

Enhanced electrochemical performance of Li-ion batteries with nanoporous titania as negative electrodes

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Abstract

Nanoporous anatase TiO₂ (np-TiO₂) electrodes have been developed via the anodization of titanium foils in fluoride containing electrolytes, and its application in rechargeable lithium-ion batteries (LIBs) was investigated. Four different types of np-TiO₂ electrodes with different pore diameters of 14.7±8.2 nm, 12.8±6.8 nm, 11.0±5.5, and 26.7±13.6 nm were fabricated for evaluating the effect of nanoporous characteristics on the LIB performance. The discharge capacity of the four battery types 1, 2, 3, and 4 were 132.7 mAh·g⁻¹, 316.7 mAh·g⁻¹, 154.3 mAh·g⁻¹, and 228.4 mAh·g⁻¹, respectively. In addition, these electrodes 1, 2, 3, and 4 exhibited reversible capacity of 106.9 mAh·g⁻¹ after 295th, 180.9 mAh·g⁻¹ after 220th, 126.1 mAh·g⁻¹ after 150th, and 206.7 mAh·g⁻¹ after 85th cycle at a rate of 1 C, respectively. It was noted that the cyclic life of the batteries had an inverse relationship, and the capacity had a proportional relationship to the pore diameter. The enhanced electrochemical performance of the nanoporous electrodes can be attributed to the improved conductivity and the enhanced kinetics of lithium insertion/extraction at electrode/electrolyte interfaces because of the large specific surface area of np-TiO₂ electrodes.

Key words

nanoporous TiO₂; negative electrode; capacity; lithium-ion batteries

1. Introduction

Lithium-ion batteries (LIBs) are one of the most promising energy storage systems for the portable power market [1], which have attracted enormous attention for several years because of their large-scale energy storage applications, such as for solar and wind power [2], electric vehicles (EV) and hybrid electric vehicles (HEV) [3]. LIBs have been very successful in the division of portable electronics since their first commercialization by Sony in the early 1990s [4]. However, further improvements in terms of power densities, safety, cost effectiveness, and lifetime require new materials or new structures with a higher storage capacity, faster charge/discharge rates and desirable potential for wider applications [5,6]. In principle, the thermodynamics of lithium insertion into the electrochemically active phase is affected by the nanosized structure of the host materials [7–9]. Extensive investigations have been carried out on the nanostructured materials because of their beneficial properties, such as shortened diffusion paths for both electronic and ionic transport, and also a large electrode-electrolyte contact area [10–12]. Among various

kinds of nanostructured materials, nanoporous materials have received particular attention since they can be more effective in increasing the electrode stability and Li intercalation capacity, especially at high charge/discharge rates. Electrodes of nanoporous, especially mesoporous (2–50 nm) materials for lithium batteries have short transport lengths for Li⁺ ions due to their nanosized grains (10–20 nm), and easy access for electrolytes due to their nanopores (5–10 nm) [13]. Therefore, attempts have been made to synthesize hierarchical, porous, nanometer-sized materials for applications in negative electrode materials for stationary energy storages with high discharging potential [14–18].

Transition-metal oxides (TMOs) have been extensively studied as negative electrodes since the reaction of nanosized TMOs with Li⁺ in the solid state was reported [19]. The nanosized pores play a considerable role in shortening the lithium-diffusion length in the solid phase, as long as the electrolytes can penetrate the pores, thus enabling fast transport towards the interior of the solid. Among various TMOs, TiO₂ has been considered as one of the promising electrode materials for LIBs. Various polymorphs of titania such as rutile [20], anatase [18,21] and TiO₂ (B) [22–25] have been studied as

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electrode materials for LIBs. The theoretical capacity of TiO₂ is low but the overall safety of the cell is greatly improved [26]. In addition, anatase TiO₂ is a stable, low cost, non-toxic, and environmentally friendly material for use as anode material in LIBs [27,28]. In comparison with the normally used carbonaceous materials, anatase TiO₂ has a lithium insertion voltage around 1.8 vs. Li/Li⁺ which is far above the lithium plating voltage that ensures the safety of LIBs [29–31]. Furthermore, anatase TiO₂ offers a higher capacity and high cycling stability, and due to the oxidic framework, the anode cannot contribute to the combustion reactions, which leads to improved cell safety [32]. The main drawback of anatase TiO₂ based anode electrodes in LIBs is the poor chemical diffusivity of lithium; both electron and lithium ion transport are extremely slow, leading to the limited lithium storage kinetics and rate performance [33]. However, a simple way of improving lithium ion transport in battery materials is the introduction of open porosity [7]. Recently TiO₂ and TiO₂ based materials have been demonstrated as promising anodes in rechargeable LIBs [34,35]. In particular, these nanostructured TiO₂ materials are regarded as promising active lithium intercalation anode materials with fast Li-intercalation/deintercalation [36]. They provide shorter pathways for both electronic and Li ionic transport, a higher electrode/electrolyte contact area and better accommodation of the strain of Li ion intercalation/deintercalation [37,38]. Practical applications of TiO₂ for LIBs, however, still present a challenge due to the low chemical diffusivity of Li in TiO₂, although promising electrode systems have recently been proposed [21,39].

