

The 65th special feature "Fluorine Chemistry and Materials for Electrochemistry"

Deoxofluorination of Activated Carbon Electrode with Sulfur Tetrafluoride for Electric Double Layer Capacitor

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ABSTRACT

Electric double layer capacitors are energy storage devices with advantages of fast charge-discharge and long life span. Surface modification of activated carbon electrodes is an effective way to improve their performance. For this purpose, deoxofluorination of activated carbon with sulfur tetrafluoride was attempted in this study. Successful introduction of fluorine atom on the surface of activated carbon resulted in the increased capacitance and improved coulombic efficiencies in electrochemical tests for electric double layer capacitors.

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Keywords : EDLC, Activated Carbon, Deoxofluorination, Sulfur Tetrafluoride

1. Introduction

Electrochemical capacitors are energy storage devices with advantages of fast charge-discharge properties and long life span in contrast to secondary batteries.^{1–3} High capacitance and improvement of cycle performance is required to widen their application field. Out of various electrode materials,^{4–8} the most common and widely used one is activated carbon (AC), which has large surface area, high mechanical stability, and low cost,^{9–11} and is suitable for electric double layer capacitors (EDLCs) storing energy at the electrode surface based on adsorption of ions. The surface of AC is typically covered with oxygen-containing functional groups such as hydroxy, epoxy, and carbonyl groups, and their low resistance against oxidation often limits the operating voltage. Therefore, modification of such functional groups has been a matter of discussion to achieve high-performance operation.

There are a number of reports on surface-modification for porous carbon materials, which affects EDLC-related properties such as wettability, capacitance, and cyclability.^{11–17} Functionalization by fluorination was also reported using different fluorination techniques by elemental fluorine, hydrofluoric acid, and ammonium fluoride, resulting in change of surface morphology and increase in capacitance.^{18–22} Fluorination is also expected to improve the oxidation resistance because it can reduce HOMO energy level. However, high oxidation power of elemental fluorine could worsen the performance by the introduction of too much F atom in the bulk along with destructing the carbon skeleton. Difficulty in optimization of its reaction conditions is also problematic for the use of elemental fluorine.¹⁸ For fluorinating agents without strong oxidation power, on the other hand, not sufficient examples and discussion have been reported so far, and exploration of new fluorinating agents is required.^{19–21} In the present study, sulfur tetrafluoride (SF₄) is used for this purpose, focusing improvement of oxidative resistance. It has a deoxofluorination (substitution of oxygen-containing functional groups with F atom) ability with a weak oxidation power, and is widely established especially in organic chemistry.²³ Successful introduction of F atom into carbon materials by the use of SF₄ was also reported for a few cases such

as graphite oxide and graphene oxide.^{24,25} Although there was a report about reactions of AC with SF₄, it did not focus on electrochemical performance but water adsorption properties and surface acidity.²⁶ Sulfur tetrafluoride is expected to deoxofluorinate only the oxygen-containing functional groups on the AC surface without destructing the carbon skeleton, and its effect on EDLC performance, especially on oxidation resistance, is an interesting topic to be investigated.

2. Experimental

Volatile materials were handled in a reaction manifold made of 316 stainless steel and tetrafluoroethylene-perfluoroalkylvinylether copolymer (PFA).²⁷ Nonvolatile materials were handled under dry Ar atmosphere in a glove box. Sulfur tetrafluoride was synthesized according to the previous works.^{23,28} A sheet of a mixture (0.2 mm in thickness, 85 wt% of activated carbon (AC, surface area: 2050 m² g^{−1}, mean pore diameter: 2.14 nm, and total pore volume: 1.10 cm³ g^{−1}, 10 wt% of polytetrafluoroethylene as a binder, and 5 wt% of carbon black as a conductive additive) was used for electrochemical measurements after drying under vacuum at 150 °C for 1 day. Silver trifluoromethanesulfonate (Ag[TfO], FUJIFILM Wako Pure Chemical Corporation, purity > 97%) for reference electrode (R.E.) was dried at 80 °C for 1 day under vacuum. A solution of 1 mol dm^{−3} [TEA][BF₄]/PC ([TEA][BF₄]: tetraethylammonium tetrafluoroborate, PC: propylene carbonate, Kishida Chemical Co., Ltd., CPG-00005, water content < 10 ppm) was used as an electrolyte.

Activated carbon (powder and sheet) was treated with 1.0 atm of SF₄ in a PFA reactor (typically 100 cm³ in volume) and with 5.0 atm of SF₄ in a Ni reactor (100 mL in volume) at 25 °C for 3 h. The products obtained by reactions of 1.0 atm and 5.0 atm of SF₄ are denoted as F1-AC and F5-AC, respectively.

