

第7講義
2012, Dec. 18

エネルギー・環境を支える 新規機能性活性炭

(Novel Functional Activated Carbons for the Applications to
Energy and Environmental Devices)

尹 聖昊

九州大学 先導物質化学研究所

yoony@cm.kyushu-u.ac.jp

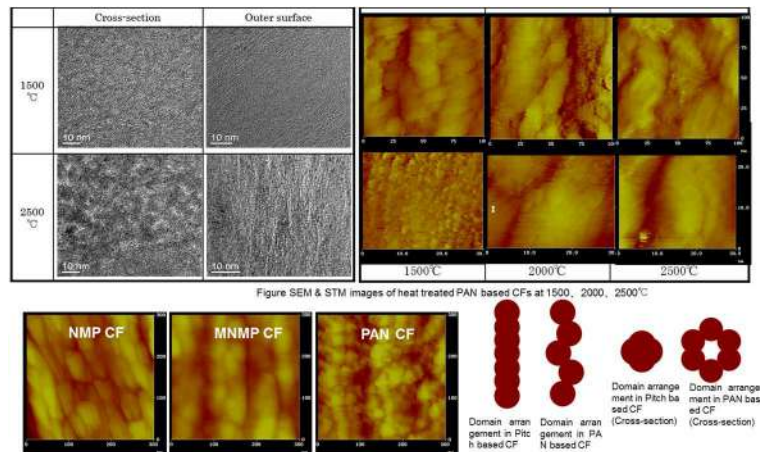
Contents:

1. 活性炭の構造、細孔分析及び応用
2. 繊維状ナノ炭素の調製、構造及び応用

活性炭を用いた水の浄化

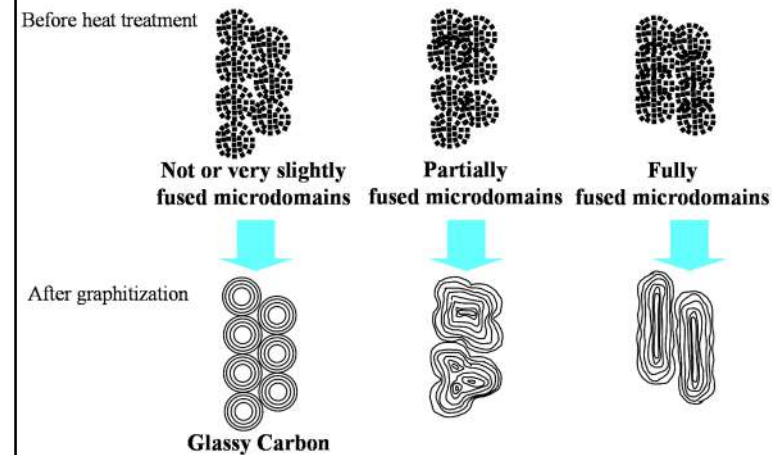


Structure of PAN based carbon fiber



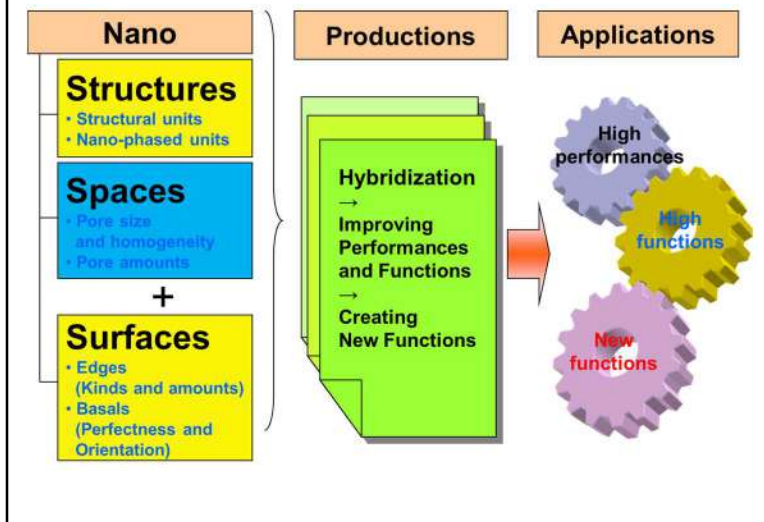
"Structural comparison of mesophase and PAN based carbon fibers"
S.H. Hong, S.H. Yoon, I. Mochida Carbon 2006, 32(10), 1171-1178

Control of structural units



IAMS, Kyushu University "Axial nano-scale microstructure in the graphitized fiber inherited from liquid crystal mesophase pitch"
Carbon, 34, 83-88 (1996) S. H. Yoon, Y. Korai, K.Yokogawa, S. Fukuyama, M. Yoshimura, I. Mochida

Carbon materials from the structural points



Best carbon?

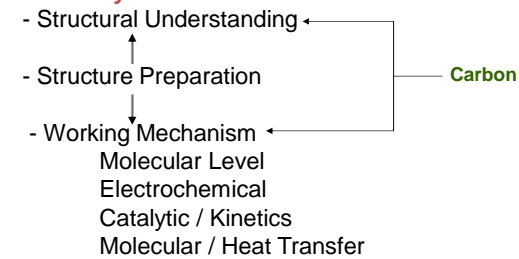
Carbon is an Indispensable Material for Energy related Devices

Best Structure for Best Performance

↕
Best Selection

Best Selection

Scientific Cycle



How to prepare the activated carbons

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

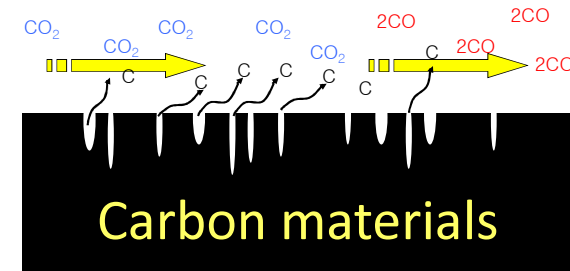
Activation Procedures

- 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

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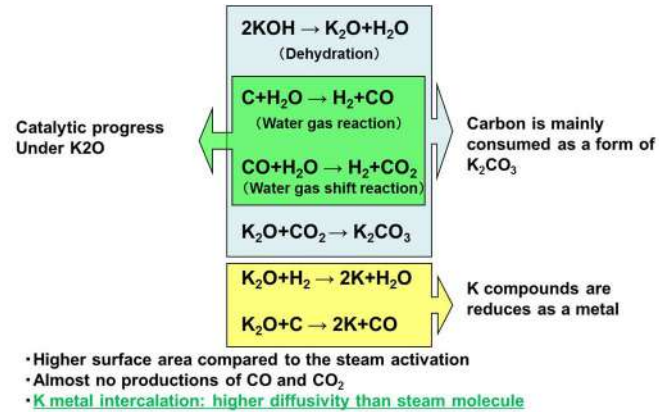
Activation



Activation reagents

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

Chemical activation



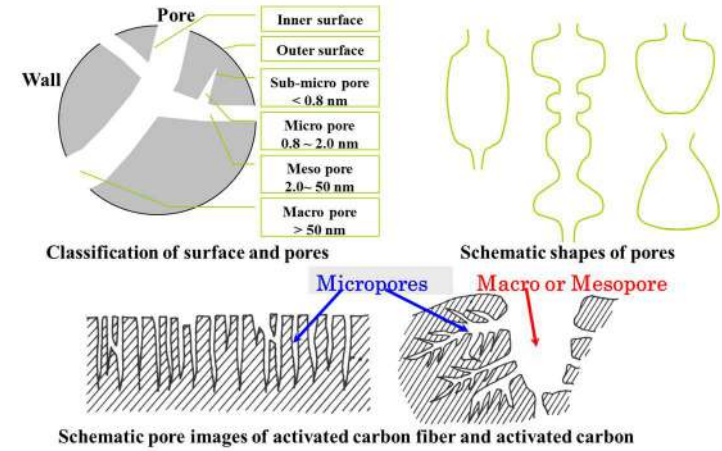
KOH
MP: 380°C
BP: 1324°C

K₂O
MP: 490°C (350°C, KO and K)

