第4講義

Carbons in Electric Double Layered Capacitor

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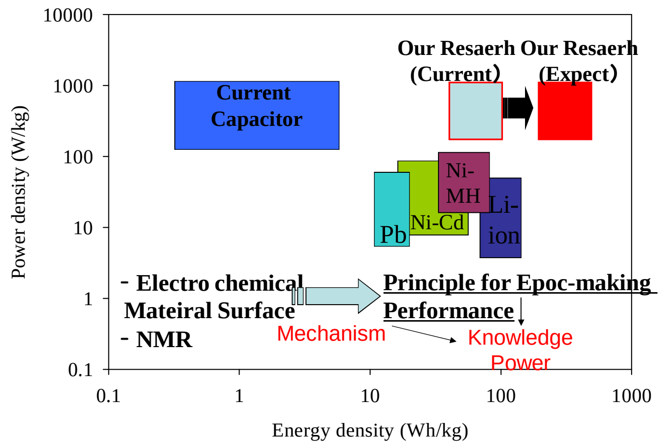
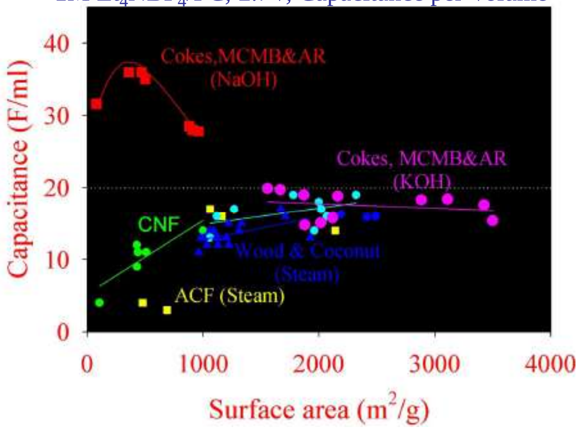
Now and Future of Capacitance



Relationship between Organic Capacitance and Surface Area

1M Et_4NBF_4/PC, 2.7V, Capacitance per Volume



Electric Storage of EDLC

Targets

Larger Capacity per Volume

High Rate of Charge-Discharge

→ Better Carbon Electrode, Guideline?

More Adsorption at Large Rate in the Adsorbent of Limited Volume

Wetting to Carbon Surface →Penetration into Pores→Adsorption on Wall Surface→Polarized Charge→Outlet from Pore→Discharge /Desorption

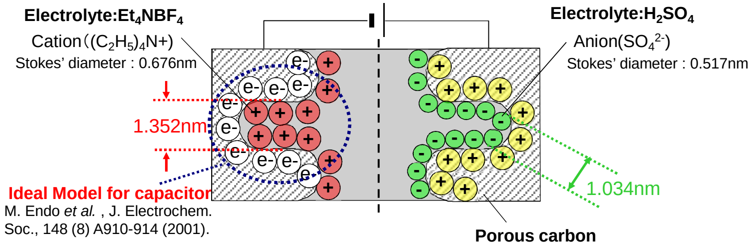
First Cycle

Sizes of Electrolyte vs. Pore for Penetration
Invasion into Matrix or very narrow pore of wall

Density Change or Expansion of Matrix,
Volumetric Change of Electrode

Mobility and Adsorbed Amount of Electrolyte as well as Structure of Electrode May Change under Electric Field

Conjecture of pore size using capacitance data



M. Endo *et al.* , J. Electrochem. Soc., 148 (8) A910-914 (2001).

In using Et_4NBF_4 as an electrolyte, at least pore size larger than 1.3nm is necessary to have electric double layered capacitance.

In using H_2SO_4 as an electrolyte, pore size of about 1.0nm is enough to have electric double layered capacitance.

Capacity governing factors

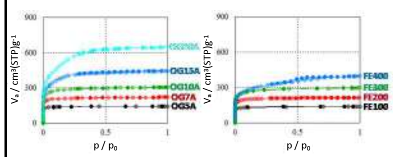
- Surface area
- Pore size and its distribution
- Surface (Edge and Basal, Heterogeneous atom functional groups)
- Crystallinity of carbons (Resistivity)
- …

Best Carbon

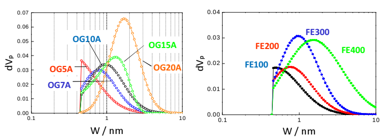
- Pore structure: Right pore exclusively
  - » Too large or small pores are useless
- Pore wall : Hexagonal edge
  - » Graphitizable carbon (Higher conductive)
- Density : Least closed pore
  - » Finer particles are desirable, but packing density should be maximized in the electrode
- Functional groups : Effectiveness
  - » Oxygen functional groups have to be minimized
  - » Other heterogeneous groups are still on studying.

Characterizations of Pitch and PAN based ACFs

N_2 吸脱着等温線 @77K



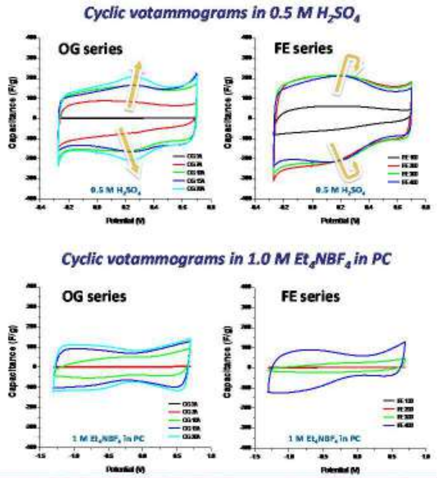
細孔径分布 (NL-DFT method)



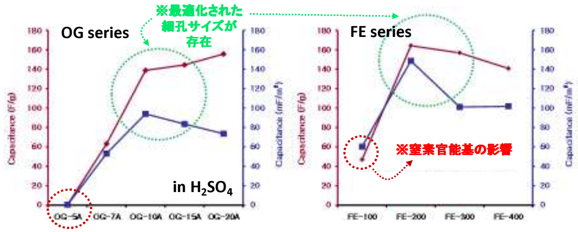
細孔特性表 (*t* -plot)

