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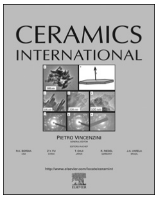

Preparation and capacitance performance of nitrided lithium titanate nanoarrays

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ABSTRACT

Nitrided lithium titanate (N-$Li_4Ti_5O_{12}$) nanoarrays with nanowire and nanotube structures were designed as the electrode materials of lithium-ion supercapacitor for electrochemical energy storage. Two types of TiO_2 nanoarrays were used as the precursor which involved TiO_2 nanowire array prepared by hydrothermal process and TiO_2 nanotube array prepared by anodization process. $Li_4Ti_5O_{12}$ nanoarrays were formed through hydrothermal reaction or sonochemical reaction of TiO_2 nanoarrays with lithium hydroxide and then calcination treatment process. Finally, N-$Li_4Ti_5O_{12}$ nanoarrays were formed through nitriding treatment of $Li_4Ti_5O_{12}$ using ammonia as nitrogen source. The electroactive N-$Li_4Ti_5O_{12}$ nanowire array and nanotube array exhibited the specific capacitance of 607.2 F g^{-1} and 814.4 F g^{-1} at a current density of 1 A g^{-1}, respectively. The corresponding capacitance retention was determined to be 92.1% and 94.2% after 1000 cycles at high current density of 5 A g^{-1}. The corresponding capacitance still kept 182.9 and 352.1 F g^{-1} at much higher current density of 20 A g^{-1}, presenting reasonable rate capability for N-$Li_4Ti_5O_{12}$ nanoarrays. The improved capacitance performance of N-$Li_4Ti_5O_{12}$ nanotube array was ascribed to the more amount of TiN and more accessible nanotube surface area, which contributed to the improved conductivity and fast diffusion of electrolyte ions on the surface of electrode. Both N-$Li_4Ti_5O_{12}$ nanowire array and nanotube array with well-aligned integrative structure exhibited an excellent cycling stability during continuous charge/discharge process. Well-designed N-$Li_4Ti_5O_{12}$ nanoarrays with high capacitance, good cycling stability and rate capability presented the promising application as feasible electrode materials of lithium-ion supercapacitors for the energy storage.

1. Introduction

The development of energy storage devices with high energy density and good cyclability has stimulated numerous research efforts on high performance electroactive materials [1,2]. Electrochemical supercapacitors and power batteries exhibit excellent properties such as cycling stability, rapid charging-discharging rate and energy density [3]. The spinel lithium titanate ($Li_4Ti_5O_{12}$) has been regarded as a promising electrode material of lithium-ion batteries because of near zero strain in the unit cell volume during the charge–discharge process. It can accommodate lithium ions during the charging process, resulting in a transition from spinel phase $Li_4Ti_5O_{12}$ to rock-salt phase $Li_7Ti_5O_{12}$ without noticeable changes in the lattice parameter ($Li_4Ti_5O_{12} + 3Li^+ + 3e^- \longleftrightarrow Li_7Ti_5O_{12}$) [4]. Normally, $Li_4Ti_5O_{12}$ is usually regarded as the anode material of lithium-ion battery. Compared to the graphite carbon electrode material, $Li_4Ti_5O_{12}$ has a relatively high operating voltage plateau, preventing effectively the decomposition of electrolyte and the formation of a solid-electrolyte interphase. Importantly, $Li_4Ti_5O_{12}$ exhibits excellent lithium-ion insertion/extraction reversibility with near zero strain in unit cell volume, guaranteeing a good charge–discharge performance by minimizing lithium dendrites growth [5]. These merits contribute to a long cycling life and cycling stability of $Li_4Ti_5O_{12}$ [6].

Nevertheless, the $Li_4Ti_5O_{12}$ has an inherently insulating property due to the empty Ti 3d state with band energy of about 2 eV, which seriously hinders its high rate performance. The lithium-ion intercalation of $Li_4Ti_5O_{12}$ involves three processes as follows. The solvated Li^+ diffuses from the bulk electrolyte solution. A charge-transfer reaction occurs at the interface between the $Li_4Ti_5O_{12}$ and the electrolyte, accompanying by accepting an electron. The Li^+ diffuses into the bulk $Li_4Ti_5O_{12}$ [7]. Till now, many approaches have been developed to improve the electrical conductivity of electrode materials [8,9]. Ions doped $Li_4Ti_5O_{12}$ can improve the electrical conductivity [10]. The bivalent metal ions such as magnesium ion

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are used to replace the lithium-ion and the trivalent metal ions such as ferric iron ion are used to replace the tetravalent titanium ion (Ti^{4+}) [11,12]. In addition, the composite materials are developed by introducing high electrical conductive carbon and metal materials (such as graphite, graphene, carbon quantum dot and silver metal) to $Li_4Ti_5O_{12}$, which can improve surface conductive ability of electrode materials [13–16]. In addition, it was reported that the nitrogen doped carbon and titanium nitride (TiN) was used to form homogeneous distribution on the surface and in the bulk of spinel $Li_4Ti_5O_{12}$ nanoparticles. This nitrogen modified $Li_4Ti_5O_{12}$ nanoparticle material had a high capacity and substantial capacity retention, showing excellent electrochemical performance [17]. Usually, the well-designed nanoarray structures are able to well promote the electrochemical performance of various functional electrode materials [18,19]. Our previous research work proved that TiN and even nitridization treatment of TiO_2 could well improve the electrical conductivity of electrode materials [20–22]. Significantly, TiN composites could act well as supercapacitor electrode materials [23–26]. TiN modified $Li_4Ti_5O_{12}$ composite was prepared using thermal nitridation approach arouses intensive interests because of its high electrical conductivity [27]. On the other hand, nanostructured $Li_4Ti_5O_{12}$ can increase the specific surface area. Specially, the nanoarray material can shorten the lithium ion diffusion path, so that it can further improve the capacitance performance.