K₂CO₃
MP: 891°C

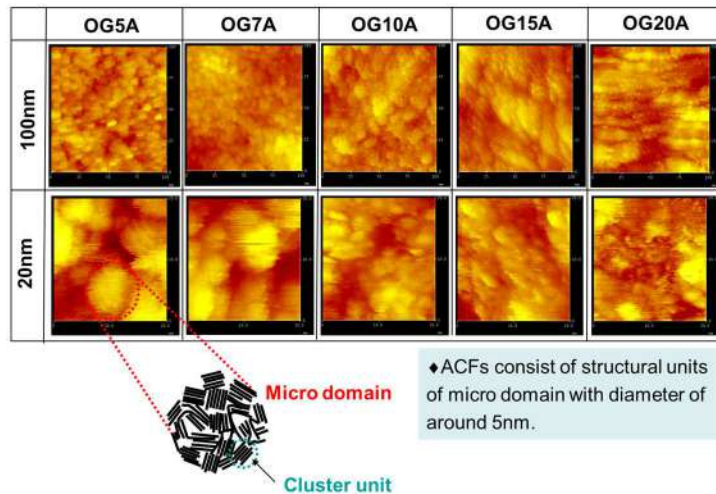
K
MP: 64°C
BP: 774°C

Conventional concept of activated carbons

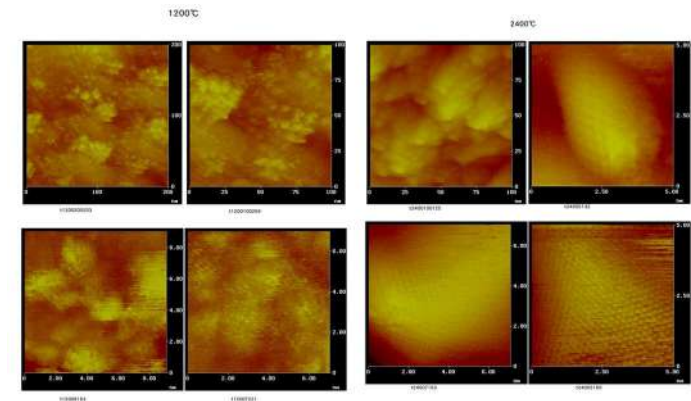


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STM images of ACFs



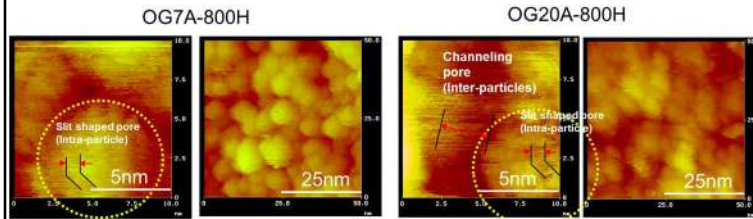
Structure of glassy carbon



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Pore nucleation in activated carbon

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 ($H_2/He = 1/4$).



- ▲ 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.

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Novel concept of activated carbon

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

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Novel concept of activation

Precursor of ACF has been composed of nano-structural primary units

Structural factor should be understanding of activated

the better heir applications.

Size and arrangement of BSU
Etching and diffusion of oxidative agent against BSU

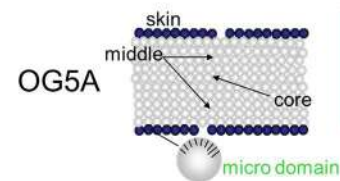
Pores from intraparticles (Slit shaped? Micropores less than 2 nm)

Pores from interparticles (Channeled shaped having wider pore size distributions (0.2 ~ 50 nm))

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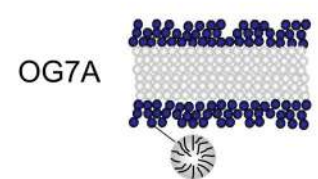
Novel understanding of activation mechanism

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.

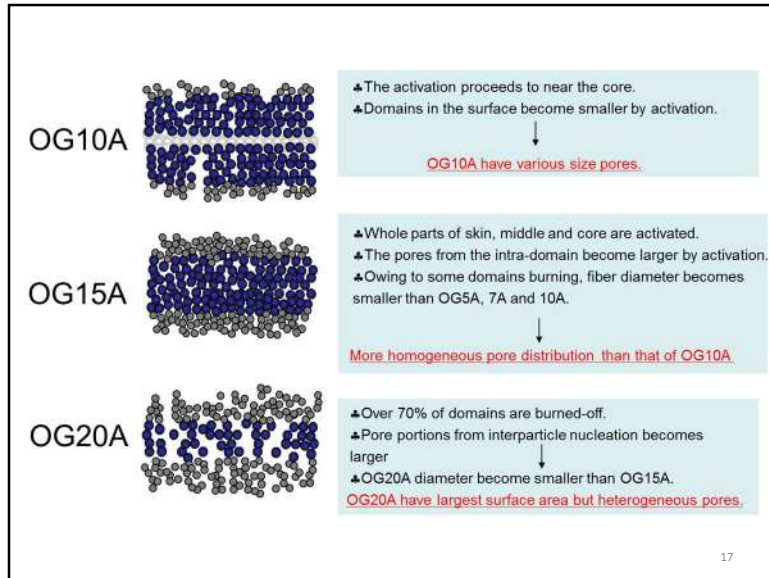
OG5A has smallest surface area but homogeneous pores.



- ▲ 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.

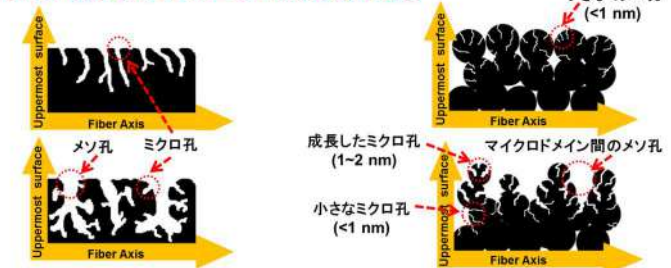
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Novel recognition of the structure of ACs

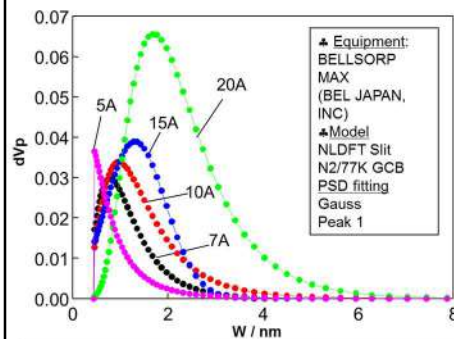
多孔性炭素材料: 乾燥・精製・分離・貯蔵などに利用

効果的な性能向上のために
詳しい細孔発達メカニズムの解明が必要



N.Shiratori, et al., *Langmuir* 2009, 25(13), 7631-7637. 1

Pore size distribution (NLDFT)



▲Advantage of DFT method

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

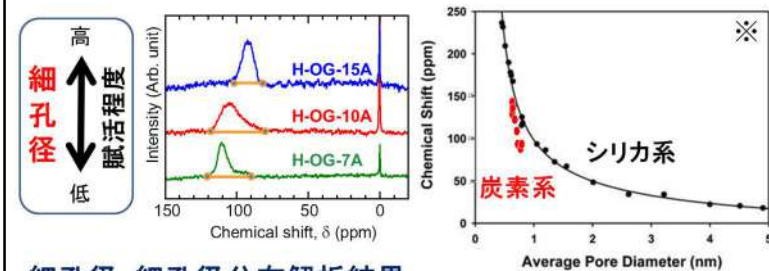
▲Disadvantage

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.

