

## ELECTROCHEMICAL BEHAVIOR OF HALOGEN-DOPED CARBON MATERIALS

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### Introduction

Electric double-layered capacitor (EDLC) usually uses high-surface area carbon materials as the electrodes, and the authors have reported that single-walled carbon nanotube (SWCNT) is a promising material for the electrode of EDLC [1-3]. For the further improvement of capacitance, modification of the electrode carbon materials is important. Doping is one of the methods to modify the carbons, and lithium doping is a recent hot topic to modify the negative carbon electrode which is the core technique of so-called lithium-ion capacitor, as a new strategy of high-rate energy storage device. On the other hand, some of halogen is known to react with carbon strongly with p-doping. In particular, p-doping of SWCNT by bromine and iodine vapor has been investigated widely from the viewpoints of increase the carrier of SWCNT [4,5]. We focus the p-doping by halogens to challenge the modification of positive carbon electrodes for capacitor system. In the present work, bromine and iodine vapors were reacted with various carbon materials such as SWCNT, graphite, and activated carbon to modify their electronic states, and their electrochemical behaviors in 1M  $\text{Et}_4\text{NBF}_4/\text{PC}$  were investigated. The stability of halogens remained in the carbon materials was also confirmed in the electrolyte and the halogen-predoped carbon materials were characterized as electrodes of capacitor on their capacitance, initial potential, and cyclic reversibility.

### Experimental

Carbon materials used in the present work are HiPco™ single-walled carbon nanotube (SWCNT, Unidym), activated carbon (YP17, Kuraray), and graphite sheet (grafoil, UC). SWCNT powder purchased was suspended in ethanol with ultrasonic treatment and filtered to make the SWCNT paper. YP17 was mixed with 10 wt.% binder PTFE and roll-pressed to make the carbon sheet. Grafoil sheet was used as it was. Halogen species used are  $\text{Br}_2$ , IBr, and  $\text{I}_2$ .  $\text{Br}_2$  is liquid and the others are sublimation solids under room temperature.

In Fig. 1, a schematic illustration of halogen doping procedure is shown. First, carbon materials are enough dried under vacuum, and next they are separately placed with halogen in closed glass tube. After 1 hour exposure with halogen vapor at room temperature, carbon samples were heated at 150 °C in vacuum to remove excess halogen adsorbed on their surface.

The carbon samples after the halogen treatment were brought into Ar-filled glove box without exposing to air to make electrochemical test cells. Three-electrode test cells were constructed; carbon samples were working electrodes, platinum foil was counter, and  $\text{Ag}/\text{Ag}^+$  was reference one. The current collector for carbon sheets or paper was platinum foil, and electrolyte was 1M  $(\text{C}_2\text{H}_5)_4\text{NBF}_4/\text{Propylencarbonate}$  ( $\text{Et}_4\text{NBF}_4/\text{PC}$ ). Cyclic voltamograms (CVs) of the test cells were measured.

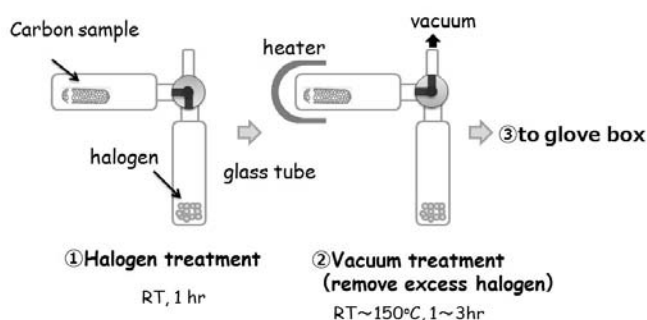


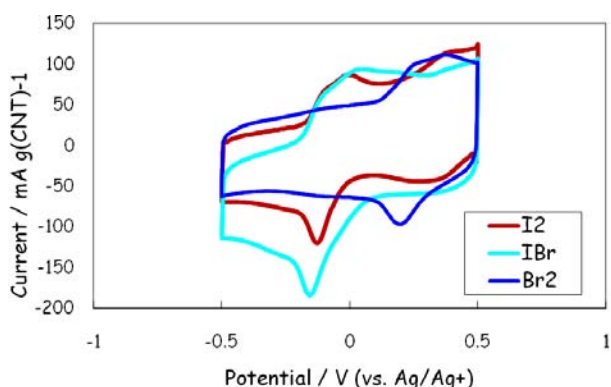
Fig. 1 Schematic illustration of the present halogen treatment.

### Results and Discussion

In Table 1, the initial potentials of SWCNTs treated by  $\text{Br}_2$ , IBr and  $\text{I}_2$  just before the electrochemical measurement are listed, and CVs of them are compared in Fig. 2. The initial potentials are dependent on the halogen. It is reasonable to suppose that the stronger dopant gains the potential of SWCNT to more positive, dependently on the Lewis acidity of each halogen species. Therefore, the most reactive bromine gains the potential of SWCNT up to +0.167 V compared with the least reactive iodine shows small gain of the potential. In the CVs, a pair of redox reaction peaks is obtained in all the three, which corresponds to undoped/redoped of halogen into/from electrolyte. Thus, the halogen species predoped in SWCNTs are found to be electrochemically released into the electrolyte. It is remarkable that the redox potential of  $\text{Br}_2$ -treated SWCNT in the CV is higher than other two. Such the potential difference probably means Br is intercalated into the bundle space of SWCNT and other two are adsorbed on the SWCNT surface. Actually, it is well agreed with the fact that bromine is well known to intercalate into graphite layer but iodine is not. In these ways, behavior of predoped halogen in SWCNT is governed by the electrochemical potential, dependently on the reactivity of halogen.

