Materials Research Bulletin 50 (2014) 240–245

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Activated carbon aerogel containing graphene as electrode material for supercapacitor

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ARTICLE INFO

Article history:
Received 3 September 2013
Received in revised form 30 October 2013
Accepted 5 November 2013
Available online 12 November 2013

Keywords:
A. Composites
A. Microporous materials
A. Nanostructure
B. Sol–gel chemistry
D. Energy storage

ABSTRACT

Resorcinol–formaldehyde aerogel containing graphene oxide (RFGO) was prepared by a sol–gel polymerization of resorcinol with formaldehyde using polyethyleneimine (PEI)-modified graphene oxide, and activated carbon aerogel containing graphene (ACAG) was then prepared by a chemical activation with K_2CO_3. For comparison, graphene-free activated carbon aerogel (ACA) was prepared by the same method using graphene oxide-free resorcinol–formaldehyde aerogel. Non-activated carbon aerogel (CA) was also prepared. BET surface area and pore volume of ACA and ACAG were remarkably enhanced with well-developed porous structure compared to those of CA. Electrochemical performance of CA, ACA, and ACAG electrodes were measured by cyclic voltammetry and galvanostatic charge/discharge methods. ACAG showed higher specific capacitance than ACA with excellent supercapacitive behavior (300 F/g vs. 271 F/g). Equivalent series resistance (ESR) of ACAG (0.40 Ω) was smaller than that of ACA (0.57 Ω). The enhanced electrochemical performance of ACAG electrode was due to graphene layer of ACAG.

1. Introduction

Supercapacitor is commonly used as an electrochemical energy storage device, which is ideally suitable for rapid storage and release of energy [1–4]. To develop supercapacitors with high performance, a large number of carbonaceous materials have been examined [5–12]. Conventional carbon materials, however, not only have low surface area for electric double layer (EDL) but also show limited power density and energy capacity. In order to overcome these problems, various modification methods of carbon materials have been suggested [13–25]. Among these modifications, chemical activation has been recognized as a feasible method for increasing specific surface area of carbon materials. Activation by chemical agent increases surface area and pore volume of carbon materials due to formation of micropores [26]. It is known that large amount of micropores improves the performance of carbonaceous materials as an electrochemical capacitor by increasing EDL [27]. However, the increase of internal resistance was inevitable when these micropores were formed. High internal resistance acted as an obstacle in generating power of supercapacitor [26].

Carbon aerogel has been widely employed as an electrode material of supercapacitors because of high surface area, fine pore size, and high porosity. Resorcinol–formaldehyde (RF) method is known to be a simple route for the preparation of carbon aerogel [21]. Furthermore, textural properties of carbon aerogel can be easily controlled in the RF method by changing preparation conditions, such as gelation temperature, pH, and reaction time [28]. Recently, composite materials based on a combination of carbon aerogel and various materials have been developed to obtain excellent supercapacitor electrodes [29,30].

Two-dimensional graphene with one atom thickness has attracted much attention due to its outstanding electrochemical properties. It has lower resistance than any other carbonaceous materials, which makes it a promising additive in the preparation of various composite materials [31,32]. However, pure graphene generally exhibits poor electrochemical performance because of its agglomerative behavior. In order to overcome this problem, graphene oxide (GO) has been widely used for the preparation of composite materials for supercapacitors.

In this work, we attempted to prepare an activated carbon aerogel containing graphene (ACAG) by a simple method to improve electrochemical performance of activated carbon aerogel as a supercapacitor. For this purpose, resorcinol–formaldehyde aerogel containing graphene oxide was prepared and it was activated with K_2CO_3 for use as an electrode of supercapacitor. For comparison, graphene-free activated carbon aerogel (ACA) and

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http://dx.doi.org/10.1016/j.materresbull.2013.11.021

non-activated carbon aerogel (CA) were also prepared. Through this work, we have demonstrated that graphene played an important role in enhancing supercapacitive electrochemical performance of activated carbon aerogel.

2. Experimental

2.1. Preparation of activated carbon aerogel containing graphene (ACAG)

Graphene oxide (GO) was synthesized from commercially available graphite powder according to the modified Hummers method in the literature [33]. Resorcinol–formaldehyde aerogel containing graphene oxide (denoted as RFGO aerogel) was prepared by a polycondensation of resorcinol ($C_6H_6O_2$, Sigma–Aldrich) with formaldehyde ($C_6H_6O_2$, Sigma–Aldrich) in a polyethyleneimine (PEI)-modified GO solution, as reported in our previous work [30]. In order to prepare activated carbon aerogel containing graphene, partially carbonized RFGO aerogel was used. Fig. 1 shows the preparation procedures for activated carbon aerogel containing graphene (denoted as ACAG). In short, known amounts of sodium carbonate (a base catalyst) and resorcinol were dissolved in a PEI-modified GO solution. Concentration of PEI-modified GO in DI water was fixed at 45 wt%. After stirring the solution, formaldehyde was added into the mixed solution to form a RFGO (resorcinol–formaldehyde and graphene oxide) solution. Molar ratio of resorcinol with respect to formaldehyde was fixed at 1:2. R/C (resorcinol/catalyst) ratio was fixed at 1000. After stirring the RFGO solution, it was cured in a vial at 80 °C to form RFGO wet gel. Solvent exchange was performed with acetone at 50 °C for one day. Ambient drying was then done at room temperature for one day to obtain RFGO aerogel. Partially carbonized RFGO aerogel was obtained through carbonization of RFGO aerogel at 500 °C under N_2 flow. Activation agent (K_2CO_3) was dissolved in DI water, and then partially carbonized RFGO aerogel powder was added into the solution. Weight ratio of K_2CO_3 with respect to partially carbonized RFGO aerogel was fixed at 1. After stirring the mixture for 1 h, the solid was recovered and dried at 120 °C for 6 h. The resultant was reacted at 800 °C for 1 h under N_2 atmosphere. Activation agent-containing ACAG was washed with DI water till the pH value of solution reached ca. 7 to remove the residual activation agent. The resulting material was finally dried at 120 °C for 1 day to obtain ACAG. For comparison, graphene-free activated carbon aerogel was prepared using RF aerogel by the same chemical activation method with K_2CO_3. Graphene-free activated carbon aerogel and non-activated carbon aerogel were denoted as ACA and CA, respectively.