Pore size distribution (Xe-NMR)

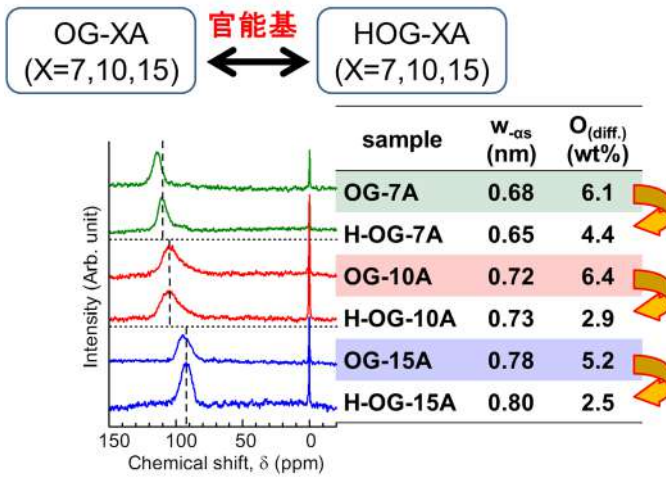


細孔径・細孔径分布解析結果

sample	¹²⁹ Xe-NMR		N ₂ adsorption		
	Avg.	range	α_s	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

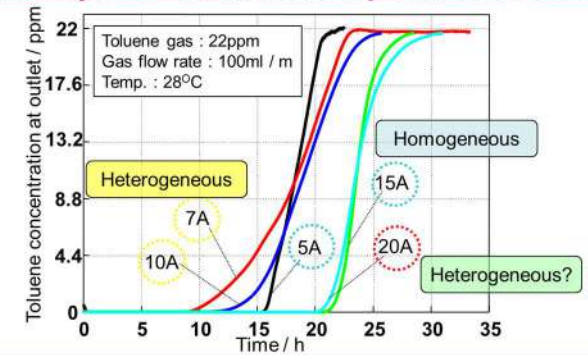
※N.Shiratori, et al., *Langmuir* 2009, 25(13), 7631-7637.

Effect of functional groups (Xe-NMR)



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Adsorption of toluene by various ACFs

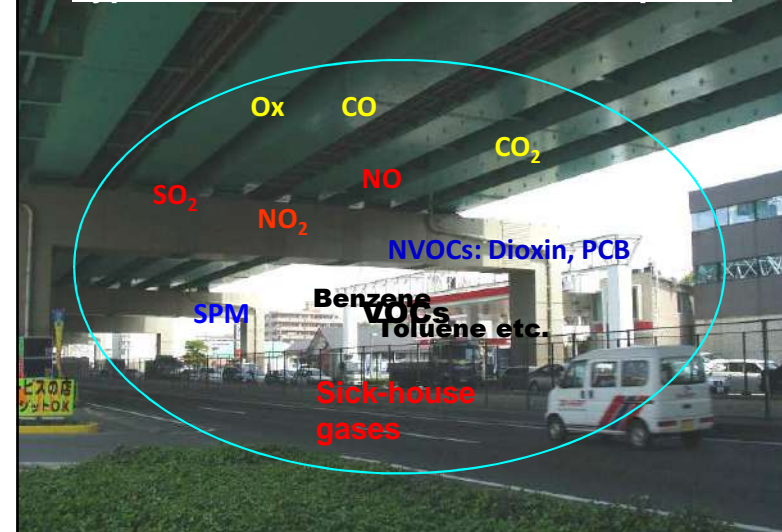


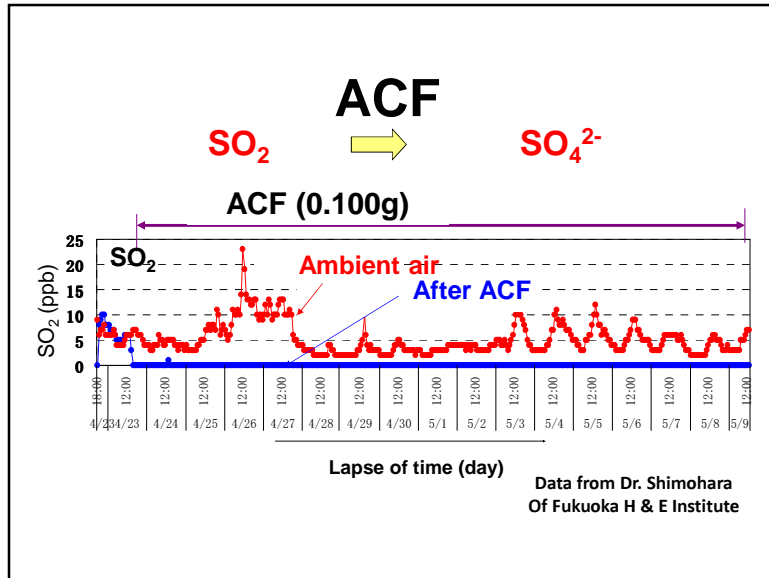
- ♦ The slopes of breakthrough curves for 5A and 15A were steeper than those of curves for 7A and 10A.
- ♦ ACFs with homogeneous pores (5A and 15A) showed rapid toluene adsorption and larger capacity per unit area and longer breakthrough time, whereas ACFs with heterogeneous pores (7A and 10A) showed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

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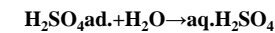
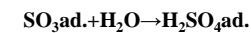
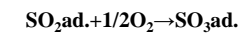
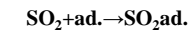
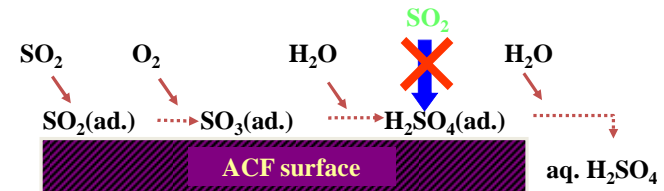
Removal of SO_x and NO_x Using ACFs

Typical Hazard Gases in the Atmosphere





DeSOx mechanism using ACF



Active Sites on Carbon Surface

Oxygen functional group Acidic nature: Oxidative
Basic nature: Reductive

Free valence

Benzyne bonds on edge Oxygen activation

Hetero-atoms in edge Zigzag or Armchair

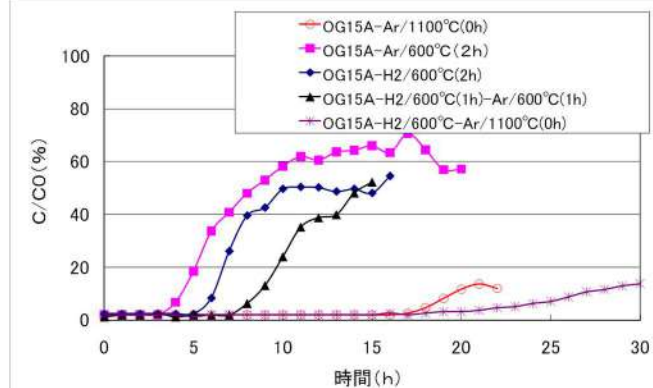
Hexagon stacking height

Hydrophilic/Hydrophobic
Small surface energy

How to control ?

