

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)

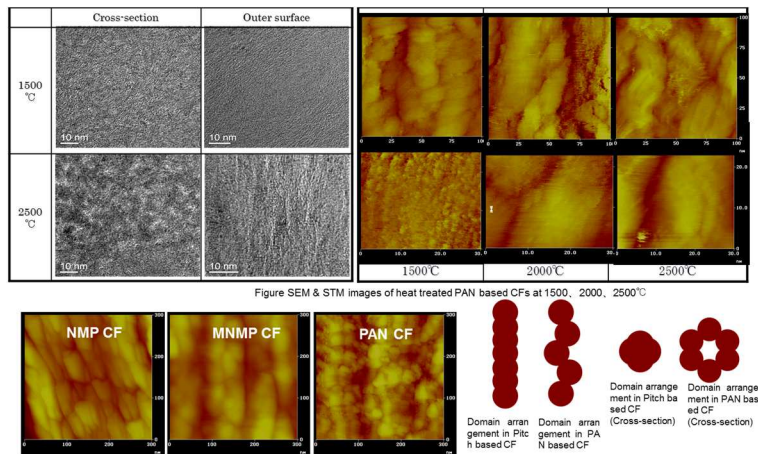
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- Contents:
1. 活性炭の構造、細孔分析及び応用
 2. 繊維状ナノ炭素の調製、構造及び応用

活性炭を用いた水の浄化

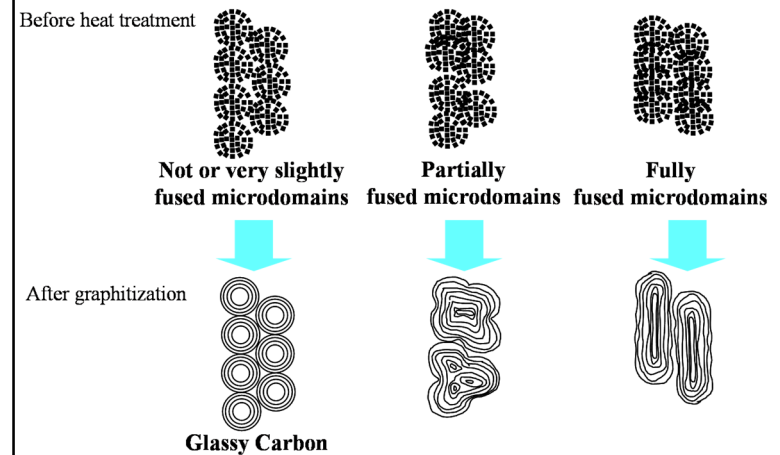


Structure of PAN based carbon fiber

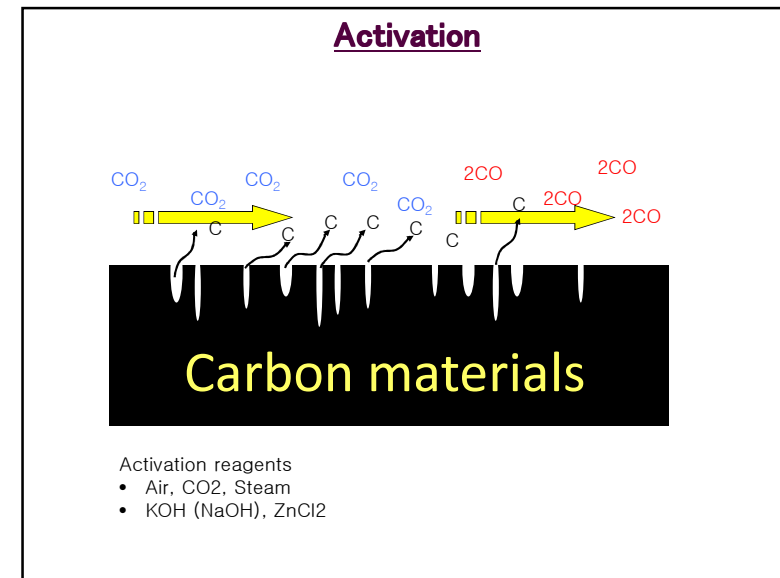
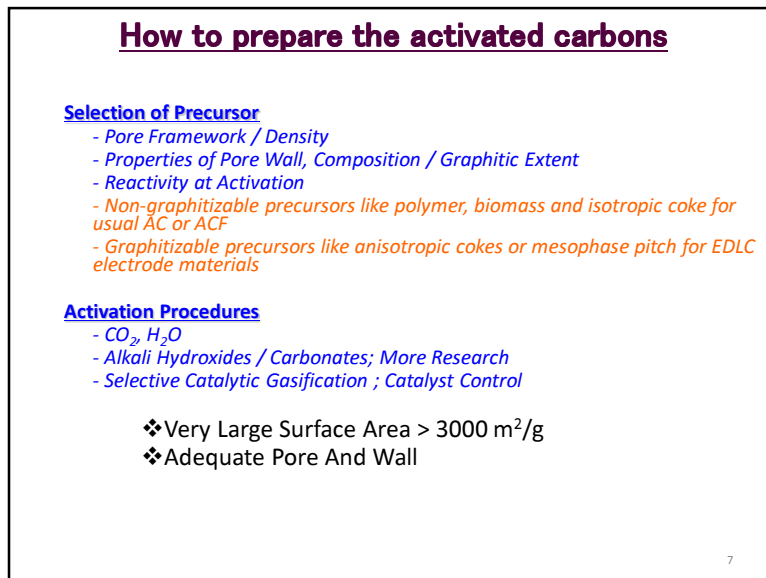
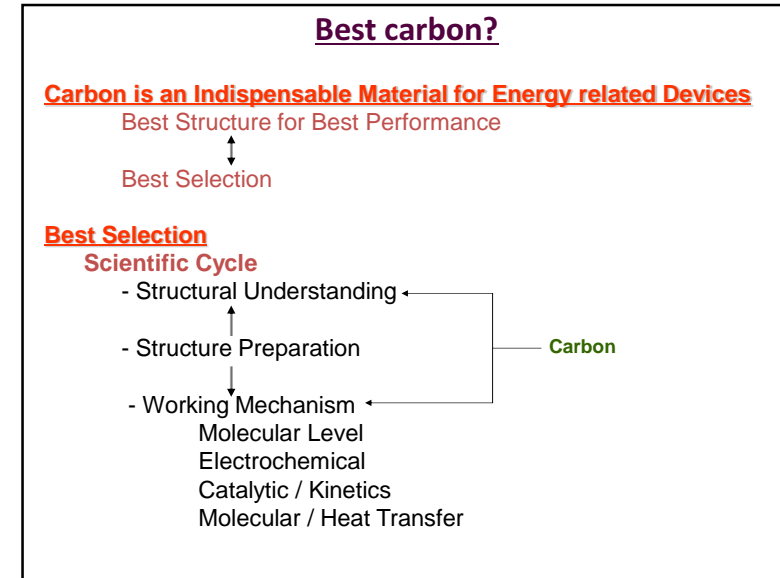
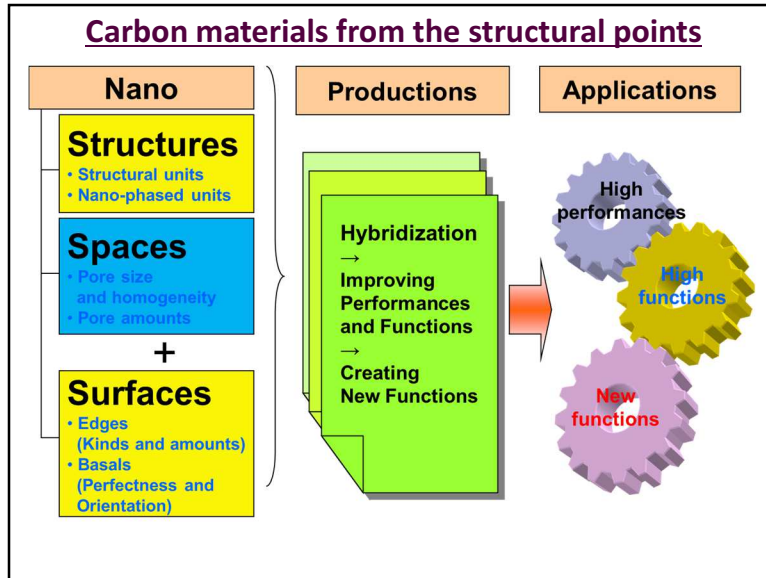


