Electrochimica Acta 208 (2016) 202–210

Contents lists available at ScienceDirect

Electrochimica Acta

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

Improving the Electrochemical Performance of Hybrid Supercapacitor using Well-organized Urchin-like TiO_2 and Activated Carbon

Hyeong-Jong Choi[a], Jin Hyeon Kim[a], Hong-Ki Kim[a], Seung-Hwan Lee[b,*], Young-Hie Lee[a,*]

[a] Dept. of Electronic Materials Engineering, Kwangwoon University, Republic of Korea
[b] Center for Advanced Life Cycle Engineering, University of Maryland, Room 1103, Building 89, College Park, MD 20742, USA

ARTICLE INFO

Article history:
Received 15 February 2016
Received in revised form 29 April 2016
Accepted 6 May 2016
Available online 9 May 2016

Keywords:
Cylindrical Hybrid Supercapacitor
Electrochemical Performance
TiO_2
Negative electrode
Activated Carbon
Urchin

ABSTRACT

TiO_2 of various morphologies was synthesized by a hydrothermal method. Among them, urchin-like TiO_2 exhibited the largest BET [Brunauer–Emmett–Teller] specific surface area. In this paper, the full-cell was fabricated using Urchin-like TiO_2 as negative electrode and the activated carbon as positive electrode and measured electrochemical properties for cell balancing of cylindrical hybrid supercapacitors. The hybrid supercapacitor using urchin-like TiO_2 with a large specific surface area had a discharge-specific capacitance of 61.1 Fg^{-1} and excellent cycle life. Also, the hybrid supercapacitor with an urchin-like TiO_2 negative electrode showed a maximum power density of 12224.356 W kg^{-1} at an energy density of 10.134 Wh kg^{-1} and maximum energy density of 50.648 Wh kg^{-1} at a power density of 194.412 W kg^{-1}. Thus, urchin-like TiO_2 showed potential as a material for the negative electrode of hybrid supercapacitors.

1. Introduction

Eco-friendly energy conservation and storage systems are required due to increased damage to the natural environment and fossil-fuel depletion. Especially, hybrid electric vehicles (HEVs), energy-storage systems (ESSs), and electric vehicles (EVs) have been a focus of attention in the field of energy-storage systems. Among energy-storage systems, lithium ion batteries and supercapacitors are the most commonly used; these store energy via different mechanisms. A high energy density and high power density power source is required for HEVs and EVs. The energy of lithium ion batteries is stored by Faradaic redox reaction during Li^+ insertion/extraction, which has a high energy density (~200 Wh kg^{-1}) [1,2]. However, problems such as low power density, short cycle life, and poor safety also occur [3,4]. Supercapacitor was classed as electrical double layer capacitor (EDLC) and pseudo-capacitor by mechanism of charge/discharge [5,6]. For EDLC, capacitance implementation was caused via physical absorption-desorption at the surface of the electrode [6,7]. This enables the high power density but energy density is low [6]. On the other hand, transition metal oxides and conducting polymers are used as electrode of pseudo-capacitor. The capacitance implementations are occurred by faradaic redox reaction [5]. This leads to high energy density than that of EDLC [7]. However, it reversely represents the poor rate capability and cyclability [5]. A new type of device, a hybrid supercapacitor, was designed for use by HEVs and EVs. One electrode of hybrid supercapacitors is the electrode used in lithium ion batteries, and the other electrode is that used in supercapacitors. As a result, hybrid supercapacitors have higher power density, higher energy density, and longer cycle life [6–8] than lithium ion batteries and supercapacitors. The development of electrode materials with excellent reversible capacity, rate capability, and cyclability is essential for superior hybrid supercapacitors [9–11]. Currently, it has been used a variety of materials such as NiO, $NiCo_2O_4$ and TiO_2. The theoretical capacitance of NiO and $NiCo_2O_4$ is higher than that of TiO_2. So, they can be regarded as a promising candidate. However, the high rate performance is one of the most important factor for hybrid supercapacitors and supercapacitors [12]. The rate capability of NiO and $NiCo_2O_4$ electrode is still limited [12,13]. However, TiO_2 has excellent intrinsic safety and rate capability [14]. Thus, we used TiO_2-based materials. In addition, prepare processes of $NiCo_2O_4$ are complicated, and large portion of electroactive $NiCo_2O_4$ is "dead surface" and blocked form the contact with the electrolyte to participate in the faradaic reactions for energy storage [12,15,16]. Also, TiO_2 polymorphs have a higher theoretical capacity (335 mAh g^{-1}) than