Breakthrough of SO_2 Removal

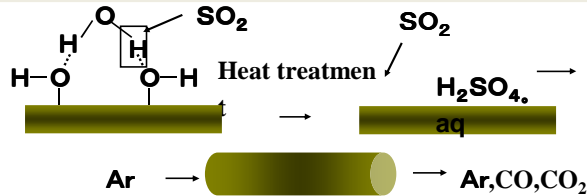
Optimum Post-Heat treatment with Reductive Oxygen Removal



SO_2 1000ppm, O_2 5vol.%, H_2O 10vol.%, N_2 balance, Flow rate: 100ml/min, Temperature: 50°C

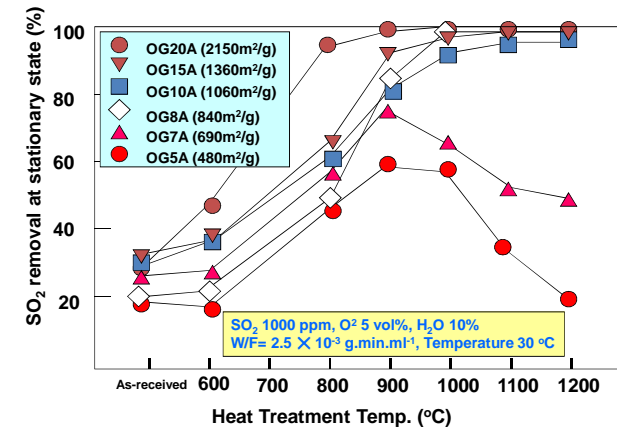
Effect of Heat Treatment

Removal of Functional Groups
with Least Changes of Carbon Structure
Surface Area and Hexagon Stacking



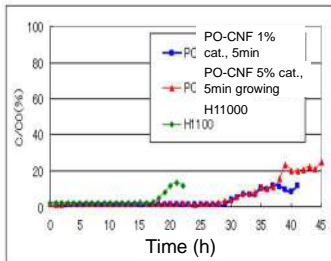
Carbon	C	H	N	O	Ash (%)
	(wt.%, dry)				
OG-15A	93.5	0.6	0.5	5.5	0.0
OG15A-H1100(0min)	97.0	0.4	0.5	2.2	0.0
OG-15A-H1100(1h)	96.8	0.2	0.3	2.7	0.1

The Effect of Heat Treatment for SO₂ Removal



DeSOx by ACF and CNF-ACF Composite

DeSOx Properties of ACF and ACF-CNF

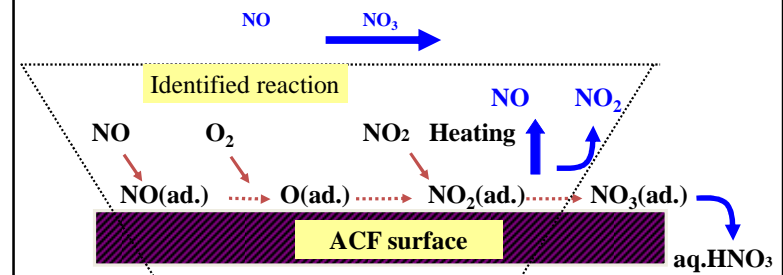


DeSOx condition: SO₂ 1000ppm, O₂ 5vol%,
H₂O 10vol%,
N₂ balance, Total flow rate: 100 ml/min
Reaction Temperature: 50 °C



PDU for SOx Removal by ACF

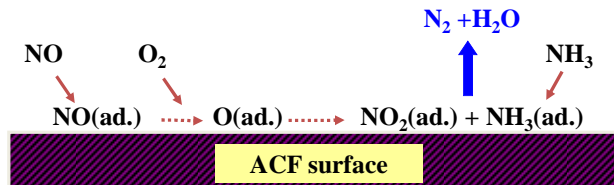
NO & NO₂ Oxidation over ACF



Strong Inhibition of H₂O

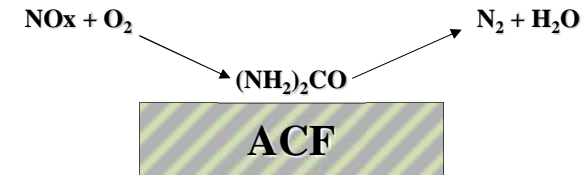
The oxidation of NO₂ always produces NO And NO₃ through the disproportionation.

The Mechanism of NO Reductive Removal



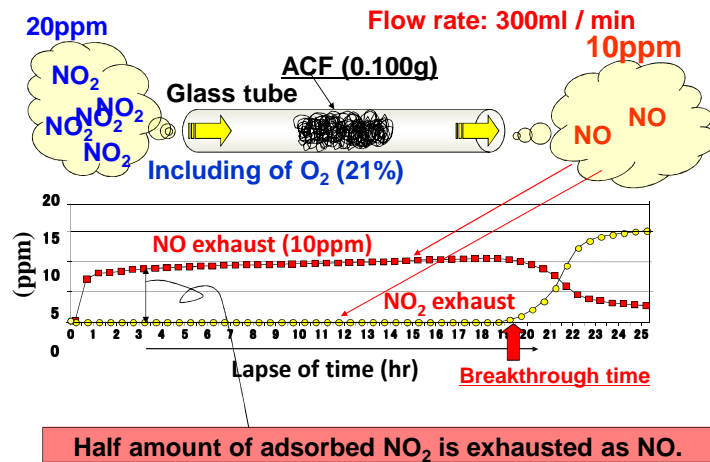
The mechanism of NO removal consists of adsorption and oxidation of NO into NO₂ which is reduced with NH₃

NOx Reduction at Room Temperature

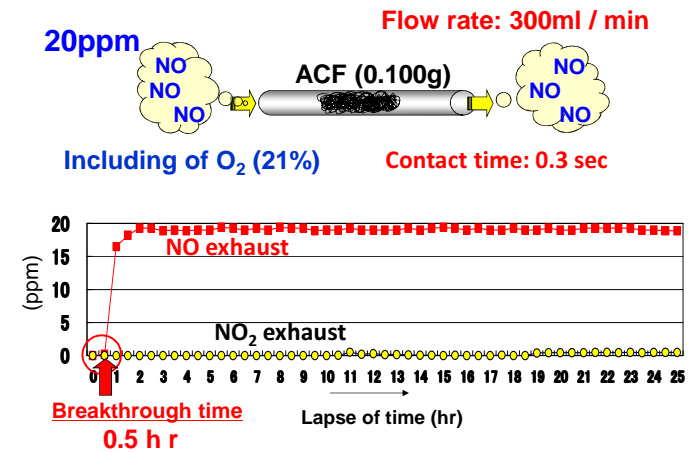


- NO_x oxidation
- Urea Activation
- NO_x in Environment
- Roles of ACF : More variety of ACF

