第9講義
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知の新世紀を拓く

Preparation and application of activated carbon

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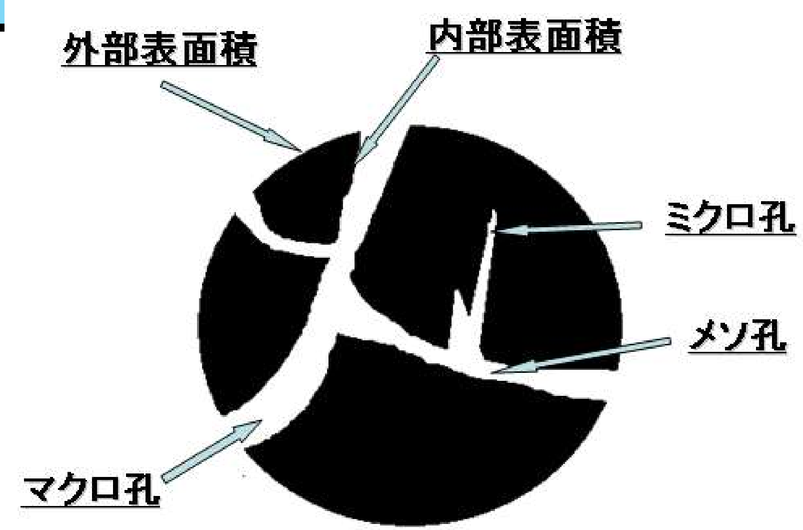
Activated Carbon

Typical porous carbon material which can be prepared through the activation of organic materials. AC is usually used as adsorption material.



Application

- Water purification
- Air pollution protection
- EDLC etc.

Activation

Gas
- Steam
- Air, CO_2 etc.

Chemical
- Alkali（KOH、NaOH）
- Salt, etc.

Classification of pores

Macropore	w > 50nm
Mesopore	2nm < w <50nm
Micropore	w < 2nm

Preparation of Activated Carbons

Selection of Carbon Precursor

- Pore Framework / Density
- Properties of Pore Wall, Composition / Graphitic Extent
- Reactivity at Activation

Activation

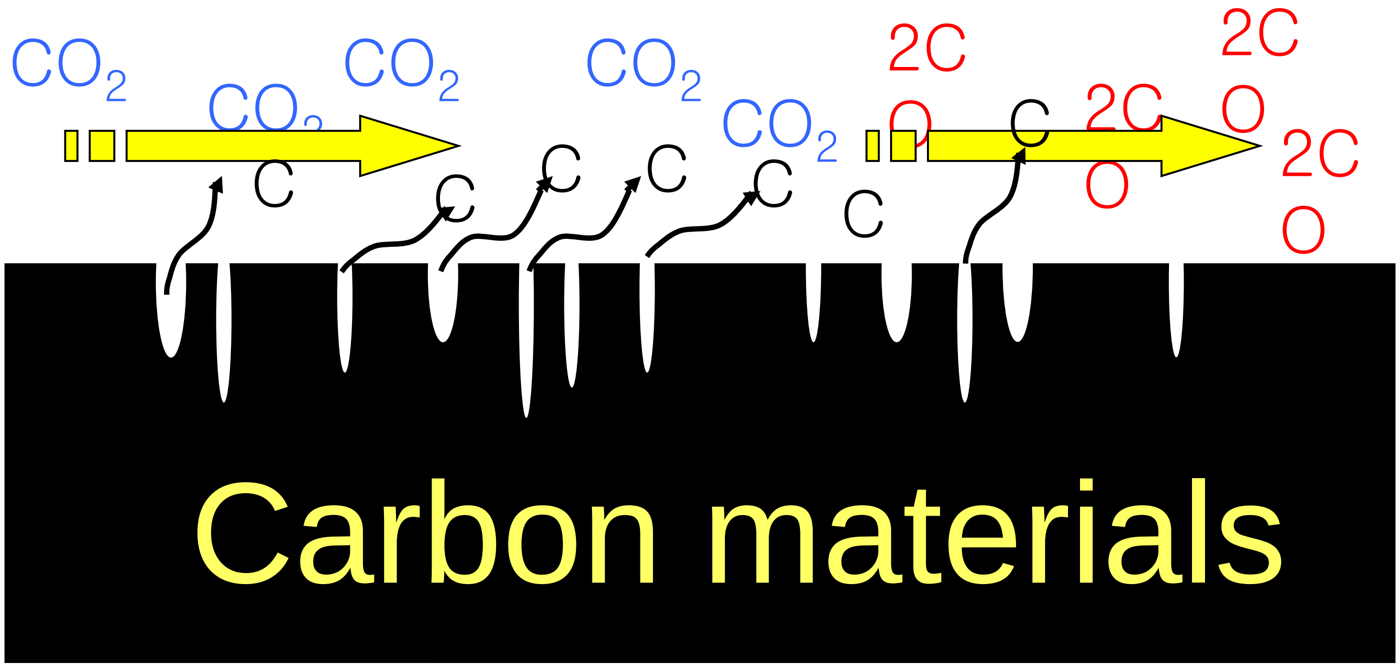
- CO_2, H_2O
- Alkali Hydroxides / Carbonates; More Research
- Selective Catalytic Gasification ; Catalyst Control

Very Large Surface Area > 3000 m^2/g
Adequate Pore and Wall

Post-Treatment

- Pore Adjustment
- Functional Groups, Introduction, Adjust and Removal
- Post-Graphitization

Activation



Activation reagents

- Air, CO2, Steam
- KOH (NaOH), ZnCl2

Mechanism of steam activation

$C+H_2O = H_2+CO$ -29.4kca

$C+2H_2O = 2H_2+CO_2$ -19.0kcall

Basically exothermic reaction
Occurring over 750℃

$C+H_2O \rightleftarrows C(H_2O)$

$C(H_2O) \rightarrow H_2+C(O)$

$C(O) \rightarrow CO$

Steam reacted with carbon
Steam decomposed into gases
CO emitted

$C+H_2 \rightleftarrows C(H_2)$

Produced hydrogen controls reaction to decrease the active site of carbon

$CO+C(O) \rightarrow C+O_2$

$CO+(H_2O) \rightarrow CO_2+H_2+9.6kcal$

Nucleated CO reacted with surface oxygen and reacted With steam to produce CO2

※(　)shows the state of molecules

・Hydrogen reacted with carbon and decreased the active site of carbon, but did not affect the CO amount.

・Ashes contained carbon materials played as catalyst for gasification which can change the rate of activation.

Mechanism of KOH activation

$2KOH \rightarrow K_2O+H_2O$
（Dehydration）

Catalytically proceeded under potassium oxide

$C+H_2O \rightarrow H_2+CO$
（Water gas reaction）

$CO+H_2O \rightarrow H_2+CO_2$
（Water gas shift reaction ）

$K_2O+CO_2 \rightarrow K_2CO_3$

Carbon mainly consumed as K_2CO_3

$K_2O+H_2 \rightarrow 2K+H_2O$

$K_2O+C \rightarrow 2K+CO$

K metal produced by the reduction with hydrogen and carbon.

- Higher surface area compared to steam activation.
- Almost no CO, CO_2 emitted.
- Potassium metal can broaden the stacking interlayers through the intercalation over 800℃.

KOH
MP：380℃
BP：1324℃

K_2O
MP：490℃

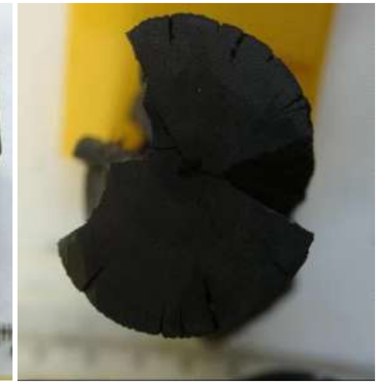
K_2CO_3
MP：891℃

K
MP：64℃
BP：774℃

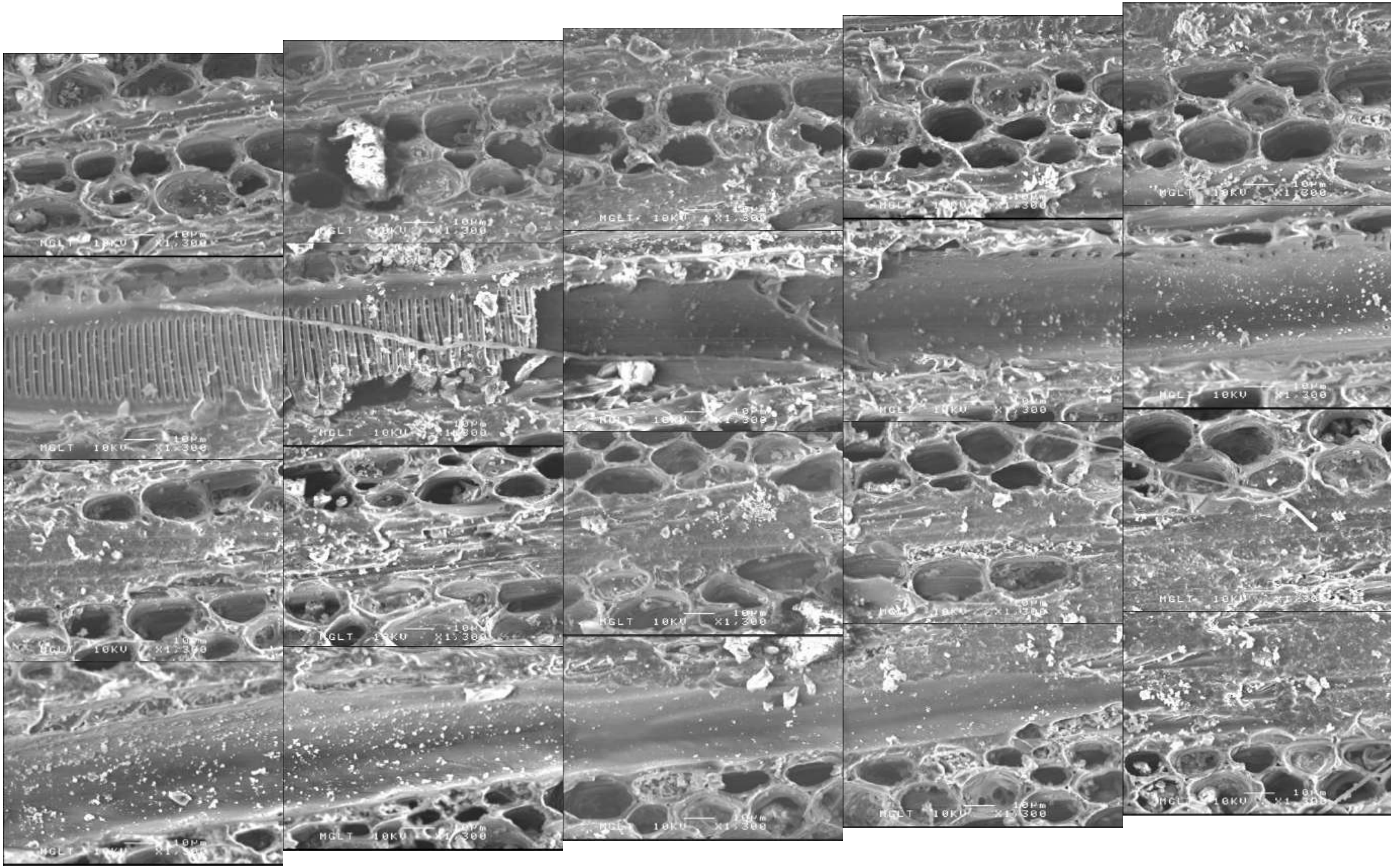
Shapes and Forma of Activated Carbon

As-Produced or Fabricated Shapes

1. **Powder**
2. **Tubular**
3. **Granular**
4. **Extrudate**
5. **Fiber**
6. **Cloth**
7. **Disk**
8. **Filter Honey Comb**

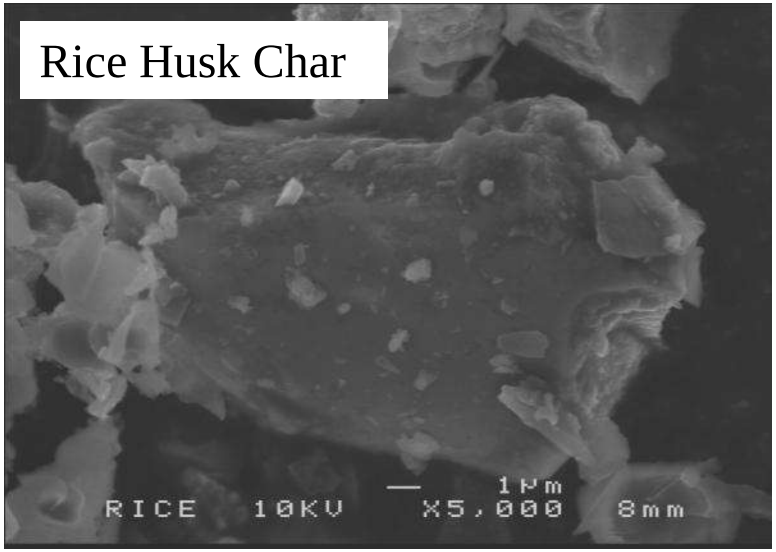
Indonesia Mangrove Char		
Yukari Char		
備長炭		

Morphology of Charcoals

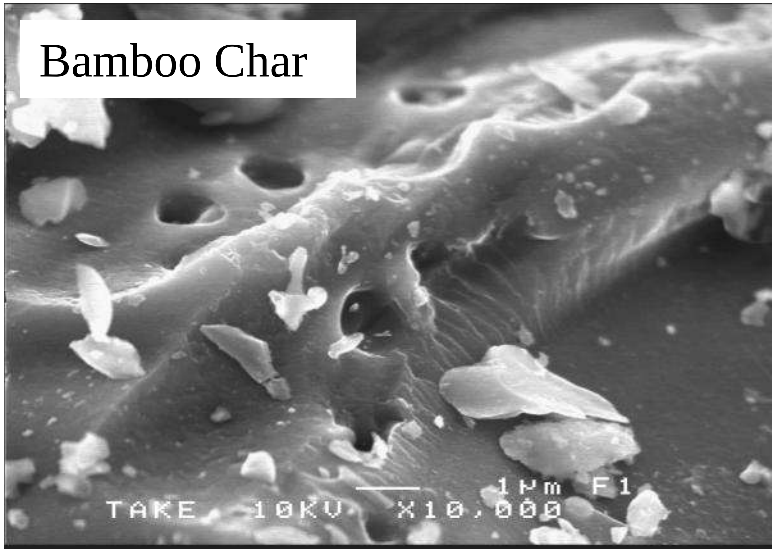


SEM montage of Indonesia mangrove charcoal (longitudinal section)

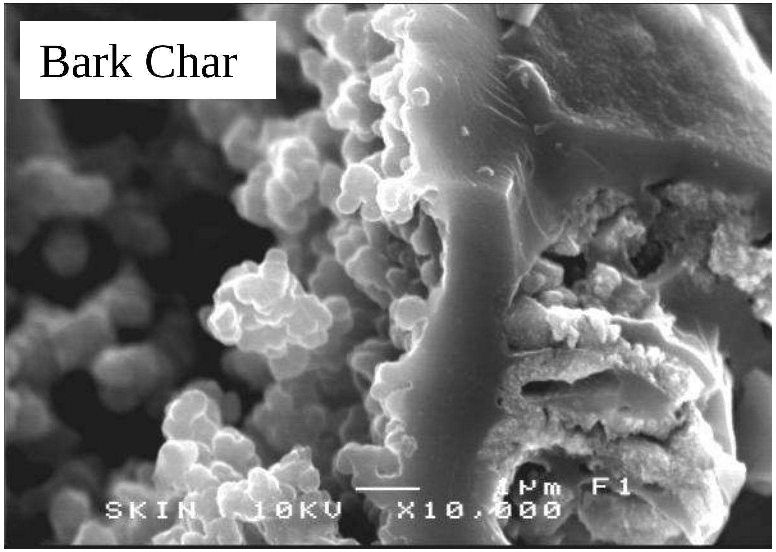
Morphology of Biomass Chars



Rice Husk Char



Bamboo Char

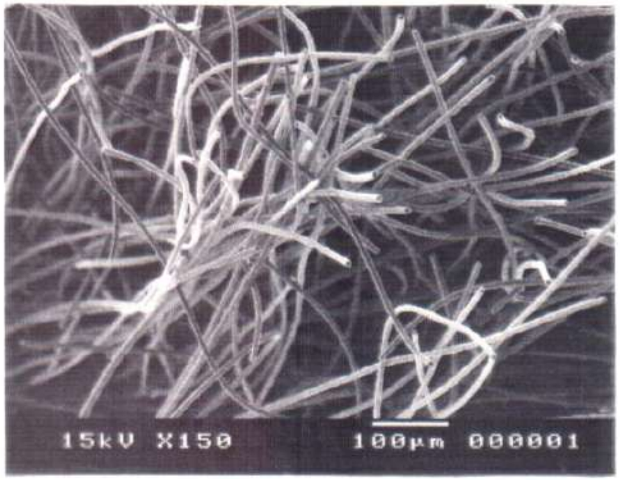


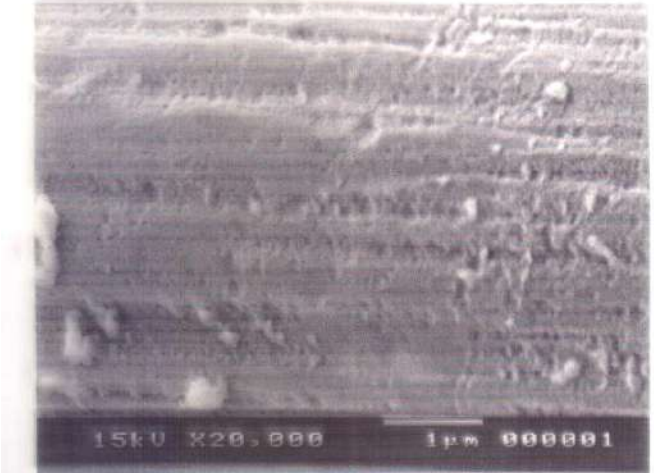
Bark Char

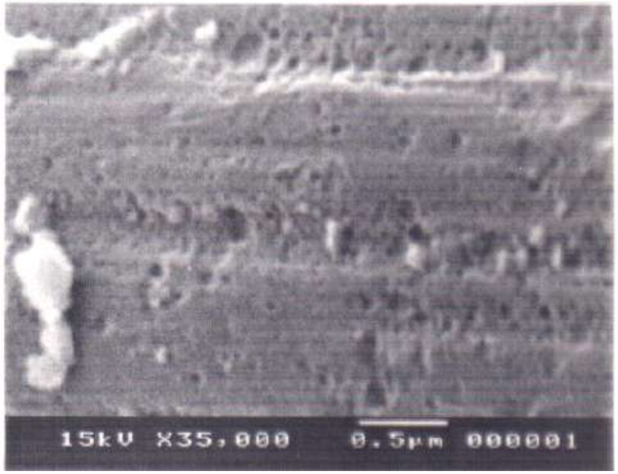
Chip's Dust Char

(Bark and Chip's Dust are from Acacia Mangium)

SEM Photographs of PAN-based CF

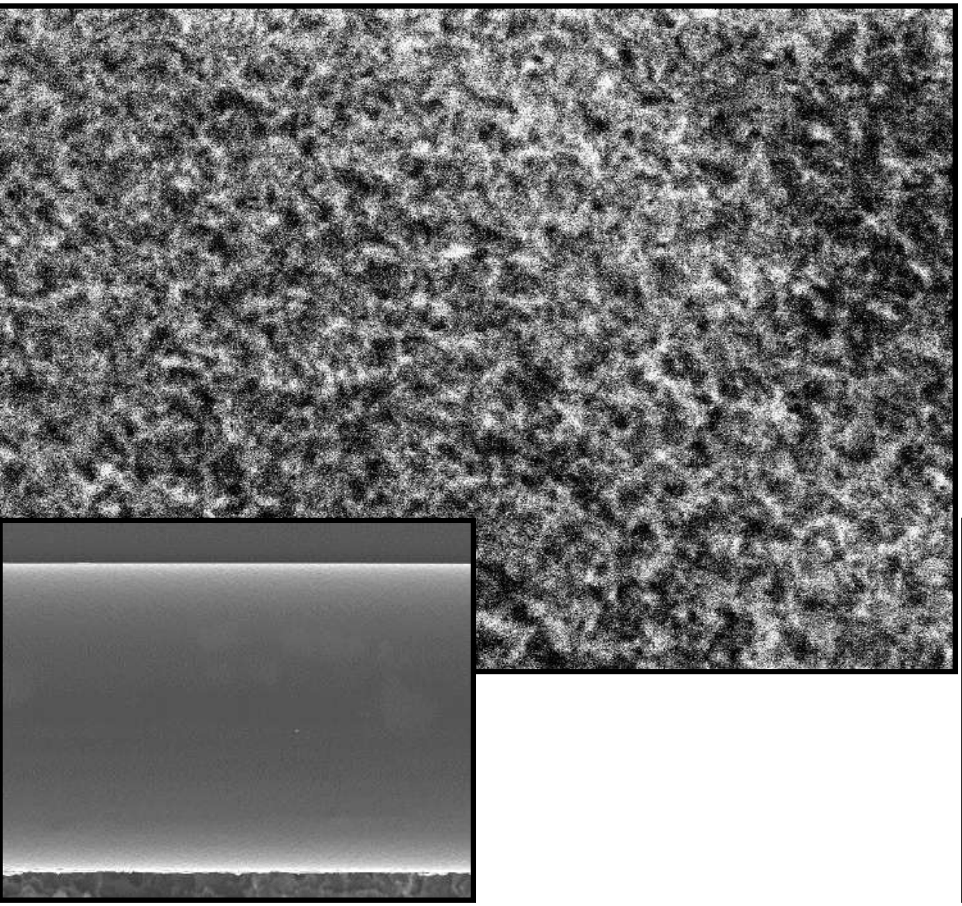




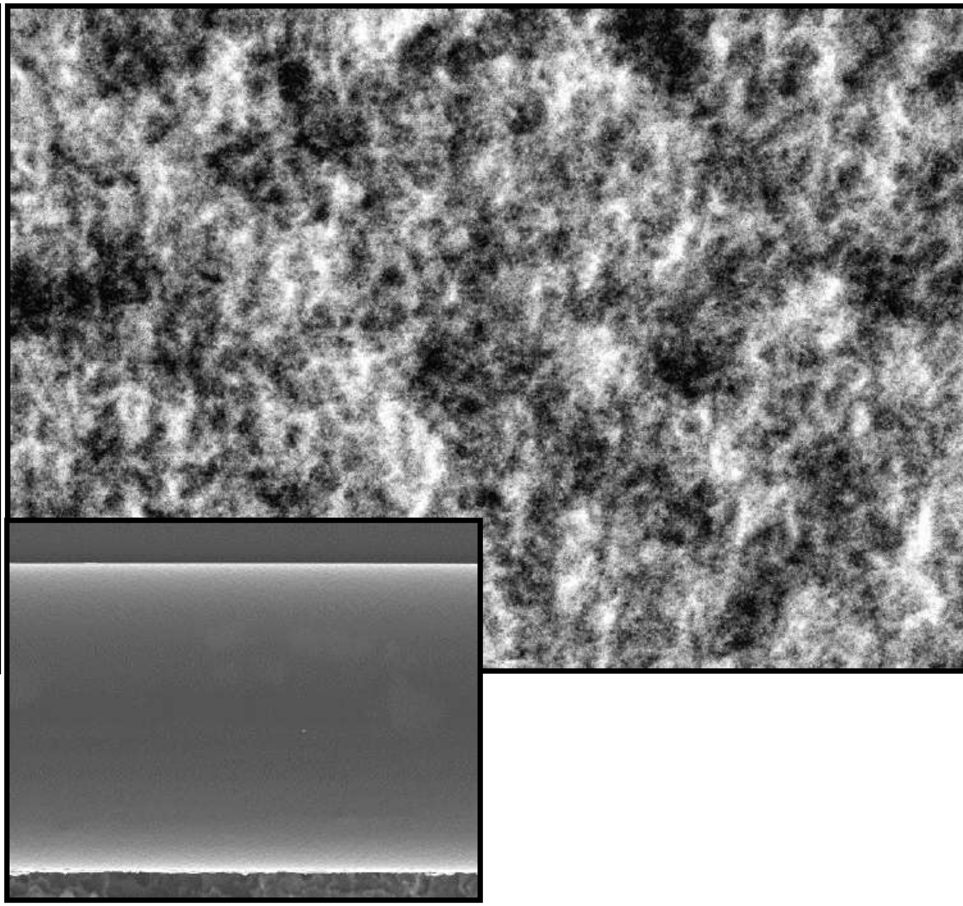


Surface Morphology of Pitch based ACFs

OG5A

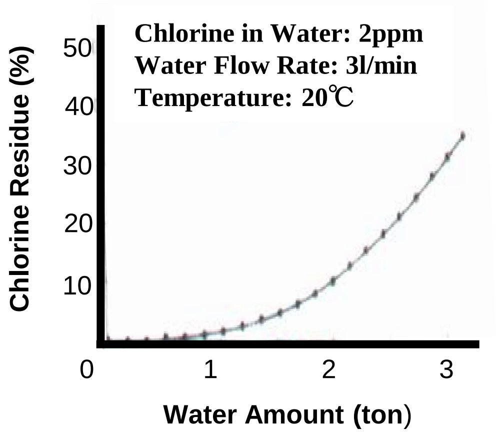


OG-15A

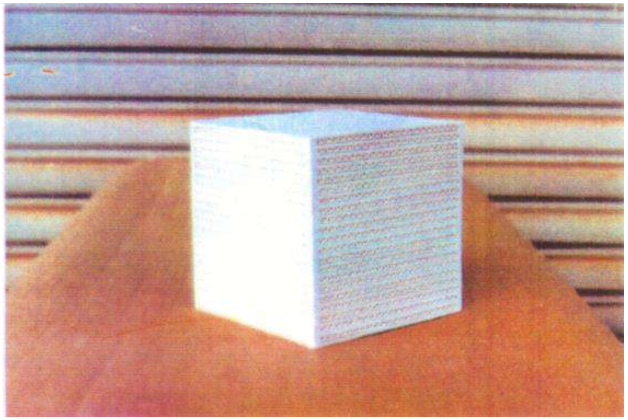


ACF Products in Particular Forms

Felt	Paper	Manufacturing Products	
		 Water Filter	 Small Water filter
• Thickness 1~8 mm ACF Coat 60~100% • Mixing organic fibers to improve the strength and dimension stability. • Needle punched felt (FN type) heat-processed felt (FH type). • Selection according to the concentration and amount of the contaminant.	• Thickness 0.2~0.8 mm ACF Coat 60~70% • Anti-water • Anti-chemicals • Easy formation into any shapes	• Columnar • Low resistivity	• Chlorine removal

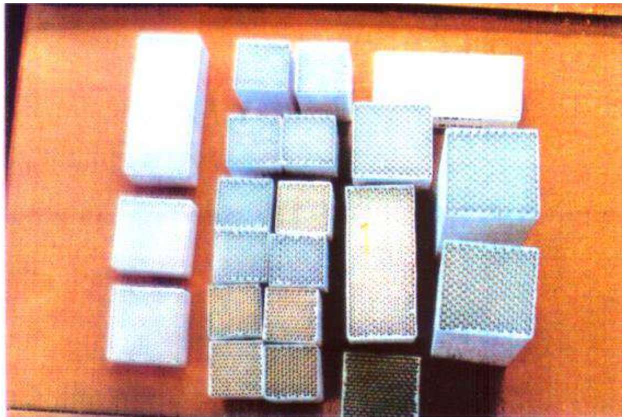


Sintered Honeycomb-shaped Ceramic Products

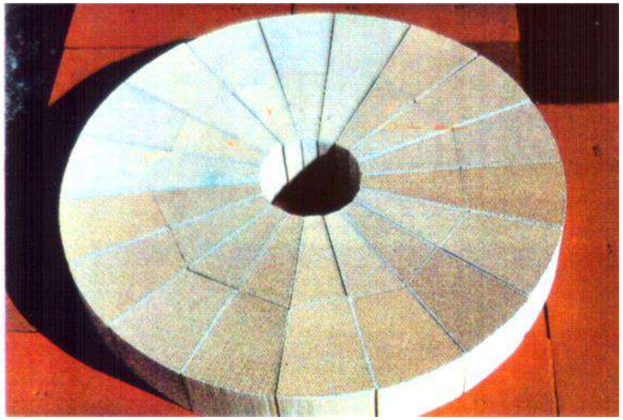


Cross-flow Sensible heat exchanger element

Material:
Silica alumina
Size: W300×L300
×H300 mm
Temperature
800℃max



Catalyst carrier



Rotor for heat exchanger

DIA: 1,900 ø
THK: 200 mm

Analyses of Pores

Adsorption　Volumetric

Prove Molecules

Interaction with Surface

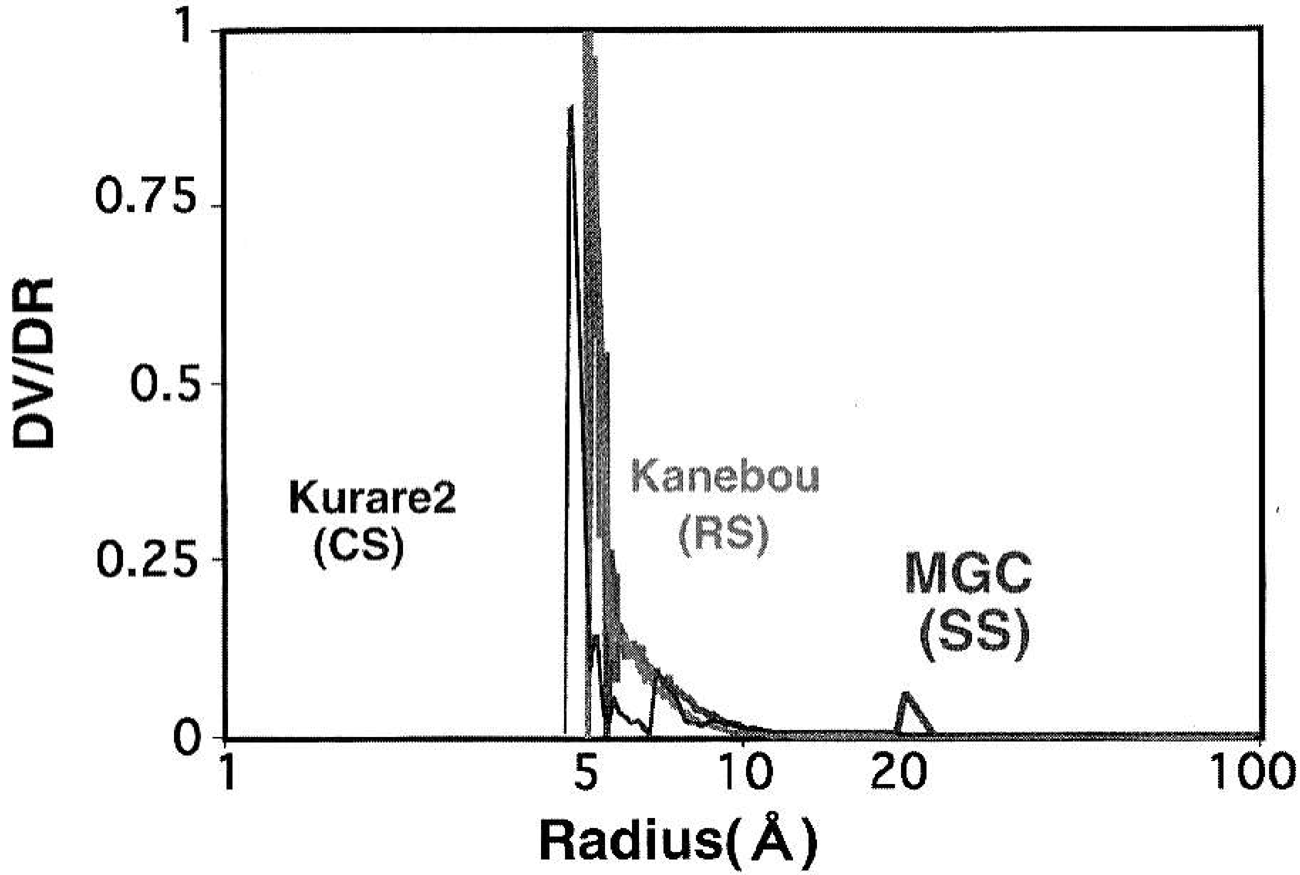
Xe-NMR

Chemical Adsorption

Direct Observation

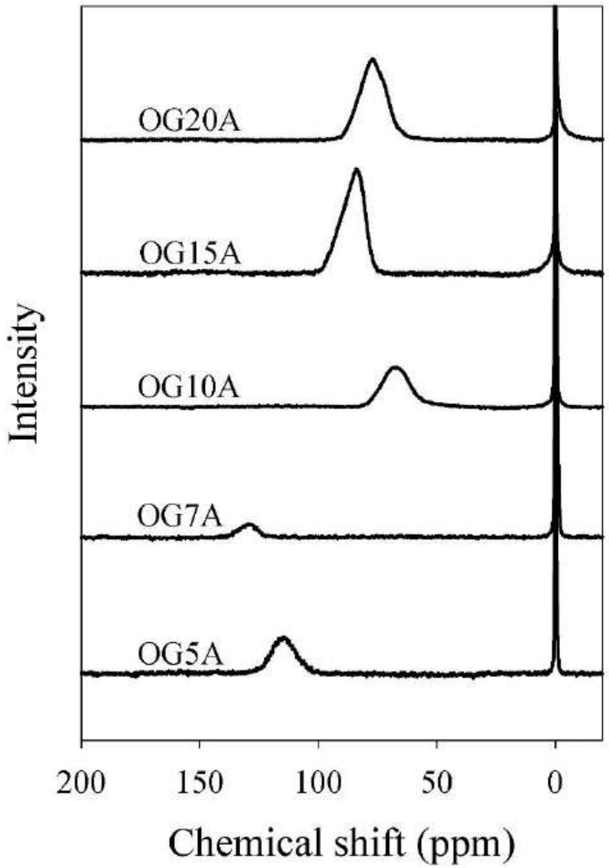
HR-SEM, HR-TEM and STM

Pore Size Distribution of AC

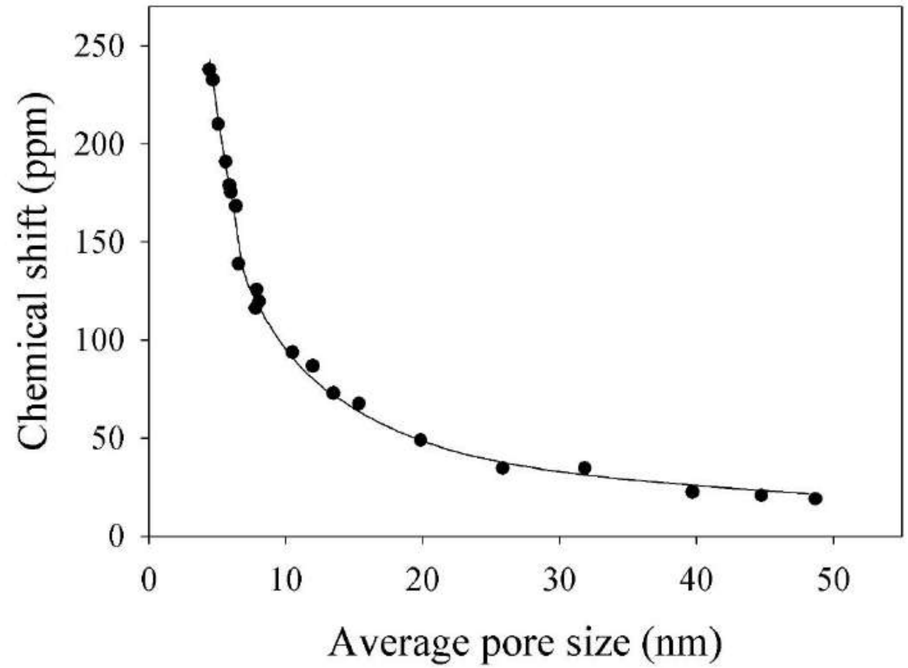


^{129}Xe-NMR Spectroscopy

^{129}Xe-NMR spectra of ACFs



Master curve between average pore size and chemical shift



Average pore size of ACFs

Some physical properties of OG-ACFs

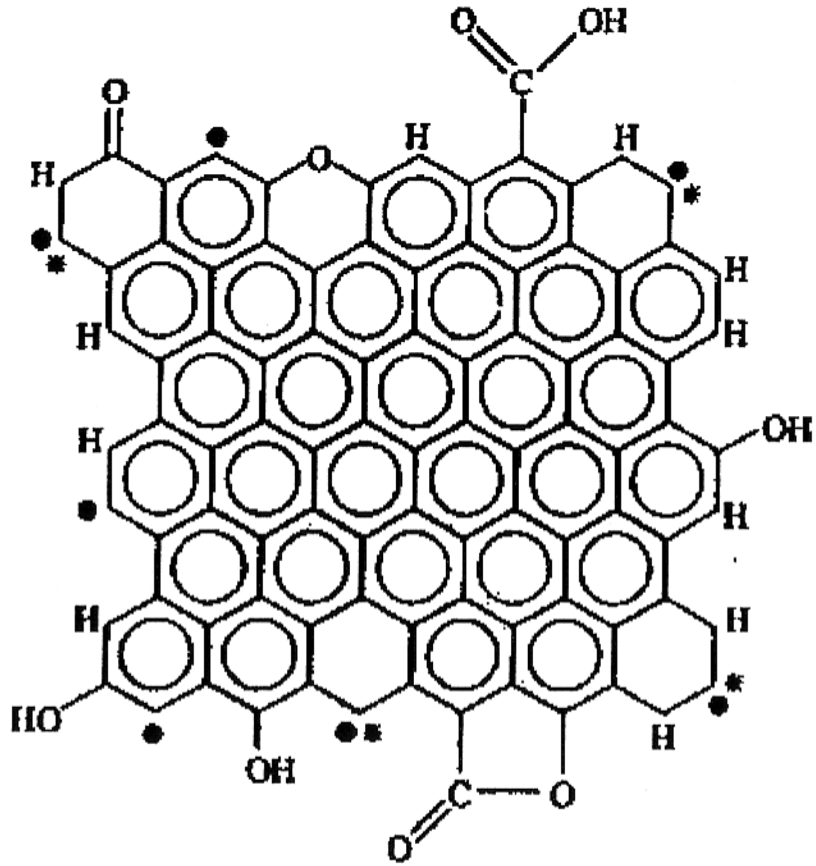
Sample	S_{BET} (m^2/g)	V_{total} (cm^3/g)	Average diameter (nm)
OG5A	573	0.31	0.9
OG7A	690	0.36	0.8
OG10A	953	0.52	1.5
OG15A	1390	0.75	1.2
OG20A	1862	1.00	1.3

S_{BET}: surface area calculated between (0.05-0.35)P/P_0 using nitrogen adsorption at 77K ;

V_{total}: total pore volume calculated at P/P_0=0.98;

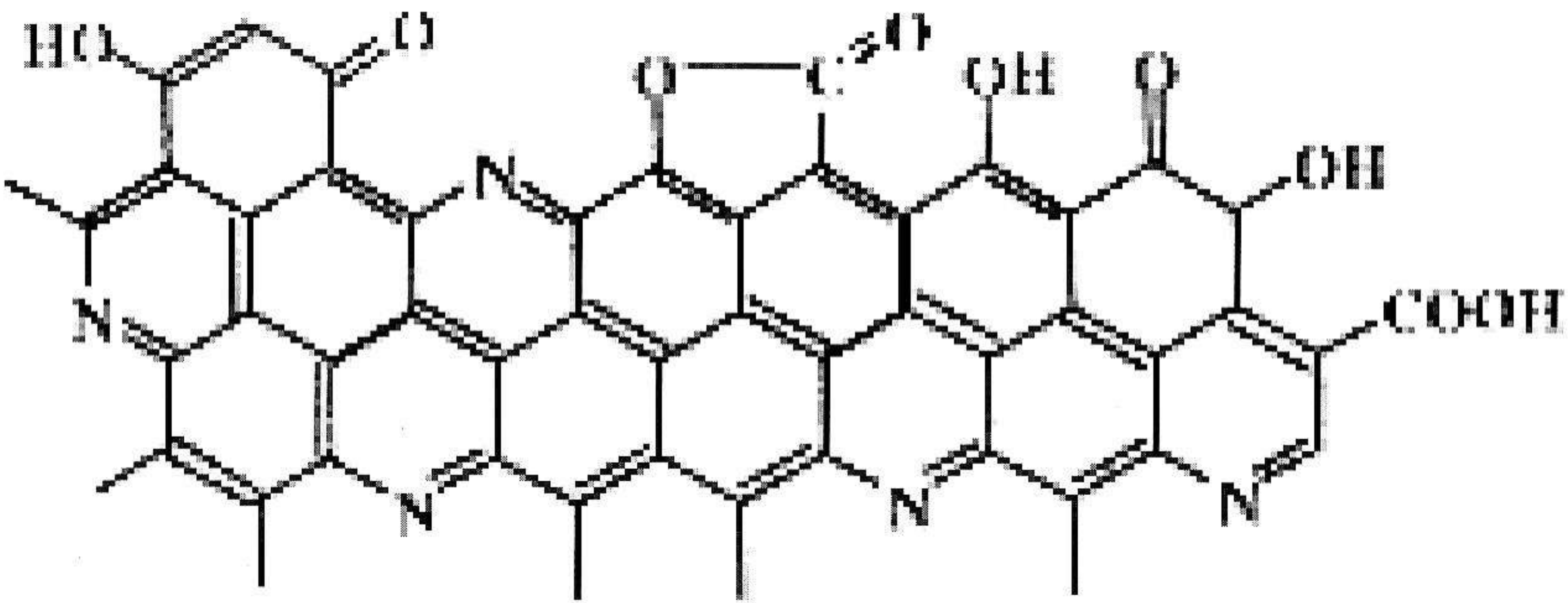
Average diameter of pore was determined by ^{129}Xe-NMR measurement .

