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Oxygen group-containing activated carbon aerogel as an electrode material for supercapacitor

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ABSTRACT

Carbon aerogel was prepared by a sol–gel polymerization of resorcinol–formaldehyde (RF) method, and it was activated with CO_2 to obtain activated carbon aerogel (ACA). A series of modified activated carbon aerogels (MACA-*X*, *X* = 3, 6, 9, and 12 h) were then prepared by HNO_3 oxidation of ACA with a variation of oxidation time (*X*) in order to investigate the effect of surface oxygen group on their electrochemical performance as supercapacitor electrode material. Electrochemical properties of ACA and MACA-*X* were measured by cyclic voltammetry, galvanostatic charge/discharge, and EIS (electrochemical impedance spectroscopy) measurements. Among the samples, MACA-6 h showed the best rate capability and the highest specific capacitance. Thus, an optimal HNO_3 oxidation condition was required for the highest supercapacitive electrochemical performance of modified activated carbon aerogel.

1. Introduction

During a few decades, supercapacitors have attracted much attention as an electrochemical energy storage device due to their unique properties such as long life cycle, rapid storage, and lossless release of energy [1,2]. Generally, supercapacitors can be classified into two categories according to the energy storage mechanism; electrochemical double-layer capacitors (EDLCs) and pseudocapacitors. In case of electrochemical double-layer capacitors, electronic and ionic charges are accumulated at the interface between electrode material and electrolyte [3,4]. In pseudocapacitors, on the other hand, electric energy is generated by fast and reversible faradaic redox reactions induced by electro-active species on the surface of the electrode [5,6]. Therefore, various materials ranging from porous carbons for EDLCs to oxygen- and nitrogen-containing surface functional groups, metal oxides, and conducting polymers for pseudocapacitors have been investigated as electrode materials for supercapacitors [7–10].

Carbon aerogels have been recognized as promising electrode materials because of their outstanding electrical conductivity and textural property [11]. These excellent properties of carbon aerogels are due to three-dimensional mesoporous network of carbon nanoparticles [12,13]. However, carbon aerogels not only have lower surface area for EDL than activated carbon but also show limited power density and energy capacity. To overcome these problems, various activation methods of carbon aerogels have been investigated. Activation of carbon aerogel with KOH and CO_2 increases surface area and micropore volume [14,15]. However, the large amount of micropores in activated carbon causes high internal resistance. In addition, hydrophobic property of activated carbon also decreases wettability of electrode in aqueous electrolyte solution, resulting in suppressed electrolyte accessibility and high internal resistance [16,17]. To overcome these drawbacks, various modification methods of activated carbon surface chemistry have been investigated [18,19]. It is known that the existence of surface oxygen group on carbon surface not only provides pseudocapacitive reactions for specific capacitance but also improves affinity of carbon electrode to aqueous electrolyte for rate capability [20,21].

In this work, a series of modified activated carbon aerogels were prepared to improve electrochemical performance of activated carbon aerogel (ACA). For this purpose, carbon aeroge
l was prepared by a sol–gel polymerization of RF (resorcinol–formaldehyde) and it was activated with CO_2. A series of modified activated carbon aerogels (MACA-*X*, *X* = 3, 6, 9, and 12 h) were then prepared by HNO_3 oxidation of activated carbon aerogel (ACA)

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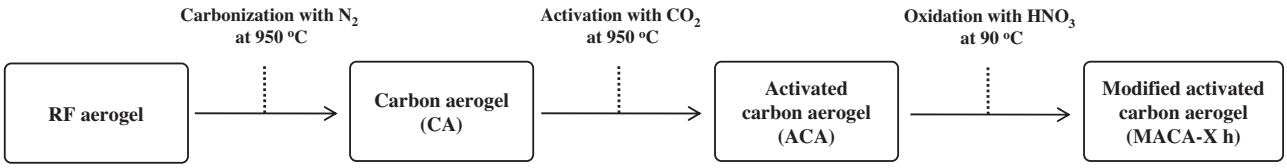

Fig. 1. Preparation procedures for modified activated carbon aerogel.

with a variation of oxidation time (*X*). For comparison, activated carbon aerogel (ACA) without HNO_3 oxidation was also examined. Through this work, we have demonstrated that surface oxygen group played an important role in determining supercapacitive electrochemical performance of modified activated carbon aerogel. We have also found that an optimal HNO_3 oxidation condition was required for the best electrochemical performance of modified activated carbon aerogel.

