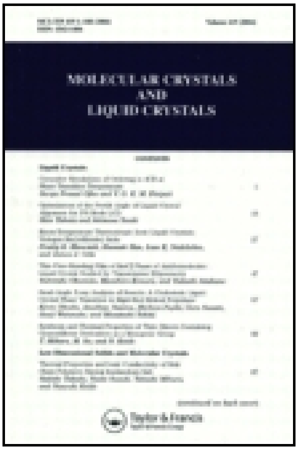

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# DOUBLE LAYER CAPACITANCE OF POROUS CARBONS DERIVED FROM DEFLUORINATION OF PTFE

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*Highly mesoporous carbon material was prepared from defluorination of PTFE with lithium naphthalenide ($LiC_{10}H_8$; radical anion), and its double layer capacitance was measured in 1.0 M $LiClO_4$/propylene carbonate. The reaction product of PTFE film with $LiC_{10}H_8$ had micro/nano domain structure consisting of one dimensional carbon chain (carbyne-like structure) and LiF. Although the carbon chain easily decomposed to amorphous carbon structure by chain crosslinking and LiF condensation through air exposure, highly mesoporous carbon was obtained by removal of fine LiF particles with dilute HClaq. This mesoporous carbon (PCPTFEr) showed larger capacitance (BET surface area: $1137\,m^2\,g^{-1}$, capacitance: $123\,F\,g^{-1}$) than activated carbon fiber with the almost same BET surface area ($1151\,m^2\,g^{-1}$, $74\,F\,g^{-1}$). Additionally, PCPTFEr maintained the capacitance even at high current density. These properties of PCPTFEr can be due to the matrix carbon structure and, especially, the pore structure.*

*Keywords*: PTFE; defluorination; carbyne; mesopore; electric double layer; capacitance

## INTRODUCTION

Since energy density of electric double layer capacitor (EDLC) [1] is quite lower than that of rechargeable batteries, the double layer capacitance

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must be increased considerably in order to apply EDLC to energy storage system such as a hybrid electric vehicle (HEV) [2]. On the other hand, it is known that a characteristic porous carbon can be prepared by defluorination of polytetrafluoroethylene (PTFE) with Li-amalgam [3]. Recently, our group also found that highly porous carbons prepared by defluorination of PTFE with lithium metal [4] or lithium naphthalenide (radical anion) showed high specific surface area and large capacitance in dilute $H_2SO_4$ aqueous electrolyte [4]. In this paper, pore structure of the porous carbon derived from PTFE with radical anion (referred to as PCPTFEr) and its double layer capacitance in nonaqueous electrolyte are discussed based on the comparison with those of conventional activated carbon fiber (ACF).

## EXPERIMENTAL

Defluorination (carbonization) or PTFE with lithium amalgamate in a vacuum system produces a micro/nano domain structure of LiF and carbonaceous matrix consisting of an one-dimensional carbon structure (carbyne-like structure: $(-C{\equiv}C-)_n$ or $(=C{=}C=)_n$) [3]. However, the one-dimensional carbon decomposes immediately to an amorphous graphite structure because of facile condensation of LiF into fine particles and cross-linking reaction of the carbon chains under the presence of oxygen such as air. Dousek and Jansta [5] also suggested that porous carbons with high specific surface area were obtained by removal of fine LiF particles in the defluorinated PTFE with $H_2O$. In our preparation method, which is similar to that of Dousek and Jansta, lithium napthalenide (radical anion: $LiC_{10}H_8$) is used instead of lithium amalgamate. PTFE film was used as precursor. Naphthalene and lithium metal (excess) were dissolved in dimethoxyethane to prepare $LiC_{10}H_8$. The PTFE film was immersed in dimethoxyethane solution containing $LiC_{10}H_8$. The defluorination reaction (carbonization) proceeds as shown in the following scheme.

$$-(CF_2CF_2)_n- + 4nLiC_{10}H_8 \rightarrow (-C{\equiv}C-)_n\ (\text{or}(=C{=}C=)_n) + 4nLiF + 4nC_{10}H_8$$

The defluorinated sample was washed by $CH_3OH$ and dried at 70°C in air. It was also heated at 700°C for 1 h to eliminate surface oxygen functional groups and to develop the crystallinity of carbon. LiF in the sample were extracted by the immersion in diluted hydrochloric acid. The sample (PCPTFEr) was dried at 200°C for 2 h under about 1 Pa.

The measurement of the double layer capacitance was conducted under galvanostatic conditions (cut off potential; 2.0 V and 4.0 V vs. $Li/Li^+$) in propylene carbonate containing $1.0\,\mathrm{mol\,dm^{-3}}$ $LiClO_4$ (1.0 M $LiClO_4$/PC) [6,7]. In this paper, the process of electrons passing from (to) the carbon electrode is referred to as a positive (negative) process.

