

ELECTRIC DOUBLE LAYER CAPACITANCE OF POROUS CARBON DERIVED FROM PTFE WITH LI METAL

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Introduction

Recently, electric double layer capacitor (EDLC) with high capacitance [1] has been proposed as a sub-power source for a pure electric vehicle (PEV) or a hybrid electric vehicle (HEV) because power density of EDLC is high enough to use as the power source at start-up of the electric vehicles. However, since energy density of EDLC is quite lower than that of rechargeable batteries, the double layer capacitance must be increased considerably in order to apply EDLC to PEV or HEV. The high capacitance of EDLC is related to high specific surface area of activated carbon electrode. The high surface area is derived from many micropores. Therefore, the improvement of the capacitance has been conducted with increasing the surface area and modification of the pore size distribution. However, it seems to be difficult to improve the low energy density of EDLC using activated carbon electrode because the double layer capacitance is not always proportional to specific surface area of the activated carbons [2-5]. As one of the reasons for this, the effective surface area, which is an available surface area of micropores to form the electric double layer, is quite low due to low permeability of the electrolyte into micropores. Generally, activated carbons are prepared by activation process such as gasification reaction of carbon. So, new porous carbon materials prepared by the other processes except the activation can be candidates of porous carbon electrodes with high capacitances. On the other hand, Jansta and Dousek reported in 1980 that porous carbon could be prepared by defluorination of polytetrafluoroethylene (PTFE) with Li-amalgam [6]. From this literature, the material was microporous and its BET surface area was higher than $2500 \text{ m}^2 \text{ g}^{-1}$ [6]. Therefore, adsorption behavior and electrochemistry of the porous carbon derived from PTFE are very interesting. This carbon is expected to be used practically as an EDLC electrode, a lithium ion battery anode, a storage medium for methane or hydrogen, or an adsorbent of toxic

substance. However, the possibility has never been clarified yet. Recently, our group also found that highly porous carbons for EDLC can be prepared by defluorination of PTFE with lithium metal or lithium naphthalenide (radical anion) in ether solution. In our previous paper [4], we already reported that the porous carbons prepared from PTFE with Li metal showed high specific surface area and large capacitance in dilute H_2SO_4 aqueous electrolyte. 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 is discussed based on the comparison with those of activated carbon fiber (ACF) prepared from phenol resin with steam activation.

Experimental

Kavan, et al., reported that the reaction product from defluorination (carbonization) of PTFE with lithium amalgamate in a vacuum system had a micro/nano domain structure of lithium fluoride and carbonaceous matrix consisting of a one-dimensional carbon structure (carbyne-like structure: $-(\text{C}\equiv\text{C})_n-$ or $=(\text{C}=\text{C})_n-$) [7]. The carbyne is known as one type of carbon allotrope such as fullerene, diamond, and graphite. 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 [6] 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 . Our preparation method of porous carbon derived from PTFE (PCPTFEr) is similar to that of Dousek and Jansta, in which lithium naphthalenide (radical anion) is used instead of lithium amalgamate. A schematic illustration for our preparation method is shown in Figure 1

