Electrochimica Acta 142 (2014) 101–107

Contents lists available at ScienceDirect

Electrochimica Acta

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

Nitrogen rich graphene-cross-linked melamine formaldehyde carbon cryogels for supercapacitors

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ARTICLE INFO

Article history:
Received 27 May 2014
Received in revised form 9 July 2014
Accepted 19 July 2014
Available online 4 August 2014

Keywords:
Melamine formaldehyde
Graphene
Cryogel
Nitrogen content
Capacitance

ABSTRACT

A new nitrogen rich porous graphene-cross-linked melamine formaldehyde carbon cryogel (GCMFCC) was successfully prepared by a sol-gel poly condensation reaction catalyzed by Na_2CO_3; it was subsequently converted to a cryogel by freeze-drying. The melamine formaldehyde carbon cryogel (MFCC) and GCMFCC-x were synthesized and characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermo gravimetric analysis (TGA) and scanning electron microscopy (SEM). XPS and BET analysis showed that the as- prepared GCMFCC-5% cryogel had a highest nitrogen content of 14.29% with surface area of 261.33 m^2/g and unimodal meso-pore volume of 0.36 cm^3/g. The electrochemical behavior of MFCC and GCMFCC-x samples was investigated by cyclic voltammetry and charge/discharge cycles. GCMFCC-5% achieved highest capacitance of 313.24 F/g. Hence, GCMFCC is a promising electric double-layer capacitor material with low production costs and the ability to avoid supercritical drying.

1. Introduction

Supercapacitors as electrical capacitors have received a considerable attention due to their energy storage mechanism with the advantages of high performance and low cost as compared to secondary lithium ion batteries and conventional capacitors. On the basis of the charge storage mechanism supercapacitors are mainly categorized into two types: electric double-layer capacitors (EDLCs) and redox pseudocapacitors. Porous carbon materials with effective surface areas, pore textures, and surface chemistry are highly desired as electrical double-layer capacitor active materials [1,2]. However, with the disadvantage of the low energy density of carbon as an EDLS electrode as compared to secondary batteries has hindered some of its applications [3,4]. The literature shows that the performance of carbon materials has been improved by optimizing the pore structure [5–7]. Moreover, the presence of functional groups containing hetero atoms such as boron, oxygen and specially nitrogen leads to a desirable interaction with the solvated ions of a polar solvent. This phenomenon generates a pseudo effect which improves the accessibility of ions to improve the capacitance. Therefore, the presence of such functional groups in carbon materials changes the electron donor aptitude of the electrolyte ions, resulting in enhanced capacitance and power [8,9]. Carbon gels produced by the carbonization of organic gels using Pekala's method have been used in adsorption and energy storage [10–15]. Due to their versatility in terms of surface area, pore texture and surface chemistry they have got a considerable attention among the researchers now a day. The improved catalytic and adsorption properties of nitrogen containing modified carbon xerogels has been investigated [16,17]. The introduction of nitrogen groups on carbon xerogels causes a surface basicity, thereby enhancing the adsorption properties. The polymeric reaction between resorcinol and formaldehyde involves aromatic electrophilic substitution, followed by a poly-condensation reaction that leads to cross-linking [18]. In a similar approach nitrogen-containing precursors such as melamine have been used in a reaction with formaldehyde, to prepare meso-porous carbon aerogels with nitrogen content around 3% [19,20].

Inspired by the importance of nitrogen in carbon aerogels and its role in the adsorption of ions in polar electrolytes, we have prepared a new graphene based melamine formaldehyde carbon cryogel with higher nitrogen through a poly condensation sol-gel method. Therefore, we used melamine along with formaldehyde and graphene to prepare a graphene-cross-linked melamine formaldehyde carbon cryogel (GCMFCC) with higher nitrogen content ever. For structural enhancement i.e. to achieve better porosity

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http://dx.doi.org/10.1016/j.electacta.2014.07.102
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and adsorption properties, graphene oxide (GO) was added as a cross-linking species in the melamine-formaldehyde (MF) sol gel process. It is mainly believed that lone-pair of electrons of nitrogen can infuse an additional negative charge in to the graphene π electron system. However, such increase in negative charge leads to an enhanced conductive behavior along with stronger interaction with foreign molecules (i.e. metals particles, ions, acidic compounds). In our experiments it was observed that the addition of graphene to the MF gel not only improved the structure, surface area, and porosity, but also led to a remarkable increase in the N-content along with enhanced capacitance. Nitrogen contents and states of N-atom were determined by X-ray photoelectron spectroscopy (XPS). The electrochemical behavior of the samples as electrode material in electric double-layer capacitors (EDLCs) was investigated by cyclic-voltammetry and charge/discharge experiments.

2. Experimental

2.1. Preparation of the porous carbon cryogel

The GO was synthesized by the modified Hummers method [21]. First an organic sol-gel was synthesized by a poly-condensation reaction between melamine (M) and formaldehyde (F) catalyzed by Na_2CO_3. The molar ratio of M to F in MF solution was taken as 1:3.7 and the pH was set at 10 by using Na_2CO_3. The solution was heated at 70-75 °C in a water bath until it became clear, then cooled to room temperature and the pH reduced to 2 by the drop wise addition of 30% HCl. 1%, 3% and 5% of GO as a total mass of both M and F were added to the MF solution while maintaining the pH at 2 and stirred for 1 h. The resulting homogenized solutions were sealed in glass vials (8 cm length × 2 cm internal diameter) and cured in a water bath at 85 °C for 3 days to obtain sol-gels. All gels were placed in separate glass bottles of de-ionized water and changed the water for several days until the pH value reached to 6 or 7. Sol-gels were freeze dried to obtain the GO cross-linked MF organic cryogels (GOCMFOC-x). The reduction of GO to graphene was achieved in a tubular furnace at a heating rate of 5 °C/min and kept at 800 °C for 1 h. Then the furnace was allowed to cool down to room temperature under N_2 and the samples were collected on the next day. The as prepared GCMFCC were identified as GCMFCC-x where x is the mass percentage of GO.