* Corresponding authors.
E-mail addresses: shlee83@umd.edu (S.-H. Lee), yhlee@kw.ac.kr (Y.-H. Lee).

http://dx.doi.org/10.1016/j.electacta.2016.05.039
0013-4686/

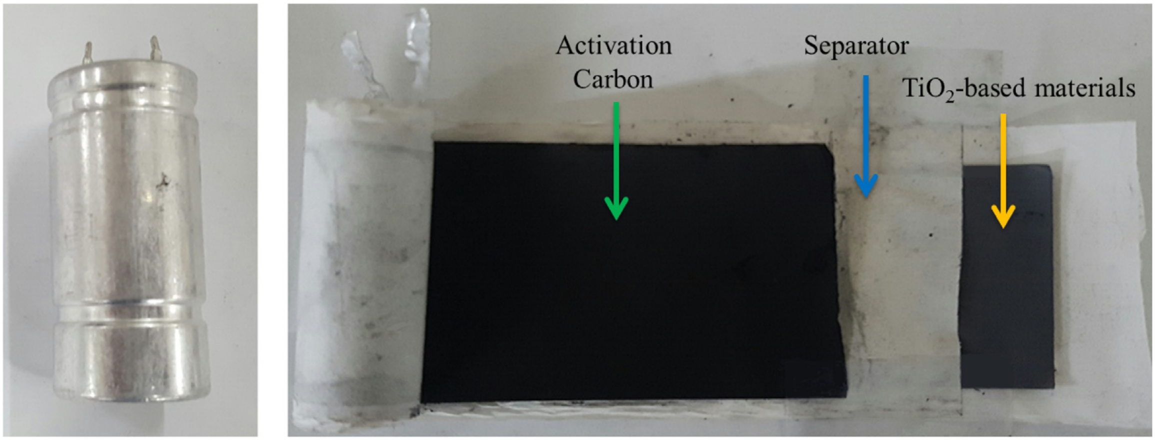

Fig. 1. Optical image of cylindrical cell of hybrid supercapacitor consisting of negative electrode/separator/positive electrode.

that of carbon [14,17]. The reaction between TiO_2 and Li-ion during the charge-discharge process is described by equation [18]:

$$xLi^+ + TiO_2 + xe^- \leftrightarrow Li_xTiO_2\ (0 \leq x \leq 1)$$

However, lithium-ion storage performance of TiO_2 and other metal oxide was limited by the poor Li^+ conductivity, electronic conductivity and volume effect [19,20]. Especially, to overcome Li^+ conductivity and volume effect, the nanocrystallization of metal oxide particles is an ideal strategy [20]. To overcome this issue, TiO_2 polymorphs have been fabricated with mesoporous or nanosize particles via a synthetic method. As a result, the capacities of TiO_2 polymorphs increased with increasing surface area [21]. In previous papers [22,23], 3D nanostructures with superior electrochemical performance and high surface area were demonstrated. In this paper, we fabricated urchin-like rutile TiO_2 microspheres and investigated the physical properties and electrochemical performances of hybrid supercapacitors that made use of urchin-like rutile TiO_2 microspheres as a negative electrode.

