# NANOWINDOW-DEPENDENT SPECIFIC CAPACITANCE OF SINGLE-WALL CARBON NANOHORN ELECTRODES OF SUPERCAPACITOR

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## Introduction

Supercapacitors have attracted much interest as energy storage devices for electric vehicle and hybrid electric vehicle. For fabricating high-performance supercapacitors, several parameters of electrode materials are recognized as key factors, which are specific surface area, pore size, conductivity, and surface chemical structures. Selection of optimal electrolyte has been also demonstrated to be an important factor for maximizing the performance of the supercapacitors. Recently, several attempts have been reported on application possibilities of nanostructured carbons to electrode materials for supercapacitors. In particular, single-wall carbon nanohorns (SWCNHs), being one of the single-wall nanocarbons, can be considered as a promising candidate for electrode material of supercapacitors, owing to their porous structure and novel physical properties. An individual SWCNH with closed tubular structure has 2-4 nm in diameter and 30-50 nm in length, and several thousand of the SWCNHs form stable spherical bundle structure whose diameter is 80-100 nm. The space between adjacent walls of SWCNHs provides interstitial nanopores. The interstitial and latent internal nanopores of the SWCNHs could provide attractive potential fields for various guest molecules. Therefore, efficient utilization of the internal spaces accessible to the guest molecules is extremely critical for application of the SWCNHs as energy storage media. For this reason, various approaches to open the SWCNHs have been attempted to increase available internal nanopores. Oxidation treatments of SWCNHs with oxygen gas or acids could create nanoscale holes, so-called "nanowindows", on the caps or sidewalls of the closed SWCNHs, resulting in highly porous SWCNHs.

Our previous study clearly revealed that the solvated ions of large size could not pass through the narrow nanowindows of SWCNHs, because the nanowindows can function as a repulsive barrier in accessibility of the solvated ions. Therefore, the size difference between the nanowindows of SWCNHs and the solvated ions of electrolytes plays an important role in the accessibility of the ions to the internal spaces through the nanowindow. Here, we report enhanced specific capacitance of SWCNH electrode of supercapacitor by controlling the nanowindow size of the SWCNHs.

## Experimental Section

The dahlia-like structured SWCNHs were synthesized with $CO_2$ laser ablation of a graphite target in Ar atmosphere (101 kPa) (as-grown SWCNHs). The as-grown SWCNHs were heat-treated in $O_2$ atmosphere at 823 and 923 K for 10 min, respectively ($O_2$-823 K and $O_2$-923 K). The pore structures were investigated by $N_2$ adsorption at 77 K using a volumetric equipment (Quantachrome AS-1-MP), after pre-evacuation for 2 h at 423 K, while maintaining the base pressure at $10^{-4}$ Pa. Pore structure parameters were determined by the subtracting pore effect (SPE) method that was performed by using high-resolution $\alpha_s$ plots constructed for standard adsorption data.

The SWCNH electrode weight was adjusted to 40 mg. The SWCNH powders were mixed with 5 wt.% of poly(tetrafluoroethylene) (PTFE) binder without a conducting material. Samples were subsequently pressed into the shape of a disk, 13 mm in diameter and *ca.*0.4 mm in thickness. The capacitor consists of a couple of electrodes which are arranged face to face, with a separator (glass paper) inserted between these electrodes. Glassy carbon was used as current collector. Electrolyte used in this study was organic electrolyte of 1M tetraethylammonium tetrafluoroborate ($Et_4NBF_4$) with propylene carbonate (PC). The charging voltages have been limited at 2.5 V to ensure the stability of the solvents. The capacitance (C) of the electrodes was calculated on the basis of the following equation, $C = (I \times \Delta t)/(W \times \Delta V)$, where $I$ is the current at discharge, $\Delta t$ is the time variation between 40 % and 60 % of the initial voltage, $\Delta V$ is the voltage variation from 40 % to 60 % of the initial voltage, and $W$ is the weight summed the both of electrodes in the cell composition. All specific capacitances were calculated from following relationship; $\text{Capacitance}_{3E}$ (in 3-electrode) = 4 × $\text{Capacitance}_{2E}$ (in 2-electrode); for comparing the $\text{Capacitance}_{2E}$ with the $\text{Capacitance}_{3E}$.