	Surface area (m^2/g)				Pore volume (cm^3/g)			Pore width (nm)	
	A_{total}	$A_{external}$	A_{micro}	A_{meso}	V_{total}	V_{micro}	V_{meso}	W_{micro}	W_{meso}
OG-5A	676.8	1.2	675.6	0	0.22	0.22	0	0.65	0.0
OG-7A	987.6	3.4	984.2	0	0.34	0.34	0	0.68	0.0
OG-10A	1211.7	5.4	1206.3	0	0.46	0.46	0	0.77	0.0
OG-15A	1488.0	13.9	1474.1	0	0.66	0.66	0	0.90	0.0
OG-20A	1817.4	15.9	1801.5	0	0.97	0.97	0	1.08	0.0
FE-100	636.9	1.2	635.7	0	0.21	0.21	0	0.67	0.0
FE-200	909.2	2.2	907.0	0	0.33	0.33	0	0.72	0.0
FE-300	1130.6	3.8	1099.7	27.1	0.45	0.43	0.02	0.78	1.82
FE-400	1187.1	5.2	931.2	250.7	0.60	0.38	0.22	0.82	1.73

CV results of Pitch & PAN based ACFs



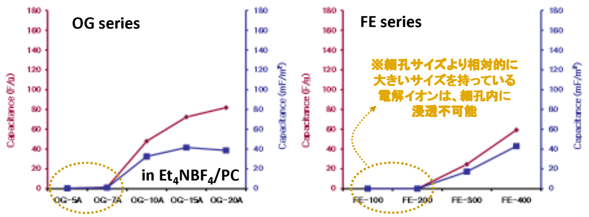
Pore size vs. Capacitance (Non-organic system)



	Specific capacitance		Surface property			
	Per weight	Per surface area	Surface area	Average pore size	O contents	N contents
	F/g	mF/m²	m²/g	nm	%	%
OG-5A	0.6	0.5	677	0.65	4.8	1.1
OG-7A	63.3	53.2	988	0.68	5.3	0.7
OG-10A	138.8	94.0	1212	0.77	6.1	0.5
OG-15A	144.4	83.5	1488	0.90	8.3	0.5
OG-20A	155.6	73.6	1817	1.08	6.7	0.3

	Specific capacitance		Surface property			
	Per weight	Per surface area	Surface area	Average pore size	O contents	N contents
	F/g	mF/m²	m²/g	nm	%	%
FE-100	47.1	60.3	637	0.67	6.2	10.1
FE-200	164.2	148.6	909	0.72	7.4	6.1
FE-300	156.8	101.1	1131	0.78	7.9	4.1
FE-400	140.7	101.8	1187	0.82 / 1.73	9.3	2.5

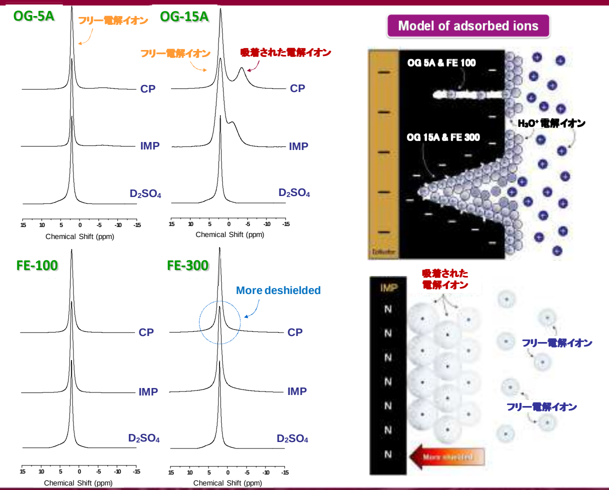
Pore size vs. Capacitance (Organic system)



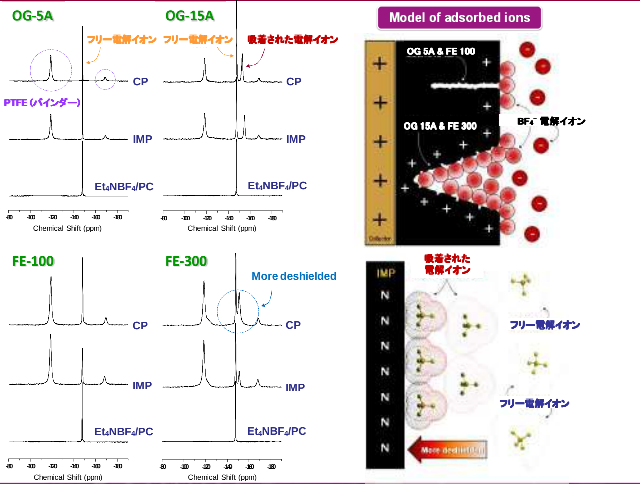
	Specific capacitance		Surface property			
	Per weight	Per surface area	Surface area	Average pore size	O contents	N contents
	F/g	mF/m²	m²/g	nm	%	%
OG-5A	0.5	0.6	677	0.65	4.8	1.1
OG-7A	1.6	1.2	988	0.68	5.3	0.7
OG-10A	48.1	32.6	1212	0.77	6.1	0.5
OG-15A	72.5	41.7	1488	0.90	8.3	0.5
OG-20A	81.9	38.7	1817	1.08	6.7	0.3

	Specific capacitance		Surface property			
	Per weight	Per surface area	Surface area	Average pore size	O contents	N contents
	F/g	mF/m²	m²/g	nm	%	%
FE-100	0.1	0.2	637	0.67	6.2	10.1
FE-200	0.1	0.2	909	0.72	7.4	6.1
FE-300	24.7	17.3	1131	0.78	7.9	4.1
FE-400	59.3	43.0	1187	0.82	9.3	2.5