"Structural comparison of mesophase and PAN based carbon fibers"
S.H. Hong, S. H. Yoon, I. Mochida Carbon2006. (2006. 7) England

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



Chemical activation

Catalytic progress
Under K₂O

$2\text{KOH} \rightarrow \text{K}_2\text{O} + \text{H}_2\text{O}$
(Dehydration)

$\text{C} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}$
(Water gas reaction)

$\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$
(Water gas shift reaction)

$\text{K}_2\text{O} + \text{CO}_2 \rightarrow \text{K}_2\text{CO}_3$

$\text{K}_2\text{O} + \text{H}_2 \rightarrow 2\text{K} + \text{H}_2\text{O}$

$\text{K}_2\text{O} + \text{C} \rightarrow 2\text{K} + \text{CO}$

Carbon is mainly consumed as a form of K₂CO₃

K compounds are reduces 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
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Conventional concept of activated carbons

Inner surface
Outer surface
Sub-micro pore < 0.8 nm
Micro pore 0.8 – 2.0 nm
Meso pore 2.0– 50 nm
Macro pore > 50 nm

Schematic shapes of pores

Classification of surface and pores

Schematic pore images of activated carbon fiber and activated carbon

10

STM images of ACFs

	OG5A	OG7A	OG10A	OG15A	OG20A
100nm					
20nm					

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

Micro domain

Cluster unit

Structure of glassy carbon

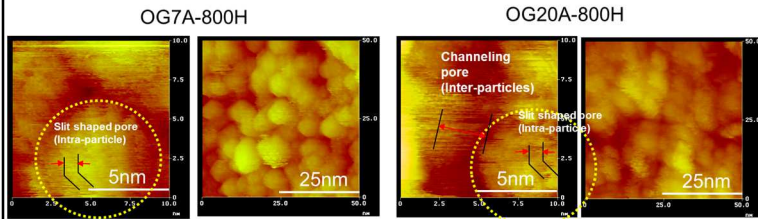
1200°C

2400°C

12

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 (H₂/ 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.

13

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

14

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

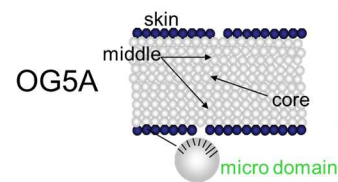
Pores from intraparticles (Slit shaped? Micropores less than 2 nm)

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

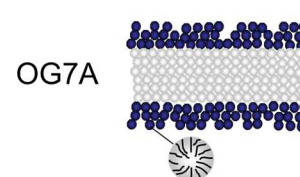
15

Novel understanding of activation mechanism

A model for cross section of ACFs

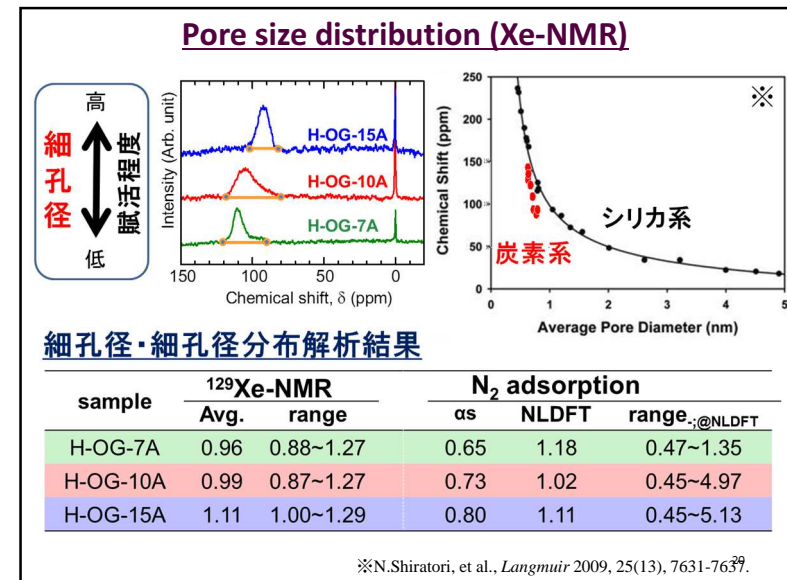
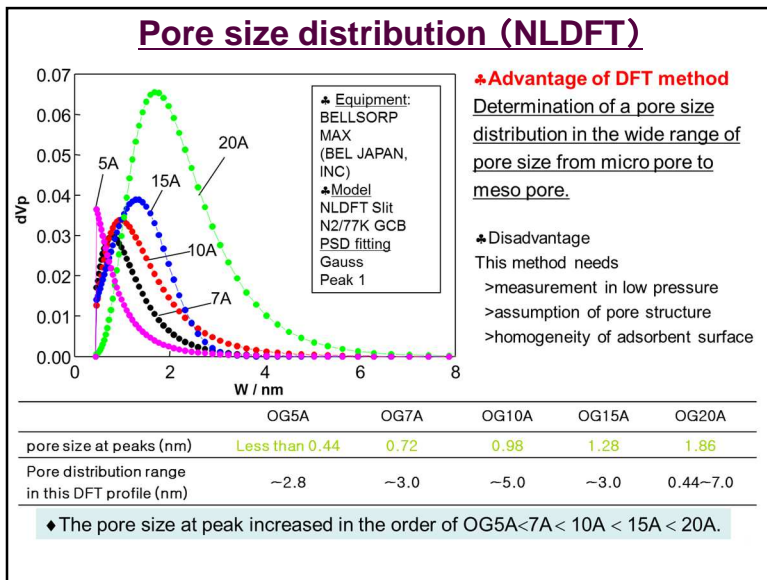
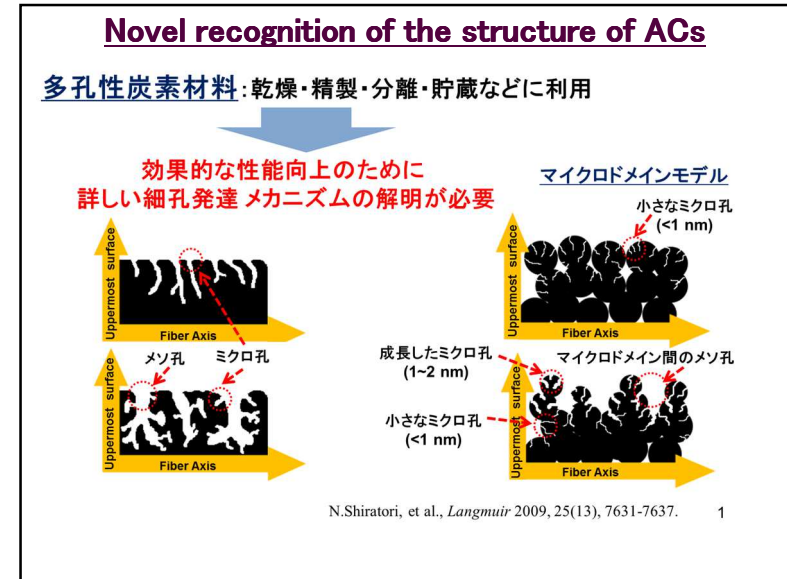
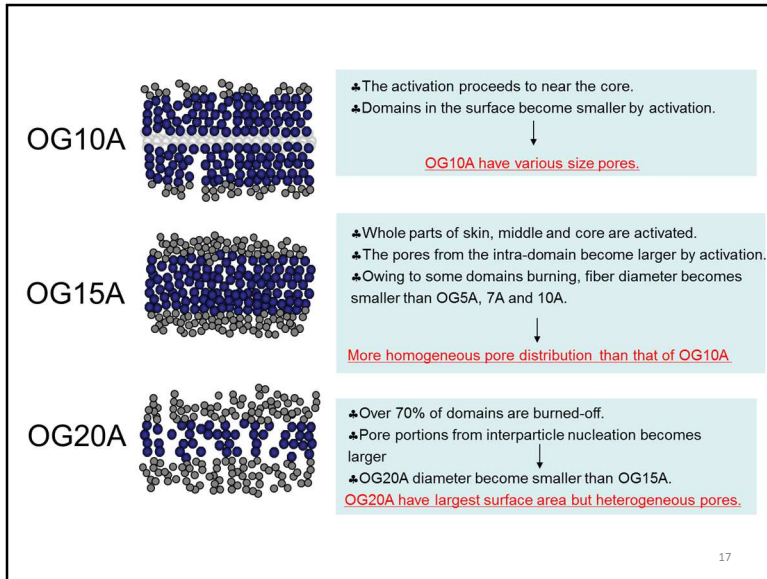


