

エネルギー・環境を支える 新規機能性炭素材

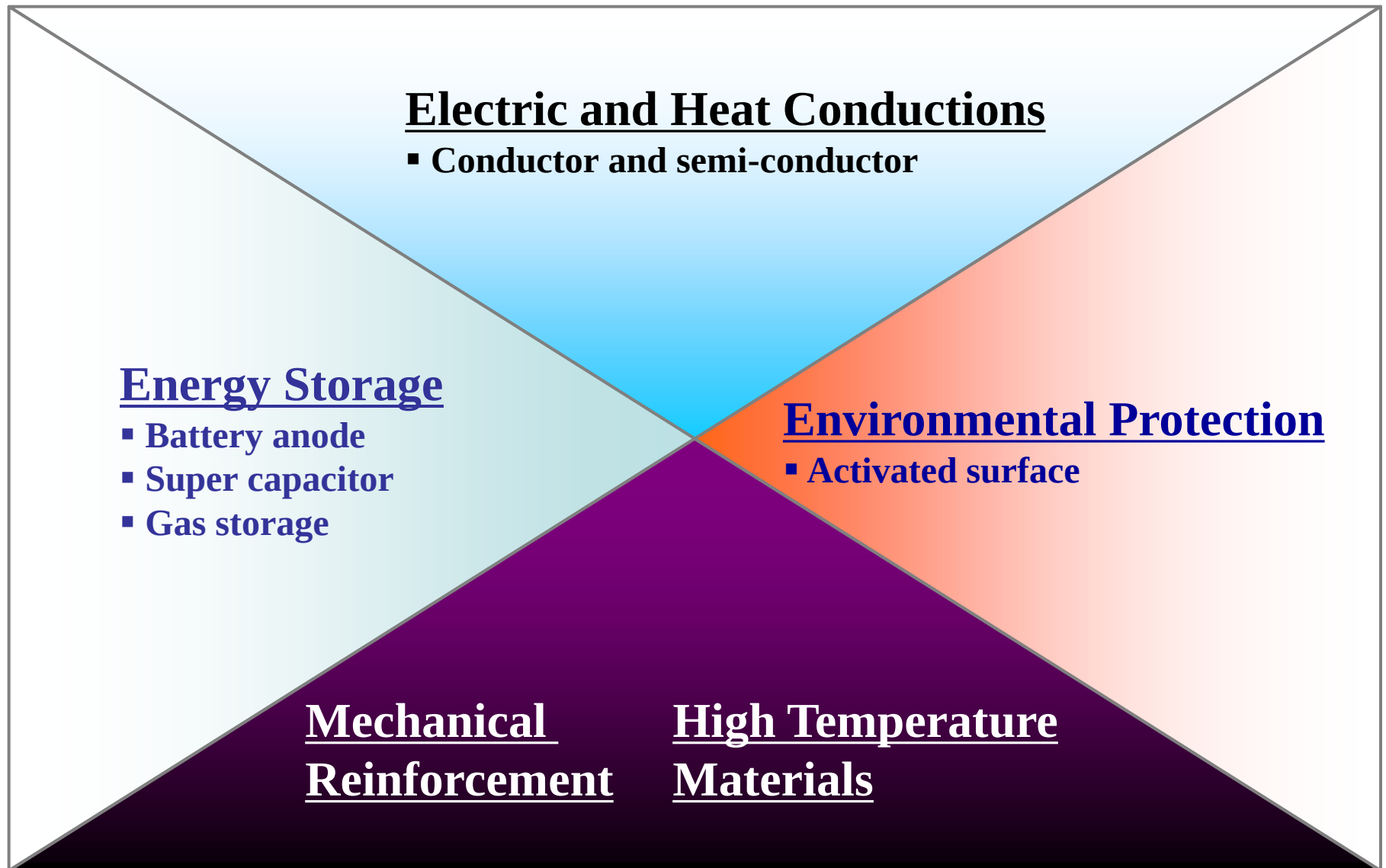
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<http://carbon.cm.kyushu-u.ac.jp/>

炭素材の応用分野



Raw materials

Coal tar

Polymer: Thermosetting and thermoplastic

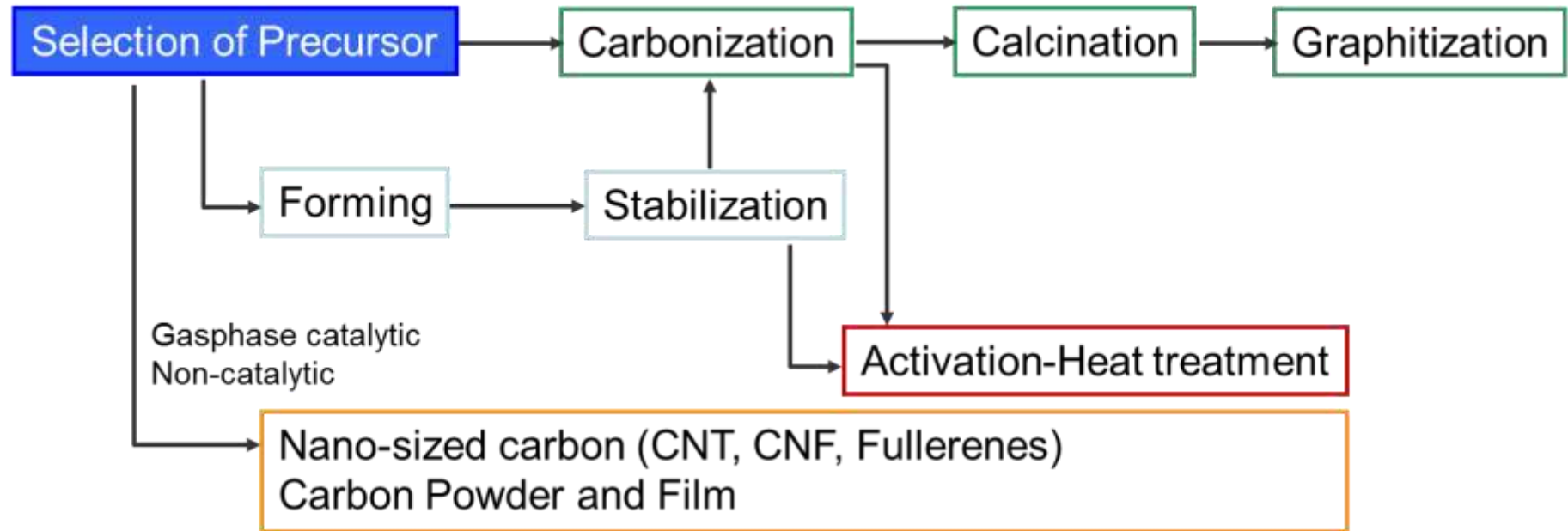
Heavy oil and residues

Biomass

Precursor

- Pitches: CF, ACF, MCMB, AC, Binder pitch, Additives
- Polymer: AC, ACF, Glassy carbon, CF
- Cokes: Electrode, Capacitor, Battery anode, AC, Additives
- Char: AC, Additives, Reducer for Solar cell

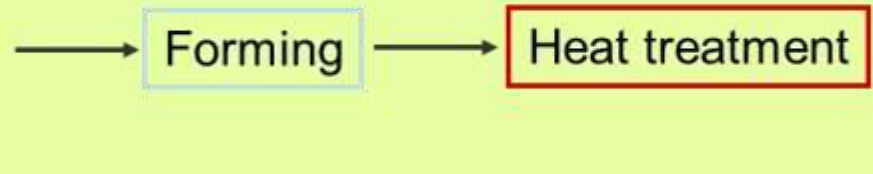
炭素材の製造



Preparation of Composite

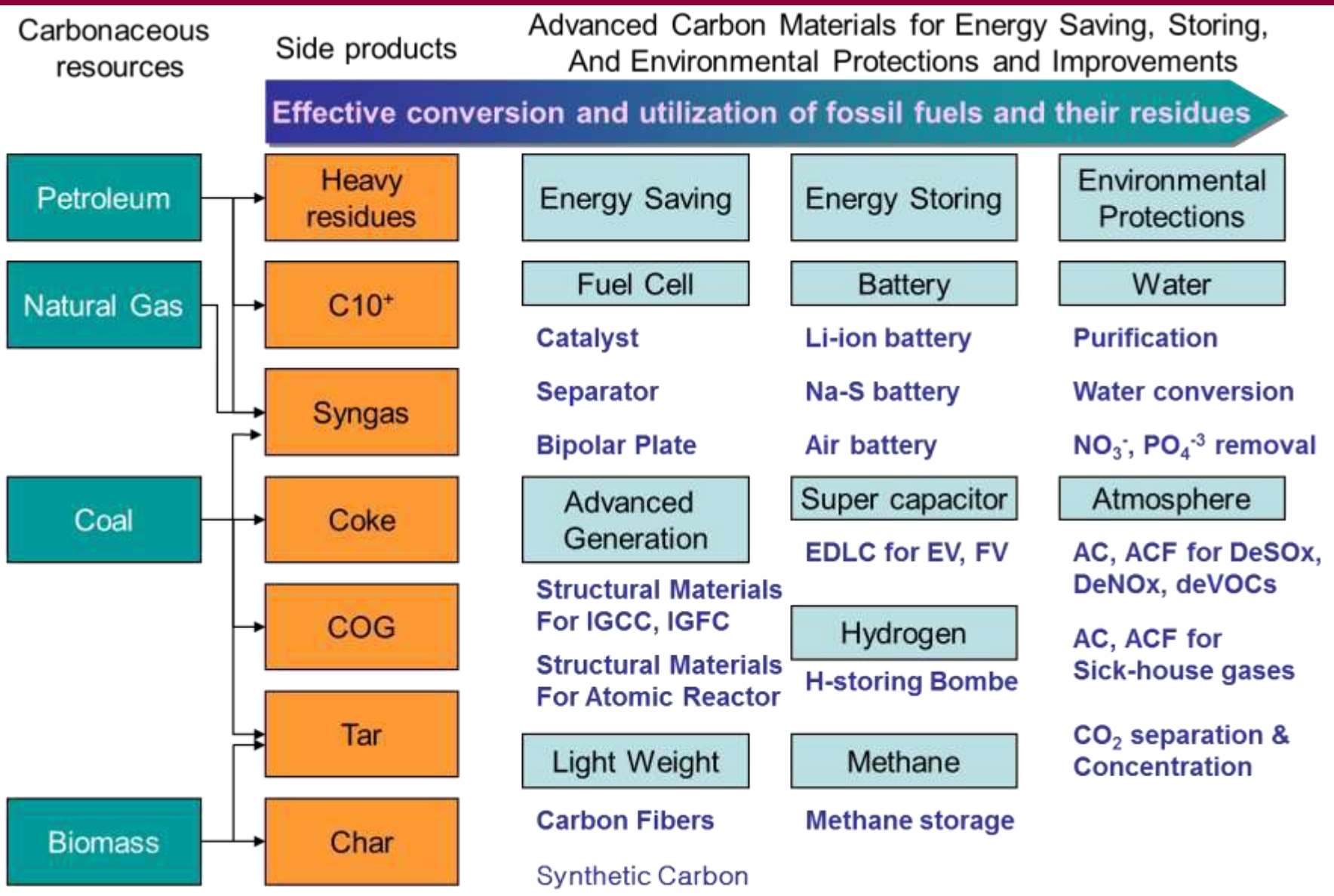
Carbon and Pitch

Polymer
Metal
Ceramic



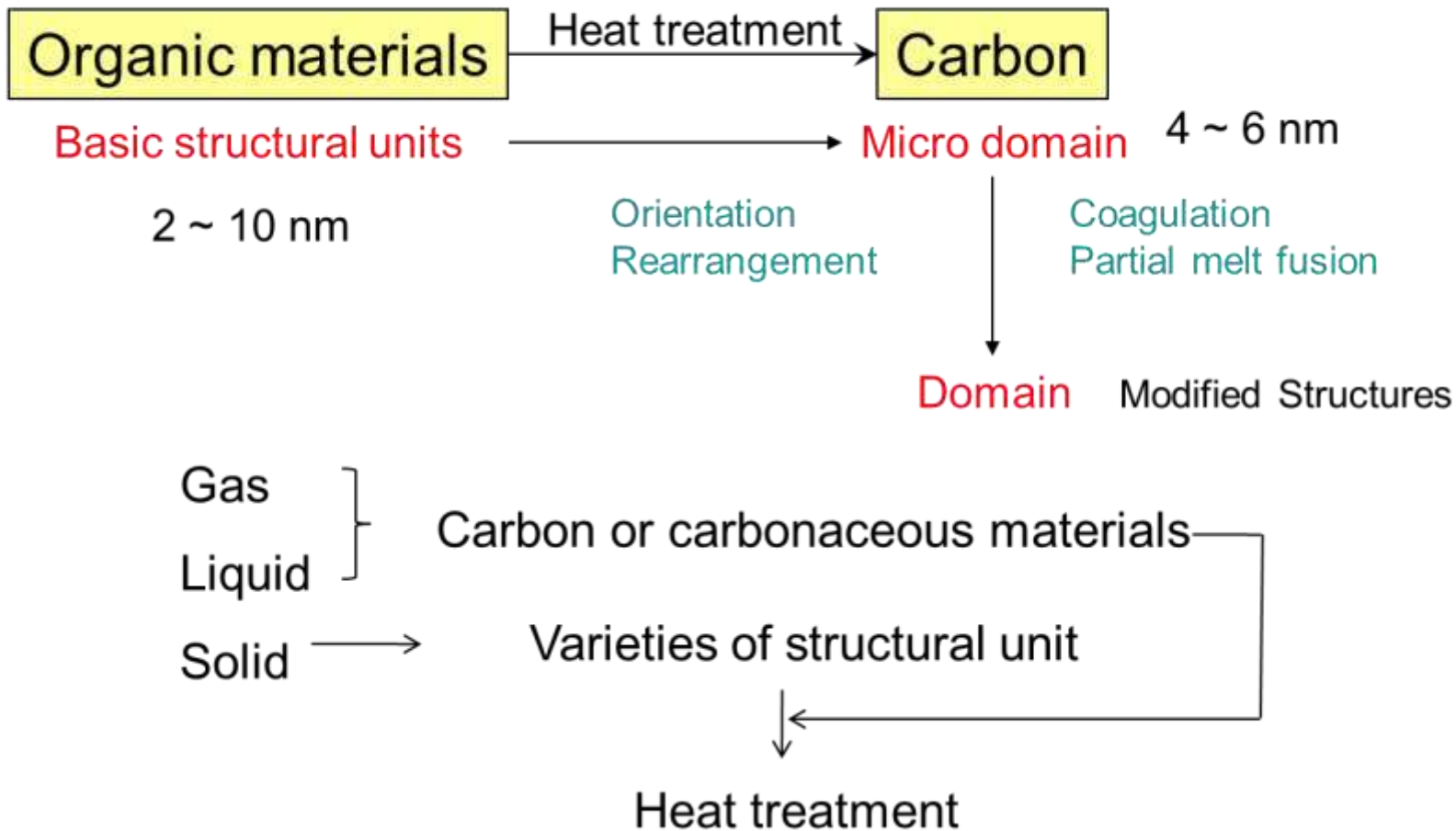
Carbon Growth on the Substrate

化石燃料からの高機能性炭素材の製造と応用

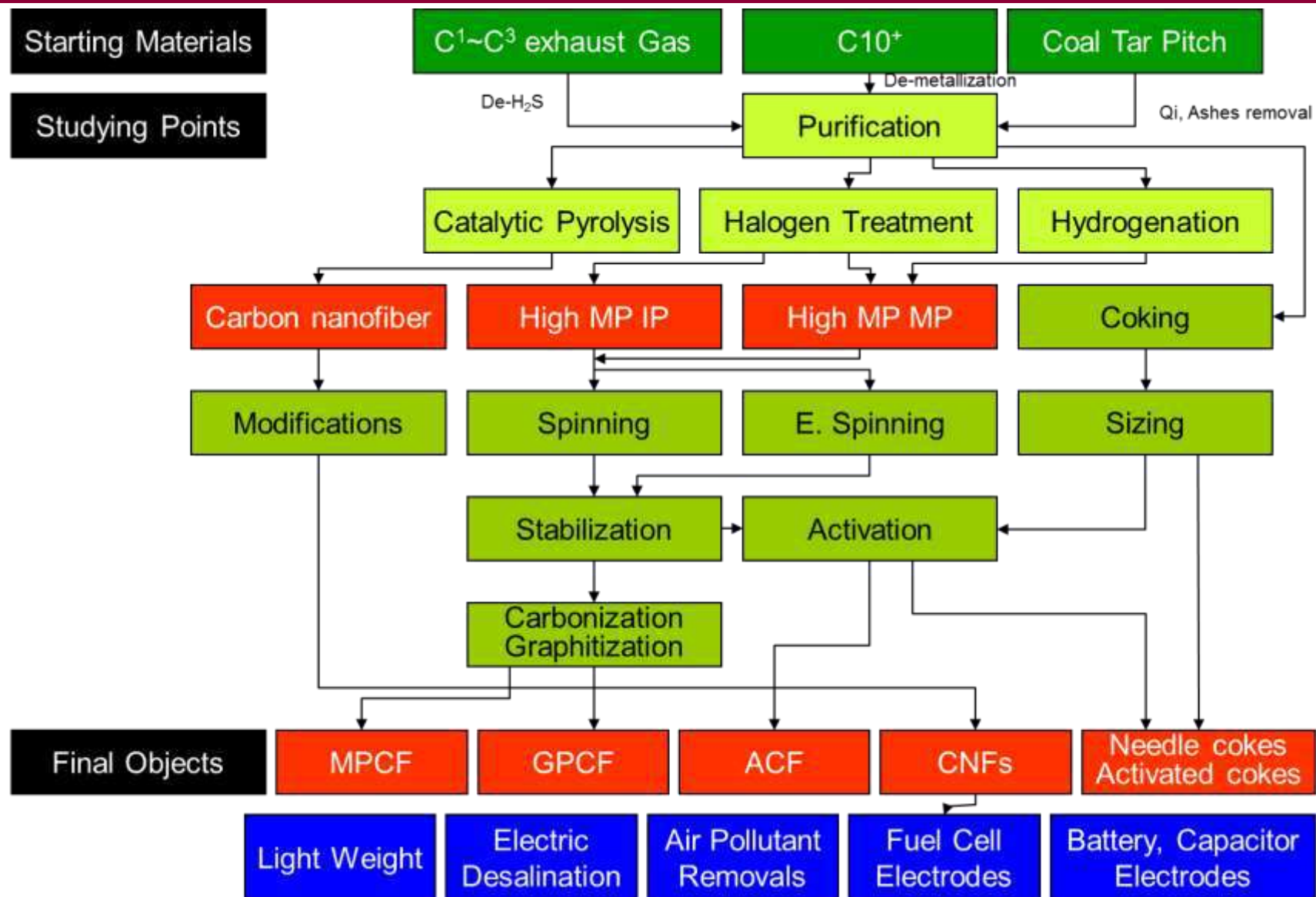


人造カーボンの構造の由来

Origin of Structural Units And Crystalline Defects



構造の制御はどこから？



PAN系炭素繊維の構造

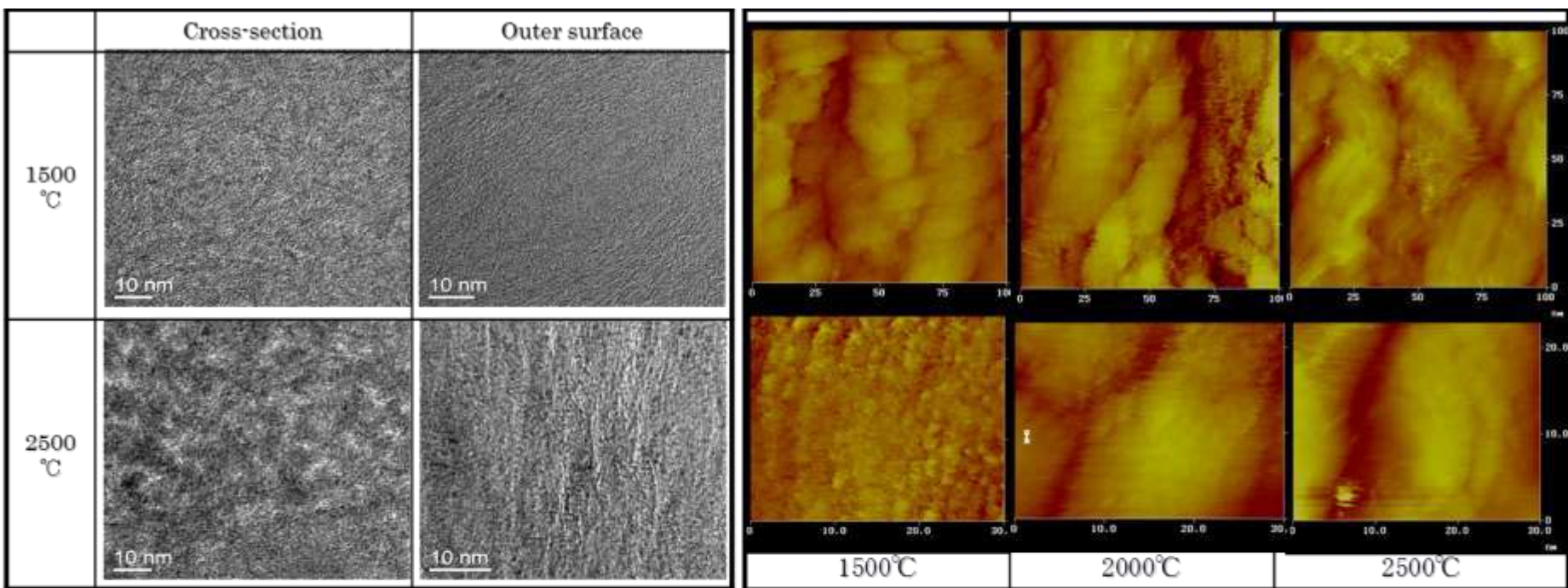
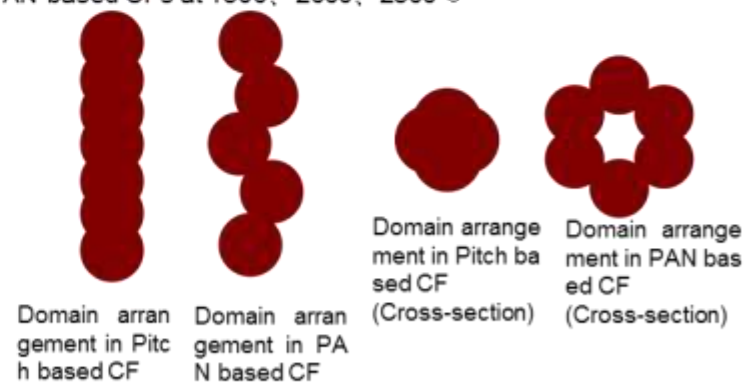
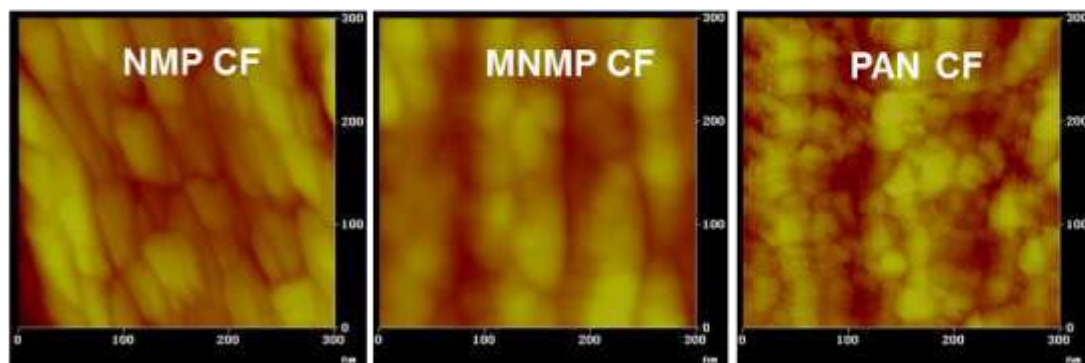
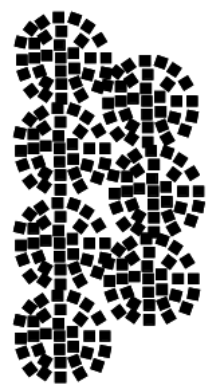


Figure SEM & STM images of heat treated PAN based CFs at 1500、2000、2500 °C

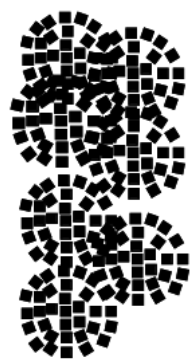


単位構造と構造の制御

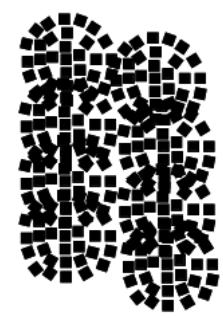
Before heat treatment



Not or very slightly fused microdomains

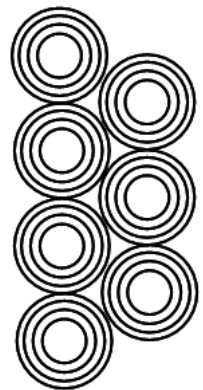
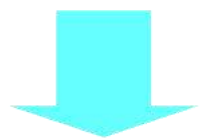


Partially fused microdomains

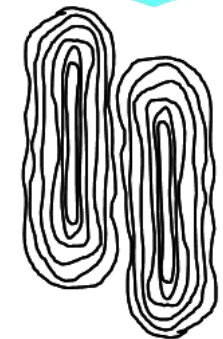
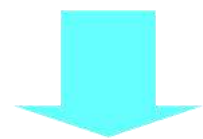


Fully fused microdomains

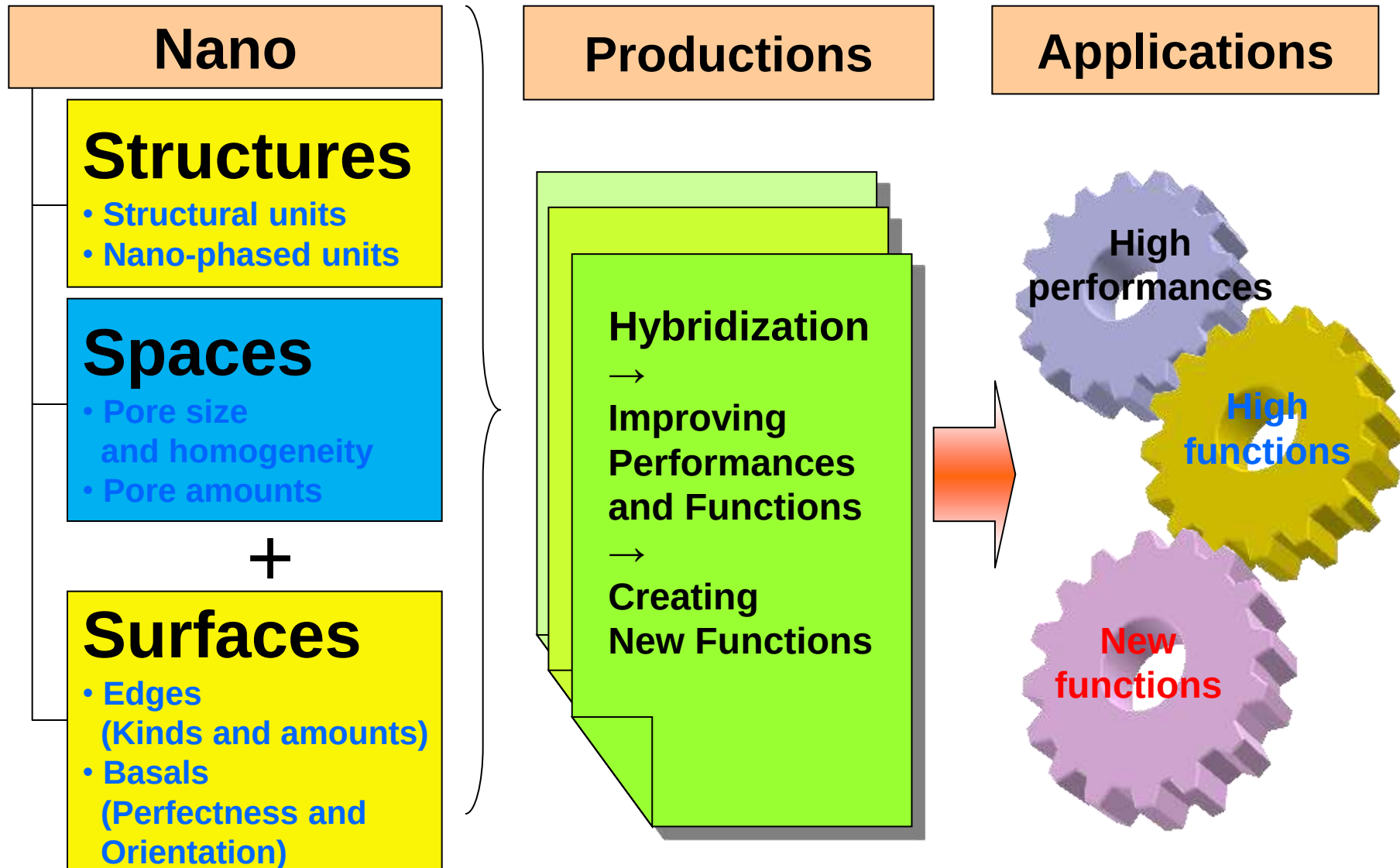
After graphitization



Glassy Carbon



構造概念からの炭素材



Carbon is an Indispensable Material for Energy related Devices

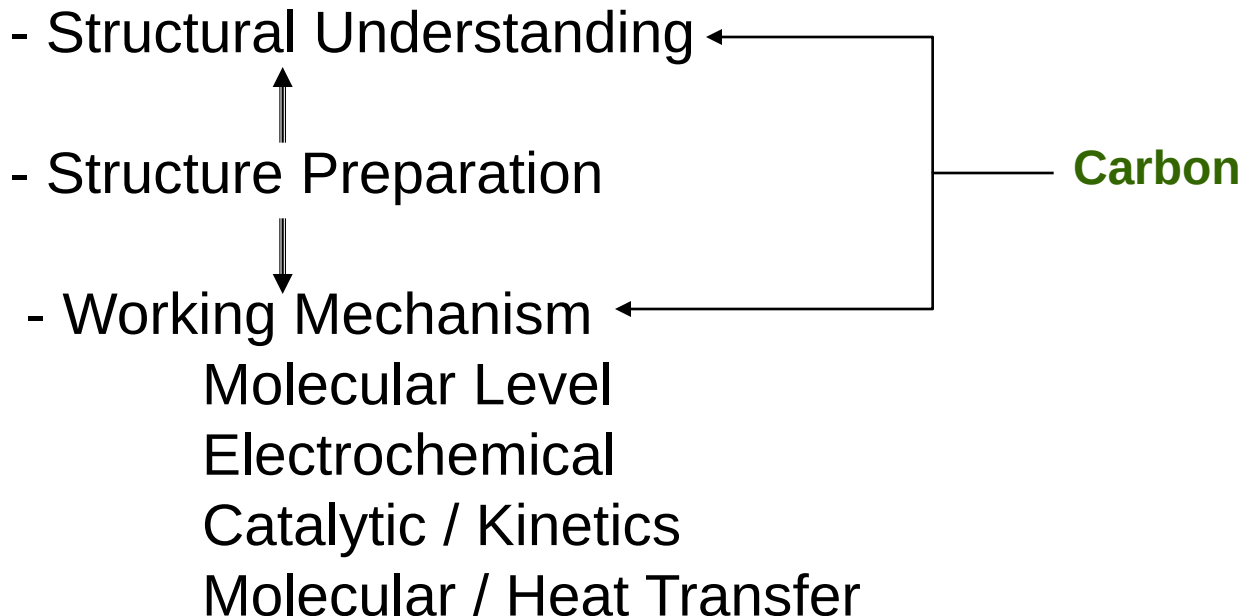
Best Structure for Best Performance



Best Selection

Best Selection

Scientific Cycle



Surface Area, Pore: *Depth & Volume*

Surface Structure

Surface Chemistry

Based and Edge Plane, Substituents

Hetero Atoms in Hexagon

Carbon Structure of Wall

Micro, Nano, Macro Structure of Carbon Wall

-Graphitization Extent

-Domain Structure

Density, Reactivity (Activated Surface)