^{2}D NMR (Non-organic system)



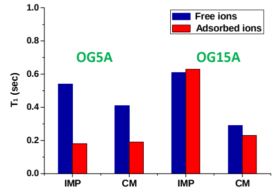
^{19F} NMR (Organic system)



ACFの細孔内電解イオン挙動に関する²H固体NMR解析（T_1値/水系）

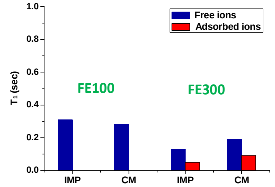
T_1 (sec) for OG series

OG5A				OG15A			
IMP		CM		IMP		CM	
Free	Adsorbed	Free	Adsorbed	Free	Adsorbed	Free	Adsorbed
0.54	0.18	0.41	0.19	0.61	0.63	0.29	0.23



T_1 (sec) for FE series

FE100				FE300			
IMP		CM		IMP		CM	
Free	Adsorbed	Free	Adsorbed	Free	Adsorbed	Free	Adsorbed
0.31	-	0.28	-	0.13	0.05	0.19	0.09

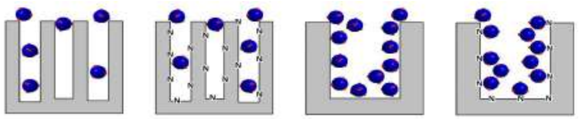


1. 緩和時間、T_1は短いほどより強く吸着をしていることを意味する。
2. T_1の値は、充電の前に比べて充電後に、より短くなる。
3. 全体的に、OGシリーズに比べてFEシリーズのT_1値が短い。

Pores vs. capacitances

1. To examine the effect of pore size and surface composition of activated carbon fibers on EDLC
2. 2. To draw out the best pore and surface images of ACFs for better performance

Model of adsorbed ions on the surface of OG and FE series



OG-5A FE-100 OG-15A FE-300

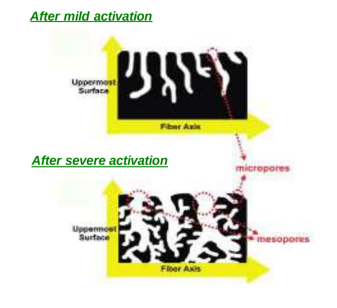
	Ion size (nm)		Reference
	Non-solvated	Solvated with solvent (PC)	
$(CH_3CH_2)_4N^+$	0.74	1.96	*Carbon*. 2002, 40, 2613
BF_4^-	0.49	1.71	
$(CH_3CH_2)_4N^+$	0.68		*Science*. 2006, 313,1760
BF_4^-	0.33		
Et_4N^+•4PC		1.35	*J. Electrochem. Soc*. 2004, 151, E199
BF_4^-•8PC		1.40	

Cf. Hydrate sulfate ion size of $SO_4^{2-}(H_2O)_{12}$: 0.53 nm *J. Electrochem. Soc*. 2001,148(8), A910

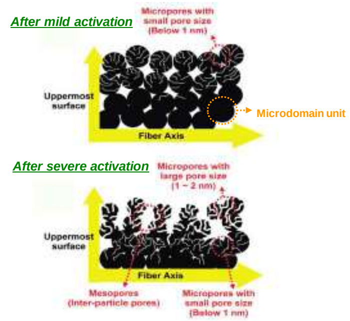
Model structures of pores

Yoon group of Kyushu university, *Langmuir*, 2009, in press
DOI: 10.1021/la9000347

Conventional Hierarchical Structure Model

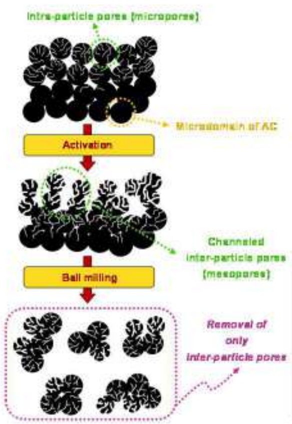


Proposed Structure Model



1. Under mild activation condition, each of the microdomains on the uppermost surface contains the slit-shaped micropores, leading to micropore-rich.
2. With increase of activation degrees, the size of uppermost microdomains reduces and the pore width of micropores becomes widened. Simultaneously, micropores are freshly generated in core part.

Two kinds of pores



Maxsorb-III

(Kansai coke and chemicals Co.)

- ✔ derived from petroleum coke
- ✔ high surface area (over 3000 m^2/g)

M-30

(Osaka gas chemicals Co.)

- ✔ derived from mesophase carbon micro beads
- ✔ high surface area (over 3000 m^2/g)

1. Novel pore structures of activated carbons, also, were suggested with microdomain units through the inter- and intra-particular mechanism.
2. From this idea, *ball mill treatment* on ACs can bring the selective removal of inter-particle pores without destroying the intra-particle pores.
3. We tried to elucidate the roles of the inter- and intra-particle pores on capacitance with two super-activated carbons (with high surface area over 3000 m^2/g) in organic and inorganic electrolytes.

Removal of pores from inter-domain nucleation

Maxsorb-III
(Kansai coke and Chemicals Co.)

M-30
(Osaka gas chemicals Co.)