2.2. Characterization

BET surface area and N_2 adsorption–desorption isotherm were measured with an ASAP 2010 (Micromeritics) instrument. Pore volume and pore size distribution of CA, ACA, and ACAG were determined by the BJH method applied to the desorption branch of N_2 isotherm. Raman spectra were obtained with a Jobin Yvon T6400 spectrometer using an Ar laser light source (wave length = 514.5 nm). Graphitization of CA, ACA, and ACAG was investigated by X-ray diffraction (Rigaku, D/MAX-2000). Morphology of carbon aerogel matrix and location of reduced GO on ACAG were confirmed by HR-TEM (Jeol, JEM-3010).

2.3. Preparation of CA, ACA, and ACAG electrodes

CA, ACA, and ACAG were casted using polytetrafluoroethylene as a binder. A mixture of each carbon material and binder with weight ratio of 90:10 was dispersed in 2-propanol. The resultant was mixed using mortar and pestle, and then it was rolled to be 8–10 μm thickness. The electrode material was cut into 1 cm × 1 cm and pressed onto nickel foam electrode. It was finally dried at 100 °C for 12 h in a vacuum oven. The weight of electrode was ca. 2.5 mg.

2.4. Measurement of electrochemical properties of CA, ACA, and ACAG

Electrochemical properties of CA, ACA, and ACAG electrodes were measured with a conventional three-electrode cell system in

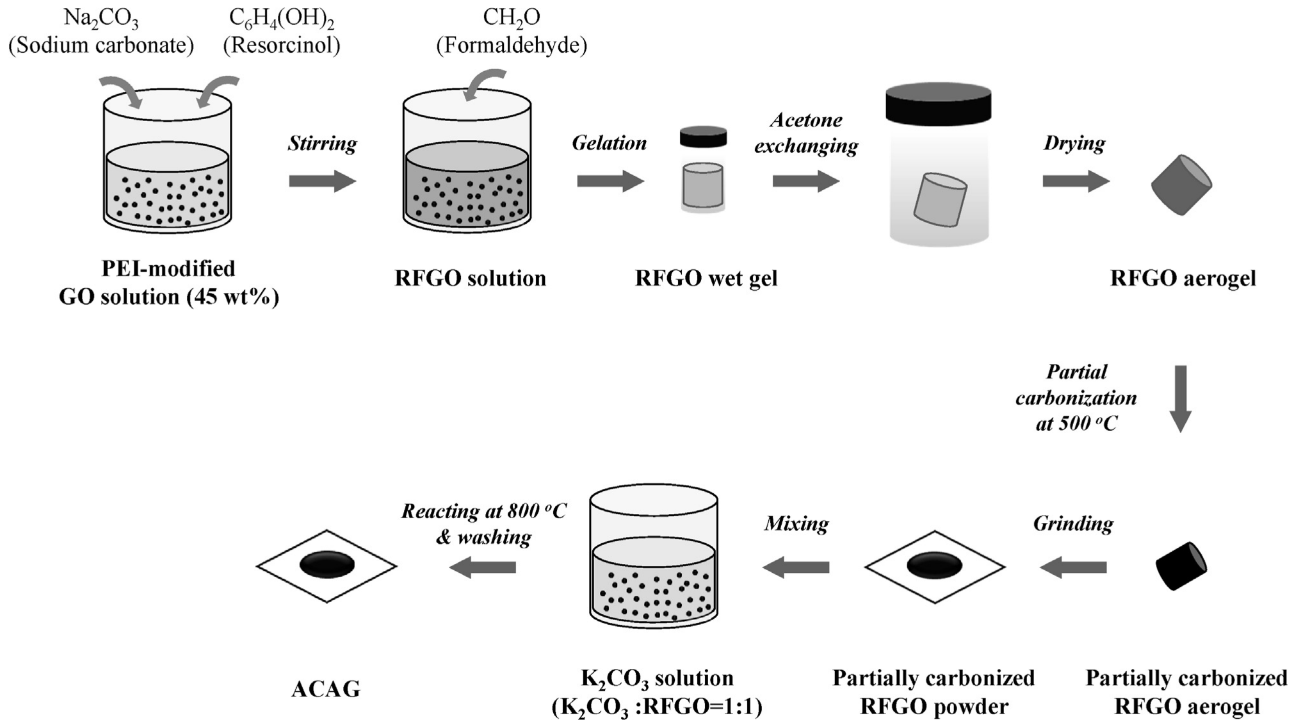

Fig. 1. Preparation procedures for activated carbon aerogel containing graphene (ACAG).