→ *Precursor : Structure and Reactivity*

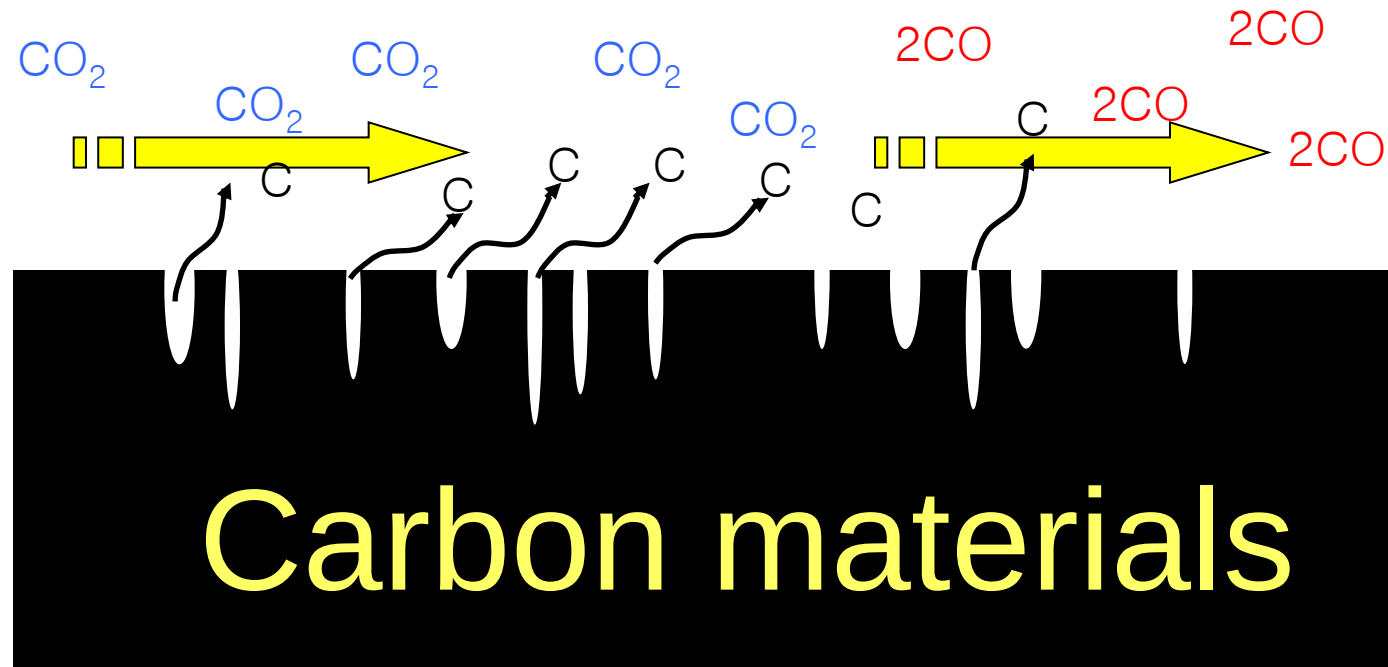
Selection of Precursor

- *Pore Framework / Density*
- *Properties of Pore Wall, Composition / Graphitic Extent*
- *Reactivity at Activation*
- *Non-graphitizable precursors like polymer, biomass and isotropic coke for usual AC or ACF*
- *Graphitizable precursors like anisotropic cokes or mesophase pitch for EDLC electrode materials*

Activation Procedures

- *CO₂, H₂O*
- *Alkali Hydroxides / Carbonates; More Research*
- *Selective Catalytic Gasification ; Catalyst Control*

- ❖ *Very Large Surface Area > 3000 m²/g*
- ❖ *Adequate Pore And Wall*

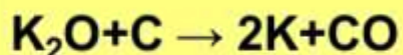
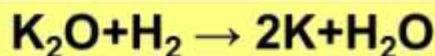
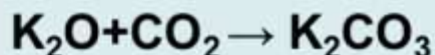
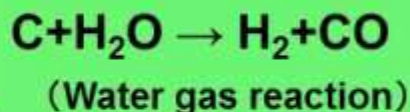
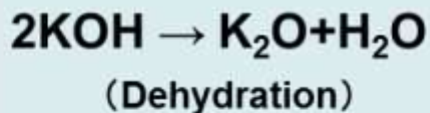


Activation reagents

- Air, CO_2 , Steam
- KOH (NaOH), ZnCl_2

化学賦活法

Catalytic progress
Under K₂O



Carbon is mainly
consumed as a form of
K₂CO₃

K compounds are
reduced as a metal

- Higher surface area compared to the steam activation
- Almost no productions of CO and CO₂
- **K metal intercalation: higher diffusivity than steam molecule**

KOH
MP: 380°C
BP: 1324°C

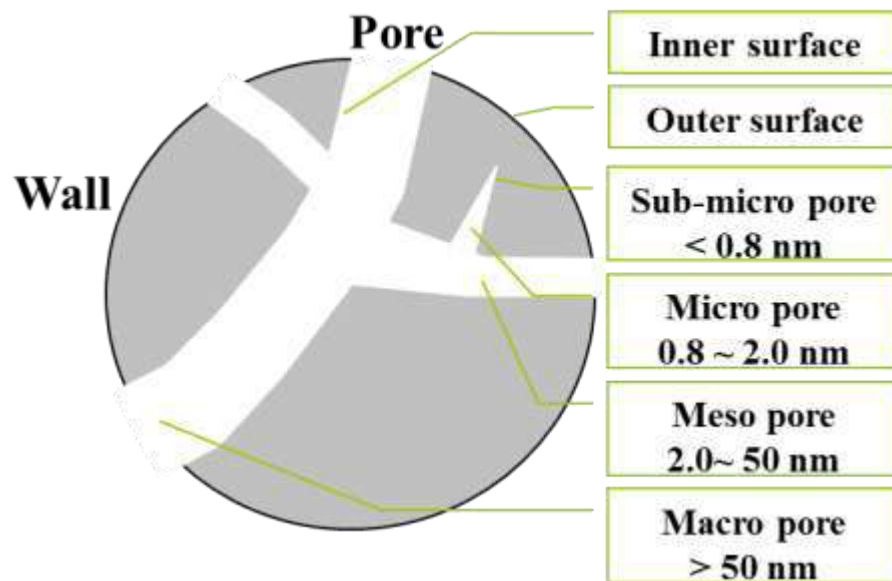
K₂O
MP: 490°C (350°C, KO and
K)

K₂CO₃
MP: 891°C

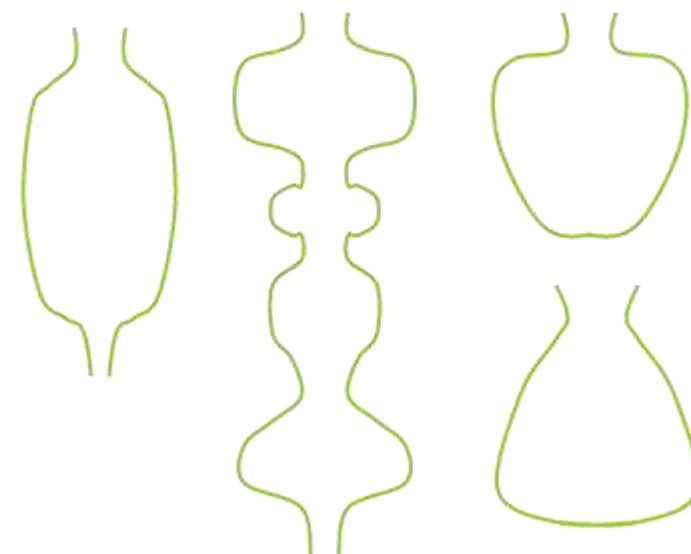
K
MP: 64°C
BP: 774°C



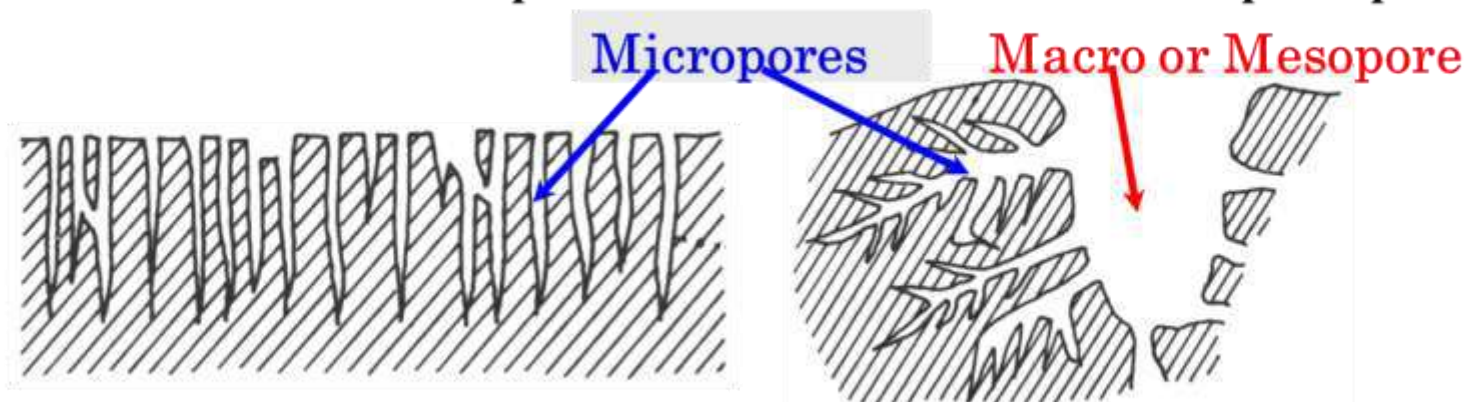
活性炭の細孔構造: 既存のイメージ



Classification of surface and pores

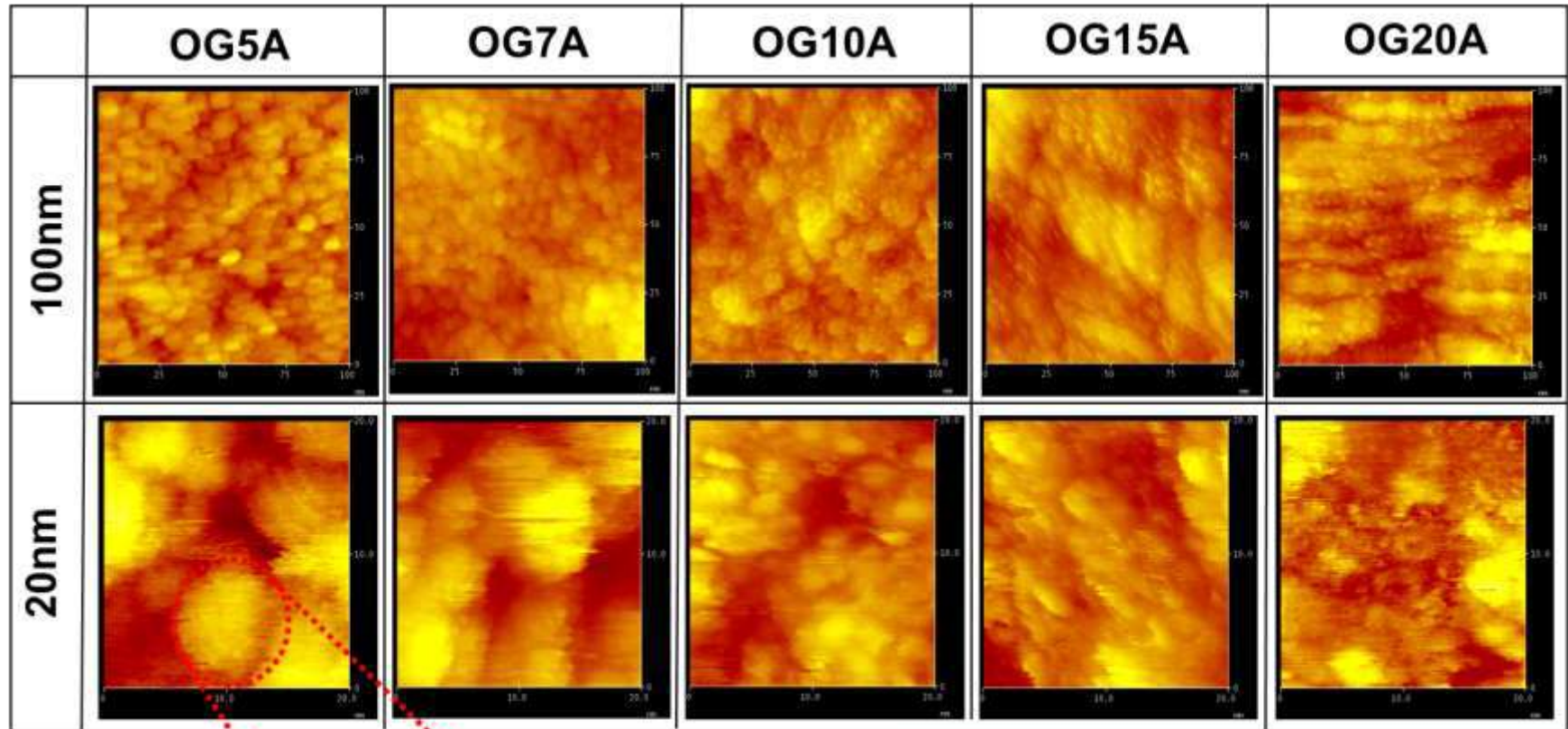


Schematic shapes of pores



Schematic pore images of activated carbon fiber and activated carbon

STM images of ACFs



Micro domain

Cluster unit

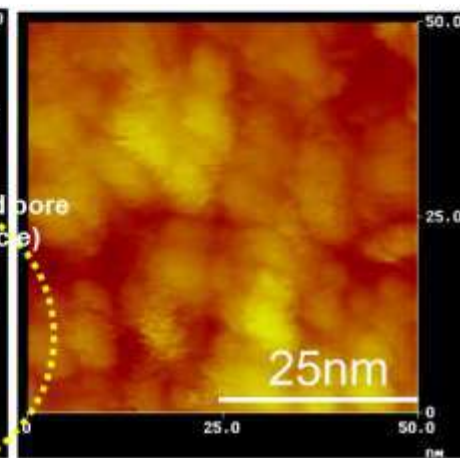
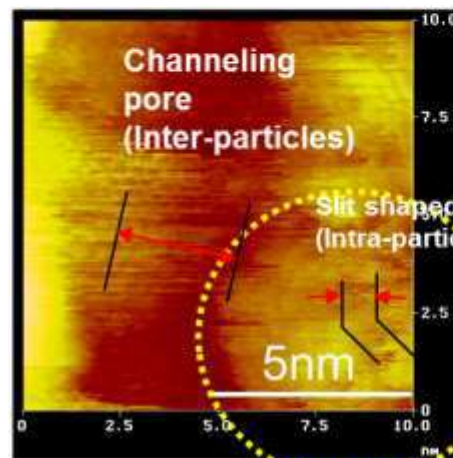
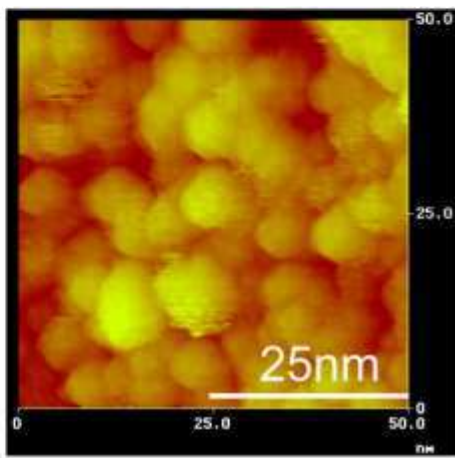
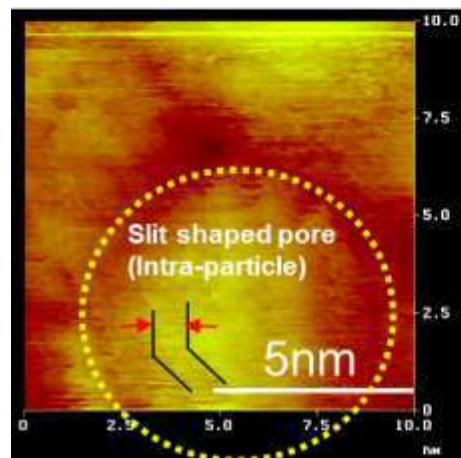
◆ ACFs consist of structural units of micro domain with diameter of around 5nm.

活性炭素繊維の細孔形成

In order to remove oxygen containing functional groups for removing the heterogeneous effect of STM, OG7A and OG20A were heat-treated at 800°C in a hydrogen atmosphere ($H_2/He = 1/4$).

OG7A-800H

OG20A-800H



♣ Vacant spaces between the two domains of OG20A are larger than that of OG7A.

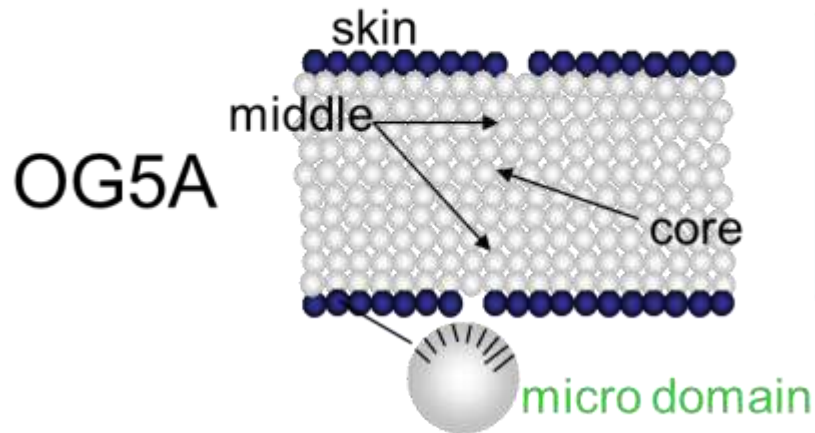
♣ Domain size of OG20A is a little smaller than that of OG7A.

♣ Slit type pores were observed in domains of OG7A and OG20A.

♣ It can be presumed that almost pores larger than 2nm nucleated by the inter-particle mechanism.

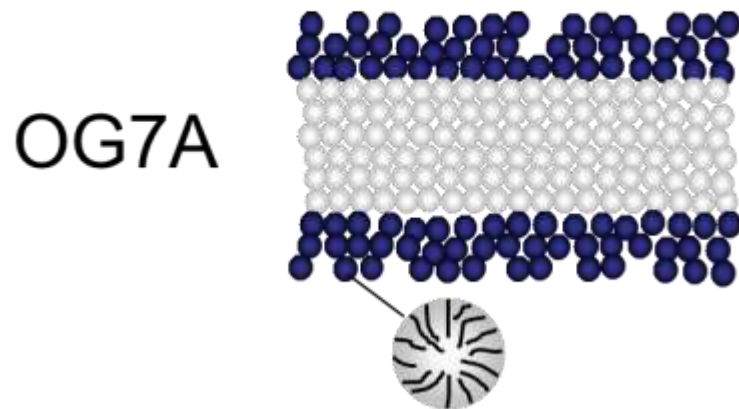
細孔生成機構

A model for cross section of ACFs



- ♣ Only skin is activated, homogeneous narrow pore exist on the surface of domains.
- ♣ The activation does not reach to the middle and core parts.

OG5A has smallest surface area but homogeneous pores.

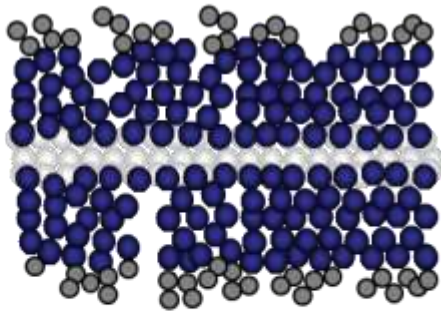


- ♣ Skin and middle parts are activated.
- ♣ Pores in domain become wider and longer than that of OG5A because of the pores formed by inter-domain mechanism.
- ♣ Pores are formed by the intra-domain and inter-domain mechanisms.

Heterogeneous pores exist.

細孔生成機構

OG10A

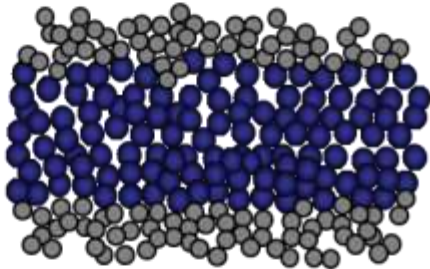


- ♣ The activation proceeds to near the core.
- ♣ Domains in the surface become smaller by activation.



OG10A have various size pores.

OG15A

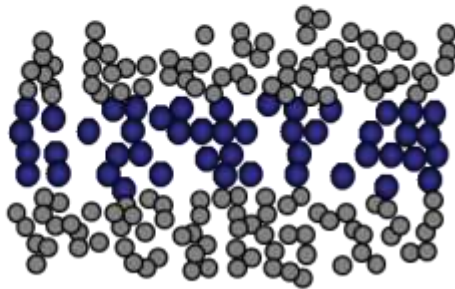


- ♣ Whole parts of skin, middle and core are activated.
- ♣ The pores from the intra-domain become larger by activation.
- ♣ Owing to some domains burning, fiber diameter becomes smaller than OG5A, 7A and 10A.



More homogeneous pore distribution than that of OG10A

OG20A

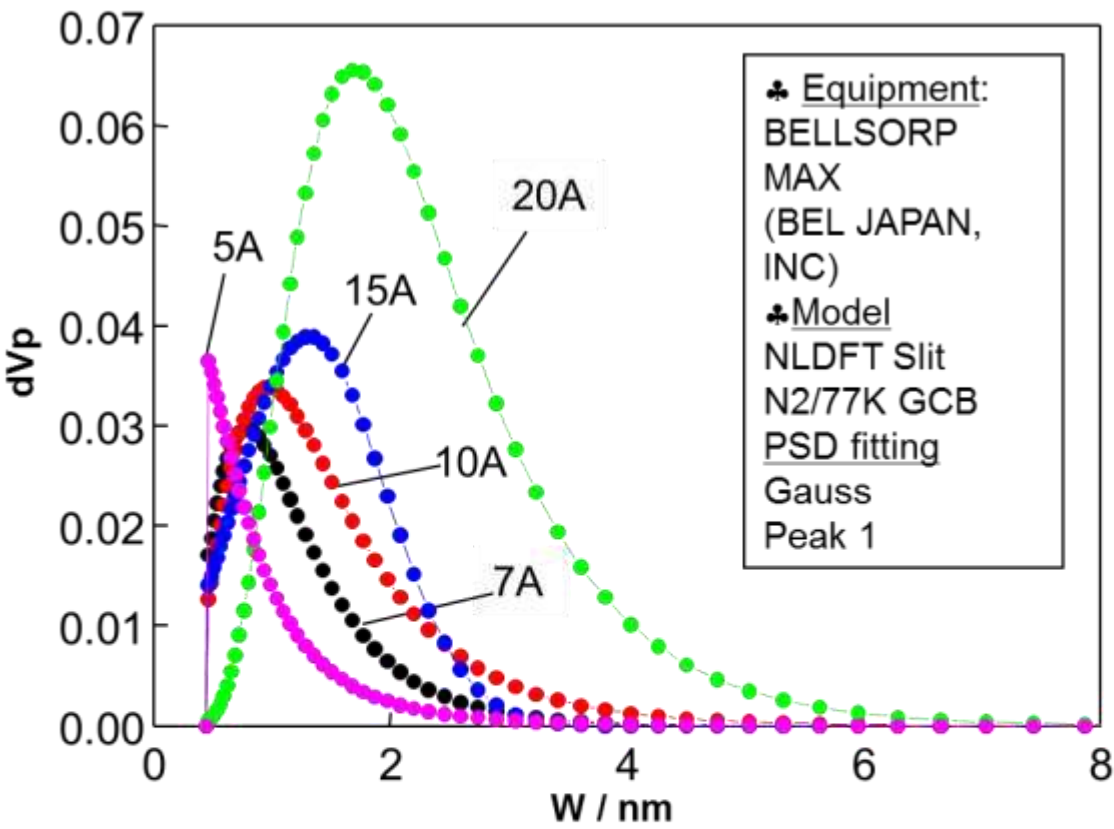


- ♣ Over 70% of domains are burned-off.
- ♣ Pore portions from interparticle nucleation becomes larger
- ♣ OG20A diameter become smaller than OG15A.



OG20A have largest surface area but heterogeneous pores.

細孔サイズと分布 (NLDFT法)



Advantage of DFT method

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

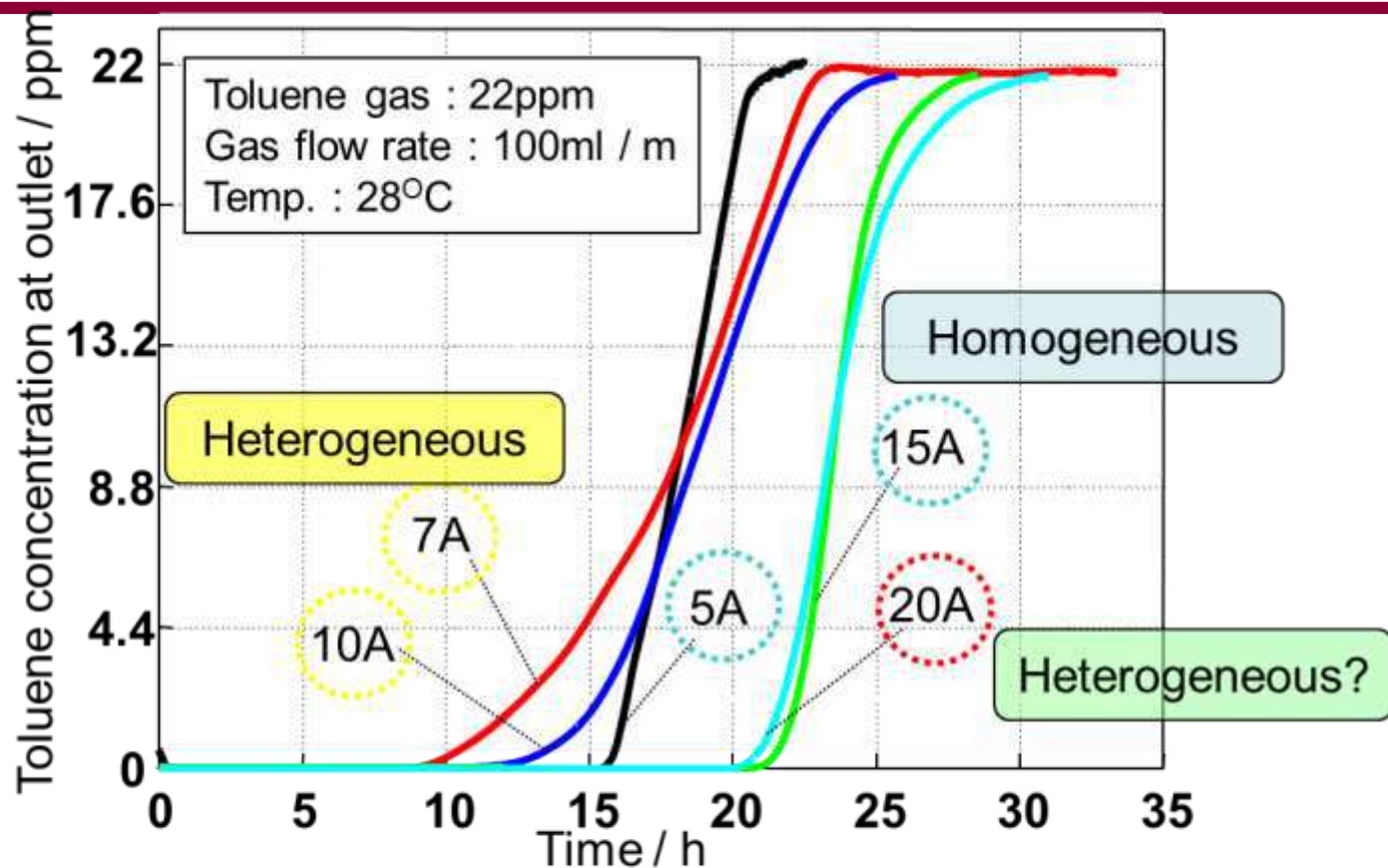
Disadvantage

- 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.