↓

Ball-mill
(for 1, 3, 5, 10 and 20 days)

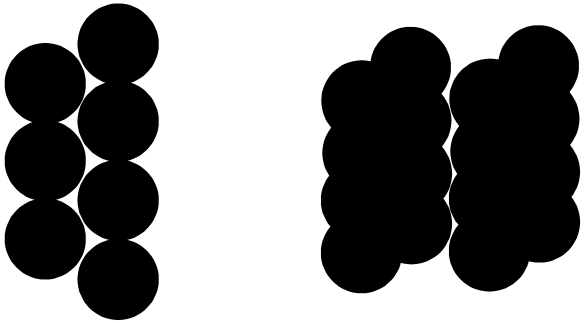
Milling conditions :
at 200 rpm of pot mill rotator (ASH, AV-400)
with zirconia balls (each 5 / 10 mm in diameter)

↓

Physical Properties
SEM, N_2 adsorption/desorption at 77 K,
Elemental analysis

Electrochemical Properties
Cyclic voltammetry
in 0.5 M H_2SO_4 and 1 M Et_4NBF_4/PC

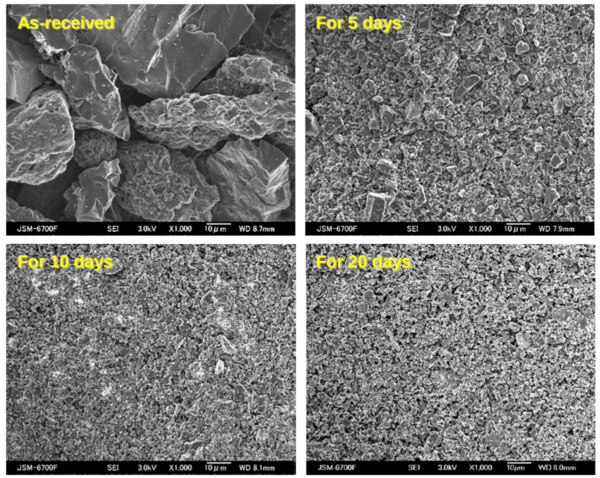
Structural Characteristics of MSCIII & M30



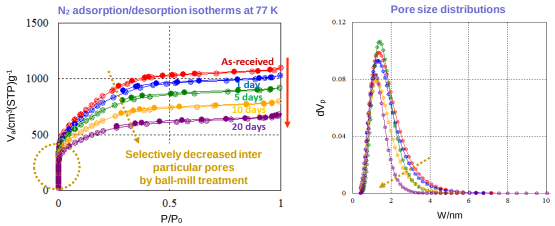
MSCIII:
Raw materials: resin
Microdomain ≈ Domain

M30:
Raw materials: Mesophase
Microdomain << Domain

SEM images of ball-milled Maxsorb-III series



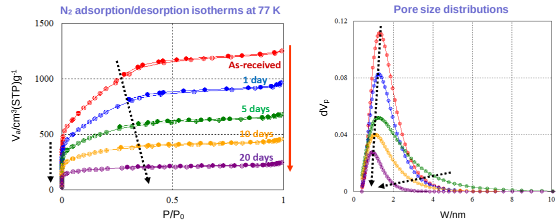
N2 adsorption/desorption of ball-milled Maxsorb-III series



	m²/g			cm³/g		nm
	Area (total)	Area (external)	Area (micro)	Vol (total)	Vol (micro)	W (micro)
As-received	2856.8	37.6	2819.2	1.60	1.60	1.14
Ball-milled for 1 day	2557.8	40.0	2517.8	1.50	1.50	1.19
Ball-milled for 3 days	2417.9	37.1	2380.8	1.39	1.39	1.17
Ball-milled for 5 days	2358.8	36.4	2322.4	1.34	1.34	1.16
Ball-milled for 10 days	2115.5	33.8	2081.7	1.15	1.15	1.11
Ball-milled for 20 days	1852.6	32.5	1820.1	0.96	0.96	1.05

1. By ball-mill treatments, the inter-particle pores (cylinder-like mesopores) were selectively removed without destroying the intra-particle pores (slit-like micropores).
2. Such novel pore models may be proved from N_2 adsorption/desorption isotherm at 77K by ball-mill treatment.

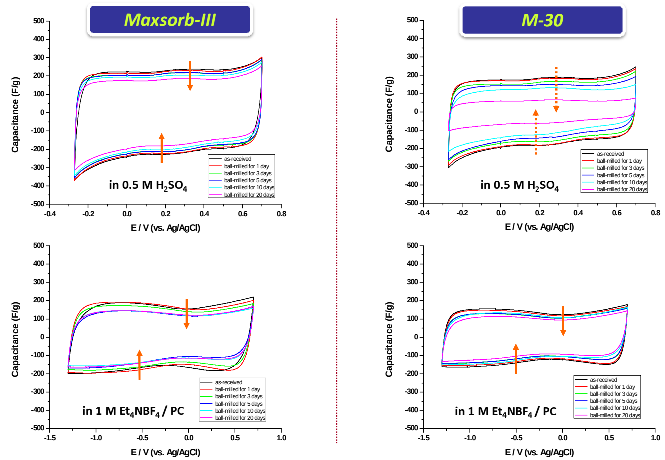
N2 adsorption/desorption of ball-milled M-30 series



	m²/g			cm³/g		nm
	Area (total)	Area (external)	Area (micro)	Vol (total)	Vol (micro)	W (micro)
As-received	2948.1	51.5	2896.6	1.81	1.81	1.25
Ball-milled for 1 day	2325.3	49.2	2276.1	1.36	1.36	1.19
Ball-milled for 3 days	1967.7	41.8	1925.9	1.08	1.08	1.12
Ball-milled for 5 days	1833.5	39.3	1794.2	0.95	0.95	1.06
Ball-milled for 10 days	1327.3	30.8	1296.5	0.62	0.62	0.96
Ball-milled for 20 days	776.1	22.8	753.2	0.31	0.31	0.83

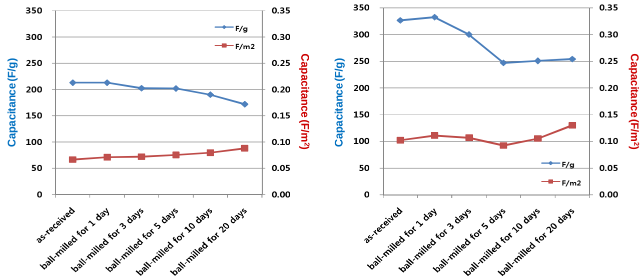
1. Both novel pore structures of M-30, inter- and intra-particle pore, were simultaneously decreased by ball-mill treatments.
2. Dramatical decrease of both pore structures in M-30 may be caused by much smaller micrographitic units derived from mesophase carbon micro beads (MCMB) which are easy to loss especially their inter-particle pores by ball-milling.