## RESULTS AND DISCUSSIONS

Figure 1 shows the Raman spectra of the defluorinated PTFE before and after the treatment for washing and drying. The reaction product (reaction time: 30 min) before the treatment has two broad peaks around 2000 cm$^{-1}$ and 1300 cm$^{-1}$, which are assigned to C≡C stretching mode and conjugated C=C stretching mode, respectively. The chain length of $(–C{\equiv}C–)_n$, that is, n was estimated to be around 6 from the peak position in the spectrum using Kastner's equation [8]. The defluorination did not finish completely during this reaction time since the peaks attributed to PTFE were also observed in the spectrum. On the other hand, the reaction product (reaction time: 2 weeks) after the treatment shows a typical spectrum for amorphous carbon prepared from thermal carbonization of an organic precursor at relatively low temperature. Two peaks around 1590 cm$^{-1}$ and 1380 cm$^{-1}$ are the G band and the D band for graphite structure, assigned to in-plane vibrations of perfect hexagonal carbon plane and imperfect one, respectively. The strong relative intensity of the D band means low crystallinity in graphite structure. So, the drastic change of the spectrum indicates that the –C≡C– chain structure in the reaction product is so unstable as to change to amorphous carbon through the cross-linking of the –C≡C– chains.

Figures 2(a) and (b) are the X-ray diffraction (XRD) patterns for the defluorinated PTFE after the washing in $CH_3OH$/drying process and after the following heat-treatment (at 700°C), respectively. The four diffraction lines can be attributed to LiF (111), (200), (220), and (311), respectively. The LiF crystal particles are derived from the reaction of lithium and fluorine in PTFE and condensation of resulting LiF. The average sizes of the

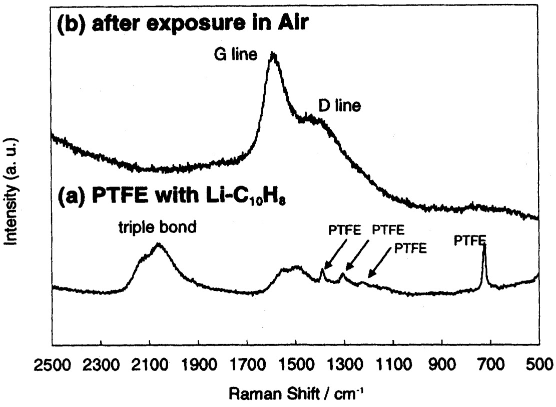

**FIGURE 1** Raman spectra of the defluorinated PTFE (a) before and (b) after the washing in $CH_3OH$/drying in air. Excitation laser: 532 nm.

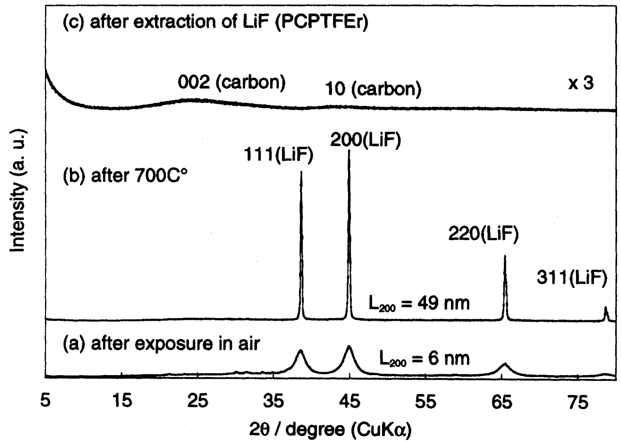

**FIGURE 2** XRD patterns for the defluorinated PTFE (a) after washing in $CH_3OH$/drying in air, (b) after heat-treatment at 700°C, and (c) PCPTFEr (the defluorinated PTFE after extraction process of LiF).

crystallite were estimated to be about 6 nm and 50 nm by Scherrer equation. This suggests that the particle (or domain) size grew by the heat-treatment. Figure 2(c) is the XRD pattern for PCPTFEr (the sample in Figure 2(b) after the immersion in a diluted HCl aqueous solution). There were no peaks of LiF except for the broad (002) line and (10) line of micrographite structure. So, the LiF particles were extracted by the immersion in diluted HCl aqueous solution.

The $N_2$ adsorption and desorption isotherms (77 K) was conducted to analyze the pore structure. The isotherms of ACFs prepared from phenolic resin with steam activation (800°C) are typical ones (Type I) for microporous carbons. On the other hand, PCPTFEr indicated a isotherm like Type IV, where hysteresis between the adsorption and desorption branches was clearly observed. The hysteresis are related to be the existence of many pores of large size such as mesopores or macropores. The characteristics of pore structure estimated by the isotherms are summarized in Table 1. PCPTFEr had larger amount of mesopore volume than various ACFs. The average micropore width of PCPTFEr was estimated to be 1.2 nm, which was larger than that of ACF (120) with the same surface area and the same micropore volume. Consequently, PCPTFEr is a characteristic mesoporous carbon containing also relatively larger micropores compared with ACFs.