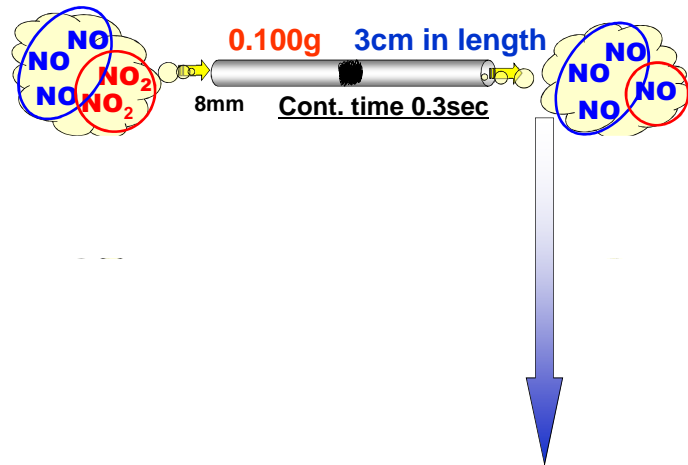
Adsorption of NO₂ in ACF



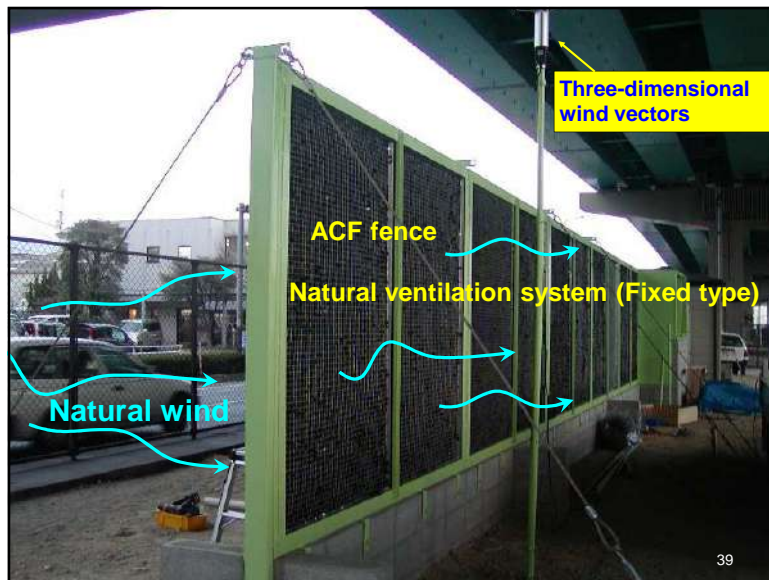
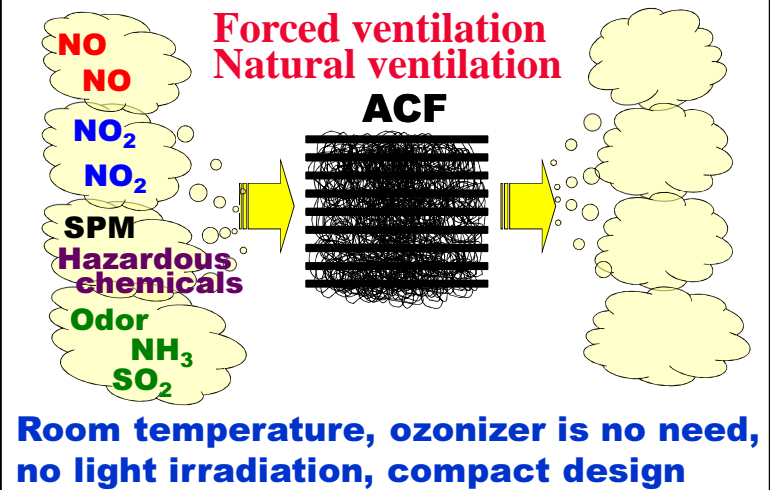
Scavenging activities against NO



The characteristics of NOx purification



Characterization of ACF purification



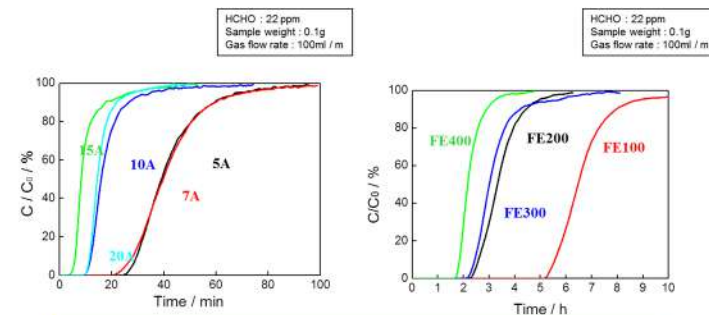
Novel applications of ACs

1. HCHO (Removal of sick-house gases)
2. Super capacitor
3. Medicine
4. Capacitive De-ionization (CDI)
5. Heat Pump (adsorptive heat pump)

1. HCHO & Toluene (Sickhouse gases)

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Removal of HCHO using ACs



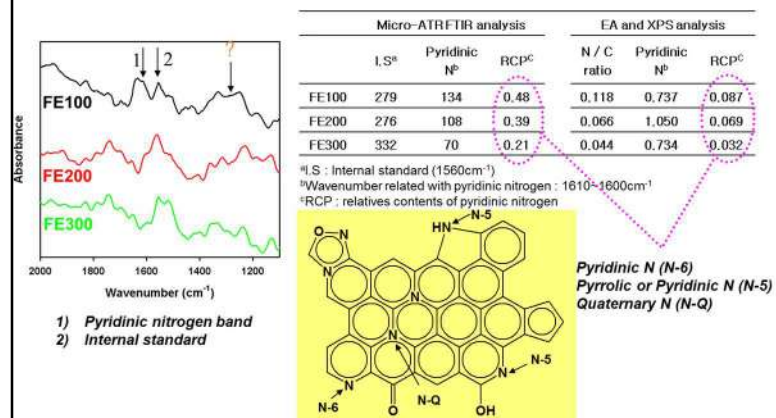
Break through time

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

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

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Micro ATR-FTIR analysis of ACs



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Micro-ATR FTIR

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

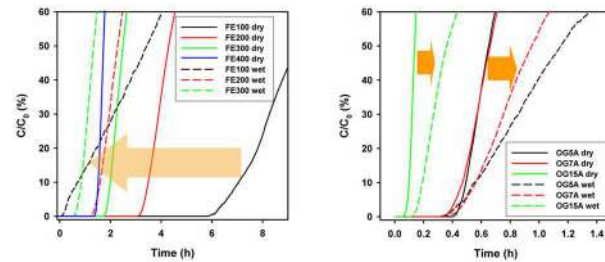
^a Wavenumber related with pyridinic nitrogen: 1610 ~ 1600 cm⁻¹

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Effect of humidity

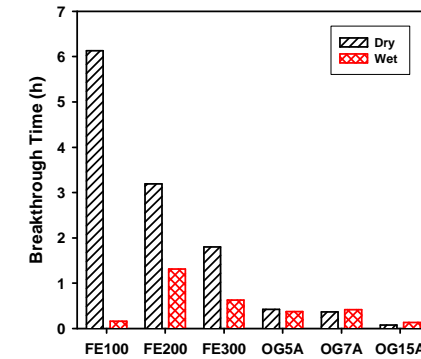
WATER Competitive adsorption decreases the adsorption amount of HCHO.

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

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Novel concept of pore (shallow pore)

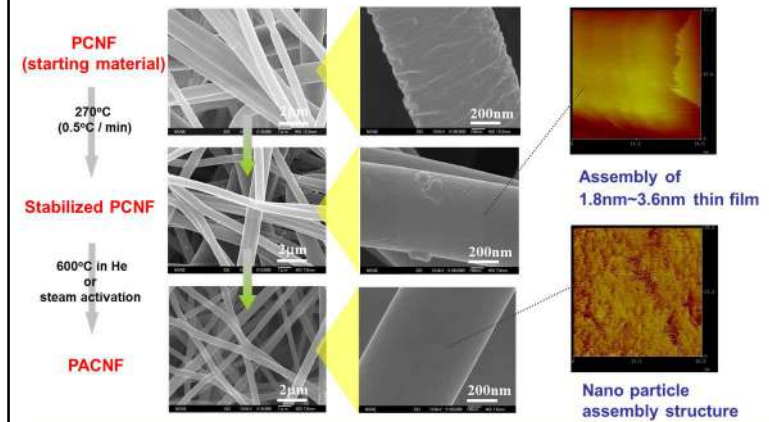
♦ Electrospun PAN based nanofiber (100% PAN)
Diameter: 800 nm, Nanotechnics (Korea)

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



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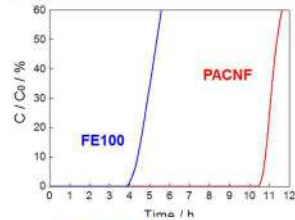
PAN based activated carbon nanofiber



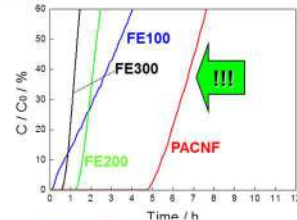
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Removal of HCHO using PAN-ACNF

RH	BET	Elemental analysis (wt%)						Microporous	
	(m ² / g)	C	H	N	Odif	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%



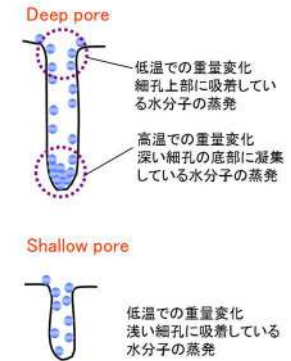
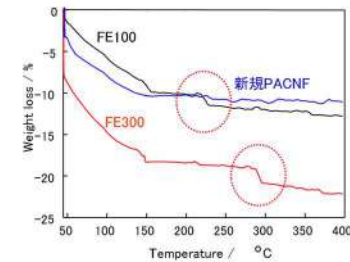
Experimental
HCHO : 11 ppm
Sample weight : 0.05g
Gas flow rate : 100ml / ml
Humidity of condition : 50%

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

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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).