活性炭素繊維のToluene吸着特性



- ◆ 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.

活性炭の新規応用

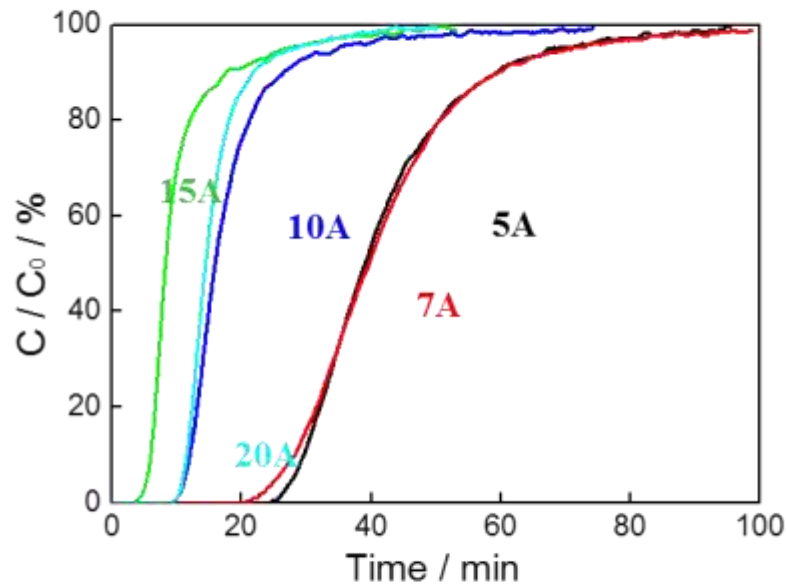
1. HCHOガス(シックハウスガス)の除去
2. 高性能キャパシタ電極材
3. 経口用薬
4. Capacitive De-ionization (CDI)
5. Heat Pump (省エネルギー応用)

1. HCHOガス(シックハウスガス)の除去

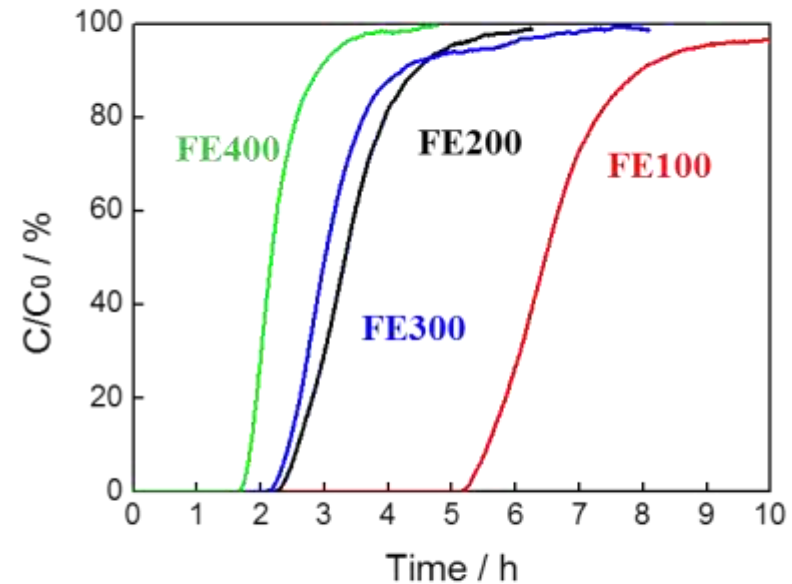


活性炭素繊維を用いたHCHOの除去

HCHO : 22 ppm
Sample weight : 0.1g
Gas flow rate : 100ml / m



HCHO : 22 ppm
Sample weight : 0.1g
Gas flow rate : 100ml / m

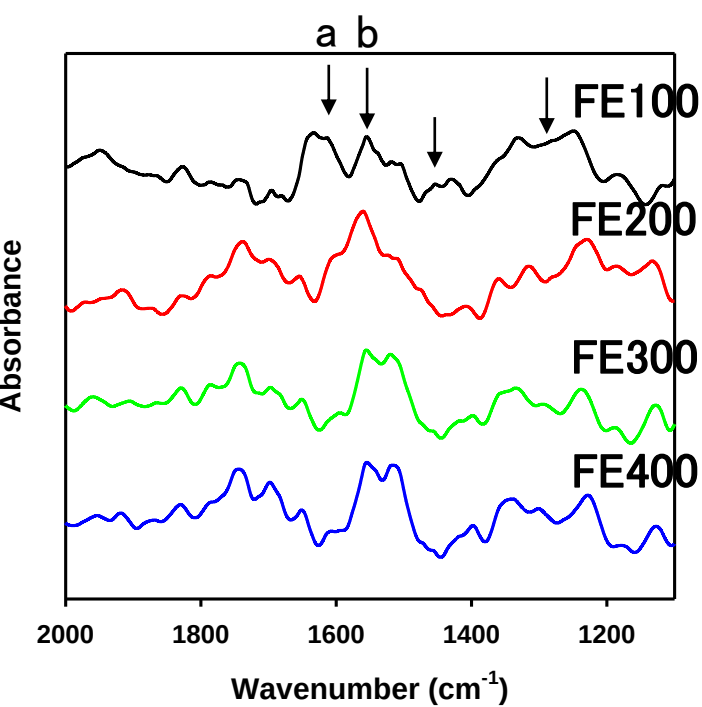


Break through time

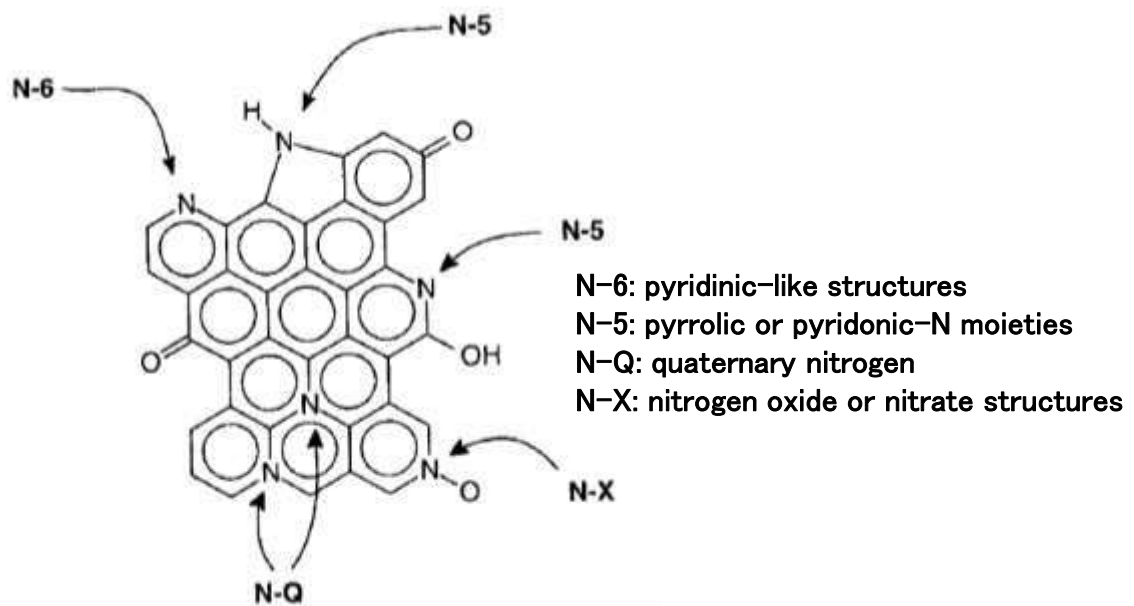
◆Pitch-based ACF : $15A < 20A < 10A < 7A < 5A$

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

Micro ATR-FTIRによるPAN系炭素繊維の表面分析



a: Pyridinic N
b: Internal standard
(C=C stretching vibration mode)

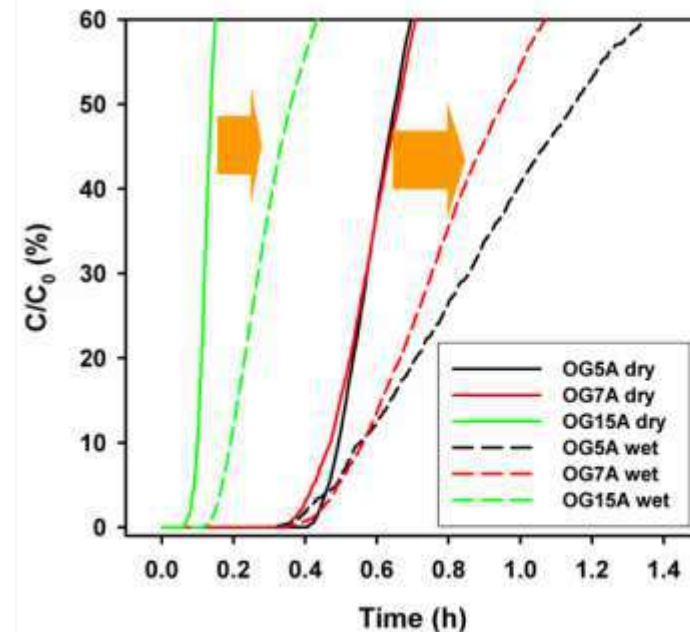
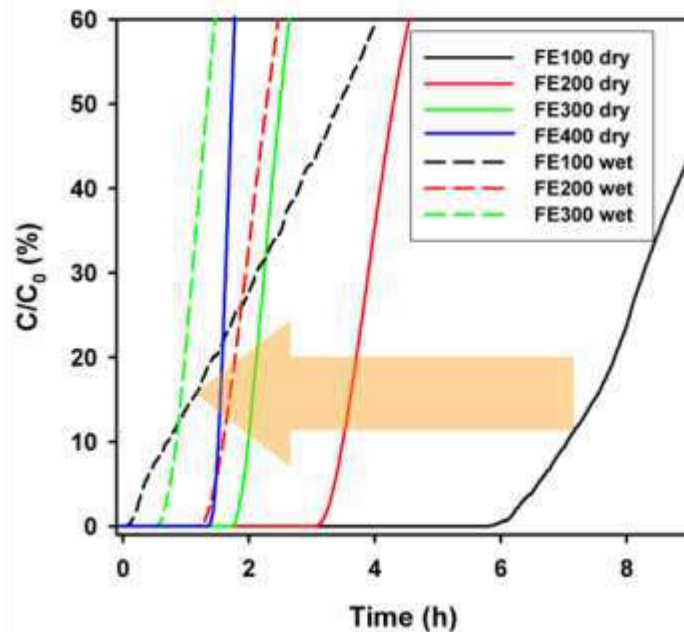


Sample	Internal standard	Pyridinic N	Pyridinic N / Internal standard
FE100	279	134	0.48
FE200	276	108	0.39
FE300	332	70	0.21
FE400	330	64	0.19

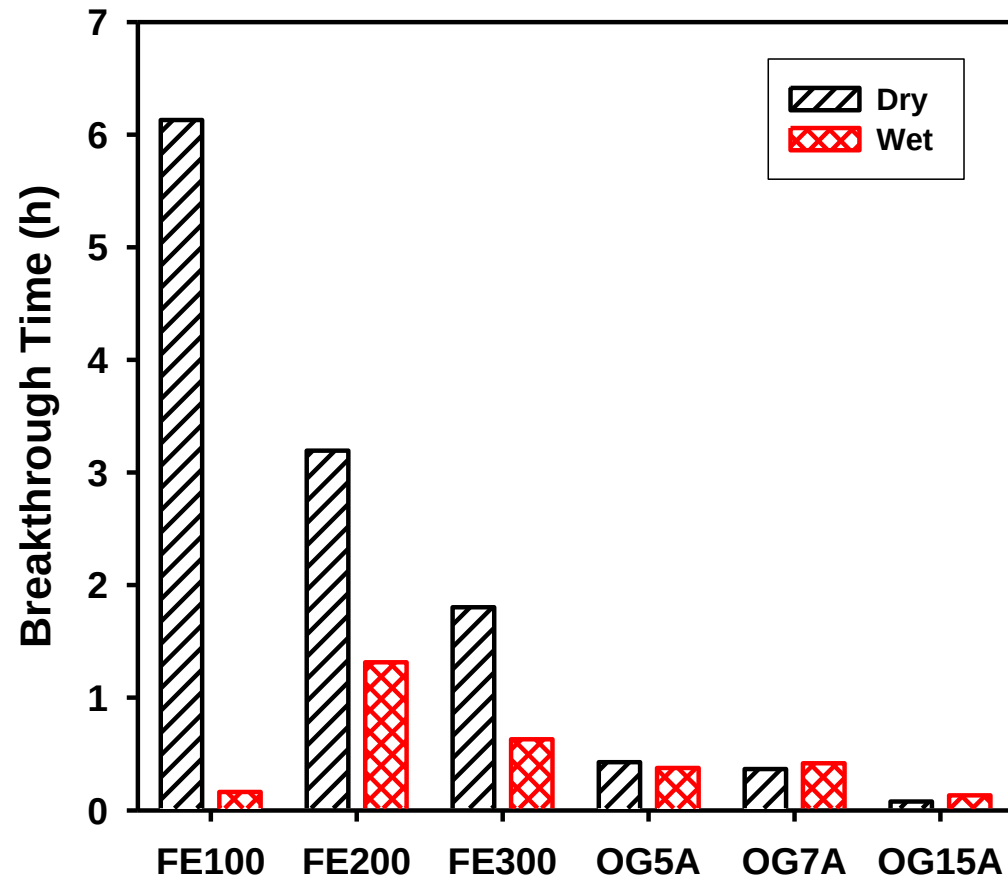
活性炭素繊維を用いたHCHOの除去(湿度の影響)

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



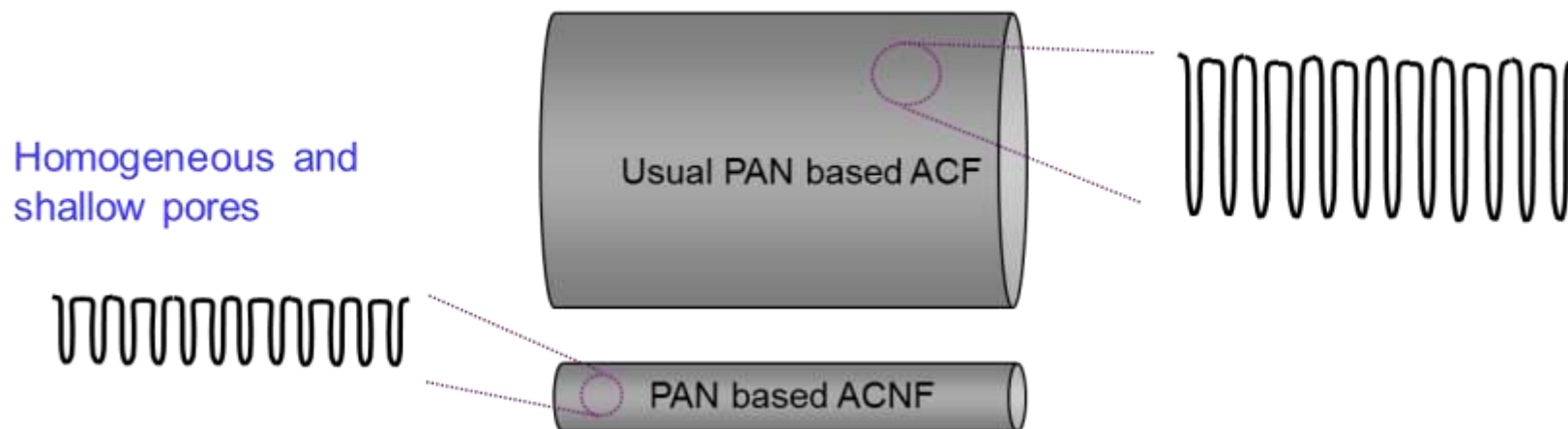
活性炭素繊維を用いたHCHOの除去(湿度の影響)



新規活性炭の概念導入(浅い細孔)

- ◆ 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系活性ナノ炭素繊維

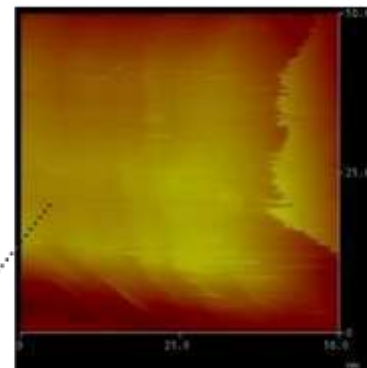
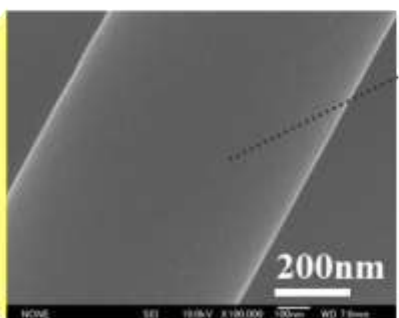
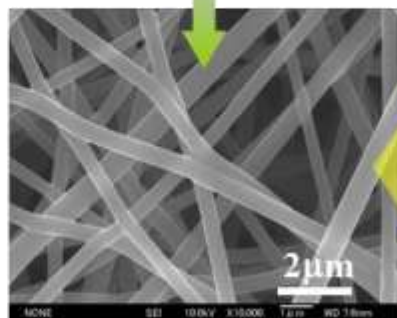
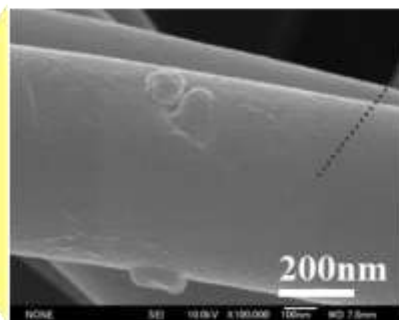
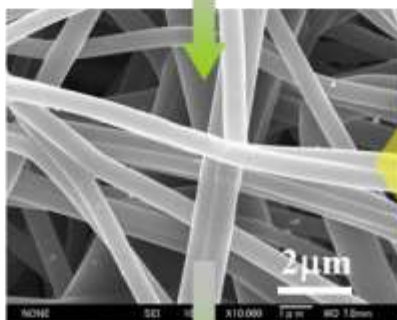
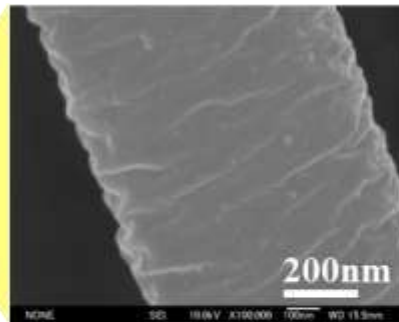
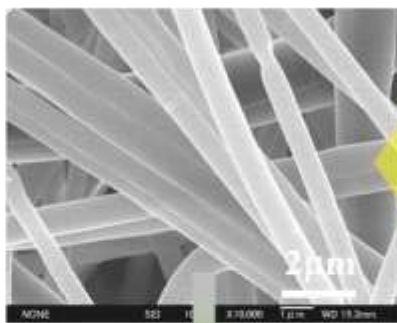
PCNF
(starting material)

270°C
(0.5°C / min)

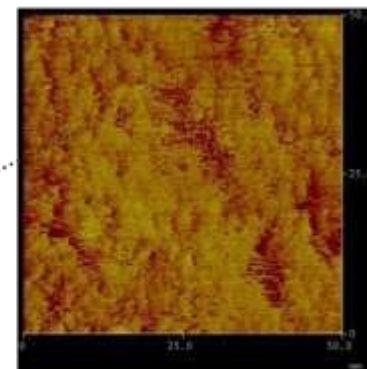
Stabilized PCNF

600°C in He
or
steam activation

PACNF



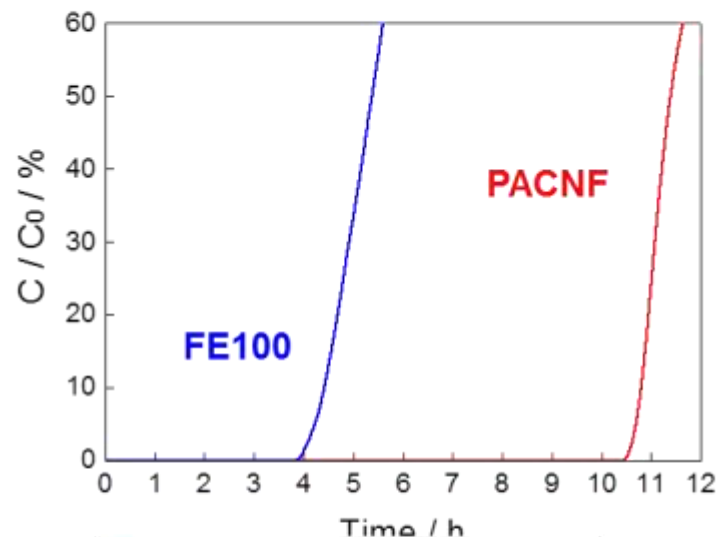
Assembly of
1.8nm~3.6nm thin film



Nano particle
assembly structure

活性炭素ナノ繊維を用いたHCHOの除去

RH	BET	Elemental analysis (wt%)						Microporous ratio (%)
	(m ² / g)	C	H	N	O _{diff}	ash	N / O	
90%	375	68.06	1.19	18.02	11.41	1.32	1.80	94.7%



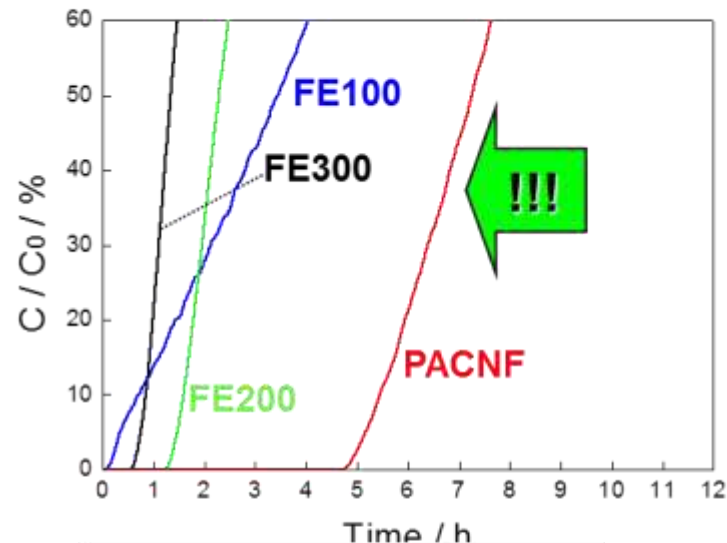
Experimental

HCHO : 11 ppm

Sample weight : 0.05g

Gas flow rate : 100ml / ml

Humidity of condition : 0%



Experimental

HCHO : 11 ppm

Sample weight : 0.05g

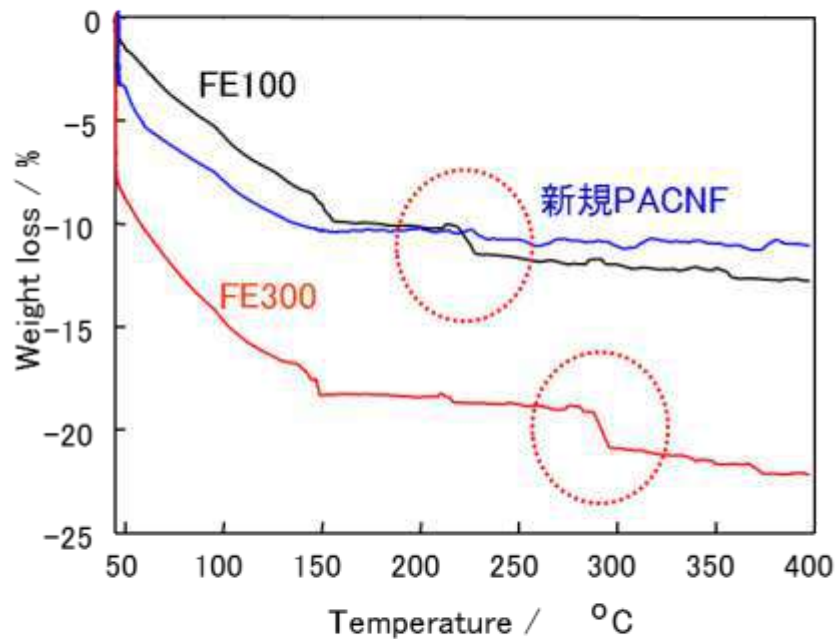
Gas flow rate : 100ml / ml

Humidity of condition : 50%

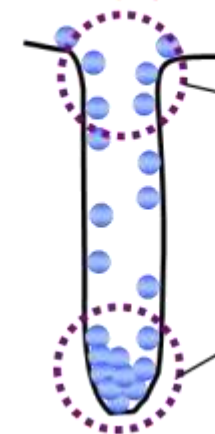
**Under the circumstances of humidity (RH=50%),
PACNF shows specific prominent adsorption characteristics for formaldehyde.**

浅い細孔(?)

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



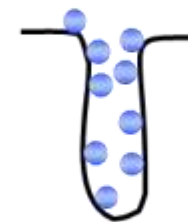
Deep pore



低温での重量変化
細孔上部に吸着してい
る水分子の蒸発

高温での重量変化
深い細孔の底部に凝集
している水分子の蒸発

Shallow pore



低温での重量変化
浅い細孔に吸着してい
る水分子の蒸発

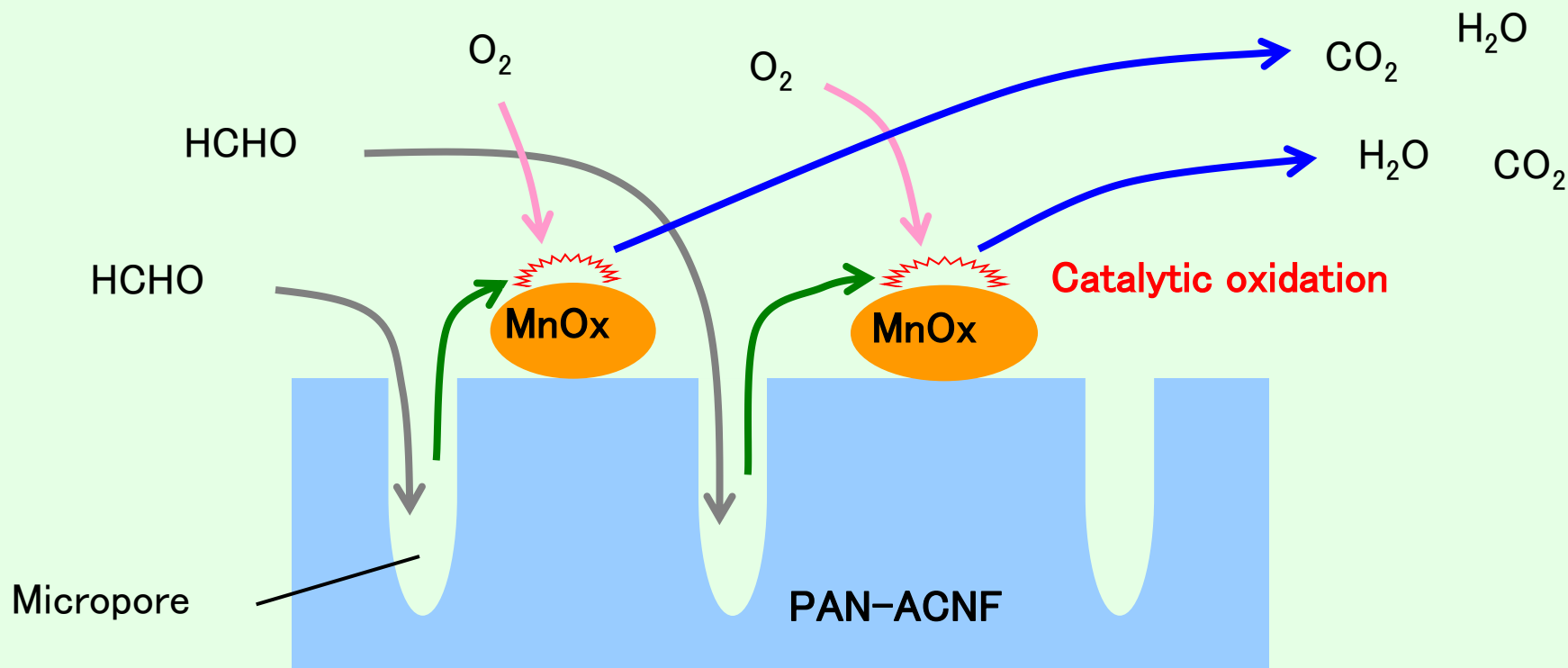
MnO_x/ACNFによるHCHOの完全無害化除去

① PAN-based Activated Carbon Nanofiber

② MnO_x catalyst

Hybridization

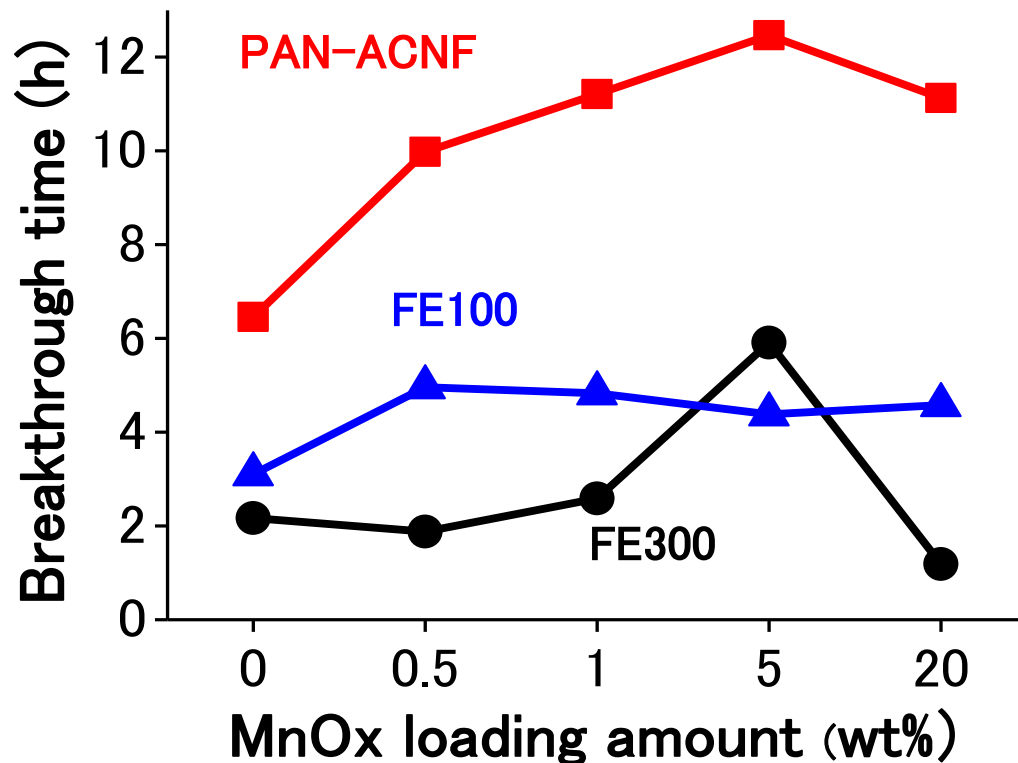
- Clean removal by MnO_x into H₂O and CO₂
- Lifetime prolongation



Conceptual illustration of MnO_x@PAN-ACNF catalyst

MnO_x/ACNFによるHCHOの完全無害化除去

Dry condition (R.H. = 0%)



MnO_x alone breakthroughed within 1 h.