## Results and Discussions

We measured $N_2$ adsorption isotherms at 77 K to determine pore structure of the SWCNHs. $N_2$ adsorption amounts of oxidized SWCNHs at low relative pressure considerably increase compared to that of as-grown SWCNHs, indicating nanowindow formation on caps or sidewalls of the SWCNHs. Pore structure parameters determined from $N_2$ adsorption

isotherms are summarized in Table 1. Oxidation treatments of SWCNHs dramatically develop microporosity, which should be contributed to increase of internal nanopores accessible to the $N_2$ molecules. The pore structure of SWCNHs strongly depends on the oxidation temperature. After oxidation treatment of SWCNHs at 823 K, total surface area increases from 300 to 1206 $m^2/g$. On the other hand, oxidized SWCNHs at 923 K give lower total surface area of 953 $m^2/g$, compared to that at 823 K, which should be related to excess burning of SWCNH walls due to high oxidation temperature.

Figure 2(a) shows specific capacitances per unit weight of the SWCNH electrodes as a function of oxidation temperature. Oxidized SWCNH electrodes exhibit considerably enhanced specific capacitances compared to as-grown one. This enhanced specific capacitance should be attributed to accessibility of electrolyte ions to the internal nanopores through the nanowindows of SWCNHs. Our previous study presented that, for organic electrolyte ($Et_4NBF_4$/PC) with solvated ions of large size ($Et_4N^+$·4PC: 1.35 nm, $BF_4^-$·8PC: 1.40 nm), SWCNHs oxidized at 693 K did not give notable enhancement in the specific capacitance, compared to as-grown SWCNHs. This result is because nanowindow size of SWCNHs is too small for the organic electrolyte ions to pass through the nanowindow. In the present study, enhanced specific capacitance of $O_2$-823 K electrode should stem from presence of large size nanowindows on SWCNHs. On the other hand, the specific capacitance of $O_2$-923 K electrode is slightly lower than that of the $O_2$-823 K electrode. Figure 2(b) shows specific capacitances per unit surface area of the SWCNH electrodes. Despite lower surface area of the $O_2$-923 K, the specific capacitance per unit surface area of the $O_2$-923 K electrode is higher than that of the $O_2$-823 K electrode. This should come from large size nanowindows of SWCNHs oxidized at higher temperature. Therefore, our results reveal that the nanowindow size of SWCNHs is a key factor to improve the specific capacitance of SWCNH electrode for supercapacitors.

**Table 1.** Pore Structure Parameters of SWCNHs before and after Oxidation Treatments.

| ample | $N_2$ (77 K) SPE method | | | |
|---|---|---|---|---|
| | total surface area ($m^2/g$) | micropore surface area ($m^2/g$) | micropore volume (mL/g) | external surface area ($m^2/g$) |
| As-grown SWCNHs | 300 | 167 | 0.10 | 133 |
| $O_2$-823 K | 1206 | 826 | 0.53 | 381 |
| $O_2$-923 K | 953 | 454 | 0.40 | 499 |

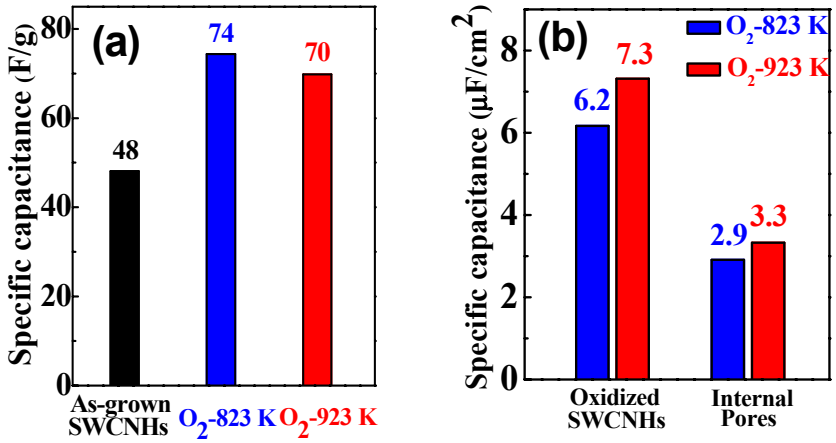


**Figure 1.** Specific Capacitances per (a) Unit Weigh and (b) Unit Specific Surface Area of the SWCNH Electrodes at Discharge Current Density of 1 $mA/cm^2$.

## References


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