2. Experimental

2.1. Preparation of activated carbon aerogel (ACA)

Carbon aerogel (CA) was prepared by a sol–gel polymerization of resorcinol and formaldehyde according to the method in our previous work [22]. Activated carbon aerogel was then prepared by CO_2 activation. In short, RF (resorcinol–formaldehyde) aerogel (4 g) was carbonized at 950 °C for 1 h under N_2 stream (30 ml/min) to obtain carbon aerogel. The carbon aerogel (2 g) was then activated at 950 °C for 1 h using CO_2 stream (30 ml/min). The prepared activated carbon aerogel was denoted as ACA.

2.2. Preparation of modified activated carbon aerogels (MACA)

Modified activated carbon aerogels were prepared by chemical oxidation of ACA with HNO_3 solution. Fig. 1 shows the preparation procedures for modified activated carbon aerogel. The activated carbon aerogel (ACA) powder (0.5 g) was stirred in 100 ml of concentrated 5 M HNO_3 solution and refluxed at 90 °C with a variation of oxidation time. After oxidation, it was filtered and washed with deionized water to remove residual HNO_3 from the sample. The resulting material was then dried at 100 °C for 12 h. The modified activated carbon aerogels were denoted as MACA-*X* (*X* = 3, 6, 9, and 12 h), where *X* represented HNO_3 oxidation time.

2.3. Preparation of ACA and MACA-X electrodes

MACA-*X* was casted using Super PTM conductive carbon (Timcal) and polytetrafluoroethylene (PTFE) as a conductive additive and a binder, respectively. A mixture of modified activated carbon aerogel, conductive additive, and binder with weight ratio of 8:1:1 was dispersed in 2-propanol. The resultant was mixed with mortar and pestle, and then it was rolled to be 8–10 μm thickness. The active material was cut into 1 cm × 1 cm and pressed onto nickel foam, which was used as an electrode. Weight of the electrode was ca. 2.5 mg. For comparison, activated carbon aerogel (ACA) electrode was also prepared by the same method described above.

2.4. Measurement of electrochemical properties of ACA and MACA-X electrodes

Electrochemical properties of ACA and MACA-*X* were measured with a two-electrode cell system in 6 M KOH aqueous electrolyte. Cyclic voltammetry, galvanostatic charge/discharge, and electrochemical impedance spectroscopy measurements were carried out to investigate the electrochemical properties of the samples. The cyclic voltammetry measurements were carried out within potential range of −1.0 to −0.2 V by varying scan rate from 10 to 200 mV/s. Galvanostatic charge/discharge measurements were carried out at constant current of 1 A/g and 5 A/g within potential range of −1.0 to 0 V. EIS (electrochemical impedance spectroscopy) measurements were also carried out within frequency range from 100 kHz to 0.01 Hz at open circuit potential with an ac perturbation of 5 mV.

2.5. Characterization

N_2 adsorption–desorption isotherms were measured with an ASAP 2010 (Micromeritics) instrument and surface areas were derived from Brunaur–Emmett–Teller (BET) method [23]. Pore volume was determined by the Barrett–Joyner–Halenda (BJH) method applied to the desorption branch of the N_2 isotherm [24]. Surface morphologies of ACA and MACA-*X* were examined by transmission electron microscopy (TEM) (Jeol, JEM-2100). FT-IR analyses (Nicolet, Nicolet 6700) of ACA and MACA-*X* were performed to analyze oxygen-containing functional group. Oxygen contents of ACA and MACA-*X* were quantitatively determined by CHN elemental analyses (CHN 932, Leco).

2.6. Calculation

At cyclic voltammetry measurements, specific capacitances of the electrodes were calculated according to the following equation. Where I_a and I_c represent anodic current and cathodic current, respectively. *W* is weight of electrode material and d*V*/d*t* represents scan rate.

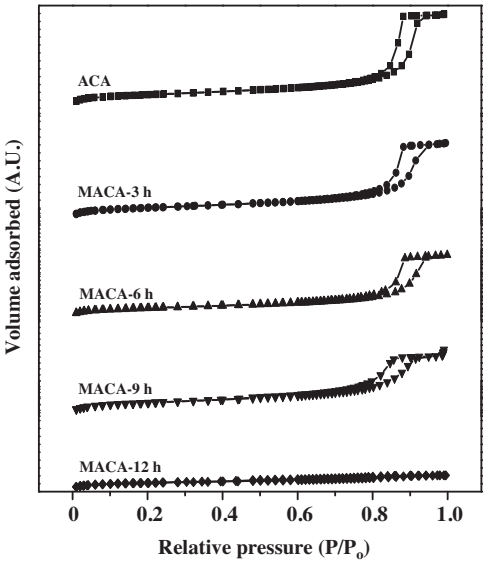

Fig. 2. N_2 adsorption–desorption isotherms of ACA and MACA-*X* (*X* = 3, 6, 9, and 12 h).