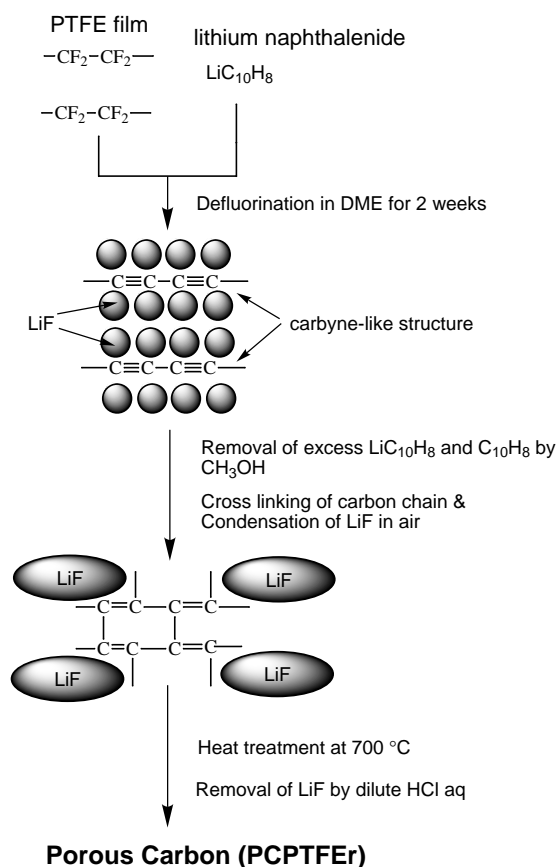


Figure 1. Schematic illustration for the preparation method of PCPTFEr.

PTFE film (50 μm thickness, 3g) was used as precursor of PCPTFEr. Naphthalene (2.56g) and lithium metal (excess) are dissolved in dimethoxyethane (DME, 100 cm^3) to prepare lithium naphthalenide. The PTFE film was immersed in dimethoxyethane solution containing lithium naphthalenide for 2 weeks. The defluorinated (carbonized) sample was immersed in CH_3OH to remove excess lithium naphthalenide and naphthalene. After the removal of the lithium metal, the sample was dried at 60 $^\circ\text{C}$ for 24h in air. The sample was heated at 700 $^\circ\text{C}$ for 1h to eliminate surface oxygen functional groups and to develop the crystallinity of carbon because excess amount of the surface functional groups or the ill-crystalline structure of carbon often cause low electron conductivity of the carbon sample. LiF in the carbonized sample were extracted by the immersion of diluted hydrofluoric acid (3wt%) for 24h. The sample (PCPTFEr) was dried at 200 $^\circ\text{C}$ for 2h under about 1Pa after the removal of hydrofluoric acid by pure water. The physicochemical condition of carbon and fluorine atoms in the defluorinated PTFE before and after the extraction of LiF was analyzed using Raman spectroscopy

(NRS-1000, JASCO, Japan) and X-ray diffraction (XRD, RINT 2100V/PC, Rigaku, Japan). The N_2 adsorption/desorption measurement at 77K was conducted using N_2 adsorption/desorption system (BELSORP28SA, BEL Japan Inc., Japan) to characterize the pore structure of PCPTFEr and ACF. The PSD of mesopores was obtained from Dolimore-Heal (DH) method using the adsorption branch [24]. The average micropore width was estimated by Dubinin-Radushevich (DR) equation.

A composite pellet electrode was prepared from ground PCPTFEr or ACF fiber (about 50 mg), carbon black, and binder (86:10:4wt%) to measure the electric double layer capacitance. A standard three-electrode cell was used to measure the electric double layer capacitance of a single ACF electrode. 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 mol dm^{-3} LiClO_4 electrolyte (1.0M LiClO_4/PC). In this paper, the process of electrons passing from (to) the carbon electrode is referred to as a positive (negative) process. The electric double layer capacitance was calculated by the amount of electricity passed during a positive or negative process according to the following equation.

$$C = i t / m \Delta V \quad (1)$$

where C ; electric double layer capacitance [F g^{-1}], i ; current [A], t ; positive (or negative) duration [s], m ; weight of ACF in the electrode [g], and ΔV ; potential change during positive (or negative) process [V] (= 2 V, in this study).