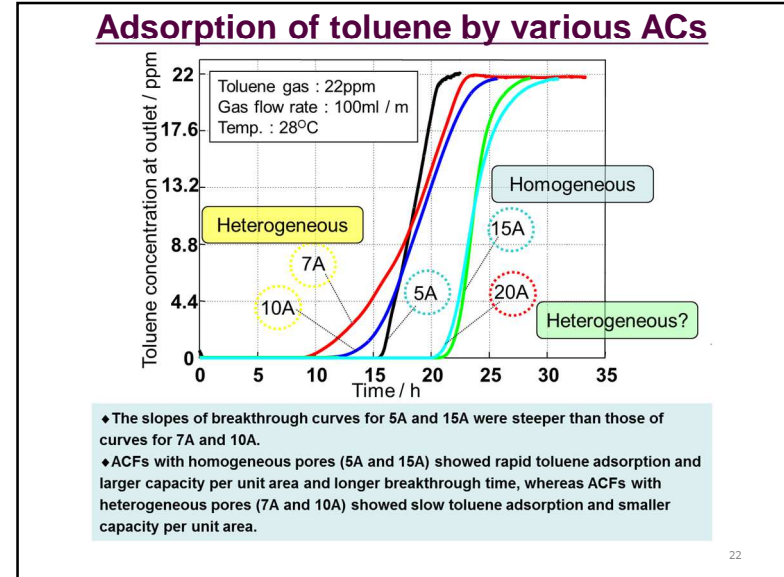
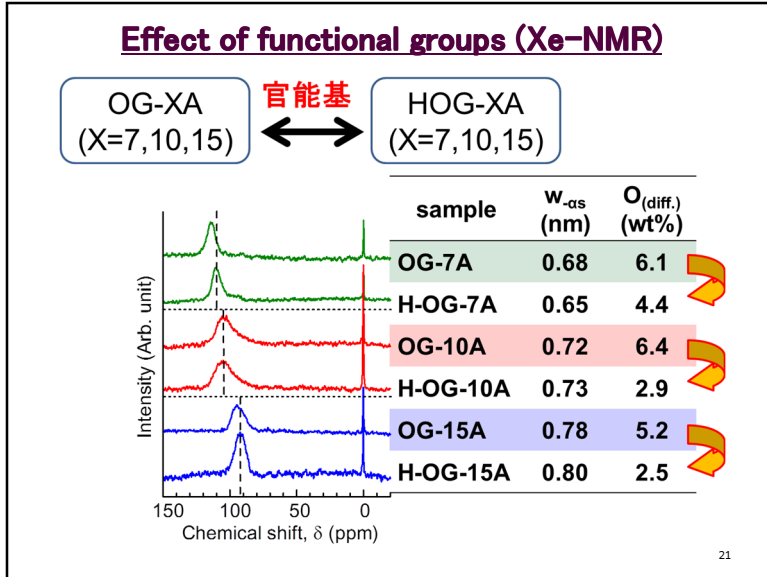
- ▲ Only skin is activated, homogeneous narrow pore exist on the surface of domains.
- ▲ The activation does not reach to the middle and core parts.
- OG5A has smallest surface area but homogeneous pores.



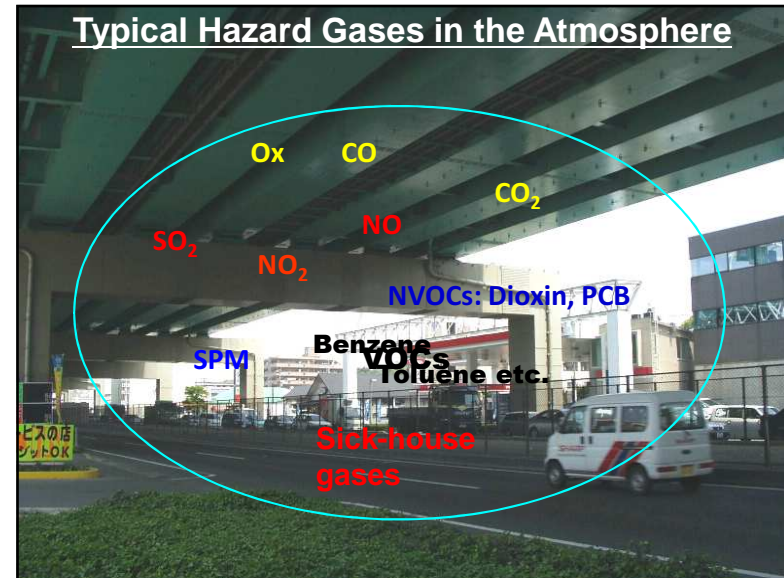
- ▲ Skin and middle parts are activated.
- ▲ Pores in domain become wider and longer than that of OG5A because of the pores formed by inter-domain mechanism.
- ▲ Pores are formed by the intra-domain and inter-domain mechanisms.
- Heterogeneous pores exist.

