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High-Performance Supercapacitor of Functionalized Carbon Fiber Paper with High Surface Ionic and Bulk Electronic Conductivity: Effect of Organic Functional Groups

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ABSTRACT

Although carbon fiber paper (CFP) or nonwovens are widely used as a non-corrosive and conductive substrate or current collector in batteries and supercapacitors as well as a gas diffusion layer in proton exchange membrane fuel cells, the CFP cannot store charges due to its poor ionic conductivity and its hydrophobic surface. In this work, the chemically functionalized CFP (f-CFP) consisting of hydroxyl and carboxylic groups on its surface was produced by an oxidation reaction of CFP in a mixed concentrated acid solution of H_2SO_4:HNO_3 (3:1 v/v) at 60 °C for 1 h. Other amide and amine groups modified CFP were also synthesized for comparison using a dehydration reaction of carboxylic modified CFP with ethylenediamine and n-butylamine. Interestingly, it was found that hydroxyl and carboxylic groups modified CFP behave as a pseudocapacitor electrode, which can store charges via the surface redox reaction in addition to electrochemical double layer capacitance. The aqueous-based supercapacitor of f-CFP has high areal, volumetric, and specific energy (49.0 μW.h/cm^2, 1960 mW.h/L, and 5.2 W.h/Kg) and power (3.0 mW/cm^2, 120 W/L, and 326.2 W/Kg) based on the total geometrical surface area and volume as well as the total weight of positive and negative electrodes. High charge capacity of the f-CFP stems from high ionic charge and pseudocapacitive behavior due to hydroxyl and carboxylic groups on its surface and high bulk electronic conductivity (2.03 mS/cm) due to 1D carbon fiber paper. The acid treatment process here could be used to improve the charge storage capacity of other carbonaceous materials such as carbon nanotubes.

1. Introduction

Supercapacitors are very attractive energy storage devices because they have higher power density than batteries and higher energy density than capacitors. They are used in many applications such as hybrid electric vehicles, public transportation buses, and portable electronic devices [1,2]. Supercapacitors can be classified by their charge storage mechanisms including electrochemical double layer capacitors (EDLCs) and pseudocapacitors [1]. EDLCs are based on a physical adsorption at an interface of solid electrode and liquid electrolyte. Carbon materials (i.e., carbon aerogel, carbon hydrogel, activated carbon, carbon nanotubes, reduced graphene oxide (rGO), and graphene) are typically used as active materials in EDLCs due to their high surface area and porosity as well as structural stability [3,4]. In addition to the physical adsorption, pseudocapacitors can store electronic charges via a fast redox reaction at the active surface area of the electrode. In general, metal oxide and conducting polymer are used as the active electrode materials in pseudocapacitors [5,6]. A major advantage of carbon-based EDLCs over the pseudocapacitors is their higher cycling stability up to >100,000 cycles. However, its capacitance is significantly lower than that of pseudocapacitors. A challenge in

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the development of EDLCs is about how to improve the specific capacitance and specific energy of EDLCs by keeping their high cycling stability and high specific power [7,8].

In addition to the active materials used in the supercapacitors, the current collectors e.g., Ni foam, Ti foam, Al foil, Cu foil, carbon fiber paper (CFP), carbon cloth, which are conductive materials, are so important for electronic charge transfer. Metal current collectors can however contribute the heavy weight to the whole device. More importantly, the stability of the metal current collectors are rather poor when used in aqueous-based super-capacitors since the corrosion of metal with anions of the electrolytes (e.g., NO_3^-, Cl^-, SO_4^{2-}) spontaneously occurs limiting the practical use of the aqueous-based supercapacitors. In fact, the diffusion of the electrolyte in water is much faster than that in organic solvents leading to higher areal and specific power.

On the other hand, carbon-based current collector such as CFP is rather stable in all electrolytes [9–13]. CFP has many advantages suitably to be used as the conductive substrate or current collector including high flexibility, corrosive resistance, porosity, and con-ductivity. However, CFP consisting of sp^2 carbon fiber (90–95 wt.%) and adhesive material PTFE (5–10 wt.%) can be used only as a conductive current collector since it cannot store charge and its hydrophobic surface in nature, which cannot adsorb/absorb the aqueous electrolyte. CFP is therefore used as the conductive substrate and/or current collectors of the supercapacitors and fuel cells [9–13].

In this work, the chemical surface functionalization of CFP (f-CFP) was finely tuned using a mixed acid treatment by keeping high bulk conductivity of the CFP. f-CFP mainly consisting of hydroxyl (-OH) and carboxyl (-COOH) on the surface of CFP was then chemically changed to the amide and amine functionalized CFP to investigate the effect of organic functional groups. Interestingly, it is found that oxygen containing groups on the f-CFP surface can introduce the pseudocapacitance due to a surface redox reaction at a solid-liquid interface. This finding could provide a new function of the CFP as an active electrode material of the supercapacitor. The as-fabricated supercapacitor exhibits high charge storage performance and stability. Eight supercapacitors of the f-CFP in a coin cell size (CR2016) connected in parallel can supply electricity to a spinning motor (RF-300CA-11400, Mabuchi Motor Co., Ltd. Japan) with a nominal voltage of 3 V over 355 s.