Results and Discussion

Figure 2 shows the Raman spectra of the reaction product of PTFE with lithium naphthalenide before and after the immersion in CH_3OH and drying in air. The reaction

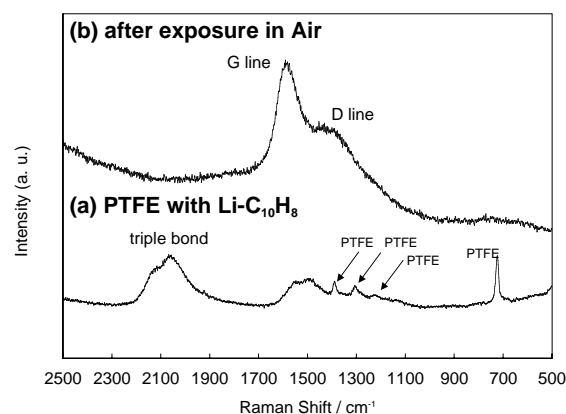


Figure 2. Raman spectra of the reaction product of PTFE with $\text{LiC}_{10}\text{H}_8$ (a) before and (b) after the washing in CH_3OH and drying in air. Excitation laser: 532 nm.

product (reaction time : 30 min) before the treatment has two broad peaks around 2000 cm^{-1} and 1300 cm^{-1} , which are assigned to $\text{C}\equiv\text{C}$ stretching mode and conjugated $\text{C}=\text{C}$ stretching mode, respectively. The chain length of $-(\text{C}\equiv\text{C})_n-$, 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 washing in CH_3OH and the exposure in air shows a typical spectrum for amorphous carbon prepared from 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

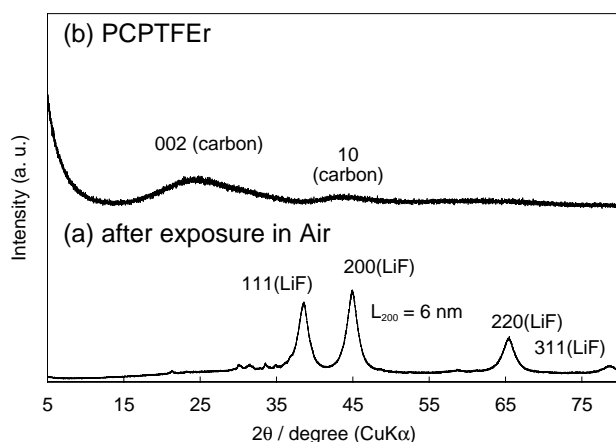


Figure 3. XRD patterns for (a) the reaction product of PTFE with $\text{LiC}_{10}\text{H}_8$ after the washing in CH_3OH and drying in air and (b) PCPTFEr (the reaction product after the heat treatment at $700\text{ }^\circ\text{C}$ and the extraction process of LiF).

intensity of the D band means low crystallinity in graphite structure. So, the drastic change of the spectrum indicates that the $-\text{C}\equiv\text{C}-$ chain structure of the reaction product is so unstable to form amorphous carbon through the cross-linking of the $-\text{C}\equiv\text{C}-$ chains.

Figure 3 shows the X-ray diffraction (XRD) patterns for the reaction product of PTFE with lithium naphthalenide. Fig.3 (a) is the pattern for the product after the washing in CH_3OH and drying process (corresponding to Fig.2 (b)). The four diffraction lines observed in Fig.3 (a) can be attributed to LiF (111), (200), (220), and (311), respectively. The LiF crystal particles (the average size of the crystallite can be estimated to be about 6 nm by Scherrer equation)

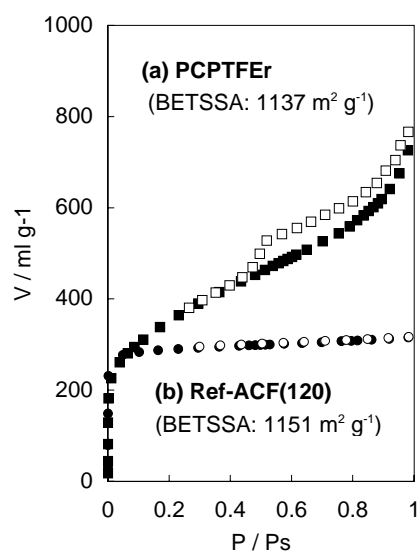


Figure 4. N_2 adsorption and desorption isotherms of (a) PCPTFEr and (b) Ref-ACF(120). Filled symbols: adsorption isotherms, open symbol: desorption isotherms.