X-ray photoelectron spectra (XPS) were obtained with a JPS-9030 MC spectrometer (JEOL, Ltd., MgK α radiation). Samples were placed on indium foil and introduced into the equipment using an airtight cell to avoid the exposure to air. Elemental analysis of bulk samples was performed at the Elemental Analysis Center at the

Institute for Chemical Research, Kyoto University (combustion analysis and ion chromatography).

Electrochemical measurements were performed using a three-electrode beaker cell with the aid of a VSP electrochemical measurement system (Bio-Logic Sciences Instruments Ltd.). The AC sheet was punched into disks into 6 mm in diameter (surface area: 0.283 cm² on one-side) as working electrodes (W.E.) and into 16 mm in diameter (surface area: 2.01 cm² on one-side) as counter electrodes (C.E.). The pristine or deoxofluorinated AC sheet was pressed on Al mesh for W.E. and immersed in the electrolyte overnight for impregnation and purification. Two pristine AC sheets with a diameter of 16 mm were pressed on Al mesh (both sides) for C.E. Electrode potential was referenced to the Ag⁺/Ag redox couple. The reference electrode was made of Ag wire immersed in the electrolyte (1 mol dm⁻³ [TEA][BF₄]/PC) containing 0.01 mol dm⁻³ of Ag[TfO] and was separated from the electrolyte by a porous glass frit (RE-6, EC Frontier Co., Ltd.). Charge-discharge tests were performed with a lower cutoff potential of 0.0 V and upper cutoff potentials varying from 0.5 to 1.5 V at intervals of 0.1 V. Positive and negative polarizations are defined as charge and discharge, respectively, in this study. The cell was charged and discharged for 10 cycles for each upper cutoff potential consecutively at a constant current density of 235 mA (g-AC)⁻¹. Capacitance was calculated based on the slopes of the discharge curve.

3. Results and Discussion

Figure 1 shows C1s and F1s XPS of AC before and after reacting with 1.0 or 5.0 atm of SF₄ at 25 °C for 3 h. In the C1s spectra (Fig. 1a), there is a peak at 284.3 eV corresponding to the C–C bonds for AC, F1-AC, and F5-AC.^{19,20,22,26} Although this peak has a weak shoulder at the high energy region corresponding to oxygen-containing functional groups, clear differences are not observed in any cases. On the other hand, the F1s region (Fig. 1b) of F1-AC and F5-AC has a peak at 686.1 eV in contrast to the pristine AC, which confirms the introduction of fluorine by the reactions with SF₄. Table 1 lists the chemical composition and F/C and O/C atomic ratios on the surface of the samples based on the peak area obtained by XPS. These results indicate that increase in SF₄ pressure causes a higher degree of deoxofluorination; the F/C ratio increases and the O/C ratio decreases with increasing SF₄ pressure. Whereas XPS provides chemical compositions on the surface, combustion analysis shown in Table 1 provides information of the bulk. The F/C ratio on the surface is larger than that of the bulk, suggesting successful deoxofluorination of surface oxygen-containing functional groups without destructing carbon skeleton. Although surface modification was tried to confirm by infrared spectroscopy, there was no noticeable difference in the obtained spectra before and after the treatment by SF₄.

Effects of deoxofluorination of AC with SF₄ on the electrochemical performance were investigated by galvanostatic charge-discharge tests. Figure 2a shows charge-discharge curves of AC, F1-AC, and F5-AC at the 10th cycle of the different cutoff potentials (0.0–0.5 V, 0.0–1.0 V, and 0.0–1.5 V vs. Ag⁺/Ag). These charge-discharge curves show typical shapes of an AC electrode in EDLCs. Figure 2b shows the resulting capacitances of the discharge process. The capacitances obtained for F1-AC and F5-AC are larger than that of AC in the high cutoff potential range and the entire cutoff range, respectively, and deoxofluorination with SF₄ effectively increases capacitances of the AC electrodes. Figure 2c shows the calculated coulombic efficiencies during cycling, which suggests that coulombic efficiencies are also improved by deoxofluorination in the entire range for F5-AC and in the high cutoff potential range for F1-AC. Although the relatively low coulombic efficiencies observed are due to small cycle numbers and are expected to be improved by longer cycling.

