carbon-coated $Nb_2O_5/TiNb_2O_7$ porous spheres for high performance Li-ion batteries are attributed to the synergistic effects of the porous, two-phase structure of the material. Furthermore, the conductive carbon matrix on the spheres provided facile electron transport and an effective alleviation of mechanical strain during cycling. The high electrochemical performance of the dual-phase carbon-coated $Nb_2O_5/TiNb_2O_7$ porous spheres recommends them as a promising anode material for future Li-ion batteries.

1. Introduction

Transition metal oxides have been extensively explored as replacements for carbon-based anodes in Li-ion batteries due to their attractive physicochemical properties. These materials react with Li via two different mechanisms, i.e., by intercalation and conversion reactions [1–3]. Intercalation-type materials (e.g., $Li_4Ti_5O_{12}$, TiO_2, MoO_2) with multidimensional structures can reversibly insert Li-ions into their lattices without destroying the crystal structure, but their specific capacities are limited. Conversion-type materials such as CuO, NiO, Co_3O_4, and Fe_3O_4 are usually decomposed as metallic particles embedded in an insulating Li_2O matrix. However, although these materials have a higher gravimetric specific capacity than already commercialized graphites, there are drawbacks in terms of structural instability and poor electrical conductivity during cycling [4–6].

Among the transition metal oxides, niobium-based oxides have been extensively investigated as intercalation-type anode materials for Li-ion batteries [7–12]. They offer a safety advantage because of their low surface reactivity with the electrolyte toward forming a solid-electrolyte interphase (SEI) layer. Additionally, in the case of orthorhombic Nb_2O_5, a stable charge–discharge process is permitted by its crystal structure because empty octahedral sites between the (001) planes provide Li-ion transport pathways [13]. However, many bulk niobium-based oxides are primarily disadvantaged by their poor intrinsic electrical conductivity (3×10^{-1} S cm^{-1}), which results in a low diffusion rate and restricts their use as a replacement for commercialized graphite anode materials [14].

Various approaches have been used to solve these intrinsic electronic/ionic conductivity limitations, including: selecting a favorable crystal structure (polymorph); optimizing particle size and controlling of morphology to reduce Li-ion diffusion pathways; and coating the particle with electronically conductive materials [15–18]. The niobium oxides are known to crystallize in various

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polymorphic forms, including pseudohexagonal (H-type), orthorhombic (O-type), tetragonal (T-type), and monoclinic (M-type) Nb_2O_5 phases. These crystal structures have different thermodynamic stabilities, and can be easily transformed, as evidenced by the conversion from monoclinic to tetragonal phases with increasing sintering temperature [10,14]. Nb_2O_5 polymorphs have been investigated as anode materials for Li-ion batteries, and structural changes have been observed during the charge–discharge process. Furthermore, the orthorhombic and tetragonal structures have been found to exhibit better cycle performance [7]. The electrochemical properties also deeply depend on the size and morphology of the particles. The architectural structure of Nb_2O_5 can slightly modulate the stresses that occur during cycling and enhance the Li-ion transport kinetics [19]. In addition, carbon composites as conductive materials can be incorporated to overcome their intrinsic conductivity limitations [11,20].

Another niobium-based oxide, monoclinic $TiNb_2O_7$, was recently introduced by the Goodenough group as an alternative anode material [21,22]. $TiNb_2O_7$ can theoretically accommodate five Li per formula unit as $Li_xTiNb_2O_7$ ($0 \leq x \leq 5$) via multiple redox couples ($Ti^{4+/3+}$, $Nb^{5+/4+}$, and $Nb^{4+/3+}$), and consequently, has a higher theoretical capacity (388 mA h g^{-1}) than graphite. Moreover, its safety characteristic, related to the prevention of SEI layer formation due to the higher operating potential, is also attractive. However, the intrinsic low electronic conductivity and poor ionic diffusivity in the $TiNb_2O_7$ lattice have restricted its electrochemical performance, such as its capacity retention and rate capability. Consequently, the kinetic issues associated with $TiNb_2O_7$ must be resolved before it becomes commercially applicable [23]. Interestingly, the kinetics of Li insertion/extraction can be enhanced significantly by several approaches [24–27], and the electronic conductivity can be effectively improved by the incorporation of a conductive material (i.e., carbon) or cation/anion doping [26,28]. In addition, nano-structured materials with large surface areas are expected to exhibit increased Li-ion insertion/extraction kinetics through shorter diffusion pathways, resulting in excellent power densities [25,29].

In this study, we successfully prepared dual-phase carbon-coated $Nb_2O_5/TiNb_2O_7$ porous spheres through a solvothermal synthesis without any surfactant assistance, and explored their use as anode materials for Li-ion batteries. The as-synthesized porous spheres consisting of two intercalation-type materials worked synergistically to improve electrochemical performance, and consequently, the material achieved superior electrochemical properties compared to Nb_2O_5 spheres. These results indicate that dual-phase carbon-coated $Nb_2O_5/TiNb_2O_7$ porous spheres have potential for future practical application in Li-ion batteries as anode materials.