Cyclic voltammograms of ball-milled AC series



Specific capacitances of ball-milled Maxsorb-III series

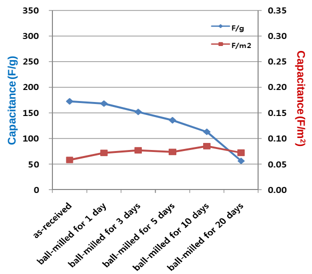
In inorganic electrolyte (0.5 M H_2SO_4) *In organic electrolyte (1 M Et_4NBF_4/PC)*



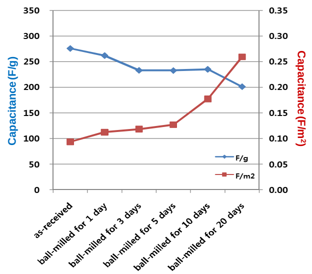
1. The capacitances in inorganic electrolyte with smaller size than intra-particle pores (micropores) were gradually decreased with increase of ball-mill times.
2. The capacitances in organic electrolyte with relatively larger ion size than that of inorganic electrolyte were steeply decreased up to 5 days and then continuously kept, with increase of ball-mill times.
3. From harsh decrease of capacitance in 1 M Et_4NBF_4/PC, we found out that the inter-particle pores selectively removed by ball-milling play an important role for EDLC in organic electrolyte.

Specific capacitances of ball-milled M-30 series

In inorganic electrolyte (0.5 M H_2SO_4)



In organic electrolyte (1 M Et_4NBF_4/PC)



1. The capacitances of M-30 in 0.5 M H_2SO_4 were largely decreased with increase of ball-mill times because both of inter- and intra-particle pores were simultaneously decreased by ball-milling.
2. The capacitances of M-30 with smaller micrographitic units which are easily destroyed by severe ball-milling for 20 days, comparing with Maxsorb-III, were dramatically decreased in both of organic and inorganic electrolytes.

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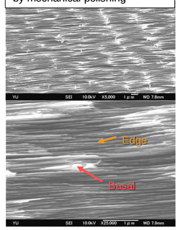
Capacitance vs. defined surfaces

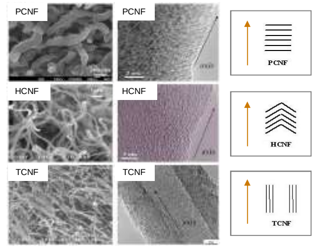
Capacitance
- Structural or its derived factors
  - Surface area & pore structure
  - Surface state – edge and basal
  - Electrical conductivity
- Surface chemistry
  - Functional groups
  - Hetero atoms on the surface
  - Metal or metal oxide on the surface

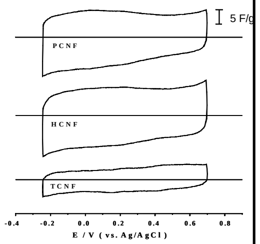
Well-defined CNF series

Capacitive performance :
Edge surface > Basal plane
Edge surface is more effective than basal plane by a factor of 3-5.

SEM images of HOPG surface by mechanical polishing







S.-H. Yoon et al. *Carbon*, 2005, 43, 1828

T.G. Kim et al. *Langmuir*, 2006, 22, 9086

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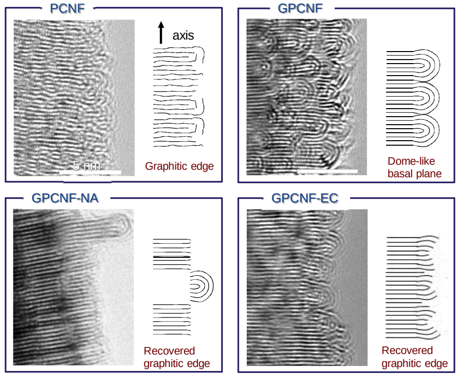
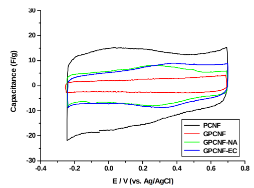
Surface-modified PCNF series



Cyclic voltammogram of GPCNF series



Elemental analysis of GPCNF series

Samples	Elemental analysis (wt%)			
	H	C	N	O (diff.)
PCNF	0.33	98.15	0.05	1.47
GPCNF	0.10	99.90	0	0
GPCNF-NA	0.15	99.12	0.06	0.67
GPCNF-EC	0.13	98.50	0	1.37

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Electrochemical oxidation by treatment

(1) **In anode (+ electrode),** treated samples by different potentials

	Results of elemental analysis (%)				Ratio of O/C
	H	C	N	O (diff.)	
as-prepared	0.81	96.88	0.00	2.31	0.02
1.0 V	1.08	93.31	0.49	5.12	0.05
1.5 V	1.07	94.68	0.45	3.80	0.04
2.0 V	0.98	91.14	0.36	7.52	0.08
2.5 V	0.99	91.11	0.37	7.53	0.08

(2) **In cathode (- electrode),** treated samples by different potentials

	Results of elemental analysis (%)				Ratio of O/C
	H	C	N	O (diff.)	
as-prepared	0.81	96.88	0.00	2.31	0.02
1.0 V	1.10	95.01	0.42	3.47	0.04
1.5 V	1.10	95.15	0.41	3.34	0.04
2.0 V	0.99	95.72	0.24	3.05	0.03
2.5 V	1.01	95.62	0.22	3.15	0.03