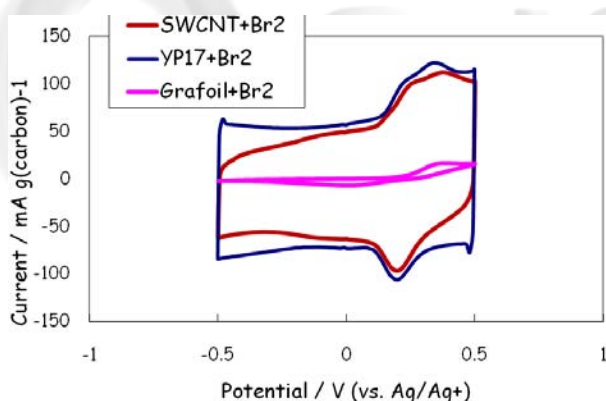
Table 1 Initial potential of halogen treated SWCNTs in 1M  $\text{Et}_4\text{NBF}_4/\text{PC}$ .

	Initial potential / V (vs. $\text{Ag}/\text{Ag}^+$ )
Untreated SWCNT	-0.14
$\text{I}_2$	-0.07
IBr	+0.085
$\text{Br}_2$	+0.167



**Fig. 2** CVs of halogen-treated SWCNTs in 1M  $\text{Et}_4\text{NBF}_4/\text{PC}$  electrolyte. The scan rate is 1mV/sec.

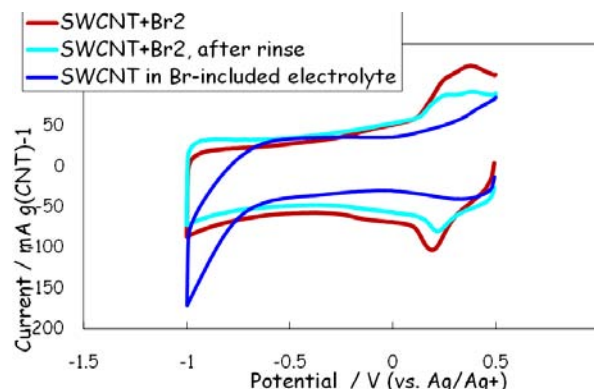
As the CVs are compared in Fig. 2, bromine treatment gives a redox reaction at higher potential, which is more promising than others as a pseudocapacitance reaction. In Fig. 3, CVs of various carbon materials bromine-treated are shown. The redox reaction is obtained in the all carbon materials. The currents of the peaks are large for SWCNT and YP17, but small for grafoil, which means the high surface area carbon can accept more bromine. Further relation between the capacitance of bromine and the surface area is being in consideration.



**Fig. 3** CVs of various bromine-treated carbon materials in 1M  $\text{Et}_4\text{NBF}_4/\text{PC}$  electrolyte. The scan rate is 1mV/sec.

We checked a rinse effect of the bromine treated sample before the measurement of CV. After the rinse of bromine-treated SWCNT by pure PC solvent, the redox peak became smaller, as shown in Fig. 4. It indicates that the some amount of bromine predoped in SWCNT is removed by the rinse, but other is still remained in SWCNT after the rinse, revealing that the former is bromine on the SWCNT surface and the latter is that in van der Waals space of SWCNT bundle. We also checked whether the bromine pre-solved in the electrolyte can be doped into SWCNT or not. The CV of pristine SWCNT in Br-included electrolyte did not show any redox peak as shown in Fig. 4. From this experiment, we suppose bromine predoped in SWCNT by the vapor phase is strongly ionized and

undoped electrochemically, but that pre-solved in electrolyte is not so ionized in which the electrochemical responsibility is little.



**Fig. 4** CVs of Br-treated SWCNT before (red) and after (pink) rinse by pure PC, and that of SWCNT in Br-included electrolyte (blue). The scan rate is 1mV/sec. The Br-included electrolyte was made by adding a few drops of liquid bromine into 50 mL of 1M  $\text{Et}_4\text{NBF}_4/\text{PC}$  electrolyte.

### Conclusive remarks

Halogen-doped carbon materials were synthesized through exposing the carbon to the halogen vapor, and the electrochemical behavior of them was clarified and compared. A redox reaction was created in the electrode due to the undope/redope of halogen in the carbon, and the potential was dependent on the halogen species.

The redox reaction of bromine predoped carbons seems to have a possibility as a source of pseudo capacitance, because it is achieved at relatively high potential compared with others are at low potentials. In addition, the bromine anion seems to be smaller than other intercalate anions such as  $\text{BF}_4^-$ , which is better for the pseudo capacitance because excess expansion of electrode by large ions is avoided. Further examination to use the halogen-doped carbons for capacitor system is being challenged.

### References

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