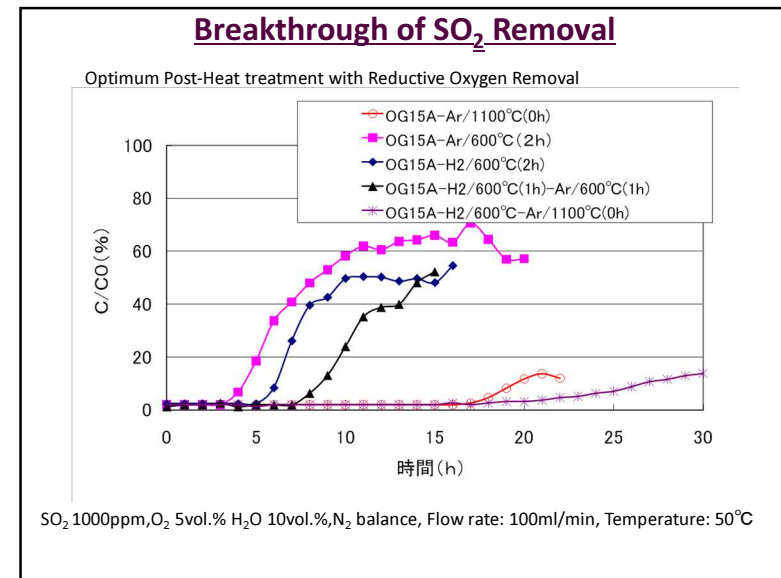
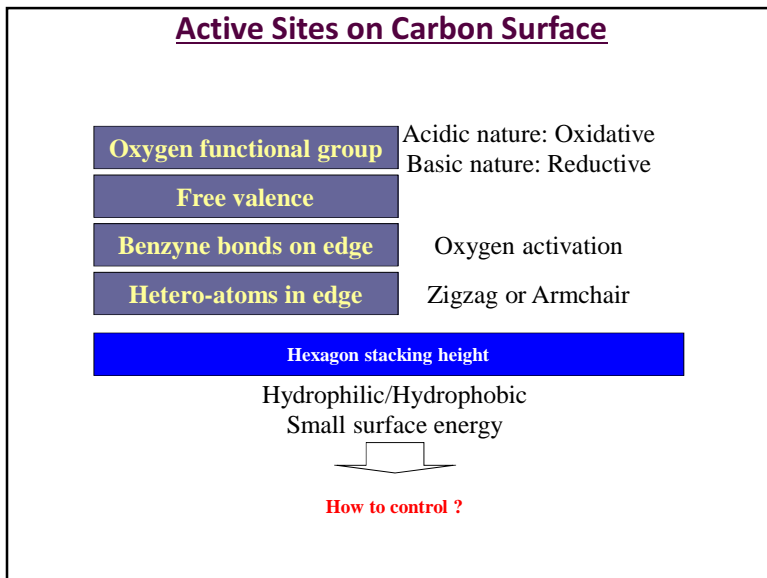
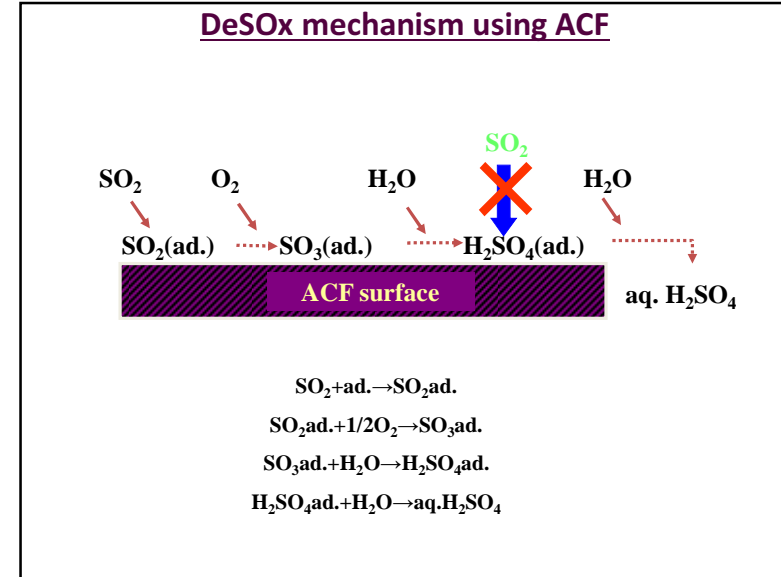
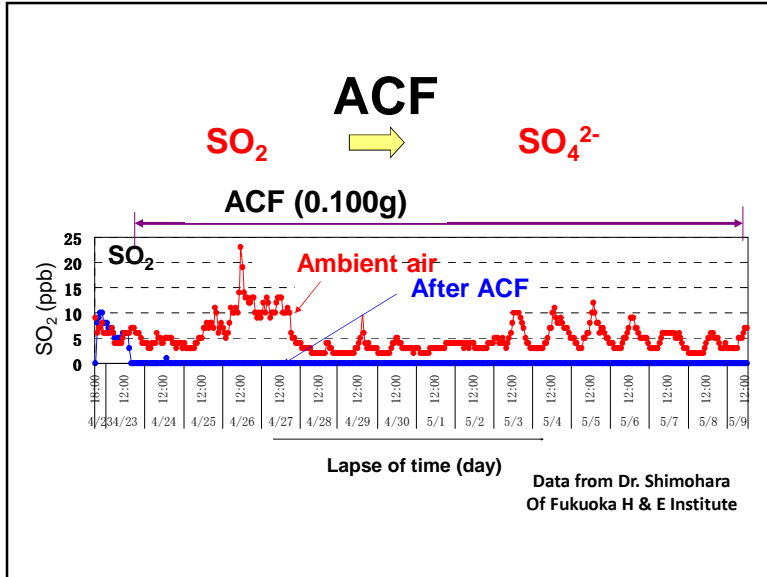
16