Surface oxygen functional groups of ACF



This structure is representative of an activated carbon with a crystallite width of 15 Å and an elemental analysis (by weight) of 87.5% C, 11.3% O, 1.2% H, ● represents an unpaired σ electron ; ● * represents an "in-plane σ pair" with * being a localized π electron. (Radovie)

Surface functional groups of PAN-based ACF



Domain structures of activated carbons

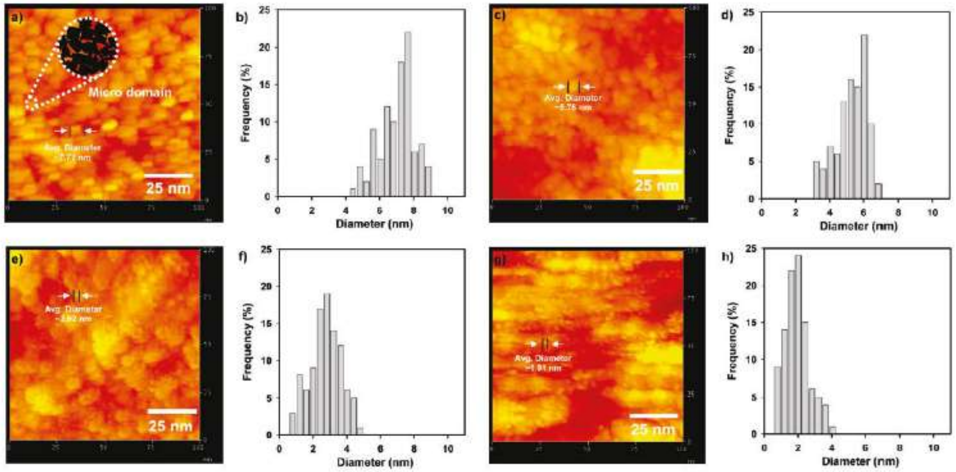
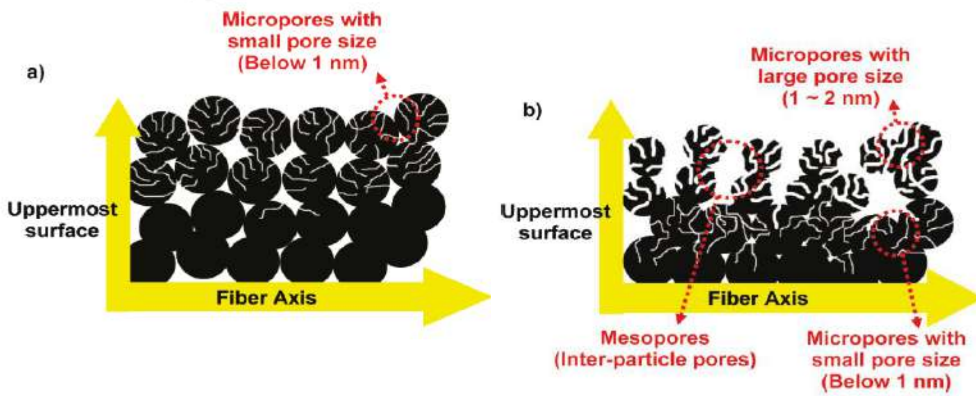
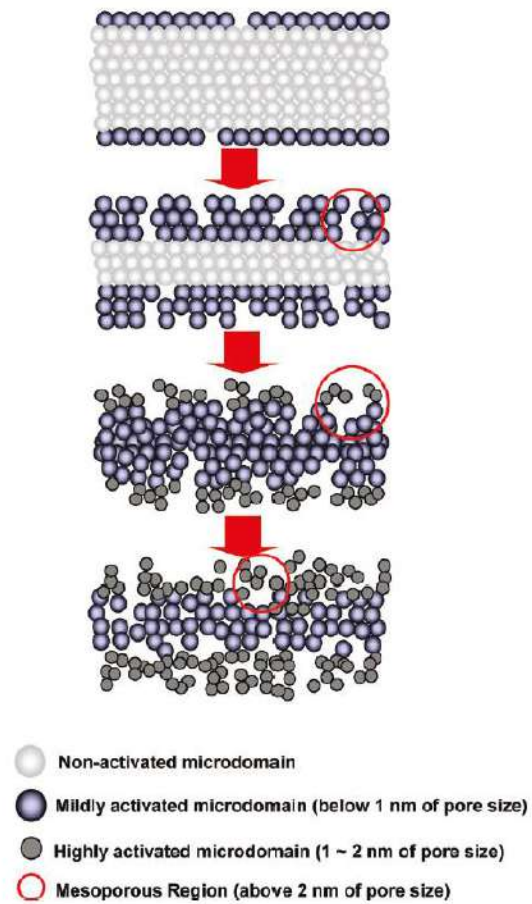


Figure 3. STM images of (a) OG5A, (c) OG7A, (e) OG10A, and (g) OG20A. The surface of ACF is composed of a microdomain with a few nanometers of diameter, and the diameter is reduced with an increasing degree of activation. (b, d, f, and h) Histograms showing particle size distributions of microdomains corresponding to samples of panels a, c, e, and g, respectively.

Scheme 3. Proposed Models for the Pore Structure of Activated Carbons Based on the Microdomain Component: (a) Mild Activation Condition and (b) Severe Activation Condition

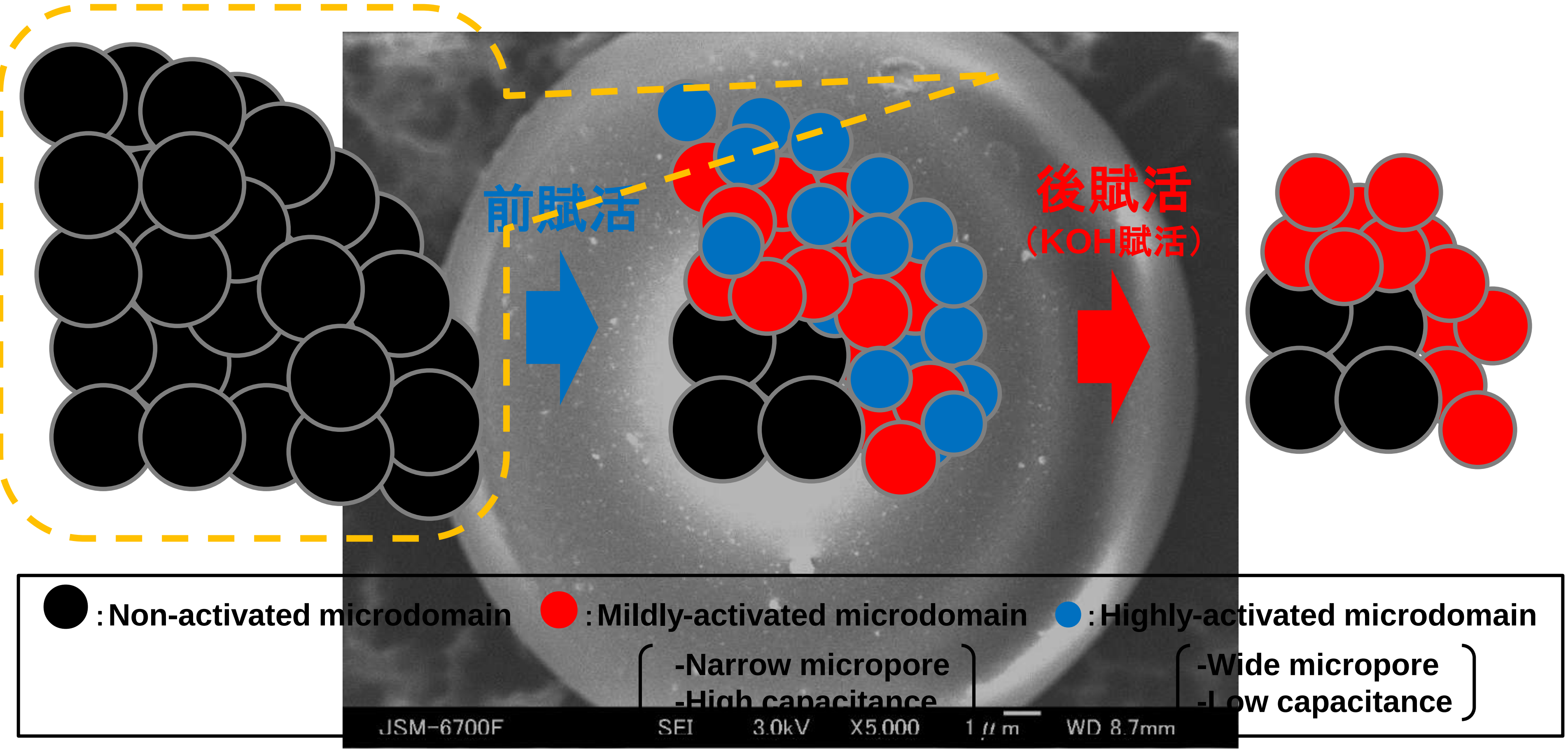


Scheme 2. Schematic Diagram of the Activation Process Based on the Microdomain Structure



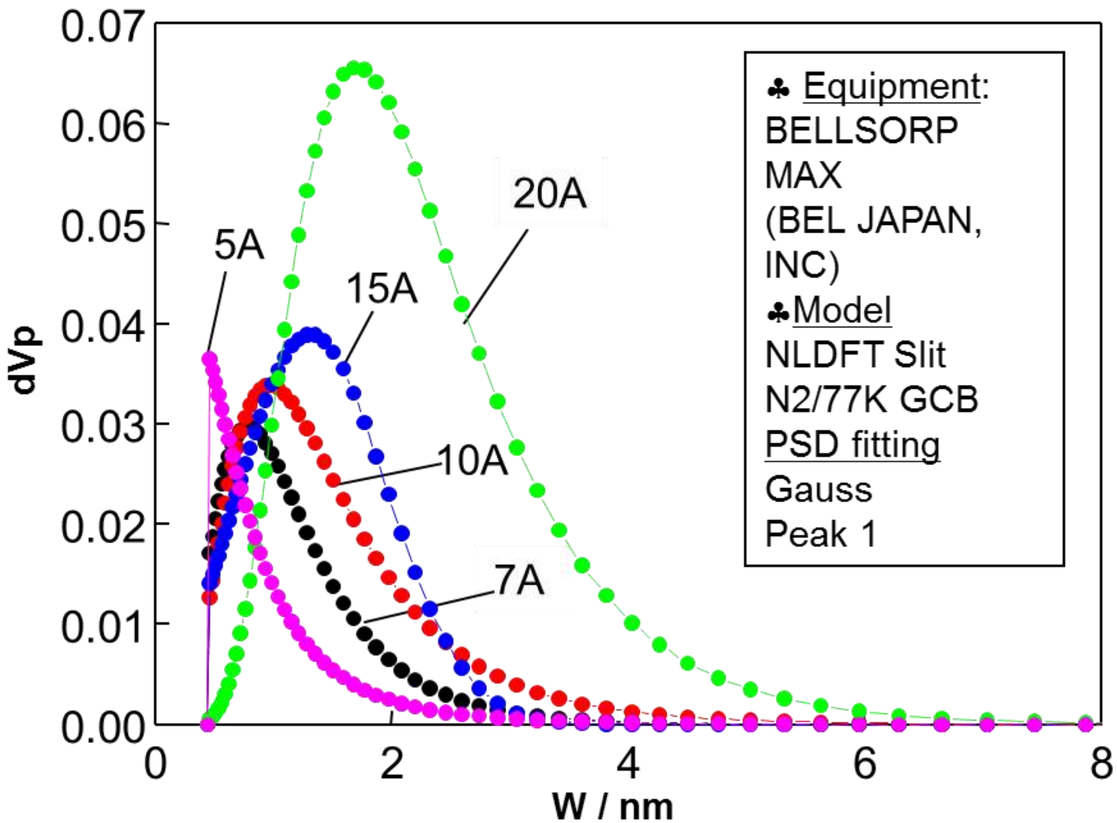
Nanako Shiratori, Kyung Jin Lee, Jin Miyawaki, Seong-Hwa Hong, Isao Mochida, Bai An, Kiyoshi Yokogawa, Jyongsik Jang and Seong-Ho Yoon, Langmuir, 25(13), 7631-7637 (2009).

Schematic model of after-activation base on domain theory



・Activated can makes micropores in every domain, but relatively larger micropores formed at outside located domains. After-activation effectively removes the domain located at outside, and finally increases the micropore efficiency to capacitance.

Pores and their distribution（NLDFT method）



♣Advantage of DFT method

Determination of a pore size distribution in the wide range of pore size from micro pore to meso pore.

♣Disadvantage

This method needs

>measurement in low pressure

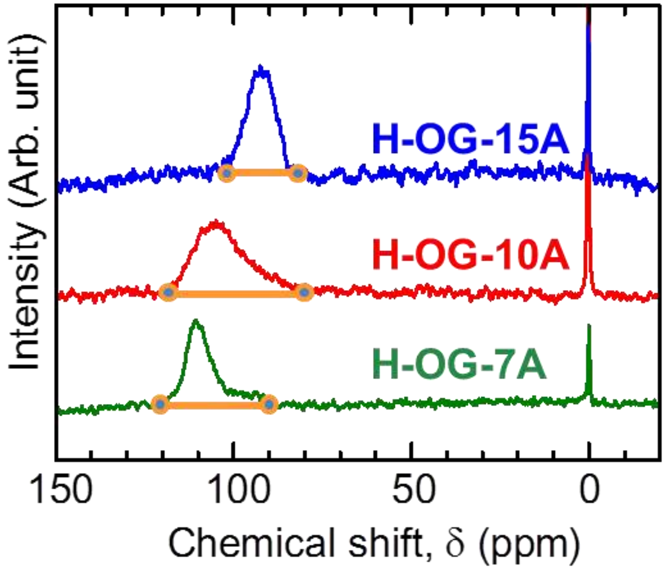
>assumption of pore structure

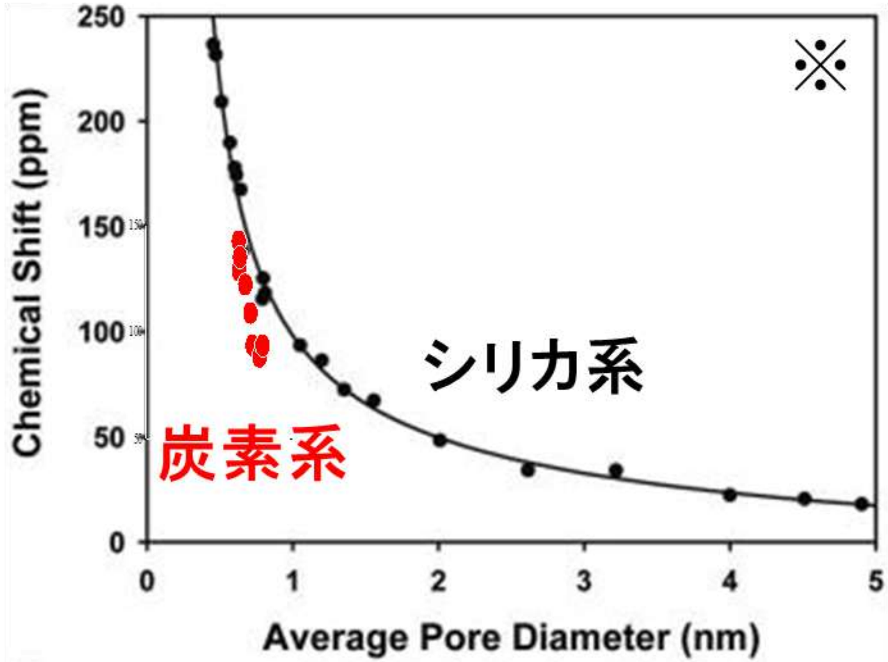
>homogeneity of adsorbent surface

	OG5A	OG7A	OG10A	OG15A	OG20A
pore size at peaks (nm)	Less than 0.44	0.72	0.98	1.28	1.86
Pore distribution range in this DFT profile (nm)	~2.8	~3.0	~5.0	~3.0	0.44~7.0

◆The pore size at peak increased in the order of OG5A<7A < 10A < 15A < 20A.

Xe-NMR





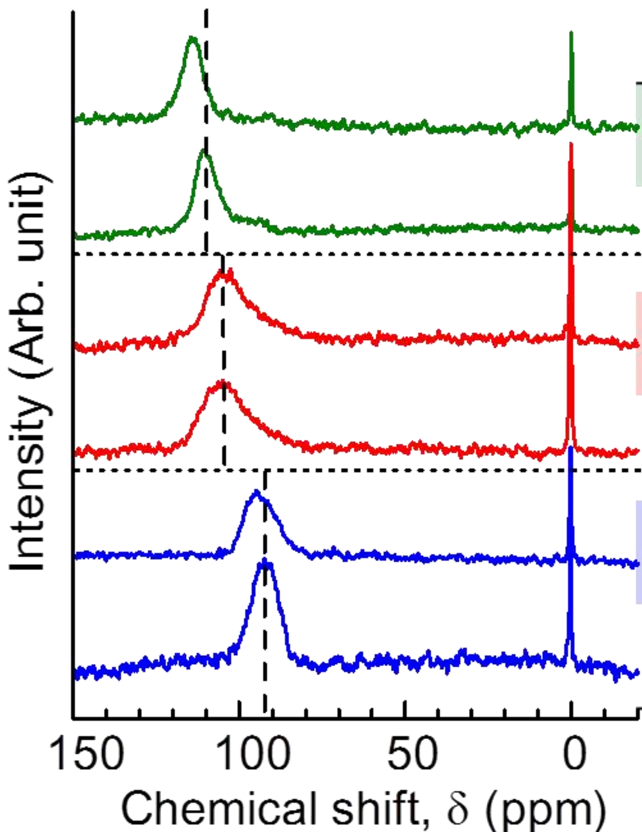
細孔径・細孔径分布解析結果

sample	^{129}Xe-NMR		N_2 adsorption		
	Avg.	range	αs	NLDFT	range-;@NLDFT
H-OG-7A	0.96	0.88~1.27	0.65	1.18	0.47~1.35
H-OG-10A	0.99	0.87~1.27	0.73	1.02	0.45~4.97
H-OG-15A	1.11	1.00~1.29	0.80	1.11	0.45~5.13

※N.Shiratori, et al., *Langmuir* 2009, 25(13), 7631-7637.

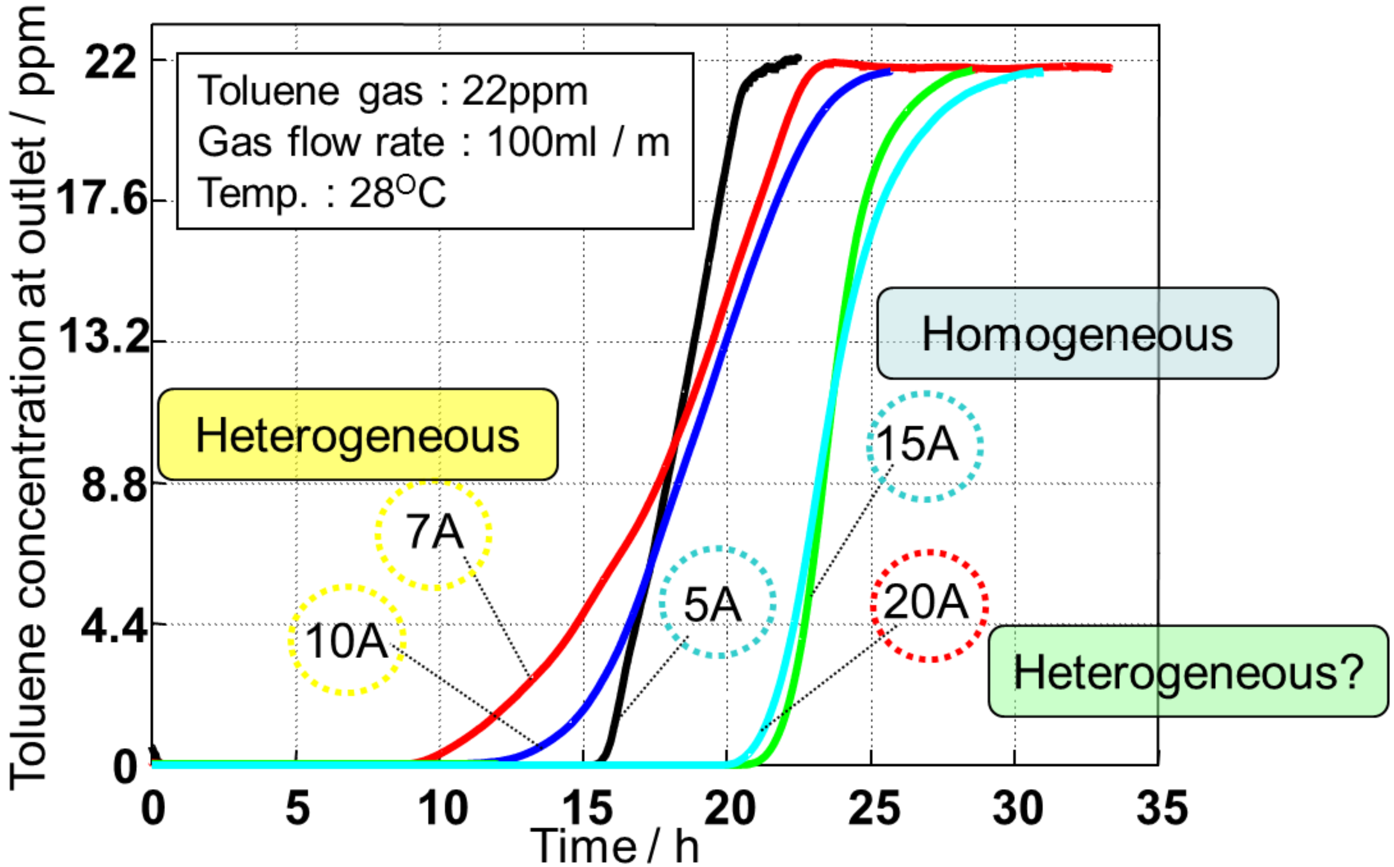
Xe-NMR method

OG-XA (X=7,10,15) ⟷ 官能基 ⟷ HOG-XA (X=7,10,15)



sample	$w_{\text{-}\alpha s}$ (nm)	$O_{(diff.)}$ (wt%)
OG-7A	0.68	6.1
H-OG-7A	0.65	4.4
OG-10A	0.72	6.4
H-OG-10A	0.73	2.9
OG-15A	0.78	5.2
H-OG-15A	0.80	2.5

Adsorption performances of toluene



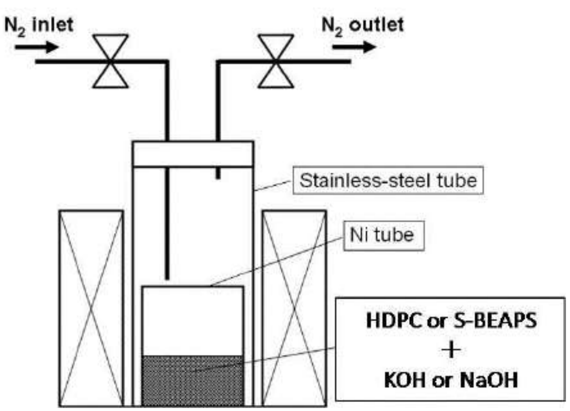
- The slopes of breakthrough curves for 5A and 15A were steeper than those of curves for 7A and 10A.
- ACFs with homogeneous pores (5A and 15A) showed rapid toluene adsorption and larger capacity per unit area and longer breakthrough time, whereas ACFs with heterogeneous pores (7A and 10A) showed slow toluene adsorption and smaller capacity per unit area.

Activated Carbons for EDLC Applications

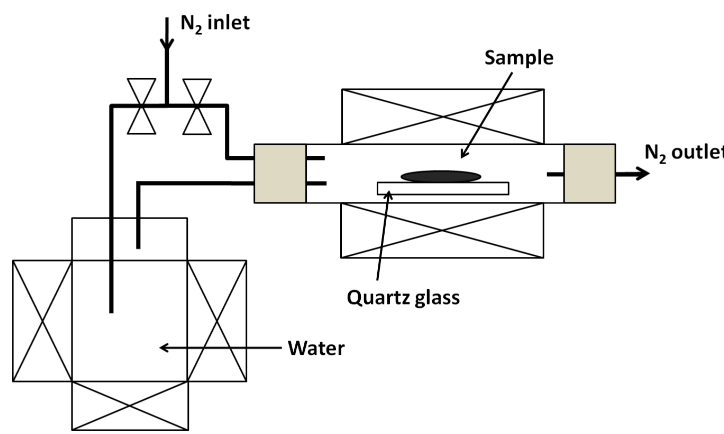
Raw materials

Mosaic cokes (HDPC) & Isotroic ball type resin (S-BEAPS)
KOH, NaOH and steam activations

KOH activation



Steam activation



Alkali activation

Alkali

KOH, NaOH

Activation temperature

600℃ ～ 800℃

Amounts of alkali

2 ～ 8 times by weight

Activation time

1h

Atmosphere

N_2 (100ml/min)

Temperature rate

5℃/min

Raw material ← KOH or NaOH

↓

Mixed in Ni crucible（Photo 1）

↓

Setting up in SS tube（Photo 2）

↓

Heat treating under N_2（Photo 3）

↓

Deceasing to RT at inside of GB

↓

HCl cleaning

↓

Filtering, watering, drying,（80℃,3h, 105℃ under Vccuo）

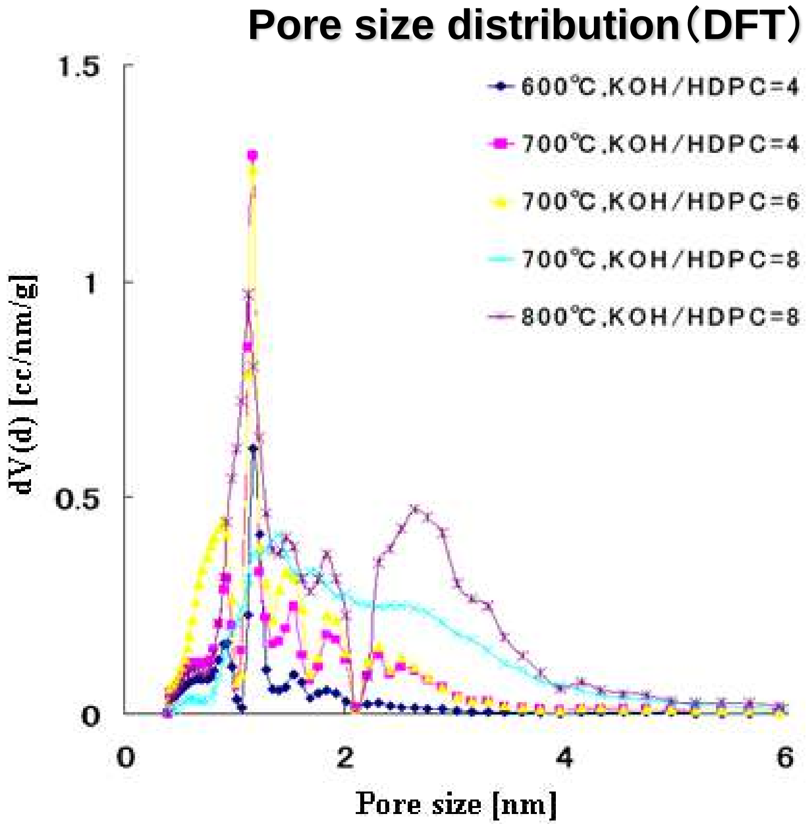
1

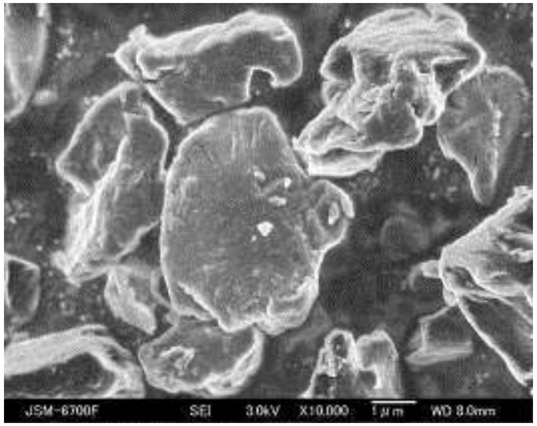
2

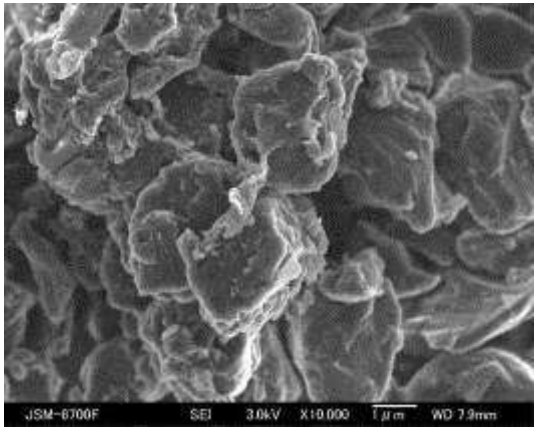
3

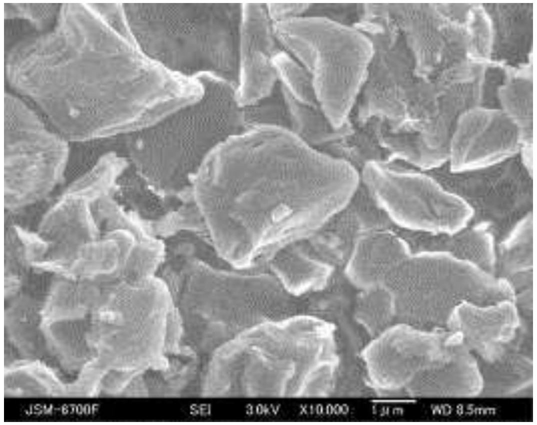
KOH activation of HDPC

Conditions	Yield [wt%]	BET SA [m^2/g]
600℃,KOH×4	62	430
700℃,KOH×4	55	920
700℃,KOH×6	41	1230
700℃,KOH×8	30	1530
800℃,KOH×8	19	2060




Raw HDPC

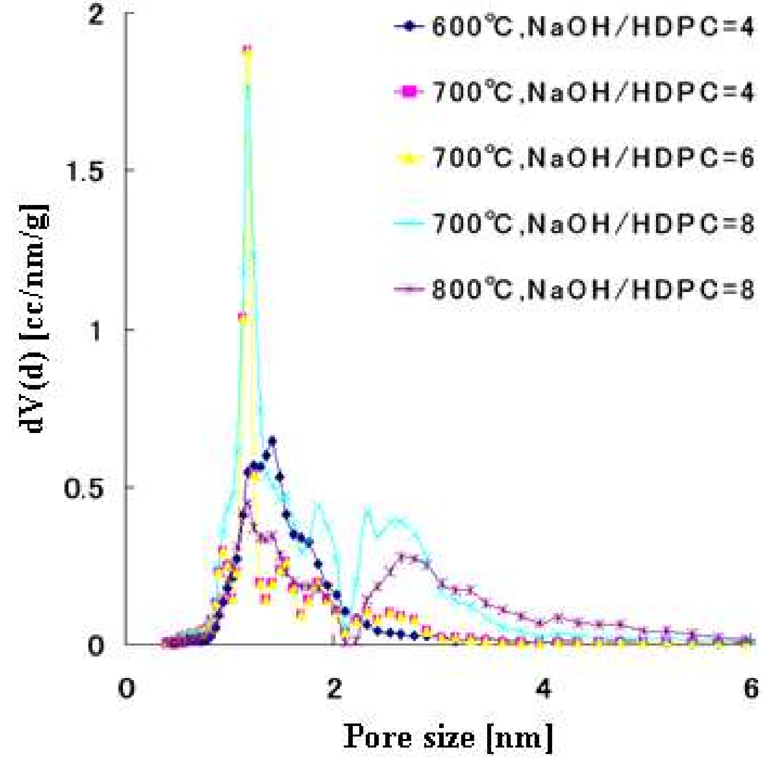

700℃,1h,KOH×6

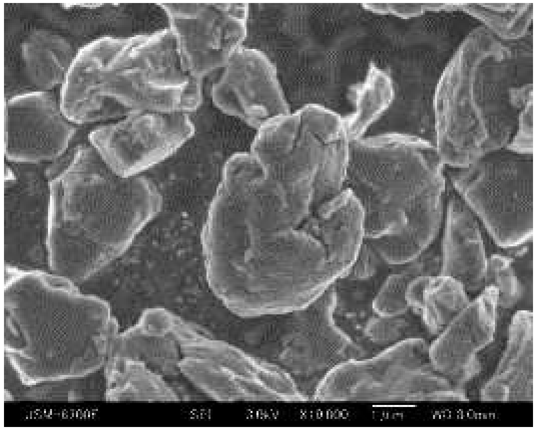

800℃,1h,KOH×8

NaOH activation of HDPC

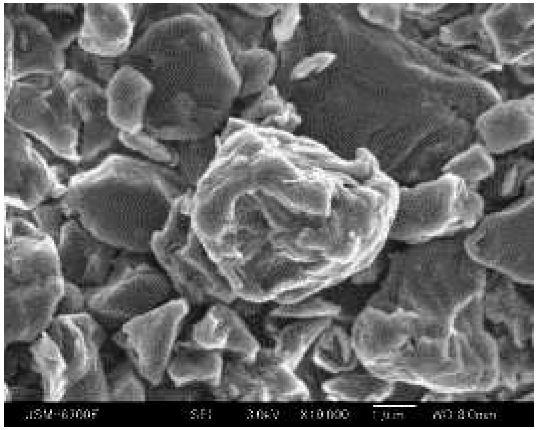
Conditions	Yeild [wt%]	BET SA [m²/g]
600℃,NaOH×4	81	934
700℃,NaOH×4	60	1062
700℃,NaOH×6	44	1678
700℃,NaOH×8	31	2234
800℃,NaOH×8	3	1162

