

PREPARATION AND DOUBLE LAYER CAPACITANCE OF POROUS NITROGENOUS CARBONS

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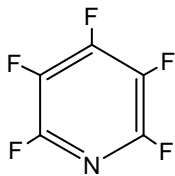
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Introduction

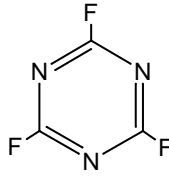
The electric double layer capacitor (EDLC) is based on electro-sorption of porous carbon electrode. The electric charge is stored on the electric double layer that is two array layers of opposite charges at the interface between carbon and electrolyte. It is well known that the pore structure influences the double layer capacitance. The capacitance corresponds to the product of the surface area and the specific capacitance per surface area for porous carbon electrode. The former is the effective surface area for adsorption/desorption of ions, which is related to pore structure. So, the optimization of pore structure has been performed to improve the energy density of EDLC. For example, mesoporous carbons has been expected as new electrode materials since ion adsorption/desorption process goes better in wider nanospace of mesopores than micropores. The authors have prepared the mesoporous carbons by the catalytic activation [1] and defluorination of perfluoropolymer [2-4] to investigate the double layer capacitance. The mesoporous carbons showed good capacitance properties, however it was also revealed that the capacitance properties of the mesoporous carbons are still not much enough at the viewpoint of volumetric-specific capacitance. Therefore, we have to consider not only pores structure but also other factors, i.e., specific capacitance per surface area. This can be modified by the surface atomic structure of carbon electrode. One of the ways is heteroatom doping to the porous carbons. In this paper, the preparation of nitrogenous porous carbons by defluorination method and the capacitance properties are discussed.

Experimental

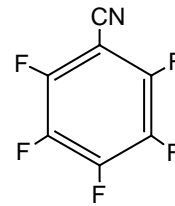
The nitrogenous porous carbons were prepared by the same way of the porous carbons derived from poly-terafluroethylene (PTFE) with alkaline metal [4]. The defluorinated of PTFE products contain the micro-domain structure of alkaline fluorine and carbon network.



Pentafluoropyridine
(PFP)



Cyanuric fluoride
(CYF)



Pentafluorobenzonitrile
(PFBN)

The removal of the alkaline fluoride from the defluorinated product gives micro/mesoporous carbon structure. In this paper, the perfluorocarbons containing nitrogen were used as start materials. Pentafluoropyridine (PFP), cyanuric fluoride (CYF), pentafluorobenzonitrile (PFBN) were defluorinated by the 1,2-dimethoxyethane mixture solution of $\text{NaC}_{10}\text{H}_8$ and KC_{10}H_8 . The defluorinated products were heated at 800°C for 1 hour in N_2 and washed with HCl_{aq} under ultrasonic waves to remove KF and NaF as by-products. The obtained porous materials were heated again at 800°C or 1000°C in N_2 for 1 hour. The obtained samples are labeled as follows, ex, PC-PFBN1000 : porous carbon from defluorination of PFBN and the second heat-treatment at 1000°C . The pore structure was characterized by N_2 adsorption method at 77K. The double layer capacitances were measured with three-electrode cell under galvanostatic condition. The propylene carbonate solution of 0.5M $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ (TEABF_4/PC) was used as electrolyte.

Results and Discussions

The XPS spectra are shown in Fig.1. The $\text{N}1\text{s}$ peaks were observed in all samples, which means that nitrogen atom can be doped in carbon matrix by our defluorination method. The atomic ratio of N/C is around 0.02~0.15 and the chemical states are the pyrrole or quaternary like and the pyridine like, depending on the kind of the precursors and the heat-treatment temperature. The samples heated at 1000°C have higher content of nitrogen than those at 800°C .

The BET specific surface area and the average micropore width are summarized in Table1. The data of the reference nitrogen-free samples as porous carbons (activated carbons and porous carbon black) are also shown. The nitrogenous carbons have around $1000\text{ m}^2\text{g}^{-1}$ and 1nm of average micropore width. They are so porous as to measure the double layer capacitance.

