

The reduction effect of oxygen functional groups in activated carbon for supercapacitor electrode

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Oxygen functional groups were removed from activated carbon in order to improve the electrochemical supercapacitor performance. Commercially available and surface-modified activated carbon electrodes were compared in non-aqueous electrolyte, which allowed stable experimentation at high voltages. N₂-adsorption, FT-IR, and elemental analyzer were used to characterize the surface areas, pore volumes, surface chemical compositions, and oxygen content. Surface area and oxygen content were decreased by heat-treatment at high temperature. Despite the decreased surface area, both of the commercially available and surface-modified activated carbons showed similar specific capacitance of 18.6 Fcc⁻¹ and 18.2 Fcc⁻¹, respectively. Also electrochemical impedance spectra, stability at high voltage and cycle performance showed that surface-modified activated carbon had outstanding electrochemical performance due to the decrease in oxygen content of the commercial activated carbon.

Key words: Supercapacitor, Activated carbon, Surface-modified activated carbon.

Introduction

Supercapacitors are energy storage devices with applicability in the development of smart grid energy systems. Their electrochemical characteristics are mostly determined by their electrodes' active material, usually activated carbon - a material with excellent electrochemical properties, high surface area, and relatively low cost [1]. Oxygenated functional groups in the surface of activated carbon can age cells through gas evolution during use with non-aqueous electrolytes [2]. This is particularly pronounced with alkali-treated activated carbon electrodes.

In this work, high temperature treatment (HTT) was applied to reduce the oxygen content of activated carbon. Surface modification by HTT has been previously reported, but its effects on electrochemical behavior at high voltages were not investigated because the electrodes were tested in aqueous systems [3]. Commercial alkali-activated carbons were heated under an argon atmosphere to reduce its oxygen content and the electrochemical properties were compared with those of the untreated product.

Experimental

Preparation of MSP20-HTT

Commercial activated carbons (MSP20, Osaka Gas

Company, Japan) were heated under an argon atmosphere, followed by heating in a pipe furnace at 900 °C for 1 hour. After being heated, the product was cooled down to room temperature.

The chemical composition and oxygen content of the specimen were determined by the infrared spectra with Fourier transform spectroscopy (FTIR, IR Prestige-21, Shimadzu, Japan) and an elemental analyzer (2400 series II, Perkin Elmer, USA). The Brunauer-Emmett-Teller (BET) method was used to measure the surface areas and pore volumes of samples (Belsorp-Mini II, Belsorp, Japan).

Electrochemical tests

Electrochemical characterization was performed on the electrodes prepared as follows. Active carbons (MSP20 or MSP20-HTT), super-P conductive carbon blacks (MMM, Belgium), and polytetrafluoroethylene (PTFE D-60, Daikin, Japan) in a given ratio (90 : 5 : 5) and an ethanol (Samchun Chemical, 99.9%) dispersion medium was used. The mixtures were prepared in a three-dimensional mixer and stretched by a heated roller press. Electrodes were prepared as rubber types with a thickness of 200 μm, dried at 150 °C for 12 hours under a vacuum atmosphere, and then punched to a diameter of 12 mm. The coin-type cells (CR-2032) were assembled with prepared electrodes, and TF4035 (NKK, Japan) as the separator, in a glove box with argon atmosphere. The capacitive performance of all samples was investigated in 1.8 M triethylmethylammonium tetrafluoroborate (TEMABF₄) in acetonitrile (AN).

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Cyclic voltammetry (CV) and impedance spectroscopy were characterized using a potentiostat (EC-Lab, France). CV was carried out at a scan rate of 5 mVs^{-1} between 0 V and 3.3 V. Impedance spectroscopy was carried out between 100 kHz and 100 mHz. Supercapacitor charge-discharge tests were conducted using a battery tester (Maccor series 4000, USA). In each cycle, the samples were charged at constant current (1 mAcm^{-2}) to 2.7 V. Then, 2.7 V constant voltage was maintained while the charge current at 0.1 mAcm^{-2} . Cells were then discharged to 1.0 V at constant current (1 mAcm^{-2}).

Results and Discussion

Structures of the carbon materials

Pore structure parameters and elemental composition of the samples are listed in Table 1. After HTT, the carbon showed the reduced specific surface area and total pore volume, while the average diameter was unchanged. Liu *et al.* [3] reported that HTT can decrease total pore volume and surface area due to the expanding and reorganization of the crystallite structures of the porous carbon.

Table 1 compares the carbon and oxygen contents of two samples with the elemental analyses. The oxygen content decreased after HTT, resulting in the increase of carbon content which is associated with higher electronic conductivity.

Fig. 1(a) shows the FT-IR spectra of MSP20 and MSP20-HTT. The band around 3450 cm^{-1} corresponds to -OH stretching vibrations of hydroxyl group [5]. The peak at 1629 cm^{-1} is characteristic of C=O stretching vibrations of lactonic and carbonyl groups [6, 7]. The removal of oxygen-containing groups during heat treatment greatly reduced the bands associated with those structures, resulting in a relative increase of carbon content.