Table 1 BET specific surface area (BET-SSA), average micropore width [2χ], micropore volume [W], and mesopore volume (DH-PV).

Sample	BET-SSA [m^2g^{-1}]	W [ml g^{-1}]	2χ [nm]	DH-PV [mlg^{-1}]
PCPTFEr	1137	0.47	1.16	0.87
Ref-ACF(10)*	654	0.28	0.64	0.06
Ref-ACF(60)	934	0.37	0.80	0.03
Ref-ACF(120)	1151	0.47	0.85	0.08
Ref-ACF(240)	1475	0.60	0.94	0.09
Ref-ACF(480)	1776	0.73	1.07	0.16

* (time) means the activation duration [min]

BET-SSA: specific surface area calculated by BET plot in the region of 0~0.05 P/P_s

2χ : average micropore width calculated from DR method

W: Pore volume of micropore calculated from DR method

DH-PV: Pore volume of mesopore (1.6nm~40nm) calculated from DH method of adsorption branch

are derived from the reaction of lithium and fluorine in PTFE and condensation of resulting LiF. Fig. 3 (b) is the XRD pattern for PCPTFEr (the sample in Fig.3 (a) after the heat treatment (at 700 °C) and the following 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.

Figure 4 shows the N₂ adsorption and desorption isotherms of PCPTFEr. The isotherm of ACF with the almost same BET specific surface area is also shown for comparison. The isotherm of the ACF is a typical one (Type I) for microporous carbon because a large amount of N₂ was adsorbed remarkably at low relative pressure (P/Ps) and the N₂ adsorption was saturated at middle and high P/Ps. The former is due to the micropore filling effect. On the other hand, in the case of PCPTFEr, the amount of N₂ adsorption still increased in the region of middle and high P/Ps. Hysteresis between the adsorption and desorption branches was also observed in the isotherm. This increment of N₂ adsorption and the hysteresis are related to be the existence of many large size pores such as mesopores or macropores. The same isotherms were obtained in porous carbon prepared from PTFE and Li metal [4]. The characteristics of pore structure are summarized in Table 1. The average micropore width (2χ) of PCPTFEr is estimated to be 1.2 nm by DR method. Consequently, PCPTFEr is highly porous carbon composed of relatively large micropores and meso/macro pores.

Figure 5 shows the relationship between the BET specific surface area and electric double layer capacitance of PCPTFE and various ACFs in 1.0 M LiClO₄/PC (current density ; 40 mA g⁻¹). Additionally, the results in Fig.8 revealed that the capacitance of ACFs was not linearly proportional to the BET specific surface area. This may be caused by insufficient electrolyte penetration into the developed micropore structure or the low mobility of the ion in the narrow micropores. On the other hand, the capacitance of the PCPTFE was higher by approximately 70 F g⁻¹ than that of ACF with almost the same BET specific surface area (1151 m²g⁻¹). The reason for the high capacitance of PCPTFE can be arisen as the follows.

(a) Pore size distribution : the presence of many meso/macropores and the relatively large mesopores 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 increased more 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 has larger than that of basal plane. Since the precursor and preparation of PCPTFE are quite different from those of ACF, the orientation, size, and accumulation of the micrographite structure in PCPTFEr should be particular.

In general, it is known that the pseudocapacitance derived from surface functionalities may contribute to the capacitance of porous carbon. However, the XPS spectra