The gravimetric-specific capacitances were shown in Fig.2 as the correlation with the BET specific surface area (S_{BET}). The positive/negative capacitance ($C_{\text{gp}}/C_{\text{gn}}$) is obtained

from the chronopotentiograms (potential-time curves) of higher/lower electrode potential region than initial potential ($\sim 3\text{V vs. Li/Li}^+$ for all samples) before electrochemical measurement. The former corresponds to the anion adsorption capacitance and the latter the cation adsorption capacitance if the capacitance origin comes from the double layer charging-discharging. The gravimetric-specific capacitances of nitrogenous porous carbons (NPC) were lower than some porous carbons. This is due to the lower BET surface areas of NPC. In order to clarify the influence of heteroatom doping, the specific capacitance per surface area (C_{sp} and C_{sn}) was calculated by dividing the gravimetric-specific capacitances with S_{BET} . The specific capacitance per surface area are shown in Table 1. The positive capacitances are higher than the negative ones for NPC, while both of the capacitance are the almost same for reference porous carbons except of ACF1 and KOH-MCMB1. The lower capacitance of cation adsorption for ACF1 and KOH-MCMB1 is due to the ion-sieving effect of narrow micropore [1]. The specific capacitances per surface area of PC-PFP800 and PC-PFBN are higher compared with other samples. The N-effect is more prominent in positive capacitance. These NPC samples have higher content of the pyrrole or quaternary like nitrogen. It suggests that this chemical state is effective in enhancement of the capacitance.

Conclusion

The nitrogenous nanoporous carbons (NPC) were prepared by the defluorination of perfluorocarbons containing nitrogen atom with alkaline metals. NPC showed higher specific capacitance per surface area compared with activated carbons and carbon black. The N-effect can be related to the enhancement of space charge layer capacitance of carbon surface, the wettability, or the pseudo-capacitance of nitrogen functionalities. We are now investigating these points together with the electrochemical window .

References

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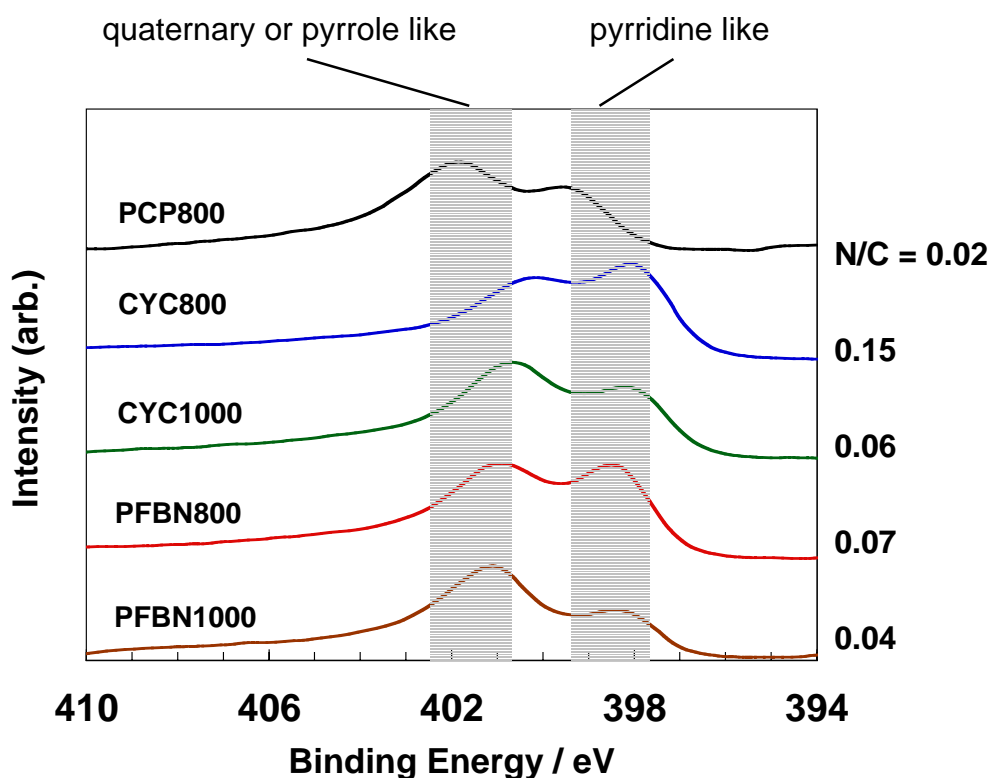


Figure 1 N1s XPS spectra of nitrogenous porous carbons (NPC). N/C is the atomic ratio of nitrogen and carbon calculated by N1s and C1s spectra.