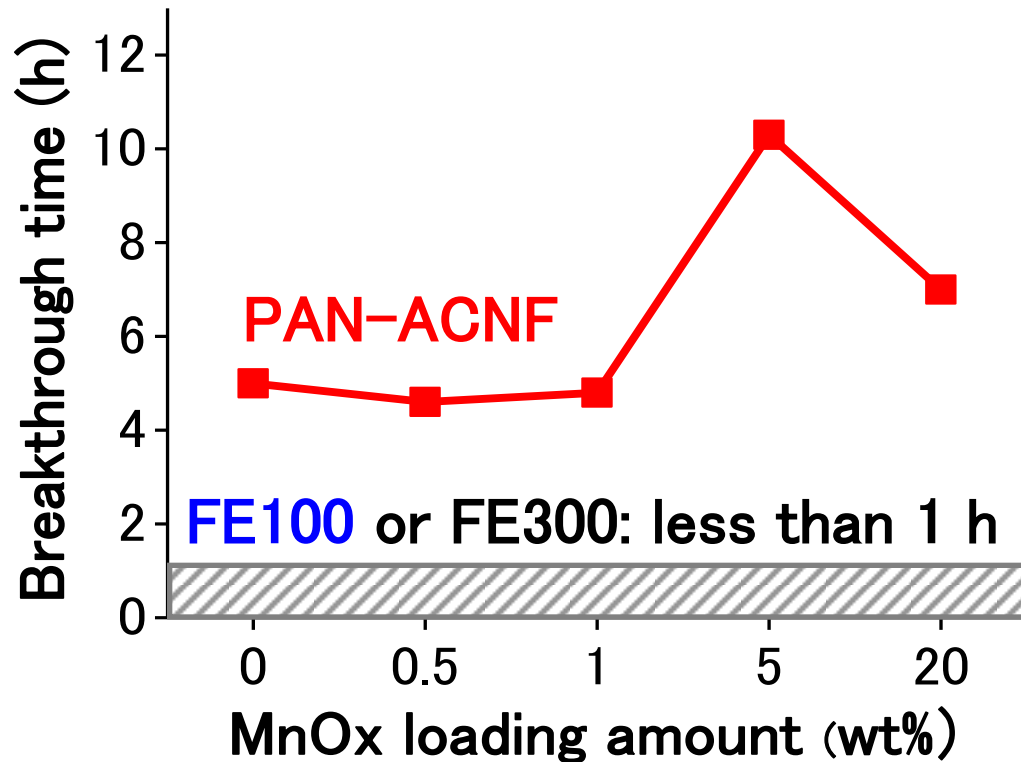
- PAN-ACNF showed the highest performance for HCHO removal at 5% MnO_x loading amount.
- Deposition of MnO_x on carbon supports improved the HCHO removal activity.

Sample weight: 50 mg
Inlet HCHO conc.: 10 ppmv

Breakthrough time was defined as the time, at which the outlet concentration reached to 0.5 ppmv.

MnO_x/ACNFによるHCHOの完全無害化除去

Wet condition (R.H. = 90%)



Sample weight: 50 mg
Inlet HCHO conc.: 10 ppmv

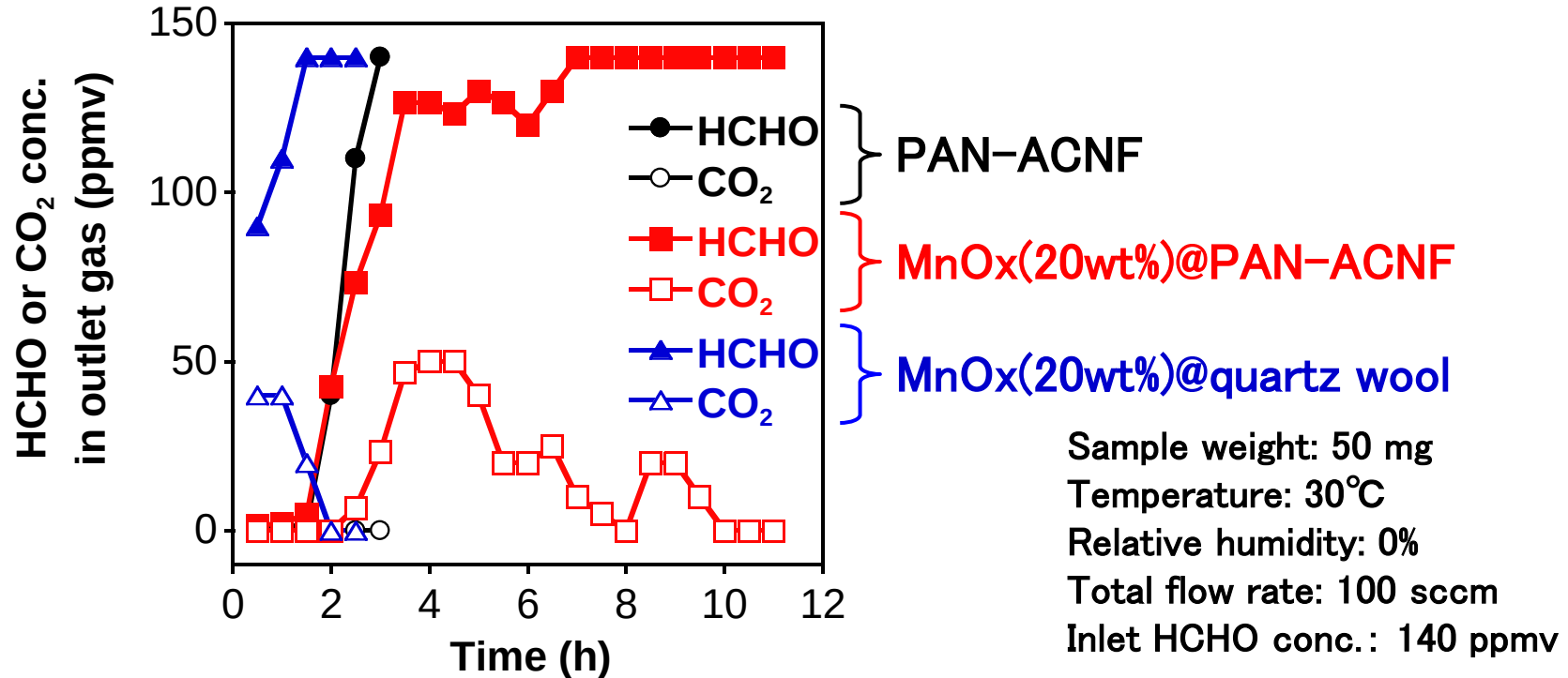
Breakthrough time was defined as the time, at which the outlet concentration reached to 0.5 ppmv.

MnO_x alone breakthroughed within 30 min.

- Humidity was fatal to HCHO removal activity as to conventional ACFs (FE100 and FE300).
- PAN-ACNFs comparatively hold strong, showing little drop with the highest activity at 5% MnO_x loading amount.

MnO_x/ACNFによるHCHOの完全無害化除去

Gas composition analysis



- Clear detection of CO₂ for MnO_x-deposited samples
($\text{HCHO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$)
- No induction period for non-porous quartz wool support
(Adsorption of HCHO in PAN-ACNF micropores)

2. 高性能キャパシタ電極材



NMRを用いたキャパシタの研究

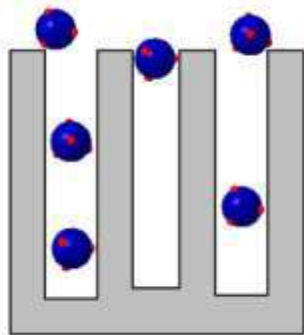
Pitch-based Activated Carbon Fibers (ACFs)

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

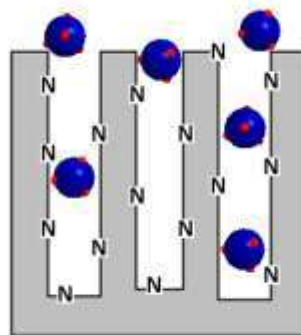
PAN-based ACFs

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

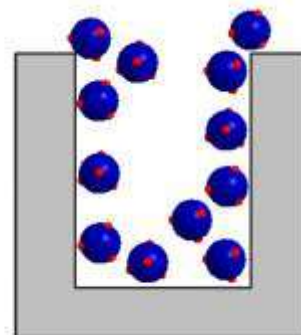
Model of micropores of OG and FE series



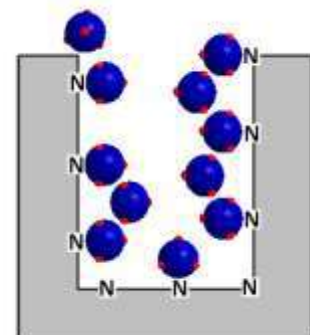
OG-5A



FE-100

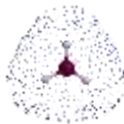


OG-15A

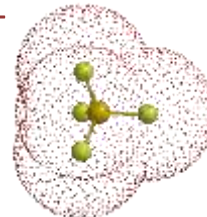


FE-300

Aqueous and non-aqueous electrolytes with different ion sizes



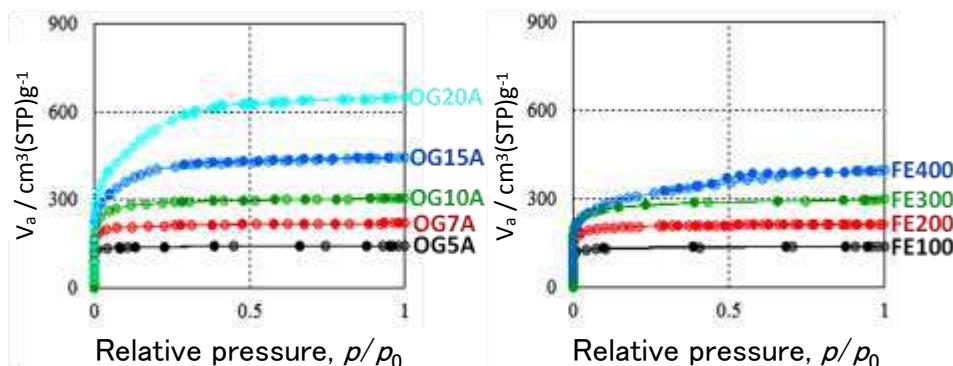
in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$



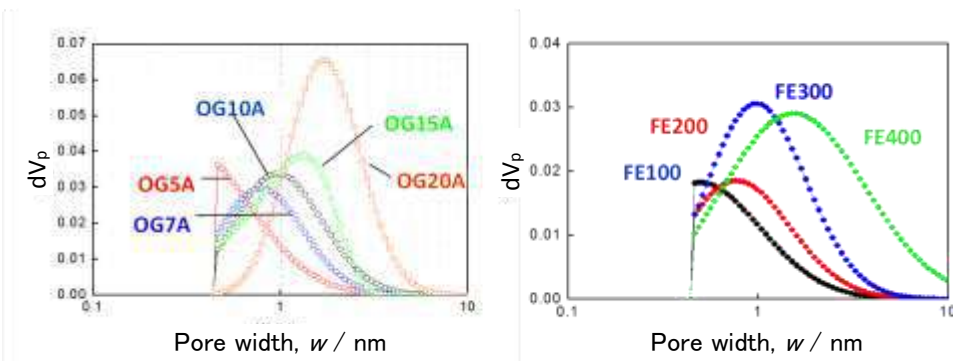
in $\text{Et}_4\text{NBF}_4/\text{PC}$

NMRを用いたキャパシタの研究

N₂ adsorption/desorption isotherms at 77K



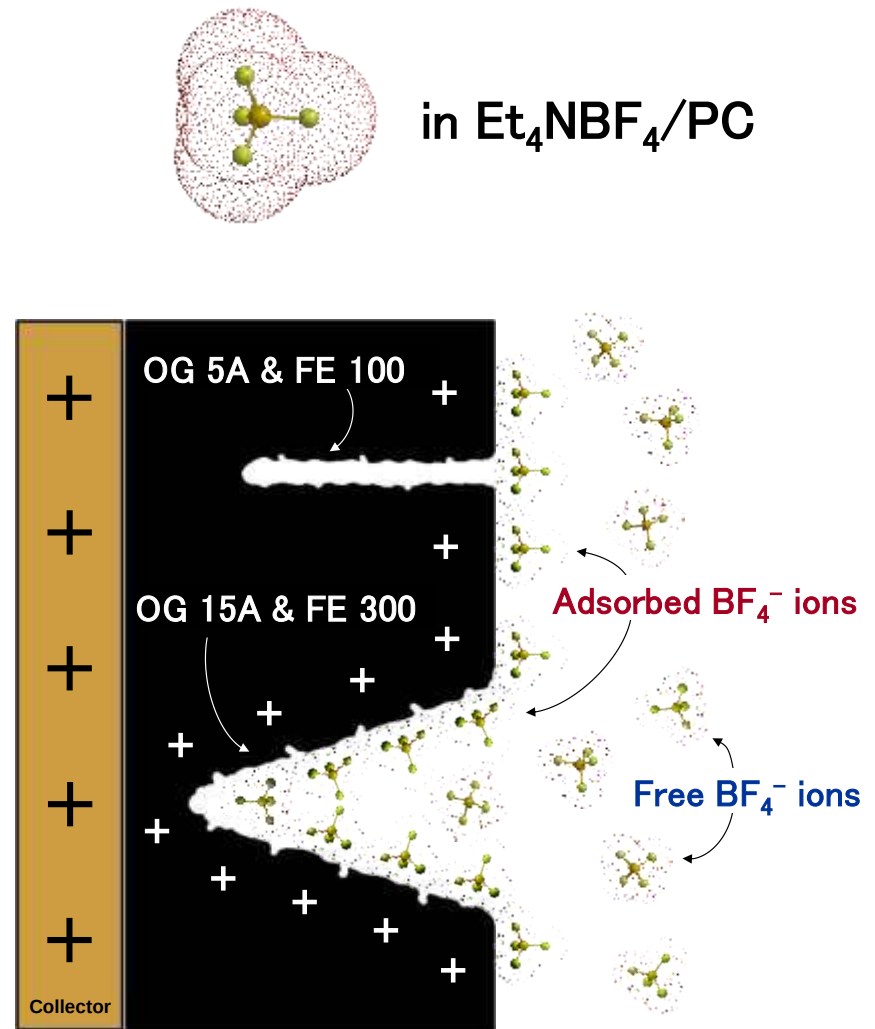
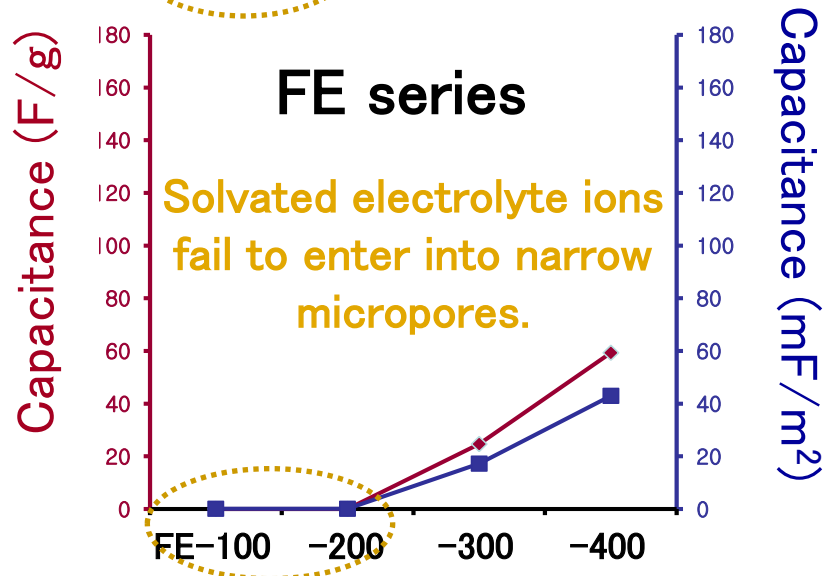
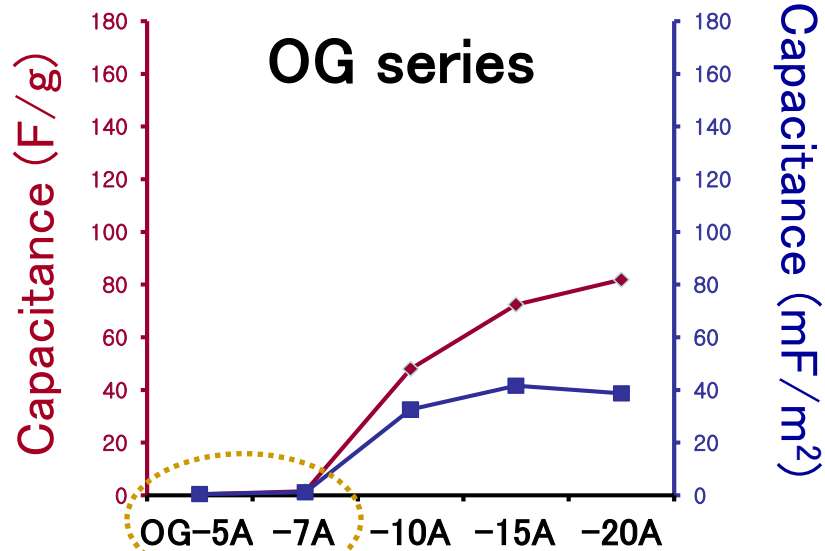
Pore size distributions (calculated by NL-DFT method)



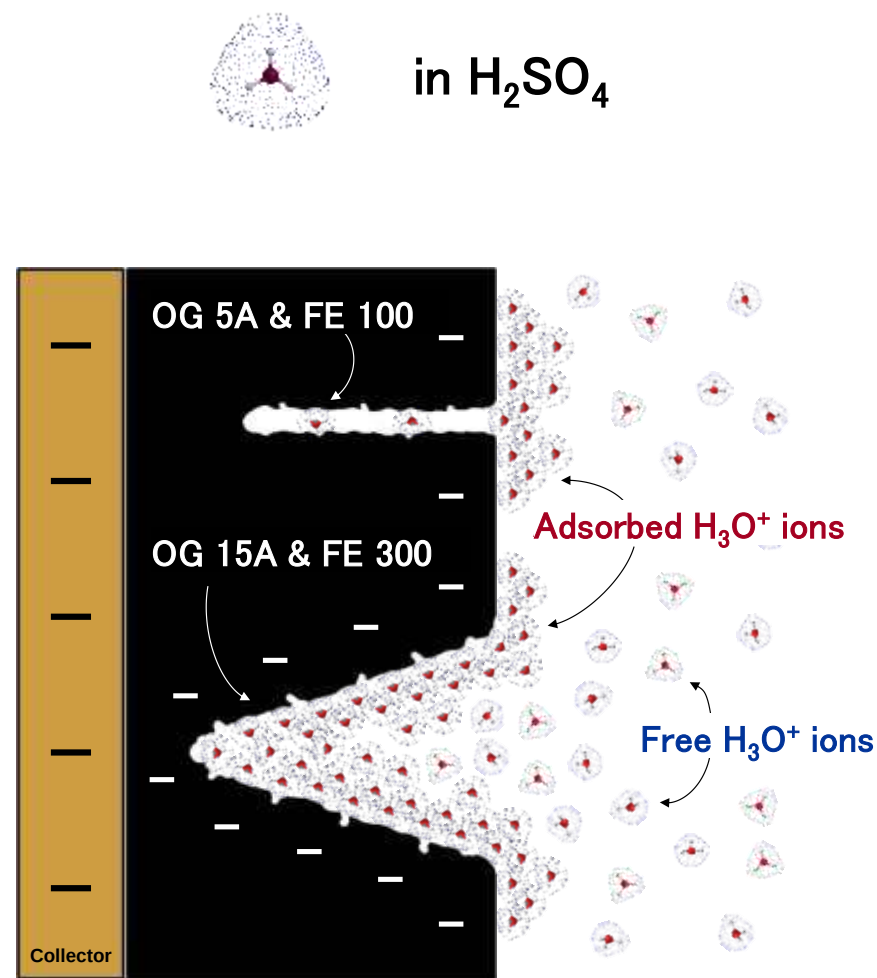
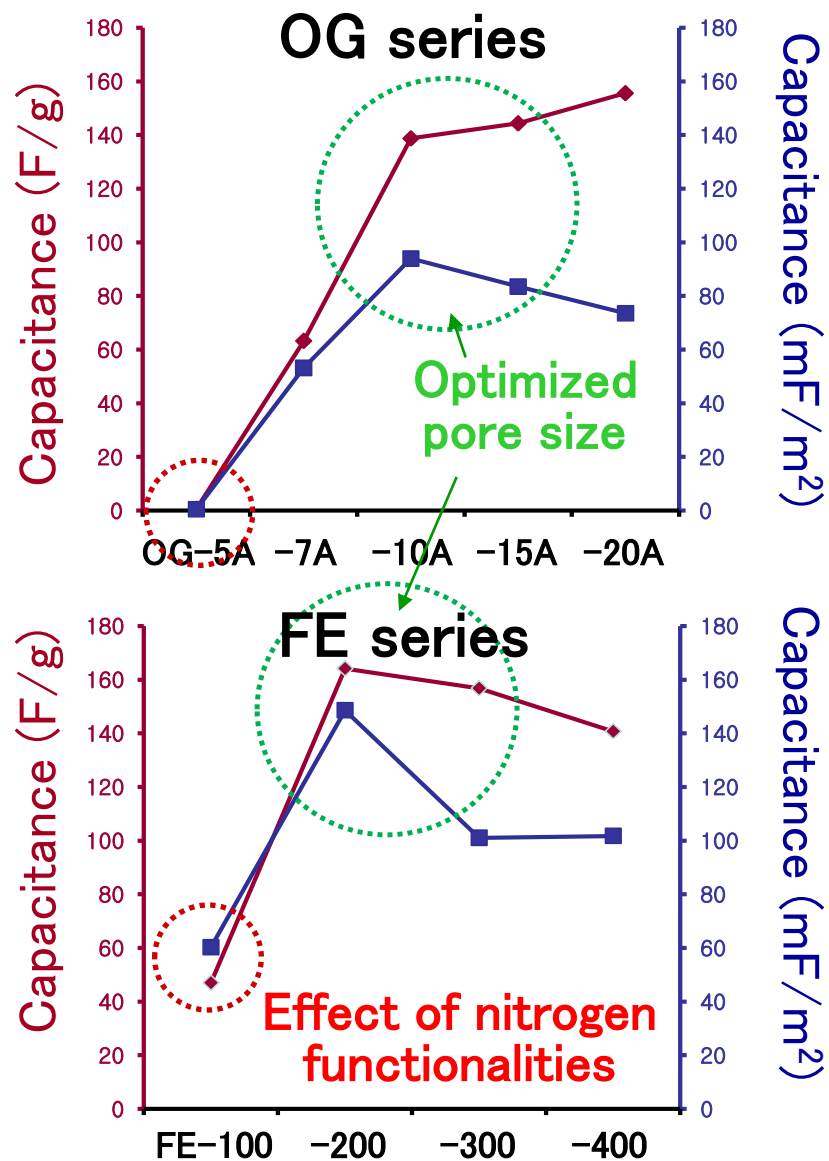
Pore structure parameters (calculated from t -plot method)

	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を用いたキャパシタの研究

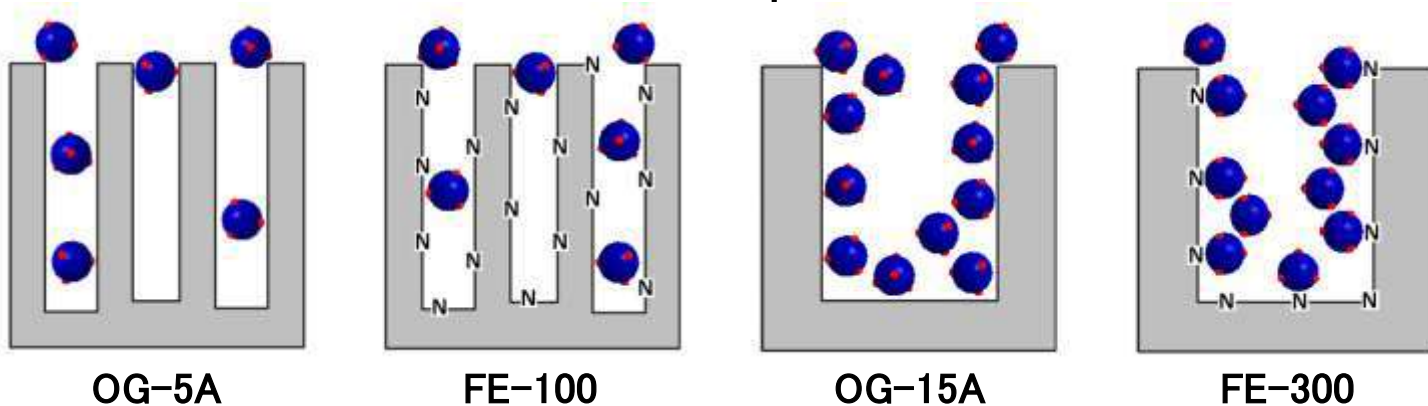


NMRを用いたキャパシタの研究



NMRを用いたキャパシタの研究

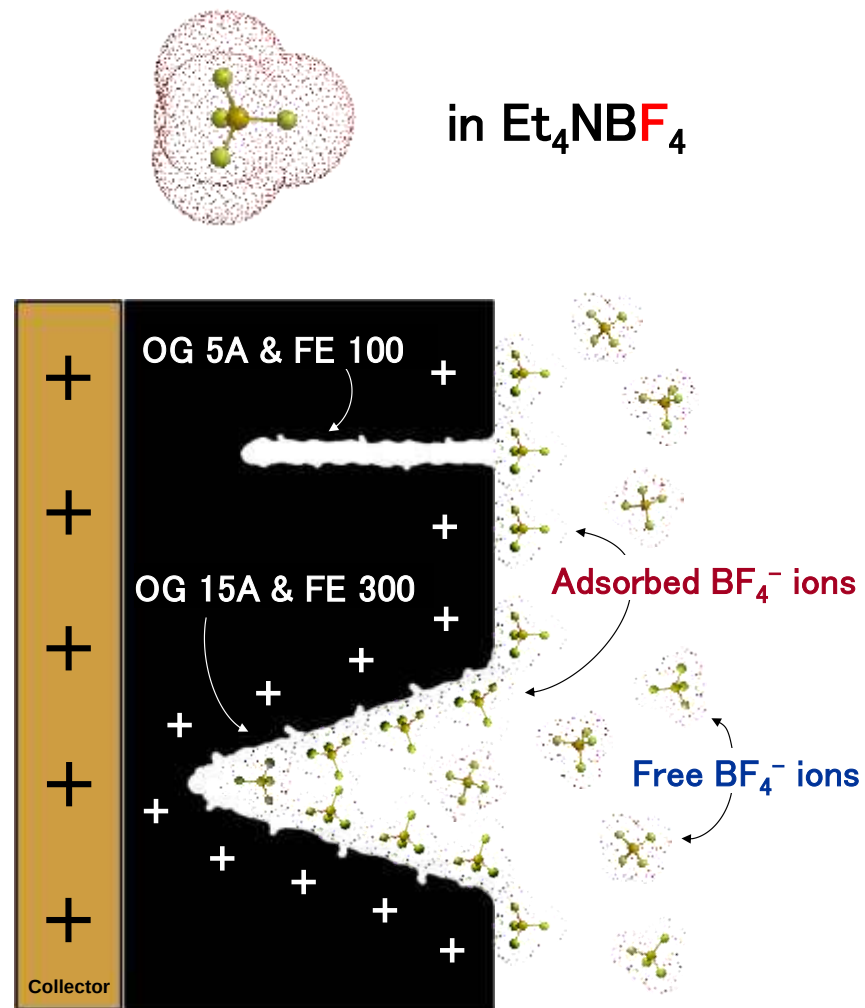
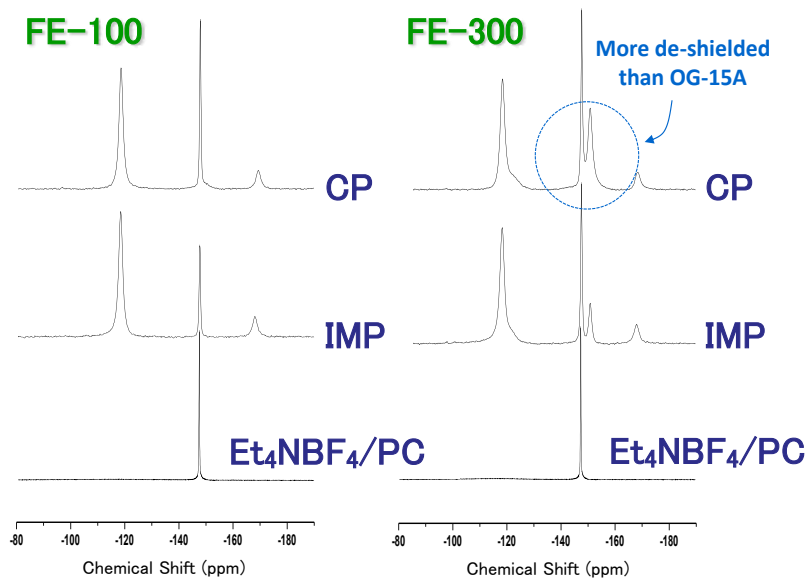
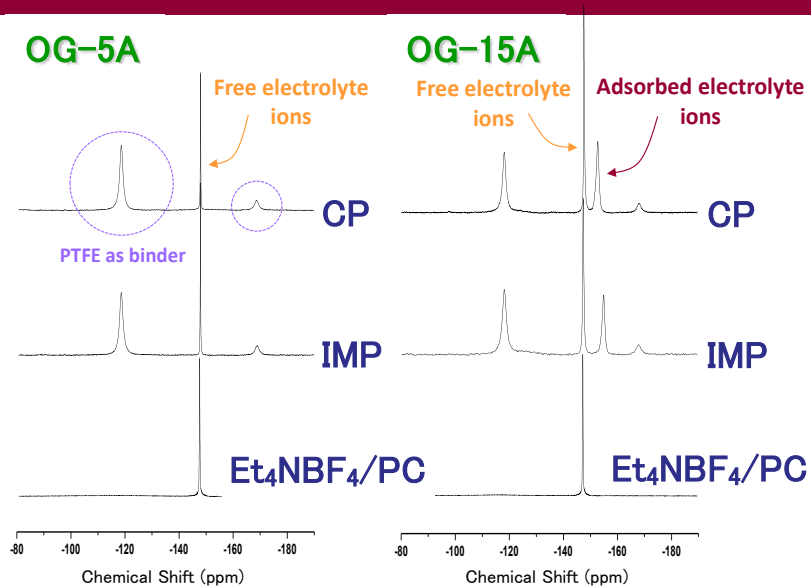
Model of adsorbed ions in micropores of OG and FE series