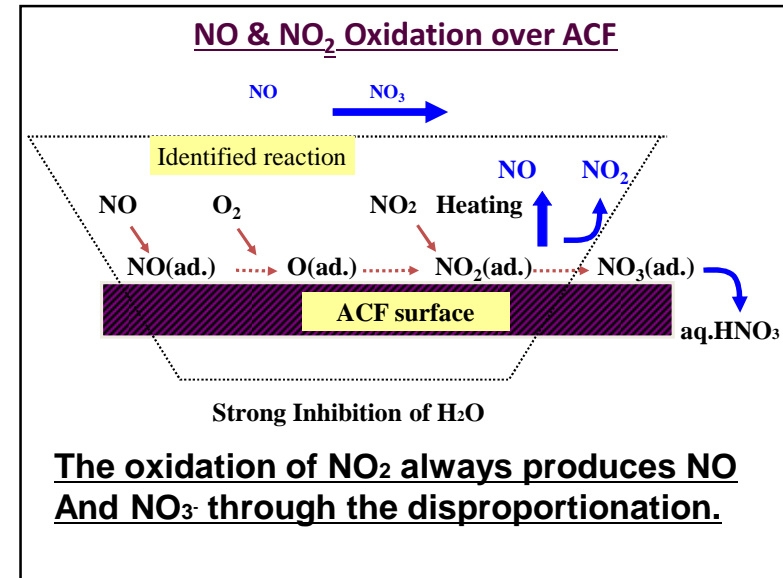
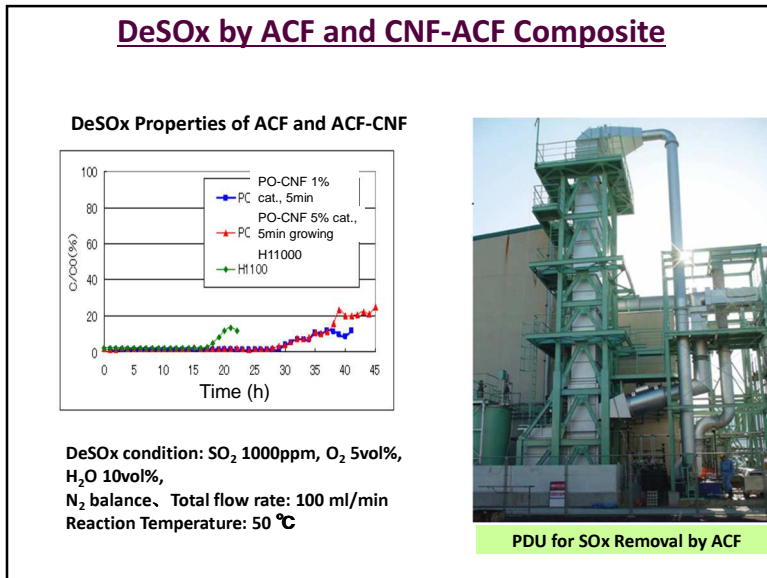
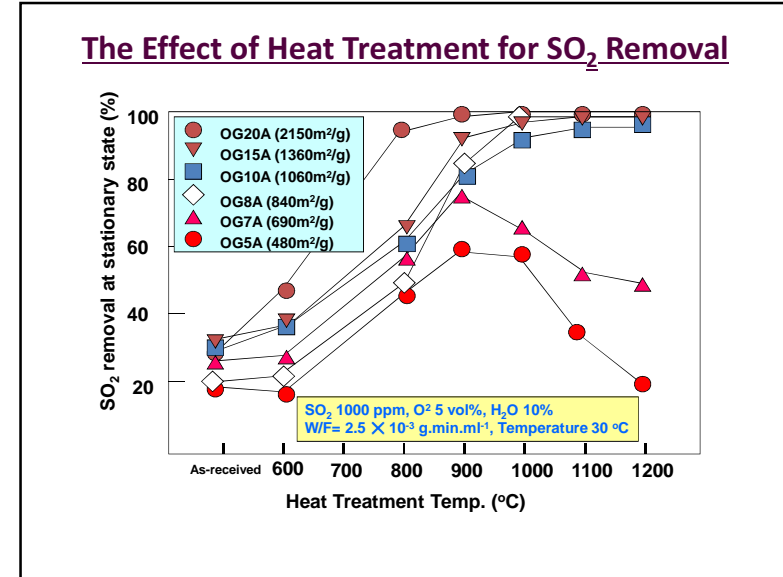
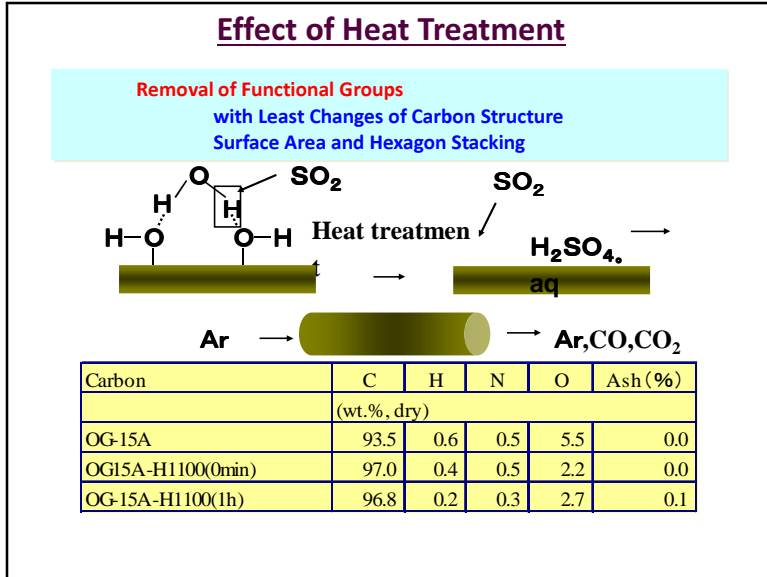




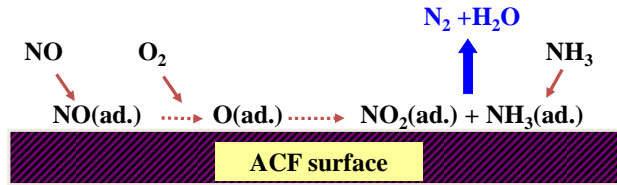
Removal of SO_x and NO_x Using ACFs





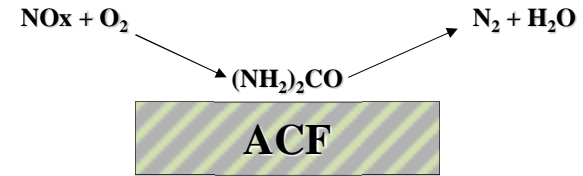


The Mechanism of NO Reductive Removal



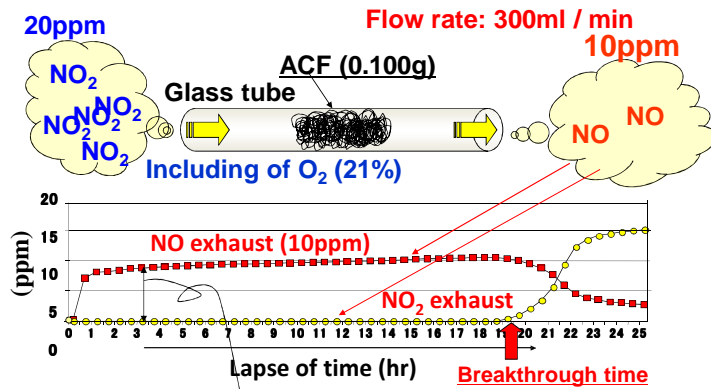
The mechanism of NO removal consists of adsorption and oxidation of NO into NO₂ which is reduced with NH₃

