Journal of Solid State Chemistry 221 (2015) 338–344

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

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

Effect of reducing system on capacitive behavior of reduced graphene oxide film: Application for supercapacitor

Hamdane Akbi [a], Lei Yu [a], Bin Wang [a], Qi Liu [a], Jun Wang [a,b,*], Jingyuan Liu [a], Dalei Song [a], Yanbo Sun [c], Lianhe Liu [a,b]

[a] Key Laboratory of Superlight Material and Surface Technology, Ministry of Education, Harbin Engineering University, Harbin 150001, PR China
[b] Institute of Advanced Marine Materials, Harbin Engineering University, Harbin 150001, PR China
[c] State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, PR China

ARTICLE INFO

Article history:
Received 28 May 2014
Received in revised form
26 September 2014
Accepted 5 October 2014
Available online 15 October 2014

Keywords:
Capacitive behavior
Reducing system
Reduced graphene oxide film
Drop-casting technique

ABSTRACT

To determine the best chemical reduction of graphene oxide film with hydriodic acid that gives maximum energy and power density, we studied the effect of two reducing systems, hydriodic acid/water and hydriodic acid/acetic acid, on the morphology and electrochemical features of reduced graphene oxide film. Using acetic acid as solvent results in high electrical conductivity (5195 S m^{-1}), excellent specific capacitance (384 F g^{-1}) and good cyclic stability (about 98% of its initial response after 4000 cycles). Using water as a solvent, results in an ideal capacitive behavior and excellent cyclic stability (about 6% increase of its initial response after 2100 cycles).

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1. Introduction

Although high energy densities can reach as high as 180 Wh kg^{-1}, Lithium batteries generally suffer from slow power delivery or uptake. Certain applications need faster and higher-power energy storage systems, a role given to the supercapacitor [1].

Supercapacitors have attracted much attention owing to their excellent power density, high rate capability, fast charging/discharging, long cycle life, ease of operation and low maintenance cost [2,3]. With a higher power density than batteries and a greater energy storage than conventional capacitors, supercapacitors are capable of bridging the power/energy gap between traditional dielectric capacitors and batteries/fuel cells. However, they are still limited by their low energy densities and slow rate capabilities [3,4]. Thus, major research on supercapacitors is directed at increasing the energy density without sacrificing other desirable properties.

The energy E stored in the supercapacitor is dependent directly on its specific capacitance and cell voltage. Consequently, enhancing the energy density can be realized by improving both the cell voltage and specific capacitance.

For supercapacitors, cell voltage can be enlarged by utilizing ionic liquid or organic electrolyte. Another way of increasing cell voltage is to develop asymmetric supercapacitors [5,6]. In other words, enhancing the specific capacitance can be achieved through increasing specific surface area and optimizing pore size by developing hierarchically porous structures, while maintaining good electrical conductivity [7].

It is well known that the electrode is the heart of the cell, and all electrochemical features, such as capacitance and charge storage of supercapacitors, essentially depend on the type of electrode material [8]. With its exceptional features, such as ultra-high electrical conductivity, high surface area (2620 m^2 g^{-1}), good theoretical capacitance (550 F/g), excellent thermal stability and outstanding mechanical properties, graphene-based materials derived from graphene oxide (GO) have aroused a great deal of interest in various applications [9–13], including solar cells [14], transparent conductors [15–17], gas sensors [18,19], and supercapacitors [4,20–22].

Among various graphene-based materials, graphene film or paper has attracted a lot of attention due mainly to its excellent mechanical properties, high electrical conductivity and high surface area [4,23,24]. Furthermore, the dispersed GO can be easily assembled into films by simple techniques such as drop-casting [4], vacuum filtering [4,25], spray coating [26], and dip-coating [27].

Because of good mechanical flexibility and high electrical conductivity the graphene film can act as both the active material and current collector in the supercapacitor, leading to simplified

* Corresponding author at: Key Laboratory of Superlight Material and Surface Technology, Ministry of Education, Harbin Engineering University, Harbin 150001, PR China. Tel./fax: +86 451 8253 3026.
E-mail address: zhqw1888@sohu.com (J. Wang).

http://dx.doi.org/10.1016/j.jssc.2014.10.004
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and lightweight supercapacitors [4]. Moreover, the oxygen-containing GO makes it practically insulated. Thus, an effective and suitable process of deoxygenation must be carried out to achieve the desired features. The epoxy and hydroxyl groups are the main oxygen-containing functional groups attached to GO [28,29]. The chemical reduction of GO film using halogen acid, including hydriodic (HI) and hydrobromic acid (HBr) as reducing agents, results in far higher efficiency compared with other agents [23,30].

Here, we focus our attention on the effect of the reducing systems, hydriodic acid/water and hydriodic acid/acetic acid, on the structure, morphology and electrochemical properties of GO film prepared using a drop-casting technique. Using HI/acetic acid as a reducing system results in a high specific capacitance as well as high electrical conductivity. Using HI/water, on the other hand, as the solvent results in an ideal capacitive behavior with excellent cyclic stability.