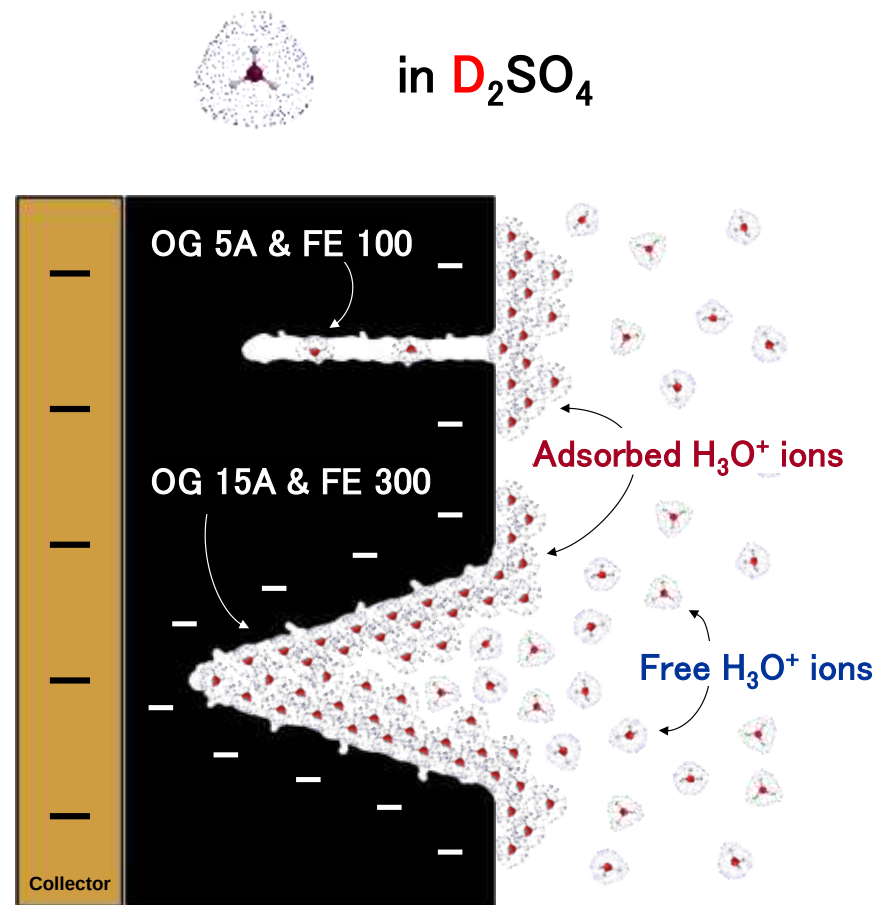
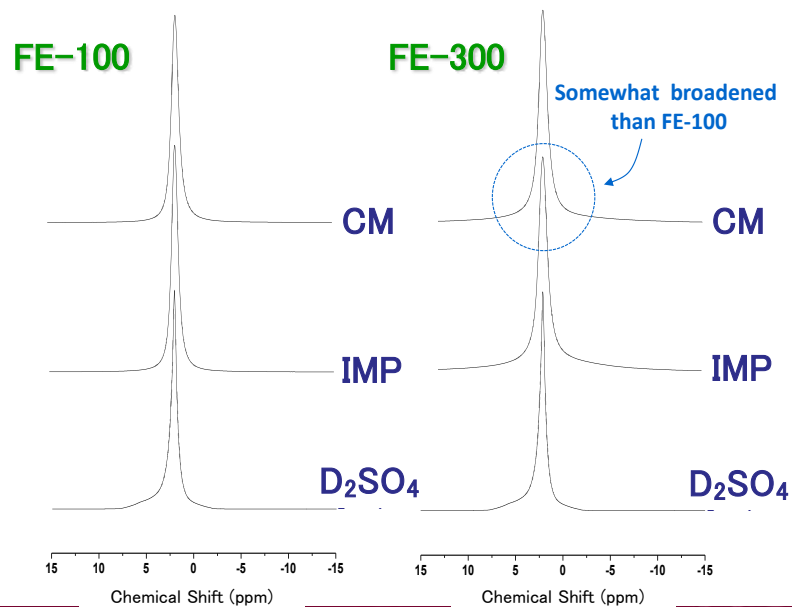
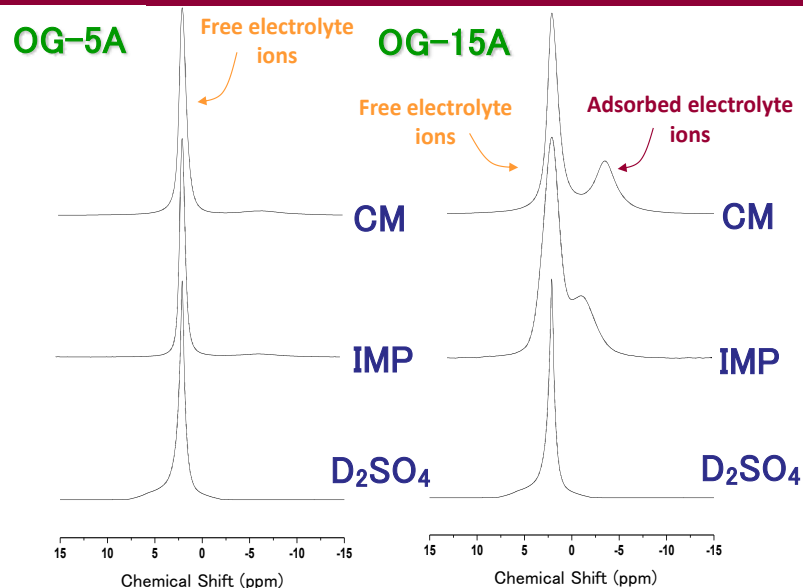
^2H or ^{19}F magic angle spinning (MAS) solid state NMR

NMR equipment:	JEOL ECA400
Electrolytes:	0.5 M D_2SO_4 (aqueous) 1 M $\text{Et}_4\text{NBF}_4/\text{PC}$ (non-aqueous)
Electrode states:	Impregnated (IMP) Charged plus (CP) Charged minus (CM)

^{19}F -MAS Solid-State NMR Spectra



^2H -MAS Solid-State NMR Spectra

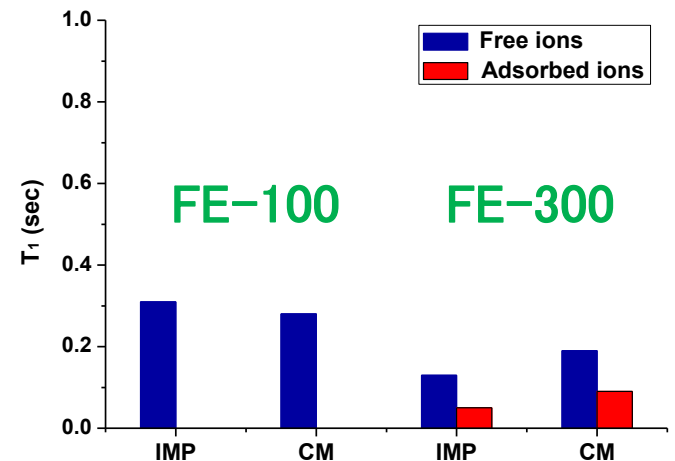
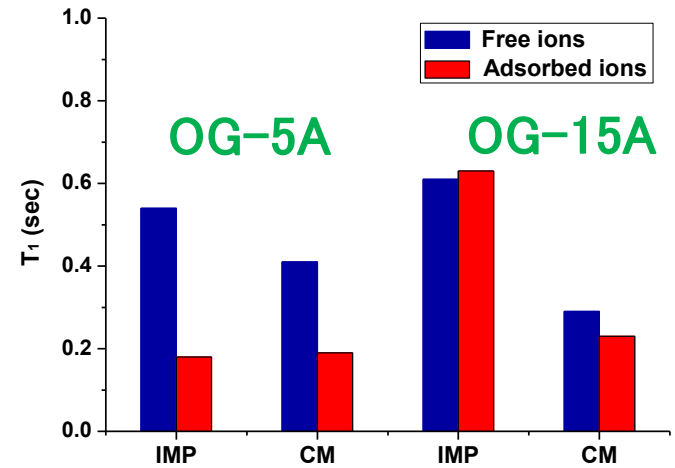


T₁ Values from ²H-MAS Solid-State NMR Spectra

The shorter the T₁ 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



水蒸気賦活と化学賦活は何が違うか？

What is the difference:

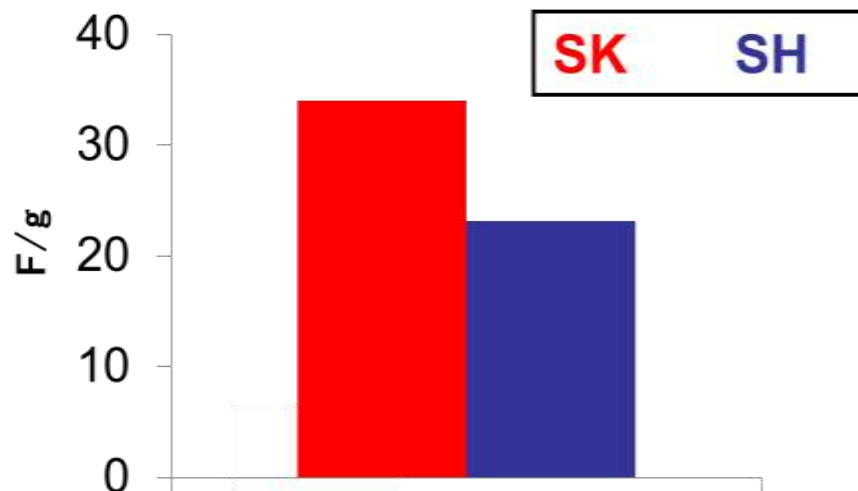
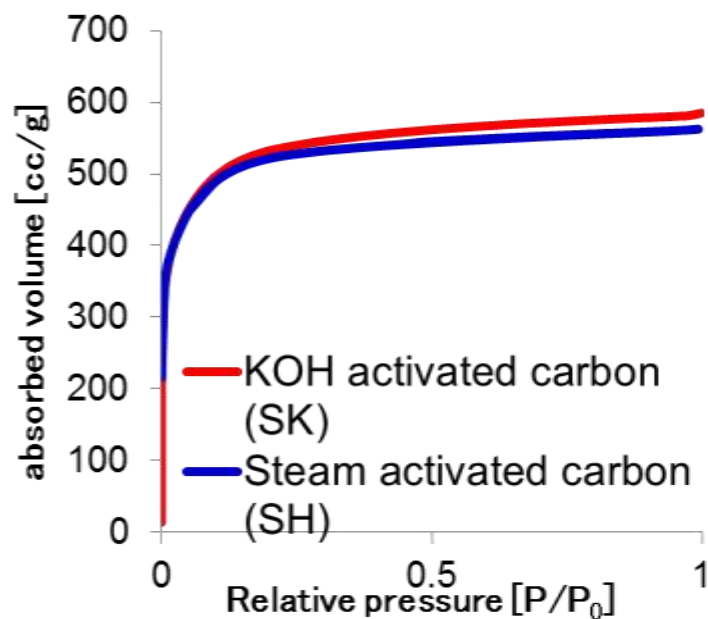
- Surface area, pore size and its distribution
- Surface compositions
- Surface structure (?)
- Cost
- Waste materials

Capacitance, cost, ...

How to overcome the differences?



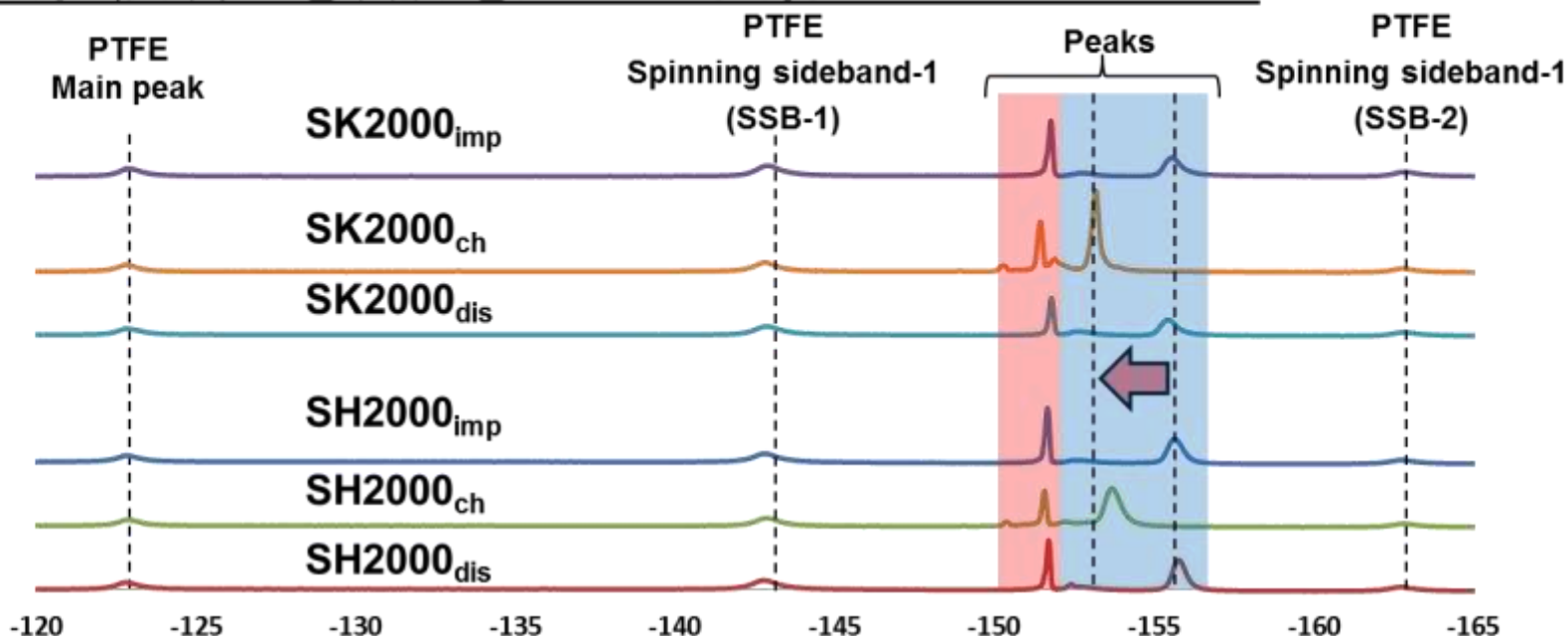
活物質の賦活方法が電気二重層キャパシタの キャパシタンスに及ぼす影響



試料名	BET 比表面積 [m^2/g]	含有率 [%]			電極密度 [g/ml]	キャパシタンス		F/g 比 (SK/SH)
		H	C	N		F/g	F/ml	
SK2000	2007	0.83	87.07	0.05	0.40	34.0	13.6	1.5
SH2000	1969	0.69	96.26	0.04	0.44	23.2	10.2	

同じ比表面積を有する活性炭であっても、水蒸気賦活したものよりも
 KOH賦活を行ったものの方がより高いキャパシタンスを示す

各状態(含浸、充電、放電)の ^{19}F 固体NMRスペクトル



	Normalized BF ₄ ⁻ 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		1.6
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		
SH2000 _{ch}	1	1.43	6.46	0.58	2.17	
SH2000 _{dis}	1	1.48	4.29	0.61		

固体NMR測定

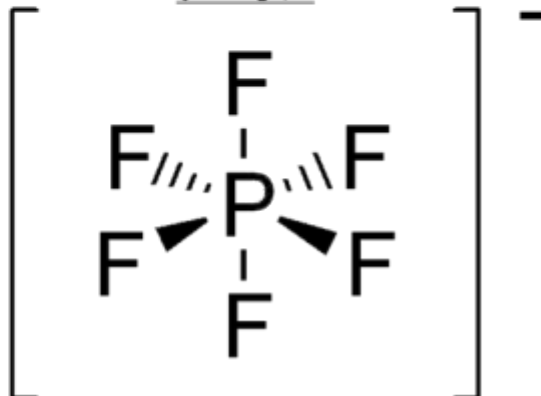
有機系電解質: LiPF_6

カチオン



Li ion

アニオン



Hexafluorophosphate ion



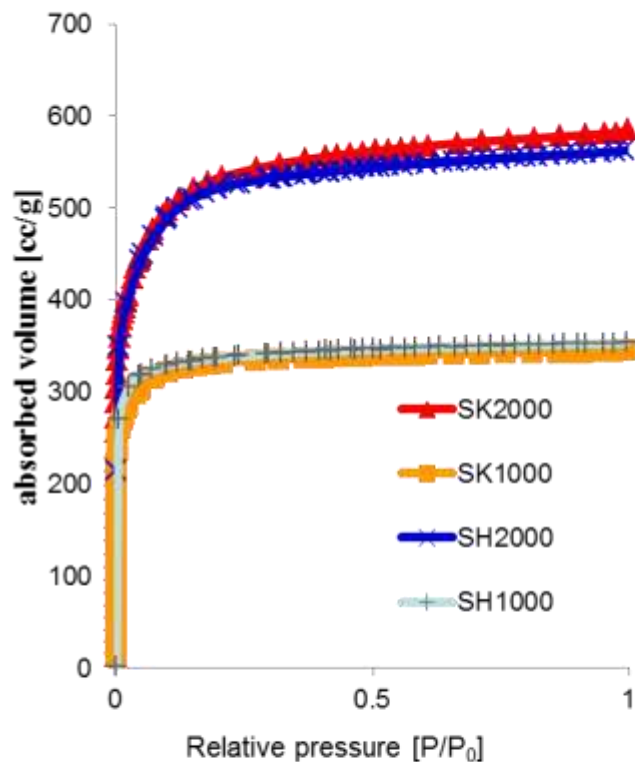
JEOL ECA800

^7Li 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。

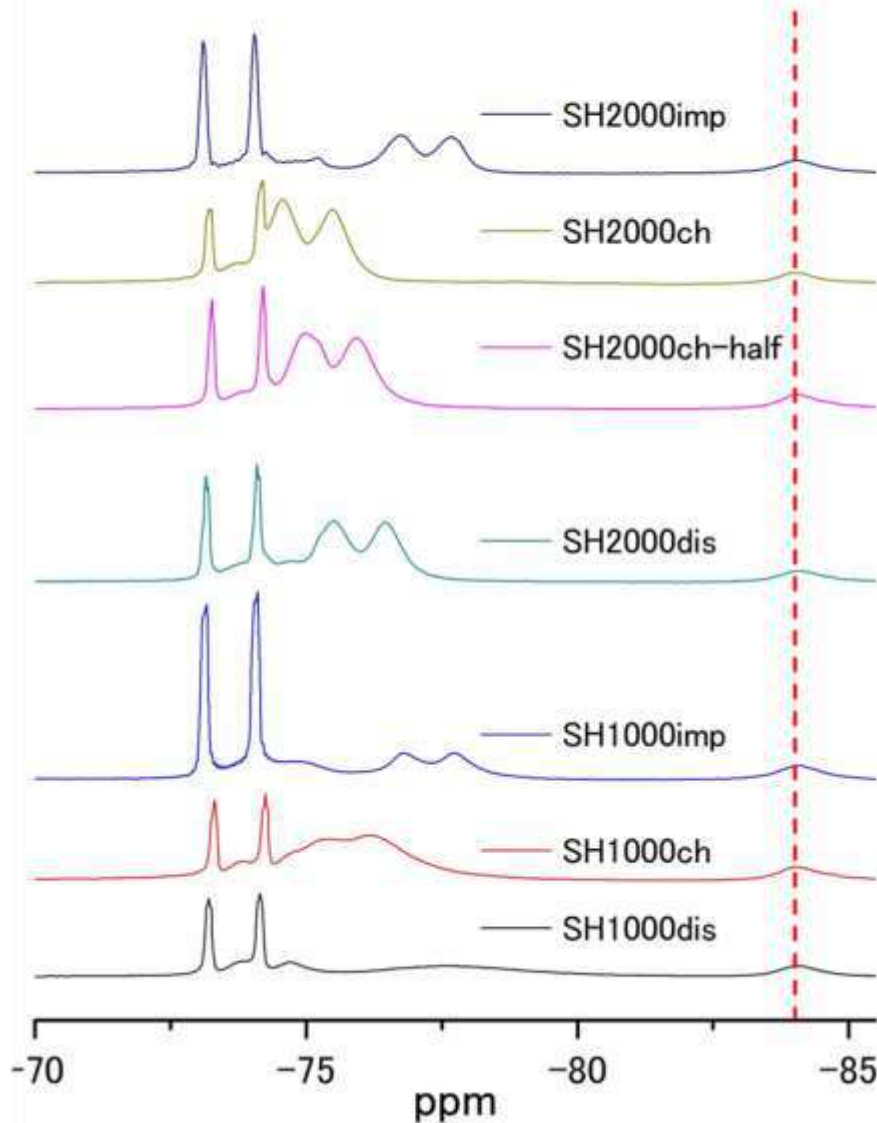
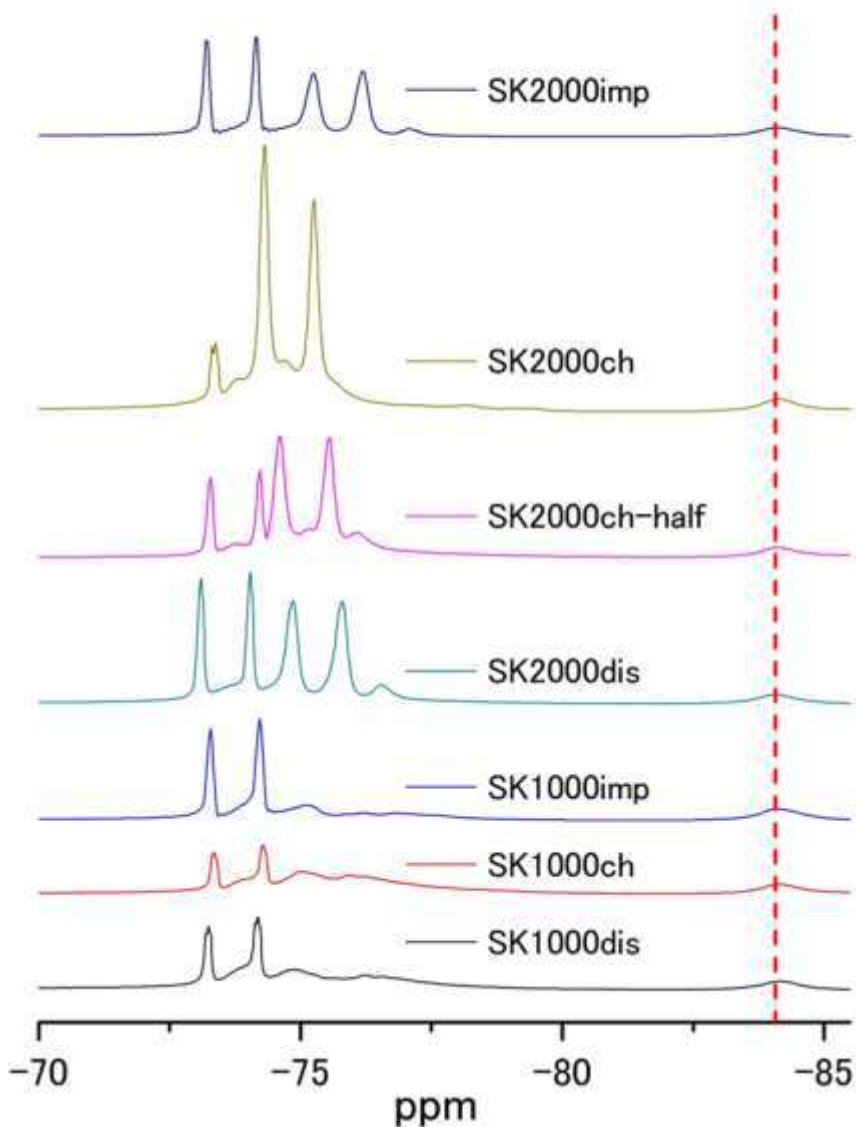
調製した活性炭の分析



サンプル	比表面積 [m ² /g]	電極密度 [g/ml]	F/g	F/ml	F/m ² 比 (SK/SH)
SK2000	2007	0.47	31.1	14.6	1.6
SH2000	1969	0.51	19.7	10.0	
SK2000 _{half}	2007	0.43	25.0	13.4	1.5
SH2000 _{half}	1969	0.49	16.4	12.1	
SK1000	1310	0.44	20.1	11.9	1.0
SH1000	1382	0.52	20.0	12.4	

細孔径分布や比表面積がほぼ揃った活性炭を調製できた。
 比表面積1000m²/gの場合、SK、SHでキャパシタンスに差はない
 比表面積2000m²/gノ場合、SKが1.5倍ほど高い値を示した。

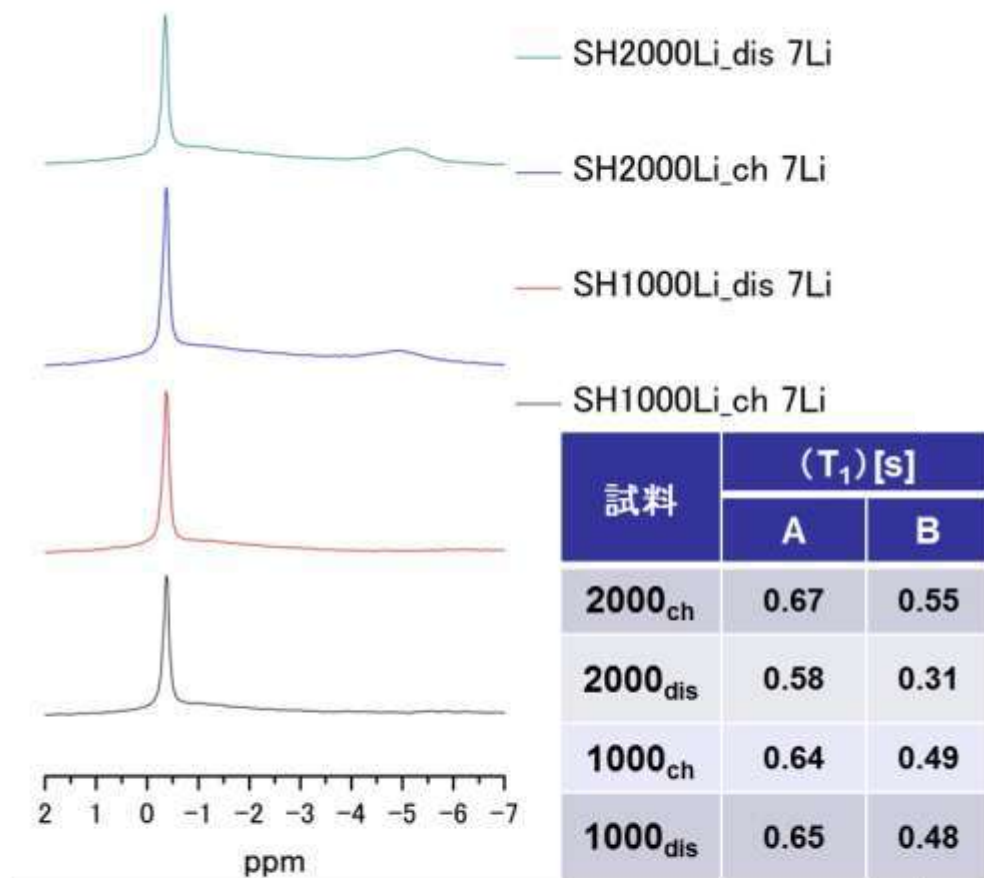
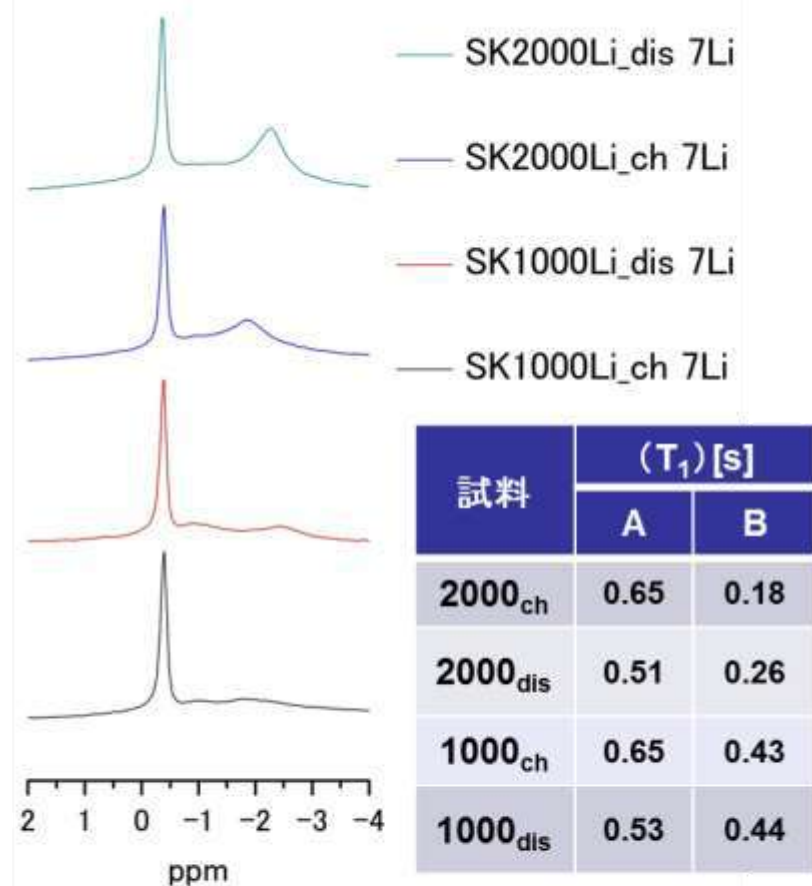
^{19}F 固体NMRスペクトル



