Electrochimica Acta 222 (2016) 27–35

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Hierarchical Hydrogen Titanate Nanowire Arrays/Anatase TiO_2 Heterostructures as Binder-Free Anodes for Li-ion Capacitors

Lan-fang Que, Fu-da Yu, Zhen-bo Wang*, Da-ming Gu

MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, No.92 West-Da Zhi Street, Harbin, 150001 China

ARTICLE INFO

Article history:
Received 2 August 2016
Received in revised form 8 November 2016
Accepted 8 November 2016
Available online 9 November 2016

Keywords:
Li-ion capacitors
hierarchical heterostructures
hydrogen titanate
anatase TiO_2
binder-free anodes

ABSTRACT

Well-aligned hierarchical heterostructures composed of hydrogen titanate ($H_2Ti_2O_5{\cdot}H_2O$, labeled as HTO) nanowire stems and anatase TiO_2 nanoparticle branches (HTO/TiO_2 NWAs) have been synthesized successfully on Ti-foil substrate as additive-free electrodes for hybrid Li-ion capacitors (LICs). The inner 3D HTO conductive scaffold consisted of vertically aligned nanowires and porous rooftop network is beneficial to large capacitance. Moreover, the countless anatase TiO_2 particles on the surface of HTO nanowires can enrich electro-active sites, reduce the ion and electron resistance, shorten Li-ion transport pathways and enhance structural stability. Owning to the synergistic effects of HTO and anatase TiO_2, the electrodes deliver large capacitance, superior rate capability and excellent cycle stability. The HTO/TiO_2//AC (activated carbon) hybrid system presents fascinating energy density (84.7 Wh kg^{-1} at 0.5 A g^{1}) and ultralong lifespan (78.5% capacity retention after 10000 cycles at 10.0 A g^{-1} within 0.0-4.0 V). Even at high power density of 20 kW kg^{-1}, an excellent energy density of 44.4 Wh kg^{-1} can be retained. Thus, the LIC assembled with HTO/TiO_2 NWAs anode and AC cathode can be a potential candidate as high-performance energy storage application.

1. Introduction

Recently, hybrid Li-ion capacitors (LICs) have attracted considerable interest as high-performance energy storage system because of their higher energy density than supercapacitors (e.g., electric double-layer capacitors, EDLC) and larger power density than the rechargeable batteries (e.g., Li-ion batteries, LIBs). [1–5] In general, the electrochemical properties of LICs highly depend on the active materials of electrodes. Therefore, it is critical to develop superior materials with large capacitance and stable construction as advanced electrodes for LICs.