In this study, N-$Li_4Ti_5O_{12}$ nanoarrays have been designed as an electrode material of lithium-ion supercapacitor for energy storage, which is formed by introducing TiN into $Li_4Ti_5O_{12}$. The electrochemical capacitance, cycling stability and rate capability of N-$Li_4Ti_5O_{12}$ nanoarrays have been fully investigated. The nanoarray structure and the nitriding treatment degree were controlled to improve the capacitance performance N-$Li_4Ti_5O_{12}$ nanoarrays.

2. Experimental

2.1. Materials

All the chemical reagents with analytical purity were purchased from Sinopharm Chemical Reagent Co. Ltd, which were used without any further purification. All solutions were prepared using distilled water with a resistivity not less than 18.2 MΩ (Synergy UV, Milipore).

2.2. Preparation of N-$Li_4Ti_5O_{12}$ nanoarrays

Fig. 1 shows the schematic illustration of the preparation of N-$Li_4Ti_5O_{12}$ nanoarrays. $Li_4Ti_5O_{12}$ nanowire array was fabricated through hydrothermal reaction, ion exchange and calcination treatment processes [28]. A piece of titanium foil was ultrasonically cleaned in water, acetone and ethanol for 15 min, respectively. The sodium titanate hydrate ($Na_2Ti_2O_5 \cdot H_2O$) was formed on the top surface of Ti foil through hydrothermal reaction, which was conducted at 220 °C for 16 h in 50 mL Teflon-lined stainless autoclave filled with 20 mL 1.0 M NaOH solution. Then, the hydrogen titanium oxide hydrate ($H_2Ti_2O_5 \cdot H_2O$) was formed through ion exchange reaction, where $Na_2Ti_2O_5 \cdot H_2O$ nanowire array was immersed in 0.5 M HCl solution for 1 h to replace Na^+ with H^+. $Li_4Ti_5O_{12}$ nanowire array was formed through ion exchange reaction, where $H_2Ti_2O_5 \cdot H_2O$ was immersed in 2.0 M LiOH solution and kept at 60 °C for 12 h to replace H^+ with Li^+. Finally, well crystalline $Li_4Ti_5O_{12}$ nanowire array was formed through a calcination treatment at 600 °C for 1.5 h in argon (Ar) atmosphere. $Li_4Ti_5O_{12}$ nanotube array was fabricated through anodic oxidation, sonochemical reaction and calcination treatment processes. Firstly, amorphous TiO_2 nanotube array was directly grown on titanium foil through the anodization process at 60 V for 3 h in the ethylene glycol electrolyte solution, which contained 0.075 M NH_4F and 6.0 M H_2O. The crystal TiO_2 nanotube array was formed through the annealing treatment of amorphous TiO_2 at 450 °C for 3 h. Then, the LiOH@TiO_2 acting as the precursor of $Li_4Ti_5O_{12}$ was formed by coating LiOH on crystal TiO_2 through the sonochemical reaction process, which was conducted at 60 °C for 40 min in 2.0 M LiOH solution under an operation condition of 40 kHz ultrasonic frequency and 100 W electric power [29]. Finally, well crystalline $Li_4Ti_5O_{12}$ nanotube array was formed through the calcination treatment at 600 °C for 1.5 h in Ar atmosphere.

The N-$Li_4Ti_5O_{12}$ nanowire array and nanotube array was prepared through the nitridation treatment of $Li_4Ti_5O_{12}$ nanowire array and nanotube array using pure ammonia with a flow rate of 55 mL min^{-1} at 800 °C for 1 h in a tubular furnace.

2.3. Microstructure characterization and electrochemical measurement

The morphology and microstructure of N-$Li_4Ti_5O_{12}$ nanoarrays were characterized by scanning electron microscopy (SEM, Zeiss Ultra Plus). The crystal phase of N-$Li_4Ti_5O_{12}$ nanoarrays were characterized by X-ray diffraction (XRD, Rigaku D/max 2550 PC, Cu Ka). N-$Li_4Ti_5O_{12}$ nanoarrays were investigated using a Raman spectrometer (Raman, Renishaw Invia Reflex System, UK) in the

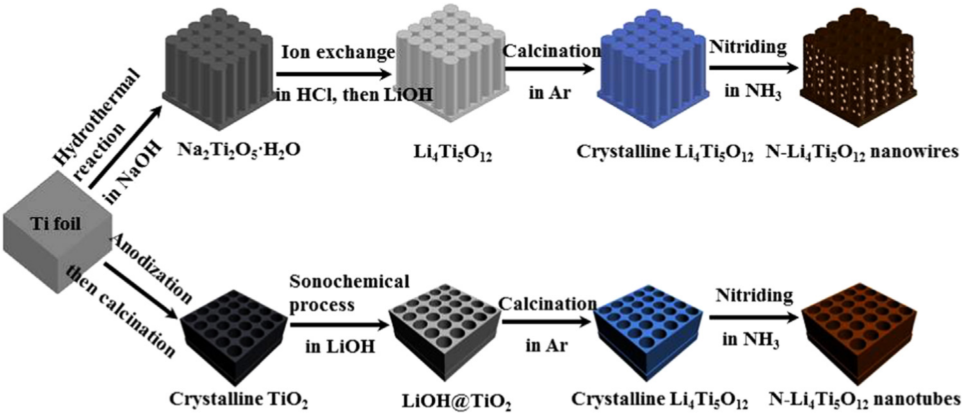

Fig. 1. A Schematic illustration of the preparation of N-$Li_4Ti_5O_{12}$ nanowire array and nanotube array.