For this paper, we fabricated np-TiO₂ film with four different types of pore size by anodizing pure Ti foils in a neutral fluoride solution, and thereafter by calcination. The controlled anodization and calcination formed nanoporous anatase structures having a substantially high specific area. This large exposed area of electrodes is the main factor for an interfacial mechanism in which lithium is stored on the surface of anatase particles [40]. The electrochemical performances of np-TiO₂ as LIB electrodes were measured over 85 to 295 cycles (varies due to four types of battery), and excellent capacity retention was observed for np-TiO₂ of the selected dimensions. Using this method, the obtained np-TiO₂ showed fully reversible capacities as high as 162.2 mAh·g⁻¹ (1 C, 80th cycle for battery type 1), 165.8 mAh·g⁻¹ (1 C, 80th cycle for battery type 2), 127.7 mAh·g⁻¹ (1 C, 80th cycle for battery type 3), and 204.2 mAh·g⁻¹ (1 C, 80th cycle for battery type 4).

2. Experimental

2.1. Preparation of nanoporous titania

Pure Ti foils (99.7%) with a thickness of 0.10 mm were used to prepare nanoporous titania (np-Titania) electrodes. The Ti samples were ultrasonically cleaned in distilled water, ethanol and acetone successively and dried in air at room temperature. Electrochemical anodization was carried out at

room temperature in a homemade cell with a two-electrode configuration. A dc power supply (GPR-3030) was used to provide a constant potential during the anodization process. Ti foils with an exposed area of 16.0 cm² acted as the anodes, and a Pt plate with an area of 2.0 cm² was used as the cathode. The distance between anode and cathode was maintained at 2.0 cm. Electrolytes were in a solution of 0.5 wt% NH₄F (supplied by VWR[®]) dissolved in 1 mol/L (NH₄)₂SO₄ (supplied by VWR[®]) with 5 vol% (electrolyte type 1), 10 vol% (electrolyte type 2), 30 vol% (electrolyte Type 3), and 50 vol% (electrolyte Type 4) of ethylene glycol (EG) (supplied by VWR[®]), respectively. Potential was increased gradually from 0 V to 32 V and then held at this potential for 2 h. After anodization, the samples were washed with deionized water for 10 min and cleaned by sonification. Finally, the samples were heated in a GERO furnace to 500 °C by 2 °C/min rate, kept for 2 h at this temperature, and then cooled to room temperature before characterization.

2.2. Materials Characterization

X-ray diffraction (XRD) analysis using Cu K_α (λ = 1.5406 Å) radiation was employed to determine the nanoporous TiO₂ crystal structure. The diffraction patterns were recorded over a 2θ range from 10° to 80° at a step size of 0.02°. Scanning electron microscope (SEM) images were subsequently collected with Zeiss SUPRA 40VP, which was combined with energy dispersive X-ray (EDX).

2.3. Electrochemical measurements

Cyclic voltametric curves (CV) and electrochemical impedance spectroscopy (EIS) were performed with a PARSTAT[®] 2273 electrochemical station. Electrochemical software PowerSine and PowerCV were employed for impedance and CV data acquisition, respectively. The amplitude for EIS measurement was 10 mV, and the range of the frequency was from 100 kHz to 10.0 mHz. The CV measurements were performed at scan rates of 0.1 mV·s⁻¹, 0.5 mV·s⁻¹ and 1.0 mV·s⁻¹ in the range of 3.0 V to 1.0 V. All the measurements were conducted at room temperature (about 25 °C).

2.4. Li-ion battery assembly

As prepared, nanoporous titania were used as the negative electrode of LIBs. The positive electrode was metallic lithium foil, about 2.0096 cm² and 0.01 cm thickness. CR2032-type coin cells were assembled glove box filled with argon gas with O₂ content below 0.1%. The electrolyte used for LIBs was 1.0 mol/L LiPF₆ (supplied by Sigma-Aldrich). Celgard 2400 polyethylene was used as the separator. The separator, current collector, battery casings, and spacer were dried at 40 °C under vacuum over 24 h. Data acquisition and analysis were performed using the battery testing instruments LANHE-CT2001A and LANDt, respectively.

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