

## Fluorinated activated carbon with superb kinetics for the supercapacitor application in nonaqueous electrolyte

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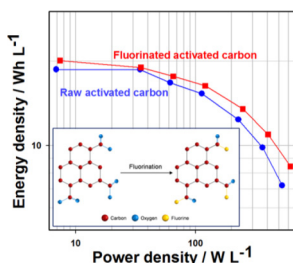
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### HIGHLIGHTS

- Fluorinated activated carbon (AC) is prepared by hydrofluoric acid treatment.
- The bonding between fluorine and carbon increases its electrical conductivity.
- Due to this ionic bonding, fluorinated AC shows an enhanced specific capacitance.

### GRAPHICAL ABSTRACT

Fluorinated activated carbon exhibits significantly improved electrochemical capacitive performance with kinetic enhancement compared to raw activated carbon. This indicates that F-AC tends to form the electric double-layer ions on its surface rapidly as a result of the increased electrical conductivity attributed to the ionic-bonding character between fluorine and activated carbon.



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### ABSTRACT

Fluorinated activated carbon (F-AC) exhibits significantly improved electrochemical capacitive performance compared to raw activated carbon (R-AC). F-AC electrode shows a specific capacitance coming up to  $19.8 \text{ F cm}^{-3}$ , whereas the capacitance of R-AC electrode is  $18.4 \text{ F cm}^{-3}$ . Besides, the kinetic enhancement of F-AC is also memorable. This phenomenon indicates that F-AC tends to form electric double-layer ions on its surface more rapidly than does R-AC. This formation is a result of the increased electrical conductivity attributed to the semi-ionic bonding character between fluorine and activated carbon. The electrochemical improvement of F-AC proves that fluorination is a very effective method for providing greater possibilities for supercapacitor applications of AC in nonaqueous electrolytes.

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## 1. Introduction

Supercapacitors are promising energy-storage devices with high power density, extreme reversibility, long cycle life, and low environmental harm [1–3]. Activated carbon (AC) has been considered as the most suitable electrode material for supercapacitors because of its large specific surface area, commercial availability, and low cost. However, the energy density stored in

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AC supercapacitors is too low to meet the energy density required for novel applications such as hybrid electric vehicles and so on [4–7]. Therefore, various attempts have been made to improve the electrochemical performance of AC for its supercapacitor applications. For this purpose, AC has been doped with heteroatom, and thereafter applied for the supercapacitors in aqueous electrolyte [8–18]. In aqueous supercapacitor, heteroatom doping significantly increases the specific capacitance of AC by evolving pseudocapacitance in addition to electric double-layer capacitance. However, the small voltage window of aqueous electrolytes is a significant obstacle in increasing the energy density of AC because it is easily decomposed at high potentials. Additionally, the oxidation or reduction of electrolyte tends to keep the cycling of AC pseudocapacitors unstable [1]. Hence, there has been a sincere need for the investigation on heteroatom-doped AC in nonaqueous electrolytes toward improving the energy density of AC supercapacitors.

Herein, we report the effects of fluorine doping on AC from a structural or electrochemical viewpoint. For the synthesis of fluorine-doped AC, hydrofluoric acid has been reduced on AC and then microwave treatment was conducted to avoid the gas evolution of fluorine-doped AC during cycling in nonaqueous electrolyte. Fluorinated AC (F-AC) exhibits significantly improved electrochemical capacitive performance compared with raw AC (R-AC) because of its enhanced electrical conductivity attributed to the semi-ionic bonding character between fluorine and AC. The structure and electrochemical properties of F-AC will be discussed in comparison with the bare one.

## 2. Experimental

### 2.1. Synthesis of materials

Fluorinated activated carbon (F-AC) was prepared using commercial activated carbon (MSP20, Kansai Coke & Chemicals Company, Ltd., Japan) as the carbon source and hydrofluoric acid (J.T. Baker, USA) as the fluorine source. F-AC was prepared by stirring R-AC (commercial AC MSP20) and 1.0 M hydrofluoric acid solution for 18 h at room temperature. Thereafter, F-AC was separated by filtration, and then dried for 24 h at 120 °C. The dried F-AC was treated by microwave heating to remove functional groups on its surface. The microwave irradiation was conducted at 400 W and 2450 MHz for 20 s in Ar atmosphere.