2. Experiments

Urchin-like and flower-like TiO_2 was prepared by a hydrothermal method. In brief, 15 mL D. I. water, 15 mL HCl (36–38%), 0.6 g, and 0.5 mL titanium (IV) n-butoxide 99% were mixed and stirred. The mixture was transferred to a Teflon-lined stainless steel autoclave. Urchin-like and flower-like TiO_2 were generated by hydrothermal synthesis at 150 °C for 10 and 20 h, respectively. Synthesized powers was washed with D.I. water and dried at 100 °C. TiO_2 nanorod was prepared by hydrothermal method. The 1 g TiO_2 (SIGMA-ALDRICH), 10 M NaOH and ethanol were mixed and stirred. The mixture was transferred in the Teflon-lined stainless steel autoclave. The autoclave was maintained at 180 °C for 15 h. And then synthesized power was washed with D.I water and dried at 100 °C. Using a method described previously, the hybrid supercapacitors were composed of urchin-like, flower-like TiO_2, commercial anatase TiO_2 (Sigma-Aldrich) and nanorod TiO_2 negative electrode, and activated carbon (AC) positive electrode to a thickness of 240 μm. To fabricate the negative electrode electrode, sample powders, conductive carbon black binder (Super P), and polyvinylidene fluoride (PVDF) were mixed at an 83:7:10 weight ratio. N-Methyl pyrrolidinine (NMP) solvent was added to produce slurry. The masses of positive and negative electrode were 2.9 g and 3.1 g, respectively. This was casted on aluminum foil to a thickness of 125 μm and then dried at 100 °C to remove the NMP solvent. The aluminum foil was pressed to a thickness of 70–80 μm. An AC positive electrode was fabricated by mixing AC (MSP-20, 90 wt%) with conductive carbon (5 wt%) and polytetrafluoroethylene (PTFE, 5 wt%). The width of the positive electrode, separator, and negative electrode were 28, 40, and 30 cm, respectively, and the heights of the positive electrode and negative electrode were both 3 cm. The fabricated positive electrodes, separator, and negative electrode were assembled into a cylindrical cell in an argon-gas-filled glove box. Before being impregnated with a 1.5 M solution of $LiBF_4$ in ethylene carbonate (EC)-dimethylcarbonate (DMC) 2:1 (v/v) as the electrolyte, to remove moisture from the cell, the fabricated cell was dried in a vacuum oven for 48 h. The electrochemical performance of the fabricated cell was evaluated by means of various tests, such as initial capacitance and rate capability, using an Arbin BT 2042 battery test system at various densities. Also, the cyclic voltammograms were measured using a three-electrode cell with a potentiostat (Iviumstat). The structure of powders was analyzed using X-ray diffraction (XRD). To confirm the powder morphology, field emission scanning electron microscopy (SEM) was used. Also, various electrochemical parameters of the hybrid supercapacitors were measured.

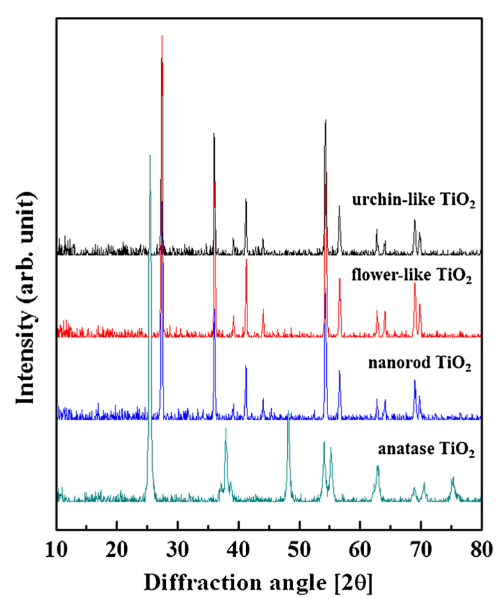

Fig. 2. XRD patterns of anatase nanoparticles, nanorods, and flower-like and urchin-like TiO_2 powders.