Applied Surface Science 285P (2013) 483–489

Contents lists available at ScienceDirect

Applied Surface Science

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

Surface modified carbon cloth for use in electrochemical capacitor

JiaXun Du, Dillip Mishra, Jyh-Ming Ting*

Department of Materials Science and Engineering, National Cheng Kung University, Tainan, Taiwan

ARTICLE INFO

Article history:
Received 20 June 2013
Received in revised form 12 August 2013
Accepted 18 August 2013
Available online 27 August 2013

Keywords:
High power supercapacitor
Carbon nanotubes
Activated carbon cloth
Electric double layer capacitor
Sputter deposition
Microwave plasma

ABSTRACT

The paper reports enhanced power densities for electrochemical capacitor through grafting carbon nanotubes (CNTs) onto the surface of activated carbon cloth (ACC). The surface-modified ACCs were first examined for their material properties and then evaluated for their electrode performance such as capacitance, equivalent series resistance, energy density, and power density. Improved electrochemical performance was obtained due to the surface modification by CNTs. In particular, the CNTs lower the contact resistance and therefore increase the power density of the electrochemical capacitor. Furthermore, we show that through such a surface modification, the specific capacitance can be increased from 108 to 117 F/g, i.e., an 8.3% increase, the energy density can be increased from 16.7 to 17.64 Wh/kg, i.e., a 5.4% increase, or the power density can be increased from 4.8 to 11.3 kW/kg, i.e., a 135% increase. To our best knowledge, the energy density and power density of a electrochemical capacitor having CNT-grafted ACC electrode have not been reported. Also, a 70% retention at a scan rate of 500 mV s^{-1} and a long cycle life of 20,000 cycles at a scan rate of 200 mV s^{-1} are demonstrated.

1. Introduction

Electrochemical capacitor (EC) is an attractive energy storage device with high energy densities and long cycle lives [1]. EC can be divided into two classes, depending on its charge storage mechanism, i.e., electric double layer capacitor (EDLC) and pseudocapacitor. In brief, an EDLC employs electrostatic forces to adsorb ions to the electrode surface to form a double layer capacitor while a pseudocapacitor relies on the use of a transition metal oxide for the occurrence of Faradaic reactions to produce charge storage. The high cost of transition metal is an obstacle for the commercial application of pseudocapacitors as compared to EDLCs. In EDLCs, mesoporous carbons (MCs), activated carbons (ACs), and activated carbon cloths (ACCs) are the most popular materials for making the electrodes due to their high specific surface areas. However, there are two potential drawbacks. One is slow or limited ion migration in micropores, resulting in poor retention, and the other one is the high contact resistance between carbon electrode and the current collector. To solve these problems, ACs and ACCs are modified through, for example, the addition of C_{60} [2], plasma surface treatment [3], and thermal activation [4–6]. A particular interest is paid to the addition of carbon nanotubes (CNTs) in ACs and surface modification of MCs or ACCs by CNT grafting.

Since 1991 [7], CNTs have been widely investigated because of their remarkable properties, such as high electrical conductivity, high strength, and high thermal conductivity [8,9]. A mixture of AC and double-walled CNTs (DWCNTs) was used as the electrode in supercapcitors [10]. The energy dissipation becomes smaller due to reduced equivalent series resistance (ESR) as a result of the addition of the DWCNTs. The retention of the DWCNT-containing capacitor was also improved. However, the specific capacitance reduces with the amount of DWCNTs. Similar results were also reported when multi-walled CNTs (MWCNTs) were added to ACs [11]. Although the ESR is reduced and the retention is improved due to the addition of the MWCNTs, the specific capacitance decreases due to the smaller specific surface area of the MWCNTs than that of the ACs. Therefore, MWCNTs were treated with nitric acid to increase the surface area [12,13]. The specific capacitance of the resulting capacitor can then be increased through the addition of MWCNTs [14]. Acid-treated CNTs were also shown to have increased pore volumes and specific surface areas, therefore giving the obtained electrochemical capacitors enhanced specific capacitance [15]. Electrochemically oxidized MWCNTs have also been investigated for use as electrodes in EDLCs [16,17]. Electrochemically oxidized MWCNT electrode was found to improve the specific capacitance by 11 times due to increased surface areas; however, the pristine MWCNT electrode has a very low specific capacitance of on 32.7 ± 7.1 F/g) [17]. The benefit of electrochemical oxidation for increased surface area has also realized elsewhere [18]. Common to these electrochemical capacitors having conductive carbon additives is the use of a binder while mixing the additive and the host carbon [10,11,14,15]. However, the use of binder often results in increased resistance [19]. For binder-free capacitors, surface modification of MCs or ACCs through the CNT or carbon nanofiber (CNF)

* Corresponding author. Fax: +886 6 238 5613.
E-mail address: jting@mail.ncku.edu.tw (J.-M. Ting).