Pore size distribution（DFT）

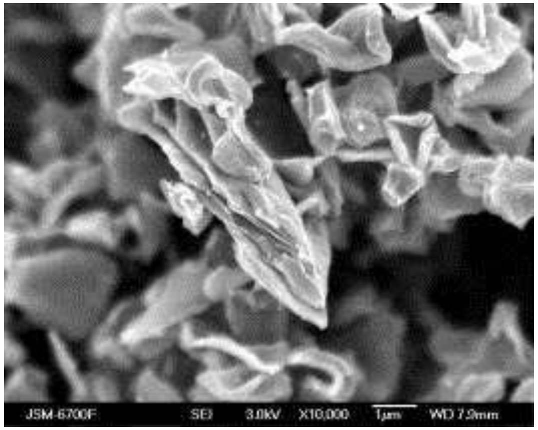




600℃,1h,KOH×4



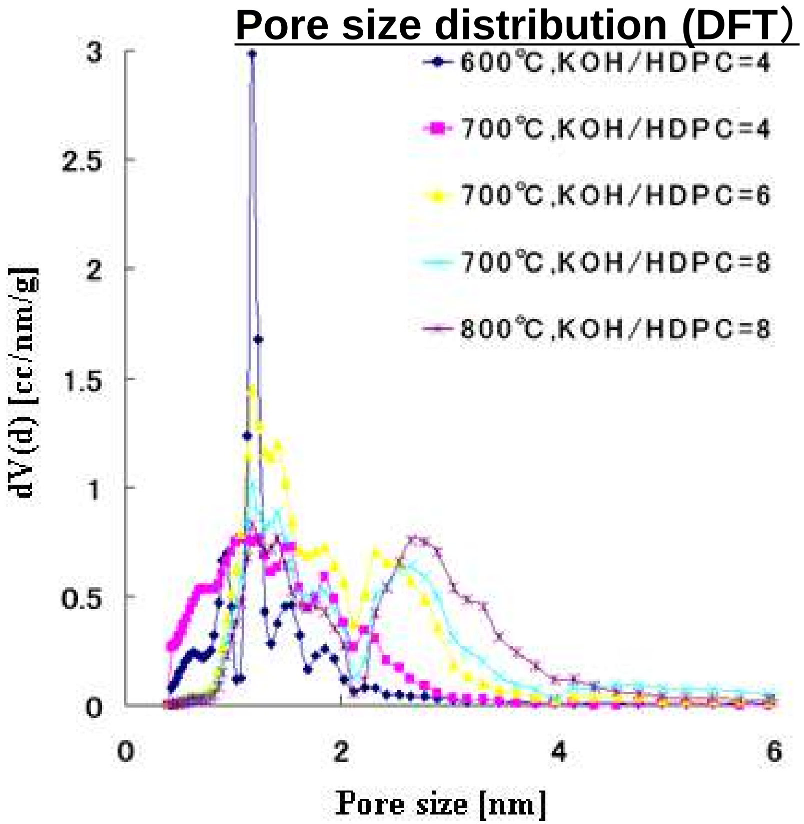
700℃,1h,KOH×6

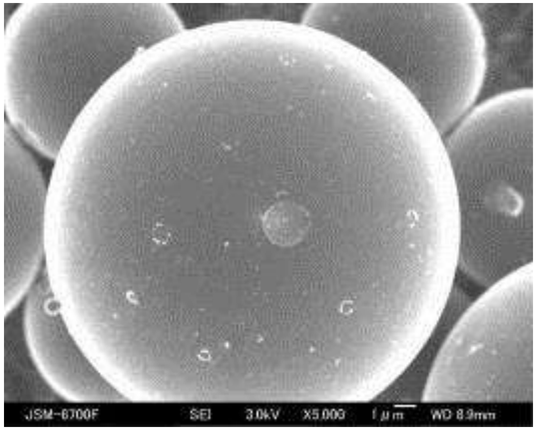


800℃,1h,KOH×8

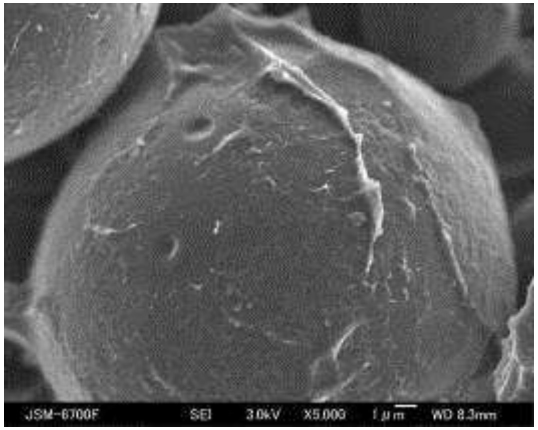
KOH activation of S-BEAPS

Conditions	Yield [wt%]	BET SA [m²/g]
600℃,KOH×4	66	1841
700℃,KOH×4	55	2247
700℃,KOH×6	41	3514
700℃,KOH×8	36	2780
800℃,KOH×8	23	2586

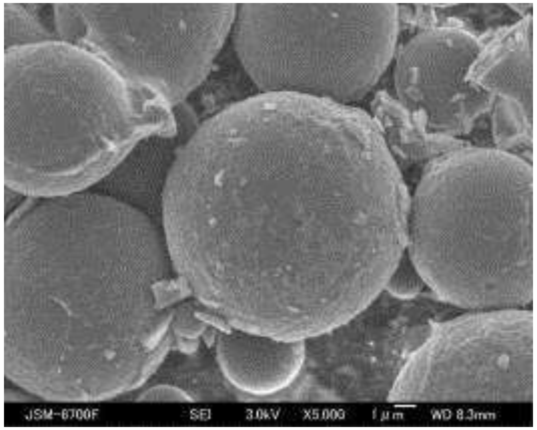




600℃ heat treated S-Beap



700℃,1h,KOH×6

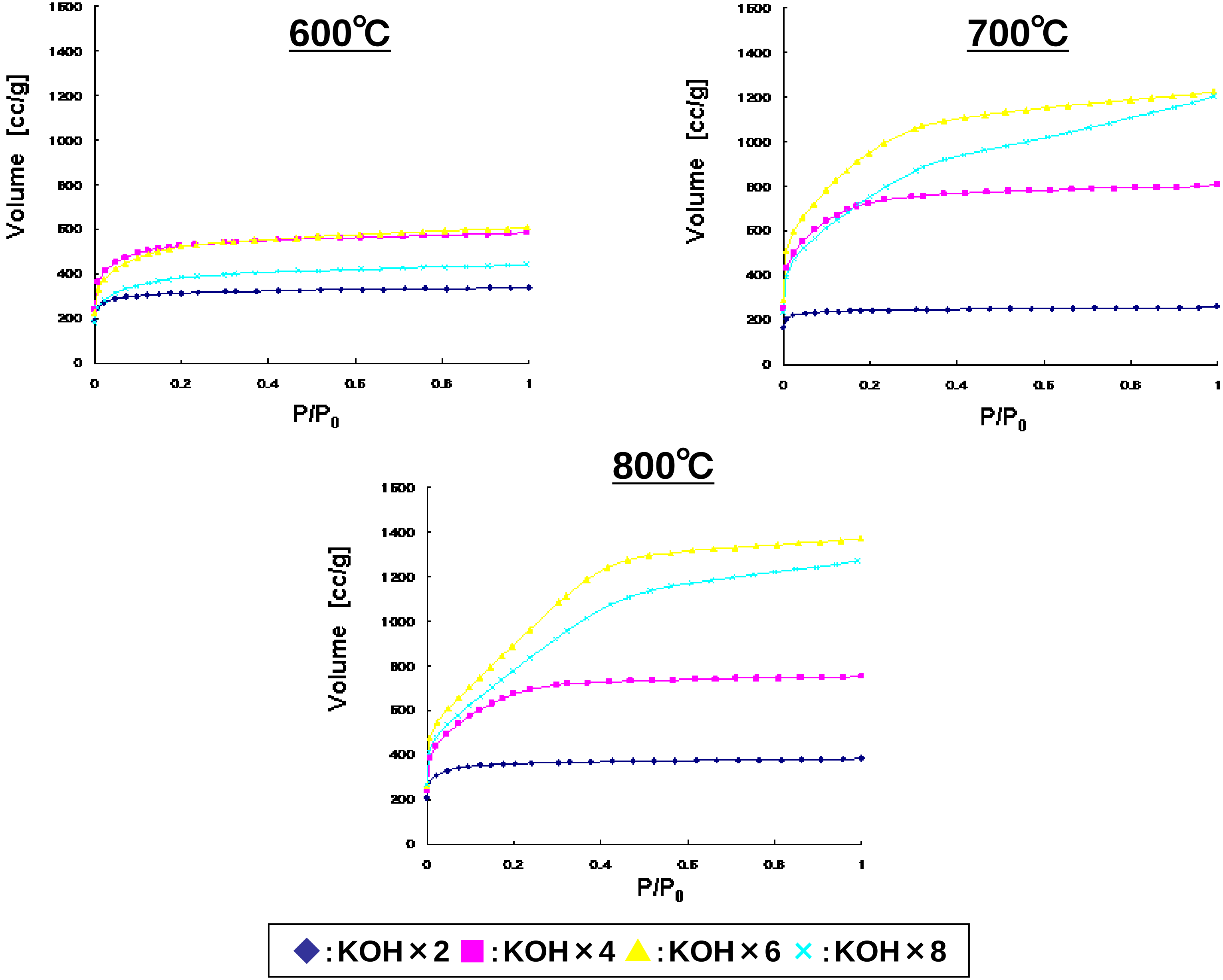


800℃,1h,KOH×8

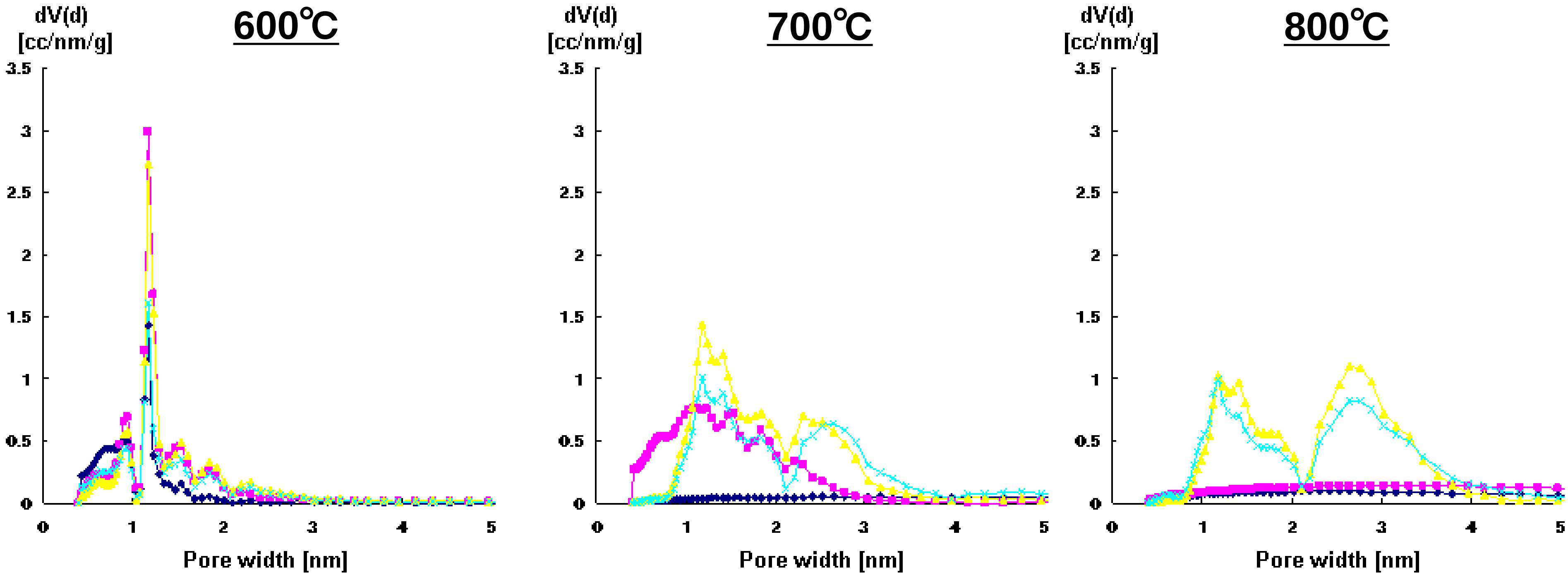
Elemental analyses

Conditions	Amounts [wt%] H	C	N	O	Ashes [%]
As-received HDPC	3.85	89.29	2.85	4.01	None
600℃、KOH×4、1h	2.2	78.44	1.93	17.43	None
700℃、KOH×4、1h	1.03	83.54	0.51	14.92	None
700℃、KOH×6、1h	0.68	86.05	0.48	12.75	0.25
700℃、KOH×8、1h	0.72	86.58	0.35	12.27	0.38
800℃、KOH×8、1h	0.99	89.04	0.29	7.32	2.36

SBEAPS – KOH activation Isotherms (77K,N2)



SBEAPS – KOH activation NLDFT



◆ : NaOH × 2 ■ : NaOH × 4 ▲ : NaOH × 6 × : NaOH × 8

Fitting error [%]

	KOH × 2	KOH × 4	KOH × 6	KOH × 8
600℃	0.31	0.431	0.39	0.304
700℃	41.702	0.219	1.48	1.167
800℃	36.425	36.085	1.53	0.885

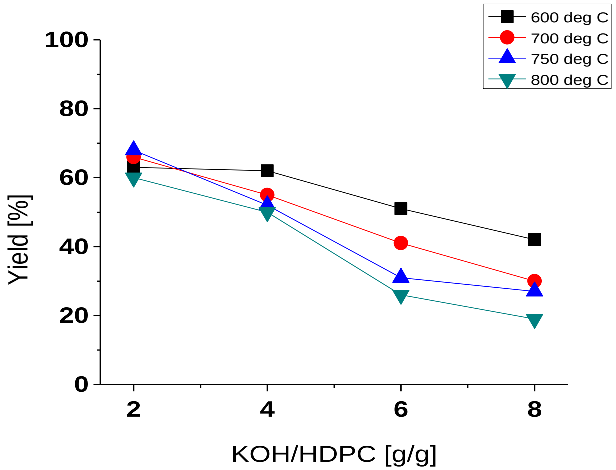
Yield vs. surface area

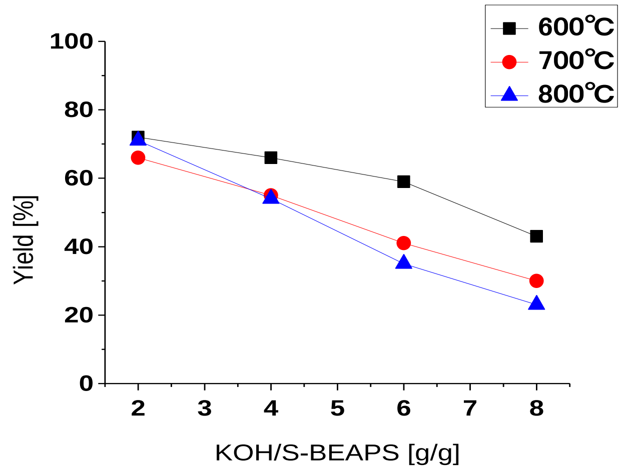
Relation btw. Activation conditions and properties

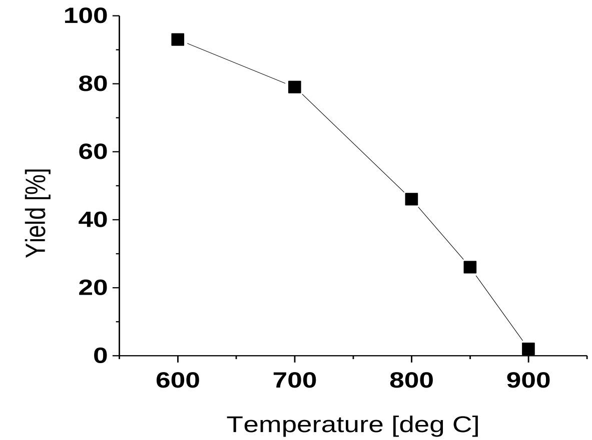
HDPC KOH

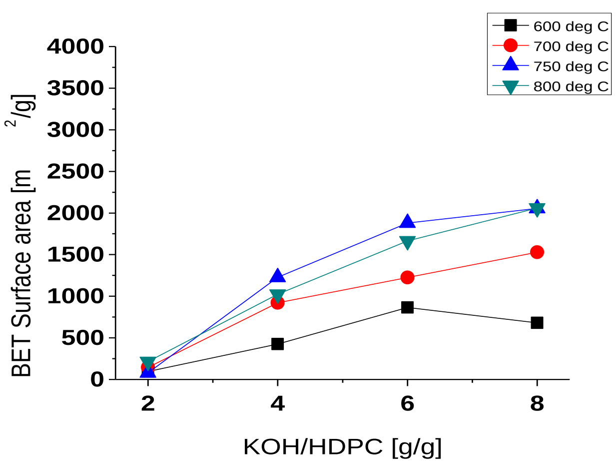
S-BEAPS KOH

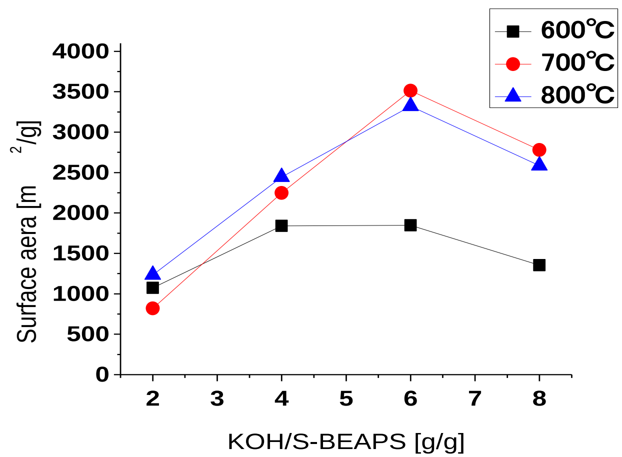
S-BEAPS steam

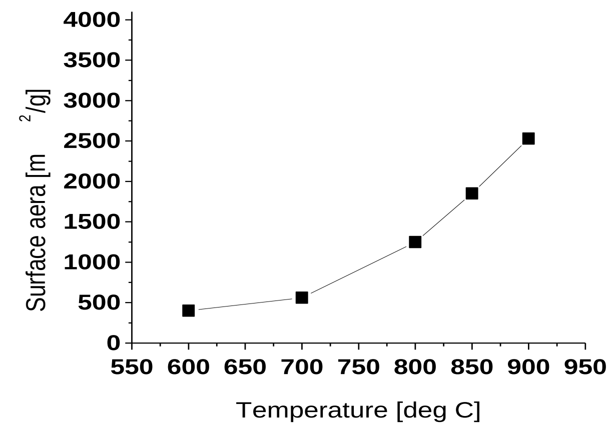




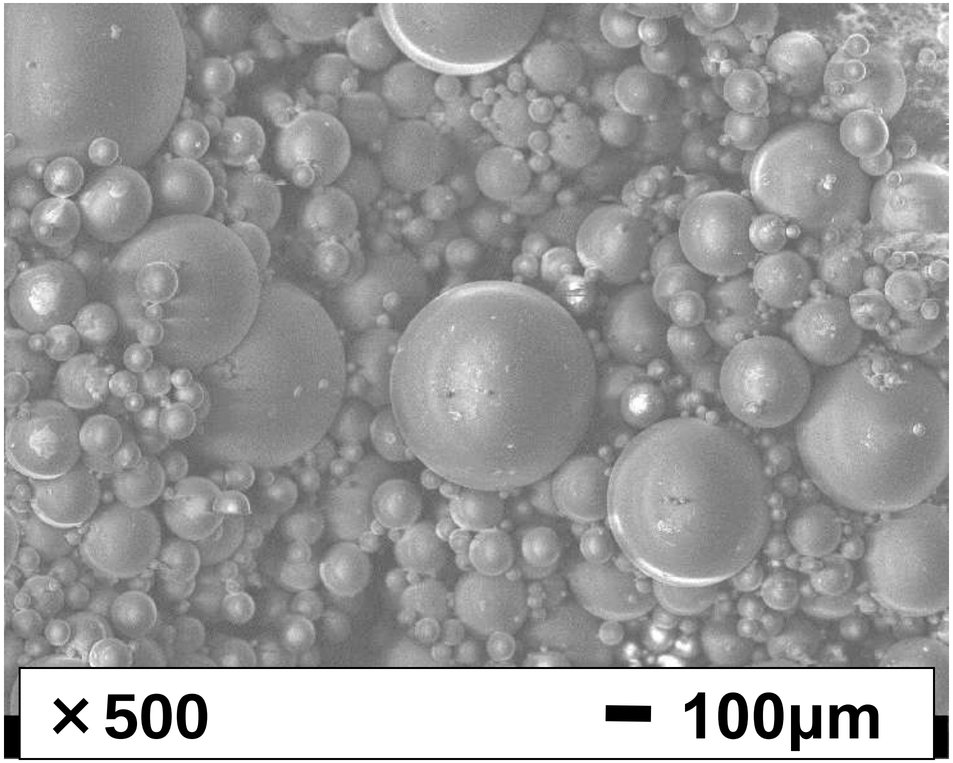


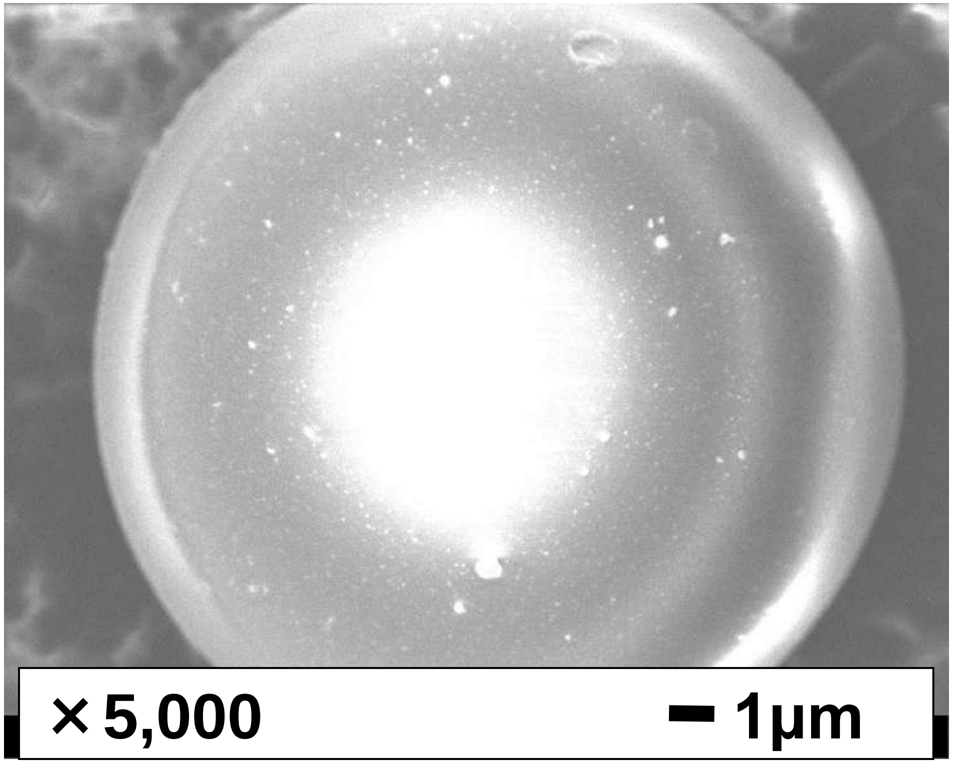




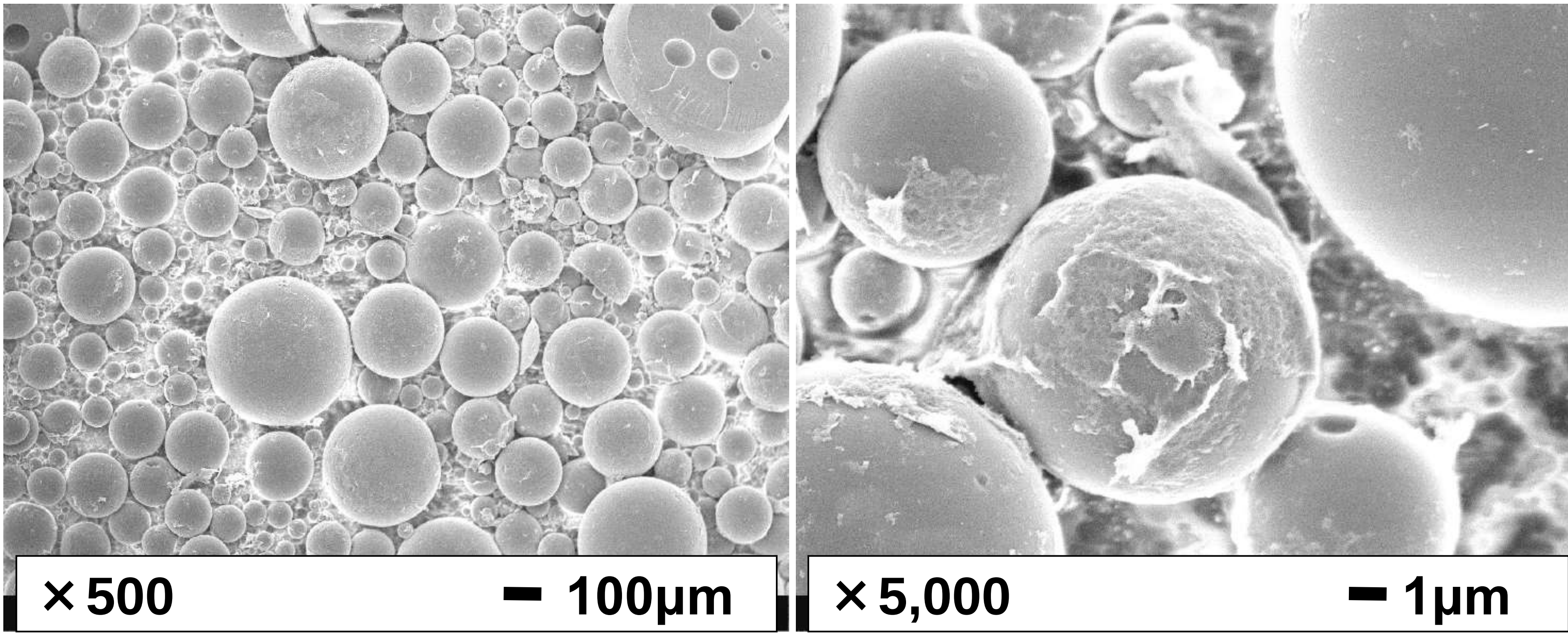


Pre heat treatment（600℃、1h）

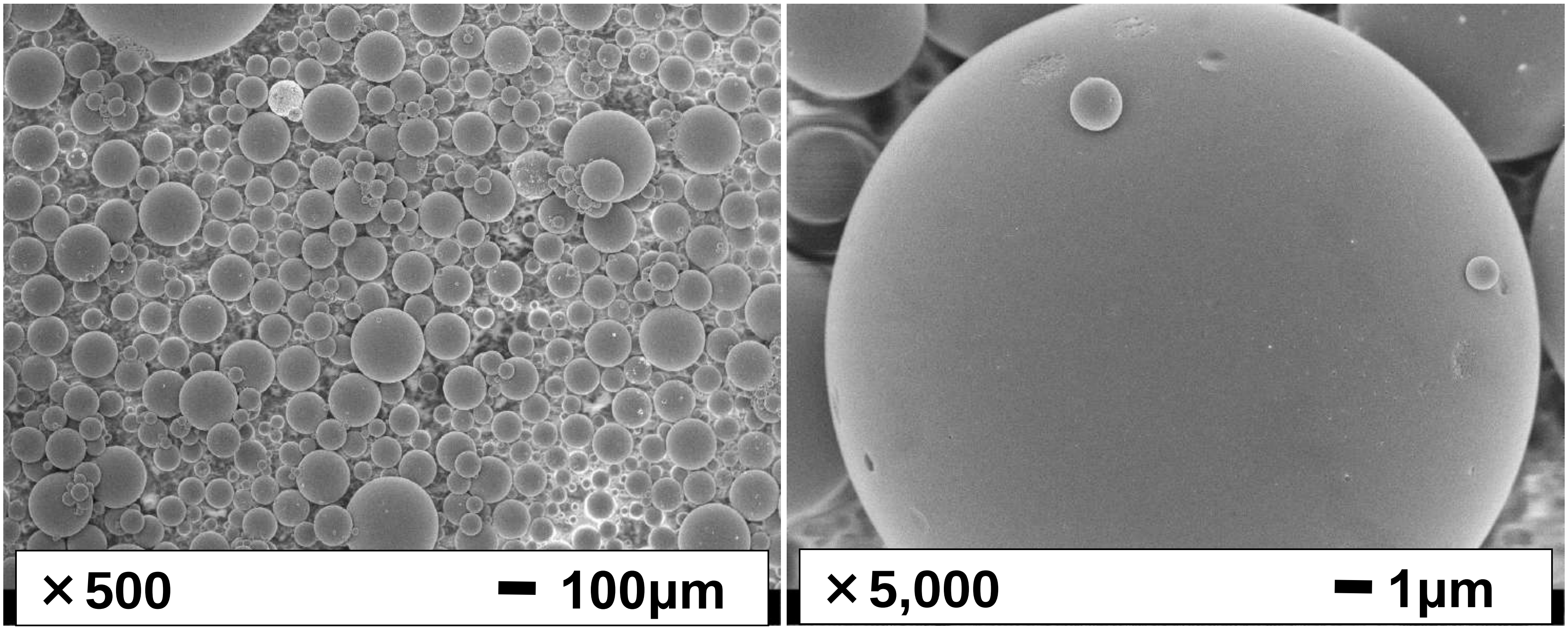




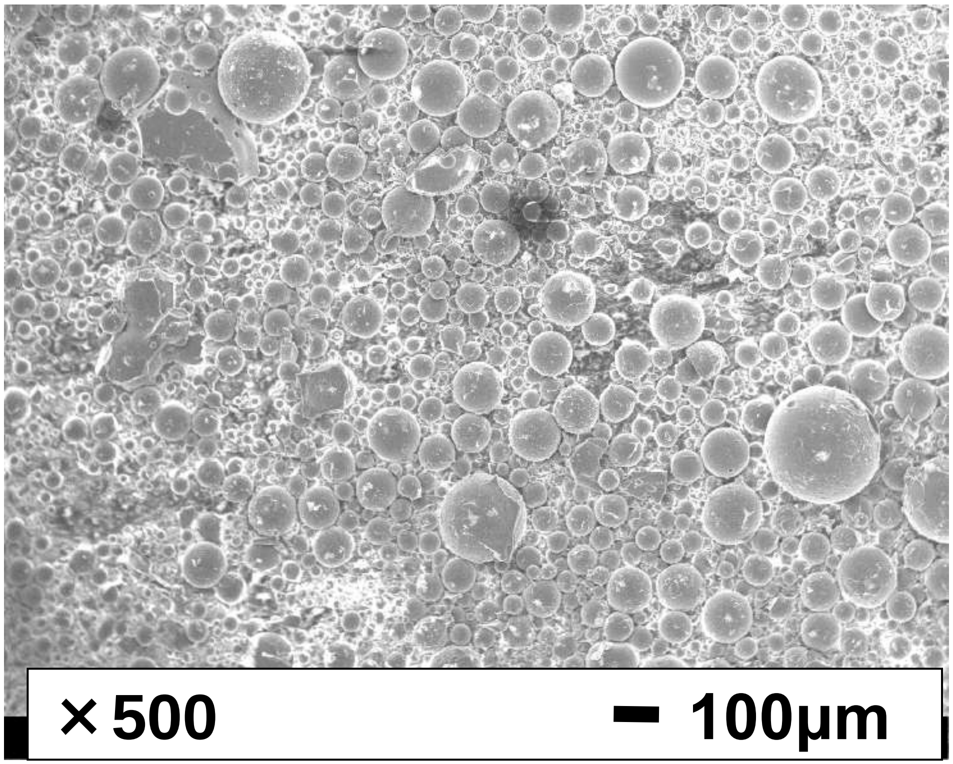
KOH activation（KOH×6、700℃、1h）

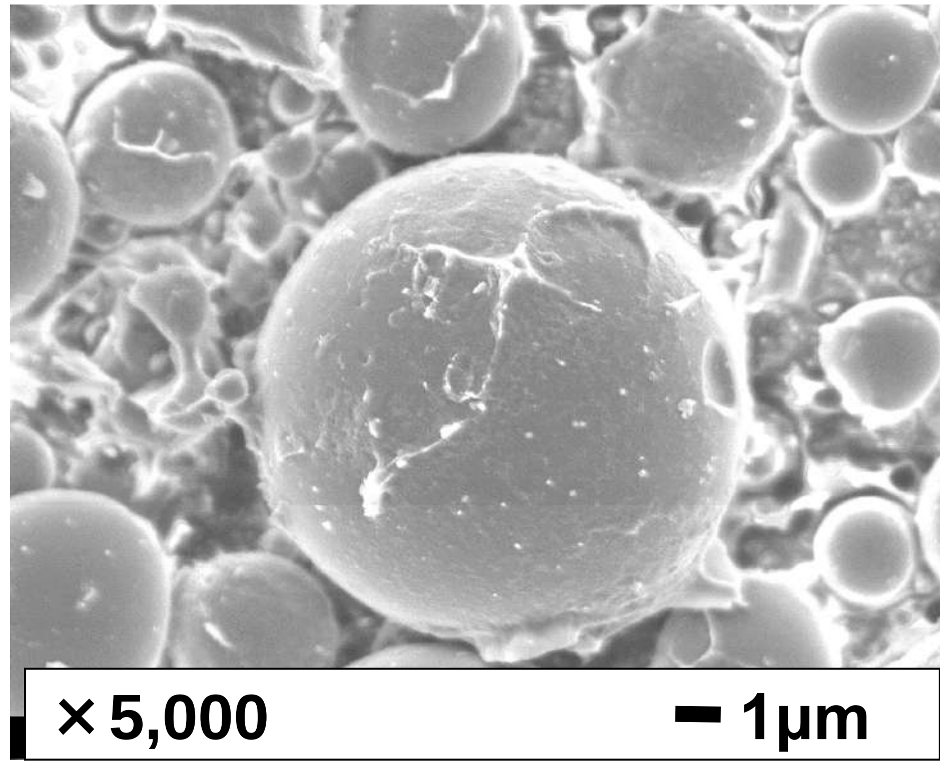


Steam activation（850℃、1h）



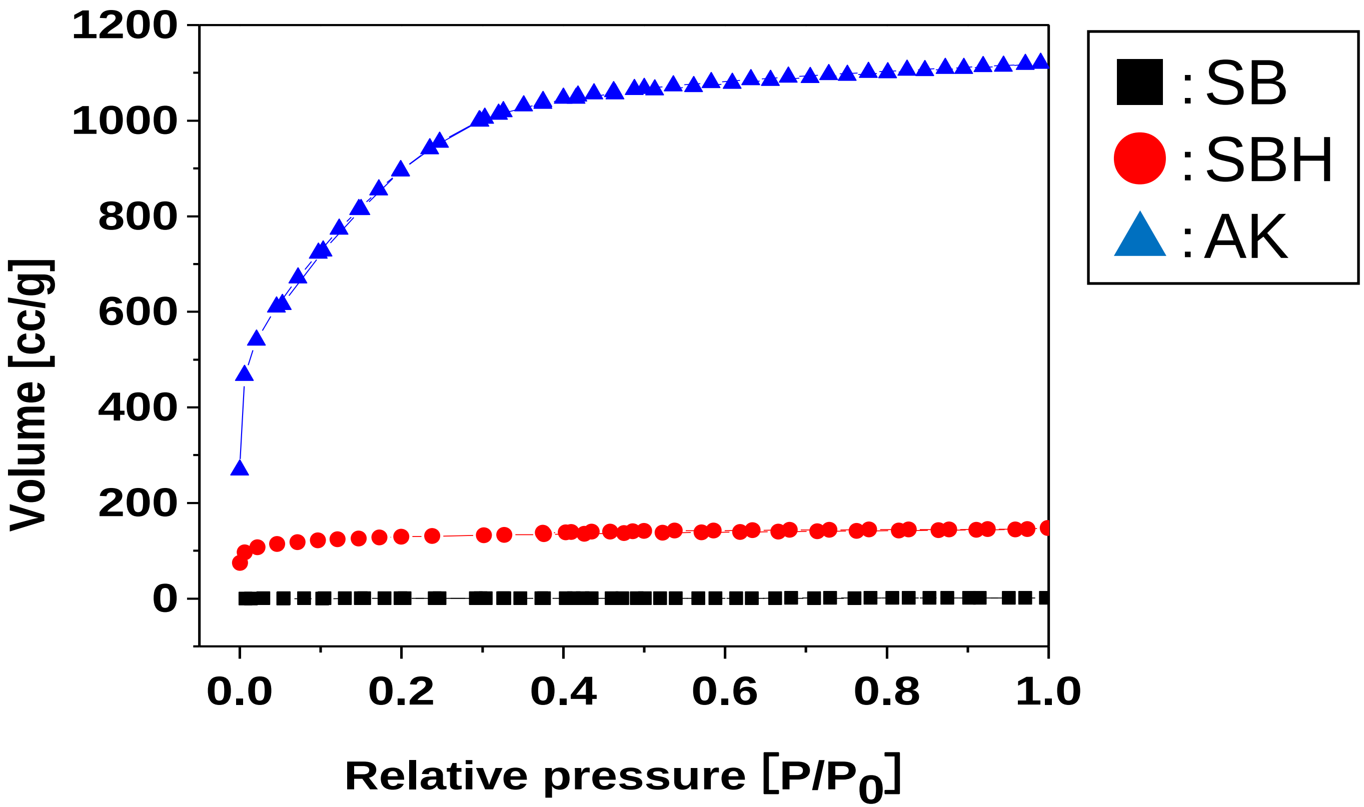
KOH after-activation（KOH×4、600℃、1h）





S-BEAPS, Preheat treatment and activation

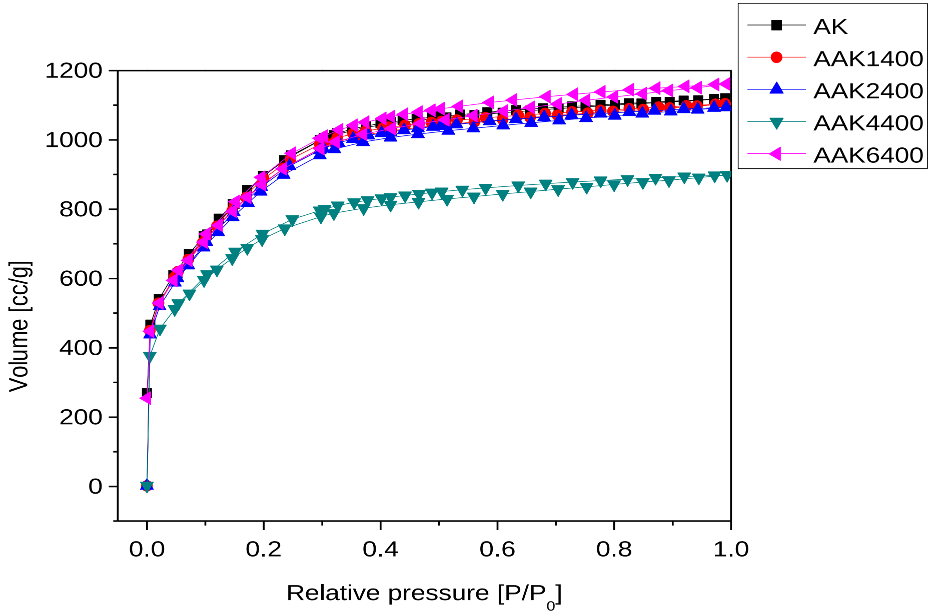
Sample	Yield [%]	Final yeild [%]	BET SA [m²/g]	Elemental analysis [%]					ED [g/ml]	Capacitance		
				H	C	N	O	Ash		F/g	F/ml	F/m²
SB	–	100	3	5.79	75.27	0.01	18.93	0.00	–	–	–	–
SBH	60	60	454	3.36	91.66	0.02	4.92	0.04	0.86	1.54	1.06	0.003
AK	40	24	3360	1.33	90.35	0.13	7.19	1.00	0.42	42.5	14.4	0.013



