Electrochimica Acta 266 (2018) 233–241

Contents lists available at ScienceDirect

Electrochimica Acta

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

Enhanced capacitance of TiO_2 nanotubes topped with nanograss by H_3PO_4 soaking and hydrogenation doping

Siwei Zhao [a, b], Ying Chen [a], Zhiyang Zhao [b], Longfei Jiang [c], Chi Zhang [a],
Jianshou Kong [c, **], Xufei Zhu [a, *, 1]

[a] *Key Laboratory of Soft Chemistry and Functional Materials of Education Ministry, Nanjing University of Science and Technology, Nanjing, 210094, China*
[b] *Tsien Hsue-shen College, Nanjing University of Science and Technology, Nanjing, 210094, China*
[c] *School of Automation, Nanjing University of Science and Technology, Nanjing, 210094, China*

ARTICLE INFO

Article history:
Received 21 November 2017
Received in revised form
5 February 2018
Accepted 6 February 2018
Available online 8 February 2018

Keywords:
Anodic TiO_2 nanotubes
Supercapacitor
Nanograss
Hydrogenation
Doping

ABSTRACT

Anodic TiO_2 nanotubes have been intensively studied for the application in supercapacitors, but the formation of nanograss is often avoided for the belief that it may retard capacitive performance. We fabricate TiO_2 nanotubes topped with nanograss by H_3PO_4 solution soaking and hydrogenation doping, which in fact increases the capacitance of nanotubes in a fast and convenient way. The new structure exhibits an enhanced areal capacitance by up to 67.7% and by up to 23.5% after 2000 times of cycling. The capacitance generally increases with the nanotube length and reaches the maximum with an optimal nanograss length. The electric charge during hydrogenation doping is determined to quantify the general doping effect. Compared with ordinary nanotubes, nanograss has larger contact area with electrolyte during doping. Therefore, the grass-topped structure yields more electric charge and Ti^{3+} during doping, which attributes to the improved capacitance.

1. Introduction

Since 1950s, supercapacitors have been widely investigated and applied due to the large power density, high cycle stability and fast charge and discharge process [1–5]. The supercapacitors are generally divided into electric double-layer capacitors (EDLC) and pseudocapacitors [6,7]. EDLCs store energy by non-faradaic reactions at electrolyte/electrode interfaces and its areal capacitance (C_s) is 20–50 nF cm^{-2} [6,8]. In contrast, pseudocapacitors show faradaic charge transfer, with C_s of ~10^3 μF cm^{-2} [6–8]. Although the capacitance of pseudocapacitors is much larger than that of EDLCs, the stability is quite poor [9].

In order to improve the capacitance and stability of supercapacitors, one-dimensional nanostructures, such as anodic titanium nanotubes (ATNTs), are studied. Compared with other electrodes, nanotubes have direct current pathways [2,8–10], high surface area [8–12], good adhesion to substrate [8,12] and relatively low cost [2]. The ATNTs resemble EDLCs and contributes almost no faradaic capacitance [2,13]. However, considering the low conductivity [2,12,14,15] and diffusion limits for electrons in nanotubes [15], modification for TiO_2 nanotubes are necessary.

There are mainly three methods to enhance capacitance of ATNTs electrode, (1) doping with other elements [16], (2) thermal annealing [13] and (3) synthesis of nanocomposites with electroactive materials (e.g. polymers and MnO_2) [7,17–20]. Specifically, hydrogenation doping has been generally used because of its more convenient and safer procedures compared with other methods [7,9,12,21,22]. After hydrogenation doping, a small percent of Ti^{4+} is reduced to Ti^{3+}, which indicates enhanced oxygen vacancy and conductivity [8,12,23]. Nevertheless, the drawback of this method is that only the top of ATNTs is sufficiently doped, so the percentage of Ti^{3+} (~1%) reduced from Ti^{4+} is much smaller than that of H_2 annealing (~30%) [22]. Also, the doping might become invalid during cycling stability test, because of the metastability of hydrogen doped into titania [24–26].

The capacitance of ATNTs is tightly related to its morphology and structure [9,22,26–28]. The aspect ratio of nanotubes positively influences areal capacitance [26,27], because tubes with longer length or smaller diameter will contain higher concentration of oxygen vacancies after hydrogenation doping [22]. Meanwhile,

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* Corresponding author.
** Corresponding author.
E-mail addresses: kongjs77@163.com (J. Kong), zhuxufei.njust@163.com (X. Zhu).
[1] Electrochemical Society Active Member.

https://doi.org/10.1016/j.electacta.2018.02.037

some new structures, such as bamboo-type tubes [9] and multilayer arrays [28] have been studied for further improvement of C_s.

TiO_2 nanograss is one of the non-ideal tops formed during the anodization of Ti substrate [29]. Compared with nanotubes, nanograss is less ordered but has a larger surface area [8,29]. The reason for the nanograss formation is the partial dissolution of nanotubes in the fluoride-containing electrolyte after a long-time anodization [30–32]. Despite the application in other materials [19,33–35], nanograss is rarely used in ATNTs supercapacitors for the belief that this less ordered structure may retard electron transfer [8]. Rather, several methods were designed to prevent the growth of nanograss, such as forming a protection layer [31] and polishing substrates before anodizing [36].