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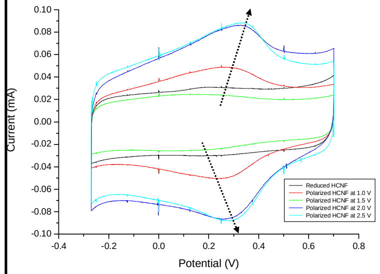
Functional Groups vs. capacitance

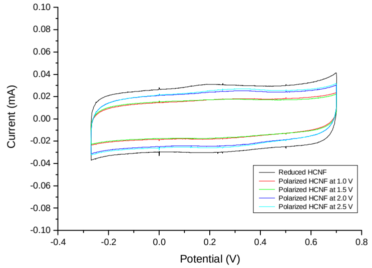
Polarized anodic HCNF by binderless polarization condition in 30 wt% H2SO4

Polarized HCNF under binderless condition in 30 wt% H_2SO_4

Anode (+ electrode)



Cathode (− electrode)



*** According to increase of the potential,**

in anode, EDLC and pseudocapacitane increased.

in cathode, capacitance decreased slightly.

Analysis of ion behaviors on the Different carbon surface using solid NMR

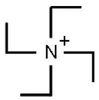
Solid-state NMR

31

Organic electrolyte：Et_4NBF_4

Cation

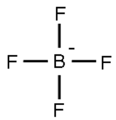
Tetra ethyl ammonium: TEA



Kinetic diam.: 0.74 nm

Anion

Tetra fluoroborate: TFB



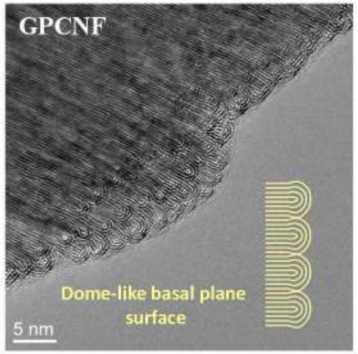
Kinetic diam.: 0.49 nm

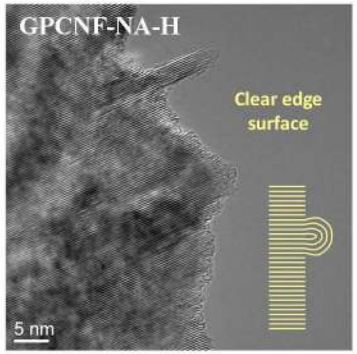
JEOL ECA400

^{11}B solid-state NMR (^{11}B:128.3 MHz)

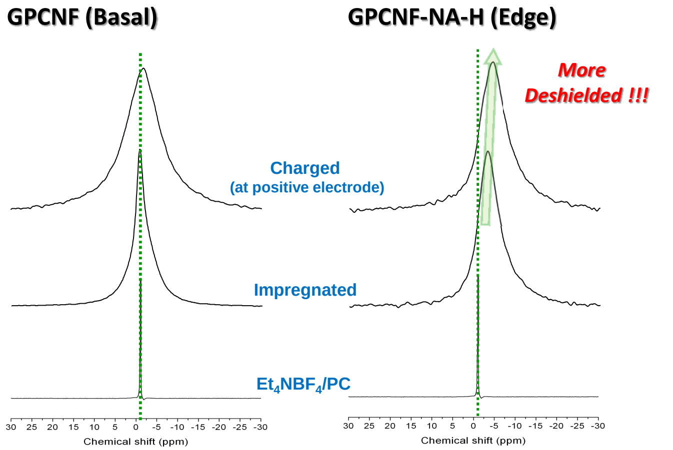
➡ **Anion behaviors in positive electrode at 3 kinds of electrode states**
- ① Impregnated state
- ② Charged state
- ③ Discharged state

Preparation of PCNFs with edge and basal planes





BF_4^- ion behaviors on the surface of GPCNFs (^{11}B-NMR)



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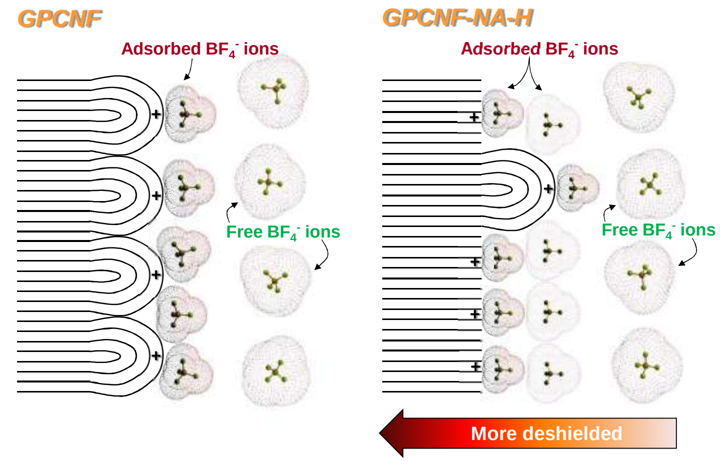
GPCNFシリーズに対するBF_4^-イオンの吸着挙動モデル



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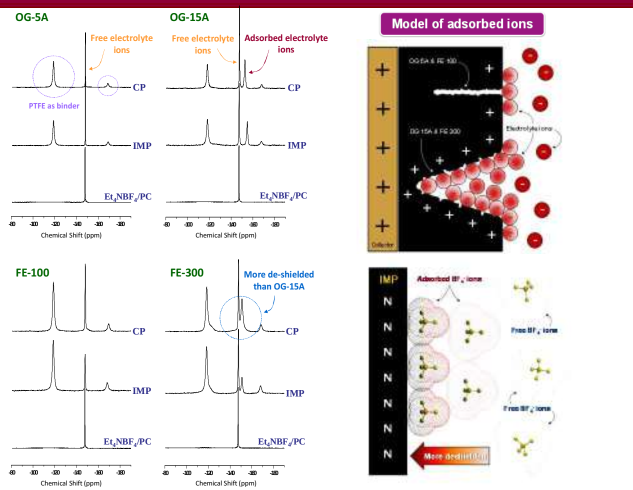
ACF vs. ^{19}F Solid NMR (Organic)



