



Activated carbon monoliths derived from bacterial cellulose/polyacrylonitrile composite as new generation electrode materials in EDLC



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ABSTRACT

Bacterial cellulose (BC) gel is synthesized by static culture process at the interface between air and medium. The solvent-exchanged BC gel is incorporated into polyacrylonitrile (PAN) copolymer solution under heating at 90 °C and subsequent cooling gives bacterial cellulose-polyacrylonitrile composite (BC-PAN) monolith. The BC-PAN monolith is carbonized at 1000 °C with physical activation in the presence of CO₂ to obtain the activated carbon monolith, BC-PAN-AC, with large surface area and high microporosity. Unique morphologies are observed for BC gel which is propagated to the BC-PAN monolith and restored in BC-PAN-AC. The BC nanofibers remain entwined throughout the porous skeleton of the PAN backbone and the entangled structure helps in retaining the continuity of the matrix of BC-PAN-AC and reduce the grain boundary impedance for electrical conduction. Cyclic voltammetry shows that these activated carbons are good electrode materials in electric double layer capacitors (EDLC) with capability of high-speed charging and discharging.

1. Introduction

Sustainable environment and energy related issues are the most important problems to be solved in the 21st century. So far, the society was predominantly based on the mass production and consumption of oil resources but now there is a great thrust of replacing them by renewable resources (Bazaka, Jacob, & Ostrikov, 2016; Jabli, Saleh, Sebeia, Tka, & Khiari, 2017; Jabli, Tka, Ramzi, & Saleh, 2018; Liang, Li, & Yang, 2017; Pandiyarasan et al., 2017; Veluswamy et al., 2017). Carbon dioxide is a greenhouse gas produced from the combustion of fossil fuels. It causes global warming and hence technologies leading to replacement of such fuels are in demand. Electric and fuel cell vehicles that do not use fossil fuels have gained increasing attention and studies on electric storage devices as an indispensable technology have been conducted actively. Among them, compact, lightweight and high-performance lithium-ion rechargeable battery (LIB) has been used in a wide range of electronic devices like mobile phones and notebook computers which support our convenient and plush life (Scrosati & Garche, 2010; Scrosati, 2000; Wang et al., 2015). Although development is underway to use LIB in electric vehicles, there are several

problems associated with it. The performance of the current LIBs needs to be improved much in terms of their efficiency, cycle life and other safety issues (Etacheri, Marom, Elazari, Salitra, & Aurbach, 2011). In this respect, an electric double layer capacitor (EDLC) can be interesting because of their higher power density and high-speed charging and discharging (Sharma & Bhatti, 2010; Simon & Gogotsi, 2008; Winter & Brodd, 2004). An EDLC has a very simple structure consisting of electrodes, an electrolytic solution and a separator. When a voltage is applied the electrodes are polarized and power storage takes place by the formation of an electric double layer in the electrolyte-liquid interface (Fig. S1). Thus, EDLC is a device that stores charges by physical adsorption and desorption of ions without any redox reaction and thus facilitates high-speed charging/discharging. It eliminates swelling of the active material and can sustain millions of cycles in comparison to a few thousands shown by regular batteries (Simon & Gogotsi, 2008). The power density and cycle life of such device is higher than conventional rechargeable battery. Such systems have already found application in PC back-up power supply and gasoline driven vehicles with regenerative braking system.

The capacitance of EDLC electrodes depend on the charge stored at

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the electrolytic liquid interface and is greatly affected by the electrode material, the electrolyte and the separator. It is facilitated by large specific surface area of the electrode material, like activated carbon (Wang, Zhang, & Zhang, 2012), with a porous structure through which electrolytes can also easily penetrate. However, the capacity of EDLC is not simply proportional to the specific surface area of the electrode material. It also depends on parameters like size and shape of the pores, conductivity of the material, its affinity towards the electrolytic solution and pseudo-capacitance due to functional groups present in the carbon material (Gu, Sevillia, Magasinski, Fuertes, & Yushin, 2013; Hsieh, Hornng, Huang, & Teng, 2015; Urita, Ide, Isobe, Furukawa, & Moriguchi, 2014). Thus, along with the development of activated carbons, new carbon materials such as ordered mesoporous carbon (Chen et al., 2015; Korenblit et al., 2010), carbon nanotubes (Futaba et al., 2006), and composite carbon materials with metal oxide (Long et al., 2014; Zhi, Xiang, Li, Li, & Wu, 2013), have been explored as electrode material. In general, the electrode material does not contain only activated carbon. It is essential to add conductive auxiliary agents like acetylene black to improve electronic conductivity (Osaka, Liu, & Nojima, 1998) and binders like polytetrafluoroethylene (which is an insulator) for molding (Tenmyo et al., 2015). Thus, if carbon materials can be synthesized with continuous and preformed molded structure and high porosity, these requirements can be met without any extra additive. In this respect, carbon monoliths with a continuous interconnected three dimensional porous structure derived from porous polymer monoliths can be useful (Nandi et al., 2012; Okada et al., 2011). Porous polymer monoliths can be fabricated either by polymerization or phase separation. In polymerization method, crosslinking agent (porogen) and the monomer are reacted in a solvent, but the operation is complicated and control of the fine structure is difficult (Kun & Kunin, 1968). On the other hand, phase separation (thermally/poor solvent induced) of a polymer solution can give porous monoliths in a neat and facile way. Polyacrylonitrile (PAN) monoliths made by thermally induced phase separation from PAN solution has been reported earlier (Nandi, Okada, & Uyama, 2011; Okada et al., 2011). PAN is a thermoplastic resin with high mechanical strength, excellent chemical stability and solvent resistance (Nataraj, Yang, & Aminabhavi, 2012). It is the main component of acrylic fibers and because of high yield in carbonization it is used as a precursor for various carbon materials (Paiva, Kotasthane, Edie, & Ogale, 2003). Monoliths of PAN can be heat treated in air to increase their stability and carbonized by physical activation to obtain carbon monoliths (Nandi et al., 2012). However, in the process of making the electrodes the carbon monoliths need to be grinded. This results in partial destruction of the co-continuous structure and thus a conductive auxiliary agent has to be added like in case of conventional activated carbon.

