Contents lists available at ScienceDirect

Synthetic Metals

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

Porous cellulose/graphene oxide nanocomposite as flexible and renewable electrode material for supercapacitor



Creative Research Center for Nanocellulose Future Composites, Dept. of Mechanical Engineering, Inha University, 100 Inha-Ro, Nam-Ku, Incheon 22212, South Korea

ARTICLE INFO

Article history: Received 3 June 2016 Received in revised form 2 November 2016 Accepted 8 December 2016 Available online 13 December 2016

Keywords: Cellulose Graphene oxide Nanocomposite Supercapacitor Flexible electrode

ABSTRACT

The increasing demand for portable, wearable, miniaturized and flexible consumer electronic devices requests the development of flexible and renewable energy storage devices. This paper reports a flexible and renewable electrode material for supercapacitor. The electrode material is made by preparing a porous structured cellulose/graphene oxide (GO) nanocomposite. The morphology of the nanocomposite is shown to be porous structure with a pore size about 10 μ m. The Fourier transform infrared spectroscopy of the nanocomposites exhibits that the cellulose and GOs are successfully grafted by a grafting agent, which results in uniform dispersion of GOs in the cellulose matrix. The electrical performance of the nanocomposite is evaluated by measuring cyclic voltammograms and galvanostatic charge-discharge curves. Low cost and sustainability of the cellulose and graphene oxide nanocomposite encourage its possible use for electrode material of flexible energy storage devices.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Electrochemical energy and conversion devices, such as supercapacitors, batteries and fuel cells are being considered seriously as alternate energy/power sources nowadays because of reducing energy sources and increasing environmental concerns caused by relying on fossil fuels. Supercapacitor, which also is called electrochemical capacitor, is a device which is able to store electrical energy in the interface of electrode and electrolyte. Supercapacitor can be divided into two kinds, electrical double layer capacitor (EDLC) and pseudocapacitor. These two categories can be distinguished by their charge storage mechanism. EDLCs are electrostatic storage of the electrical energy done by separating the charge in a double layer at the interface between electrode and electrolyte, while pseudocapacitor is electrochemical storage of the electrical energy, achieved by faradic redox reactions [1–3]. For large scale applications of portable electronic systems and automotive, development of these power sources are very useful because they have excellent properties such as high power density, reliable energy density, long cycle life and excellent reversibility. Nowadays much efforts are being given to find new ways to reduce production cost of supercapacitor with high performance, lightweight and flexibility [4–9]. For this reason, polymer based

* Corresponding author.

E-mail address: jaehwan@inha.ac.kr (J. Kim).

http://dx.doi.org/10.1016/j.synthmet.2016.12.010 0379-6779/© 2016 Elsevier B.V. All rights reserved. energy storage devices are drawing attention of researchers [10– 14]. However, limitations of polymer based energy storage devices are poor cyclic stability, self- discharge, mass transport limitations etc. [15–19]

Cellulose, most abundant organic resource on earth, is advantageous for development of many devices because of its renewability, abundance and nontoxic behavior. Besides, some great properties such as biocompatibility, flexibility, transparency, high mechanical strength, biodegradability are observed in cellulose. Discovery of cellulose as a smart material made it more favorable for the development of flexible and renewable sensors, actuators and printed electronics [20,21]. Because of its unique behaviors, cellulose has a possibility for renewable separator for supercapacitor. Once cellulose is tailored by inorganic nanomaterials, such as graphene, then its functionality for supercapacitor electrode can be improved with maintaining its renewable characteristics.

Graphene, flat monolayers of tightly packed carbon atoms in a two dimensional honey comb lattice, has shown many exclusive properties, such as the quantum hall effect (QHE), large specific surface area, high carrier mobility at room temperature, high mechanical strength, optical transparency, high flexibility, abundant surface functional groups and excellent thermal conductivity [22– 24]. Graphene can be used as electrode materials in optoelectronic devices, field effect transistors, electrochemical supercapacitor and mechanical sensors, such as gas sensor, bio sensor. [25–27]. Graphene based composite as flexible and thin supercapacitor







electrode has already been reported [28]. Recently, graphene oxide (GO) as a very good filler material in polymer nanocomposite has been demonstrated [29]. Its easy process ability in solution and rich colloidal properties make GO a smart precursor for the fabrication of functional composite materials. So far, cellulose GO composite fabrication and its application in various sensors and devices like proximity sensor, chemical sensor, temperature sensor, energy storage and memory storage device have been reported [30–32]. Active carbon based material like CNT and GO, modified graphene can be used to develop new composite for supercapacitor electrode as it is cheap and highly conductive [33–35]. Combination of carbon materials with cellulose can provide an improved conductive network as well as capacitance [36].

In this paper, we report the electrochemical characteristics of porous structured cellulose/GO nanocomposite as an electrode material for supercapacitor. Feasibility of the nanocomposite as electrical double layer supercapacitor electrode is also investigated. Morphology and structure of the nanocomposite are investigated by scanning electron microscope (SEM) and Fourier transform infrared spectroscopy (FTIR).