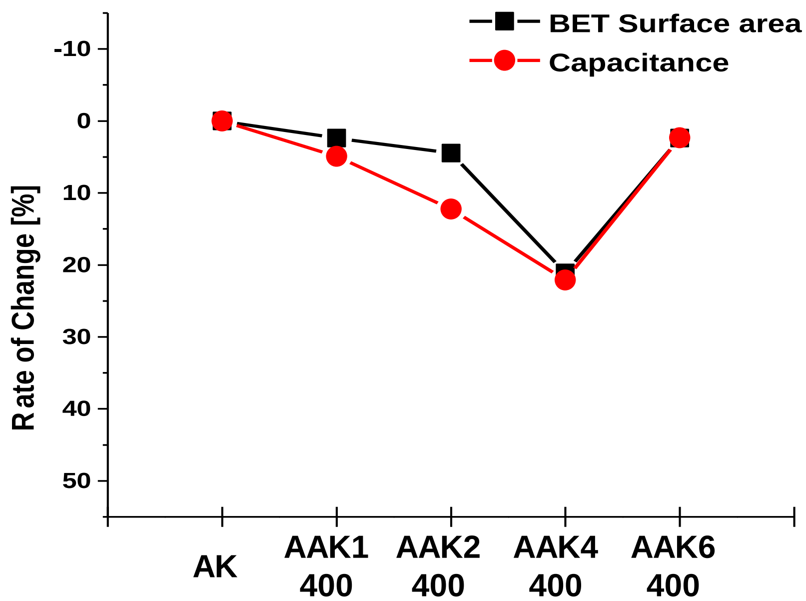
After-activation

Activation（KOH×6,700℃,1h）→ After-activation（KOH×1~6 ,400℃,1h）

Sample	Yield [%]	Final yield [%]	BET SA [m^2/g]	Elemental analysis [%]					ED [g/ml]	Capacitance		
				H	C	N	O	灰分		F/g	F/ml	F/m^2
AK	40	24	3360	1.33	90.35	0.13	7.19	1.00	0.42	42.5	14.4	0.013
AAK1400	94	23	3280	0.44	90.46	0.01	9.09	0.00	0.43	40.4	13.8	0.012
AAK2400	88	21	3210	0.42	89.38	0.02	10.14	0.04	0.46	37.3	13.7	0.012
AAK4400	84	20	2650	0.68	84.43	0.01	14.79	0.09	0.56	33.1	14.8	0.013
AAK6400	82	20	3280	0.56	90.09	0.00	9.34	0.01	0.45	41.5	15.0	0.013



N2 isotherms at 77K

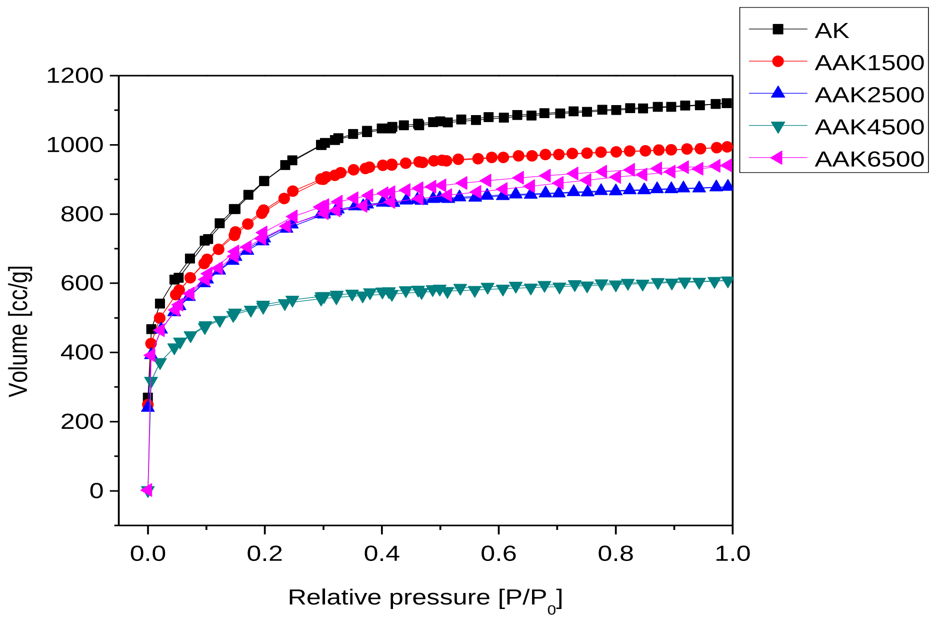


Surface area vs. capacitance after After-activation

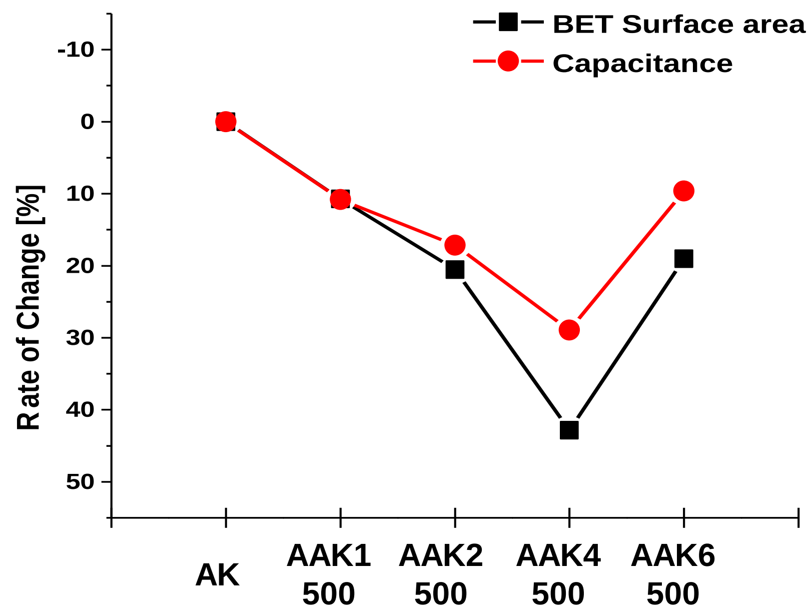
After-activation

Activation（KOH×6,700℃,1h）→after -activation（KOH×1~6 ,500℃,1h）

Sample	Yield [%]	Final yield [%]	BET SA [m²/g]	Elemental analysis [%]					ED [g/ml]	Capacitance		
				H	C	N	O	灰分		F/g	F/ml	F/m²
AK	40	24	3360	1.33	90.35	0.13	7.19	1.00	0.42	42.5	14.4	0.013
AAK1500	82	20	3000	0.45	91.03	0.02	8.50	0.00	0.45	37.9	13.6	0.013
AAK2500	73	18	2670	0.52	88.55	0.03	10.84	0.06	0.50	35.2	14.2	0.013
AAK4500	60	14	1920	0.81	84.80	0.00	14.34	0.05	0.67	30.2	16.2	0.016
AAK6500	77	18	2720	0.62	86.50	0.01	12.83	0.04	0.51	38.4	15.7	0.014



N2 isotherms at 77K

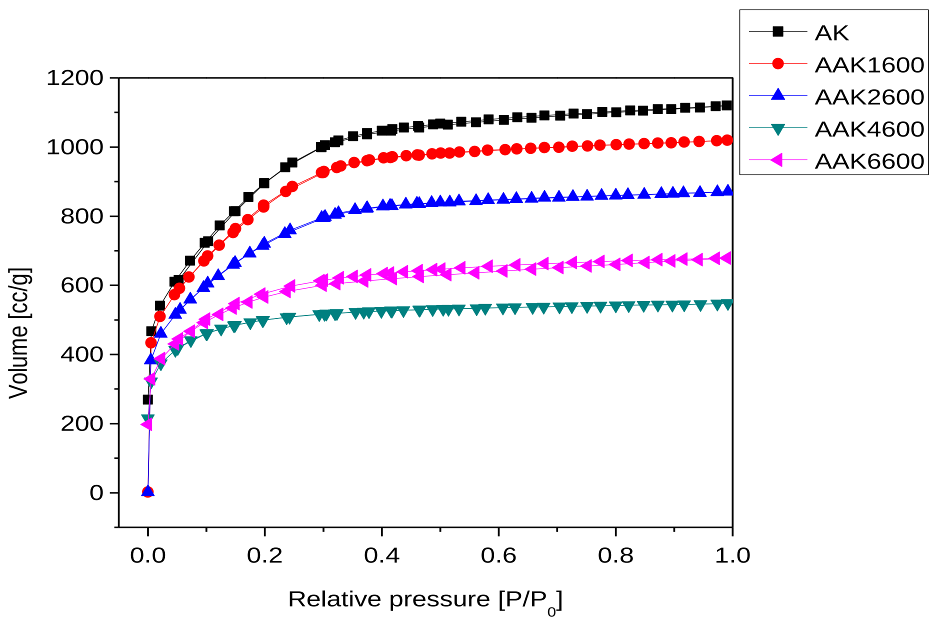


Surface area vs. capacitance after After-activation

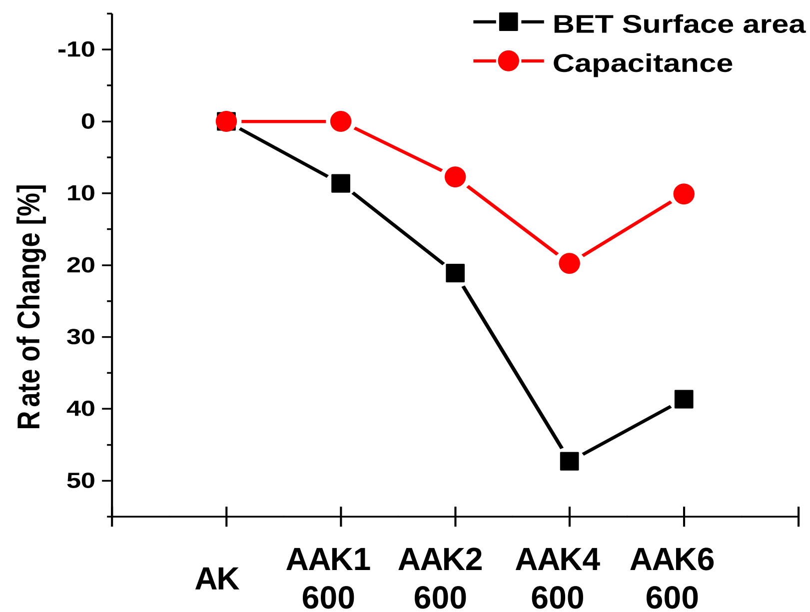
After-activation

Activation（KOH×6,700℃,1h）→After activation（KOH×1~6 ,600℃,1h）

Sample	Yield [%]	Final yield [%]	BET SA [m^2/g]	Elemental analysis [%]					ED [g/ml]	Capacitance		
				H	C	N	O	灰分		F/g	F/ml	F/m^2
AK	40	24	3360	1.33	90.35	0.13	7.19	1.00	0.42	42.5	14.4	0.013
AAK1600	78	19	3070	0.50	92.71	0.03	6.73	0.03	0.40	42.5	13.7	0.014
AAK2600	66	16	2650	0.55	91.96	0.01	7.42	0.06	0.42	39.2	13.2	0.015
AAK4600	46	11	1771	0.74	90.38	0.00	8.74	0.14	0.60	34.1	16.4	0.019
AAK6600	37	9	2060	0.83	84.25	0.01	14.78	0.13	0.57	38.2	17.4	0.019



N2 isotherms at 77K

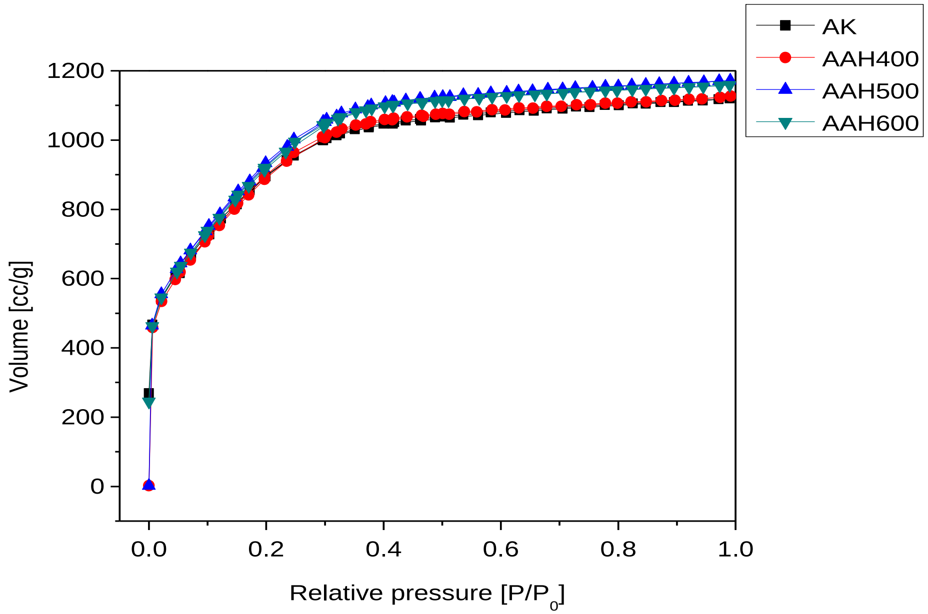


Surface area vs. capacitance After after-activation

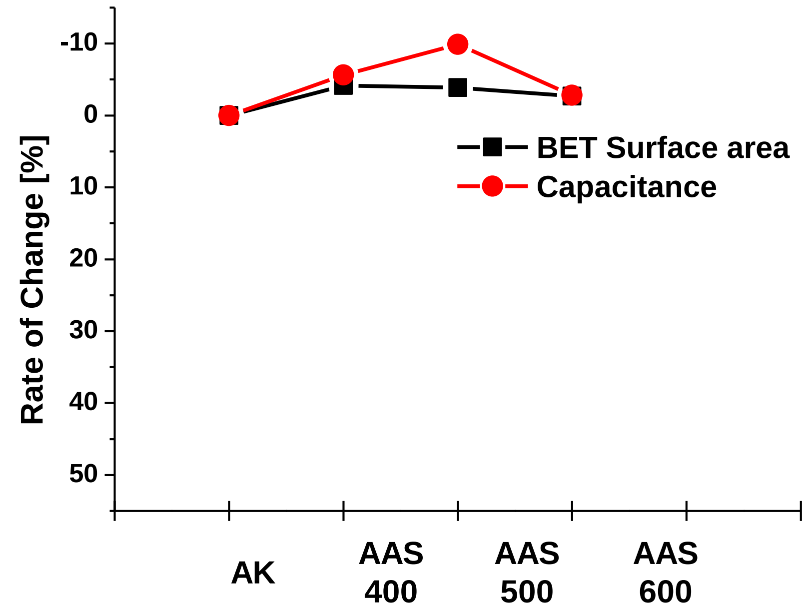
After activation

Activation（KOH×6,700℃,1h）→After-activation（Steam, 400℃～600℃,1h）

Sample	Yield [%]	Final yield [%]	BET SA [m^2/g]	Elemental analysis [%]					ED [g/ml]	Capacitance		
				H	C	N	O	灰分		F/g	F/ml	F/m^2
AK	40	24	3360	1.33	90.35	0.13	7.19	1.00	0.42	42.5	14.4	0.013
AAS400	90	22	3500	1.38	91.72	0.10	6.80	0.00	0.39	44.9	13.9	0.013
AAS500	91	22	3490	0.96	93.23	0.07	5.74	0.00	0.38	46.7	14.1	0.013
AAS600	81	19	3450	1.23	94.16	0.08	3.92	0.61	0.37	43.7	13.0	0.013

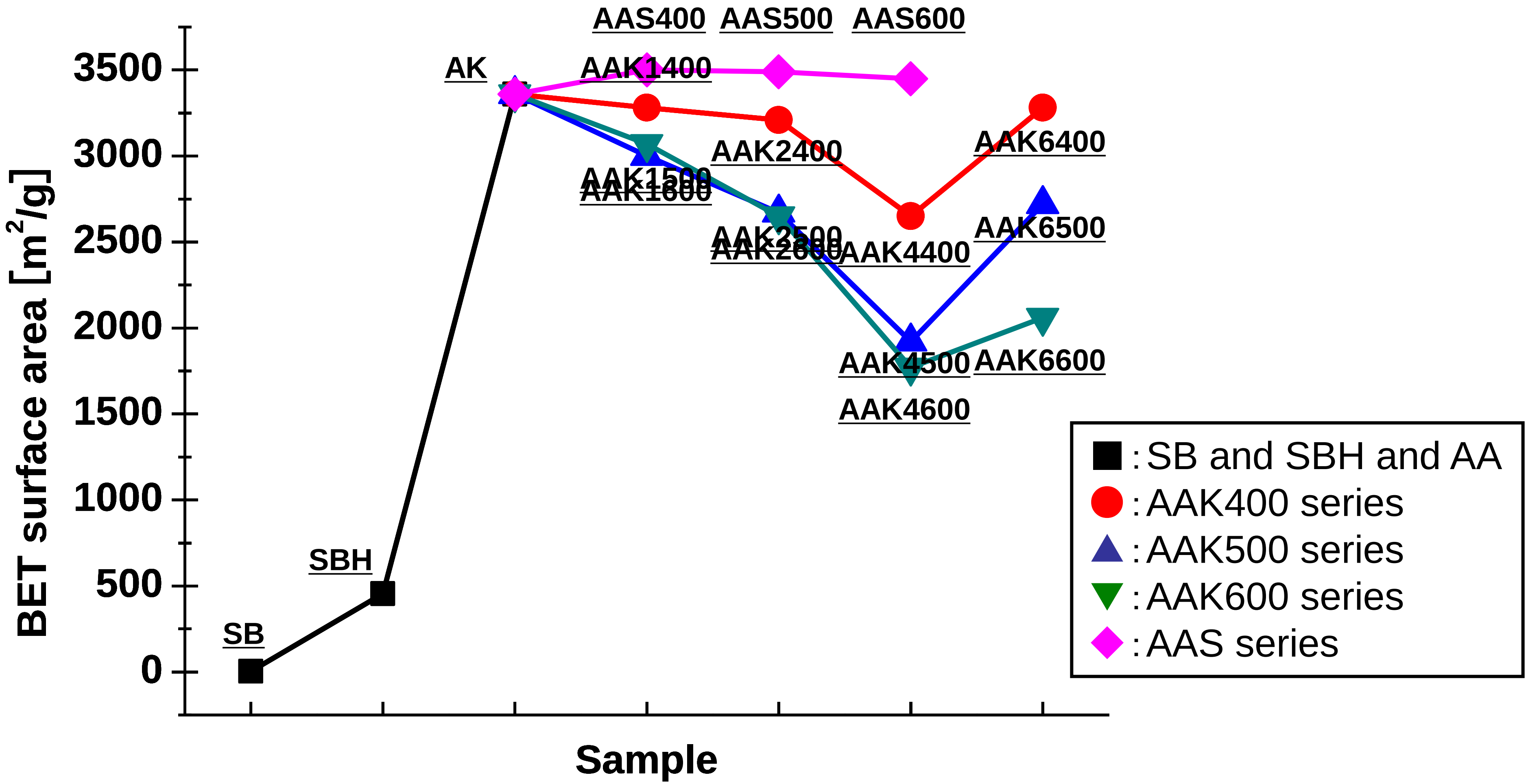


N2 isotherms at 77K



Surface area vs. capacitance
After after-activation

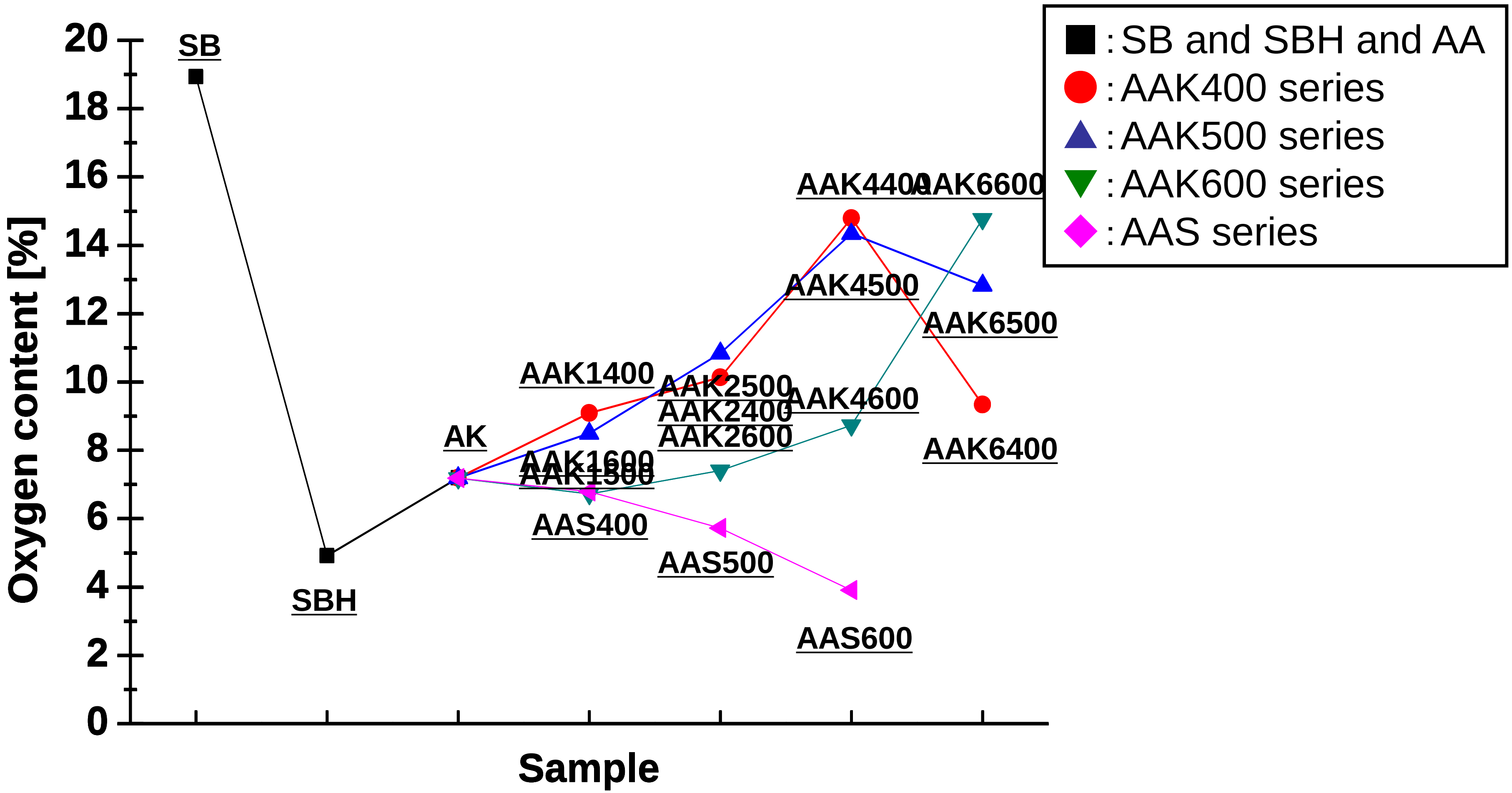
BET surface area after after-activation



＜KOH after-activation＞
Decreased - increased

＜Steam after-activation＞
unchanged

Change of oxygen amount after after-activation



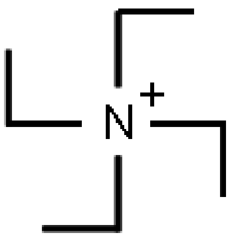
＜KOH＞
Increased

＜Steam＞
Decreased

^{11}B solid NMR

Organic electrolyte : Et_4NBF_4

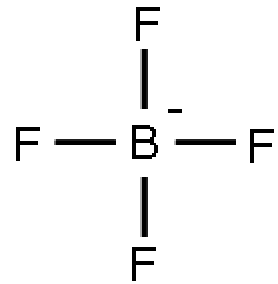
Cation



Diameter: 0.74nm

Tetra ethyl ammonium: TEA

Anion



Diameter: 0.49nm

Tetra fluoroborate: TFB

JEOL ECA400

Measurement of anionic behavior at charge by ^{11}B solid NMR

Prepared electrode

① Impregnated

② charged

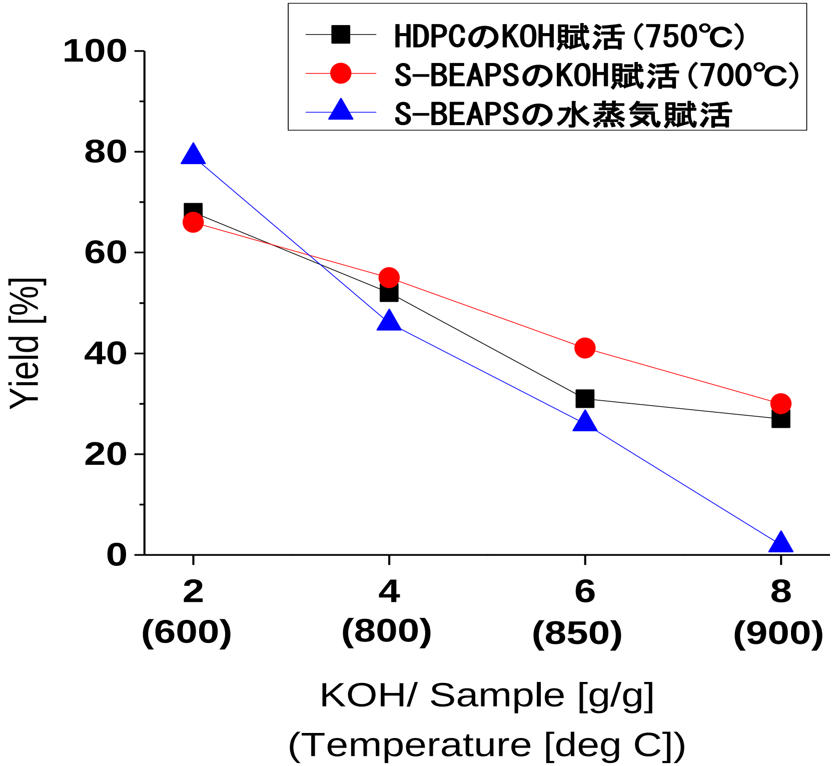
③ discharged after charged

JEOL ECA400 ^{11}B solid NMR (^{11}B:128.3MHz)

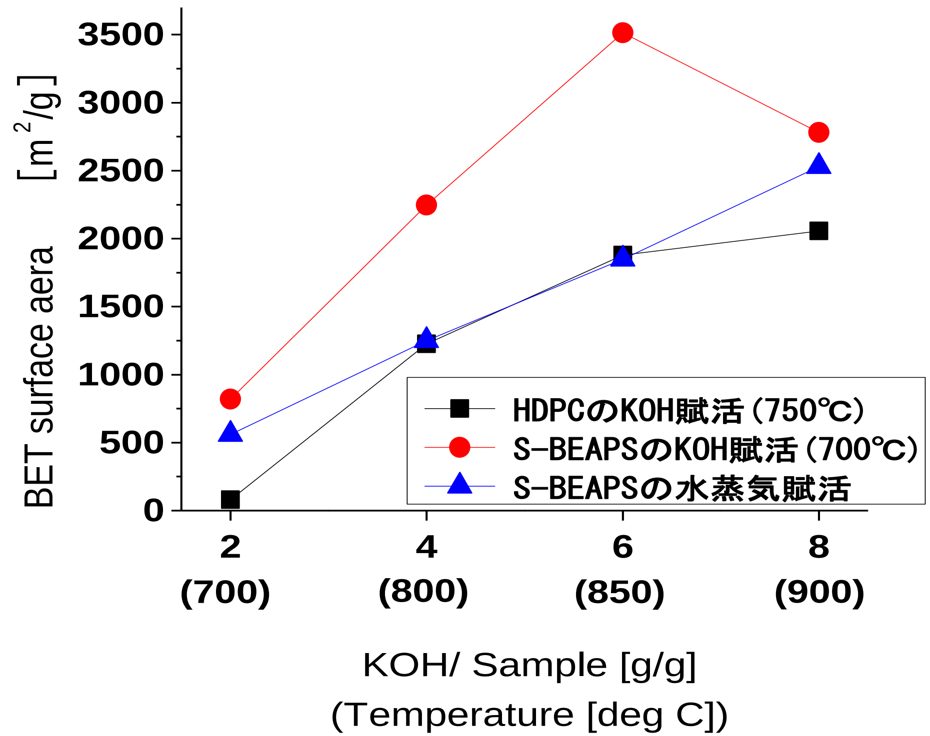
Preparation of activated carbons for EDLC and control of its properties

Yield vs. surface area

Yield



Surface area

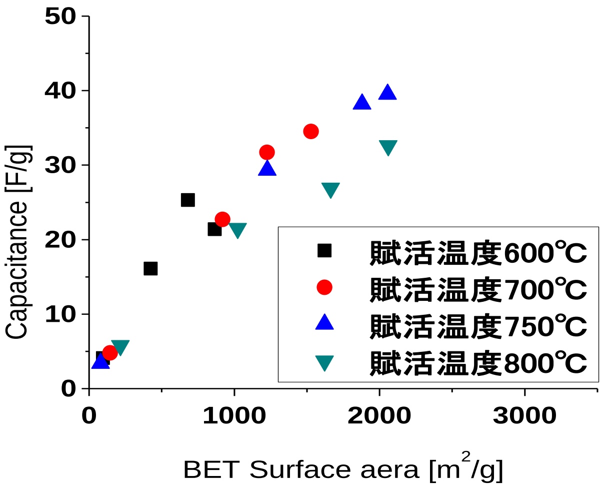


Yield linearly decreased with increasing temperature
Surface area: KOH activation HDPC → middle, S-BEAPS → high
Steam activation ＜ KOH activation

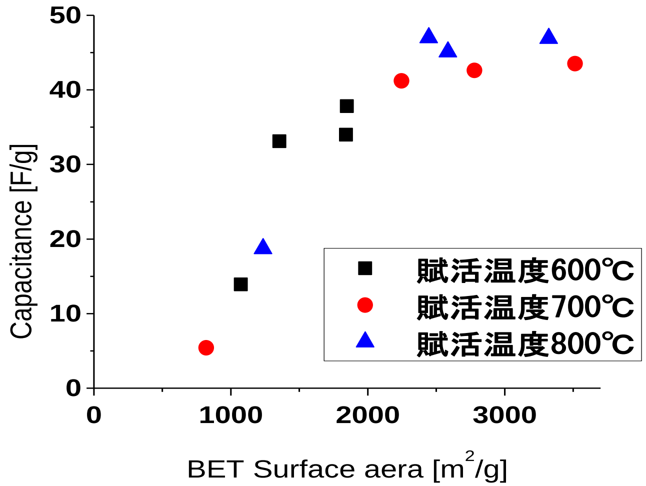
Capacitance vs. activated carbons

Capacitance vs. surface area(up: weight, down: Volume)

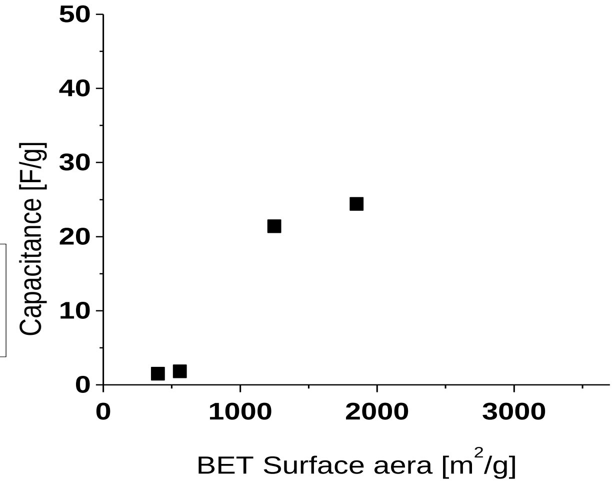
HDPC KOH

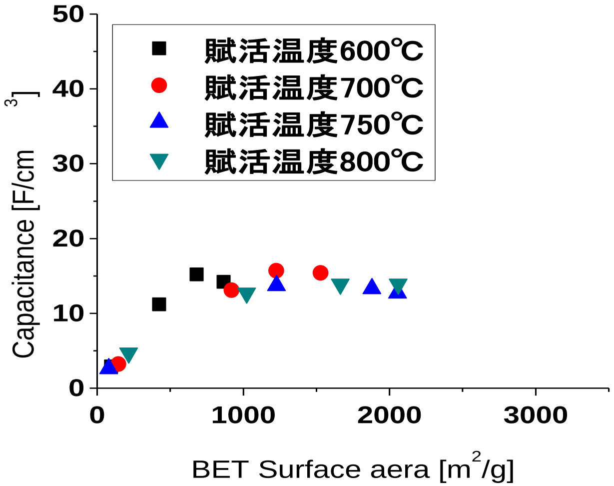


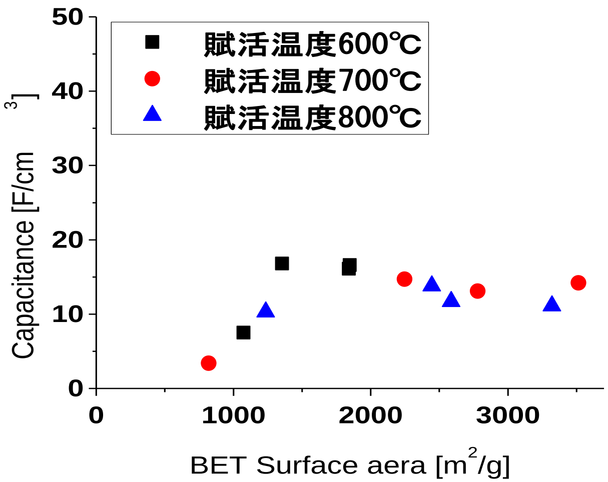
S-BEAPS KOH

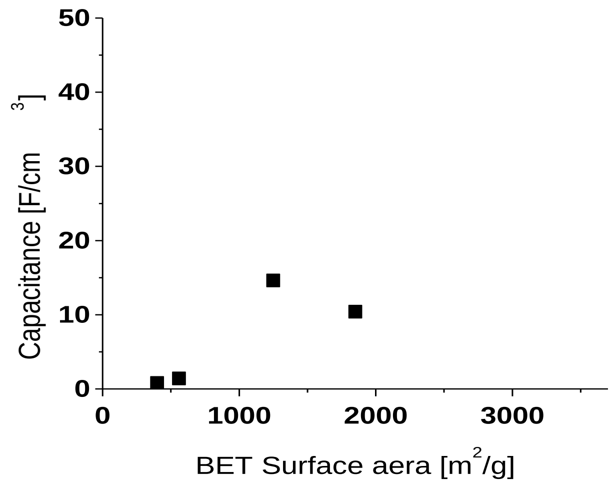


S-BEAPS steam





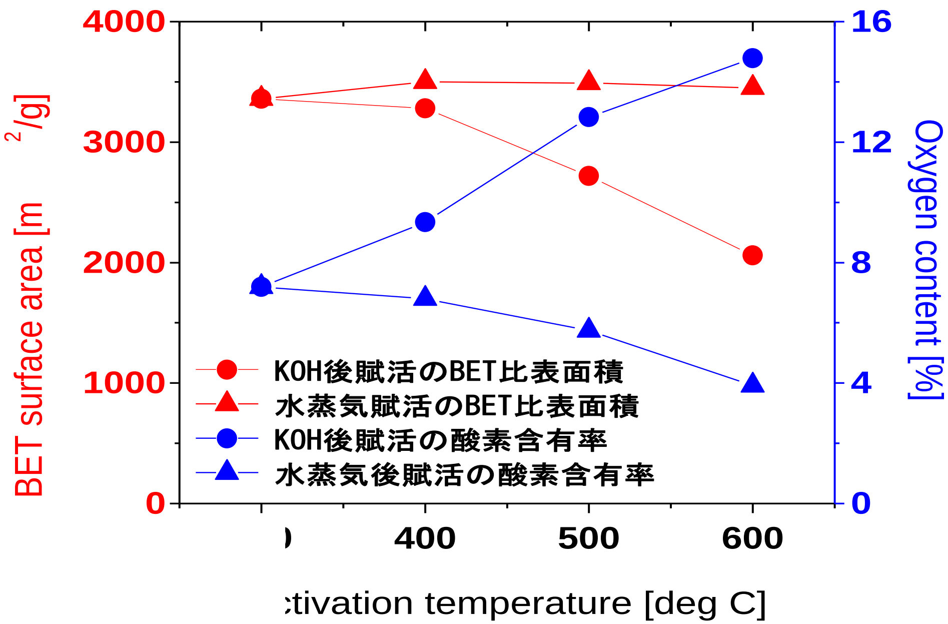




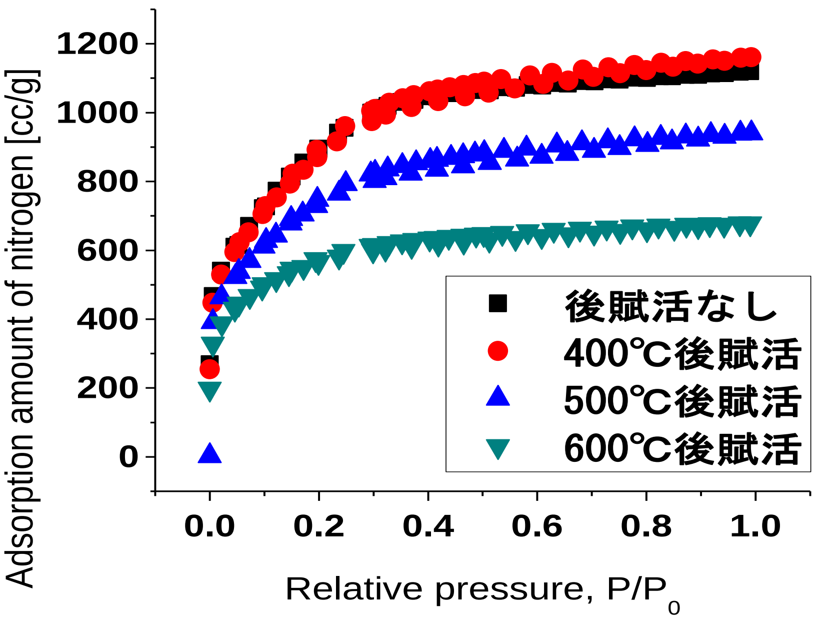
Contorl of the properties through after activation

S.A. and functional groups can be controlled through the after-activation.