Electrochemical characteristics

Capacitance testing was carried out at a current density of 1 mAcm^{-2} from 1.0 to 2.7 V to evaluate charge/

Table 1. Porous structures and chemical compositions of activated carbons

Porous structures	S_{BET}	V_T	D_A	E_D	P_R				
					micro	meso,	macro		
MSP20	2379.6	1.03	1.7	0.55	82.93	17.07			
MSP20-HTT	2105.7	0.92	1.7	0.58	82.87	17.13			
Chemical compositions (wt.%)					C	H	N	S	O
MSP20	93.68	0.19	0.21	0.02		5.9			
MSP20-HTT	95.98	0.17	0.08	0.02		3.75			

S_{BET} , specific surface area ($\text{m}^2 \text{ g}^{-1}$); V_T , total pore volume ($\text{cm}^3 \text{ g}^{-1}$); D_A , average pore diameter (nm); E_D , electrode density (g cm^{-3}); P_R , pore ratio (%).

discharge performances for MSP20 and MSP20-HTT. The specific capacitances of the cells were calculated by the following equation from the discharge profile: $C = I \cdot (T_2 - T_1) / (V_1 - V_2) \cdot (X)$, Where V_1 and V_2 are 2.16 V and 1.08 V, respectively, I is 1.13 mA and X is the volume sum of each electrodes.

Fig. 2 reveals the cycling performance of MSP20 and HTT-MSP20. The HTT-MSP20 exhibited a stable capacitance of about 18.0 Fcc^{-1} without severe fading at 1 mAcm^{-2} during 1000 cycles. The initial capacity was 18.2 Fcc^{-1} and the 1000th capacity was about 18.0 Fcc^{-1} . The total capacitance fading was only 1.1% during 1000 cycles. On the other hand, raw MSP20 displayed a rather poorer cycling performance. The 1st capacitance was about 18.5 Fcc^{-1} and the 1000th capacity decreased to 17.6 Fcc^{-1} . Thus, the specific capacitance decay increased to 5.0%, which was much larger than that of HTT-MSP20.

Electrochemical impedance was measured to compare the samples' electrical conductive properties. Nyquist plots of two-electrode systems employing the samples

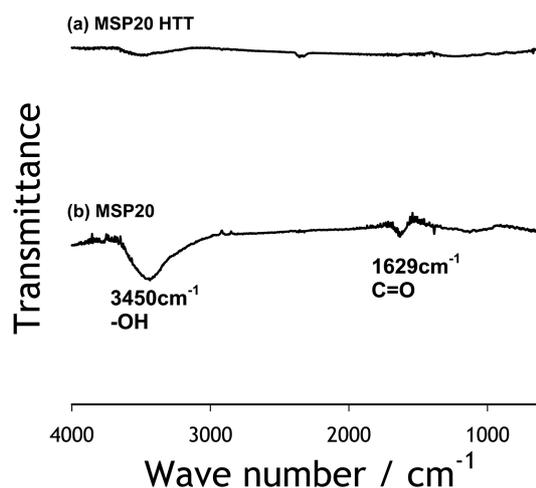


Fig. 1. FT-IR spectra of the (a) MSP20-HTT and (b) MSP20.

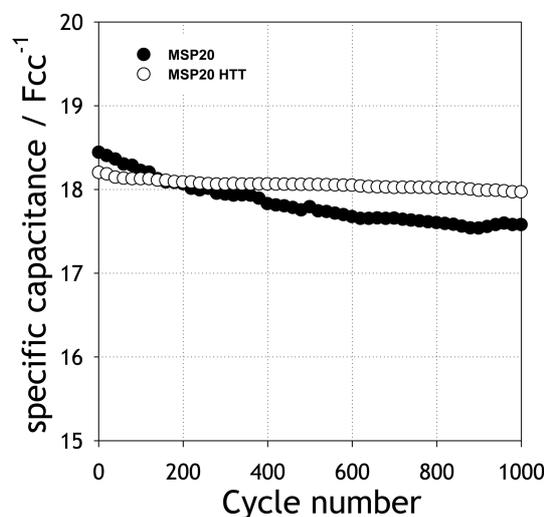


Fig. 2. Cycling performances of the MSP20 and MSP20-HTT.