2. Experimental details

2.1. Materials

Natural flake graphite, Hexamethylene-1,6-diisocyanate (HMDI), Dimethyl Acetamide (DMAc), Lithium Chloride (LiCl), Sulfuric Acid (H_2SO_4), Nitric Acid (HNO_3), Hydrochloric acid (Hcl), Sulfuric acid (H_2SO_4), Potassium permanganate (KMnO₄), Calcium Carbonate (CaCO₃) with a particle size of 10 μ m and 30% Hydrogen Peroxide (H_2O_2) solution were procured from Sigma-Aldrich. 99.5% isopropyl alcohol (IPA) was purchased from Daejung, South Korea. 98% pure and with a degree of polymerization 4500 cotton pulp was obtained from Buckeye Technology, USA.

2.2. Material preparation

1.5 wt% Cellulose solution was obtained by dissolving cotton pulp in DMAc/LiCl solvent system [20]. The whole preparation process of cellulose solution is illustrated briefly. First of all, LiCl and cotton pulp were dried in oven at 100 °C. Then, they were added in anhydrous DMAc with a ratio of (cotton pulp/LiCl/DMAc) 2/8/90 followed by heating at 155 °C with mechanical stirring for 4 h to obtain a viscous solution. Then, the solution was centrifuged at 11,000 rpm to remove undissolved parts of cellulose fibers. GOs were synthesized by the improved graphene oxide synthesis method [37]. The AFM and TEM images are shown in Supplementary information (Fig. S1). The AFM image of the GO shows that the thickness of GO layer is ~1.5 nm. The bright and smooth TEM image reveals the overlapping and barely distinguishable morphology of GOs from the slightly dark double sheet regions and its crystallinity. Functionalized Graphene Oxide (FGO) was obtained by treating GO with HMDI [38]. For this purpose, HMDI was added with GO dispersed in anhydrous DMAc by stirring at 110 °C. According to the desired wt% of GO in cellulose amount of GO (12.5 mg for 1 wt%, 25 mg for 2 wt%, 37.5 mg for 3 et%) was functionalized. The cellulose solution (80 g) was added in this GO solution followed by mechanical stirring at the same temperature for another 3 h. This high temperature is required for grafting between cellulose and GO as well as it reduces GO at some extent and increase the conductivity [39]. Then, the mixed solution was cooled down and CaCO₃ was added followed by mechanical stirring for 2 h.

A doctor blade was used to cast the mixed solution on a glass plate and cured using deionized (DI) water for 3 h. This slow curing process prevents aggregation of GOs and CaCO₃ and eliminates the remnants of LiCl and DMAc. Than the cured nanocomposite was rinsed in two different DI water baths and dried at an ambient temperature, which is named as CFGO. Finally the dried film was dipped into 5 wt% HCl to remove CaCO₃ and get a porous cellulose/ GO nanocomposite (PCFGO). CaCO₃ reacts with HCl and it produces calcium chloride which is soluble in water. Thus, CaCO₃ can be removed from the cellulose matrix so as to make PCFGO. Numbers after the abbreviation of CFGO and PCFGO represent the weight percentage of GOs in the cellulose matrix. Fig. 1 shows the reaction mechanism which takes place between the cellulose and GO as well as between CaCO₃ and HCl.

2.3. Supercapacitor electrode fabrication

To make a supercapacitor, one side of $4 \text{ cm} \times 1 \text{ cm}$ PCFGO sample was coated with a gold electrode as current collector. Then, it was glued on a PET film with epoxy so that the gold electrode placed between the nanocomposite and the PET film. Schematic diagram of the supercapacitor electrode is shown in Fig. 2. The electrode bent at 45° , 90° and 180° is shown in the Supplementary information Fig. S2 to confirm its flexibility.

2.4. Characterization

Field emission scanning electron microscope (FE-SEM) images of the samples were taken with JEOL JSM-6400F SEM to study the sample morphology. The samples were prepared by coating platinum layer using an ion sputter EMITECH, K575X. To confirm the removal of CaCO₃, Energy-dispersive X-ray spectroscopy (EDX) was taken using EDAX Ametek attached to the FESEM. To demonstrate covalent grafting of GOs to cellulose, FTIR spectra were obtained using an FTIR spectroscopy (Bruker Optics Inc.) with KBr pellet method in the spectral range of 500–4000 cm⁻¹ by averaging 25 scans with a resolution of 4 cm⁻¹/min to minimize the dynamic scanning effects. Electrochemical characterization was performed using Solartron, SI 1287 electrochemical interface

Cellulose – OH + GO-OH
$$\xrightarrow{ONC - R - CNO}$$
 Cellulose – O – C = N – R – N = C – O – GO
DMAc, 110°C

$$CaCO_{3}(s) + HCl (aq) \longrightarrow CaCl_{2}(aq) + CO_{2}(g) + H_{2}O (l)$$

Fig. 1. Schematic diagram of chemical reaction mechanism.

Download English Version:

https://daneshyari.com/en/article/5435657

Download Persian Version:

https://daneshyari.com/article/5435657

Daneshyari.com