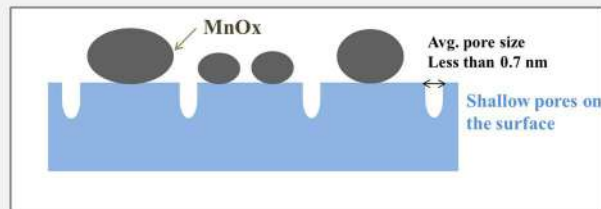
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Complete removal of HCHO using MnOx/ACNF

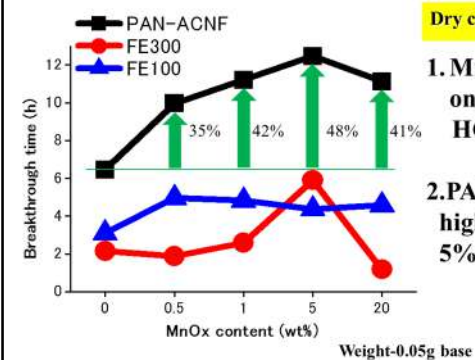
- ① Activated nano carbon fiber
- ② Catalytic decomposition of HCHO by MnOx into water and carbon dioxide

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

The conceptual model of MnOx-carbon catalyst



Catalysis Today, in press (2012).



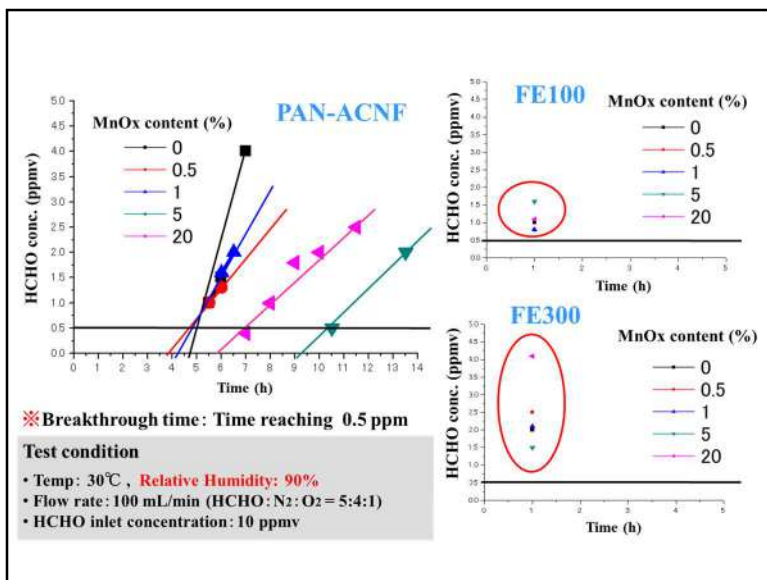
Dry condition

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

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

Mn₃O₄ or MnO₂ alone breakthrough in less than an hour.

➡ Deposition on carbon support improves catalytic activity of MnOx.



2. Super capacitor

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Study of super capacitor using NMR

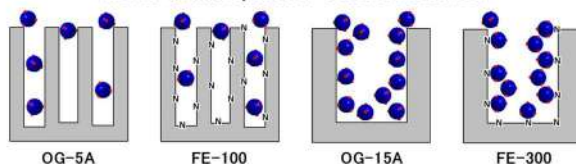
Pitch-based Activated Carbon Fibers (ACFs)

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)

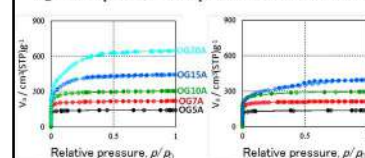
Model of micropores of OG and FE series



Aqueous and non-aqueous electrolytes with different ion sizes

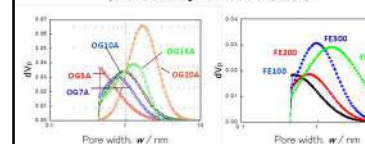


N₂ adsorption/desorption isotherms @77K



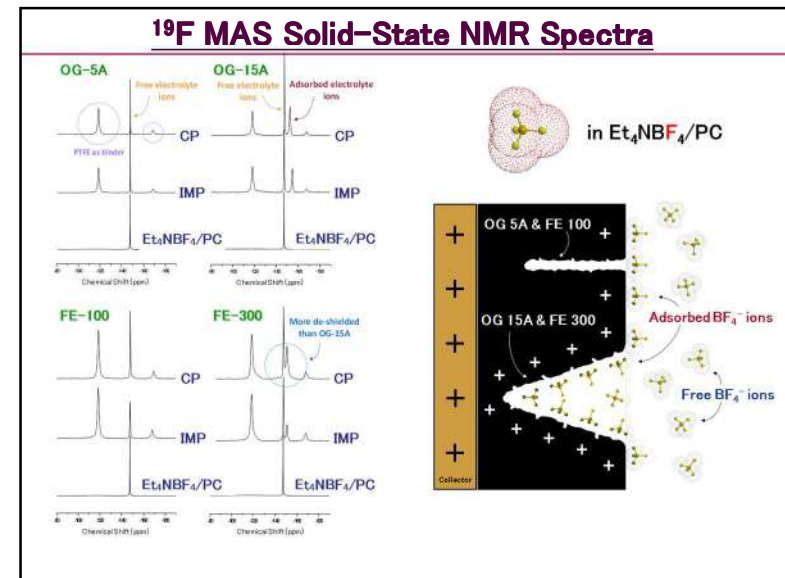
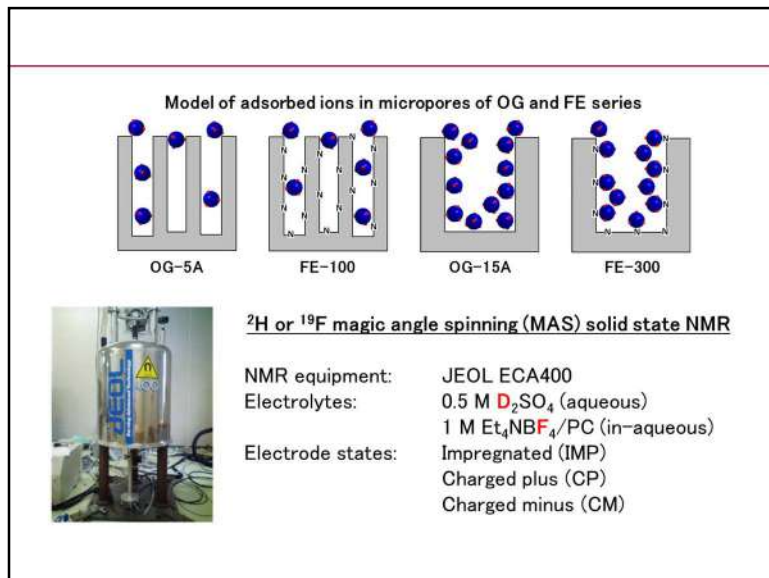
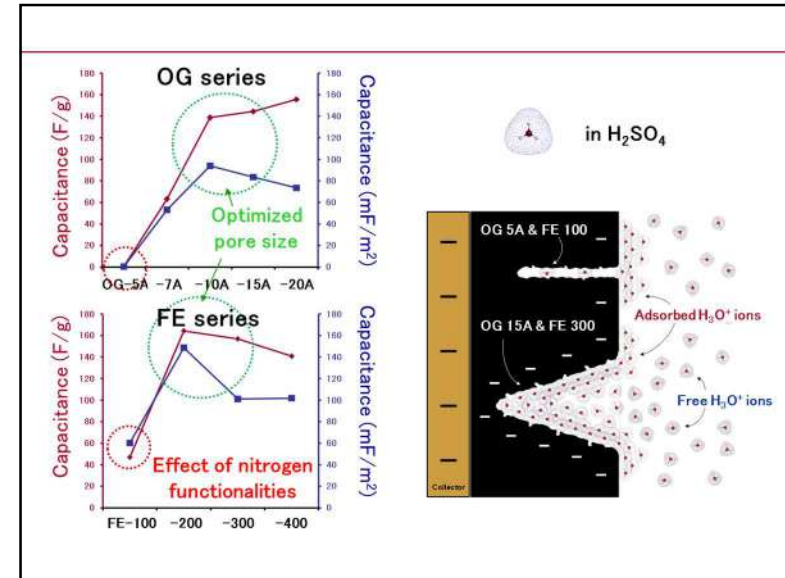
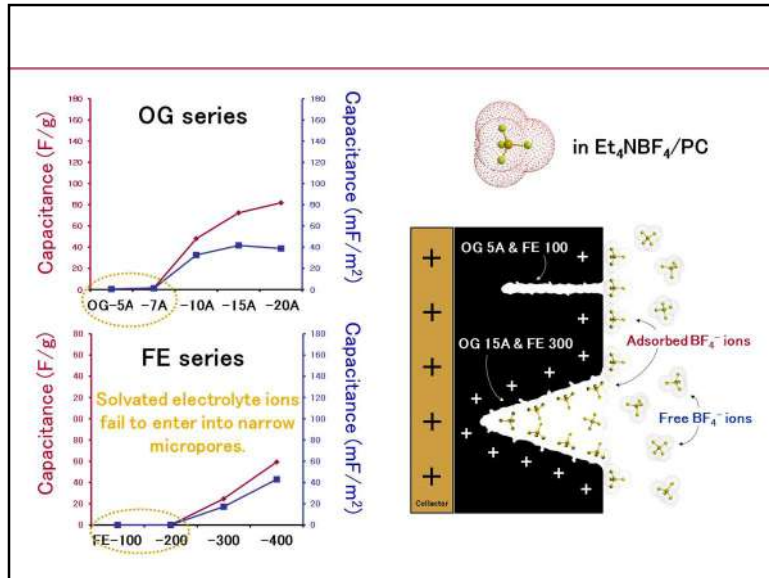
Pore size distributions