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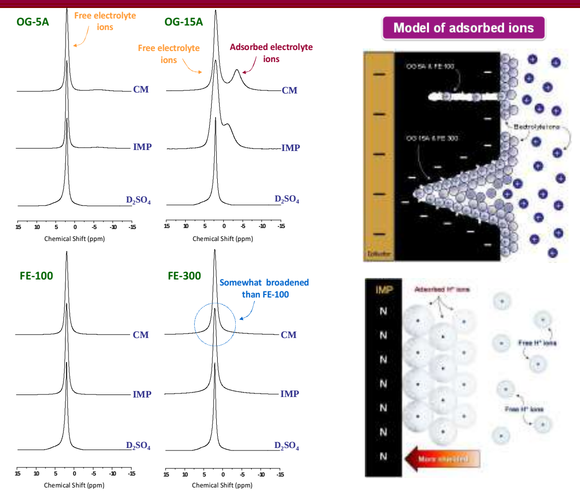
ACF vs. ^{2}H Solid NMR (Inorganic)



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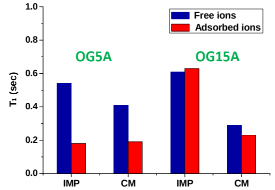
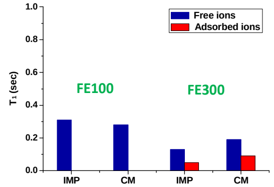
ACF vs. ^{2}H Solid NMR（T_1 value）

T_1 (sec) of OG series							
OG5A				OG15A			
IMP		CM		IMP		CM	
Free	Adsorbed	Free	Adsorbed	Free	Adsorbed	Free	Adsorbed
0.54	0.18	0.41	0.19	0.61	0.63	0.29	0.23



T_1 (sec) of FE series							
FE100				FE300			
IMP		CM		IMP		CM	
Free	Adsorbed	Free	Adsorbed	Free	Adsorbed	Free	Adsorbed
0.31	-	0.28	-	0.13	0.05	0.19	0.09



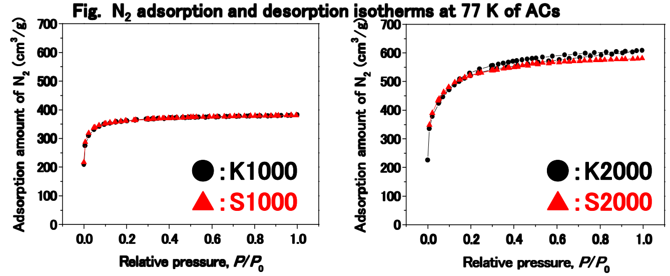
1. Small value of T1 means stronger adsorption
2. T1 goes to be short after charge.
3. T1 of FE series < T1 of OG series

Steam activation vs. KOH activation

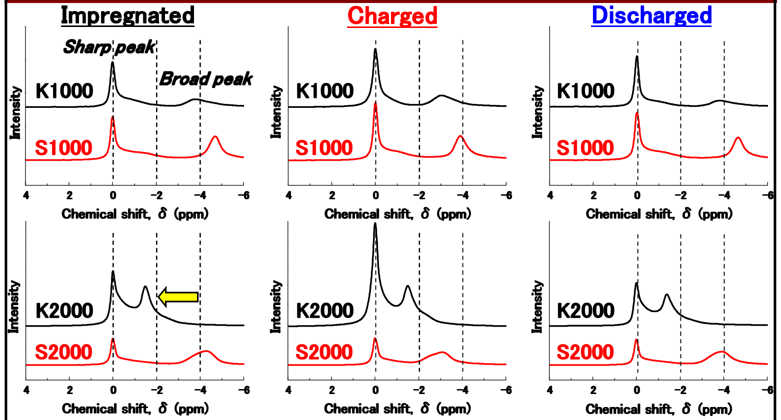
Table BET surface area, elemental composition, and capacitance of ACs

Code	Activation method (Temp., KOH/S-BEAPS ratio)	Surface area (m^2/g)	Atomic ratios (%)					Electrode density (g/cm^3)	Capacitance		
			H	C	N	O	Ash		F/g	F/cm^3	F/m^2
K1000	KOH (800℃, 2)	1240	0.70	87.6	0.18	11.5	0.00	0.69	18.7	10.3	0.015
S1000	Steam (800℃)	1250	0.82	96.1	0.00	2.94	0.18	0.73	21.5	14.6	0.017
K2000	KOH (600℃, 6)	1850	1.47	79.6	0.03	19.0	0.00	0.55	37.8	16.6	0.020
S2000	Steam (850℃)	1850	0.70	96.5	0.00	2.44	0.39	0.61	24.0	10.4	0.013

Fig. N_2 adsorption and desorption isotherms at 77 K of ACs



^{11}B solid-state NMR



※ A peak was adjusted at 0 ppm.