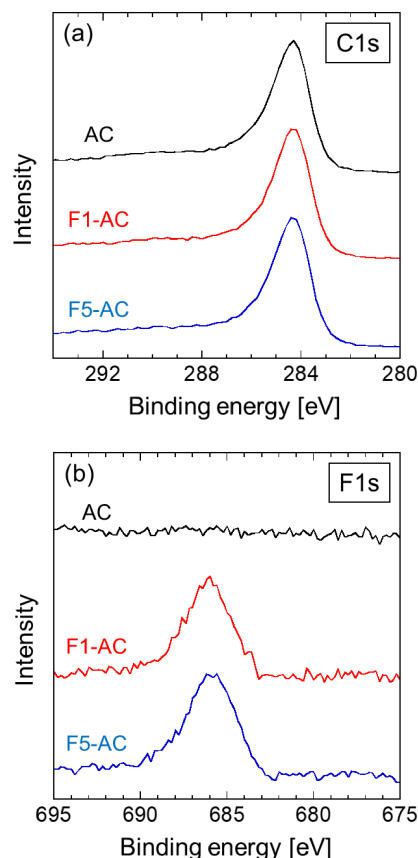


Figure 1. XPS of AC before and after reacting with 1.0 atm and 5.0 atm of SF₄ at 25 °C for 3 h in the (a) C1s and (b) F1s regions.

Table 1. Chemical compositions of AC, F1-AC, and F5-AC obtained by XPS and combustion analysis.

Samples	XPS for surface				
	Elements [at%]			Atomic ratios	
	C	F	O	F/C	O/C
AC	95.8	—	4.2	—	0.044
F1-AC	93.3	4.4	2.3	0.047	0.025
F5-AC	91.8	6.2	2.0	0.067	0.022
Samples	Combustion analysis for bulk				
	Elements [wt%]			Atomic ratio	
	C	F	H	F/C	
AC	94.3	0	0.7	—	
F1-AC	90.0	2.1	0.6	0.015	
F5-AC	89.2	2.4	0.6	0.017	

4. Conclusions

Surface modification of AC is an effective way to improve electrode performance in EDLCs. In the present study, deoxofluorination of AC with SF₄ and its effects on the electrochemical performance as an electrode material for EDLCs were investigated. The XPS analysis confirmed introduction of F atom and decrease of oxygen-containing functional groups by the SF₄ treatment, and higher pressure of SF₄ was more effective for this purpose. Comparison of elemental analysis by XPS and combustion methods revealed that F atom was selectively introduced to the surface

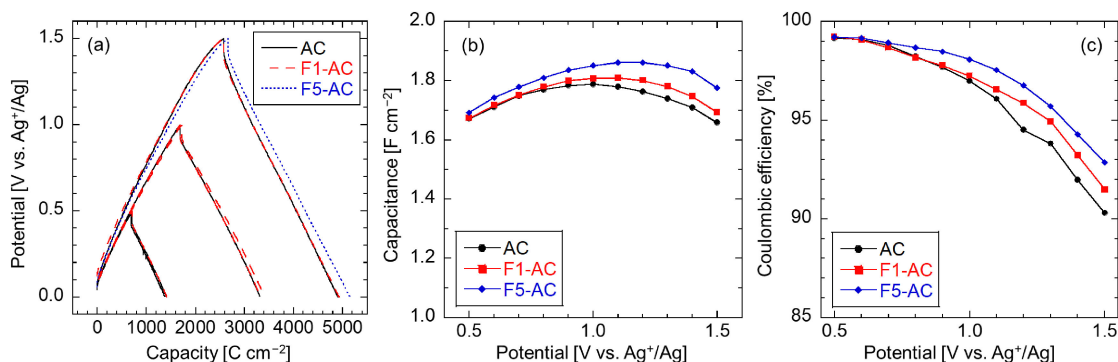


Figure 2. (a) Charge-discharge curves and potential dependence of (b) capacitance and (c) coulombic efficiencies for AC, F1-AC, and F5-AC at the 10th cycle in the cutoff range of 0.0–0.5 V, 0.0–1.0 V, and 0.0–1.5 V vs. Ag⁺/Ag.

compared to the bulk, suggesting that the reaction proceeded mainly involving deoxofluorination of oxygen-containing functional groups on the surface of AC. Charge-discharge tests indicated slight increase of capacitance and improvement of coulombic efficiency by deoxofluorination, especially the treatment at high pressure. Detailed analysis on the mechanism of the improved electrochemical performance is now under way.

Acknowledgment

This work was financially supported by the JSPS KAKENHI Grant Number JP17K14544 (K. M.).

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