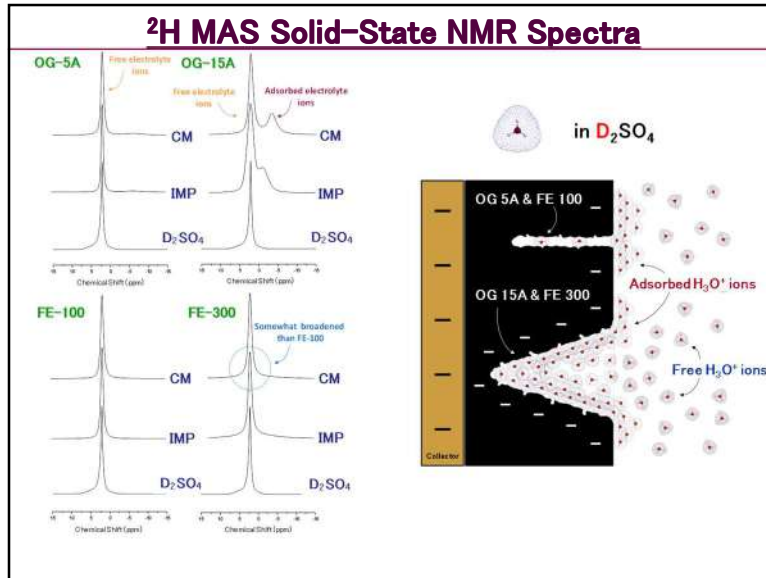
(calculated by NL-DFT method)



Pore structure parameters (calculated from t -plot method)

	Surface area (m ² /g)				Pore volume (cm ³ /g)				Pore width (nm)	
	A _{total}	A _{extreme}	A _{meso}	A _{micro}	V _{total}	V _{meso}	V _{micro}	W _{meso}	W _{micro}	
OG-5A	676.8	1.2	675.6	0	0.22	0.22	0	0.85	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	



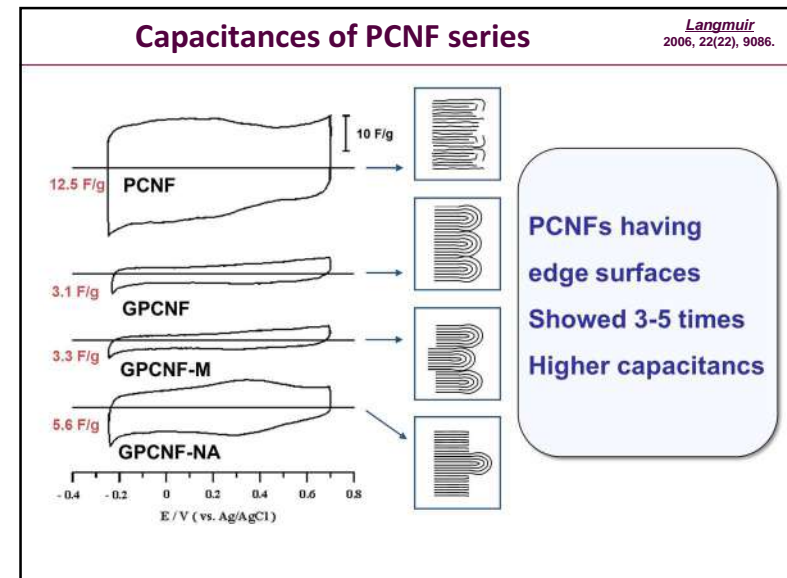
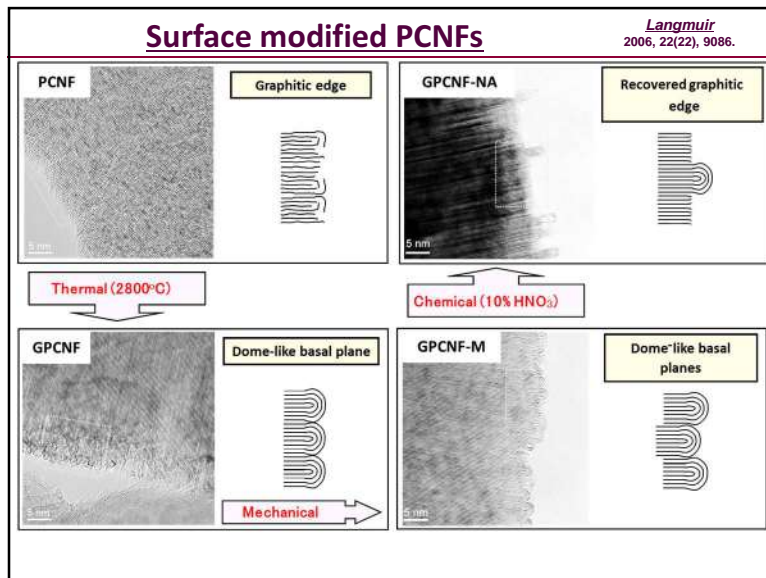
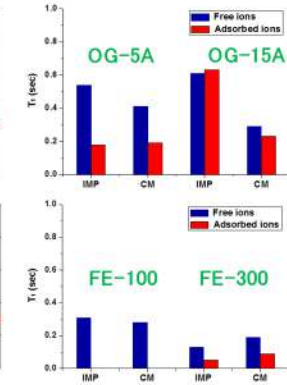