Oxygen contents change by the after activation



77K isotherms by the after-activation

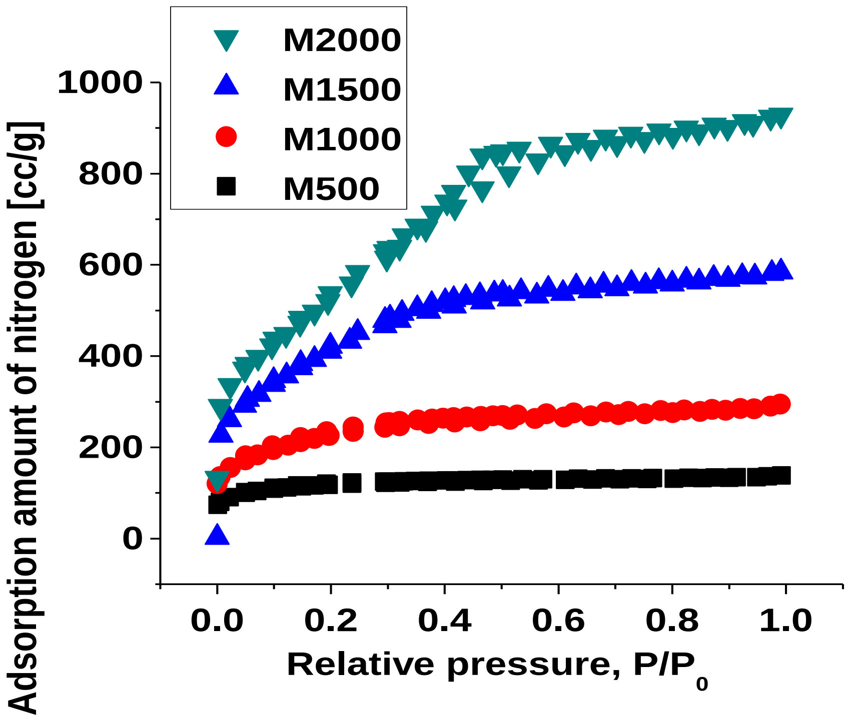


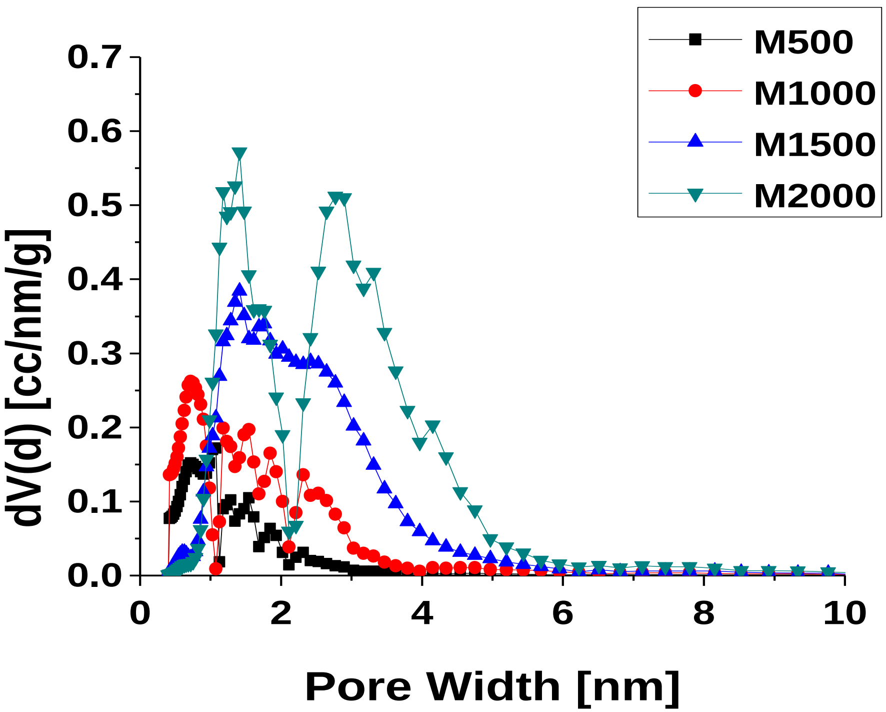
KOH after-activation：decreasing the amount of releatively larger micropores, and increasing oxygen contents on the surface

Ionic behaviors inside of the pores

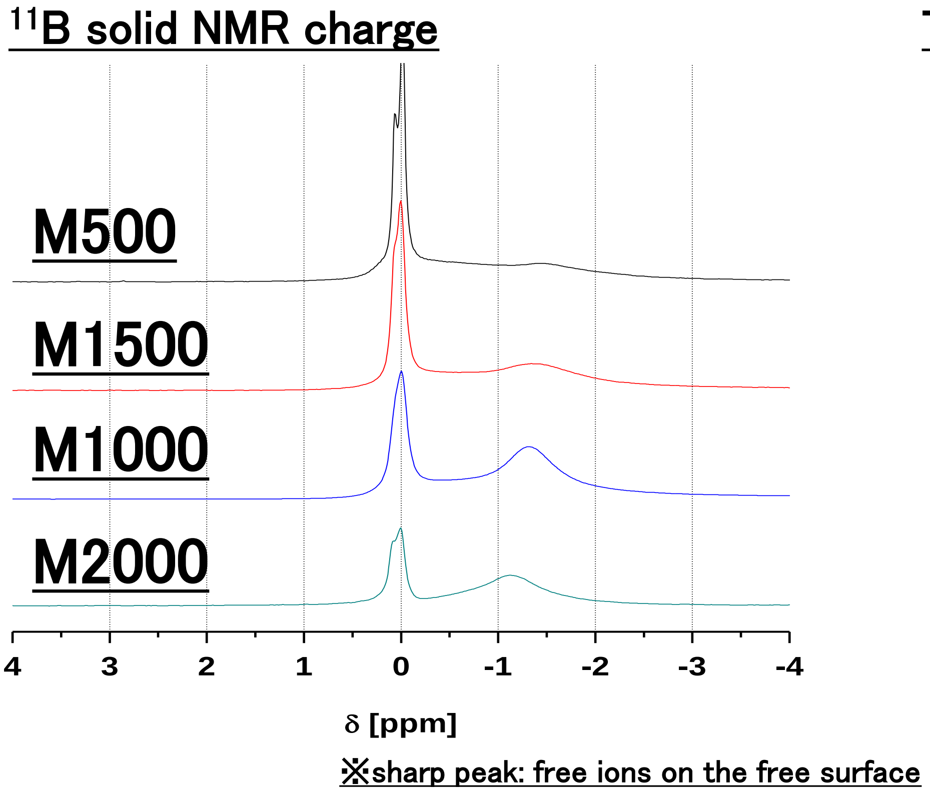
Samples

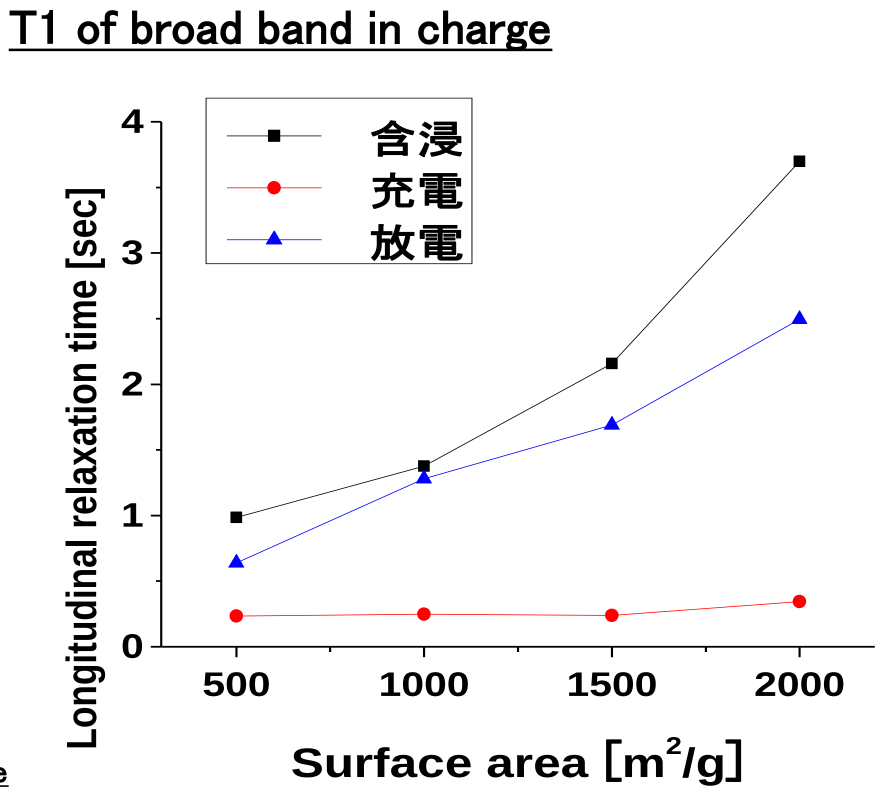
Samples	BET Surface area [m²/g]	Electrode density [g/ml]	capacitance			Amounts [wt%]				
			F/g	F/ml	F/m²	H	C	N	O	Ash
M500	420	0.84	12.0	8.10	0.029	2.20	78.4	1.93	17.4	–
M1000	820	0.65	17.3	8.90	0.021	1.03	83.5	0.51	14.9	–
M1500	1520	0.51	30.3	12.4	0.020	0.72	86.6	0.35	12.3	0.38
M2000	1930	0.38	43.2	12.9	0.022	0.99	89.0	0.29	7.32	2.36





Anionic behaviors inside of pores by 11B-NMR measurement

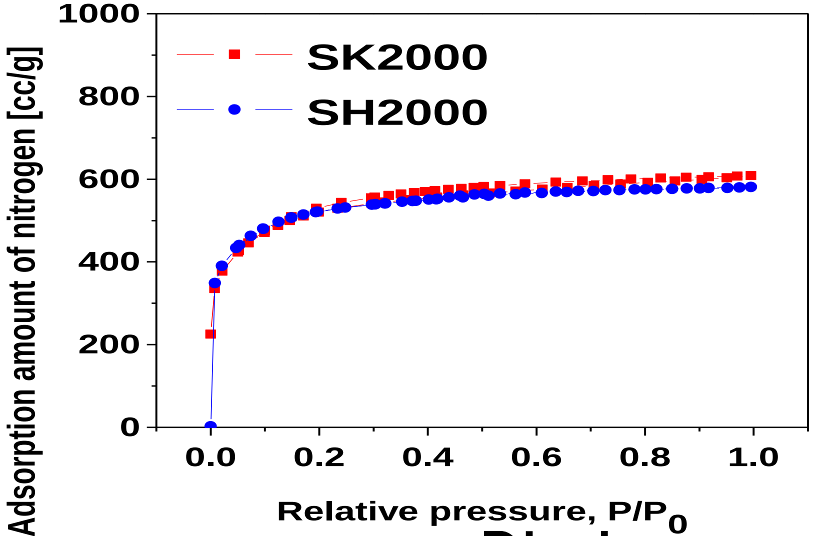


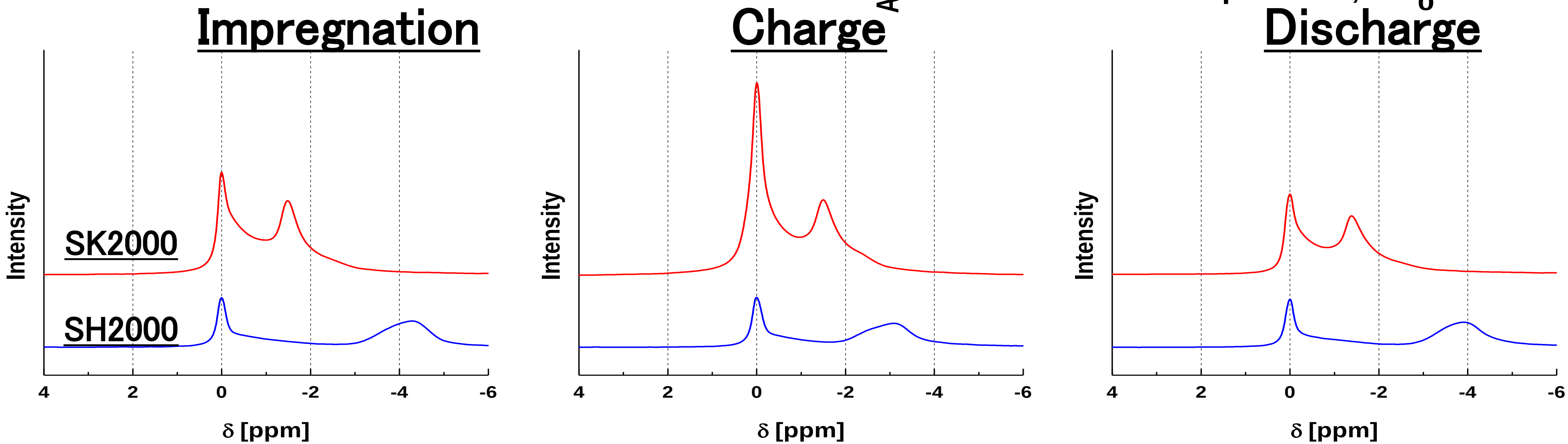


In ^{11}B-solid NMR, the adsorbed anions outside of pores appear sharp, but those inside of pores broad.
T1s were well matched with adsorbed peaks of anionic ions.

Comparison of ionic behaviors in activated carbons which have the same surface area and pore size distribution but prepared by different method

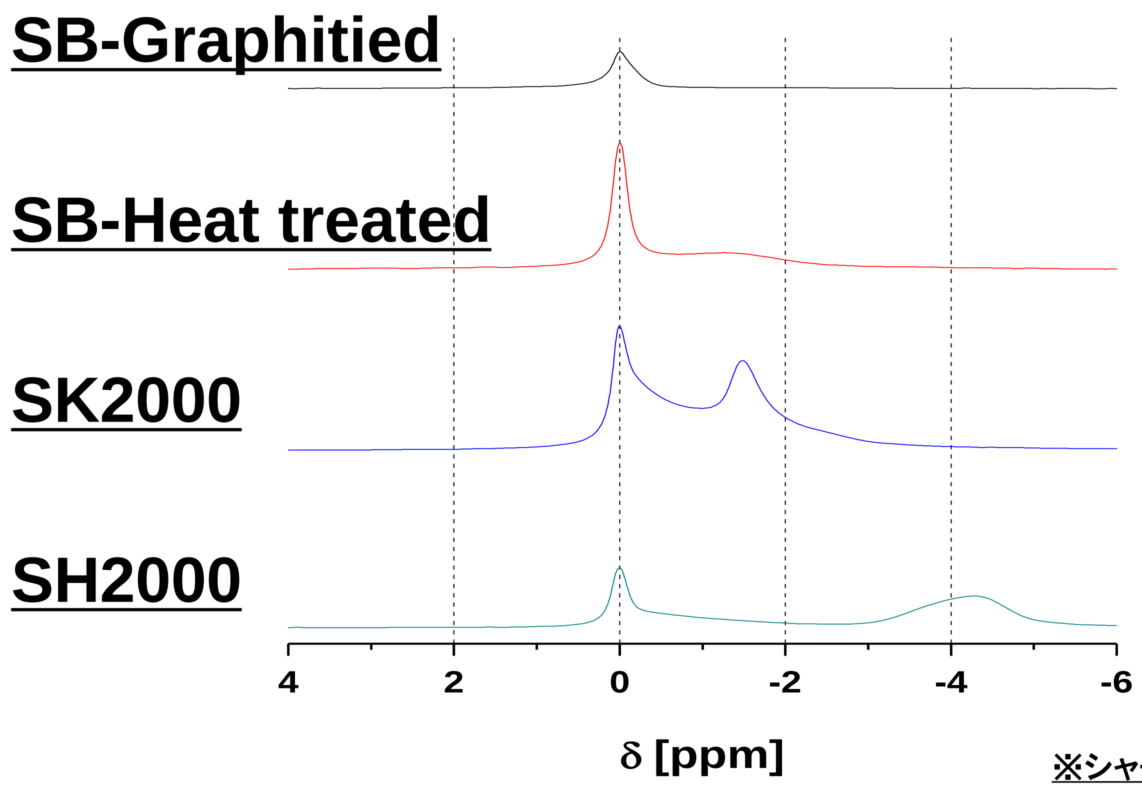
Sample	Activa-tion temp. [℃]	BET SA [m^2/g]	ED [g/ml]	Capacitance		
				F/g	F/ml	F/m^2
SK2000	600	1850	0.63	37.8	16.6	0.020
SH2000	850	1850	0.61	24.0	10.4	0.013





※シャープピークを0ppmに合わせている。

Graphitized SB, heat treated SB, SK2000, and SH2000の^{11}B NMR（Imp）

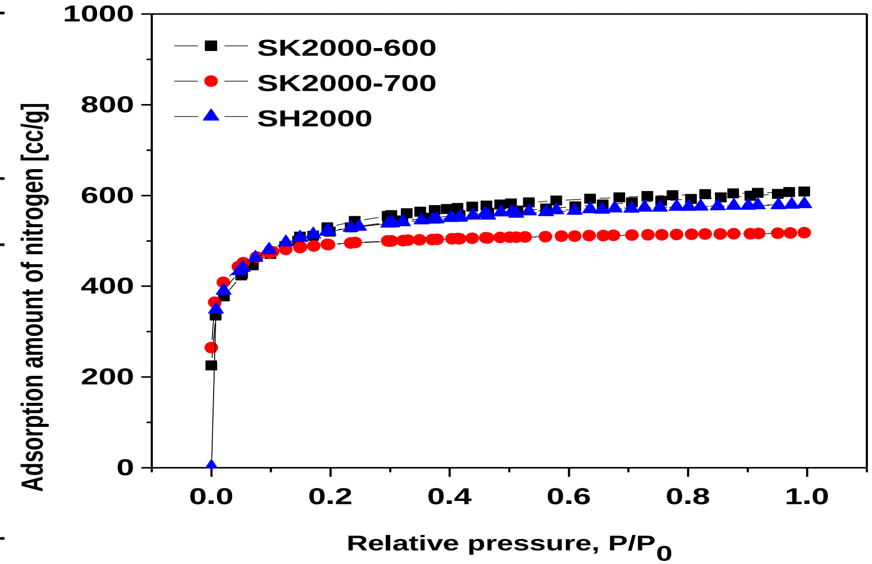


※シャープピークを0ppmに合わせている。

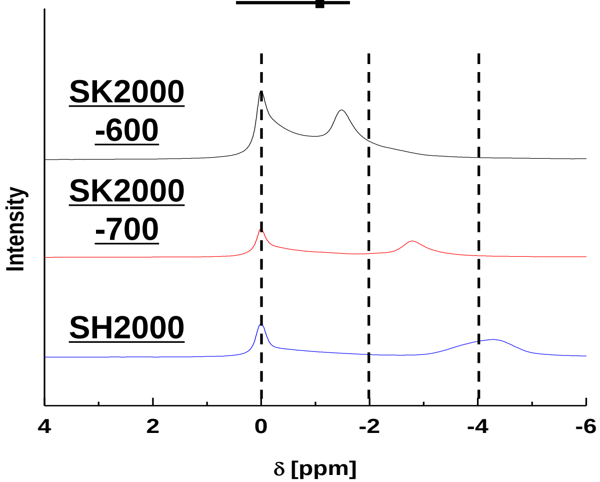
Sample	BET SA [m²/g]	Elemental analysis [%]					ED [g/ml]	Capacitance		
		H	C	N	O	Ash		F/g	F/ml	F/m²
SB−Gr	1	0.07	99.92	0.00	0.01	0.00	1.00	1.83	1.47	−
SB−HT	450	3.36	91.66	0.02	4.92	0.04	0.79	1.75	1.10	0.004
SK2000	1850	1.47	79.6	0.03	19.0	0.00	0.55	37.8	16.6	0.020
SH2000	1850	0.70	96.5	0.00	2.44	0.39	0.61	24.0	10.4	0.013

Ionic behaviors of activated carbons

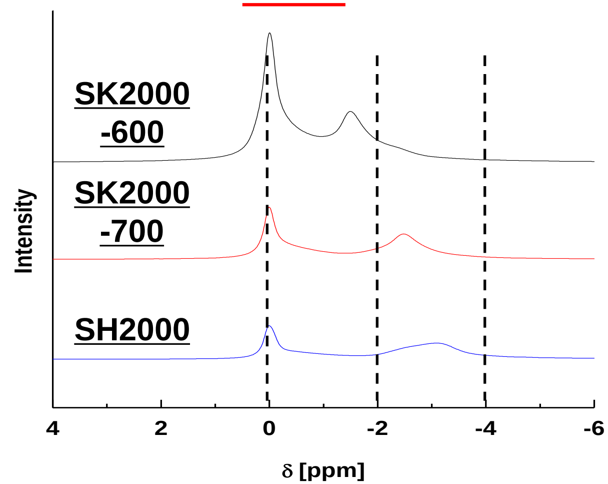
Sample	Activa-tion Temp.	BET SA [m^2/g]	ED [g/ml]	Capacitance		
				F/g	F/ml	F/m^2
SK2000 −600	600℃	1850	0.63	37.8	16.6	0.020
SK2000 −700	700℃	1700	0.60	30.2	14.5	0.018
SH2000	850℃	1850	0.61	24.0	10.4	0.013



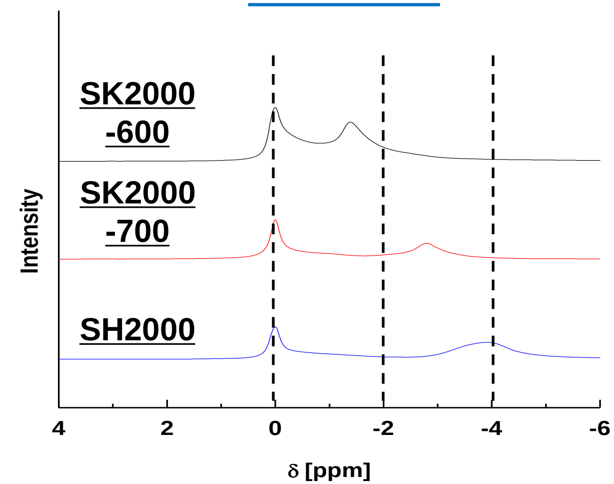
Imp



Ch.



Disch.

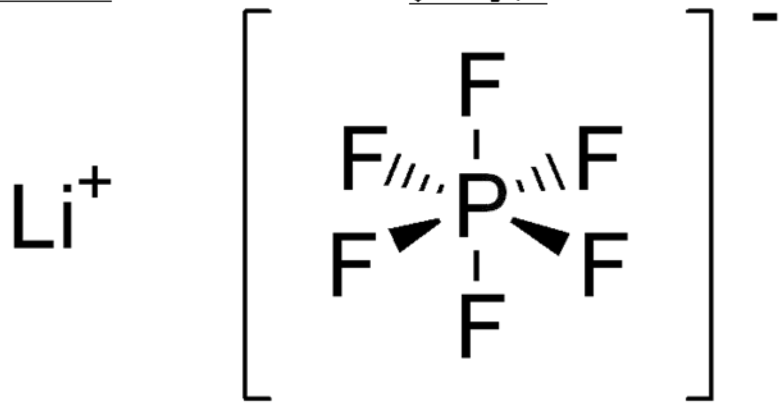


※シャープピークを0ppmに合わせている。

固体NMR測定

有機系電解質：$LiPF_6$

カチオン　　　　アニオン



Li ion　　　Hexafluorophosphate ion

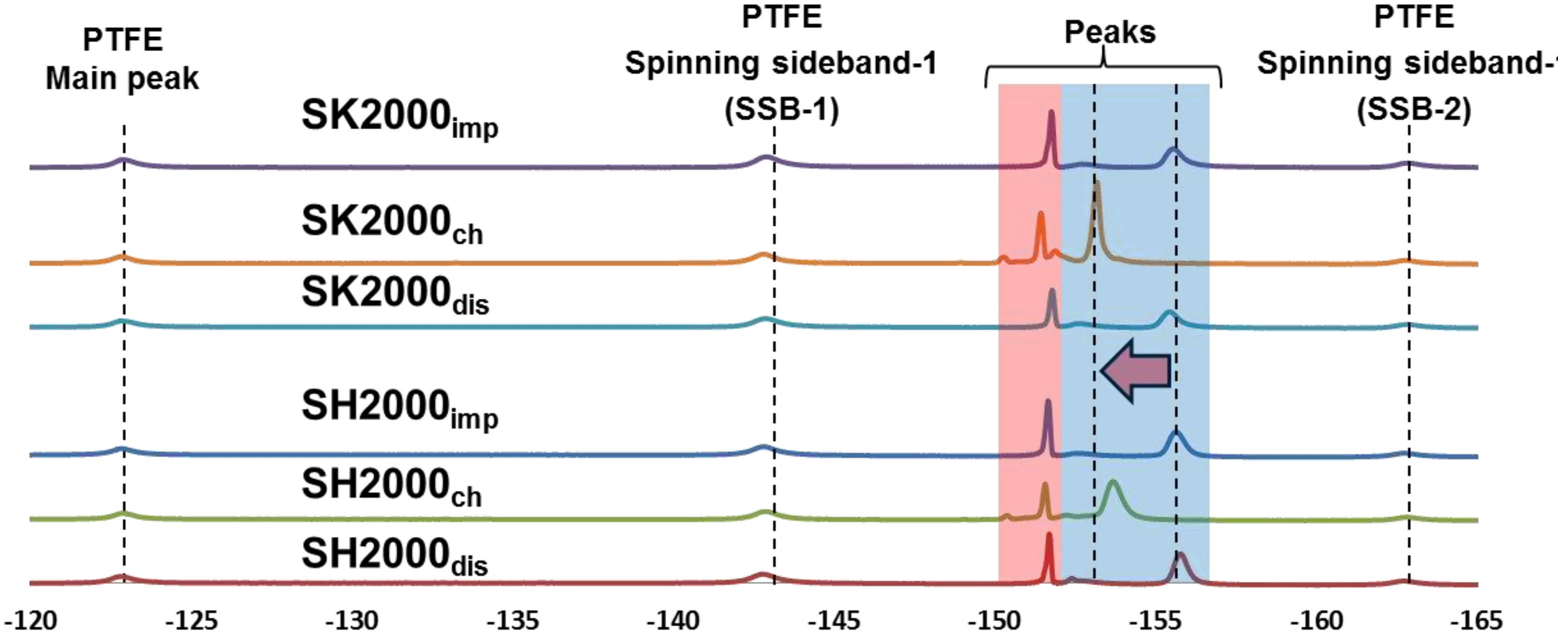
JEOL ECA800

^{7}Li固体NMRにより充放電時におけるカチオンを、
^{19}F固体NMRにより充放電時におけるアニオンを測定した。
作製した活性炭電極について

① 電解液を含浸させただけのもの
② 充電させたもの
③ 充電した後、放電させたもの

以上の状態について^{19}F固体NMR 測定を行った。

各状態（含浸、充電、放電）の^{19}F固体NMRスペクトル

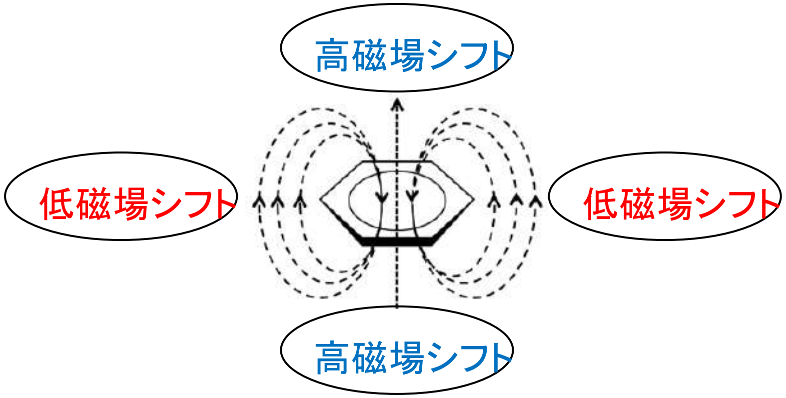


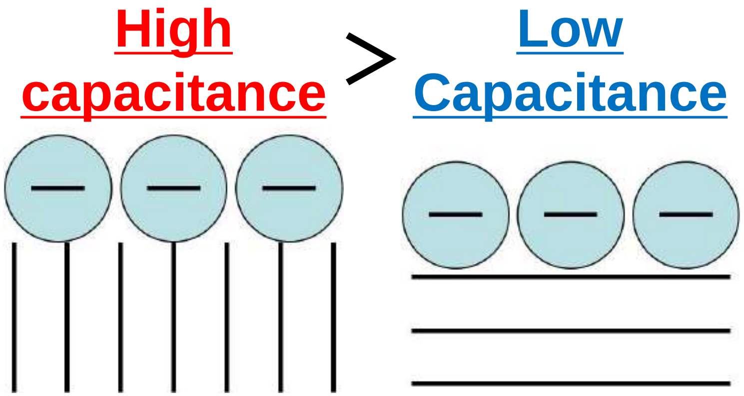
	Normalized BF4- by PTFE main peak					Peak area ratio
	PTFE Main Peak	PTFE-SSB ①	Peaks	PTFE-SSB②	ch-dis	SK/SH
$SK2000_{imp}$	1	1.44	3.22	0.58		
$SK2000_{ch}$	1	1.46	6.87	0.59	3.57	
$SK2000_{dis}$	1	1.44	3.30	0.58		
$SH2000_{imp}$	1	1.42	4.32	0.62		1.6
$SH2000_{ch}$	1	1.43	6.46	0.58	2.17	
$SH2000_{dis}$	1	1.48	4.29	0.61		

Ring current effect

Effect of edge and basal planes

Chemical shift（Ring current effect）Higher capacitance





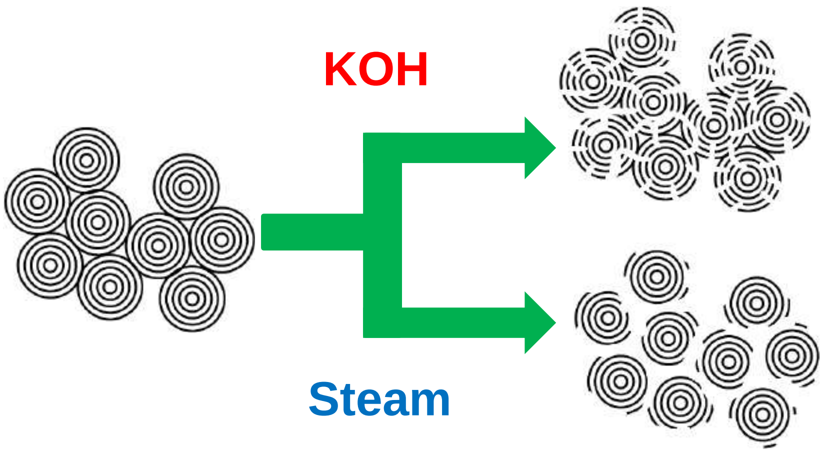
Kim T., et al.,Langmuir, 2006, 22(22), 9086-9088.