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http://dx.doi.org/10.1016/j.apsusc.2013.08.081

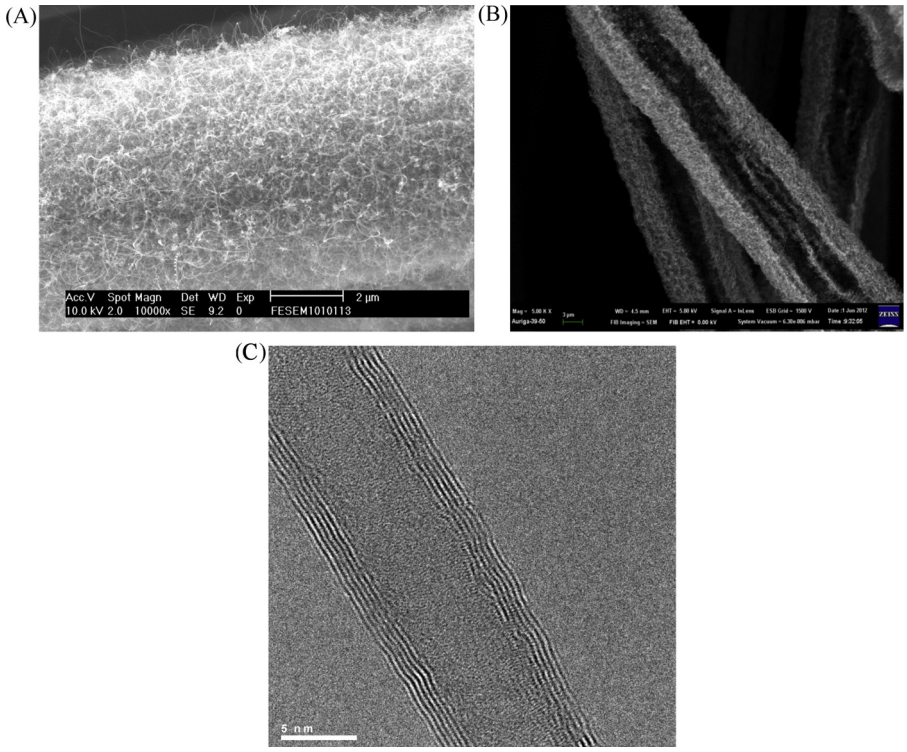

Fig. 1. Surface morphologies of (A) G1 and (B) G5-C samples. (C) HR-TEM image of a CNT showing 6 graphitic layers.

grafting on has been investigated. CNT-grafted MCs has been shown to reduce the contact resistance among the MCs in which the CNTs were believed to serve as interconnects [20]. CNT-grafted ACCs also greatly reduce the contact resistance between the electrode and the current collector, leading to improved retention of the resulting capacitors [21–23].

In this study, surface modification of ACCs by CNTs was performed using a low temperature (~500 °C) process in which a novel Fe-Si catalyst was used to grow the CNTs. The obtained CNT-grafted ACCs were then made into electrodes for use in electrochemical capacitor and their performance such as capacitance, energy density, and power density have been examined. To our best knowledge, the energy density and power density of a electrochemical capacitor having a CNT-grafted ACC electrode have not been reported. It was found that the CNTs lower the contact resistance and therefore increase the power density. Improved capacitor performance is demonstrated.

2. Experimental

Polyacrylonitrile (PAN)-based ACCs were used as the substrates for the growth of CNTs. The fiber diameter is ~7 μm. Fe-Si catalyst was deposited onto the ACCs using a dc sputter deposition technique. The deposition time and power were 3 min and 50 W, respectively, such that the thickness of the resulting Fe-Si catalyst layer was 24 nm. The detailed deposition process can be found elsewhere [24–29]. The Fe-Si deposited ACCs were cut into $1 \times 1\ cm^2$ coupons. CNTs were then grown on the coupon using a microwave plasma-assisted chemical vapor deposition. The microwave power and pressure were 500 W and 40 Torr, respectively. The hydrogen/methane ratio was 9/4. The growth took place for 1, 2, 3, and 5 min, giving samples designated as G1, G2, G3, and G5, respectively. In these samples, the CNTs were grown with the plasma ball floating slightly above the substrates. For comparison, CNTs were also grown with the plasma ball edge touching the substrate. The growth time was 5 min and the obtained sample is designated as G5-C. The morphology and microstructure of the bare and CNT-grafted ACC samples, and the diameters of the CNTs were examined using field emission scanning electron microscopy (FE-SEM) and high resolution transmission electron microscopy (HR-TEM). Micro-Raman spectrometer equipped with 633 nm He-Ne laser was used to determine the quality of the resulting CNTs. The specific surface area, pore volume, and pore size were determined using N_2 isothermal adsorption at 77 K (Mircromeritics TriStar II 3020) and the Brunauer–Emmett–Teller (BET) method, and through the Barrett–Joyner–Halenda (BJH) equations. X-ray photoelectron spectroscopy (XPS) was used to determine the surface chemistry of the CNT-grafted ACC samples.

Two-electrode electrochemical cells were constructed using stainless steel (SS316L) as the current collector, bare or CNT-grafted ACC as the electrode, and a filter paper (Advantec 5C filter paper) as the separator. The electrode area was $1 \times 1\ cm^2$. The use of a two-electrode system is that it analogs to a real capacitor. The electrochemical measurements were performed using a 2 M H_2SO_4 solution as the electrolyte at the ambient temperature. Cyclic voltammetry (CV) measurements were conducted in a potential range between −1.0 and 1.0 V [4,27] at different scan rates ranging from 5 to 500 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) was used to determine the impedance behavior of the electrodes. The measurements were performed at 0 V with an ac potential amplitude of 5 mV and frequencies ranging from 2 mHz to 100 kHz.

3. Results and discussion

Fig. 1 shows SEM images of CNT-grafted ACC samples. Homogeneous coverage of the ACCs by CNTs was obtained as shown in Fig. 1A for a G1 sample. Extremely high area densities of CNTs have been obtained. However, with the plasma ball touching the substrate, a cleavage is seen along the carbon fiber axis, as shown in Fig. 1B. Inside the cleavage, CNT growth is much less. An HR-TEM image of a CNT is shown in Fig. 1C, which indicates that the obtained