

# ELECTROCHEMICAL CAPACITANCE OF DEFLUORINATED GRAPHITE FLUORIDE

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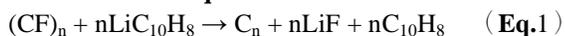
## Introduction

The electric double layer capacitor (EDLC) is an electric energy storage device based on the dielectric property of the electric double layer at the interface between the electrolyte and a nanoporous carbon electrode such as activated carbon. The EDLC is considered to be one of the promising systems for electric energy storage because of its excellent power density and cycle life, but the energy density of the EDLC is lower than that of rechargeable batteries such as the lithium ion battery, therefore it should be further improved for energy saving applications.

Graphite fluoride is one of graphite intercalation compounds and used as lubricate and cathode material of lithium primary battery. The authors recently found that the carbon product derived from the de-fluorination of graphite fluoride has highly electrochemical capacitance regardless of its low microporosity. In this paper, the author will report the correlation of the nano-structure with the electrochemical capacitance for the de-fluorinated graphite fluoride (dfGF).

## Experimental

Referring to the preparation method for nano-porous carbon derived from de-fluorinated poly-tertafluoroethylene (PTFE) [1,2], the graphite fluoride ((CF)<sub>n</sub>) was de-fluorinated by the reductive reaction with lithium metal complex. The reaction is shown in Eq.1.



Lithium metal was dissolved to dimethoxyethane (DME) solution containing 0.2M naphthalene to form lithium-naphthalene charge-transfer complex. The graphite fluoride powder was de-fluorinated by the immersion in the complex solution for two weeks under the room temperature. The de-fluorination product was washed by dilute hydrochloric acid and pure water to remove the LiF by-product. The carbon product (dfGF) was obtained with around 40wt% yield, which almost corresponded to the theoretical one (39wt%) based on the stoichiometry of (CF)<sub>n</sub>.

The composite electrodes (13mm diameter, ~35 mg weight) were prepared from the dfGF, acetylene black (Denki Kagaku Kogyo, Co. Japan) and binder (PTFE 6J, Du Pont-Mitsui Fluorochemicals Co., Ltd., Japan), in a ratio of 80:10:10 wt%, respectively. To compare the dfGF to conventional activated carbon, the composite electrode using steam-activated carbon (AC) was also prepared. The galvanostatic measurements were carried out with a standard three-electrode cell at room temperature. The electrolyte was a propylene carbonate solution containing 0.5 moldm<sup>-3</sup> (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBF<sub>4</sub>.

## Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) profiles of the graphite fluoride and the dfGF. The graphite fluoride is known to be a layered structure composed of cyclohexane-like carbon planes. The XRD profile showed the 001 interlayer spacing (d-space) is around 0.73nm. The XRD profiles indicated that the de-fluorination of the graphite fluoride and the consecutive removal process of LiF formed carbon material. The d-space of the carbon product (dfGF) was around 0.37nm, which is smaller than that of the graphite fluoride. This d-space reduction is due to the absence of the fluorine atoms. Notably, the d-space of around 0.37nm is not usual, because the carbon hexagonal planes attract each other to have narrower d-space close to 0.34 nm. Some nanoporous carbons such as activated carbon are known to have apparently the similar d-space to the dfGF, but in these cases the diffraction line is more broadened than that of the dfGF. The crystallinity of the dfGF was higher than that of the AC. Figure 2 shows the SEM images of the dfGF. The microscopic morphology of the dfGF was lamelliform, which is derived from the layered morphology of the graphite fluoride.

The pore structure parameters calculated by nitrogen adsorption measurement were summarized with the d-space (*d*<sub>002</sub>) and lattice size (*L*<sub>c</sub>) in Table 1. The dfGF-500, the dfGF-1000 means the heated-dfGF sample at 500°C or 1000°C for 1 hour at nitrogen atmosphere, respectively. The micropore and mesopore of the original dfGF were not developed and the BET specific surface area is only around 200 m<sup>2</sup>g<sup>-1</sup>. The AC is a typical microporous carbon with the BET specific surface of around 2000 m<sup>2</sup>g<sup>-1</sup>, so it can be seen that the dfGF is too less-porous carbon as electrode material for EDLC. The surface area and pore volume of the heated-dfGFs are smaller than the original dfGF. It is due to the pore shrinkage and blocking by the heat-treatment. The *d*<sub>002</sub> of the dfGF was very sensitive to the heat-treatment. The higher temperature caused the narrower d-space. This suggests that the wide d-space of the dfGF is so thermally unstable as to be easily decreased by the heat-treatment at only 500°C. The *L*<sub>c</sub> of the dfGF increased by the heat-treatment. It means that the carbon crystallite grew along c-axis due to increasing the stack number of the carbon plane.