T_1 Values Measured from ^2H MAS Solid-State NMR

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



AC- medicine

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

Research background

Chronic Kidney Disease

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 entero-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
- Not to be removed

Indole (MW: 117.15)

⇒ a kind of poisons

Amylase (MW: about 46000)

⇒ Digestive enzyme

Samples

OG series (Osaka Gas)

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

H₂-OG series

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

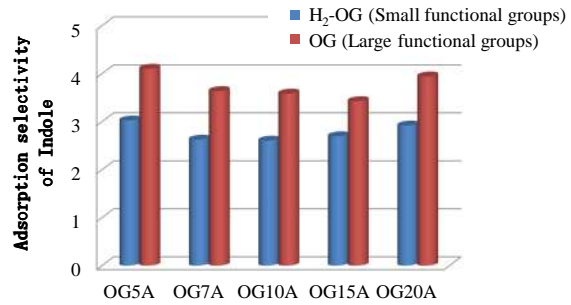
Ball type activated carbons

Ball type activated carbons with diameters of 100~300 μm

		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	Scmp	SACmp
Pore size (nm)	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
	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
Pore size (nm)	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

α_g analysis

Effect of functional groups for binary solutions

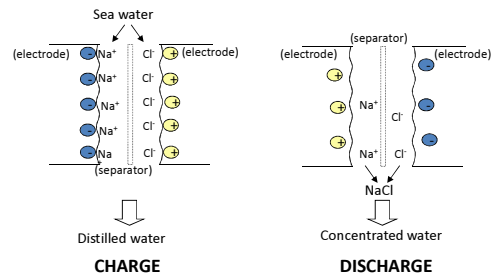


Removal ratio of Indole (%)	OG5A	OG7A	OG10A	OG15A	OG20A
Small functional groups	49.9	70.1	69.3	70.9	72.1
Large functional groups	43.1	63.3	63.8	69.9	68.6
Removal ratio of amylase (%)	OG5A	OG7A	OG10A	OG15A	OG20A
Small functional groups	16.5	26.7	26.6	26.3	24.7
Large functional groups	10.5	17.4	17.8	20.4	17.4

Capacitive De-ionization (CDI)

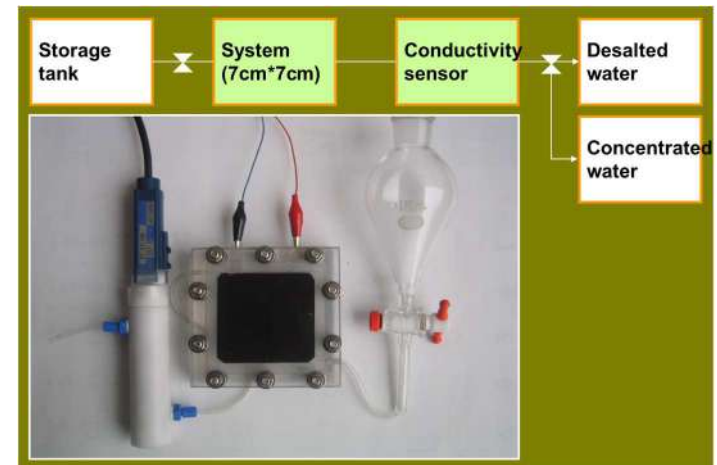
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Principle of electrical desalination

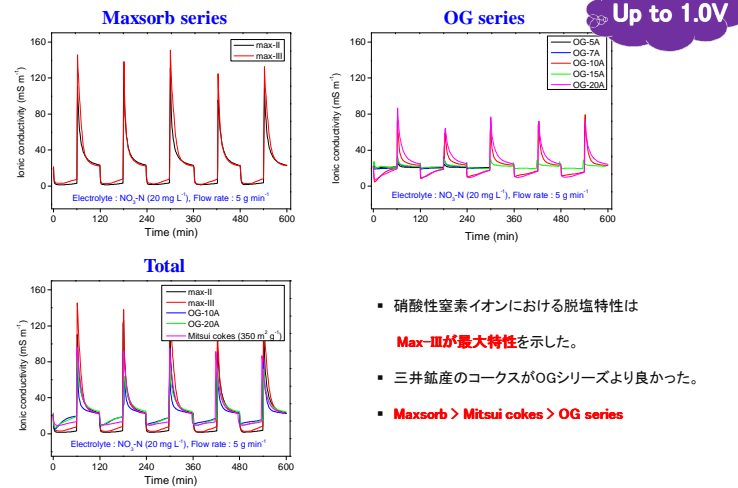


- Diffusion of ions inside of pores
- Rapid electrochemical adsorption and desorption

Experimental setup

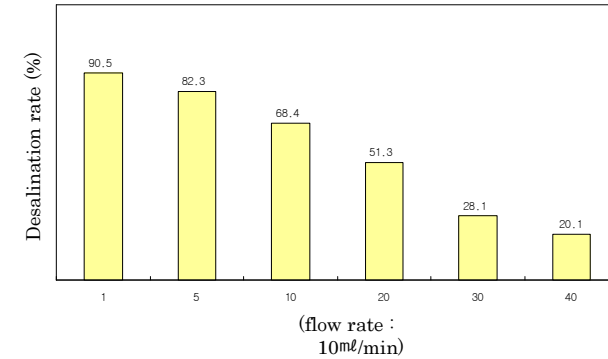


Nitric ion removal behaviors



Cl⁻ ions in the city water

Effect of flow rate

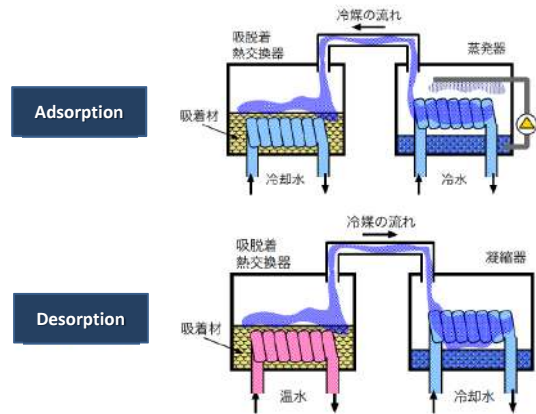


Points

- 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

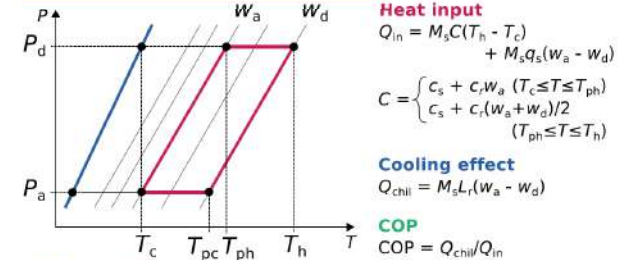
Application of activated carbons to Heatpump for energy-free operation

Principle of Heat Pump



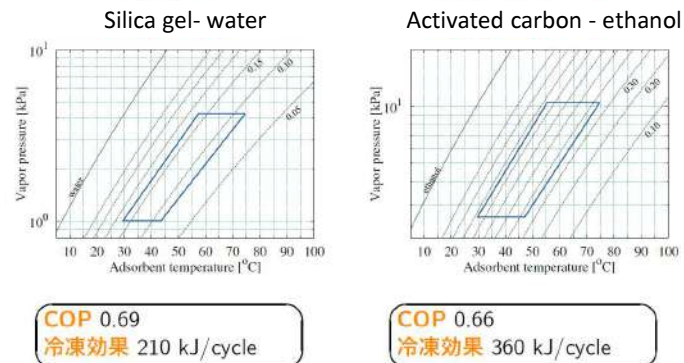
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Static analysis of adsorptive HP



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Performance test results



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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