2. Experimental

2.1. Materials and method

All chemicals were of analytical grade and were used without further purification. Graphite oxide was synthesized from natural graphite using a modified Hummers method [31]. Exfoliation of GO was achieved by ultrasonication of the dispersion in an ultrasonic bath (KQ-500DB, 250 W). GO film was made by drop-casting GO dispersions (5 mg ml^{-1}) onto the mold constructed from smooth paper [4]. The films were then allowed to dry for 48 h under ambient conditions, then for 8 h at 60 °C. The film thickness was controlled by varying two parameters: the concentration and the amount of the dispersing GO. The reduction of GO film was carried out by immersing GO films into 30% HI/water and 30% HI/Ac-OH at 70 °C.

2.2. Characterization

The crystallographic structures of the materials were determined by a powder X-ray diffraction (XRD) system (Rigaku TTR-III) equipped with Cu KR radiation (λ=0.15406 nm). X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI 5700 ESCA spectrometer with monochromatic Al KR radiation ($h\nu$=1486.6 eV). All XPS spectra were corrected by the C1s line at 284.4 eV. Raman spectroscopy measurements were taken using a Horiba HR800 micro-Raman spectrometer. The microstructure of the samples was investigated by scanning electron microscopy (SEM, JEOL JSM-6480A microscope). The sheet resistance of the reduced graphene oxide film (r-GO) was measured by a four-probe method. The thickness of the r-GO film was measured by a digital micrometer.

2.3. Preparation of electrodes and electrochemical measurement

The working electrodes were prepared by pressing the r-GO film onto nickel foam as the current collector with a pressure of 20 MPa. All electrochemical measurements were done in a three-electrode setup: Ni foam/r-GO film as the working electrode, platinum foil and SCE electrode as the counter and reference electrodes, respectively. The measurements were carried out in a 6 M KOH aqueous electrolyte at room temperature. Typically, cyclic voltammogram (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) were measured by a CHI 660C electrochemical workstation. CV tests were done between −1 and 0 V at different scan rates. Galvanostatic charge/discharge curves were measured in the potential range of −1 to 0 V at different current densities, and EIS measurements were also carried out in the frequency range from 100 kHz to 0.005 Hz at open circuit potential with an ac perturbation of 5 mV.

3. Results and discussion

GO was prepared from natural graphite by the modified Hummers methods [31]. The GO film was prepared by using a drop-casting technique (Fig. S1). The GO film was reduced chemically using hydriodic acid as a reducing agent in two different solvents (Fig. S2), water and acetic acid, at low temperature (70 °C).

The sheet resistance (R, Ω sq^{-1}) of the r-GO films was measured by a four-probe method and the corresponding volume conductivity (σ, S m^{-1}) was calculated using the formula $\sigma=1/(Rt)$, where t (unit: cm) is the film thickness. The resulting r-GO film possesses excellent properties in terms of electrical conductivity. The r-GO film reduced by hydriodic acid/acetic acid (r-GO_{HA}) displays a high electrical conductivity (σ_{HA}=5194.80 S m^{-1}) which is nearly twice the electrical conductivity of r-GO film (σ_{HW}=1984.13 S m^{-1}) reduced by hydriodic acid/water (r-GO_{HW}).

3.1. Reducing mechanism and selection of solvents

The main purpose of this work is to remove oxygen-containing groups from GO film without destroying its structure and acquisition of other desired features, a role given to some halogen acids. It has been proved that HI can catalyze epoxy group and transform it into hydroxyl group. In addition, the HI reducing agent would replace hydroxyl group with iodide, which is good leaving group, resulting in a highly-effective deoxygenation [23]. Moreover, the selection of water and acetic acid as solvents is attributed to several facts. Typically, the high proportion of functional groups in graphene oxide gave it a hydrophilic character, hence the GO film is dissolvable in water [32,33]. This feature causes an expansion in thickness of the film during the reduction process (Fig. S3). In addition, the use of water gives a desirable accessibility of HI into GO film layers, resulting in a fast and complete reduction. On the other hand, the use of acetic acid as a solvent with HI can eliminate the oxygen functional groups and replace them with organohalides, which are easily removed. As a consequence, this property leads to a high graphitization [30]. Fig. 1 clarifies the effect of each solvent on the reduction process of GO film.

3.2. Microstructure characterization

The chemical reducing process causes a remarkable change in the morphology of the GO film. Fig. 2 shows the SEM images of GO films before and after reduction. As shown, the reduction process changes the morphology of the GO film. In addition, changing the reducing system has a pronounced effect. Regarding the surface (Fig. 2a, b and c), chemical treatment causes a significant change in the morphology of GO film, from a smooth surface, prior to reduction, to a wrinkled and corrugated surface after reduction. In addition, changing the reducing system shows differences in the morphology with a greater wrinkled-surface when HI/water is used as the reducing system.

To further understand the morphology of as-prepared GO film, a cross section of GO film was investigated with SEM before and after reduction. As shown in Fig. 2d, e and f, using water as a solvent result in an expansion in thickness of the film (Fig. 2e), while using acetic acid result in a shrinkage, owing to the van der Waals force between graphene sheets. More importantly, the reduction process gives the desired structure, resulting in a high specific capacitance, energy density and excellent rate performance.

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