In the present study, our aim is to develop a new kind of conductive activated carbon from a combination of PAN monolith and bacterial cellulose gel that does not require the addition of a conductive aid. Cellulose is a water-insoluble linear homopolymer of β -1,4-linked D-glucose units that exists as crystallized Cellulose Nano-Fiber (CNF) and is the main component of plant cell walls. It is most abundant in nature and has been utilized since ancient times as wood and paper (Eichhorn et al., 2010). But in order to obtain CNF from plant cellulose it needs to be isolated from other wood-based polymer, such as pectin, hemicellulose and lignin (Abe, Iwamoto, & Yano, 2007; Isogai, Saito, & Fukuzumi, 2011). However, bacterial cellulose (BC) synthesized by cellulose-producing bacteria like *Gluconacetobacter xylinus* can be obtained in high purity with I_{α} type crystal structure (Brown, 1887; Lin et al., 2013). BC obtained from coconut water is known for a long time in South-east Asia and is used as a familiar low calorie dessert named *nata de coco*. BC can be produced by bacteria in the form of a gel swollen in water under aerobic condition from a culture medium containing sugars where it grows at the interface between culture solution and air. BC gel discharged from the body of bacteria is in the form of hydrogel nanofiber ribbons of ~ 0.89 nm width, with a three-

dimensional network structure containing more than 99% by weight of water (Hu, Chen, Yang, Li, & Wang, 2014; Huang et al., 2014). Since the biosynthesis is carried out by static culture in a liquid medium the nano-sized network structure is spread uniformly at the surface to form a lamellar structure with micron-sized thickness (Iguchi, Yamanaka, & Budhino, 2000). It is possible to control the gel thickness and shape by changing conditions like temperature, oxygen concentration and presence or absence of stirring (Hu & Catchmark, 2010). The gel has excellent solvent resistance and the solvent entrapped in it can be replaced by other solvents without shrinkage. The BC sheets obtained by drying the gel have rigid three-dimensional network of CNF with high degree of crystallinity, tensile strength, moldability, excellent mechanical properties, biocompatibility, biodegradability and moisture retention ability (Hu & Catchmark, 2010; Iguchi et al., 2000; Klemm, Schumann, Udhardt, & Marsch, 2001; Yamanaka et al., 1989). Thus by taking advantage of its unique features BC gel can either be used as a matrix itself or as a reinforcing material with other polymer matrices (Retegi et al., 2012; Yano et al., 2005).

Here, BC-PAN composite monolith has been made by introducing BC gel into PAN monolith and used as a precursor of new activated carbon monolith, BC-PAN-AC with a network of co-continuous porous structure. A simple and versatile method involving a combination of thermally induced phase separation and solvent substitution is used to prepare the composite monoliths. The composite differs from conventional BC or PAN polymer composites and exhibits interesting morphological features. While the horizontal cross-section shows three-dimensional network, the vertical cross-section suggests a layered structure. This feature is retained in BC-PAN-AC obtained by oxidative pretreatment and carbonization of the composite. Application of BC-PAN-AC as EDLC electrode material and the influence of the unique structure on the performance of the electrode have been studied (Shu, Maruyama, Iwasaki, Shen, & Uyama, 2017). The material performs very well without the addition of any conductive agent which is its uniqueness and advantage. To the best of our knowledge, this is the first report on the role of BC nanofibers in determining the morphology and shape of activated carbon particles to reduce its grain boundary impedance and hence enhance conductivity.

2. Experimental section

2.1. Materials and physical measurement

For bacterial culture polypeptone, yeast extract and D- mannitol are purchased from Wako Chemicals; glucose from MP Biomedicals, Inc. and *Gluconacetobacter xylinus* (NBRC 13,693) is purchased from National Institute of Technology and Evaluation, Japan. PAN copolymer has been procured from Mitsubishi Rayon. Magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$), sodium hydroxide (NaOH), and acetic acid are purchased from Wako Chemicals and used without further purification. The solvents are also used as-purchased. For preparation of electrodes, fine powder of polytetrafluoroethylene (PTFE) to be used as a binder and conductive auxiliary agent, acetylene black (AB) are procured from Mitsui Du Pont Fluorochemicals and Strem Chemicals, respectively. One mol/L aqueous sulfuric acid (H_2SO_4) and deionized water are purchased from Wako Pure Chemical Industries, Ltd.

The molecular structure of the samples are studied by Fourier transform-infrared (FT-IR) spectroscopy by attenuated total reflectance (ATR) method using Spectrum One FT-IR spectrometer, PerkinElmer, USA. CHN elemental analyses of the samples are carried out with a CHN Corder MT-5, Yanaco Co. Ltd., Japan. Nitrogen adsorption/desorption isotherms of the samples at liquid nitrogen temperature are measured using a surface area and pore size analyzer instrument, Nova 4200e, Quantachrome, USA. Before carrying out the analyses, the samples are activated or degassed by heating under vacuum. The specific surface areas are determined by Brunauer-Emmett-Teller (BET) multipoint method and pore-size distribution by Quenched Solid State Density

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