Sharp peak (A peak): ions on the free surface, weakly adsorbed
Broad peak (B peak): ions on the pore wall, strongly adsorbed

Relaxation time, T_1

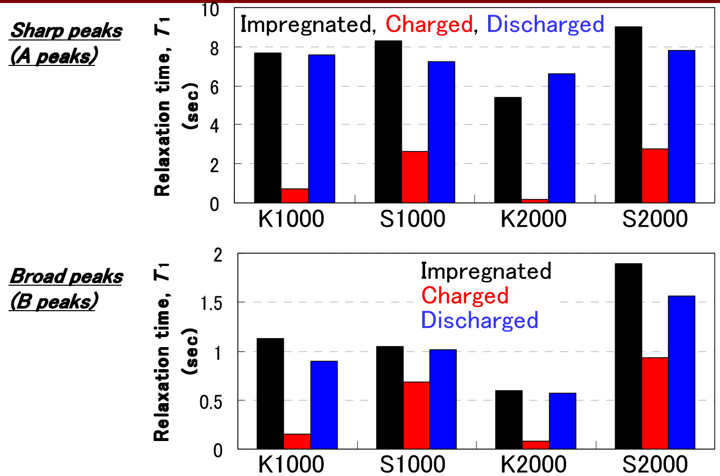


Fig. 5 Longitudinal relaxation time (T_1) of ions at various states

Discussion

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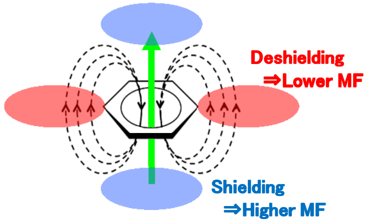
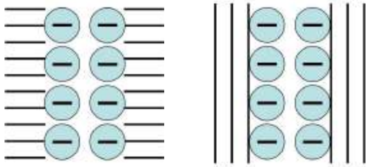
Effect of pore wall structure (Edge and Basal)

Chemical shift

Ring current effect



Capacitance



T. Kim *et al.*, *Langmuir* (2006), **22(22)**, 9086–9088.

Ion adsorbed on the edge → Low MF shift, High capacitance
→K2000 (KOH activated) has more edge walls.
Ion adsorbed on the basal→High MF shift, Low capacitance
→S2000 (steam activated) has less edges in pore walls.

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Difference of KOH & steam activations

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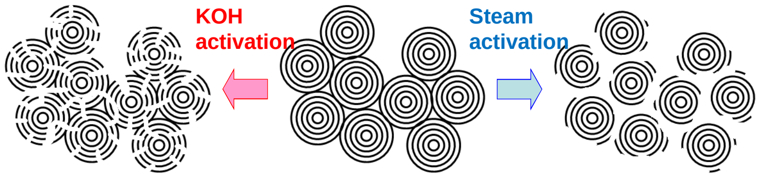
In the case of low surface area ACs (K1000 and S1000),

The activations were not much proceeded for both KOH and steam activations. Small and homogeneous pores.

In the case of high surface area ACs (K2000 and S2000),

The activations were fully proceeded for both KOH and steam activations. Large and heterogeneous pores. KOH showed the more dispersion property than steam, resulted in many edges.



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Quantitative analyses of ion behaviors on the different activated carbons using solid NMR

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Result of experiment ①

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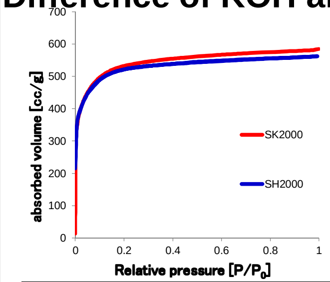
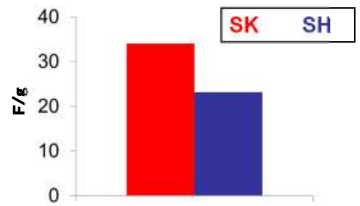
Difference of KOH and steam activations





Sample	BET S.A. [m^2/g]	Atomic ratios[%]					Electrode density [g/ml]	Capacitance		F/g ratios (SK/SH)
		H	C	N	O	ash		F/g	F/ml	
Electrolyte : Et_4NBF_4/PC										
SK2000	2007	1.47	79.6	0.03	19.0	0.00	0.40	34.0	13.6	1.5
SH2000	1969	0.70	96.5	0.00	2.44	0.39	0.44	23.2	10.2	

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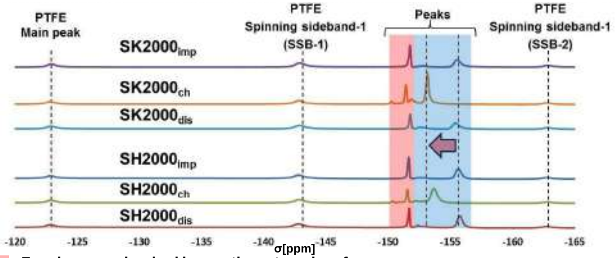
Results of experimental ①

1 M Et4NBF4/PC electrolyte, 19F-NMR



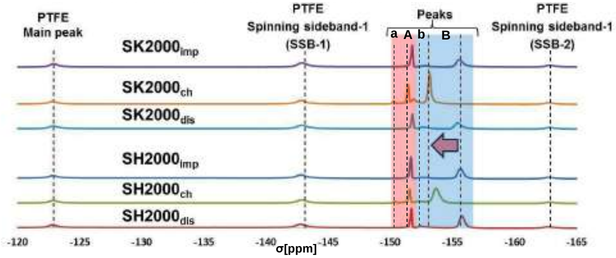
Free ions or adsorbed ion on the external surface

Adsorbed ions on the pore walls

	PTFE main peakによるBF4- normallization			Peak area ratio
	PTFE Main Peak	Peaks	ch-dis	SK/SH
$SK2000_{imp}$	1	3.49		2.5
$SK2000_{ch}$	1	8.11	2.89	
$SK2000_{dis}$	1	5.22		
$SH2000_{imp}$	1	4.32		
$SH2000_{ch}$	1	6.39	1.13	
$SH2000_{dis}$	1	5.26		

Results of experiment ①

1 M Et4NBF4/PC electrolyte, 19F-NMR



Sample	Relaxation time (T_1)[s]			
	a	A	b	B
$SK2000_{ch}$	0.27	0.34	0.14	0.13
$SK2000_{dis}$	—	2.87	1.53	1.13
$SK2000_{imp}$	-	3.25	2.47	1.37
$SH2000_{ch}$	0.41	0.50	0.41	0.57
$SH2000_{dis}$	—	3.03	1.43	1.51
$SH2000_{imp}$	—	3.10	2.21	1.78