Figure 3(a) shows the relationship between the BET surface area and the double layer capacitance of PCPTFEr and various ACFs in 1.0 M $LiClO_4$/PC (current density; 40 mA $g^{-1}$). Figure 3(a) revealed that the

**TABLE 1** BET Specific Surface Area (BET-SSA), Average Micropore Width ($2\chi$), Micropore Volume ($V_{micro}$), and Mesopore Volume ($V_{meso}$)

| Sample | BET-SSA $[m^2\,g^{-1}]$ | $V_{micro}$ $[ml\,g^{-1}]$ | $2\chi$ [nm] | $V_{meso}$ $[ml\,g^{-1}]$ |
|---|---|---|---|---|
| PCPTFEr | 1137 | 0.47 | 1.16 | 0.87 |
| ACF(10)* | 654 | 0.28 | 0.64 | 0.06 |
| ACF(60) | 934 | 0.37 | 0.73 | 0.03 |
| ACF(120) | 1151 | 0.47 | 0.85 | 0.08 |
| ACF(240) | 1475 | 0.60 | 0.94 | 0.09 |
| ACF(480) | 1776 | 0.73 | 1.07 | 0.16 |

*(time) means the activation duration [min].

BET-SSA: specific surface area by BET plot between 0 ~ 0.05 P/Ps.

$2\chi$: average micropore width by Dubinin-Radushevivh (DR) method.

$V_{micro}$: micropore volume by DR method.

$V_{meso}$: mesopore volume by Dolimore-Heal method of adsorption branch.

capacitance of ACFs was not linearly proportional to the BET specific surface area. This may be caused by insufficient penetration of (solvated) ions into the developed micropore structure or the low mobility of the ion in the narrow micropores. On the other hand, the capacitance of the PCPTFEr was higher by approximately 50 F $g^{-1}$ than that of ACF with the almost same BET surface area (1151 $m^2\,g^{-1}$). The reason for the high capacitance of PCPTFEr can be arisen as the follows.

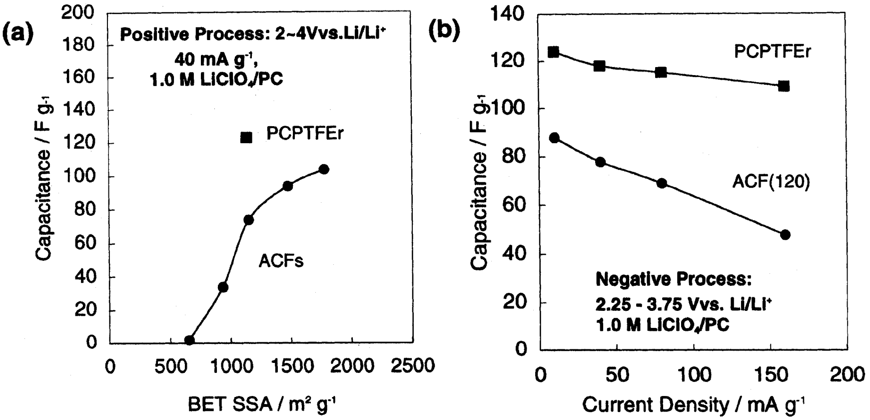

**FIGURE 3** (a) Correlation between the BET surface area and the double layer capacitance for PCPTFEr or ACFs in 1.0 M $LiClO_4$/PC, (b) Dependence of the double layer capacitance of PCPTFEr or ACF (120) on current density.

(a) Pore size distribution: the presence of many meso/macropores and the relatively large micropores can assist in the penetration of the electrolyte into micropores and the transfer of ions in narrow micropore structure. As a result, the effective surface area for double layer is larger than that of ACF.

(b) Structure of carbon: electric double layer capacitance is affected by the carbon structure. For example, it is well known that the electric double layer capacitance of edge plane of graphite was larger than that of basal plane. Since the precursor and preparation for PCPTFEr are quite different from those of ACF, the micrographite structure in PCPTFEr may be particular. Thus, the correlation between double layer capacitance and the micrographite structure has to be also investigate with other analytical methods in future.

In general, it is known that the pseudocapacitance derived from surface functionalities may contribute to the capacitance of porous carbon. However, the XPS spectra revealed that the surface functionalities on external surface of the PCPTFEr were very similar to the ACF (oxygen/carbon atomic ratio is around $0.05 \sim 0.06$). Moreover, the electrolyte is composed of Li salt and aprotic solvent such as propylene carbonate, so the influence of electrochemical redox reaction of surface functionalities on the capacitance of PCPTFEr can be ignored.

Figure 3(b) showed the dependence of the double layer capacitance of PCPTFEr or Ref-ACF (120) on current density. The capacitance of PCPTFEr did not almost decrease at high current density, while significant loss of the capacitance was observed at high current density for ACF(120). The loss of the capacitance is concerned with the larger resistance of ionic transfer in micropores. Therefore, the constant capacitance of PCPTFEr at various current densities is due to fast ion-transfer by mesopores and the micropore with large pore width.

Consequently, the new porous carbon: PCPTFE is a very atractive material for EDLC. However, there are some critical problem for practical use such as preparation cost and low bulk density. More economical way for mass production and more detailed PSD control are required.

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