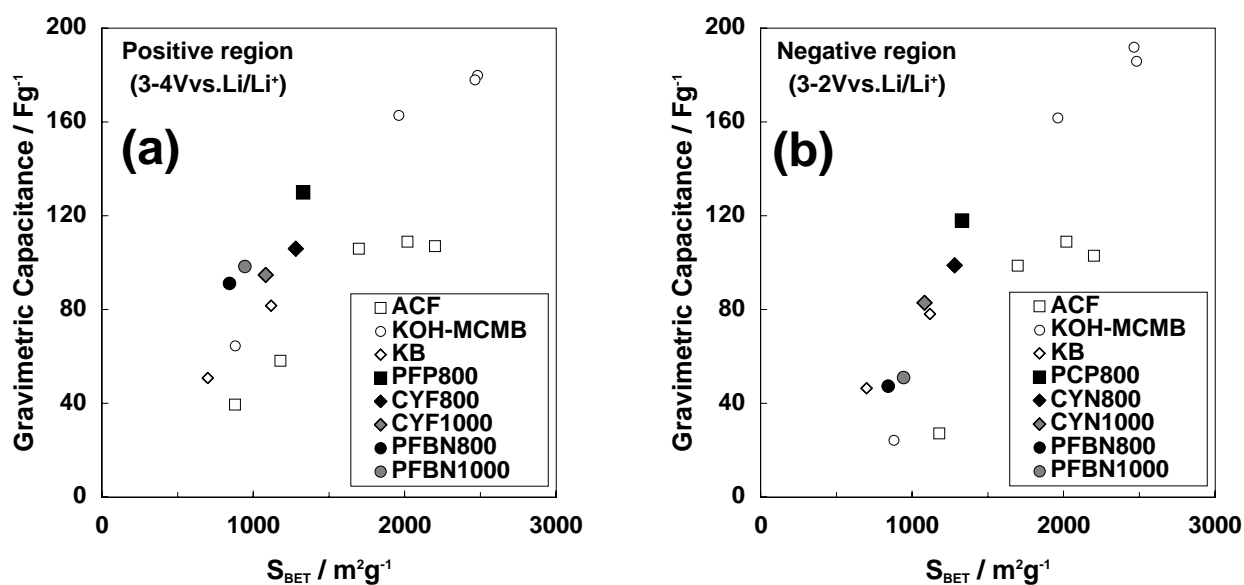


Figure 2 Correlation between BET specific surface area (S_{BET}) and gravimetric double layer capacitance in 0.5M TEABF₄/PC. Gravimetric condition (40 mA g⁻¹). (a) Positive (anion adsorption) capacitance or (b) Negative (cation adsorption) capacitance is obtained chronopotentiogram of 3-4V or 3-2 V vsLi/Li⁺, respectively.

Table 1 BET specific surface area (S_{BET}), average micropore width (w_{micro}), and specific capacitance per surface area for various porous carbons.

Sample	S_{BET} [m ² g ⁻¹]	w_{micro} [nm]	Csp [μFcm ⁻²]	Csn [μFcm ⁻²]
ACF1	1190	0.73	8.2	2.3
ACF2	1700	1.05	6.7	5.8
ACF3	2020	1.13	5.1	5.4
ACF4	2200	1.21	5.4	4.7
KOH-MCMB1	880	0.73	5.4	4.7
KOH-MCMB2	1960	0.98	8.3	8.2
KOH-MCMB3	2480	1.18	7.2	7.5
KOH-MCMB4	2470	1.18	7.2	7.8
KB1	700	1.14	7.3	6.6
KB2	1120	1.33	7.3	7.0
PC-PCP800	1330	1.06	9.8	8.9
PC-CYN800	1280	1.08	8.3	7.7
PC-CYN1000	1080	1.09	8.8	7.7
PC-PFBN800	840	0.86	10.8	5.6
PC-PFBN1000	940	1.00	10.4	5.4

w_{micro} : calculated by DR method

Csp: specific capacitance per surface area for positive potential capacitance (anion adsorption capacitance)

Csn: specific capacitance per surface area for negative potential capacitance (cation adsorption capacitance)

ACF: phenolic resin based activated carbon fiber (steam activation, 800°C)

KOH-MCMB: mesocarbon microbeads activated by KOH (800°C)

KB: Ketjen Black

Acknowledgment

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