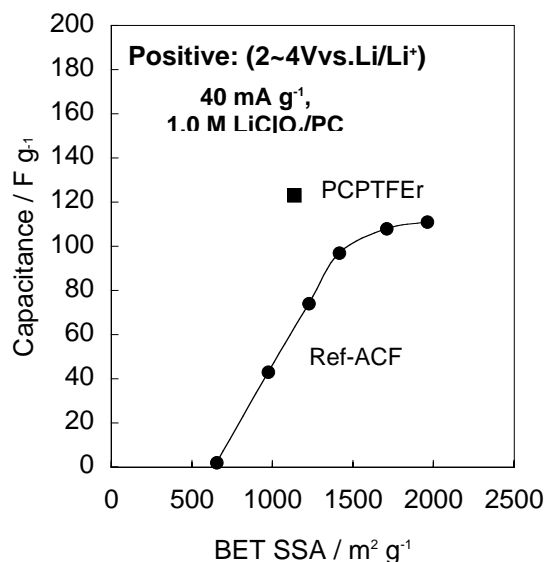


Figure 5. Relationship between the BET surface area and the double layer capacitance for PCPTFEr or Ref-ACF series in 1.0M LiClO₄/PC.

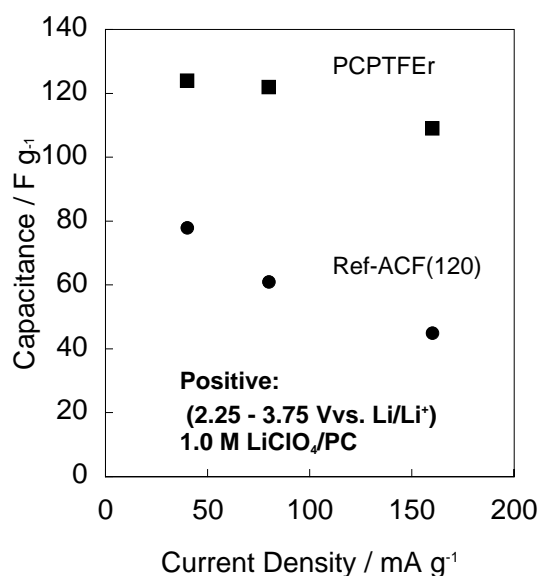


Figure 6. Dependence of the double layer capacitance of PCPTFEr or Ref-ACF (120) on current density (in 1.0M LiClO₄/PC).

revealed that the surface functionalities on external surface of the PCPTFEr were very similar to the ACF (oxygen/carbon atomic ratio is around 0.04 ~ 0.05). Moreover, the electrolyte used in this paper is composed of Li salt and propylene carbonate which is aprotic. Thus, the effect of electrochemical redox reaction of surface functionalities on the capacitance of PCPTFEr can be ignored.

Figure 6 showed the dependence of the double layer capacitance of PCPTFEr or Ref-ACF (120) on current density. The capacitance of PCPTFE did not almost decrease at high current density, while significant loss of the capacitance was observed at high current density of Ref-ACF(180). The loss of the capacitance is concerned with the large resistance of ionic transfer in micropores. Therefore, the constant capacitance of PCPTFEr at various current densities is due to the presence of meso/macropores and the micropore with large pore width.

Conclusion

Highly porous carbon material was prepared from defluorination of PTFE with lithium naphthalenide ($\text{LiC}_{10}\text{H}_8$; radical anion), and its electric double layer capacitance was measured in 1.0 M LiClO_4 /propylene carbonate electrolyte. The reaction product of PTFE film with lithium naphthalenide had micro/nano domain structure consisting of one dimensional carbon chain (carbyne-like structure) and LiF. After cross-linking of the carbon chain and condensation of LiF in the reaction product, highly porous carbon containing not only micropore but also meso/macropore was obtained by removal of fine LiF particles with dilute HCl solution. This porous carbon (PCPTFEr) derived from PTFE with $\text{LiC}_{10}\text{H}_8$ showed higher capacitance (BET surface area: $1137 \text{ m}^2\text{g}^{-1}$, capacitance: 123 F g^{-1}) than activated carbon fiber with almost the same BET surface area ($1151 \text{ m}^2\text{g}^{-1}$, 74 F g^{-1}). Additionally, PCPTFEr maintained the high capacitance at high current density. These properties of PCPTFEr can be due to the matrix carbon structure and, especially, the pore structure.

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