2. Experimental

The synthesis procedure is illustrated in Fig. 1. The $Nb_2O_5/TiNb_2O_7$ porous spheres were prepared by a solvothermal reaction. In a typical experiment, niobium chloride ($NbCl_5$, >99%, Alfa, 70 mmol) was dissolved in ethanol (20 mL) with gentle stirring. Titanium isopropoxide ($C_{12}H_{28}O_4Ti$, >97%, Aldrich, 25 mmol) was added, and the resultant solution was transferred into a Teflon-lined autoclave and heated at 180 °C for 24 h with a heating/cooling rate of 2 °C min^{-1}. The resulting slurry was then filtered and washed with distilled (DI) water before drying in a vacuum oven. The powder was finally heated at 700 °C in air for 2 h. To obtain the carbon-coated $Nb_2O_5/TiNb_2O_7$ porous spheres, the as-synthesized $Nb_2O_5/TiNb_2O_7$ porous spheres (0.5 g) were dispersed in DI water (20 mL) and sonicated for a few minutes; then, D-glucose ($C_6H_{12}O_6$, >99%, Aldrich, 0.1 g) was added. The reaction mixture was transferred to a Teflon-lined autoclave and subjected to hydrothermal treatment at 180 °C for 12 h. The resulting material was isolated by centrifugation and further carbonized under Ar flow at 700 °C for 1 h.

The phase analysis of the synthesized samples was performed using a D8-Bruker X-ray diffractometer with Cu Kα radiation. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using a Mettler-Toledo TGA/DSC 1 in air at a heating/cooling rate of 10 °C min^{-1}. Raman spectra were recorded using a Horiba Jobin Yvon Raman spectrometer with 512 nm laser excitation. The specific surface areas were evaluated with a BELSORP-mini surface analyzer based on the Brunauer–Emmett–Teller (BET) multipoint method and N_2 physisorption at 77 K. Adsorption–desorption isotherm measurements were used to determine the porosity and pore size distribution via the Barrett–Joyner–Halenda (BJH) method. The morphology, microstructure, and composition of the synthesized samples were examined with a Tescan Mira LM scanning electron microscope (SEM) and FEI Tecnai field-emission transmission electron microscope (FE-TEM).

For electrochemical evaluation, electrodes were prepared by mixing 70 wt% of the active material powder, 15 wt% carbon black (Super P) as a conducting agent, and 15 wt% polyvinylidene fluoride (PVDF) dissolved in *N*-methylpyrrolidinone (NMP) as a binder to form a slurry, followed by coating on copper foil, pressing, and drying at 120 °C for 2 h under vacuum. CR2032 coin cells were assembled in an Ar-filled glove box using Celgard polypropylene as a separator, Li foil as the counter electrode, and 1 M $LiPF_6$ in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (EC–EMC, 1:2 v/v) as the electrolyte. The charge–discharge experiments were performed galvanostatically at a constant current density of 38 mA g^{-1} (C/10) within the voltage range of 1–3 V vs. Li^+/Li. The electrochemical impedance spectroscopic analysis (EIS) was carried out with a ZIVE SP2 instrument by applying a 10 mV amplitude signal in the frequency range of 10 kHz to 0.01 Hz. For the EIS measurements, an active material content of ~0.5 mg served as the working electrode and Li foil served as the counter and reference electrodes. The impedance response was measured after 20 cycles and it was fitted with use of the ZMAN software.

3. Results and discussion

The X-ray diffraction patterns of the $Nb_2O_5/TiNb_2O_7$ and carbon-coated $Nb_2O_5/TiNb_2O_7$ samples are shown in Fig. 2(a). For each sample, every reflection could be indexed on the bases of orthorhombic Nb_2O_5 (*Pbam*, JCPDS no. 30-0873) and monoclinic $TiNb_2O_7$ (*C*2/*m*, JCPDS no. 39-1407). The XRD pattern does not show any peaks corresponding to carbon due to its amorphous nature or low content. Although the carbon coating on the surface results in slightly weakened XRD peak intensities, the XRD patterns show that the carbon coating process did not destroy the structure of Nb_2O_5 or $TiNb_2O_7$. To better characterize the carbon present in the carbon-coated $Nb_2O_5/TiNb_2O_7$ sample, TGA/DTA was performed as a function of temperature (Fig. 2(b)). One exothermic DTA shoulder is observed at ~430 °C, corresponding mainly to the loss of carbon from the sample as CO_2. No events occur after ~580 °C, and the weight loss represents ~2.5 wt% carbon. The carbon-coated $Nb_2O_5/TiNb_2O_7$ sample was further investigated by Raman spectroscopic analysis, as shown in Fig. 2(c). The modes at 1582 and 1357 cm^{-1} correspond to the G (ordered) and D (disordered) bands, respectively. The high integrated intensity ratio (I_D/I_G) of 0.82 for carbon-coated $Nb_2O_5/TiNb_2O_7$, as compared to 0.09 in ordered synthetic graphite, indicates a higher degree of disorder [30] for the carbon in the $Nb_2O_5/TiNb_2O_7$ sample.

The morphology and microstructure of the as-synthesized