2. Experimental

2.1. Acid treatment of CFP

CFP (SGL CARBON SE, Germany) consisting of 95 wt.% graphitized carbon content and 5 wt.% PTFE adhesive binder with an areal weight of ca. 85 g/m^2, a thickness of 250 μm, 88% porosity, and an electrical resistance of <12 mΩ.cm was immersed in mixture of concentrated sulfuric acid (H_2SO_4 98%, QRec) and concentrated nitric acid (HNO_3 65%, QRec) with different volume ratios of H_2SO_4: HNO_3 of 1:0, 1:1, 2:1, 3:1, 4:1, and 0: 1. The acid treatment temperature and time were also varied to find the optimum conditions. After that, treated CFP was washed by ultrapure water until the pH of washed water equal to 7 and then the treated sample was dried at 60 °C for 24 h and characterized by microscopies and spectroscopies.

2.2. Amide and amine functionalization of CFP

After the acid treatment of CFP, oxygen containing groups functionalized CFP (f-CFP) was obtained, which was then used as a precursor to prepare amide functionalized CFP (CFP-$CONHCH_2CH_2NH_2$). f-CFP was stirred in ethylenediamine (EDA, Chemie 98.0–101.0% LOBA Chemie) or n-butylamine (BTM, 99.0%

LOBA Chemie) at 70 °C for 3 h. Finally, f-CFP (EDA) or f-CFP(BTM) was washed by ultrapure water until pH 7.

2.3. Fabrication of symmetric supercapacitors in a coin cell (CR2016)

The symmetric supercapacitor was assembled using a 2016- type coin cell. The functionalized CFP samples were cut in diameter of 1.58 cm with a geometrical area of 1.96 cm^2 or a geometrical volume of 0.049 cm^3. The positive and negative electrodes consist of the same electrode materials. Cellulose paper was soaked by 1 M H_2SO_4 for 10 min and inserted between the electrodes as an electrolyte separator.

2.4. Characterizations

The morphology of the samples was characterized by field-emission scanning electron microscopy (FE-SEM). Nitrogen adsorp-tion/desorption isotherm was measured by a Brunauer-Emmett-Teller (BET) method. The surface characterization was analyzed by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) (AXIS Ultra DLD, Kratos Analytical Ltd., Manchester, UK) and static contact angle measurement. The chemical structure was analyzed by Fourier transform infrared spectroscopy (FTIR). Thermal behavior was studied by thermal gravimetric analyzer (TGA) in nitrogen atmo-sphere with heating rate 5 °C/min from 25 °C to 800 °C. Electrochem-ical property was measured by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectros-copy (EIS) with a Metrohm AUTOLAB potentiostat (PGSTAT 302 N) made in Netherlands running NOVA (version 1.10.3) software. The platinum wire and the Ag/AgCl were used as the counter and the reference electrode, respectively for the half cell testing. The areal capacitance of a single f-CFP electrode carried out from CV in a three electrode system can be calculated from Eq. (1) [14];

$$C_S = \frac{Q}{\Delta V \times S} \tag{1}$$

where C_s is an areal capacitance (mF/cm^2), Q is an average charge in the discharge process (Coulomb, C), ΔV is a potential working window (V), and S is a geometrical surface area of f-CFP electrode (cm^2). It is necessary to note here that choosing the potential window in a safety zone without gas evolution at high anodic and cathodic voltages is rather important for long cycle life of the supercapacitor.

The areal capacitance of the single f-CFP electrode also determined using the GCD measurement can be calculated from Eq. (2) [14]

$$C_S = \frac{I \times \Delta t}{\Delta V \times S} \tag{2}$$

where I is the applied constant current (A), Δt is the discharging time (s), and ΔV is the potential window (V) excluding iR drop for which the iR drop increases when increasing the charge/discharge rate. Note that the volumetric capacitance (F/cm^3) of the f-CFP electrode can also be calculated by replacing the geometrical surface area with the geometrical volume of f-CFP used.

On the other hand, the areal capacitance of the supercapacitor device (C_{cell}) consisting of two f-CFP electrodes (positive and negative electrodes) in series with an electrolyte absorbed cellulose separator in the middle of such two electrodes can be investigated by the CV, GCD, EIS, and power discharge (Ragone) techniques. As the two electrodes connected in series, C_{cell} is equal to the following Eq. (3);

$$C_{cell} = \frac{I \times \Delta t_{cell}}{\Delta V_{cell} \times S_{cell}} \tag{3}$$