2.2. Nitrogen determination

The nitrogen content of MFCC and GCMFCC-x was determined by XPS analysis carried out on a Thermo Fisher, ESCA Lab 250 spectrometer using a monochromatized Al Kα X-ray source.

2.3. Structural characterization

The cross-linking phenomenon of MF and GOMF was studied by using a NICOLET 6700 FTIR THERMO SPECIFIC spectrophotometer from 400 to 4000 cm^{-1} under vacuum. The structural and thermal stability of MFOC and GOCMFOC-x were evaluated by TGA/DSC-1(METTLER TOLEDO) instrument under N_2 flow and the mass was recorded as a function of temperature. The samples were heated from room temperature to 900 °C at a ramp rate of 10 °C min^{-1}. Powdered XRD patterns were obtained using a Japanese D/Max 2500 diffractometer (40 kV and 200 mA with Cu Kα (λ=1.54 Å)). Surface morphologies of MFCC and GCMFCC-x were observed by using Hitachi S-4700 scanning electron microscope with and an acceleration voltage of 20 kV. Nitrogen adsorption was measured using a Sorptomatic 1990 apparatus. Prior to measurement samples were heated to 200 °C under vacuum (10-5 Torr) for 2 h to remove all adsorbed species. The BET surface area S was determined by applying the Brunauer–Emmett–Teller (BET) model to N_2 adsorption data taken at 77 K.

2.4. Electrochemicals measurements

The carbon electrodes were fabricated by mixing GCMFCC-x with acetylene carbon black and polytetrafluoroethylene with a mass ratio of 75:20:5 onto nickel foam. The electrochemical measurements and galvanic cylcles were performed by using an electrochemical work station (Zahner-Electrik, Germany) in a three electrode system, in which platinum wire and a saturated calomelelectrode were used as counter and reference electrodes, respectively. Cyclic voltammograms (CV) were obtained in 5 M KOH at a scan rate of 10 mV/s. Capacitance values for all electrodes were calculated as $c = \frac{1}{m\upsilon(V_c - V_a)}\int_{V_a}^{V_c} I(V)dV$, where C is the specific capacitance (F/g), m (g), υ (V/s), Vc and Va, and I (A) are the mass of the active materials in the electrode, scan rate, high and low potential limit of potential window, and the instantaneous current on CV curves, respectively. Galvanic cycles were taken under the same conditions with three electrodes system and 30% KOH. Capacitances were determined on discharge curves by using $c = \frac{I\Delta t}{m\Delta V}$.

3. Results and discussion

Fig. 1 illustrates a simple schematic synthesis route of sol gel formation of MF-gel and GOCMFOC-x samples where (x = 1%, 3%, and 5%) is the mass ratio of GO.

3.1. Polymerization and cross-linking of MF-GO

Polymerization (curing) of melamine to formaldehyde occurs in two stages. In the first step, the methylolation reaction of formaldehyde to melamine was carried out under basic conditions at 70-75 °C [22]. The second step comprised a ploycondensation and cross-linking reaction between formaldehyde, melamine and GO, leading to the formation of methylene and a methylene ether bridge that was thermally cured under acidic conditions [23]. FTIR analysis was carried out to monitor the polycondensation and cross-linking reactions. Fig. 2 illustrates the FTIR spectra of GO, MFOC and GOCMFOC-x. The broad O–H stretching peak at 3382 cm^{-1}, strong C = O peak at 1726 cm^{-1}, O–H deformation peaks at 1620 and 1412 cm^{-1}, C–OH stretching peak at 1225 cm^{-1}, and C–O stretching peak at 1051 cm^{-1} were attributed to the presence of hydroxyl, carboxylic acid, and epoxy groups, respectively on the surface of the GO sheets [24]. The peaks at 3330 cm^{-1}

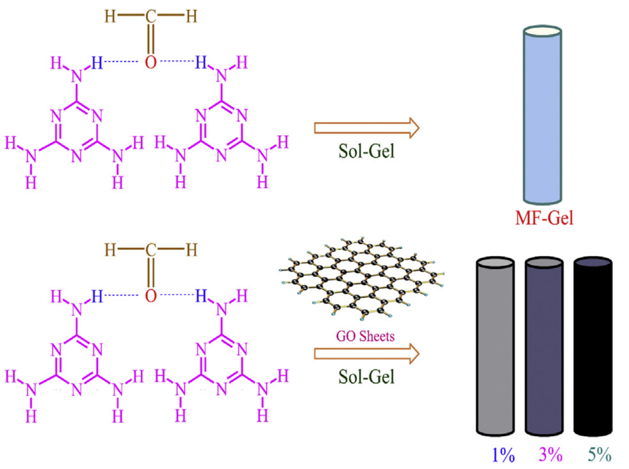

Fig. 1. Schematic illustration of synthesis of MF-gel and GOCMFOC-x through a sol gel poly condensation reaction.