¹⁹F固体NMR測定によるEDLC電極の活性炭細孔内における 電解質イオンの吸着特性

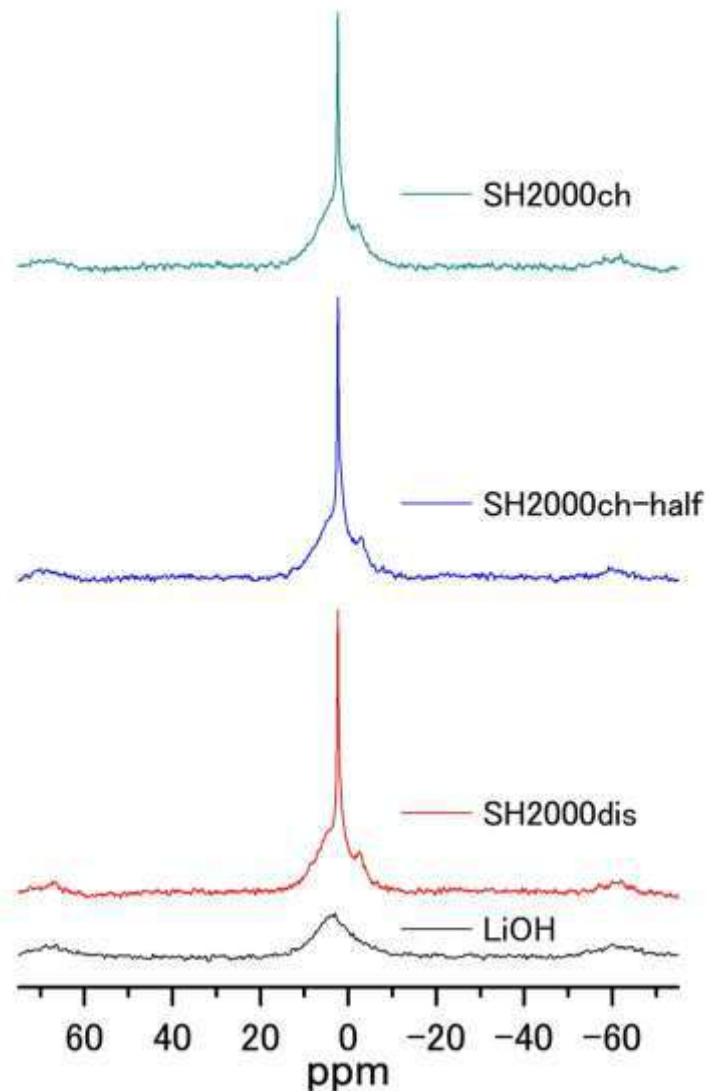
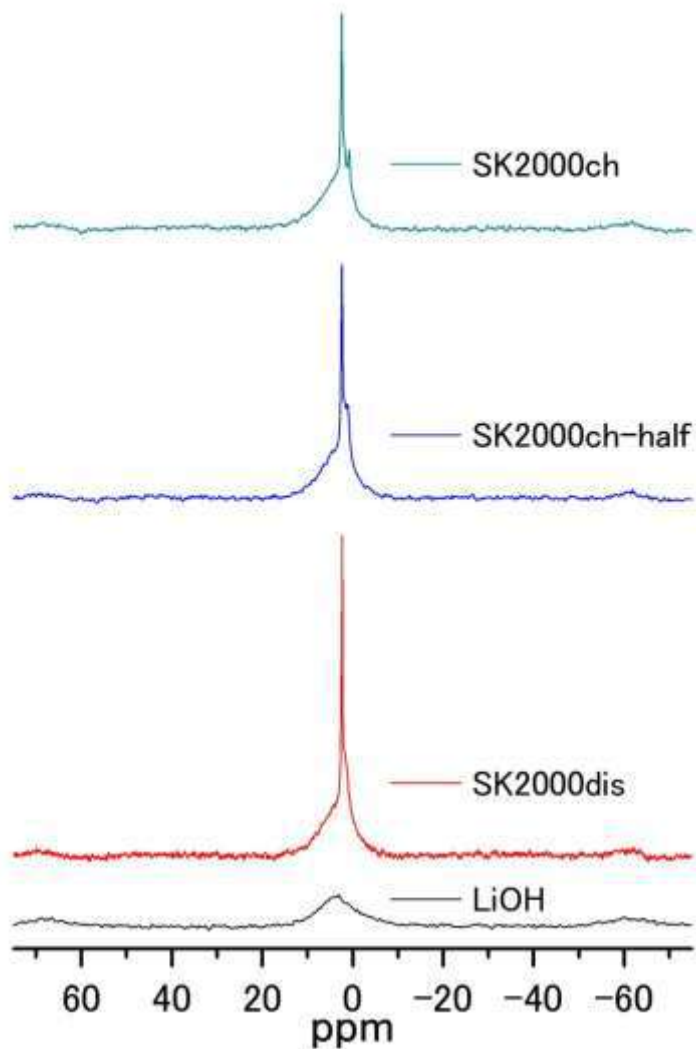
サンプル	PF ₆ ⁻ [× 10 ³]	PTFE [× 10 ³]	PF ₆ ⁻ /PTFE	PF ₆ ⁻ 吸脱着量 (ch/dis)	PF ₆ ⁻ 吸脱着量比 (SK/SH)
SK2000 _{ch}	1217.0	95.8	12.7	1.9 (SK2000 _{ch} / SK2000 _{dis})	1.6 (SK2000 / SH2000)
SK2000 _{ch-half}	912.0	74.6	12.2	1.5 (SK2000 _{ch-half} / SK2000 _{dis})	1.4 (SK2000 _{half} / SH2000 _{half})
SK2000 _{dis}	592.1	63.2	9.4	-	-
SH2000 _{ch}	620.8	67.8	9.2	1.2 (SH2000 _{ch} / SH2000 _{dis})	-
SH2000 _{ch-half}	821.5	94.3	8.7	1.1 (SH2000 _{ch-half} / SH2000 _{dis})	-
SH2000 _{dis}	548.0	70.6	7.8	-	-
SK1000 _{ch}	616.9	124.8	4.9	1.0	0.8 (SK1000 / SH1000)
SK1000 _{dis}	277.2	53.8	5.2	-	-
SH1000 _{ch}	657.9	97.5	6.8	1.3	
SH1000 _{dis}	289.1	76.6	3.8	-	-

^7Li 固体NMRスペクトル



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。

^7Li 固体NMRスペクトル



^7Li 固体NMR測定によるEDLC電極の活性炭細孔内における 電解質イオンの吸着特性

サンプル	$\text{Li}^+ (\text{LiPF}_6)$ [$\times 10^3$]	$\text{Li}^+ (\text{LiOH})$ [$\times 10^3$]	Li^+ 吸脱着量 ($\text{Li}^+ (\text{LiPF}_6)/\text{Li}^+ (\text{LiOH})$)	Li^+ 吸脱着量比 (SK/SH)
SK2000 _{ch}	738.6	525.1	1.41	1.6 (SK2000 _{ch} / SH2000 _{ch})
SK2000 _{ch-half}	756.1		1.44	1.8 (SK2000 _{ch-half} / SH2000 _{ch-half})
SK2000 _{dis}	704.1		1.34	-
SH2000 _{ch}	453.9		0.86	-
SH2000 _{ch-half}	414.6		0.79	-
SH2000 _{dis}	413.9		0.79	-

キャパシタンスと Li^+ 、 PF_6^- -イオンの移動量との関連性

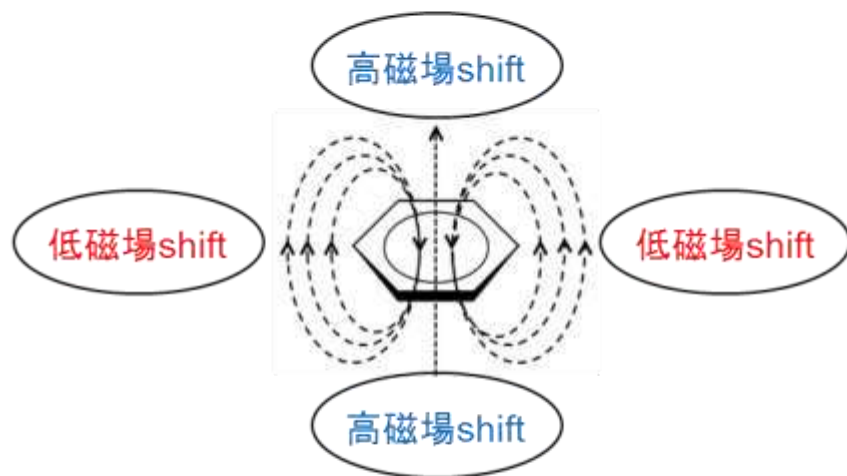
サンプル	PF_6^- 吸脱着量比 (SK/SH)	Li^+ 吸脱着量比 (SK/SH)	F/g比 (SK/SH)
SK2000/SH2000 満充電状態	1.6 (SK2000 / SH2000)	1.6 (SK2000 _{ch} / SH2000 _{ch})	1.6
SK2000/SH2000 半充電状態	1.4 (SK2000 _{half} / SH2000 _{half})	1.8 (SK2000 _{ch-half} / SH2000 _{ch-half})	1.5

PF_6^- 吸脱着量比、 Li^+ 吸脱着量比、F/g比いずれもSKの方が高い値を示し、それぞれに良い相関が見られた。これまでにPTFEを内部標準試料としてフッ素を含む電解質の定量が可能であることが分かっていたが、Liについても定量的な解析が可能であると考えられる。

端面による効果?

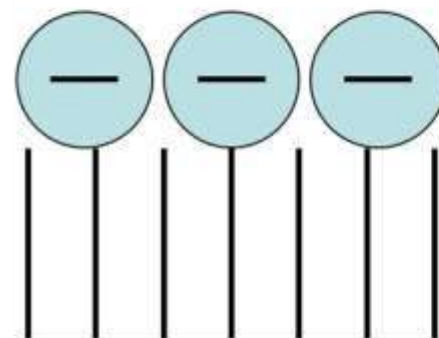
Effect of wall surface

Contribution to chemical shift (Ring current effect)

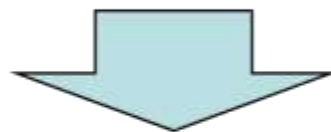
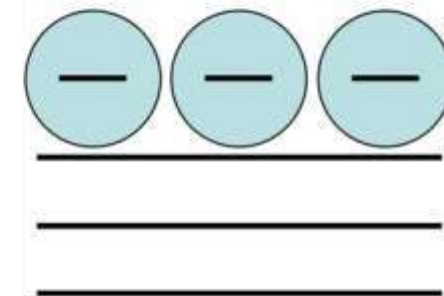


Contribution to capacitance

High capacitance



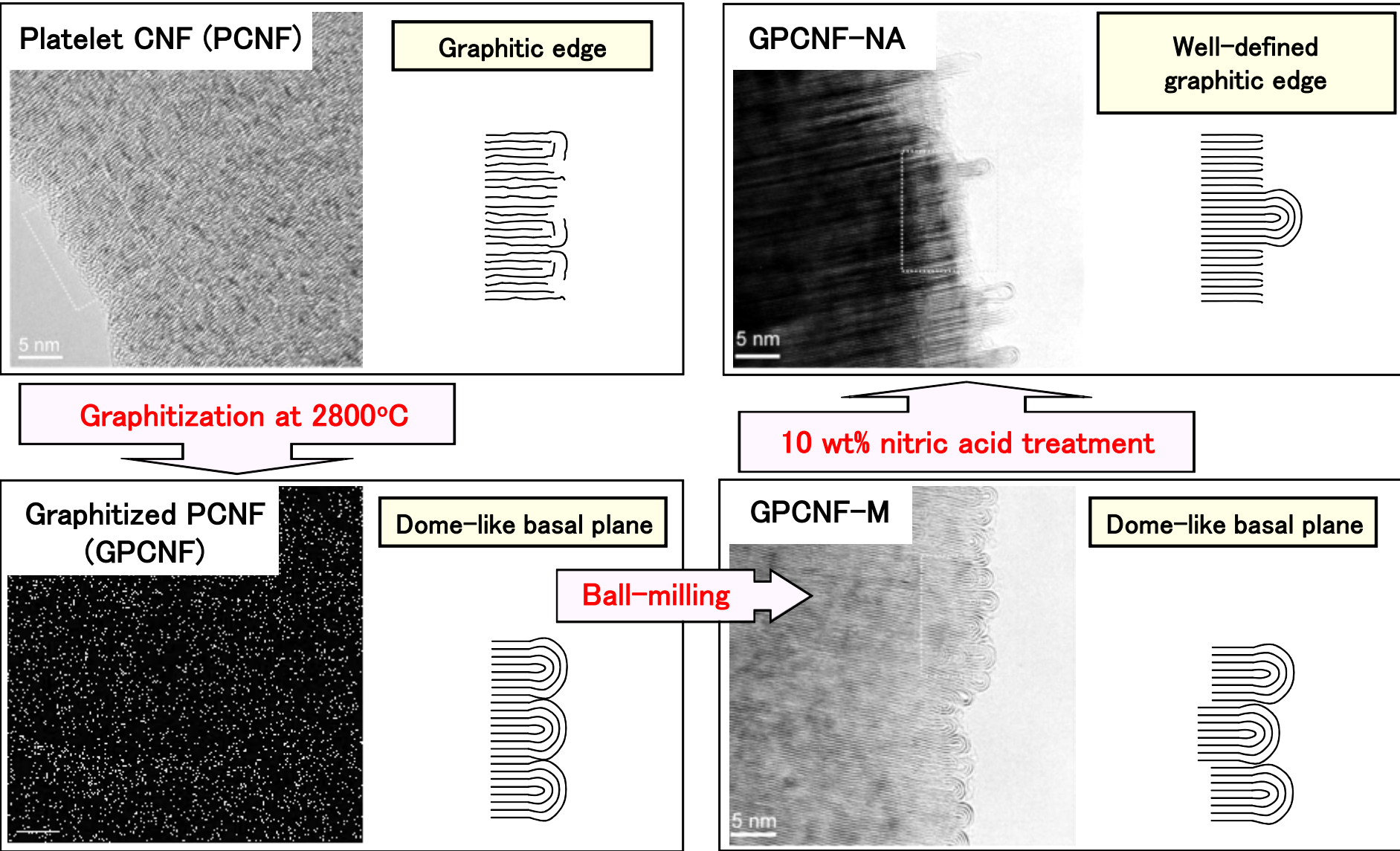
Low capacitance



Adsorption on the edge → Lower magnetic field shift, Higher capacitance
→ SK2000 is conjectured to have more edges on the pore walls

Adsorption on the basal planes → Higher magnetic field shift, lower capacitance
→ SH2000 might have less edges on the pore walls

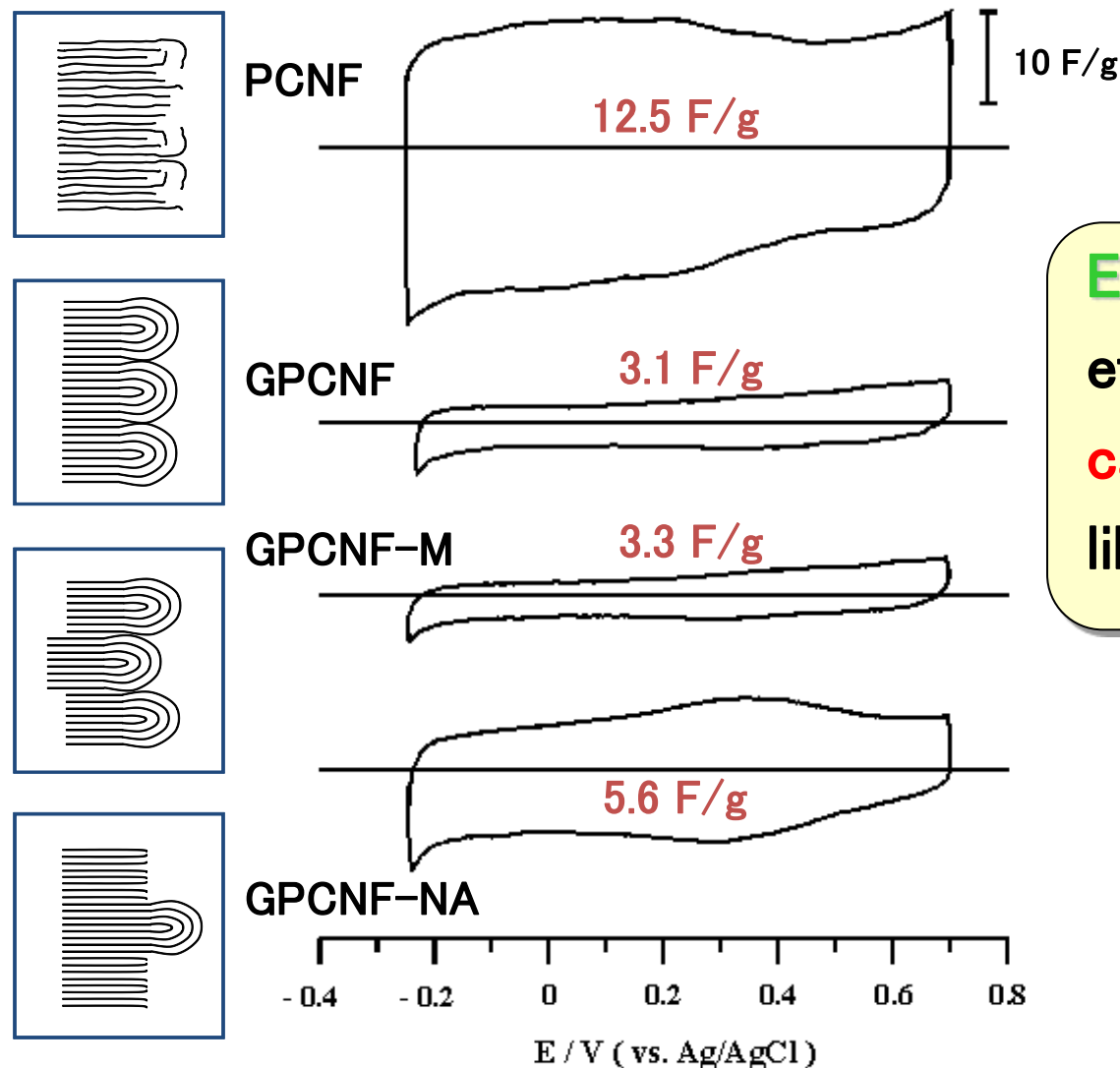
Surface modified PCNFs



Lim, S., et al., *J. Phys. Chem. B*, 2004, 108(5), 1533–1536

Capacitances of PCNF series

Cyclic voltammogram (CV) in 0.5 M H₂SO₄



Edge surface is more effective for a high capacitance than dome-like basal plane surface.

Influence of surface structure on capacitances

Surface features	Sample	BET surface area (m ² /g)	Capacitance	
			F/g	F/m ²
<i>Edge</i>	HCNF	126	23.4	0.19
	PCNF	72	12.5	0.17
	GPCNF-NA	58	5.6	0.10
<i>Basal</i>	GPCNF	51	3.1	0.06
	GPCNF-M	53	3.3	0.06
	TCNF	98	4.5	0.05

- *Capacitance per weight*: Edge is 2–5 times higher than basal plane.
- *Capacitance per surface area*: Edge is 2–4 times higher than basal plane.

3. 経口用薬

インドールとアミラーゼの選択的吸着挙動に与える
経口用活性炭の表面・細孔構造因子の解明

慢性腎不全症

体内の有害物質を除去する腎臓の機能が低下

→ 人工透析を導入し、老廃物などを除去

患者に大きな
負担をかける。

人工透析の導入時期を延期するため、**経口用活性炭薬**を服用

経口用活性炭薬

- ・腸内で選択的物理吸着を原理として、有害物質を吸着し便とともに排泄させることで、有害物質の体内への吸収を抑制することができる。
- ・体質によって便秘を起こす場合がある。
- ・1日6gという大量服用が患者に大きな負担となる。

少量で選択的かつ高い吸着能を持つ 経口用活性炭薬の開発

吸着特性に影響を及ぼす要因

- ・比表面積及び細孔径
- ・形状
- ・表面特性

モデル吸着物質

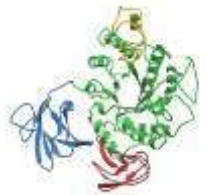
- ・除去すべき物質



インドール (分子量: 117.15)

⇒ 毒性物の一種

- ・除去してはいけない物質



アミラーゼ (分子量: 約46,000)

⇒ 膵液や唾液に含まれる消化酵素

OGシリーズ(大阪ガス(株)提供)

比較的均一なミクロ孔を持ち、賦活時間により比表面積、細孔径が制御されている活性炭素繊維

H₂-OGシリーズ

- ・比表面積及び細孔径
- ・表面特性

OGシリーズを水素中熱処理(600℃、1時間)により表面官能基を除去した活性炭素繊維

球状活性炭シリーズ

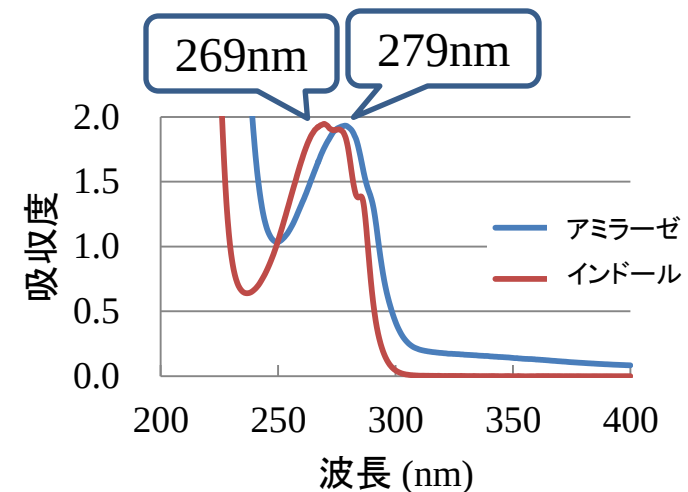
粒径約100～300μ mである球形状の活性炭

 α_s 解析

		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
比表面積 (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
細孔径 (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
表面官能基量(%)		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

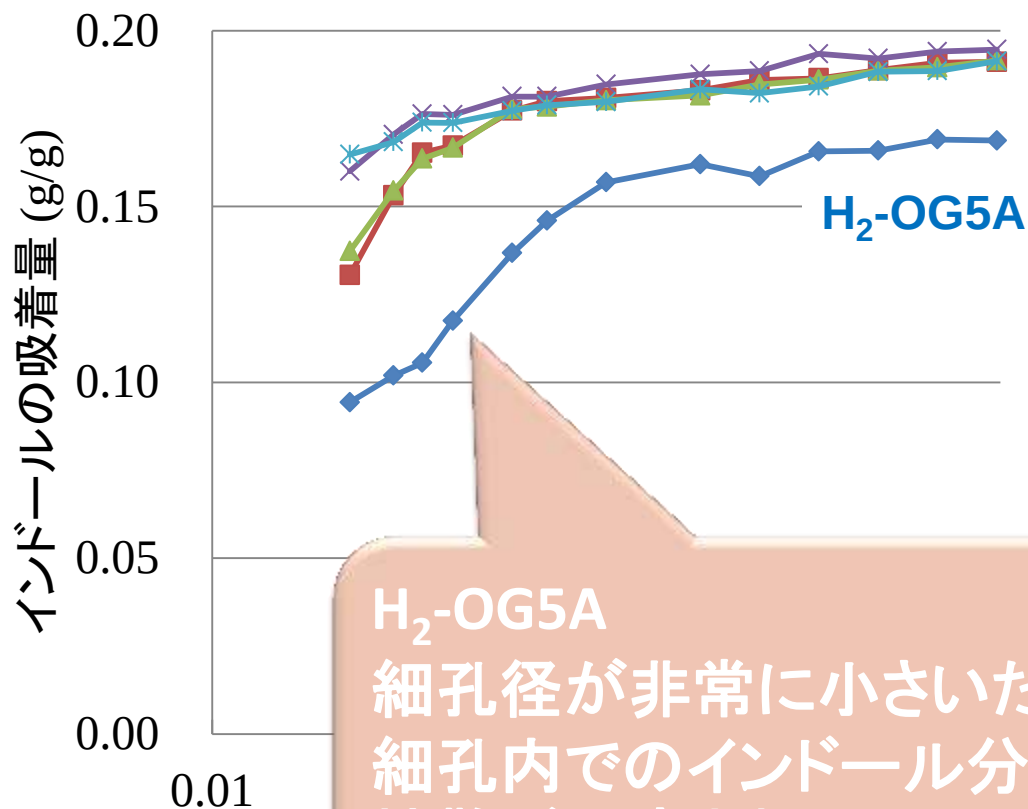
吸着量測定方法

1. インドールとアミラーゼの水溶液を製作
2. インドール及びアミラーゼ水溶液(40 ml)に活性炭素材料(8 mg)を分散
3. 25°Cで指定時間攪拌(3 min~96 h)
4. 活性炭素材料をフィルター(0.20 μ m)で除去
5. 紫外可視分光器により測定した吸光度から濃度を計算