Adsorption on edge planes→ **Chemical shift to lower magnetic place, higher capacitance**
→SK2000: more edges

Why different by activation method

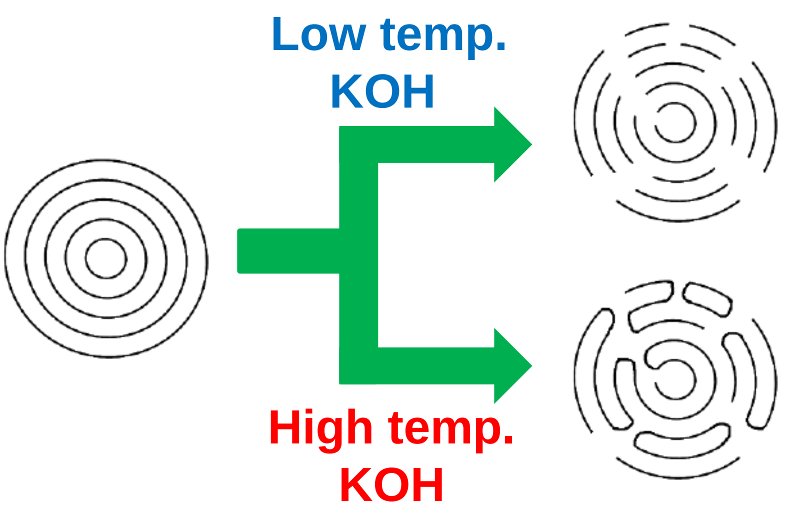
Different activation behavior

KOH: K intercalation and higher diffusion
Steam: Lower diffusivity into the inside of domain



Effect of activation temperature

KOH: lower temperature; effective to produce edge surface
Steam: higher temperature; effective to produce basal surface



Most effective pore size using NMR method

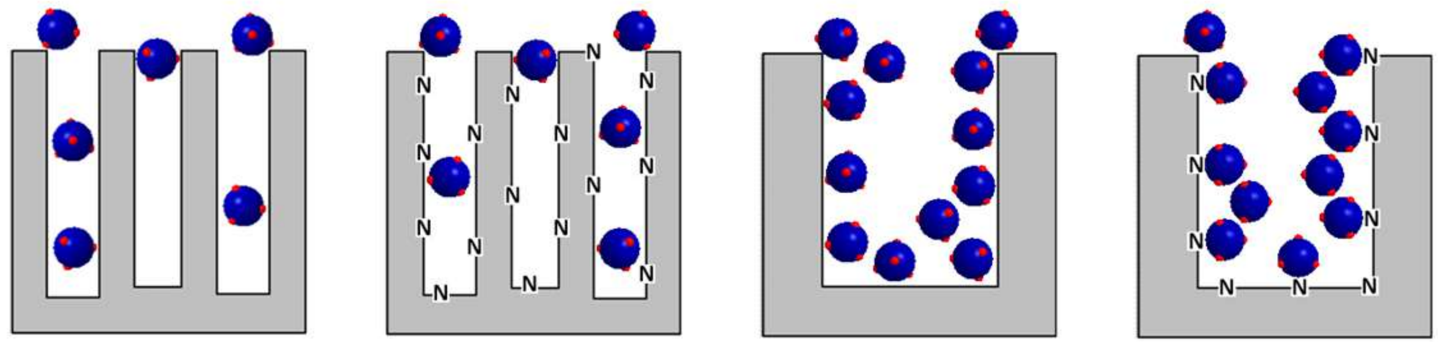
Pitch-based Activated Carbon Fibers (ACFs)

OG series : OG-5A, OG-7A, OG-10A, OG-15A, OG-20A (Osaka Gas Co., Japan)

PAN-based ACFs

FE series : FE-100, FE-200, FE-300, FE-400 (Toho TENAX Co., Japan)

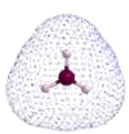
Model of micropores of OG and FE series



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

Aqueous and non-aqueous electrolytes with different ion sizes

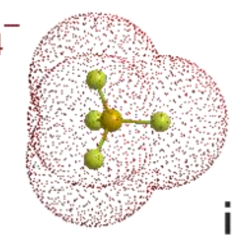
H_3O^+



in H_2SO_4/H_2O

≪

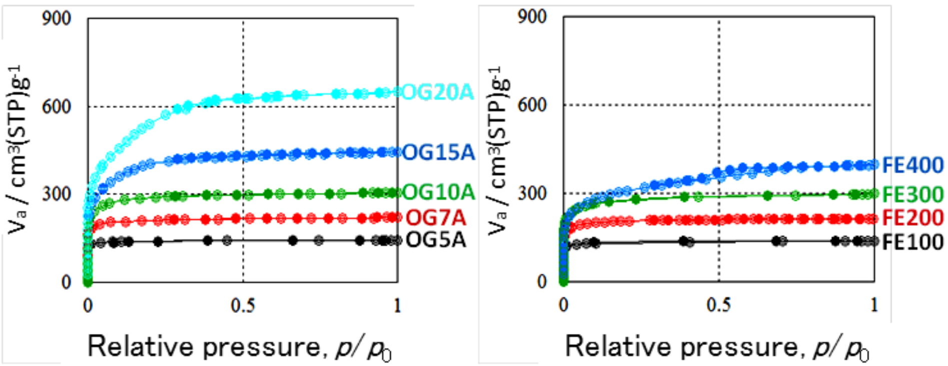
BF_4^-



in Et_4NBF_4/PC

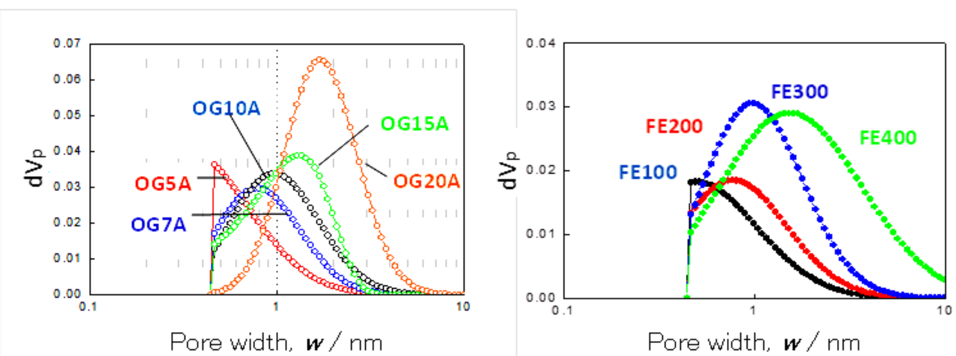
NMR method

N_2 adsorption/desorption isotherms @77K



Pore size distributions

(*calculated by NL-DFT method*)

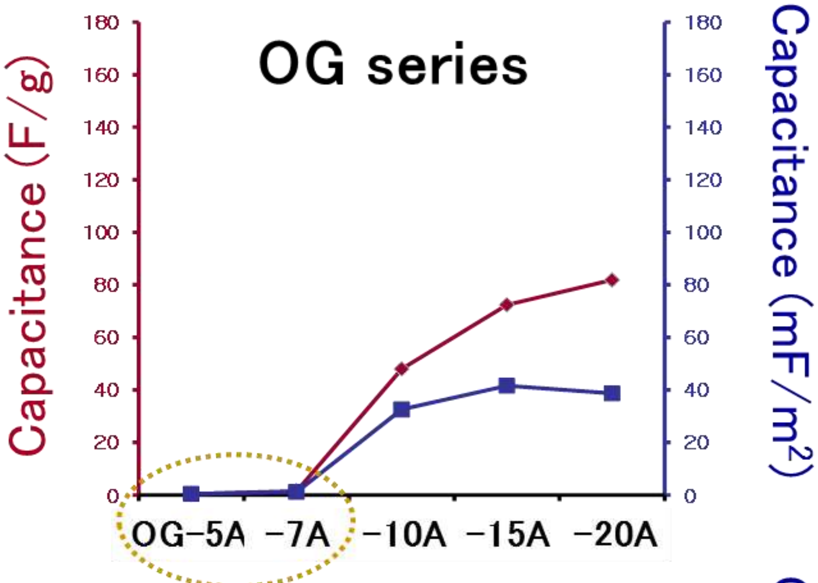


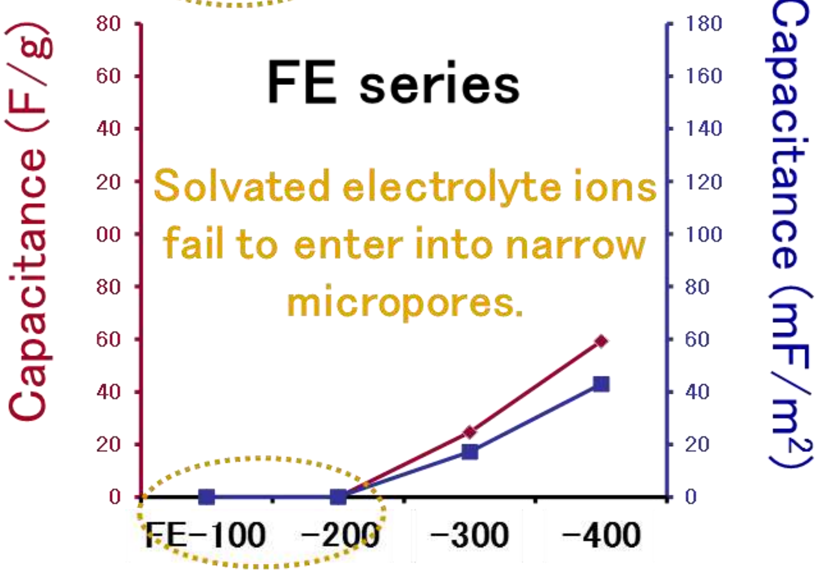
Pore structure parameters

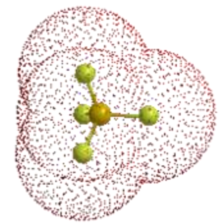
(*calculated from t-plot method*)

	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

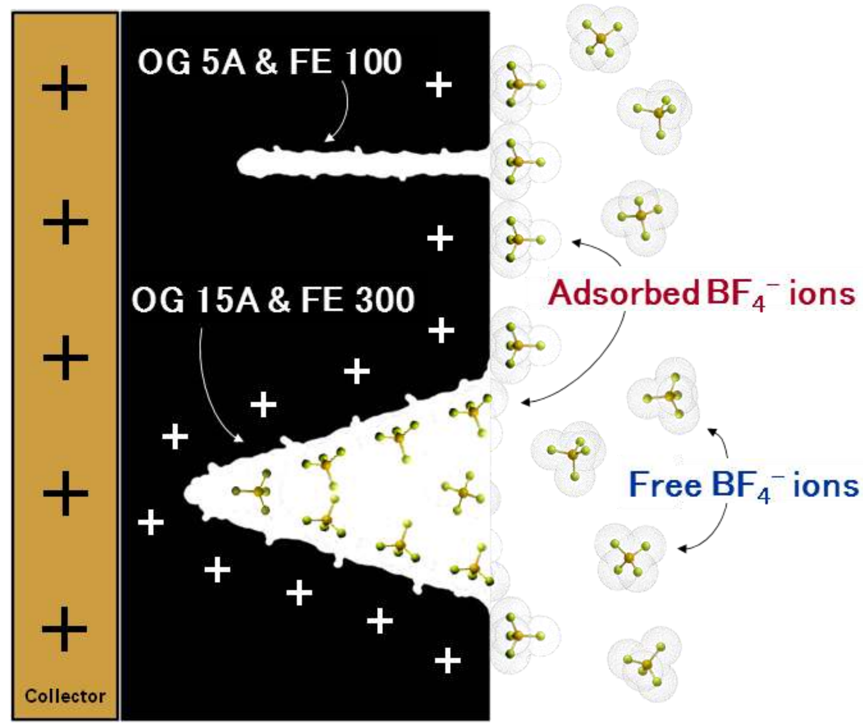
NMR method



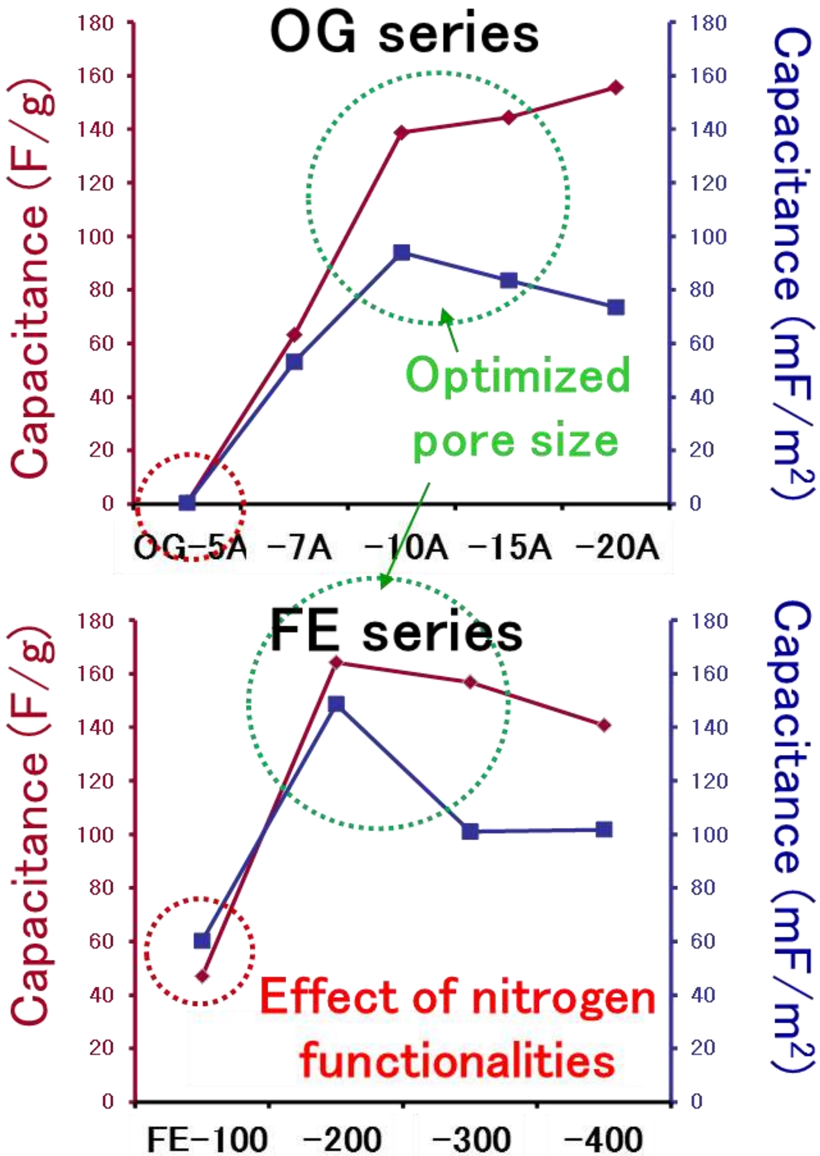


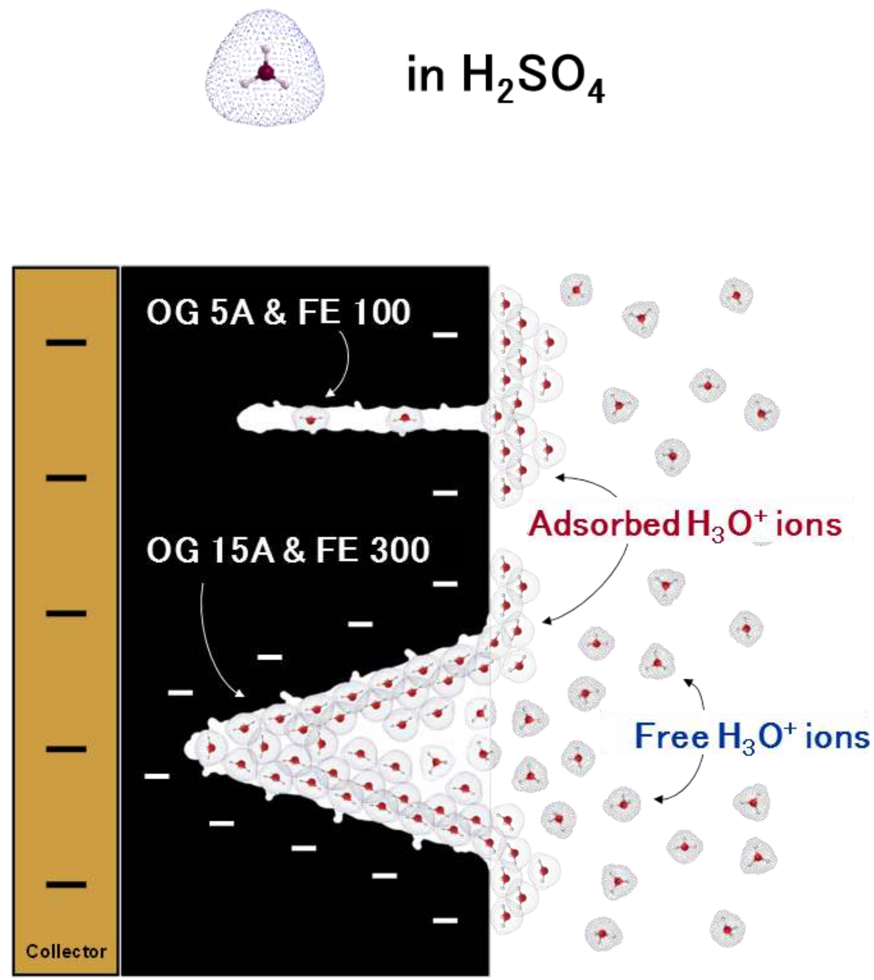


in Et_4NBF_4/PC



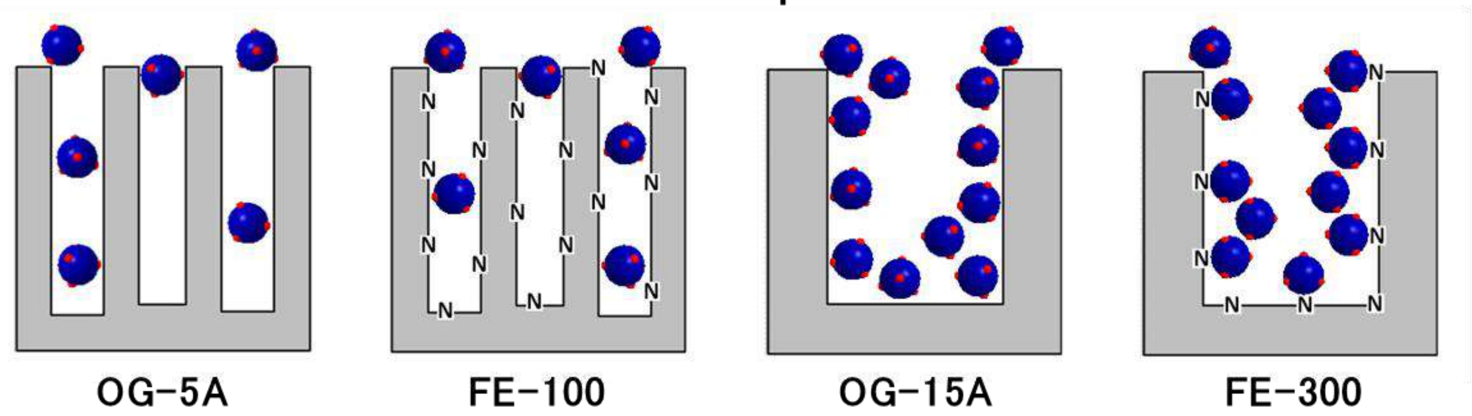
NMR method


OG series
Capacitance (F/g)
Capacitance (mF/m²)
180
160
140
120
100
80
60
40
20
0
OG-5A
-7A
-10A
-15A
-20A
Optimized
pore size
FE series
FE-100
-200
-300
-400
Effect of nitrogen
functionalities


in H_2SO_4
OG 5A & FE 100
OG 15A & FE 300
Adsorbed H_3O^+ ions
Free H_3O^+ ions
Collector

NMR method

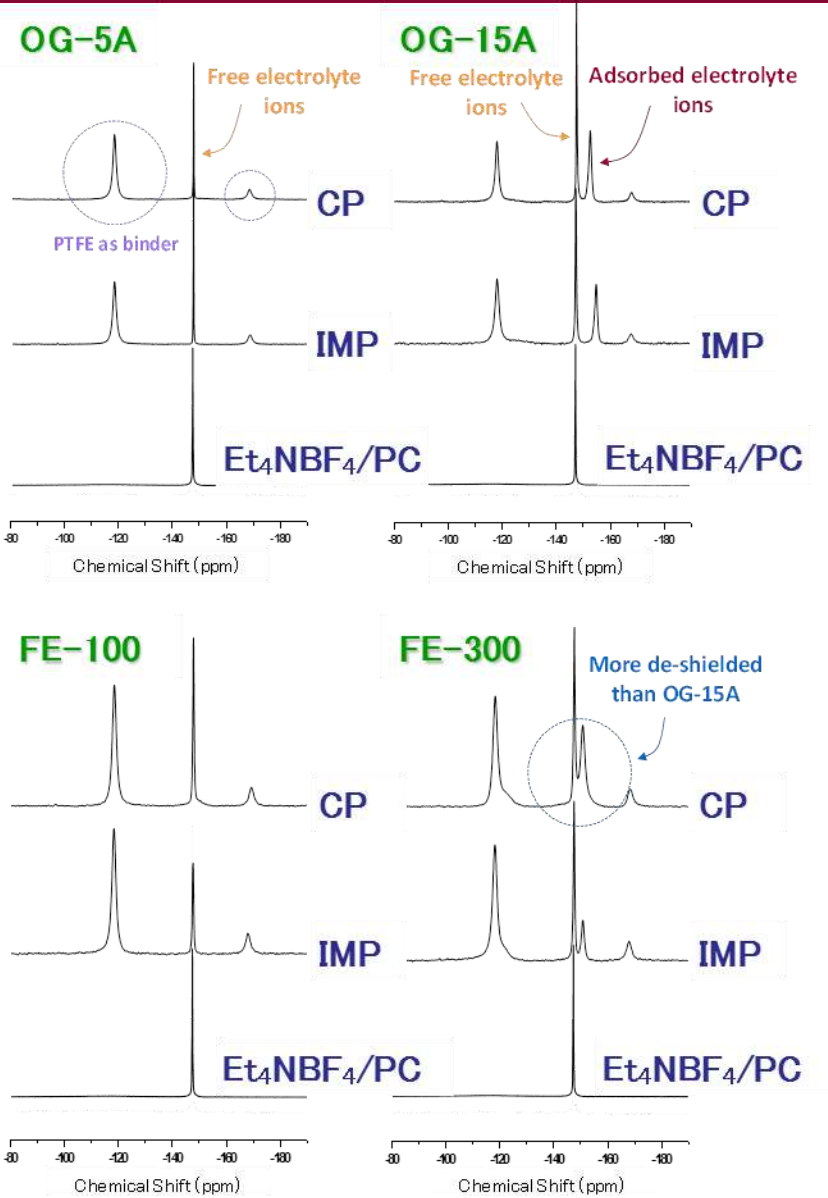
Model of adsorbed ions in micropores of OG and FE series

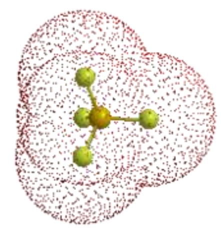


^{2}H or ^{19}F magic angle spinning (MAS) solid state NMR

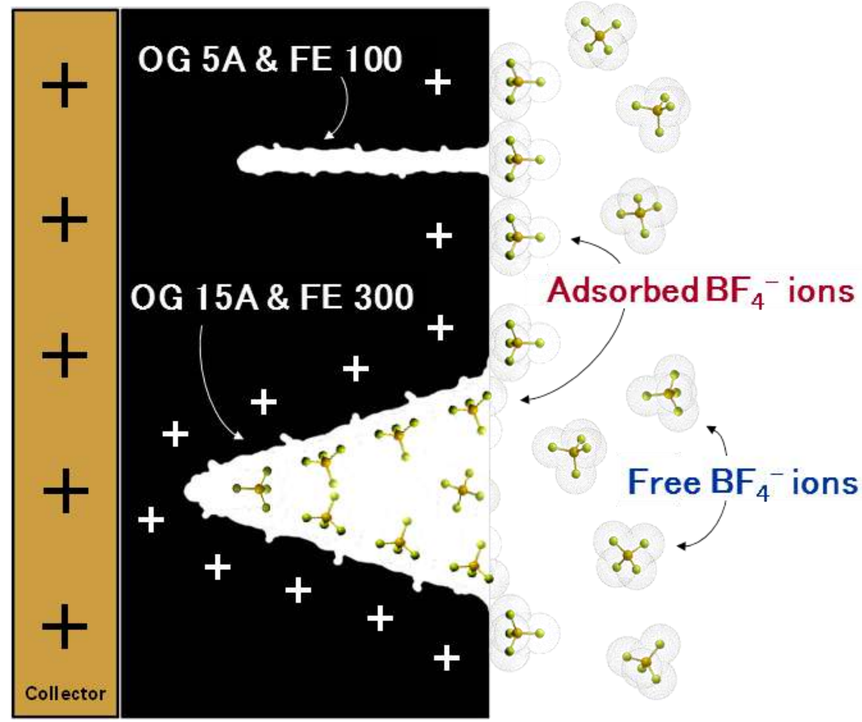
NMR equipment:	JEOL ECA400
Electrolytes:	0.5 M D_2SO_4 (aqueous)
	1 M Et_4NBF_4/PC (in-aqueous)
Electrode states:	Impregnated (IMP)
	Charged plus (CP)
	Charged minus (CM)

^{19}F MAS Solid-State NMR Spectra

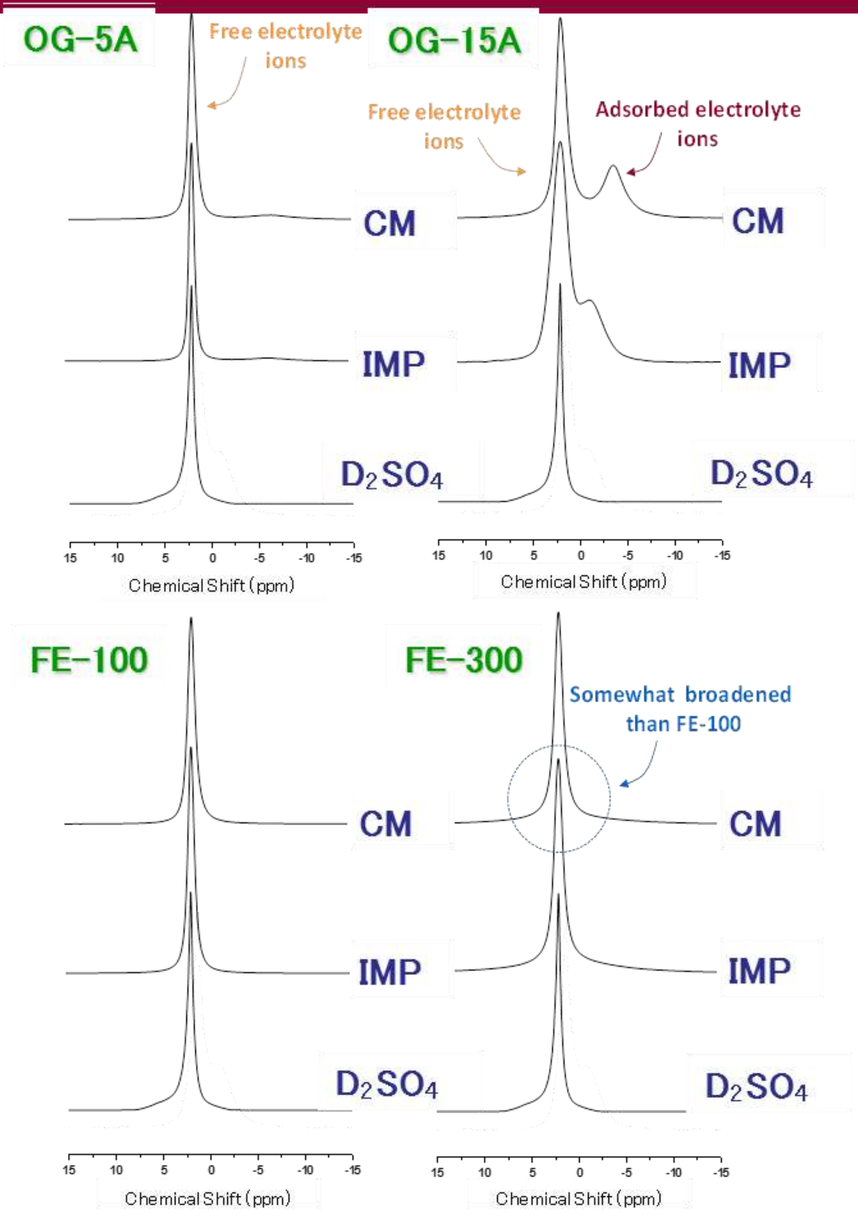


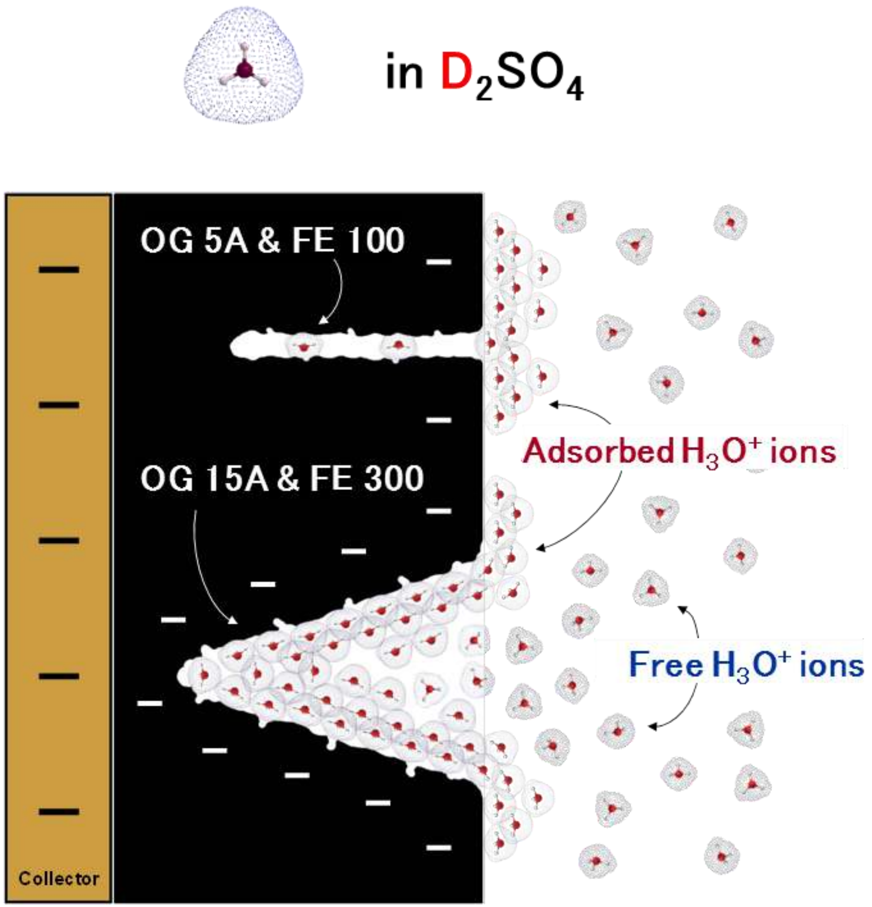


in Et_4NBF_4/PC



^2H MAS Solid-State NMR Spectra

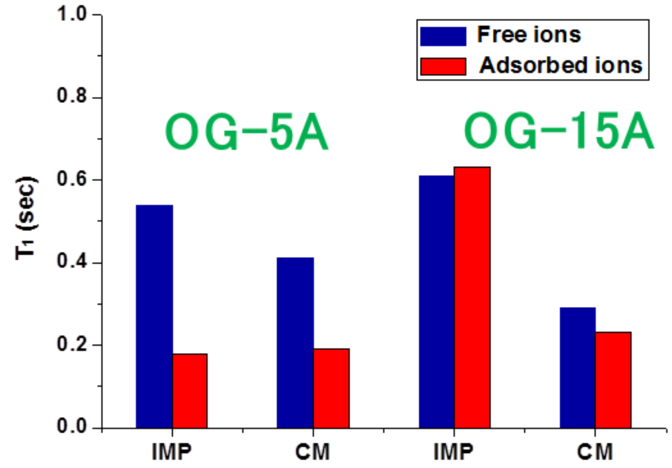




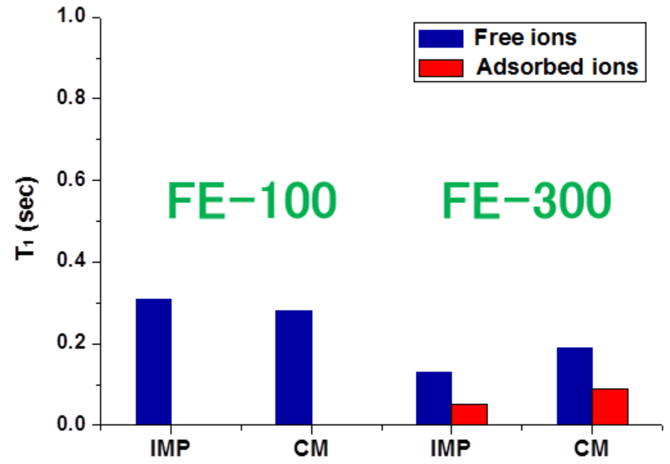
T_1 Values Measured from ^2H MAS Solid-State NMR

The shorter the T_1 value of relaxation time, the stronger the adsorption interaction between adsorbed electrolyte ions and carbon electrodes.