### 2.2. Characterization

The pore structure of the samples was analyzed by the Brunauer–Emmett–Teller (BET) method using a BELsorp-minill (BEL Japan, Inc.). The samples were outgassed at 140 °C for 18 h under vacuum prior to the gas adsorption measurements. In order to investigate the structure of the samples, X-ray diffraction (XRD, D/Max 2500/PC, Rigaku, Japan) was carried out. The atomic concentrations of carbon, oxygen, and fluorine were determined by X-ray photoelectron spectroscopy (XPS) at  $1.1 \times 10^{-7}$  Pa, using a PHI 5000 VersaProbe with Al K $\alpha$  radiation (ULVAC-PHI, Inc., Japan). Raman spectroscopy was conducted using a LabRam HR (Horiba Jobin Yvon, French) with an Ar-ion laser at 514.5 nm. XPS and Raman spectra results were fitted using a mixed Gaussian–Lorentzian curve to determine the peak intensities and shifts [19,20]. Electrical conductivity of the samples in a Teflon cylinder cell filled with the powder was measured using a current–voltage ( $I$ – $V$ ) source. Herein, 20 mm-diameter electrodes were used as probes, and the conductivities of the samples were calculated from the slope of  $I$ – $V$  curves because  $I$ – $V$  characteristics were ohmic in the measured voltage range (from 0 to 5 mV) [21–23].

### 2.3. Electrochemical measurements

Rubber-type electrodes were made using polytetrafluoroethylene (PTFE, D-60, Daikin Industries, Japan) as a binder and Super-P black (MMM Carbon Co., Belgium) as a conducting agent. The electrode was composed of 90 wt% active material, 5 wt% conducting material, and 5 wt% binder. The electrochemical tests were carried out using a coin-type cell (CR-2032) in which the electrolyte was composed of 1.8 M triethylmethylammonium tetrafluoroborate in acetonitrile. The cyclic voltammetry (CV) tests were conducted from 0 to 2.7 V using a VSP potentiostat (Biologic, France). Electrochemical impedance spectroscopy (EIS) was carried out using a beaker-type three-electrode cell in the frequency range of 100 kHz to 100 MHz. In this procedure, the reference electrode (Ag/Ag<sup>+</sup>) was inserted between two identical electrodes. All electrochemical tests were carried out at room temperature.

Volumetric specific capacitances ( $C_s$ ) were calculated from the CV curves according to the following equation:

$$C_s = \frac{\int I dV}{\nu \Delta V W}$$

where  $I$  is the response current,  $\Delta V$  is the potential window (V),  $\nu$  is the potential scan rate ( $V s^{-1}$ ), and  $W$  is the volume of two electrodes. Energy and power densities were calculated using the following formulas:

$$E = \frac{C_s (\Delta V)^2}{2}, \quad P = \frac{E}{t}$$

where  $E$  is the specific energy density ( $Wh L^{-1}$ ),  $P$  is the specific power density ( $W L^{-1}$ ), and  $t$  is the discharging time (s) [15].

## 3. Results and discussion

The N<sub>2</sub> adsorption/desorption isotherms presented in Fig. S1 shows that the specific surface areas of R-AC and F-AC are 2379 and 2312 m<sup>2</sup> g<sup>-1</sup>, respectively. The micropore and mesopore volumes were calculated according to the MP-plot and Barrett–Joyner–Halenda (BJH) methods, respectively. The micropore size distribution analysis based on the MP-plot method is shown in Fig. S1. All of the samples were microporous, suggesting that fluorination process was not accompanied by any destruction of the porous structure of R-AC.

To investigate in detail the effect of fluorine doping on the structure of AC, XPS and Raman analyses were performed. The XPS wide-scan spectra of R-AC and F-AC are shown in Fig. 1.

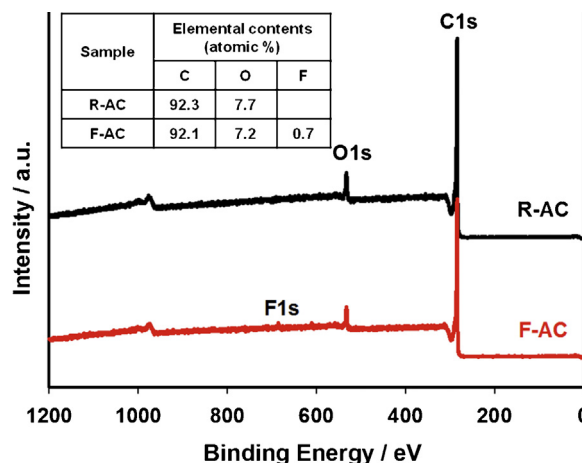


Fig. 1. XPS wide-scan spectra and elemental analysis results (inset) of raw activated carbon (R-AC) and fluorinated activated carbon (F-AC).

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