インドールとアミラーゼの最大吸光波長である269 nmまたは279 nmの値を用いて算出

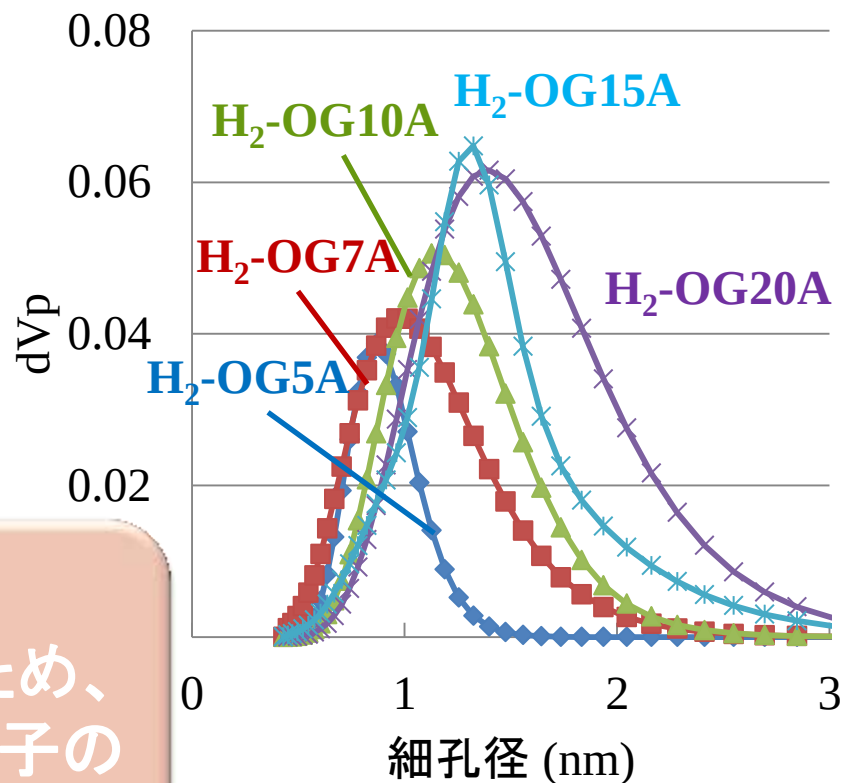
インドール水溶液の初期濃度 0.004%



H₂-OG5A

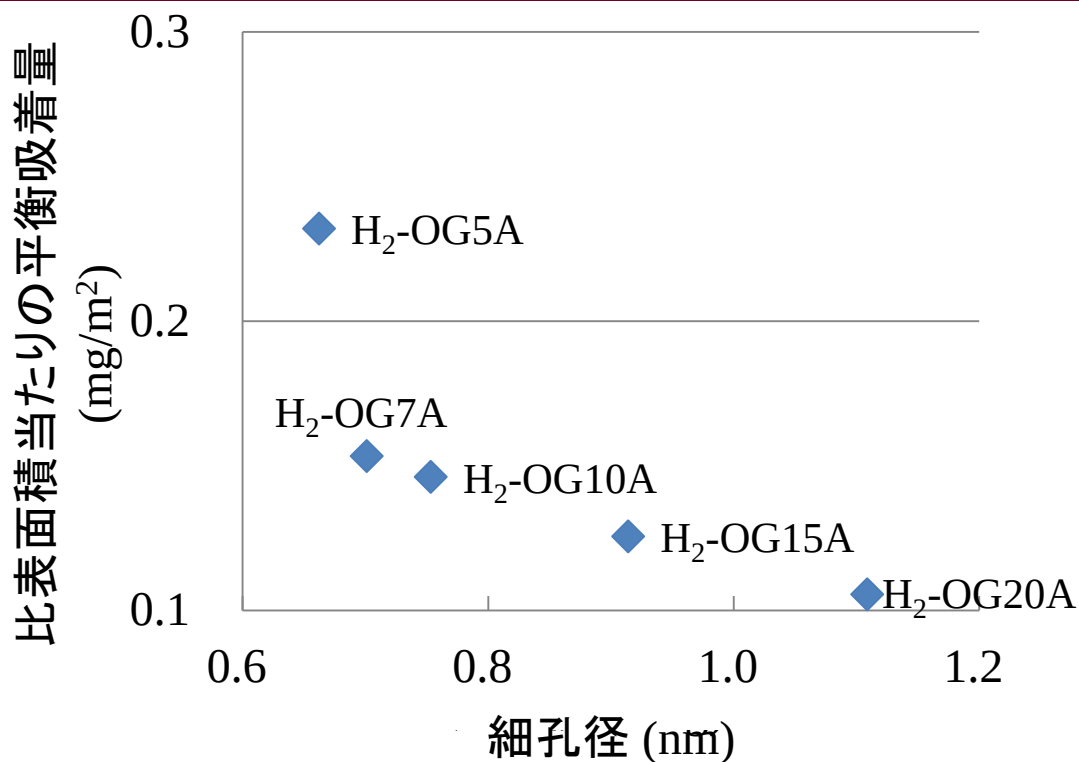
細孔径が非常に小さいため、
細孔内でのインドール分子の
拡散が阻害される。

吸着速度プロット

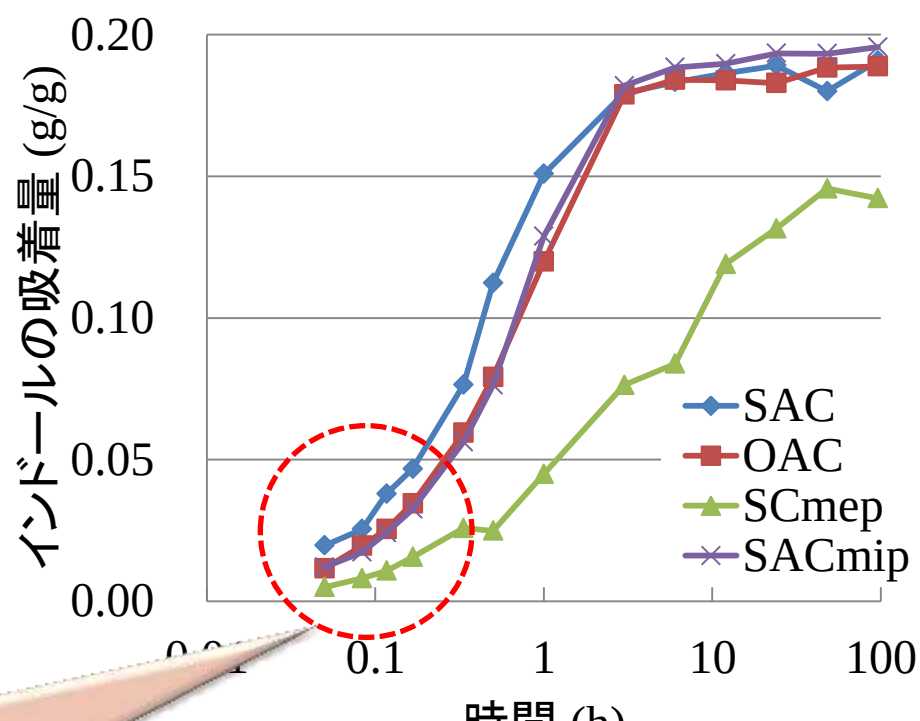
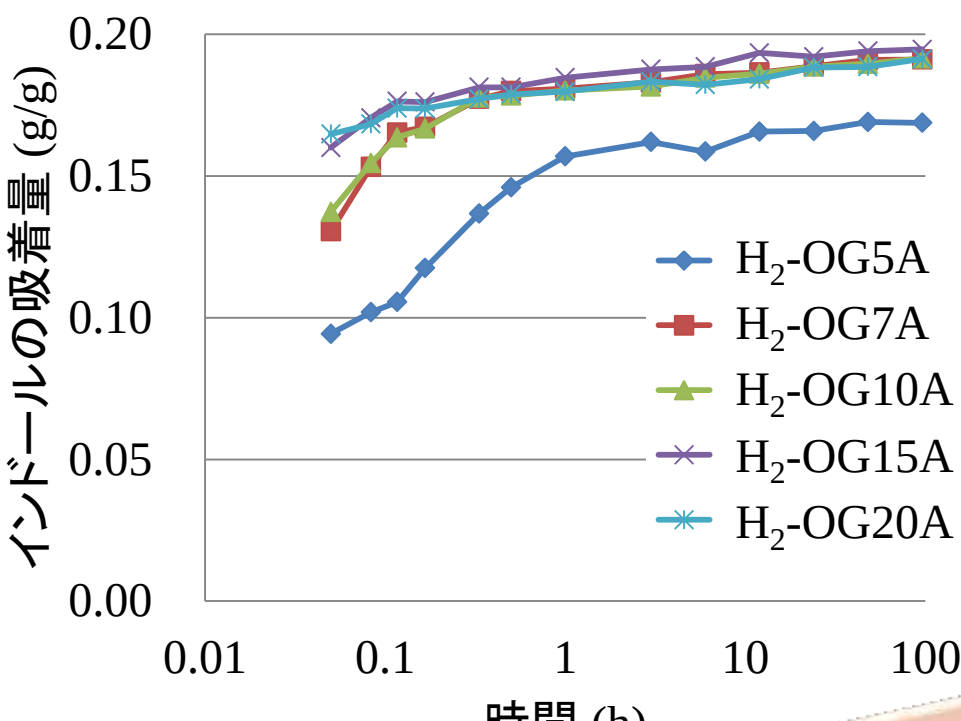


H₂-OGシリーズの細孔径分布

	OG5A	OG7A	OG10A	OG15A	OG20A
平均細孔径(nm)	0.65	0.70	0.75	0.91	1.11



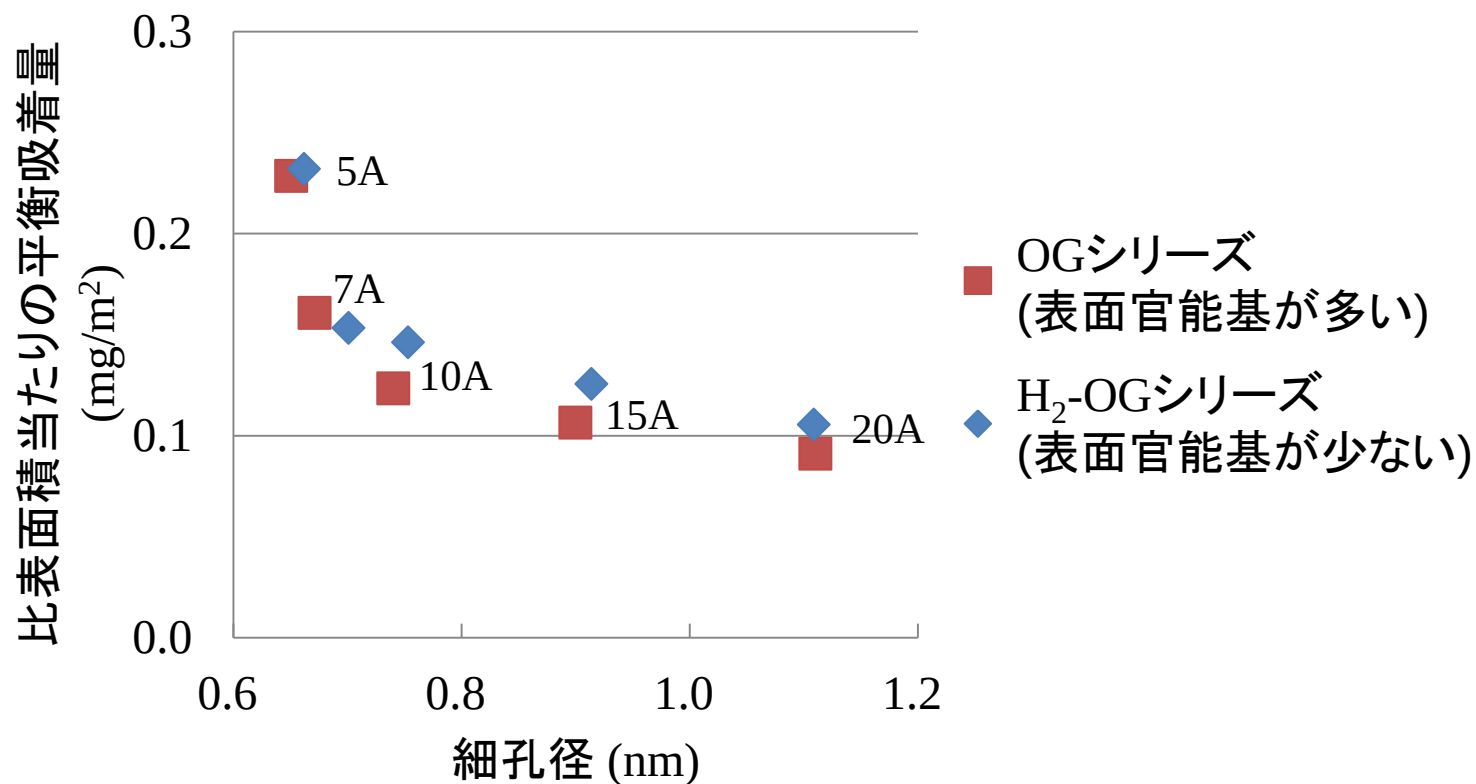
	比表面積 (m ² /g)	細孔径 (nm)	除去率 (%)	比表面積当たりの 平衡吸着量 (mg/m ²)
H ₂ -OG5A	728	0.65	83.4	0.232
H ₂ -OG7A	1247	0.70	94.4	0.153
H ₂ -OG10A	1305	0.75	94.1	0.146
H ₂ -OG15A	1548	0.91	96.0	0.126
H ₂ -OG20A	1802	1.11	93.8	0.108



粒径が大きく、細孔の深さが深い
ため細孔の奥まで溶液が浸透し
インドールが拡散するのに時間がかかる

孔径が大きく、細孔の深さが深いため
 孔の奥まで溶液が浸透しインドールが
 拡散するのに時間がかかる

				表面積当たりの 吸着量 (mg/m ²)
SAC	1254	0.69	90.9	0.253
SACmip	1409	0.74	96.3	0.143
OAC	1585	0.96	90.3	0.113

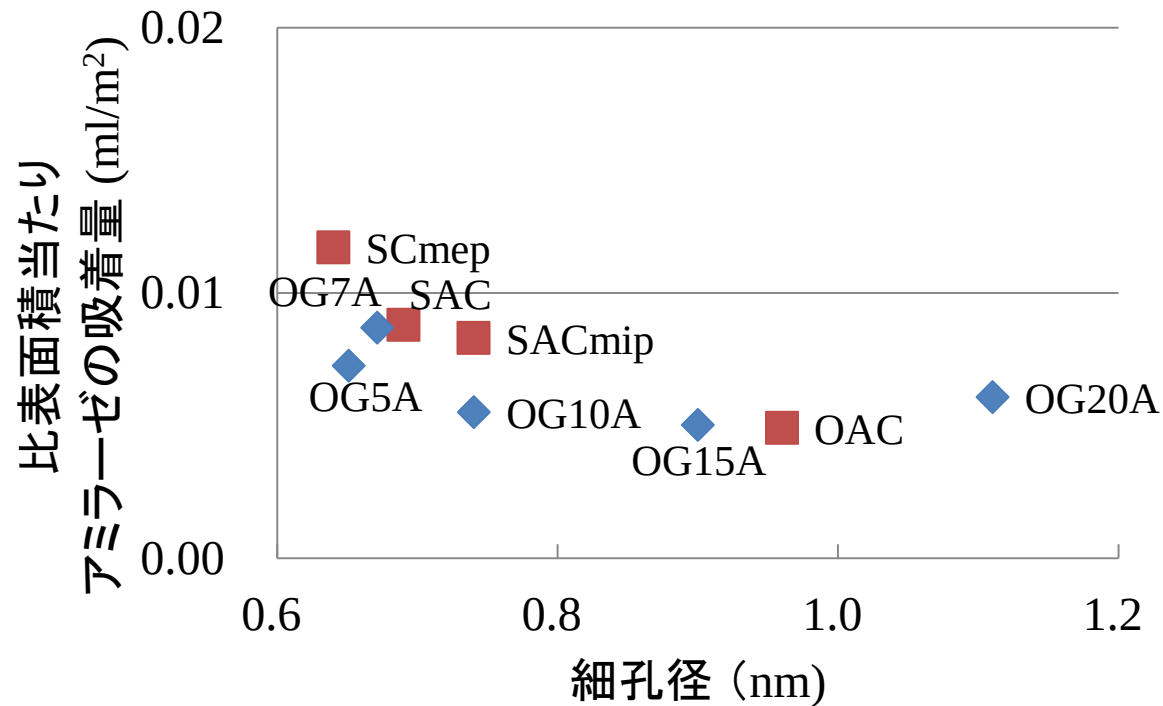


インドールの除去率(%)	5A	7A	10A	15A	20A
表面官能基が少ない場合	83.4	94.4	94.1	96.0	93.8
表面官能基が多い場合	74.3	79.5	79.6	90.3	88.3

インドールの吸着に適した活性炭は...

- 比表面積が大きい
- 細孔が浅い
- 表面官能基が少ない
- 細孔径が小さい

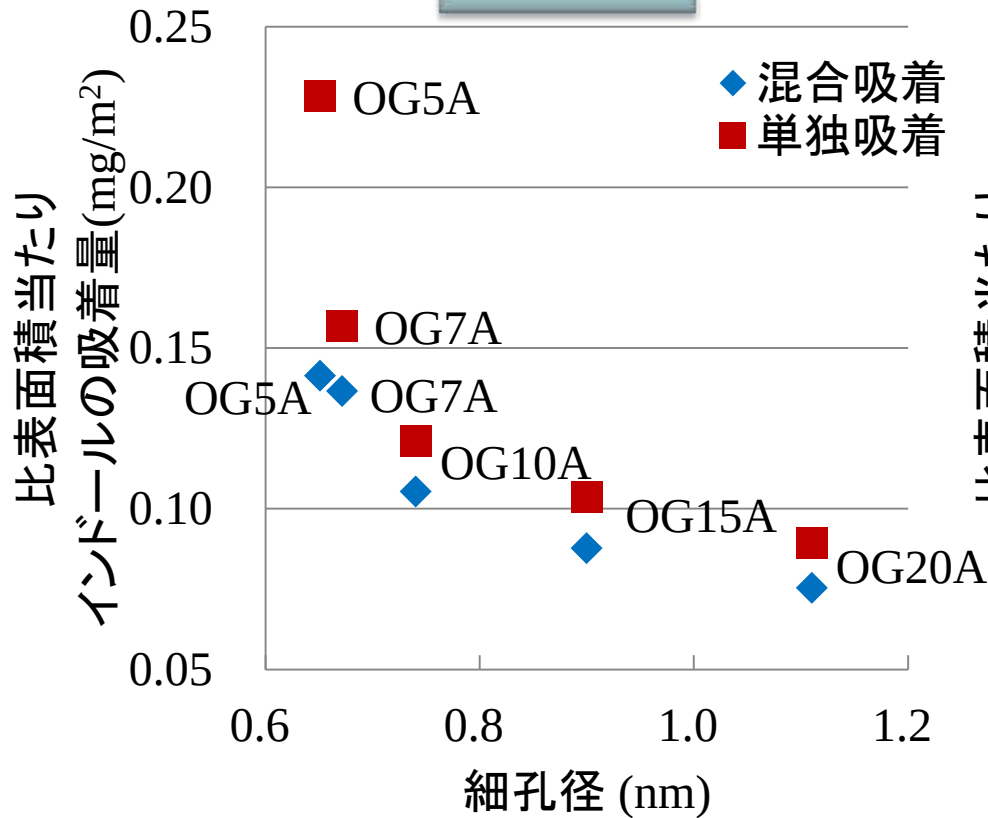
⇒ 細孔径が非常に小さい時はインドール分子の拡散阻害が観察されたため、細孔径は 0.7 nm が適している。



	OG5A	OG7A	OG10A	OG15A	OG20A	SAC	OAC	SCmep	SACmip
除去率(%)	3.9	7.2	5.9	7.1	9.8	8.2	5.8	5.0	9.2

- ・活性炭の違いによる吸着率の差は顕著ではない
- ・アミラーゼは分子量が非常に大きい物質であり、除去率は10%以下とインドールに比べ非常に低い

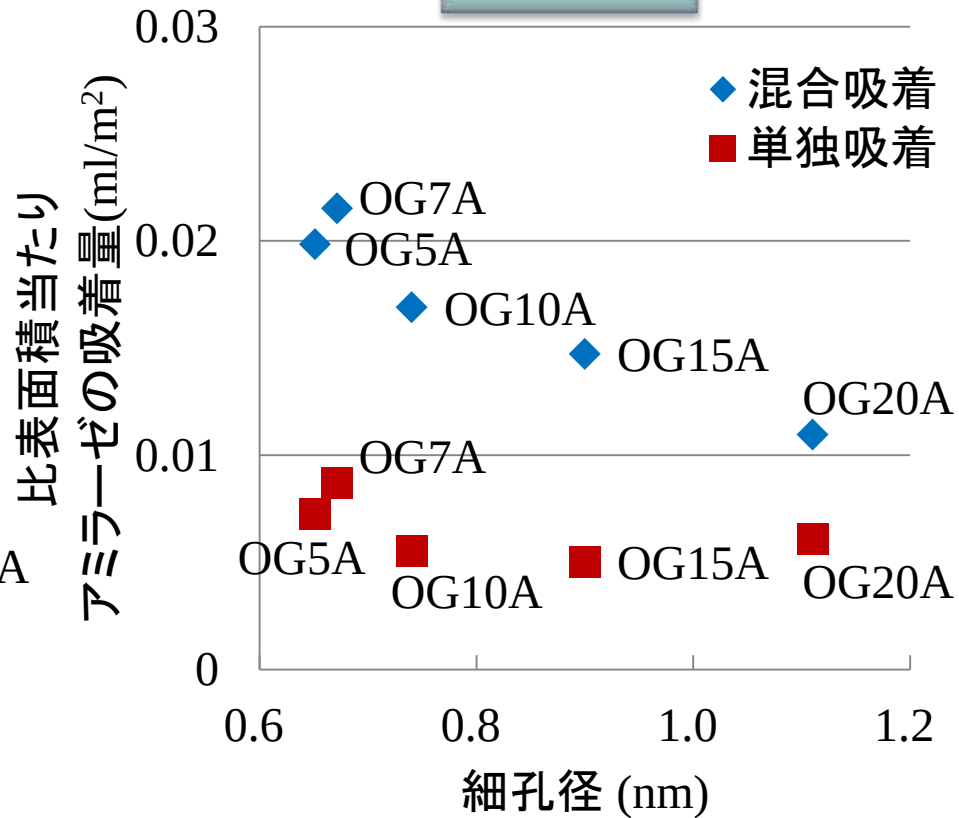
インドール



インドールの除去率の変化

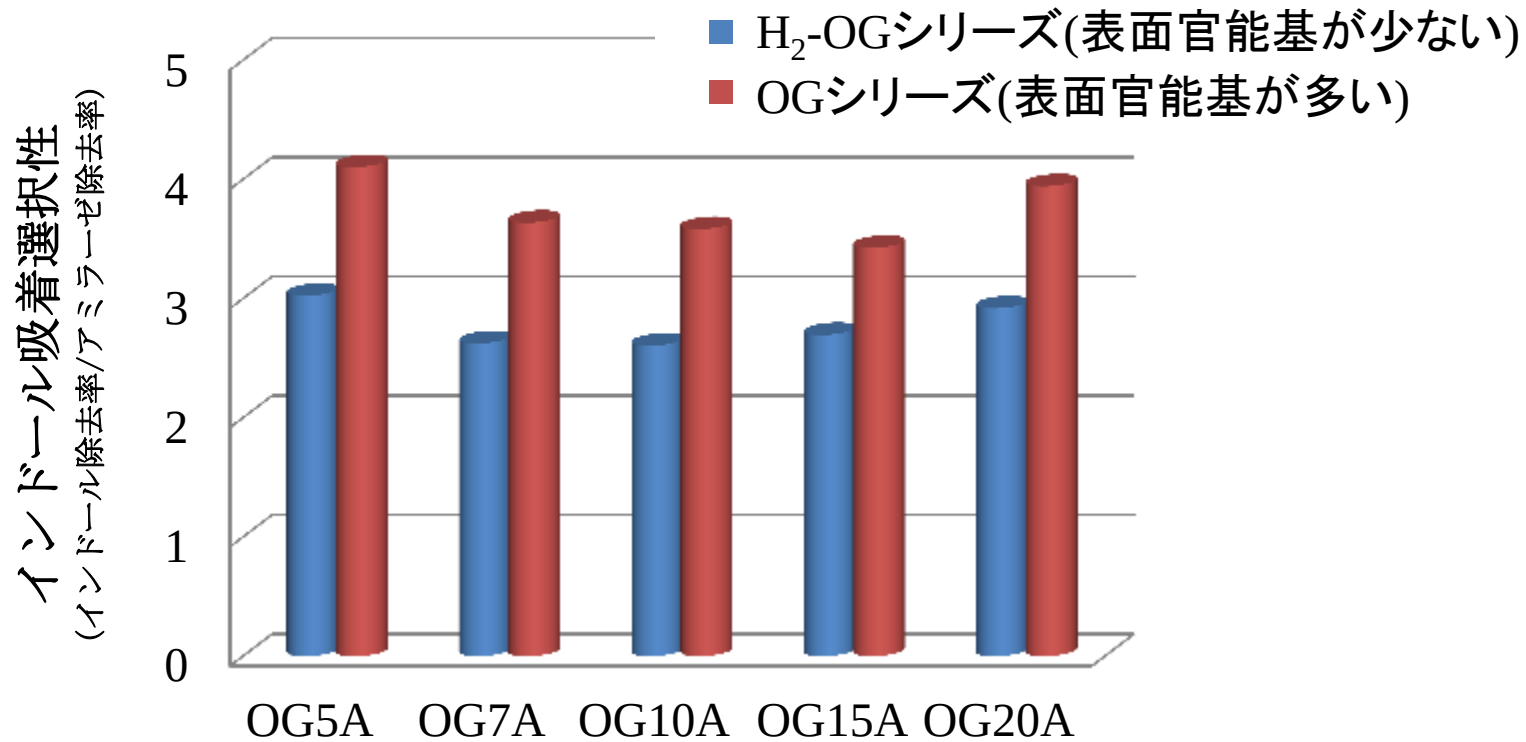
	OG5A	OG7A	OG10A	OG15A	OG20A
単独吸着	74.3	77.5	78.3	88.1	86.7
混合吸着	43.1	63.3	63.8	69.9	68.6

アミラーゼ



アミラーゼの除去率の変化

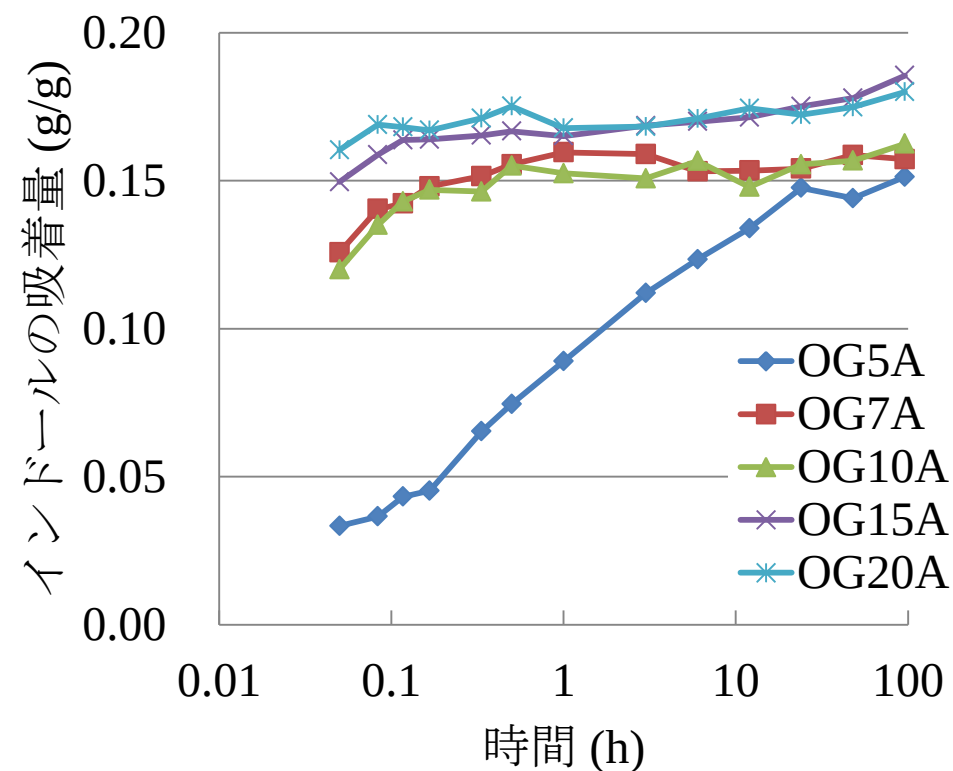
	OG5A	OG7A	OG10A	OG15A	OG20A
単独吸着	3.9	7.2	5.9	7.1	9.8
混合吸着	10.5	17.4	17.8	20.4	17.4



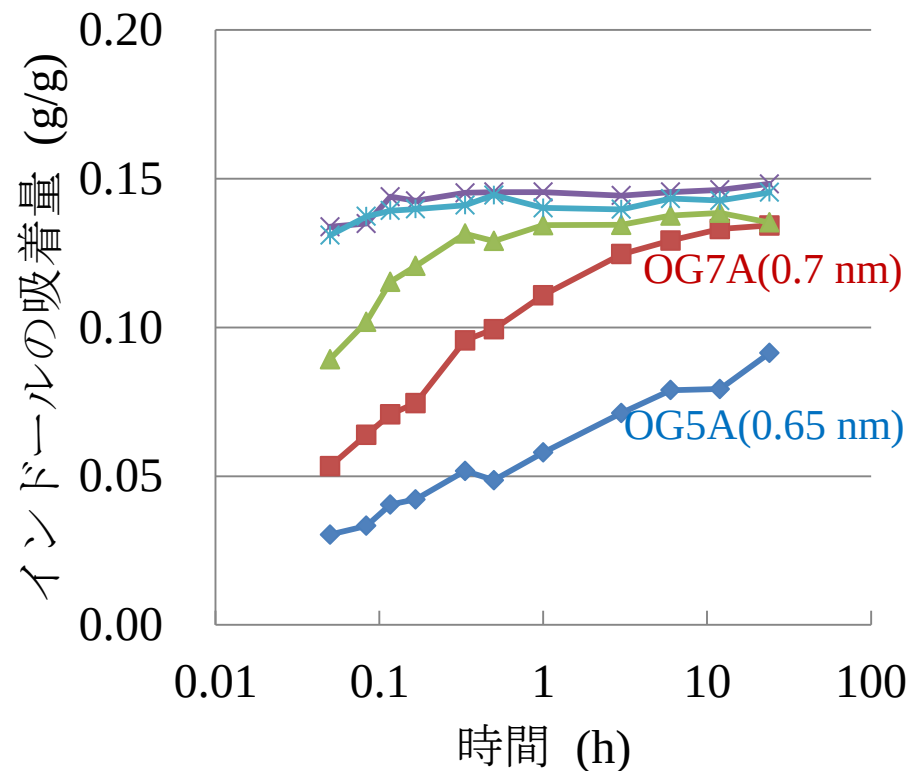
インドールの除去率(%)	OG5A	OG7A	OG10A	OG15A	OG20A
表面官能基が少ない場合	49.9	70.1	69.3	70.9	72.1
表面官能基が多い場合	43.1	63.3	63.8	69.9	68.6

アミラーゼの除去率(%)	OG5A	OG7A	OG10A	OG15A	OG20A
表面官能基が少ない場合	16.5	26.7	26.6	26.3	24.7
表面官能基が多い場合	10.5	17.4	17.8	20.4	17.4

単独吸着



混合吸着



混合吸着の時は細孔径0.7 nmのOG7Aでも拡散障害が観察される。

⇒ 0.75 nm以上のミクロ孔が適している。

1. インドールの吸着

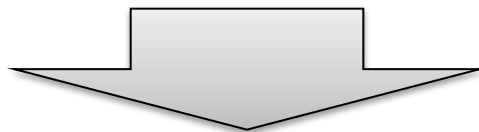
比表面積が大きく、細孔が浅く、表面官能基が少なく、かつ細孔径約0.7 nmのミクロ孔がインドールの除去に適している。

2. アミラーゼの吸着

活性炭の違いによる吸着率の差は顕著ではない。

3. アミラーゼ共存時のインドールの選択的吸着

表面官能基が多くて、細孔径0.75 nmのミクロ孔に適している。



選択的かつ高い吸着能を持つ経口用活性炭薬では...