NOx Reduction at Room Temperature



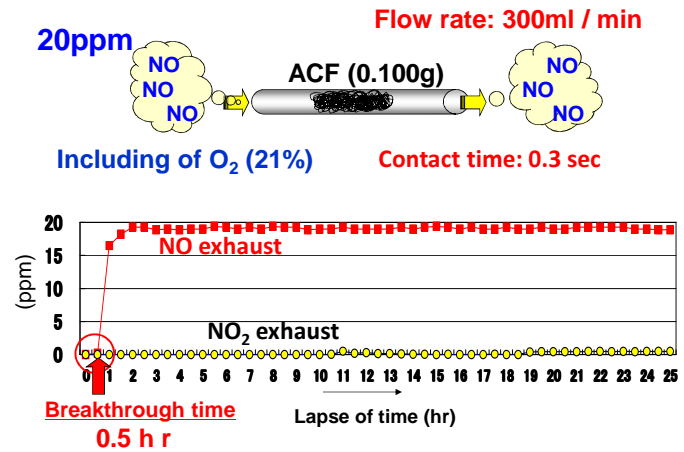
- NOx oxidation
- Urea Activation
- NOx in Environment
- Roles of ACF : More variety of ACF

Adsorption of NO₂ in ACF

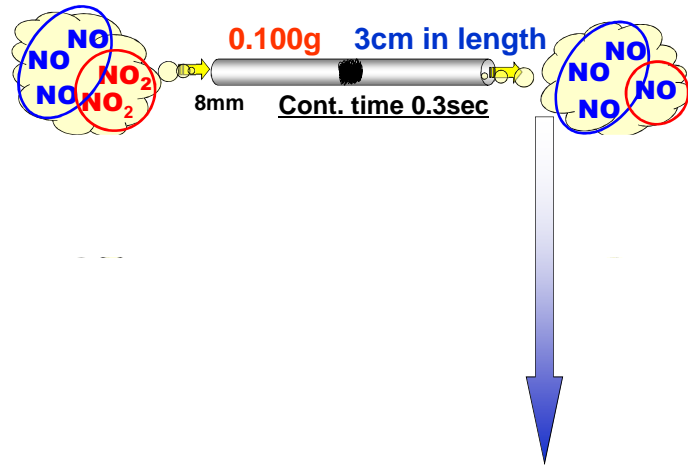


Half amount of adsorbed NO₂ is exhausted as NO.

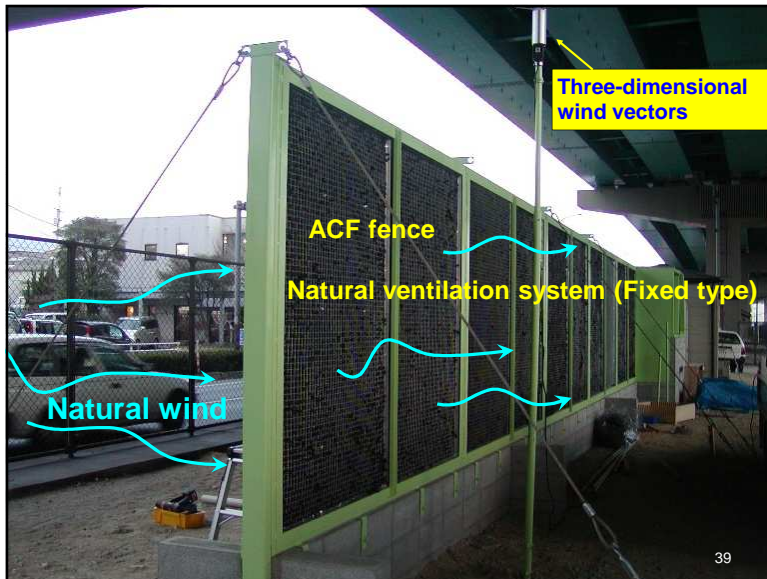
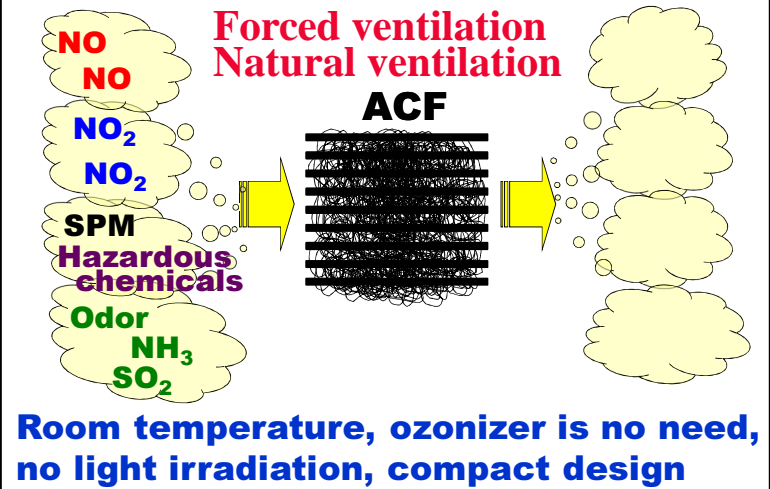
Scavenging activities against NO



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)

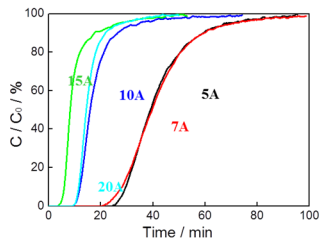
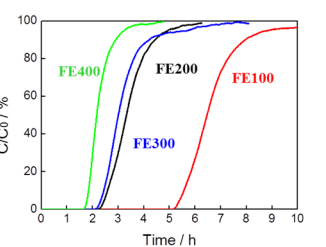
1. HCHO & Toluene (Sickhouse gases)

41

Removal of HCHO using ACs

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

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

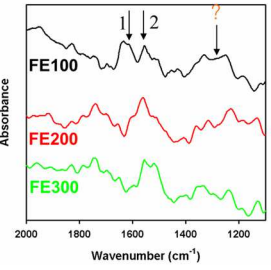



Break through time

- ◆ Pitch-based ACF : 15A < 20A < 10A < 7A < 5A
- ◆ PAN-base ACF : FE400 < FE300 < FE200 < FE100

42

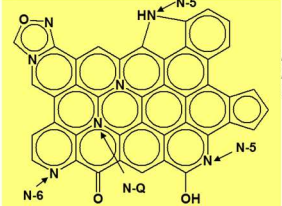
Micro ATR-FTIR analysis of ACs



1) Pyridinic nitrogen band
2) Internal standard

	Micro-ATRFTIR 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

^aI.S : Internal standard (1560cm⁻¹)
^bWavenumber related with pyridinic nitrogen : 1610~1600cm⁻¹
^cRCP : relatives contents of pyridinic nitrogen



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

43

Micro-ATR FTIR

Relative amount of pyridinic nitrogen functional groups for PAN based ACs 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

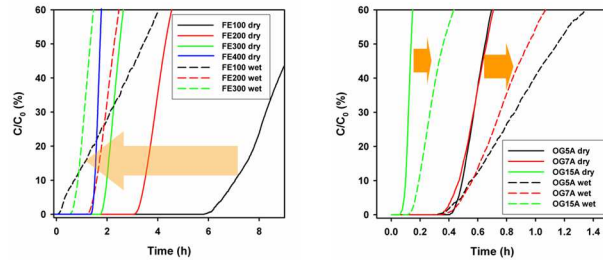
^a Wavenumber related with pyridinic nitrogen: 1610 ~ 1600 cm⁻¹