However, in terms of the large surface area, the nanograss top on nanotubes may increase the performance of ATNTs to some extent. Kim et al. [36] found that the removal of TiO_2 nanograss decreases the short circuit current of photovoltaic cells, which indicates that the nanograss has both positive and negative effects. Du et al. [8] discovered that nanotubes with nanograss top show enhanced areal capacitance (up to 43.4%).

Acid or water soaking is a convenient way to increase surface area of ATNTs. Zhang et al. [37] fabricated rough nanotubes by soaking in water for 80 h. In spite of the increased capacitance, the long-term immersion triggers serious delamination [26]. Acid soaking, specifically phosphoric acid soaking, was employed to develop hexagonal structure of porous anodic aluminia films [38,39]. Notably, acid soaking is more efficient than long-time anodizing, given the etching rate of acid solution. So far, most of the research have focused on the prevention of nanograss [31,36] and few work has been done to study the influence of nanograss on capacitive performance [8]. Additionally, nanograss is produced by long-term anodization or water soaking [37], which is time consuming.

In this article, we prove that TiO_2 nanograss can enhance the capacitance of ATNTs to some extent. By using H_3PO_4 soaking, for the first time, nanotubes topped with nanograss are fabricated in a fast period. After hydrogenation doping, the grass-topped nanotubes show enhanced areal capacitance, which is 67.7% larger compared with non-soaked nanotubes. The capacitance is positively related to nanotube length. With the growth of nanograss, the capacitance reaches the maximum and then declines. By integrating the electric charge from hydrogenation doping, it is found that nanograss is hydrogenated to a larger degree than nanotubes during doping. The better doping performance may be due to the extra surface area of nanograss.

2. Experimental

2.1. Preparation of specimens

The titanium foil (100 μm thick; purity 99.5%, anodization area is 4 cm^2) was used as a working electrode and the graphite as a counter electrode (3.0 cm apart). Before anodizing, specimens were polished in a solution (80 mL) of HF (≥40%, Shantou West Long Chemical Factory Limited), HNO_3 (65–68%, Shantou West Long Chemical Factory Limited) and deionized water (1:1:2 in volume) for 10 s, then rinsed in deionized water for 10 s and dried in the air. The polishing process is to prevent over-dissolution during anodizing [36].

The processed foils were anodized in 0.5 wt% NH_4F (AR, 98%, Aladdin) ethylene glycol (EG) solutions containing 2.0 wt% H_2O at 60 V. The anodization was performed at 30 °C (in water bath) with vigorous stirring. The anodizing time was 10 min, 20 min and 30 min respectively. All specimens were then anodized at 20 V for 5 min for good adherence to the substrate [40].

Subsequently, specimens were soaked in 6.0 wt% H_3PO_4, 6.0 wt% $H_2C_2O_4$ and 0.5% NH_4F aqueous solutions for 0 min, 20 min, 40 min, 60 min, 120 min and 180 min respectively, and then rinsed in deionized water for 10 s.

Afterwards, the H_3PO_4 soaked ATNTs were annealed in air at 150 °C for 2 h and generally up to 450 °C for another 3 h. Finally, hydrogenation doping was performed in 0.5 mol L^{-1} Na_2SO_4 aqueous solution at −1.5 V for 60 s [22]. As listed in Table 1, we labeled the doped specimens as *AxSy*, where *x* and *y* means time (min) for anodizing and soaking, respectively.

2.2. Characterisation

The ATNTs were characterized by a scanning electron microscope (SEM, Zeiss Supra 55 and Hitachi S4800). Nanotube length was measured for three times on each specimen directly on the FE-SEM, and the average value is used for study.

The electrochemical measurements were conducted by AUTOLAB PGSTAT302 N/FRA2 in 0.5 mol L^{-1} H_2SO_4 aqueous solution in a three-electrode cell. A Pt sheet worked as counter electrode, and a saturated calomel electrode worked as reference electrode. The exposure area of foils was 2 cm^2 for cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) tests, and the voltage range was from 0 V to 0.8 V. The scan rate for CV was 100 mV s^{-1} and the current density was 0.5 mA cm^{-2}. Electrochemical impedance spectroscopy (EIS) measurements were conducted in 0.5 mol L^{-1} Na_2SO_4 aqueous solution. The frequency range was between 100 kHz and 0.1 Hz, and the signal amplitude was 10 mV at 0 V bias potential. Mott-Schottky plots were measured at 1 kHz. The cycling stability was done by GCD tests for 2000 cycles at 2.0 mA cm^{-2}.

After doping, X-ray photoelectron spectroscopy (XPS, PHI Quantera) was applied for element analysis. The N_2 adsorption/desorption measurements were carried out at 350 °C and the Brunauer-Emmett-Teller (BET) surface areas of the samples were determined by BET equation.

The areal capacitance was determined from the current vs potential plot from CV test. The areal capacitance in cycling stability

Table 1
Labels of specimens for hydrogenation doping.

Label	Anodising time (min)	Soaking time (min)	Label	Anodising time (min)	Soaking time (min)
A10S0	10	0	A20S60	20	60
A10S20	10	20	A20S120	20	120
A10S40	10	40	A20S180	20	180
A10S60	10	60	A30S0	30	0
A10S120	10	120	A30S20	30	20
A10S180	10	180	A30S40	30	40
A20S0	20	0	A30S60	30	60
A20S20	20	20	A30S120	30	120
A20S40	20	40	A30S180	30	180