Figure 3 shows the dependence of the volumetric capacitance on the potential range of the dfGF series. The wider potential range on the three-electrode cell means the higher voltage charging on the two-electrode cell (corresponding to actual capacitor construction). The capacitance of the AC slightly increased by widening the potential range, but the capacitance of the original dfGF and dfGF-500 markedly increased by the potential range widening. Especially, the capacitance of the original dfGF at the range of 1.25 ~ 4.75Vvs.Li/Li<sup>+</sup> (corresponding to 3.5V charging at the two-electrode cell) was over 100 Fcc<sup>-1</sup>. The behavior of the AC in Fig.3 is usual as conventional activated carbons for EDLC, but the very high capacitance and the dependence on

the potential range for the original dfGF and dfGF-500 cannot be explained by the conventional theory of the double layer capacitance based on accessible surface area for ion adsorption/desorption. The dfGF-1000 showed very small capacitance on any potential range. The heat-treatment decreased the maximum capacitance and enhanced the threshold potential range for increasing the capacitance. Therefore, it can be said that the high capacitance needs wider d-space than around 0.35nm.

The high capacitance of the low-porous carbon such as the dfGF can be possibly explained by “electrochemical activation”. The electrochemical activation is an electrochemical behavior that high voltage charging gives low-porous carbons unexpectedly high capacitance that is comparable to that of conventional activated carbons with high surface area. The case has been reported for KOH-activated soft-carbon [3,4], exfoliated graphite [5], etc.. It is considered that the electrochemical activation is owing to the electrochemical intercalation / de-intercalation of electrolyte ion to the interlayer or the increment of ion-accessible surface area by opening the closed pores under strong electric field. It can be said that the wide interlayer spacing of the carbon plane of the dfGF causes the electrochemical activation.

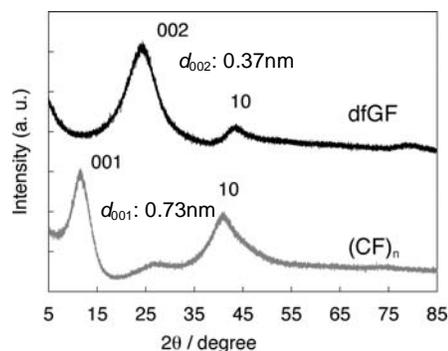
## Conclusions

A low-porous carbon (dfGF) with  $d_{002}$  of around 0.37nm was prepared by the de-fluorination of graphite fluoride using lithium charge transfer complex at room temperature. The dfGF showed a high capacitance regardless of the low specific surface area. The high capacitance of the dfGF can be explained by the electrochemical activation.

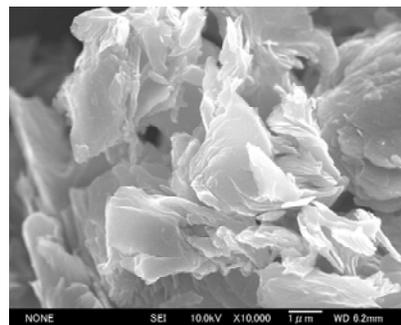
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**Table 1. BET specific surface area ( $S_{BET}$ ), mesopore volume ( $V_{meso}$ ), micropore volume ( $V_{micro}$ ), mean micropore width ( $w_{micro}$ ), d-space ( $d_{002}$ ), and lattice size ( $L_c$ ) of de-fluorinated graphite fluoride (dfGF), heated dfGF, or steam-activated carbon (AC).**

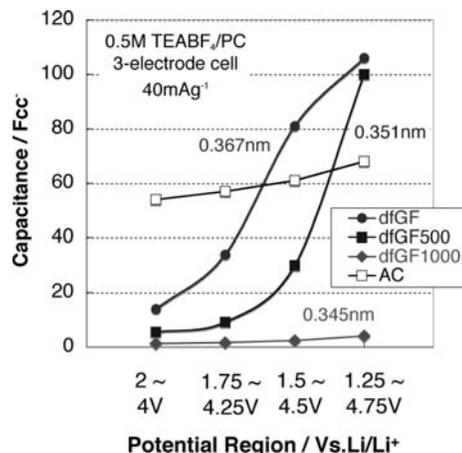
Sample	$S_{BET}$ / $m^2g^{-1}$	$V_{meso}$ / $mlg^{-1}$	$V_{micro}$ / $mlg^{-1}$	$w_{micro}$ / $nm$	$d_{002}$ / $nm$	$L_c$ / $nm$
dfGF	230	0.09	0.09	1.01	0.367	1.3
dfGF-500	44	-	-	-	0.351	2.0
dfGF-1000	27	-	-	-	0.345	2.2
AC	2100	0.39	0.85	1.06	0.39	0.82



**Fig. 1** XRD patterns of graphite fluoride ((CF)<sub>n</sub>) and de-fluorinated graphite fluoride (dfGF).



**Fig. 2** SEM image of dfGF.



**Fig. 3** Dependence of capacitance (three-electrode cell, galvanostatic) on potential range for dfGF, dfGF-500, dfGF-1000, or AC.

## References

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