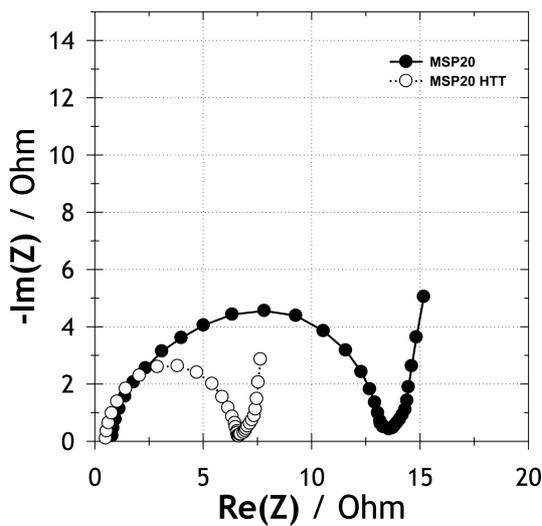


Fig. 3. Nyquist plots of the MSP20 and MSP20-HTT (100 kHz – 100 mHz).

(Fig. 3) show high frequency semicircles associated with the resistance of the electrolyte solution, the intrinsic resistance of the active material, and the contact resistance at the interface active material/current collector. The similarity between the cell assemblies and the use of the same electrolyte ensures that the differences between the high frequency semicircles resulted from the differences in the electric conductivity of the electrode materials [8]. The relative size of the semicircles shows that MSP20 has higher impedance than that of MSP20-HTT. The improved surface resistance of the HTT activated carbon is believed to be attributed to the reduction of oxygen-containing groups.

The samples' cyclic voltammograms were recorded varying upper limit voltage to 2.7, 2.9, 3.1, and 3.3 V (Fig. 4). The CV curves of MSP20 (Fig. 4(a)) do not overlap, and tails appear at higher voltage – indicating different behavior from that of a typical supercapacitor. The observed current loss implies the occurrence of side reactions, such as gas generation.

An effective approach to achieve higher energy is to increase the acceptable working voltage of conventional supercapacitors. Currently, the maximum voltage of supercapacitors is limited to 2.5–2.7 V because of significant decrease in capacitance, and continuous increase in internal resistance at applied voltage over 2.7 V. The undesired Faradaic process that leads to a capacitance fade over a certain cell voltage is the most critical factor that determines the cycle life of supercapacitors. The presence of oxygenated groups on the surface of the activated carbon causes gaseous products of CO_2 and CO at electrodes [2].

The cyclic voltammogram of MSP20-HTT (Fig. 4(b)) shows greatly reduced tails and typical rectangular shapes of the material, which exhibits only electric double layer capacitance (i.e., no apparent pseudo-capacitance from Faradaic process) in the high voltage region. This

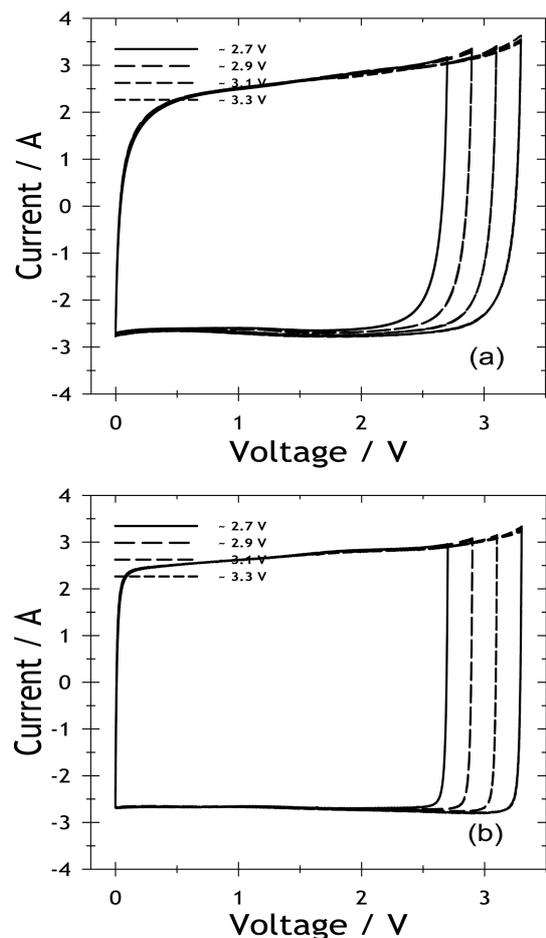


Fig. 4. Cyclic voltammograms of the (a) MSP20 and (b) MSP20-HTT (scan rate: 5 mV/s).

indicates that the removal of oxygen functional groups from the activated carbon's surface improves its cycling stability at high voltages (2.7 ~ 3.3 V).

Conclusions

Activated carbon thermally treated at 900 °C lost oxygen functional groups, which led to improved electrical conductivity and lowered impedance. Despite the decreased surface area by HTT, activated carbon showed similar capacitance and cycling performance to the commercial activated carbon. Also, a supercapacitor employing this heat-treated carbon as electrodes showed better high voltage performance than that of the untreated activated carbon. This shows that the removal of oxygen functional groups from activated carbon's surface by HTT improved its high-voltage stability in a unit cell.

Acknowledgements

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