CARBON 67 (2014) 662–672

Available at www.sciencedirect.com

ScienceDirect

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

An easy one-step electrosynthesis of graphene/polyaniline composites and electrochemical capacitor

Xiaoqing Jiang [a,b,*], Sunao Setodoi [b], Saki Fukumoto [b], Ichiro Imae [b], Kenji Komaguchi [b], Jun Yano [c], Haruo Mizota [d], Yutaka Harima [b]

[a] Jiangsu Key Laboratory of New Power Batteries, Laboratory of Electrochemistry, College of Chemistry and Materials Science, Nanjing Normal University, 122 Ninghai Road, Nanjing 210097, PR China

[b] Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

[c] Department of Engineering Science, Niihama National College of Technology, Yagumocho 7-1, Niihama, Ehime 792-8580, Japan

[d] Hakodate University, 51-1 Takaoka-cho, Hakodate 042-0955, Japan

ARTICLE INFO

Article history:
Received 27 March 2013
Accepted 16 October 2013
Available online 24 October 2013

ABSTRACT

An easy electrochemical technique is proposed to prepare electrochemically reduced graphene oxide (ERGO)/polyaniline (PANI) composites in a single step. The technique uses a two-electrode cell in which a separator soaked with an acid solution is sandwiched between graphene oxide (GO)/aniline films deposited on conductive substrates and an alternating voltage was applied to the electrodes. Successful preparations of ERGO/PANI composites were evidenced by characterizations due to UV–vis-NIR, FT-IR, XPS, XRD, and SEM measurements with free-standing films of ERGO/PANI obtained easily by disassembling the two-electrode cells. The ERGO/PANI films exhibited a high mechanical stability, flexibility, and conductivity (68 $S\ cm^{-1}$ for the composite film containing 80% ERGO) with nanostructured PANI particles (smaller than 20 nm) embedded homogeneously between the ERGO layers. The two-electrode cells acted as electrochemical capacitors (ECs) after a sufficient voltage cycling and exhibited relatively large specific capacitances (195–243 $F\ g^{-1}$ at a scan rate of 100 $mV\ s^{-1}$) with an excellent cycle life (retention of 83% capacitance after 20,000 charge–discharge cycles). Influences of the GO/aniline ratio, the sort of electrolytes, and the weight of the composite on the energy storage characteristics of ECs comprising the ERGO/PANI composites were also studied.

1. Introduction

Electrochemical capacitors (ECs) are an energy storage device utilizing an electrochemical double-layer built up at the interface between a high-surface area electrode and a liquid electrolyte [1,2], and thus called electrochemical double-layer capacitors as well. ECs are also called supercapacitors or ultracapacitors because they have extremely high energy densities compared with conventional parallel-plate capacitors. ECs have recently received a keen interest because they have clear advantages of a long cycle life and a high power capability over Li-ion batteries that have been currently used in electric vehicles, hybrid electric vehicles, and portable electronic devices. At present, however, the energy densities of

* *Corresponding author at:* Jiangsu Key Laboratory of New Power Batteries, Laboratory of Electrochemistry, College of Chemistry and Materials Science, Nanjing Normal University, 122 Ninghai Road, Nanjing 210097, PR China. Fax: +86 25 85891767.
E-mail addresses: jiangxiaoqing@njnu.edu.cn, xiaoqing_j@aliyun.com (X. Jiang).
0008-6223/$ - see front matter
http://dx.doi.org/10.1016/j.carbon.2013.10.055

ECs are inferior to those of Li-ion batteries [3] and thus a number of studies have been carried out for making the energy storage abilities of ECs closer to those of Li-ion batteries. The progress towards increasing the energy densities of ECs has benefited from the continuous development of nanostructured electrode materials. Carbon is the most investigated electrode material for ECs [4] and the use of various forms of carbon such as activated carbon, mesoporous carbon, and carbon nanotube (CNT) has promoted the development of carbon-based ECs. Among various carbon materials, graphene, a two-dimensional form of carbon with unique electronic, optical, mechanical, thermal, and electrochemical properties, has thrown a new light on the enhancement of the EC performance [5]. The specific capacitances (C_{sp}s) of ECs based on graphene converted chemically or electrochemically from graphene oxide (GO) prepared by chemical oxidation and exfoliation of graphite have been reported to exceed 100 F g^{-1} [5–9]. In view of an extremely high conductivity and a large specific surface area (2630 m^2 g^{-1}) of graphene, however, there will be still much room for improving performances of the graphene-based ECs. The relatively small capacitances of graphene-based ECs [5–9] seem to arise from an inevitable aggregation of graphene nanosheets obtained by chemical or electrochemical reduction of GO such as leading to the decrease of their effective surface area.