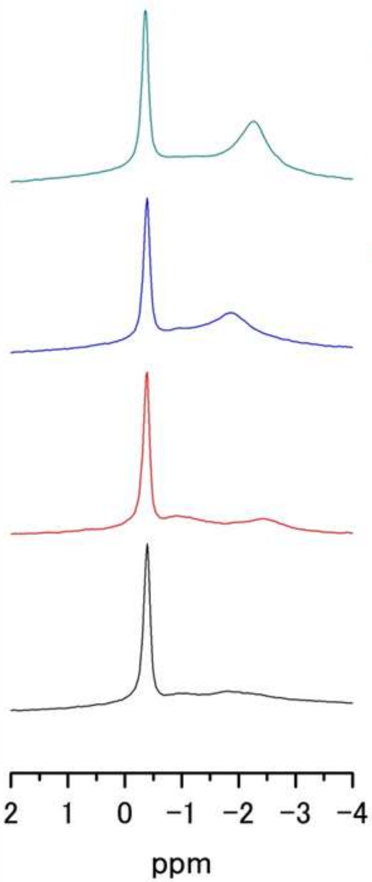
T_1 (sec) for OG series							
OG-5A				OG-15A			
IMP		CM		IMP		CM	
Free	Adsorbed	Free	Adsorbed	Free	Adsorbed	Free	Adsorbed
0.54	0.18	0.41	0.19	0.61	0.63	0.29	0.23



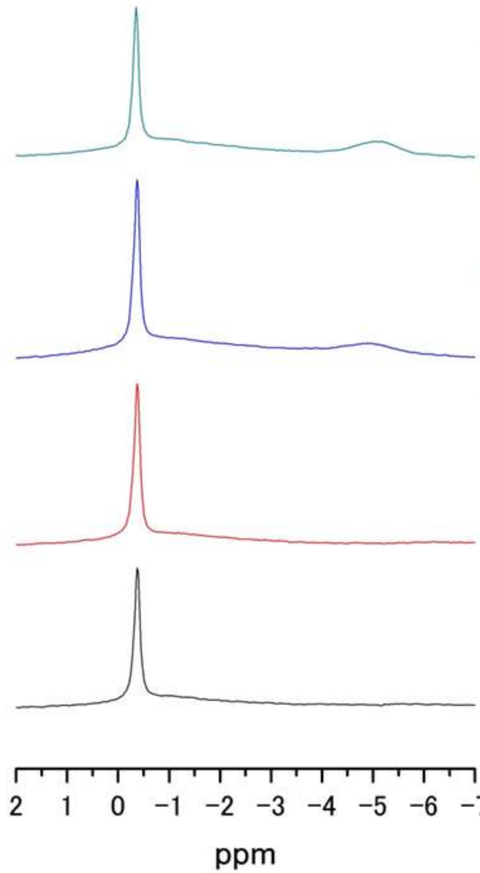
T_1 (sec) for FE series							
FE-100				FE-300			
IMP		CM		IMP		CM	
Free	Adsorbed	Free	Adsorbed	Free	Adsorbed	Free	Adsorbed
0.31	–	0.28	–	0.13	0.05	0.19	0.09



^{7}Li固体NMRスペクトル



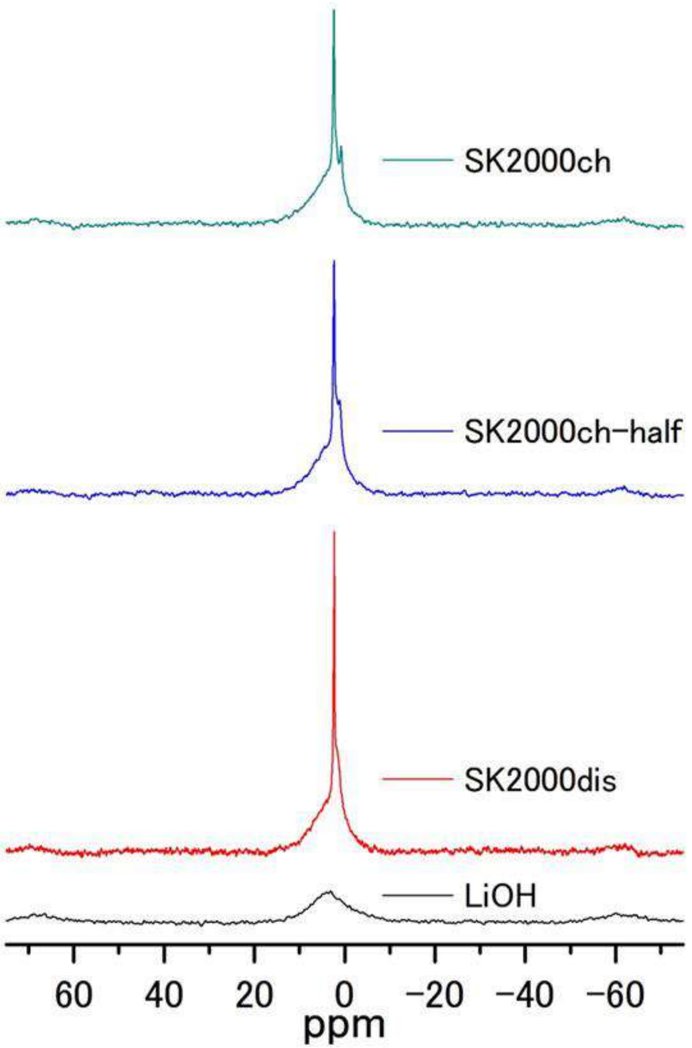
試料	(T_1) [s]	
	A	B
2000_{ch}	0.65	0.18
2000_{dis}	0.51	0.26
1000_{ch}	0.65	0.43
1000_{dis}	0.53	0.44

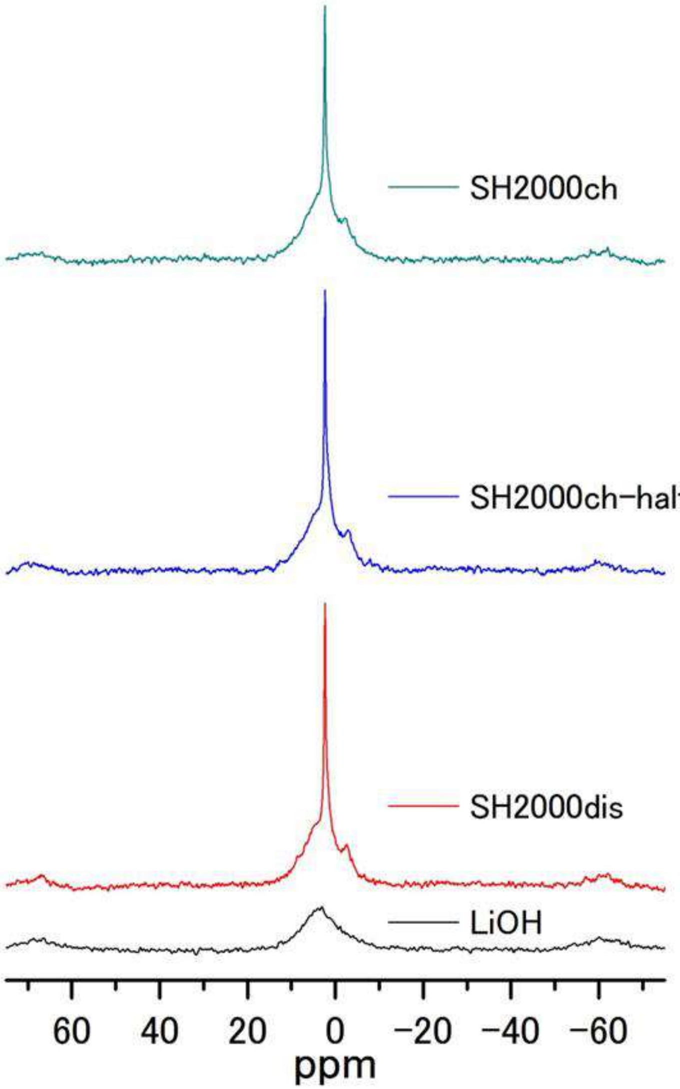


試料	(T_1) [s]	
	A	B
2000_{ch}	0.67	0.55
2000_{dis}	0.58	0.31
1000_{ch}	0.64	0.49
1000_{dis}	0.65	0.48

いずれも0ppm近傍にシャープなピークと高磁場側にブロードなピークが観測された。ブロードなピークはSK、SHではSKの方がより高磁場側に現れ、また、充電に際して低磁場側にケミカルシフトすることが確認された。

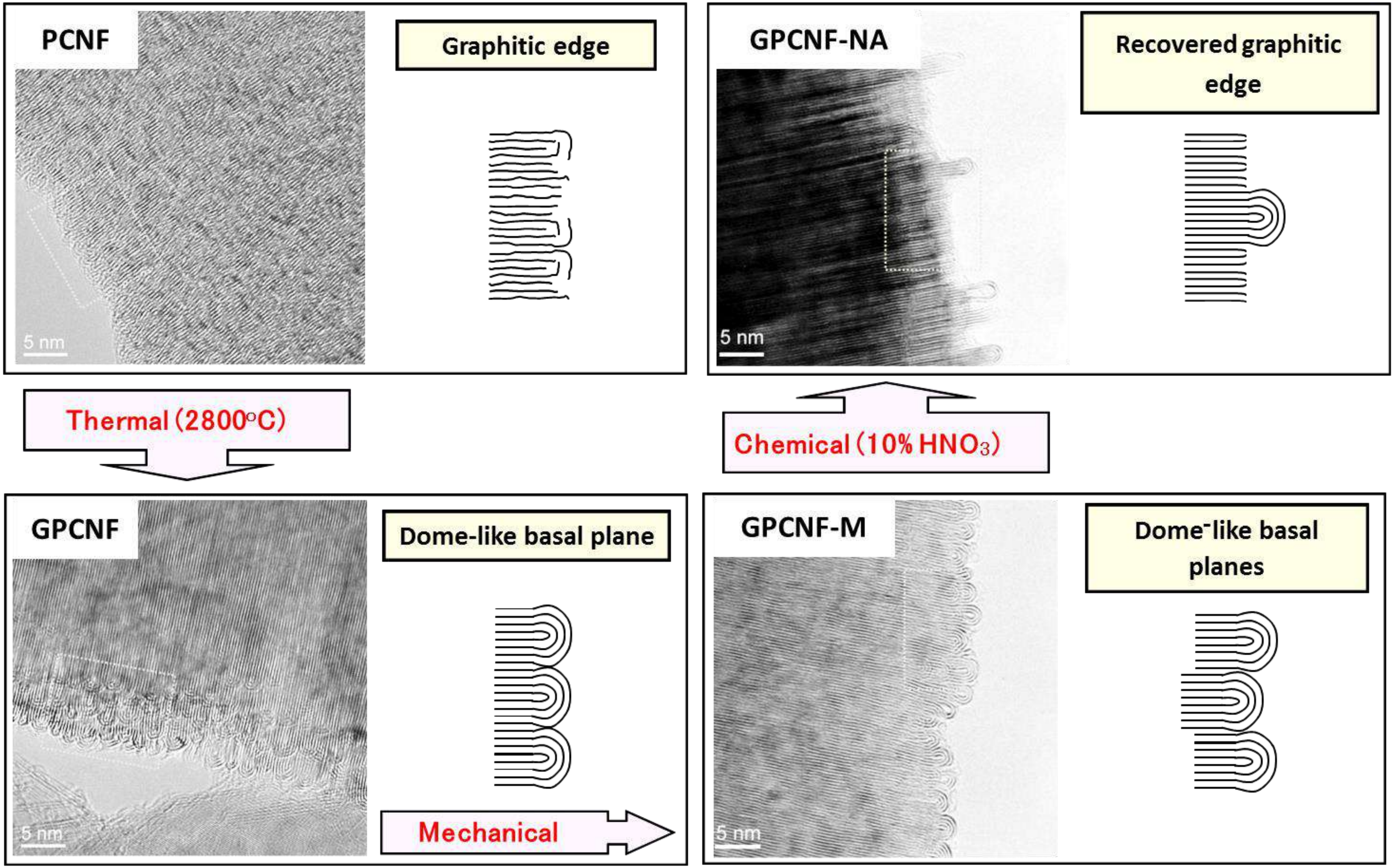
^{7}Li固体NMRスペクトル





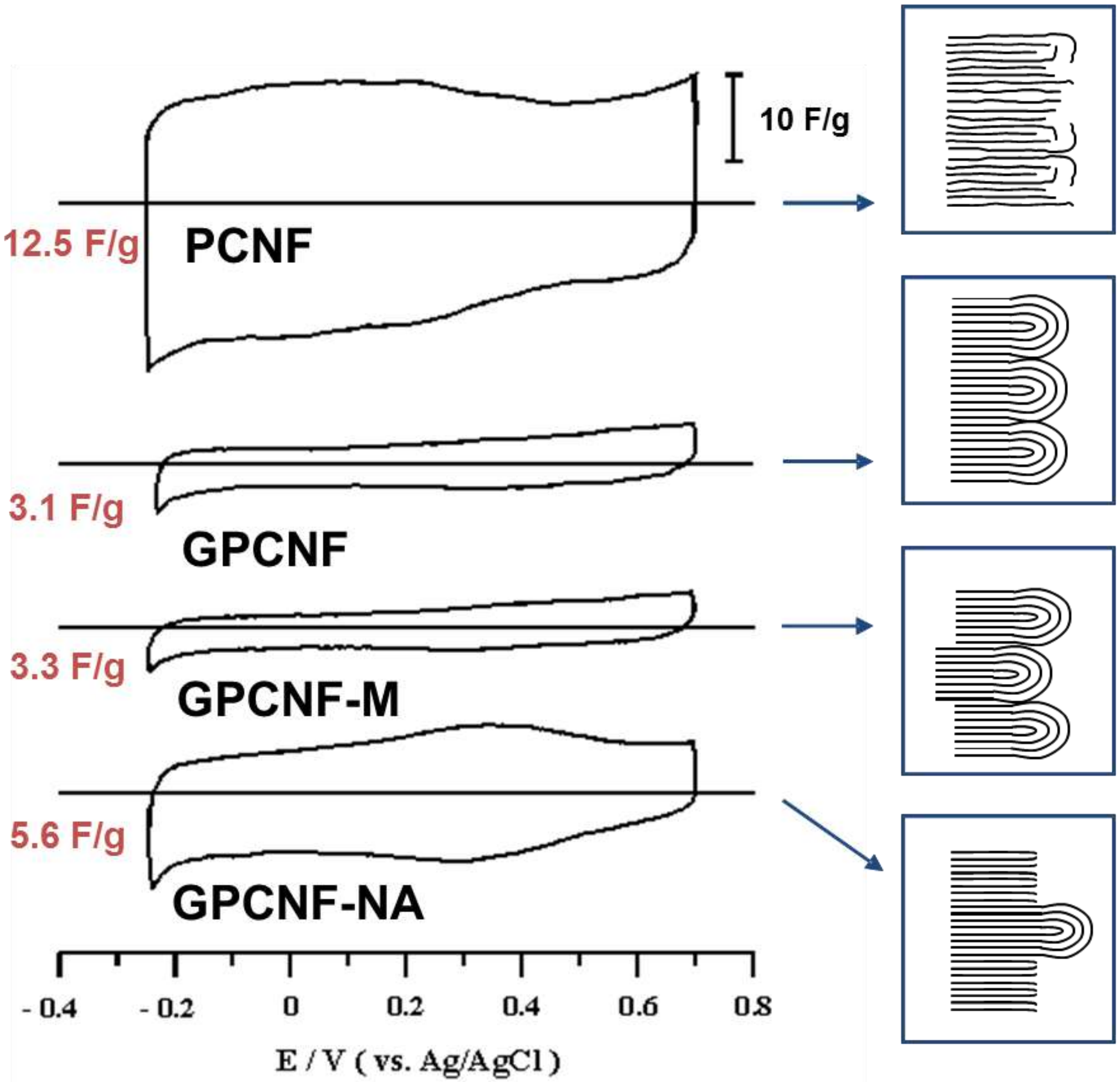
Surface modified PCNFs

Langmuir
2006, 22(22), 9086.



Capacitances of PCNF series

Langmuir 2006, 22(22), 9086.



PCNFs having

edge surfaces

Showed 3-5 times

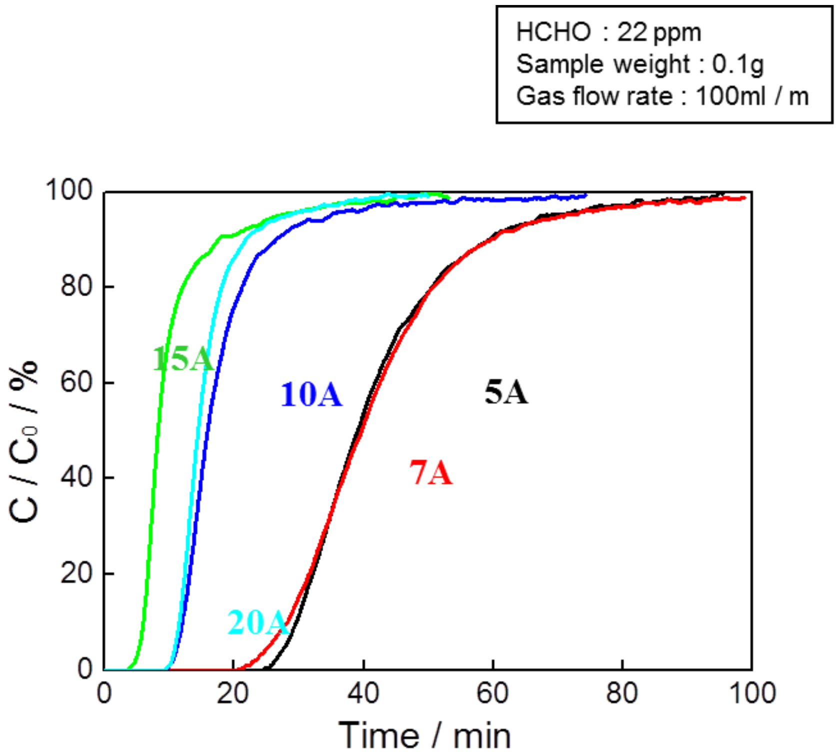
Higher capacitancs

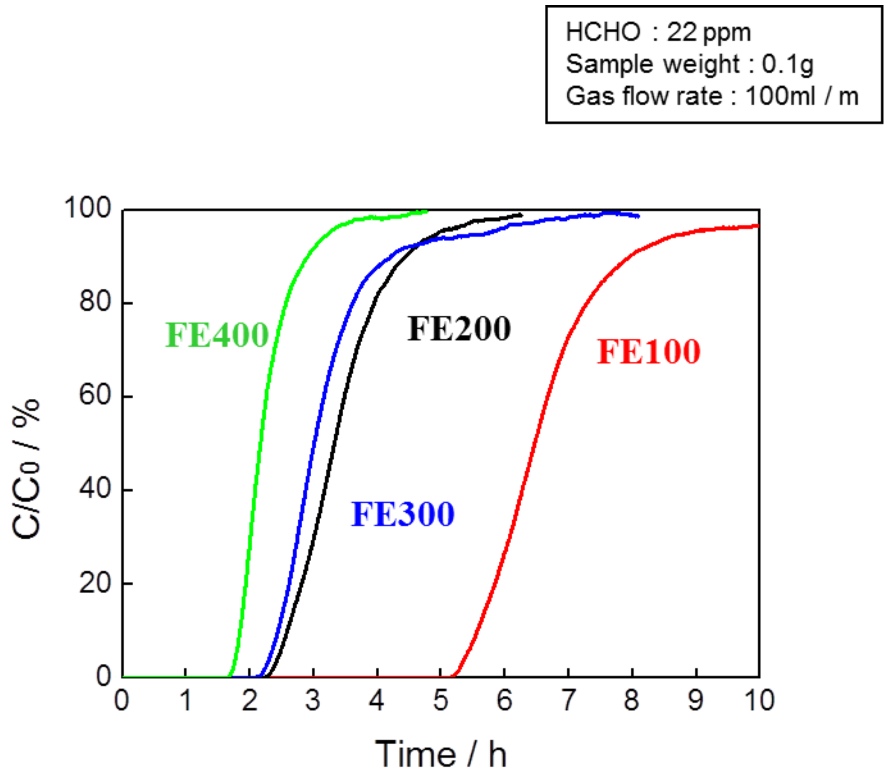
Novel applications of activated carbons

1. HCHO, removal of sickhouse gases
2. Medicine
3. Capacitive De-ionization （CDI）
4. Heat Pump（Energy saving）

1. HCHO, Removal of sickhouse gas

HCHO removal using activated carbon fibers



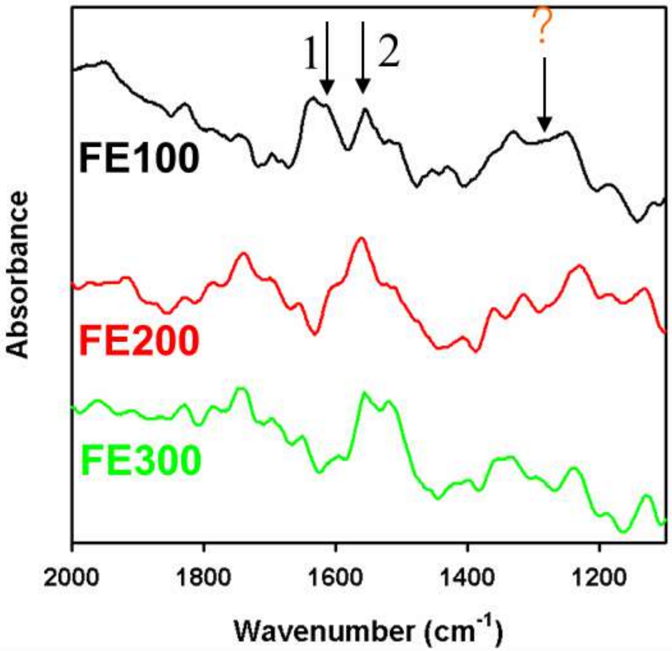


Break through time

◆**Pitch-based ACF : 15A < 20A < 10A < 7A < 5A**

◆**PAN-base ACF : FE400 < FE300 < FE200 < FE100**

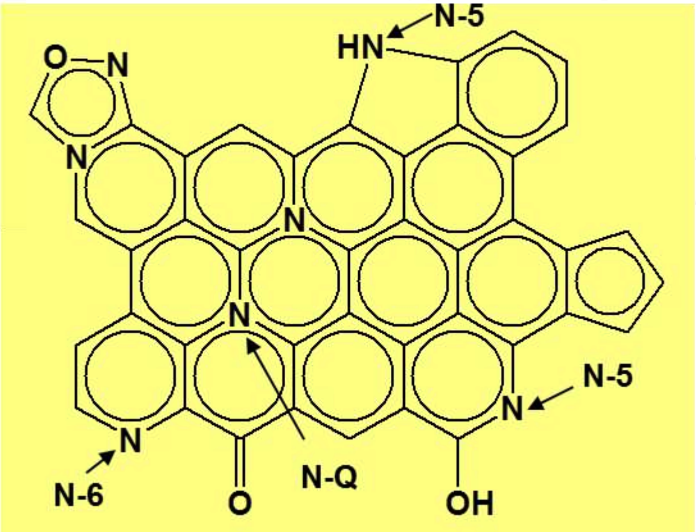
Surface analysis of PAN ACF by Micro ATR-FTIR



1) *Pyridinic nitrogen band*
2) *Internal standard*

	Micro-ATR FTIR analysis			EA and XPS analysis		
	I.S[a]	Pyridinic N[b]	RCP[c]	N / C ratio	Pyridinic N[b]	RCP[c]
FE100	279	134	0.48	0.118	0.737	0.087
FE200	276	108	0.39	0.066	1.050	0.069
FE300	332	70	0.21	0.044	0.734	0.032

[a]I.S : Internal standard (1560cm^{-1})
[b]Wavenumber related with pyridinic nitrogen : 1610~1600cm^{-1}
[c]RCP : relatives contents of pyridinic nitrogen



Pyridinic N (N-6)
Pyrrolic or Pyridinic N (N-5)
Quaternary N (N-Q)

Micro-ATR FTIR results

Relative amount of pyridinic nitrogen functional groups for PAN based ACFs by micro-ATR FTIR analysis

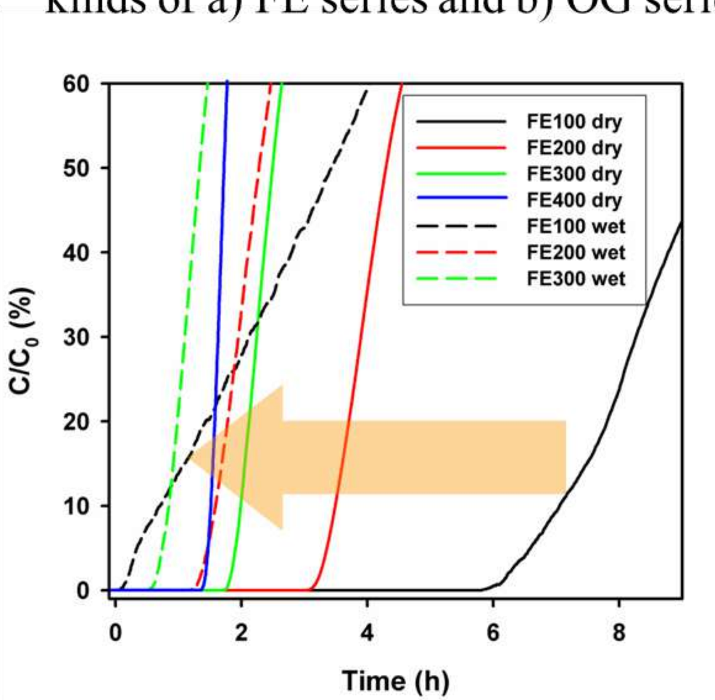
Sample	Internal Standard	Pyridinic N [a]	Internal Standard /Pyridinic N
FE100	279	134	0.48
FE200	276	108	0.39
FE300	332	70	0.21
FE400	330	64	0.19

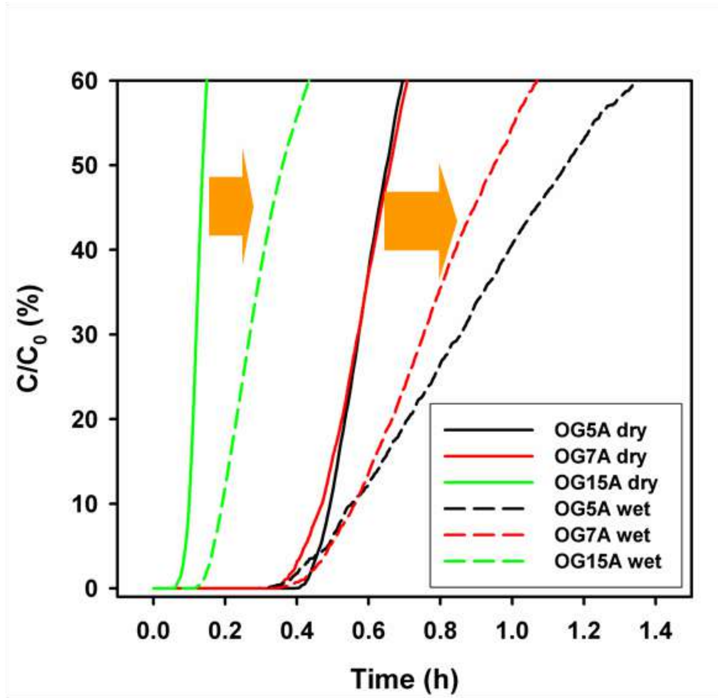
[a] Wavenumber related with pyridinic nitrogen: 1610 ~ 1600 cm^{-1}

Humidity effect for removing HCHO

WATER Competitive adsorption decreases the adsorption amount of HCHO.

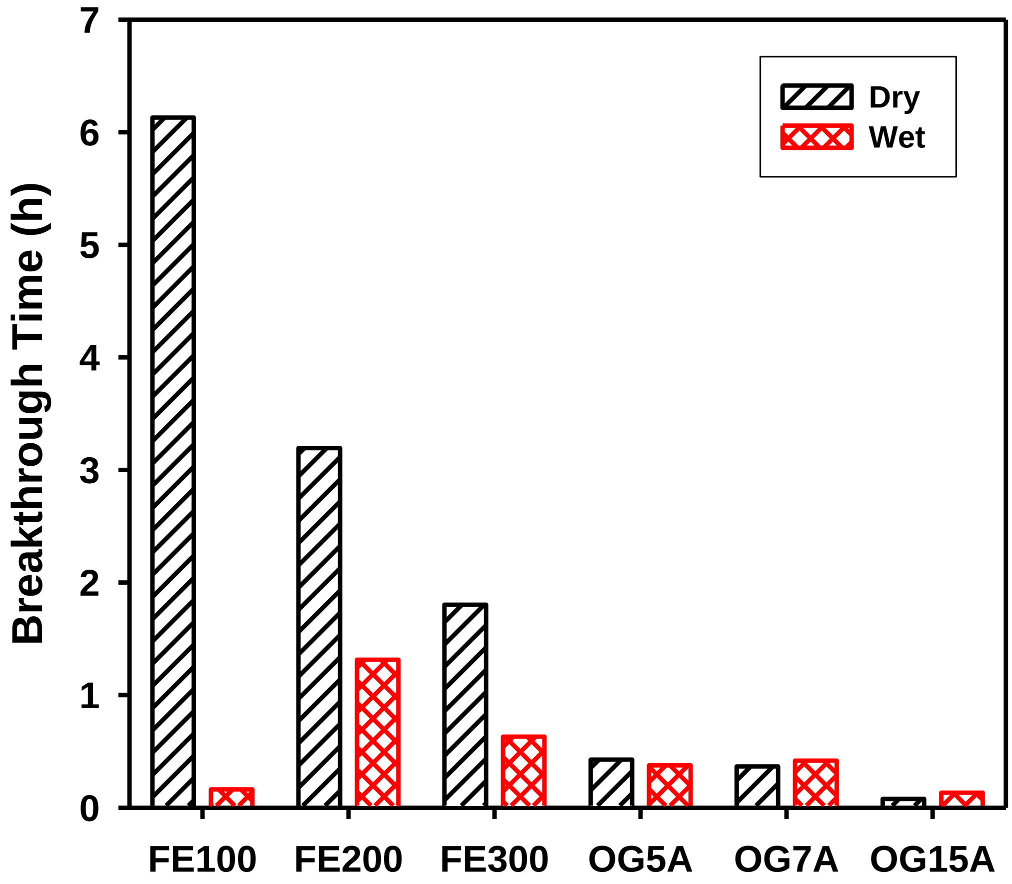
Dry condition (solid line) and wet condition (dashed line) for the different kinds of a) FE series and b) OG series





JOURNAL OF APPLIED POLYMER SCIENCE 106 (4): 2151-2157 NOV 15 2007

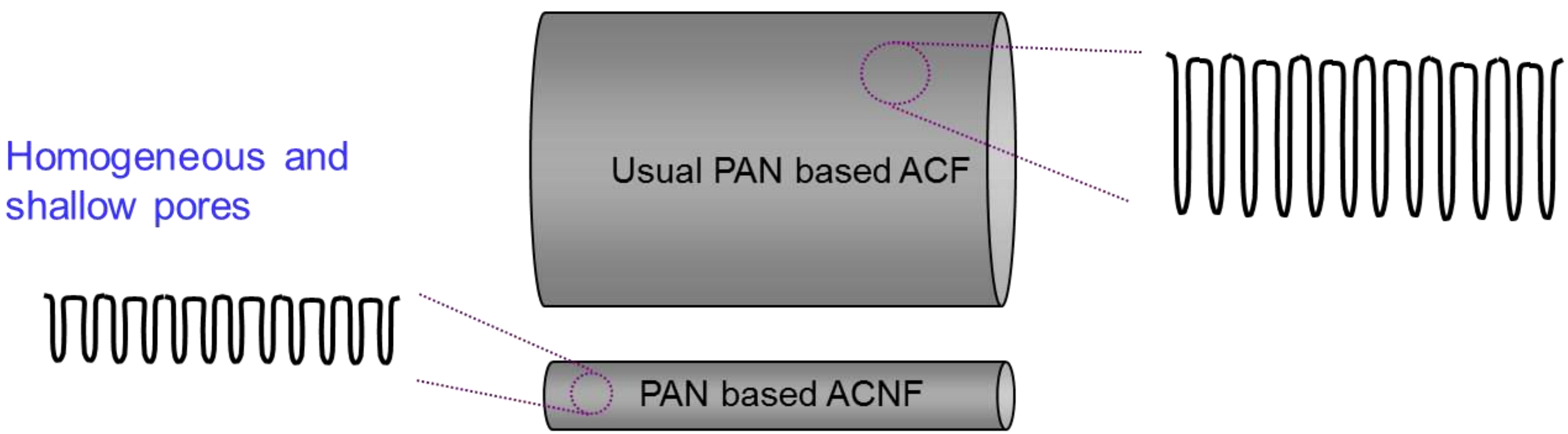
Humidity effect for removing HCHO



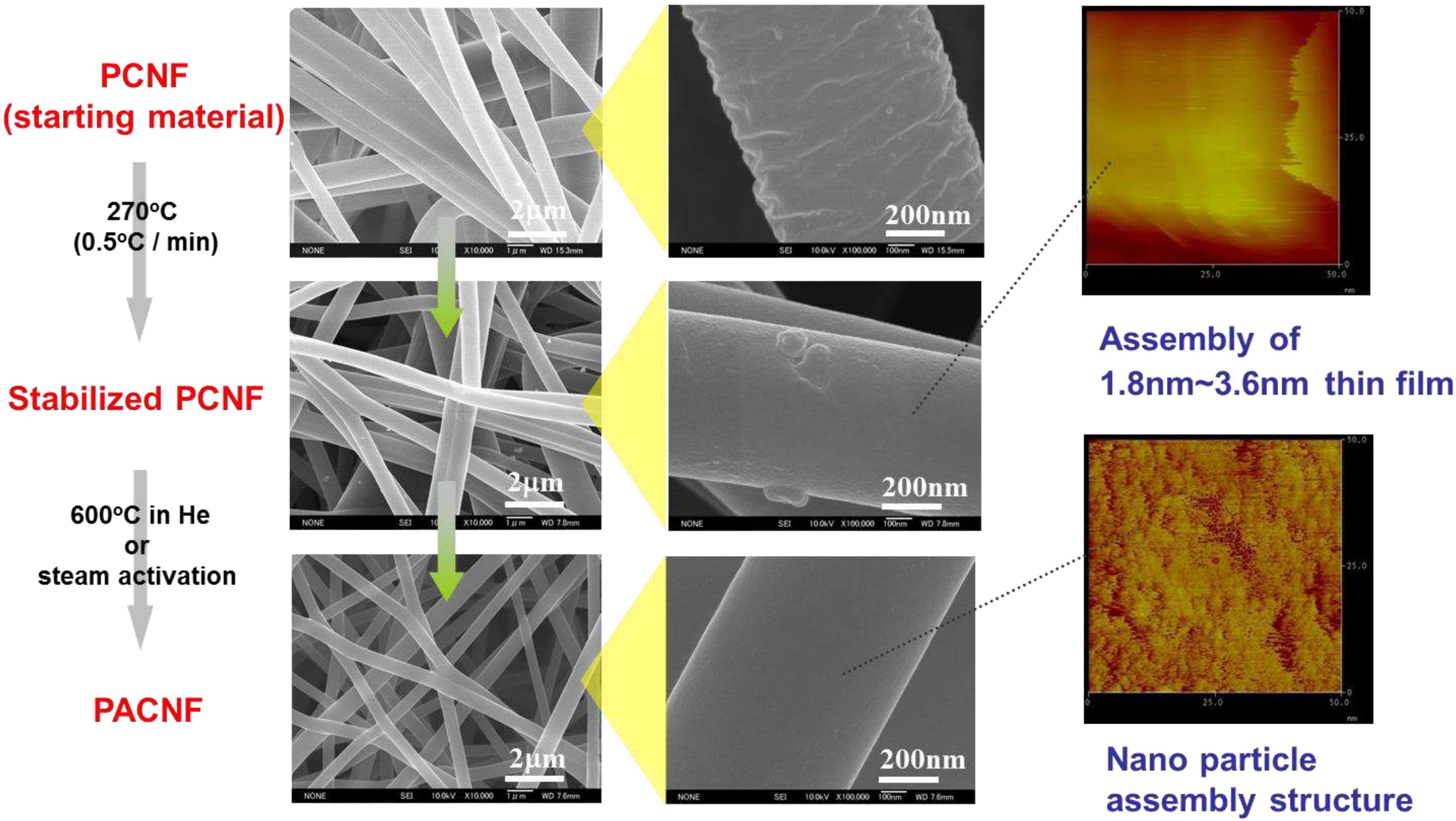
New concept (shallow pore)

- Electrospun PAN based nanofiber (100% PAN)
  Diameter: 800 nm, Nanotechnics (Korea)

100 times surface area compared to usual PAN fiber
→Can be expected very shallow and homogenous pores。

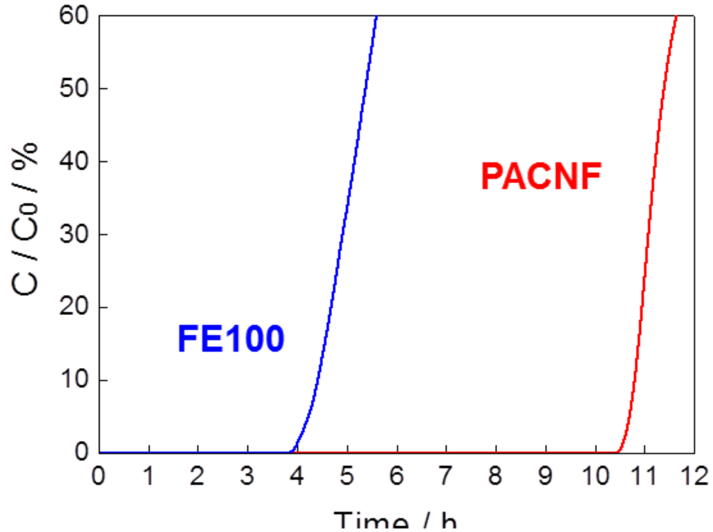


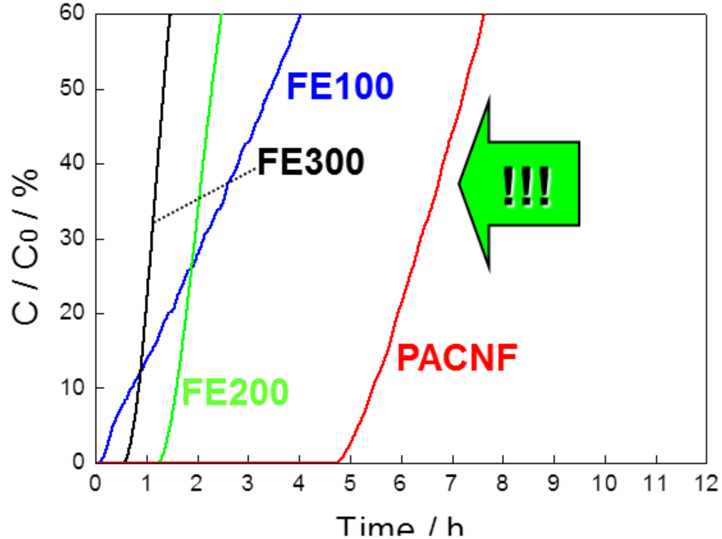
PAN based activated carbon nanofiber



HCHO removal using PAN ACNF

RH	BET	Elemental analysis (wt%)						Microporous
	(m2 / g)	C	H	***N***	***Odiff***	ash	N / O	ratio (%)
90%	375	68.06	1.19	***18.02***	***11.41***	1.32	1.80	94.7%





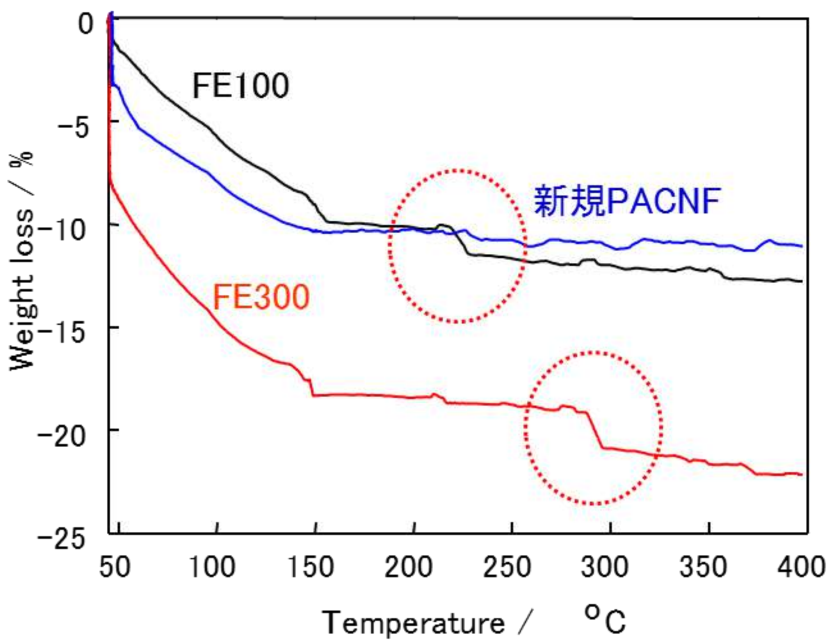
Experimental
HCHO : 11 ppm
Sample weight : 0.05g
Gas flow rate : 100ml / ml
Humidity of condition : 0%

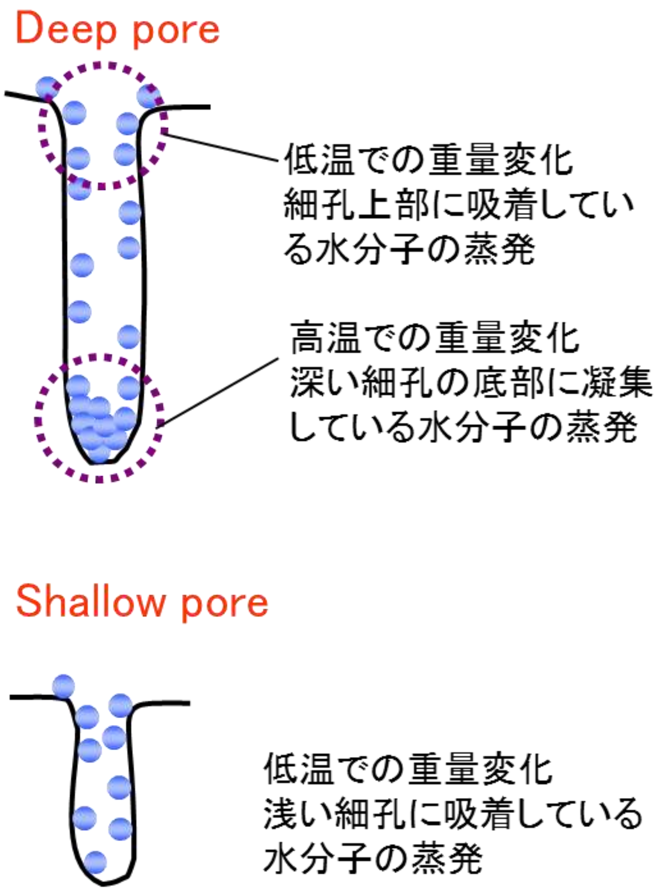
Experimental
HCHO : 11 ppm
Sample weight : 0.05g
Gas flow rate : 100ml / ml
Humidity of condition : 50%

Under the circumstances of humidity (RH=50%),
PACNF shows specific prominent adsorption characteristics for formaldehyde.