44

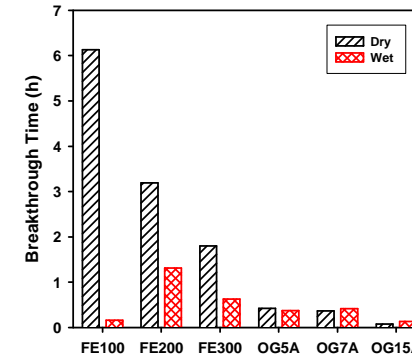
Effect of humidity

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



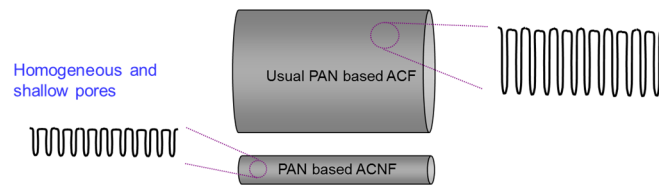
JOURNAL OF APPLIED POLYMER SCIENCE 106 (4): 2151-2157 NOV 15 2007



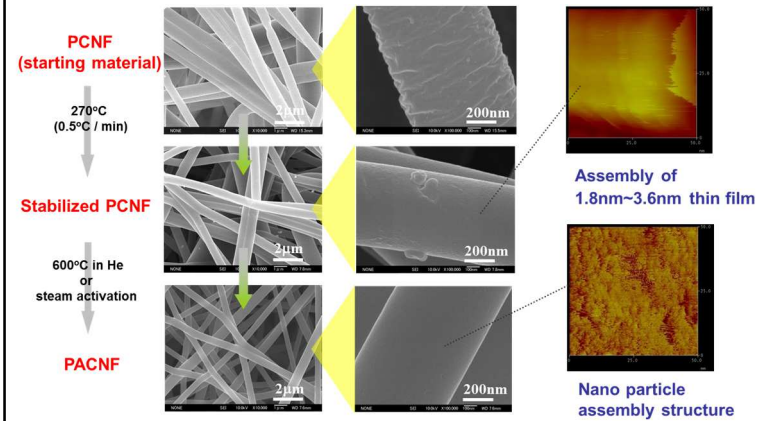
Novel concept of pore (shallow pore)

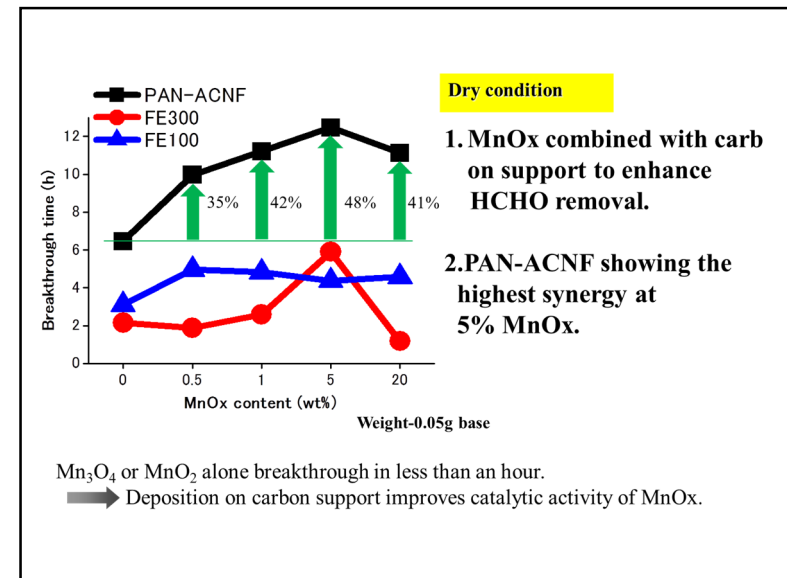
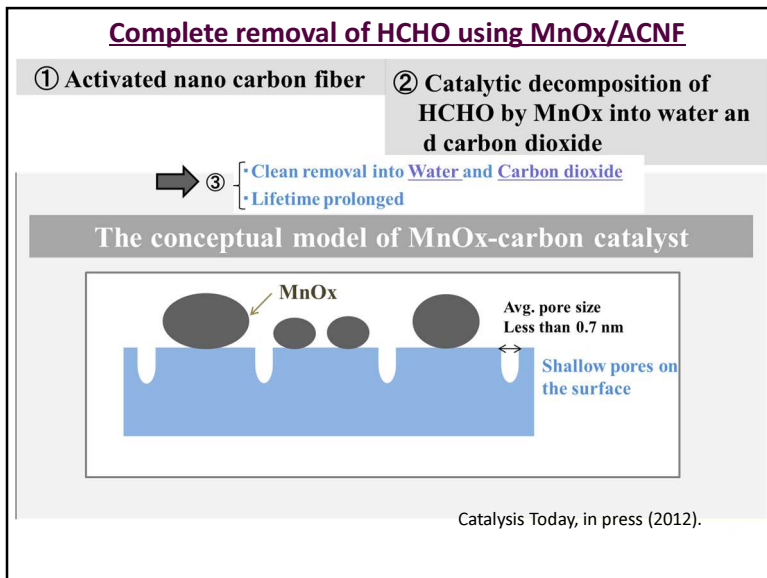
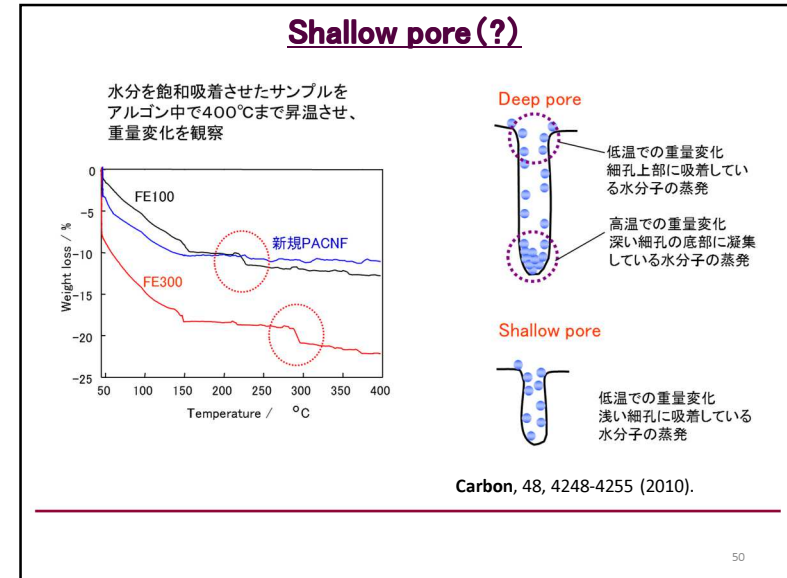
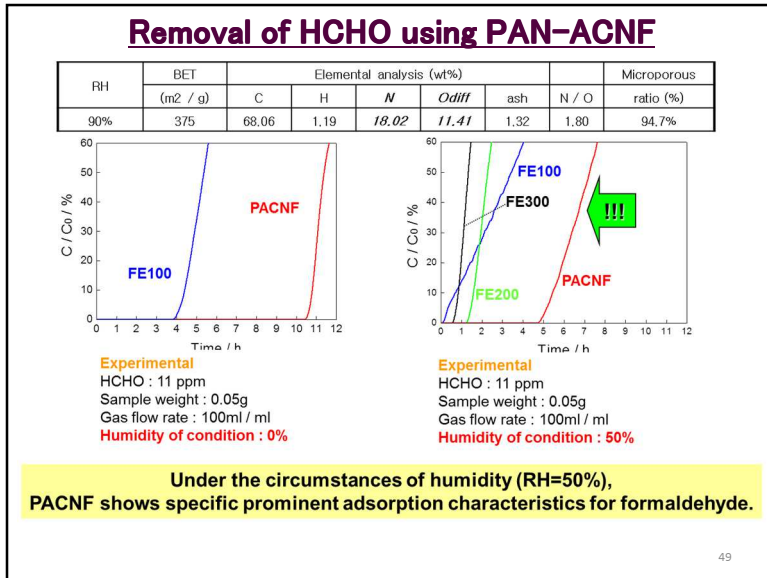
◆ Electrospun PAN based nanofiber (100% PAN)
Diameter: 800 nm, Nanotechnics (Korea)