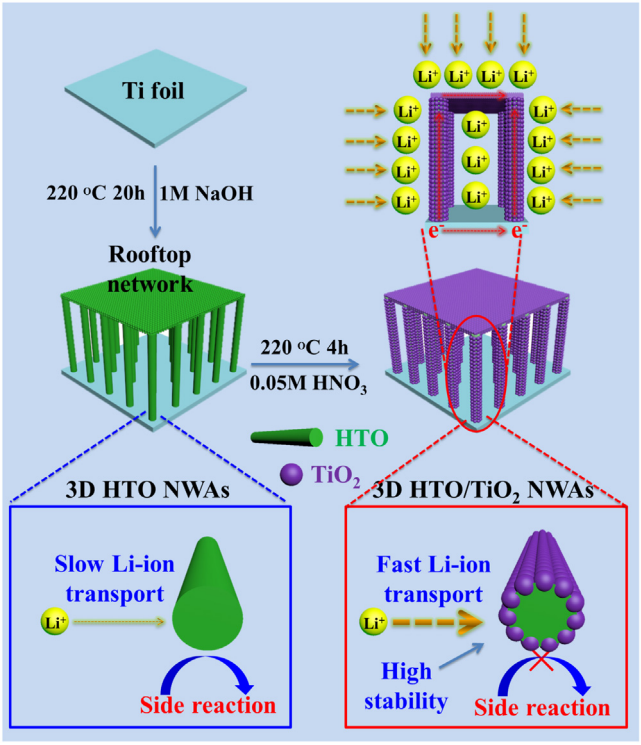
Currently, $Li_4Ti_5O_{12}$ as one of the most commonly used anode materials for LICs, has been intensively investigated due to its low cost, excellent structural stability, and high safety [6]. However, the majority of the reported $Li_4Ti_5O_{12}$-based LICs suffer from unsatisfied energy density and rate performance caused by poor electrical conductivity, which limits LICs to realize their full potential [7]. TiO_2 (e.g., anatase TiO_2 and TiO_2-B) based hybrid LICs have also been explored intensively but interfered by the same disadvantage [8–10]. In this instance, because of its fascinating characteristics including good electrical and ionic conductivity, high specific surface area and larger theoretical capacitance than that of other Ti-based compounds, layered hydrogen titanate (HTO) is particularly attractive [11,12]. As a result, various HTO nanostructures, such as nanoparticles, nanowires, and nanotubes, have been explored as negative electrode materials for Li-ion storage. [13–16] However, the application of HTO in hybrid LICs is still insufficient and there is lack of a systematic study about the electrochemical performances when combined it with AC (activated carbon) cathodes. [11] In addition, most of them are suffering from poor rate performance and cycle property due to the sluggish reaction caused by disordered nanostructures. According to ref [17] and [18], it has been proved that shortening the Li-ion diffusion pathway by fabricating well-ordered and free-standing 1D nanoarchitecture can overcome these drawbacks effectively. In our previous work, we have synthesized well-ordered and free-standing $H_2Ti_8O_{17}$ nanowire arrays and summarized the effects of different crystal structures on the electrochemical performances of LICs. [32] Through removing crystal water partially by calcining, the rate capability and cycle stability of the LIC have been improved to some extent. However, the cycle performance of the overall hybrid LIC is still insufficient. It has been proposed that hierarchical

* Corresponding author. Tel.:+ +86 451 86417853; fax: +86 451 86418616
E-mail address: wangzhb@hit.edu.cn (Z.-b. Wang).

http://dx.doi.org/10.1016/j.electacta.2016.11.049
0013-4686/

heterostructure materials consisting of oriented nanostructure arrays and a second component branches can effectively release the structure strains, buffer the volume change, stabilize the electrode integrity and prolong the lifespan during the discharge-charge processes since their special morphology and structure properties [19]. More importantly, the 3D heterostructures can simultaneously guarantee high electrical conductivity and fast electrolyte-ion transport within the whole scaffold. [20] It has been reported that hydrogen titanate ($H_2Ti_2O_5{\cdot}H_2O$) can convert into anatase TiO_2 through acid hydrothermal reaction easily. [21] Considering these aspects, combing the synergetic effects of morphologic design and crystal structure may be a promising problem-solving strategy.

Herein, we have proposed and designed 3D HTO ($H_2Ti_2O_5{\cdot}H_2O$) nanowire arrays modified with numerous anatase TiO_2 nanoparticles (HTO/TiO_2 NWAs) as binder-free anode for LIC for the first time. These novel HTO/TiO_2 NWAs were fabricated by facile two-step hydrothermal processes (Scheme 1). The intention of this work is to combine the synergetic properties of HTO nanowire arrays and TiO_2 nanoparticles. (1) The inner 3D HTO conductive scaffold consisted of porous rooftop network and well-aligned nanowire array is beneficial to realize large capacitance. (2) HTO/TiO_2 NWAs anodes without any ancillary materials can overcome the sluggish reaction by providing direct Li-ion diffusion channels. (3) Hierarchical HTO/TiO_2 NWAs anodes possess complementary characteristics in LICs: while HTO in HTO/TiO_2 NWAs electrode can provide large capacitance, the tailored anatase TiO_2 phase can be beneficial to rich electro-active sites, fast Li-ion transport and excellent structural stability. When used as binder-free anodes for LIBs, HTO/TiO_2 NWAs manifest large capacity, superior rate performance and excellent cycle property. Thus, the HTO/TiO_2 NWAs//AC LIC exhibits a maximum energy density of 84.7 Wh kg^{-1} and delivers an energy density of 44.4 Wh kg^{-1} at 20 kW kg^{-1}, which exhibits attractive capability in high-performance energy storage applications.