Shallow pore（?）

水分を飽和吸着させたサンプルを
アルゴン中で400℃まで昇温させ、
重量変化を観察





Carbon, 48, 4248-4255 (2010).

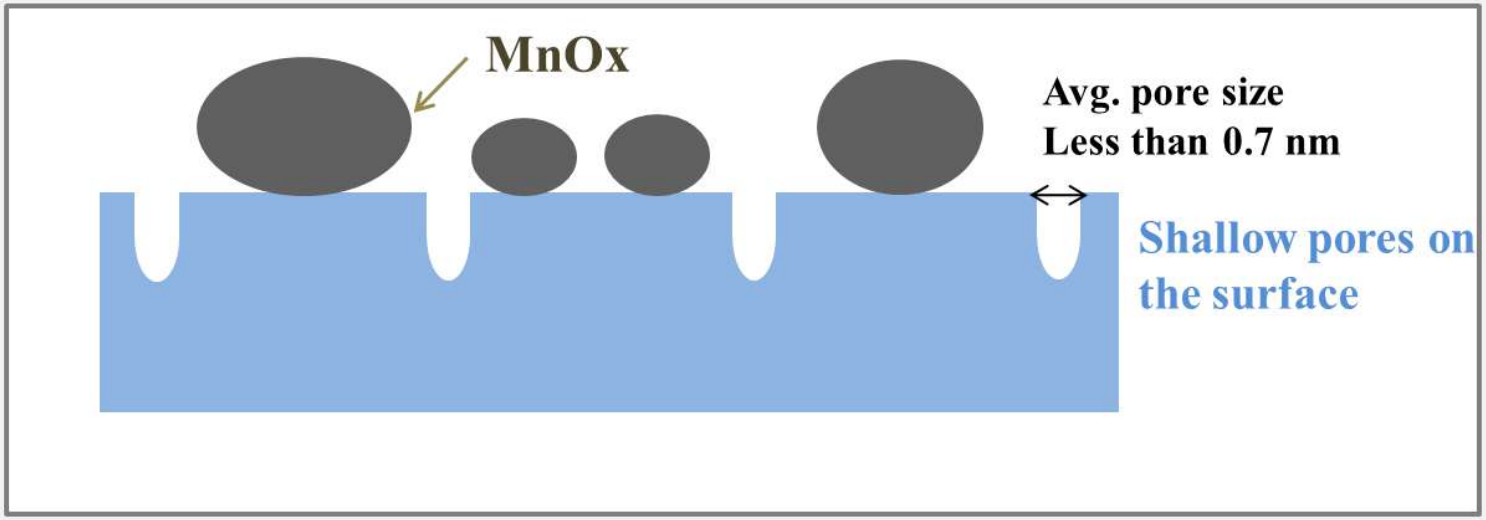
Complete removal of HCHO using MnOx/ACNF

① Activated nano carbon fiber

② Catalytic decomposition of HCHO by MnOx into water an d carbon dioxide

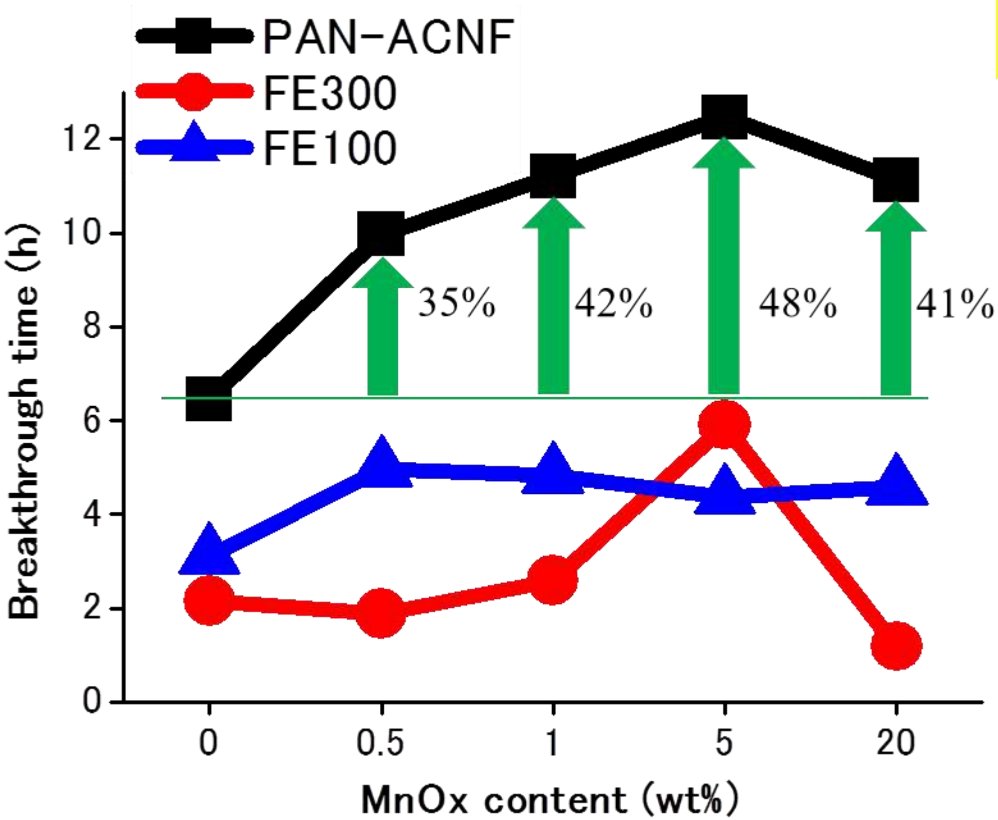
③
- Clean removal into Water and Carbon dioxide
- Lifetime prolonged

The conceptual model of MnOx-carbon catalyst



Catalysis Today (2012).

Complete removal of HCHO using MnOx/ACNF



Dry condition

1. MnOx combined with carb on support to enhance HCHO removal.

2. PAN-ACNF showing the highest synergy at 5% MnOx.

Weight-0.05g base

Mn_3O_4 or MnO_2 alone breakthrough in less than an hour.

→ Deposition on carbon support improves catalytic activity of MnOx.

AC- medicine

Characteristics of activated carbons for the selective adsorption behaviors for Indole and Amylase

Research background

Chronic Kidney Desease

Renal function decrease for removal poisons from body

➡ **Artificial dialysis**

big burden to patient

To prolong the introduction of dialysis, AC medicine was developed

AC internal medicine

・To remove the entro−poisons like indole through the excretion with activated carbon.

・Very hard to take a dose (6g/day)

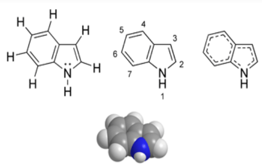
How to decrease the dosage amount

Factors for selective adsorption

- Surface area and pore size
- Shape
- Surface property

Model adsorption materials

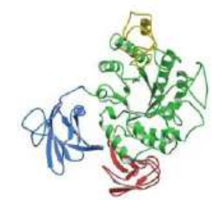
- To be removed



Indole (MW: 117.15)

⇒ a kind of poisons

- Not to be removed



Amylase (MW: about 46000)

⇒Digestive enzyme

Samples

OG series (Osaka Gas)

Relatively similar shapes of pores but different surface area and pore size distribution

H_2-OG series

- Surface area and pore
- Surface property

Hydrogenation of OG series to remove the oxygen functional groups(600℃, 1h)

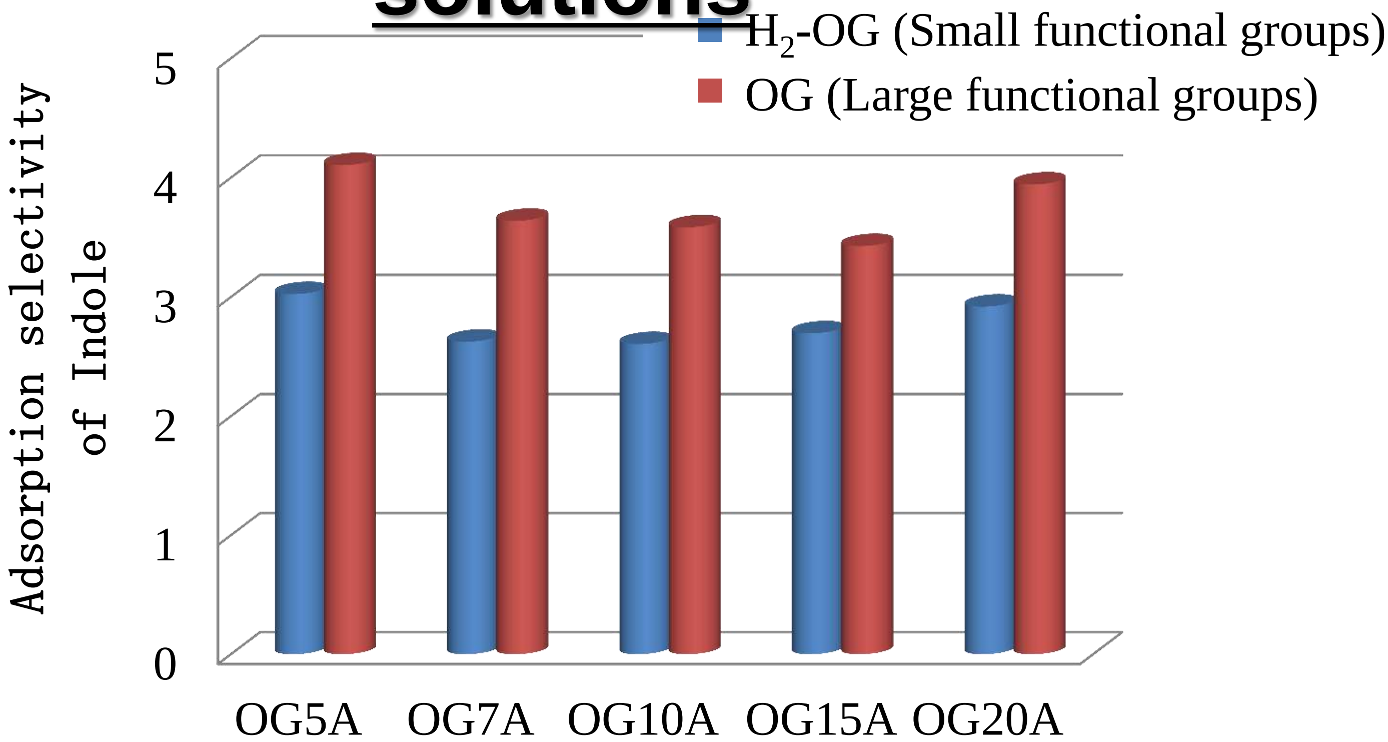
Ball type activated carbons

Ball type activated carbons with diameters of 100～300μ m

α_s analysis

		OG5A	OG7A	OG10A	OG15A	OG20A	H_2-OG 5A	H_2-OG 7A	H_2-OG 10A	H_2-OG 15A	H_2-OG 20A	SAC	OAC	Scmep	SACmip
SA (m^2/g)	A_{micro}	646	982	1283	1688	1928	728	1247	1305	1548	1802	1254	1585	570	1409
	A_{meso}	0	0	0	0	0	0	0	0	0	0	56	0	108	143
	$A_{external}$	0.3	0.3	0.1	0.3	0.3	0.4	0.1	0.3	0.3	0.5	6.6	1.4	0.2	0.4
Pore size (nm)	W_{micro}	0.65	0.68	0.74	0.90	1.11	0.65	0.70	0.75	0.91	1.11	0.69	0.96	0.64	0.74
	d_{meso}	0	0	0	0	0	0	0	0	0	0	12.0	0	5.85	3.24
Oxygen contents (%)		14.3	19.0	22.2	12.8	12.1	6.0	5.2	4.5	2.5	2.6	15.1	4.7	6.0	4.4

Effect of functional groups for binary solutions

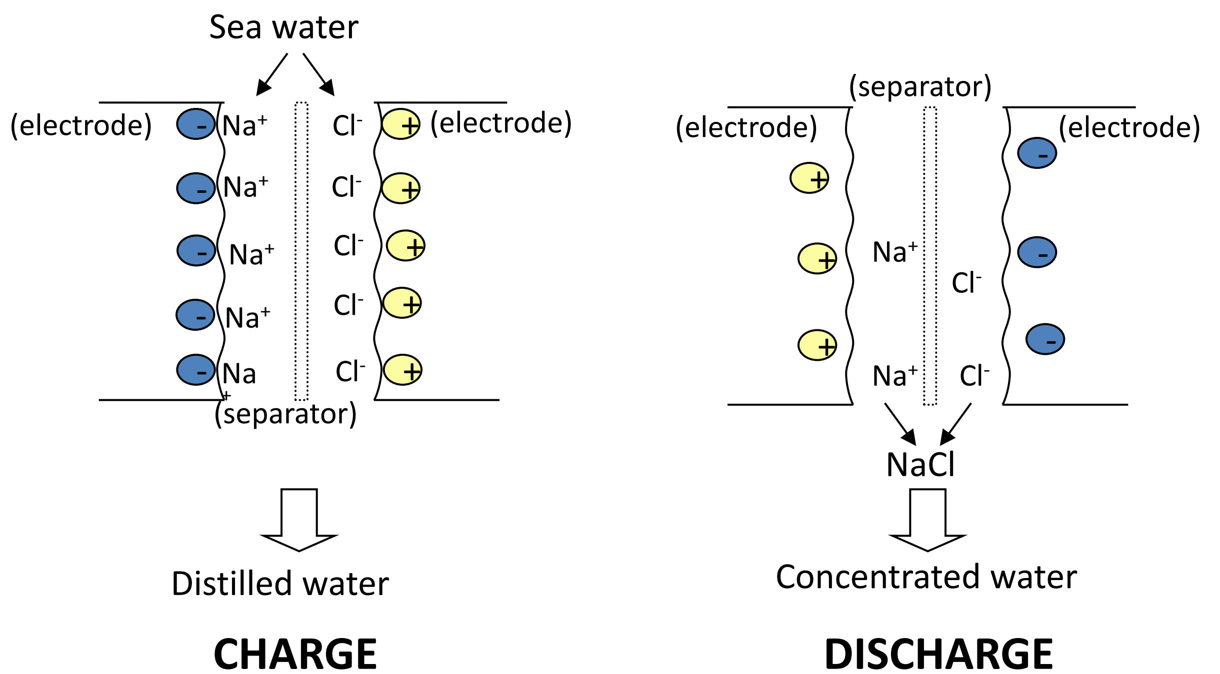


Removal ratio of Indole (%)	OG5A	OG7A	OG10A	OG15A	OG20A
Small functional groups	49.9	70.1	69.3	70.9	72.1
Large functional groups	43.1	63.3	63.8	69.9	68.6

Removal ratio of amylase (%)	OG5A	OG7A	OG10A	OG15A	OG20A
Small functional groups	16.5	26.7	26.6	26.3	24.7
Large functional groups	10.5	17.4	17.8	20.4	17.4

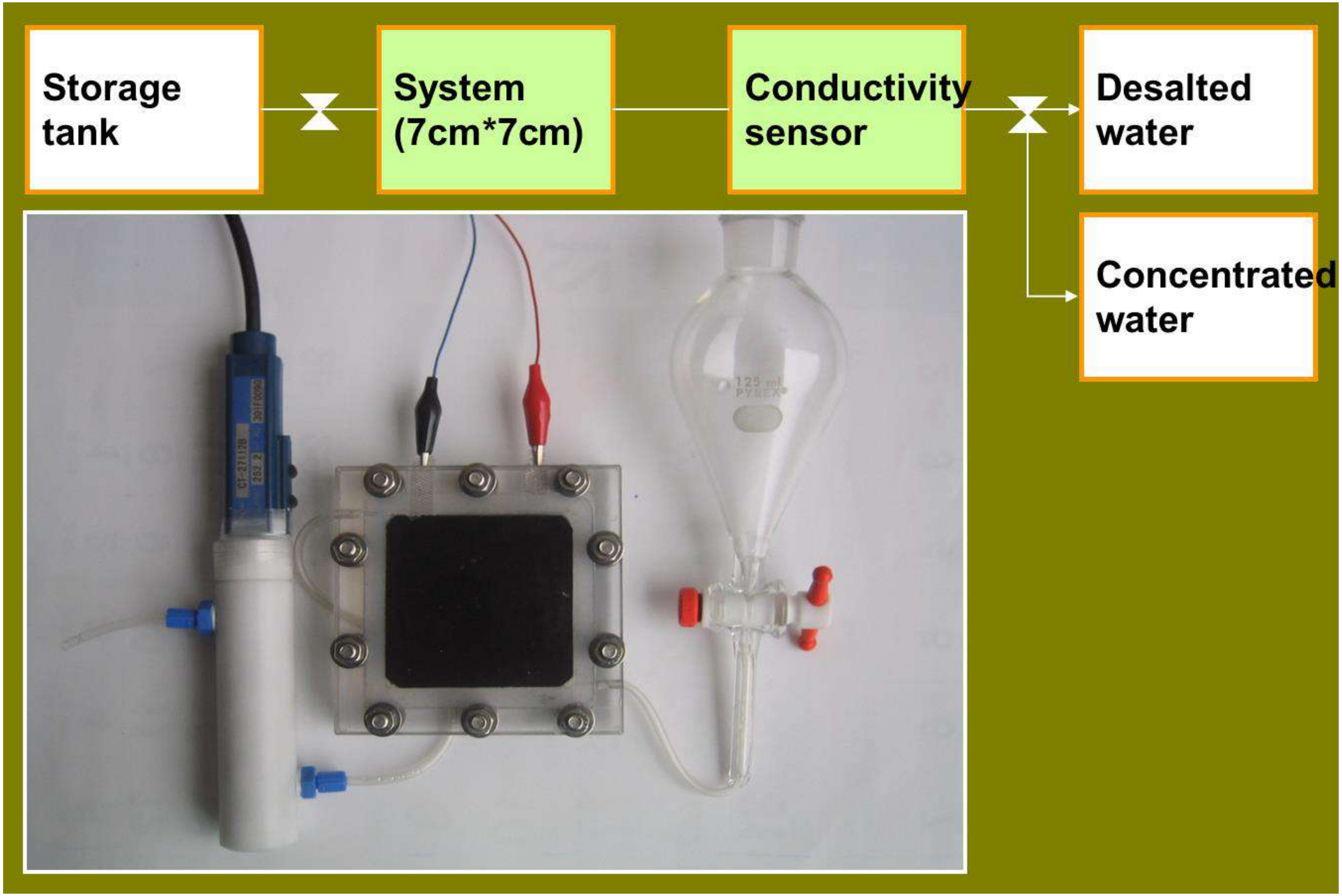
Capacitive De-ionization (CDI)

Principle of electrical desalination



- Diffusion of ions inside of pores
  - Rapid electrochemical adsorption and desorption

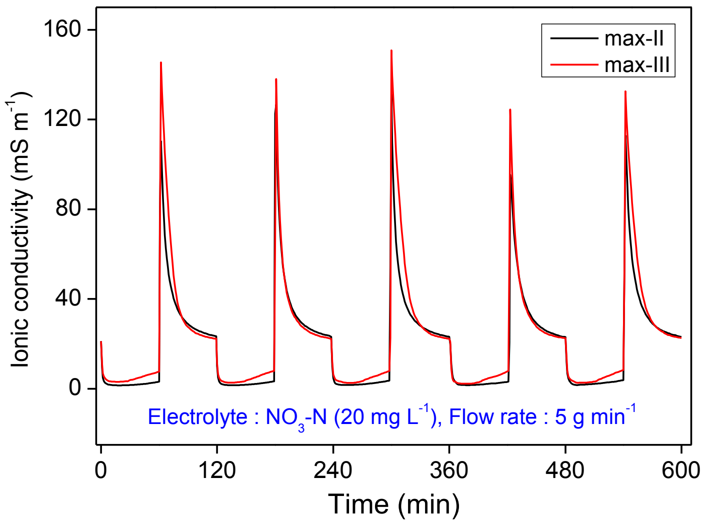
Experimental setup



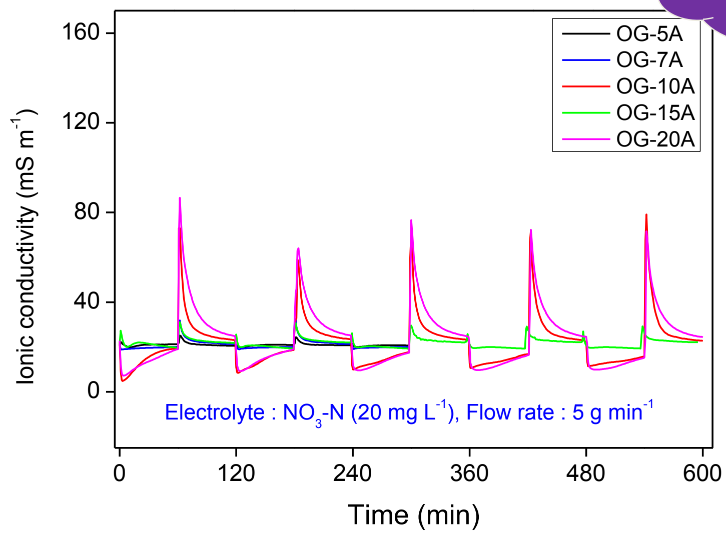
Nitric ion removal behaviors

Up to 1.0V

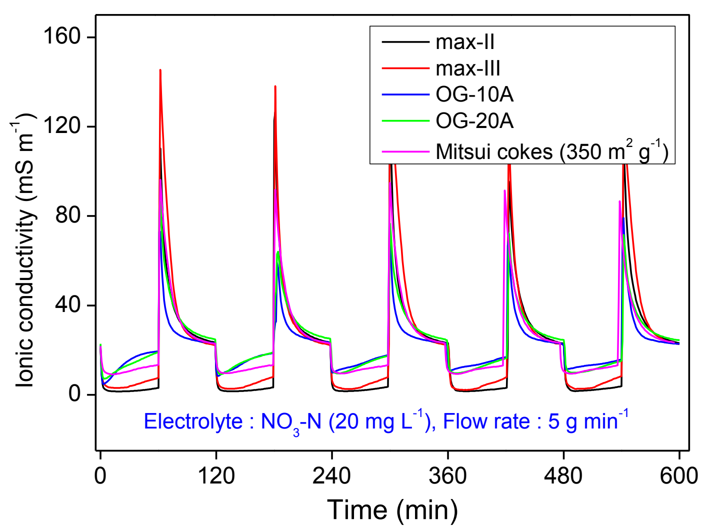
Maxsorb series



OG series



Total



- 硝酸性窒素イオンにおける脱塩特性は

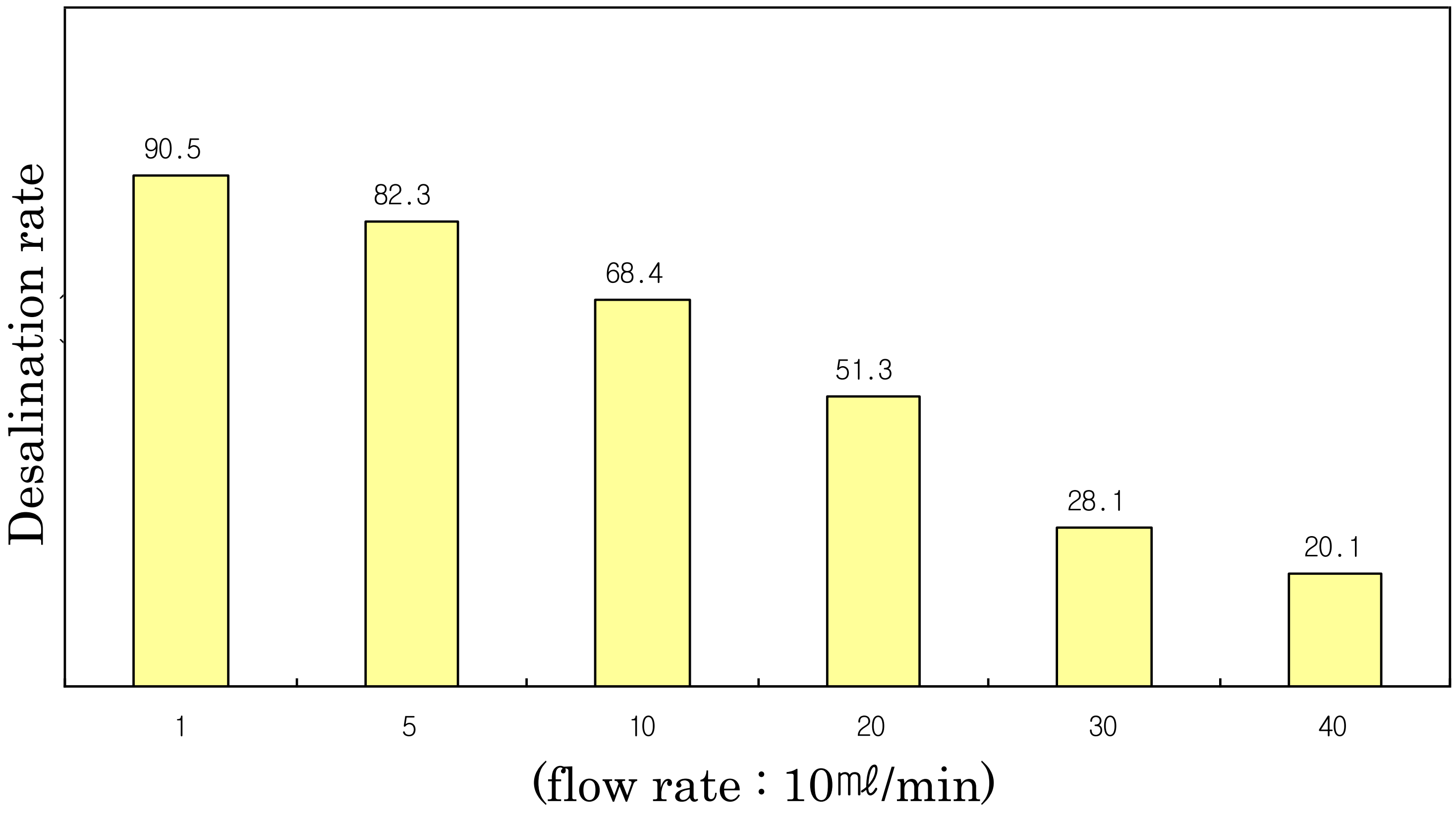
  Max–IIIが最大特性を示した。

- 三井鉱産のコークスがOGシリーズより良かった。

- Maxsorb > Mitsui cokes > OG series

Cl^- ions in the city water

Effect of flow rate



Points

- How to increase lifetime
- How to increase adsorption selectivity and amount of ions

⇒

□ Optimization of pore and its distribution

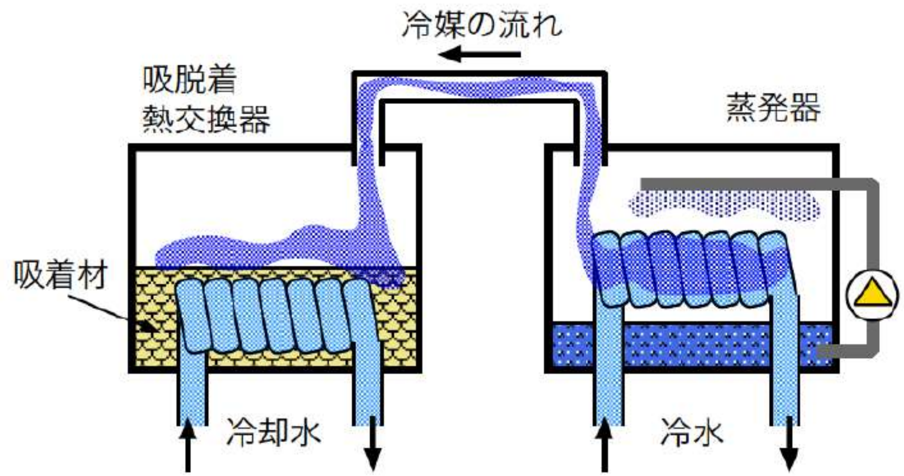
□ How to increase molecular diffusivity

□ Preparation of high electric conductive AC

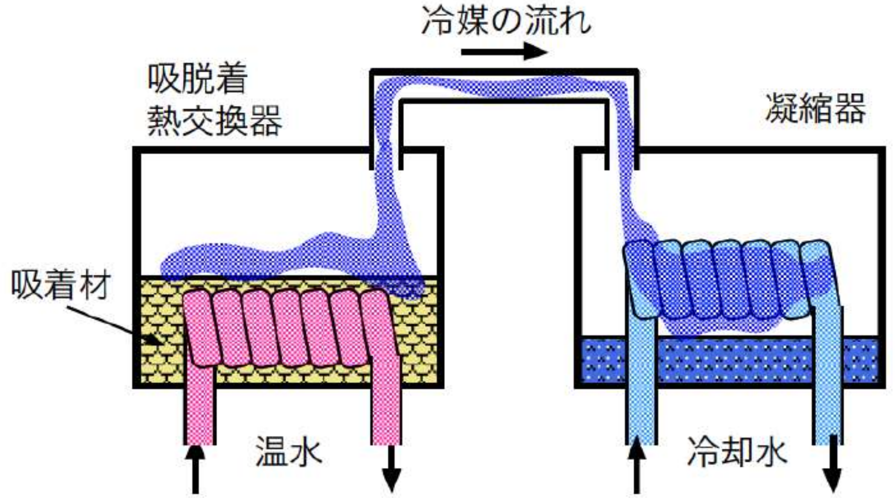
Application of activated carbons to Heatpump for energy-free operation

Principle of Heat Pump

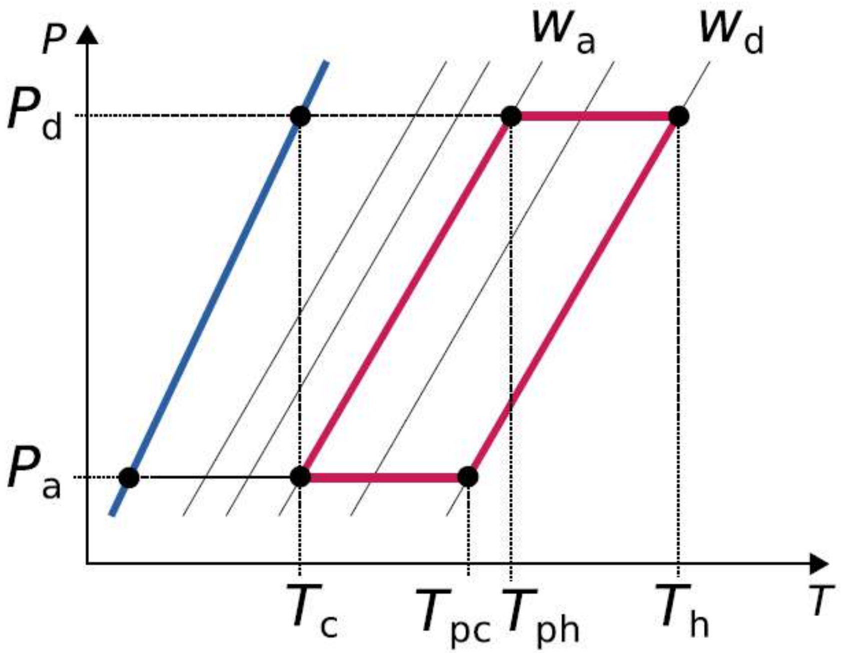
Adsorption



Desorption



Static analysis of adsorptive HP



Heat input

$$Q_{in} = M_s C(T_h - T_c) + M_s q_s (w_a - w_d)$$

$$C = \begin{cases} c_s + c_r w_a & (T_c \leq T \leq T_{ph}) \\ c_s + c_r (w_a + w_d)/2 & (T_{ph} \leq T \leq T_h) \end{cases}$$

Cooling effect

$$Q_{chil} = M_s L_r (w_a - w_d)$$

COP

$$\mathrm{COP} = Q_{chil}/Q_{in}$$

How to increase power

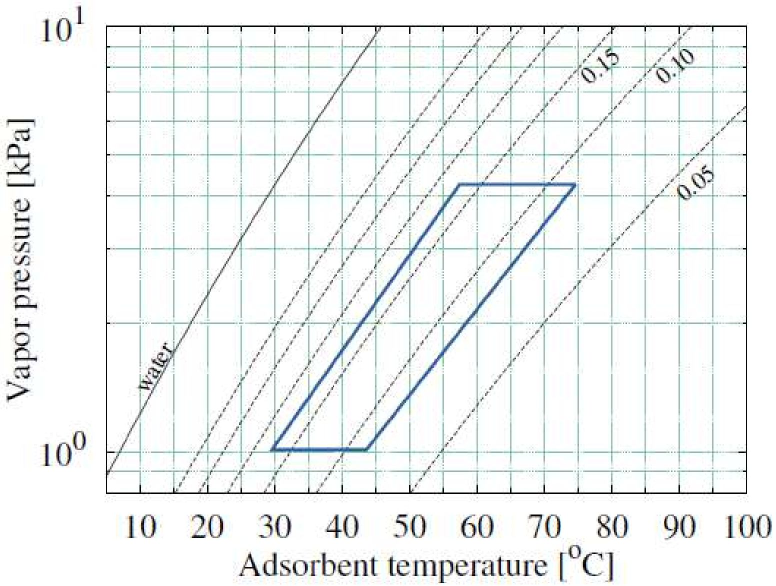
- Increasing effective adsorption

How to increase COP

- Making temperature change smaller

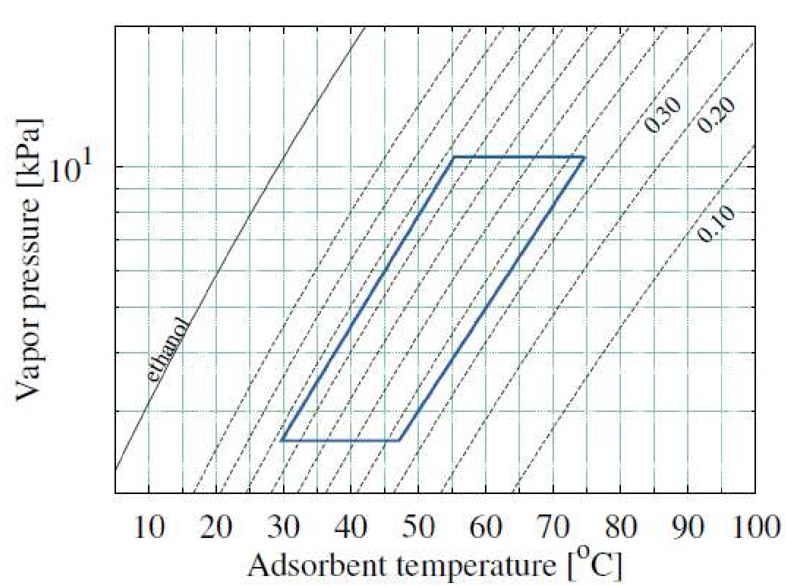
Performance test results

Silica gel- water



COP 0.69
冷凍効果 210 kJ/cycle

Activated carbon - ethanol



COP 0.66
冷凍効果 360 kJ/cycle

Points

- How to increase adsorption amount of molecules such as water, methanol and ethanol

⇒

□ Optimization of pore and its distribution

□ How to increase molecular diffusivity

□ Preparation of high thermal conductive AC

Conclusion

- **New functions, Improving conventional characteristics**

⇒

- **New analysis, New structure, surface, functional groups and properties**

✓Domain concept
✓Shallow pore concept
✓Functional groups
 - Nitrogen, oxygen … ⇒ other hetero atoms
✓High electrical conductive
✓High thermal conductive

Thank you for kind attention.