One of potential approaches to increase C_{sp}s or energy densities of ECs is to use pseudocapacitances inherent to the redox active materials such as conducting polymers and metal oxides [1,10,11], although these electrode materials giving pseudocapacitance need be nanostructured [12–14]. Various composites comprising carbon and redox active materials have been explored and applied to ECs [15–25]. Composites of graphene and polyaniline (PANI), in particular, are of scientific and industrial interest because of excellent properties of PANI such as extremely high conductivity, high specific surface area, and superior stability, along with low costs of both materials. Several techniques have been developed for preparing the graphene/PANI or GO/PANI composites, including chemical or electrochemical polymerization of aniline in the presence of graphene or GO [18–22], a direct mixing of PANI nanofiber and chemically converted graphene [23], or exfoliation of graphite oxide by polymerization of intercalated aniline [24]. In most of graphene/PANI composite studies reported so far, reduction of GO to graphene and polymerization of aniline to PANI were carried out successively [19–22] or separately [23]. Consequently, it was difficult to control aggregation of graphene nanosheets during the reduction of GO or agglomeration of PANI nanofibers during polymerization of aniline, thus leading to the lowerings of C_{sp} and the cycle durability of the graphene/PANI composites.

In the present study, a one-step electrosynthesis using a two-electrode cell is demonstrated to fabricate graphene/PANI composites from a mixture of GO and aniline. The two-electrode cell consisted of two similar GO/aniline films sandwiching a separator containing acid and an alternating voltage was applied to the cell. During a voltage cycling, GO in the GO/aniline film deposited on one electrode was reduced to graphene concurrently with oxidation of aniline to PANI at the other electrode, and vice versa in the reverse voltage application. Just by repeating a voltage cycling, GO/aniline films were completely converted to graphene/PANI composites and the sandwich-type cell configuration enabled us to prepare graphene/PANI composites of various film thicknesses. The composite films in the two-electrode cell showed C_{sp} values of 195–243 F g^{-1} at a relatively high scan rate of 100 mV s^{-1} in acid solutions. In addition, the capacitance of the composite film remained 83% of an initial value even after 20,000 charge–discharge cycles, indicating a greatly improved electrochemical stability. Free-standing graphene/PANI films with a high mechanical strength, flexibility, and conductivity (68 S cm^{-1}) were easily obtained by this very simple preparation method.

An electrochemical synthesis of the graphene/PANI composite was reported recently [26], where a drop cast or spun film of a mixture of GO and aniline deposited on a conductive substrate was reduced and oxidized in a H_2SO_4 solution by cycling a potential in the three-electrode system. At an early stage of our present study, we also prepared the graphene/PANI composite in a similar way. In this technique, however, it was difficult to prepare thick composite films because they were likely to be peeled off from the electrode surface. This inconvenience hinted us to employ a two-electrode cell configuration.

2. Experimental

2.1. *Preparation of GO/aniline films*

GO was synthesized from a natural graphite powder (SNO-10 from SEC Carbon Ltd.) by a modified Hummers method [27,28]. Typically, graphite powder (2.0 g) was put into an 80 °C solution of concentrated H_2SO_4 (5 mL), $K_2S_2O_8$ (1.0 g), and P_2O_5 (1.0 g). After being kept at 80 °C for 5 h, the mixture was cooled to room temperature, carefully diluted with deionized water (200 mL), and left overnight. The mixture was then filtrated and washed with a Buchner funnel until pH of the rinse water became neutral. The filtrate was dried in air at ambient temperature overnight and then put into a concentrated H_2SO_4 (80 mL) at 0 °C. $KMnO_4$ (8 g) was added gradually with stirring and cooling so that the temperature of the mixture was kept below 20 °C. The mixture was then stirred at 35 °C for 2 h, and deionized water (100 mL) was carefully added in an ice bath to keep the temperature below 50 °C. The mixture was stirred for 2 h. Then a large amount of deionized water (400 mL) containing 30% H_2O_2 solution (10 mL) was added to the mixture to terminate the reaction, at which bubbles were generated and the color of the mixture changed to bright yellow. The mixture was filtrated and washed with 1:10 (volume ratio) HCl aqueous solution (500 mL) to remove metal ions. However, it was difficult to remove acids from the residue by filtration with deionized water because the residue became very viscous when being washed with water. Therefore, to remove metal ions and acids completely, the residue was put in deionized water, and the viscous and brown dispersion of about 2% w/v was subjected to dialysis for one week. The stock solution (10 mg mL^{-1}, pH 2.6) was prepared and different concentrations of GO dispersions were obtained by diluting the stock solution, being followed by exfoliation due to ultrasonication