Scheme 1. Schematic of the synthetic route of a hierarchical HTO/TiO_2 NWAs film.

2. Experimental sections

2.1. Preparation of hierarchical HTO/TiO_2 nanowire membranes

All the chemicals are of analytical grade and used without further purification. Activated carbon (YEG-8B, purchased from FUZHOU YIHUAN CARBON CO., Ltd, China) is used as cathode material. Ti-foils (99%, purchased from QINGYUAN Metal MATERIALS Co., Ltd) provide Ti source for nanowire arrays and act as substrates at the same time. As illustrated in Scheme 1, HTO/TiO_2 NWAs were synthesized on Ti-foil by a two-step hydrothermal reaction. Firstly, 3D HTO nanowire arrays were synthesized by an alkali hydrothermal process combined with an ion-exchange process. [32] Briefly, after putting the Ti-foil into a 80 mL Teflon-lined stainless steel autoclave with 40 mL 1 mol L^{-1} NaOH aqueous solution and keeping at 220 °C for 20 h, the sample was immersed into 0.05 mol L^{-1} HCl solution in order to replace Na^+ ions with H^+ ions. Secondly, the as-prepared 3D HTO nanowire arrays were kept at 120 °C for 4 h in a Teflon-lined stainless steel autoclave with 0.05 mol L^{-1} HNO_3 solution. This acid treatment will cause partially phase transition from titanate to anatase on the surface of HTO nanowires to obtain hierarchical HTO/TiO_2 NWAs.

2.2. Materials Characterization

The morphologies of HTO and HTO/TiO_2 NWAs were observed by a field emission transmission electron microscopy (FETEM) (JEM-2100) and a field emission scanning electron microscopy (FESEM) (S-4800, HITACHI), respectively. X-ray diffraction (XRD) patterns were recorded with an X-ray diffractometer [Bruker D8 ADVANCE, with Cu Ka radiation (=1.5418 Å), Germany].

2.3. Electrochemical Measurements

The as-prepared HTO and HTO/TiO_2 NWAs were cut into small thin round slices as binder-free anodes. Half-cell devices were assembled using Li-metal foil as counter and reference electrodes in coin type cells. The separator was polypropylene membrane and the electrolyte is 1 mol L^{-1} $LiPF_6$ in EC-DMC mixture.

Hybrid LIC was fabricated with HTO/TiO_2 NWAs anode (mass = 1 mg) and activated carbon cathode (mass = 4 mg) by pressing them together with a polypropylene membrane as separator in 1 M L^{-1} $LiPF_6$ in EC-DMC electrolyte solution. Galvanostatic discharge–charge experiments were performed at different current densities with a multichannel battery tester (NEWWARE, China). Cyclic voltammetry (CV) and electrochemical impedance spectra (EIS) were measured by the electrochemical work station (CHI660E, Chenhua, Shanghai). The galvanostatic intermittent titration technique (GITT) test was carried out on a NEWWARE battery tester. For the GITT measurement, the battery cell was charged with a constant current flux of 40 mA g^{-1} for 10 min followed by open circuit conditions for a specified time interval of 40 min to relax the cell to a steady state.

3. Results and discussion

3.1. HTO/TiO_2 NWAs Half-Cell

As mentioned in the previous section, the hierarchical HTO/TiO_2 NWAs were synthesized via a two-step hydrothermal growth process. The crystal structures of the as-prepared samples were characterized by X-ray diffraction (XRD) patterns as illustrated in Fig. 1. Obviously, the diffraction peaks of HTO are well indexed to $H_2Ti_2O_5{\cdot}H_2O$ (JCPDS No.47-0124). Compared with the XRD pattern of HTO NWAs, the (101) lattice plane of anatase TiO_2 (JCPDS No.21-1272) can be observed clearly in the second sample, indicating the