比表面積が大きく、細孔が浅く、表面官能基が多く、かつ0.75 nmのミクロ孔を持つ活性炭が望ましい。

4. Capacitive De-ionization (CDI)

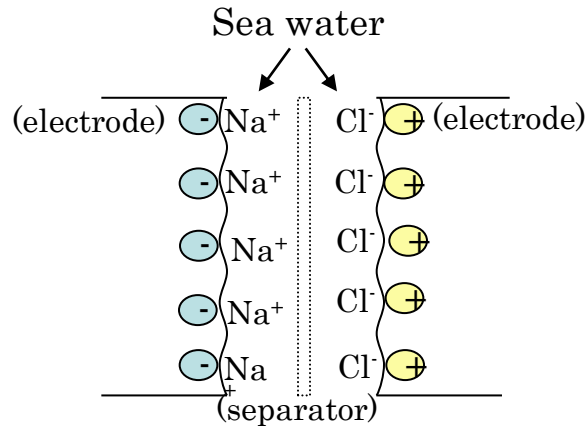


	RO (Reverse Osmosis)	ED (Electro Dialysis)	Electric Desalt
Merit	●High performance	●Selective removal of ion	●Low energy consumption ●Low fee of maintenance
De- merit	●Fouling phenomenon ●High operation cost ●Low collection ratio from non-treated water ●High cost for maintenance ●Environmental contamination	●High cost membrane ●High cost for maintenance	●Low removing performance of ion

Objective

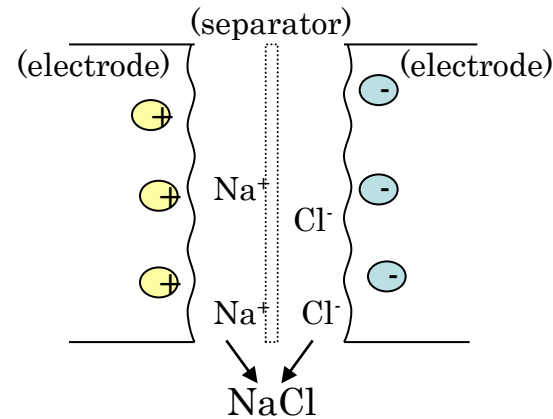
- Development of cost effective, long time maintenance free ion-removing system using EDLC principle
- Development of high performance activated carbon based thin electrode for electro-desalt system
- Investigation on the selective ion removal by structure of electrode and activated carbon

- Electric-desalt system.



Distilled water

CHARGE



Concentrated water

DISCHARGE

- Thinner electrode

- Rapid electrochemical adsorption and desorption .
- Activated carbon of large surface area and small particle size

電極の調製

Mixing of material
(Maxsorb II+ Graphite + Binder)



Make Sheets using hot press roller



Drying (200°C, 3hrs)



Rolling of sheets to control
thickness



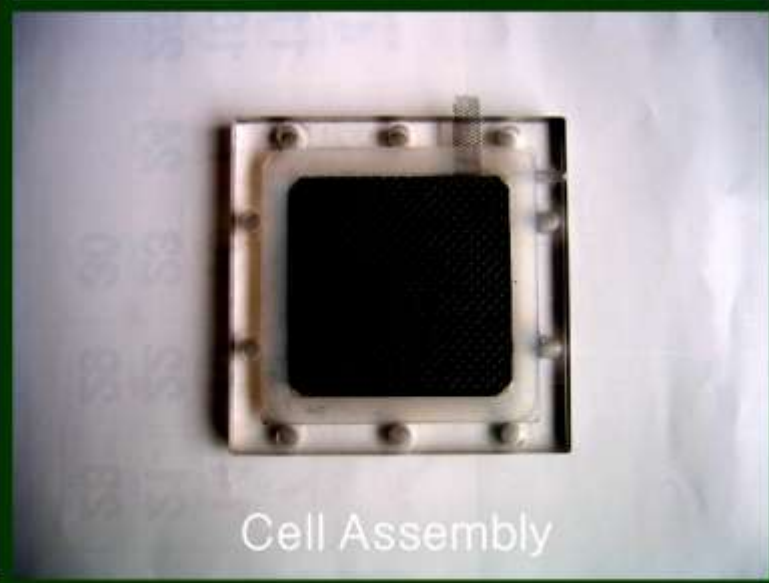
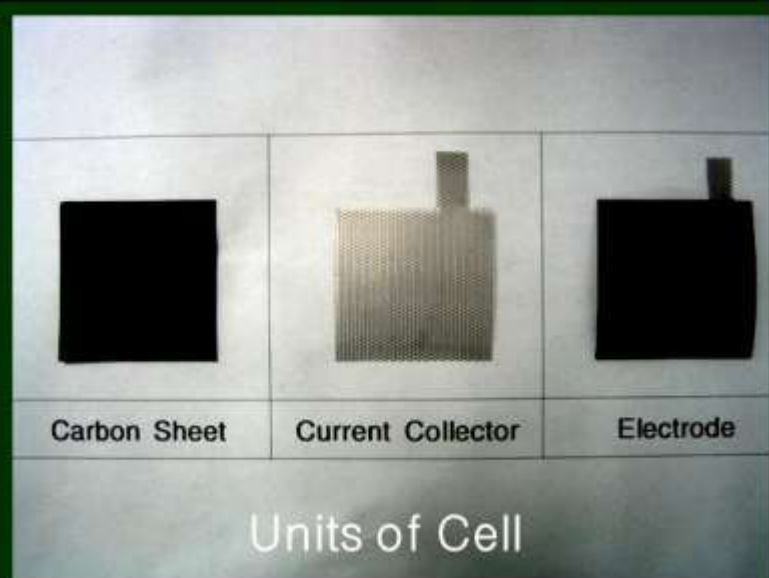
Sizing for Electrode with
current collector



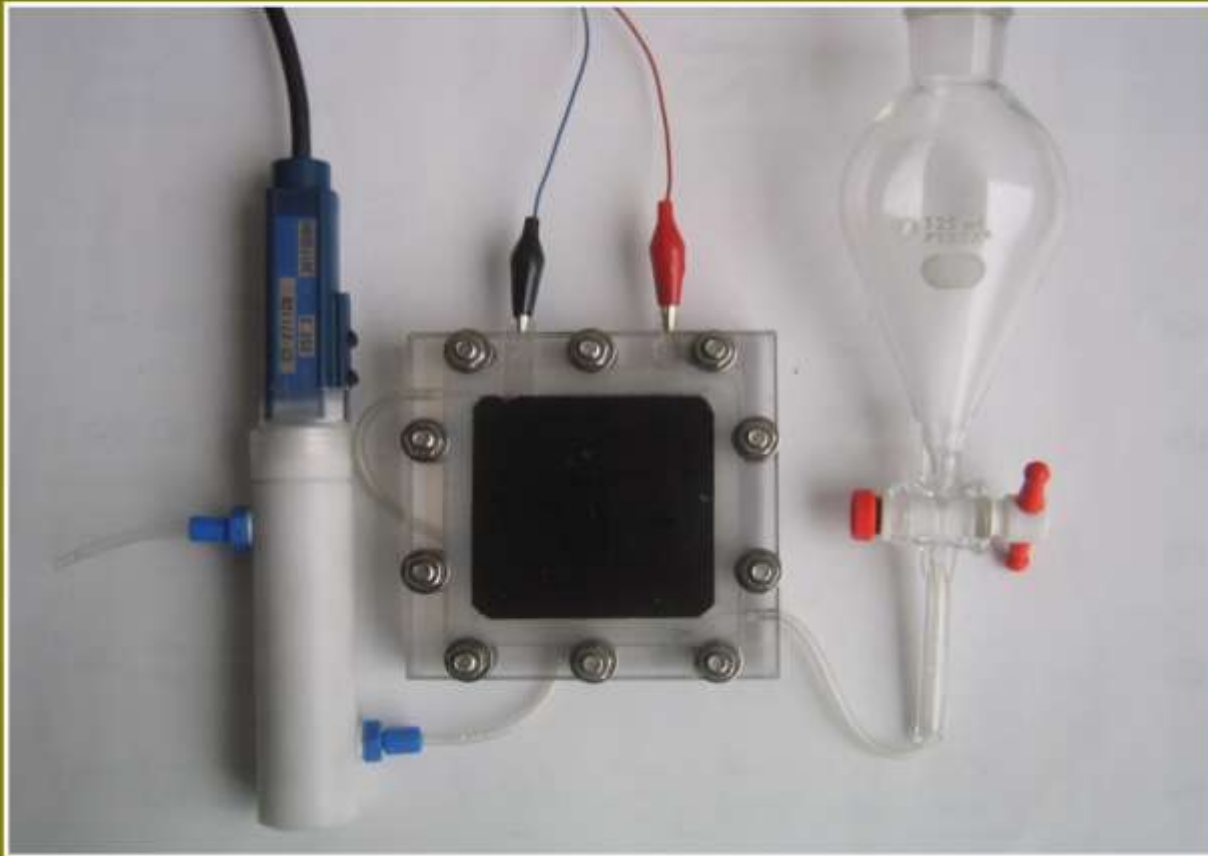
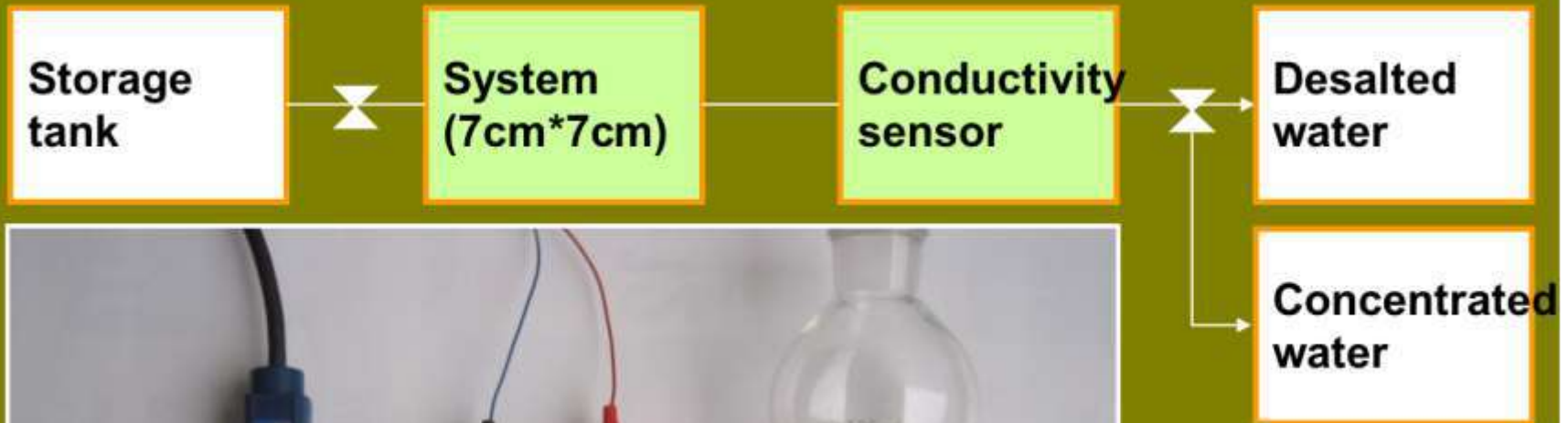
Manufacturing of Cell



Performance Evaluation

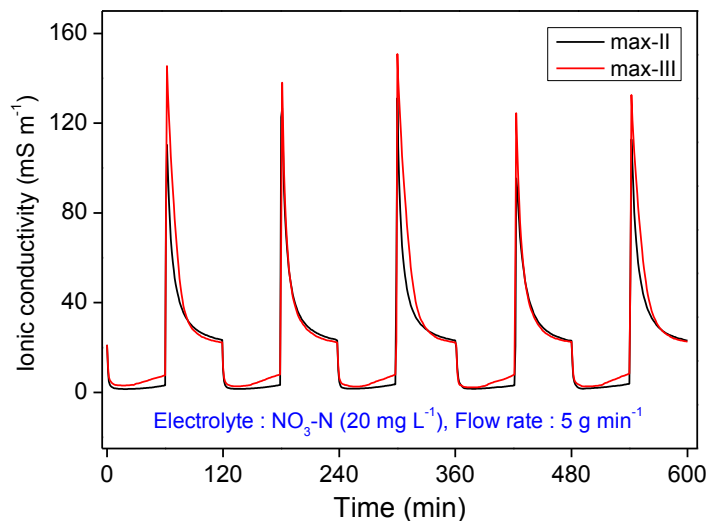


実験セッティング

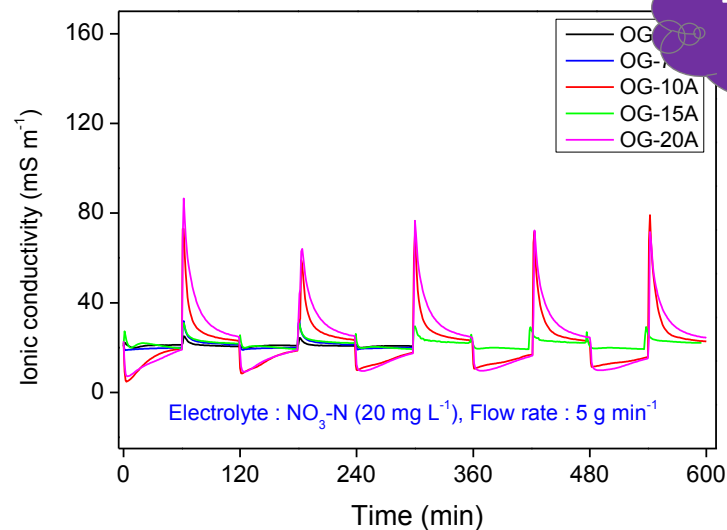


硝酸性窒素イオンの脱塩特性

Maxsorb series

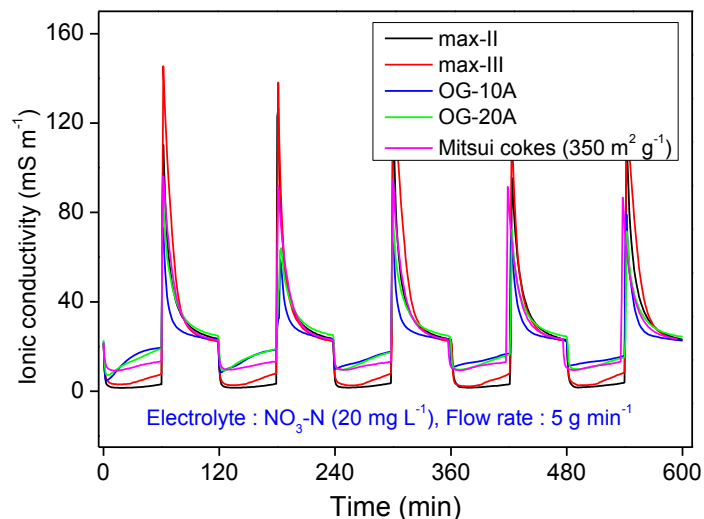


OG series



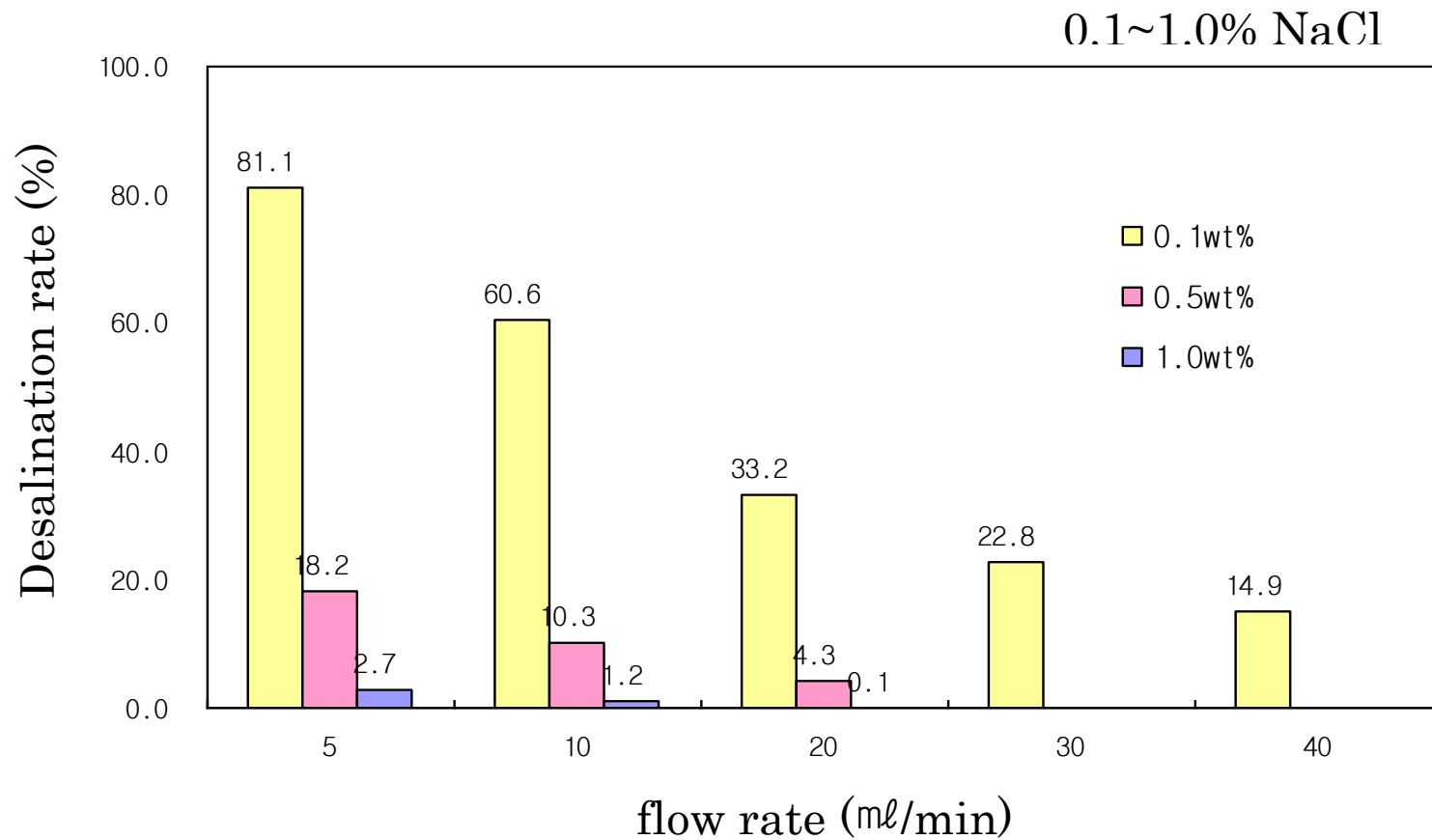
1.0Vまで

Total

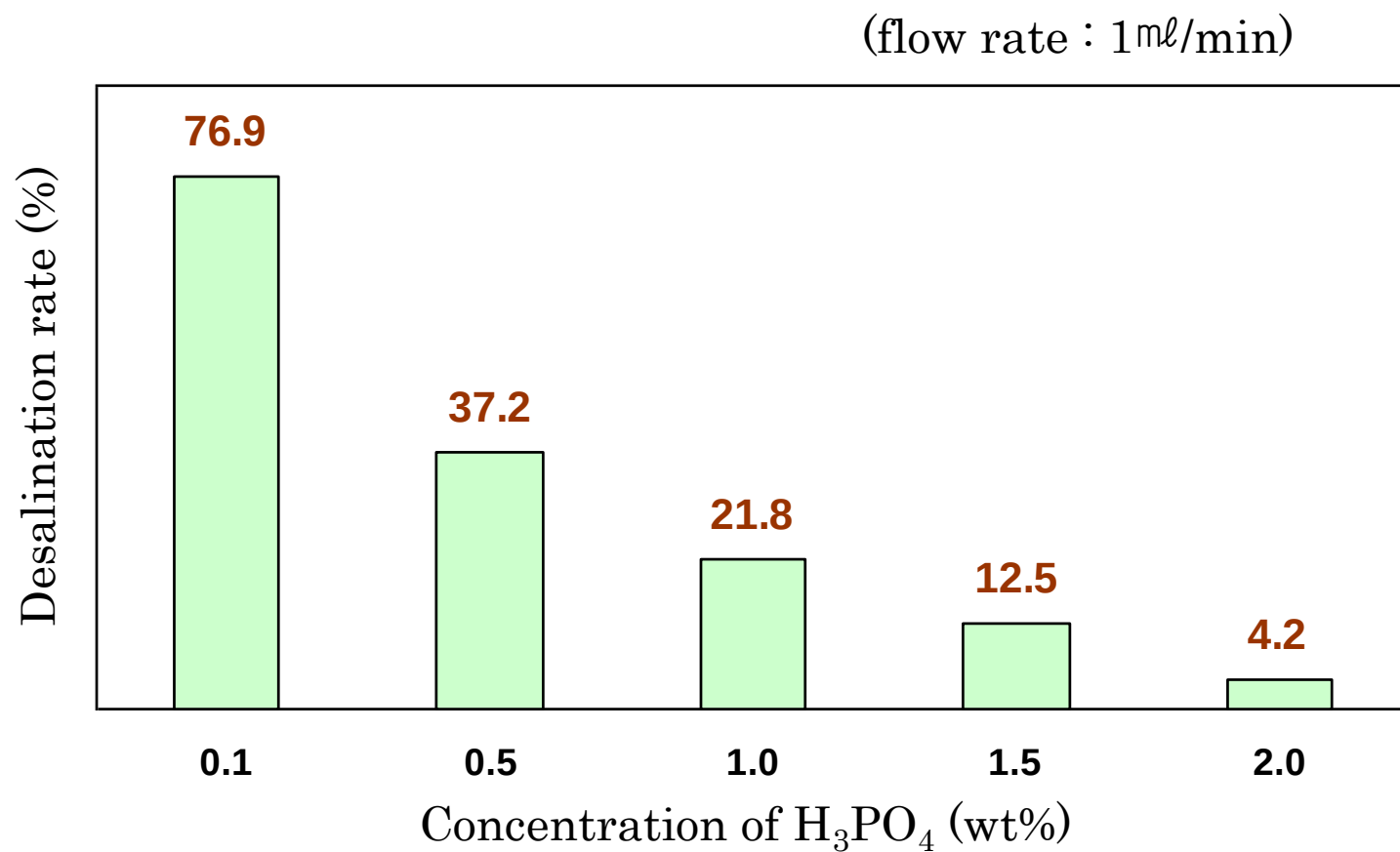


- 硝酸性窒素イオンにおける脱塩特性は
Max-IIIが最大特性を示した。
- 三井鉱産のコークスがOGシリーズより良かった。
- **Maxsorb > Mitsui cokes > OG series**

Effect of flow rate

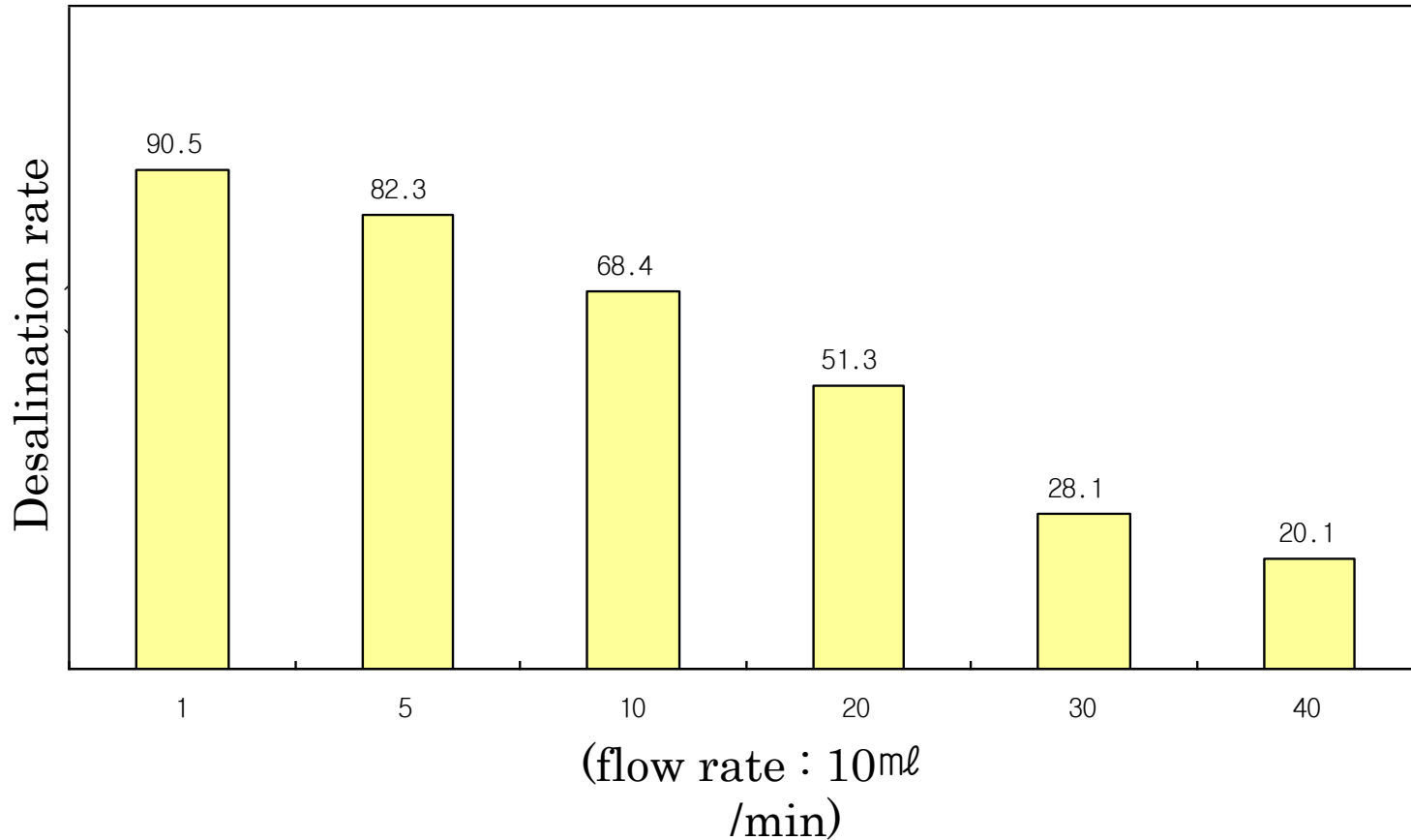


Effect of concentration



Cl⁻ ions in the city water

Effect of flow rate



CDIに適した活性炭は？

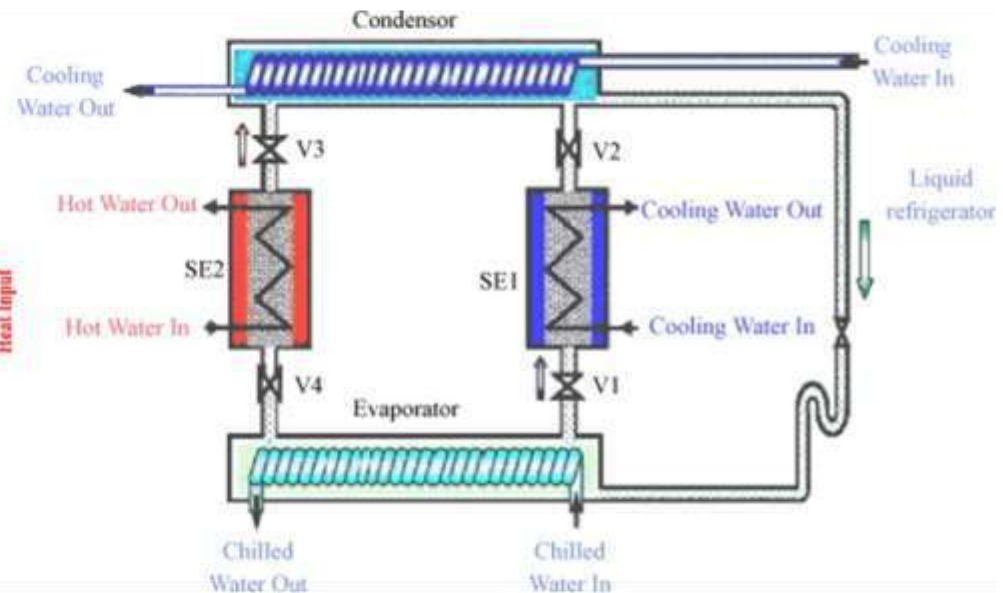
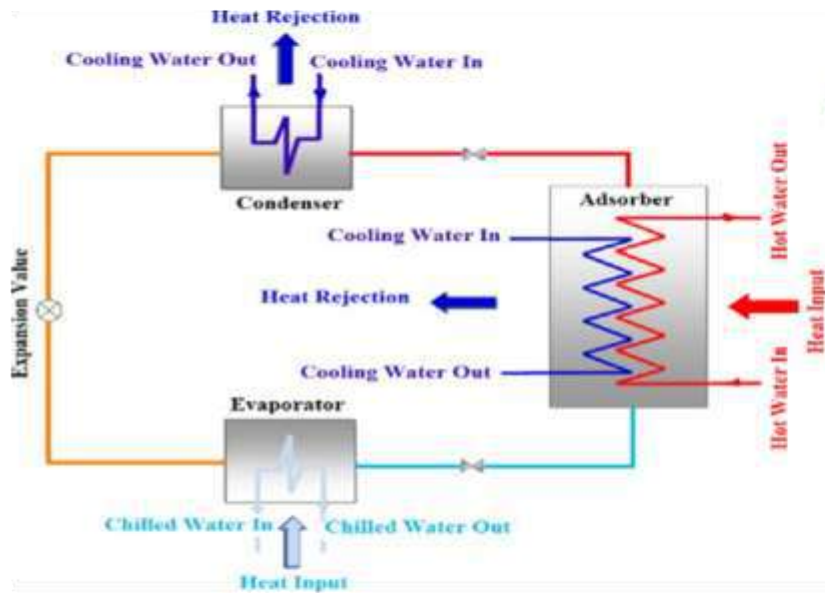
1. 高電気伝導度？
2. 高細孔内拡散性

How to solve?

5. Heat Pump（省エネルギー応用）

Thermal Powered Cooling System

ACF based adsorption system may lead to the use of unexploited low-temperature solar /waste heat that may offer an attractive possibility for improving energy conservation and efficiency.



The schematic diagram of the two-bed AC-ethanol adsorption cycle (Mode A).

Saha et al. Renewable and Sustainable Energy Reviews 15 (2011) 1708–1721

Cooling systemに適した活性炭は?

1. 大量吸着性 (Methanol, ethanol)
2. 高吸脱着レート (High efficiency)
3. 高熱伝導度?

How to solve?

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