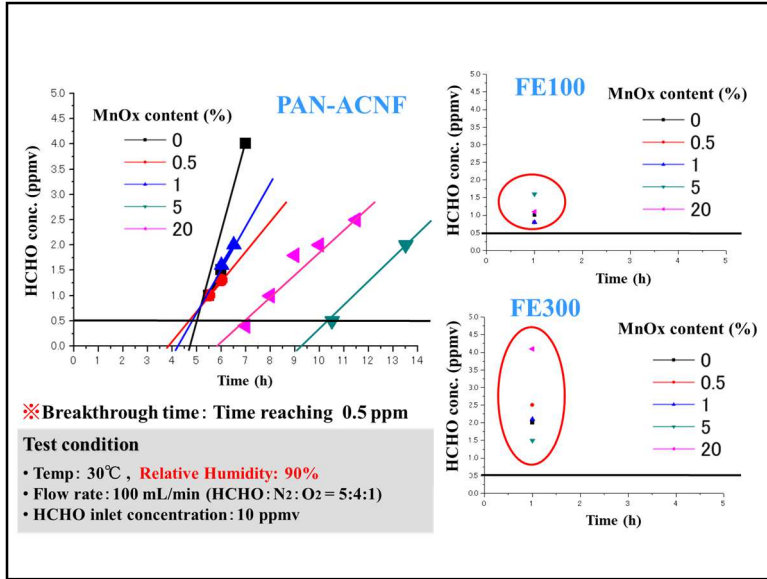
100 times surface area compared to usual PAN fiber
→ Can be expected very shallow and homogenous pores.



PAN based activated carbon nanofiber







2. Super capacitor

54

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)

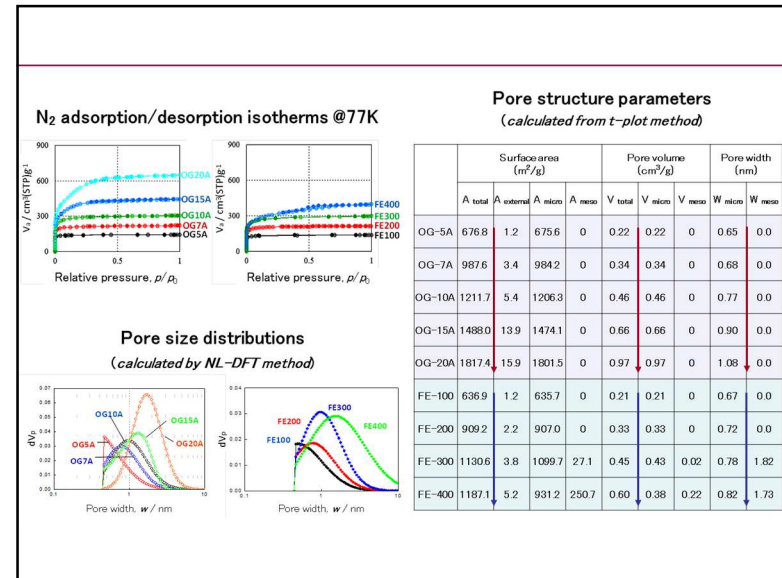
PAN-based ACFs
FE series : FE-100, FE-200, FE-300, FE-400 (Toho TENAX Co., Japan)

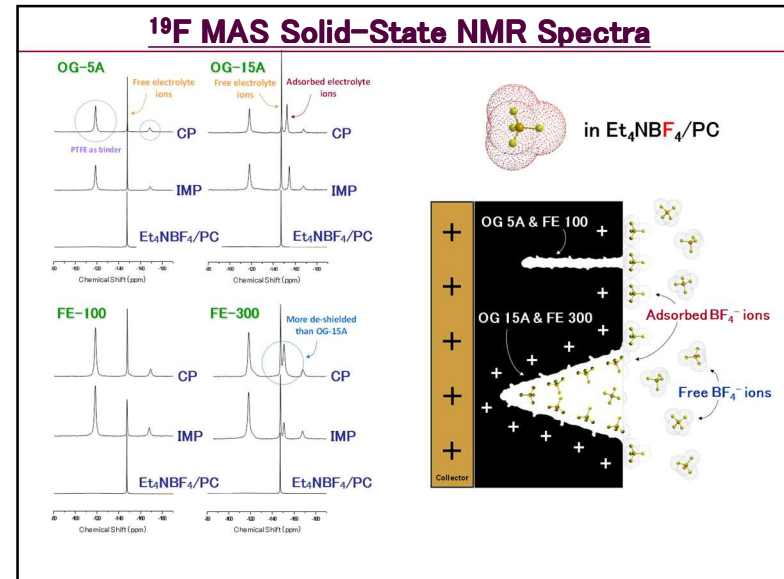
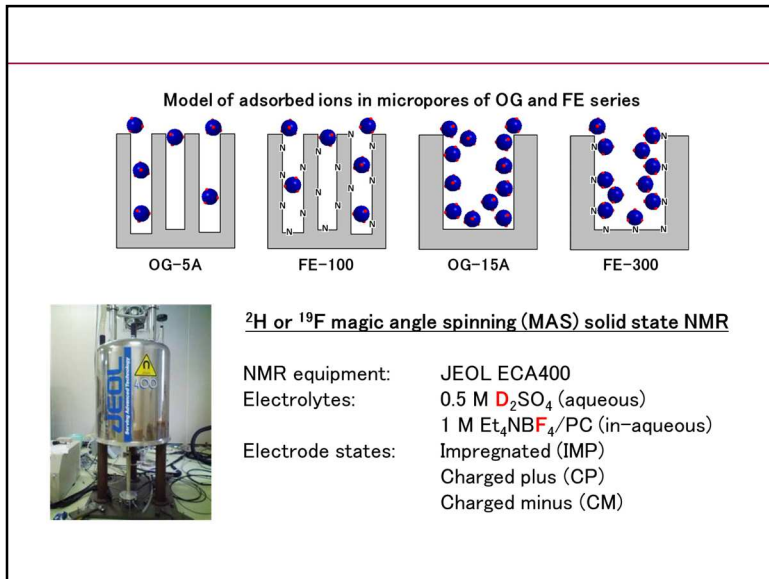
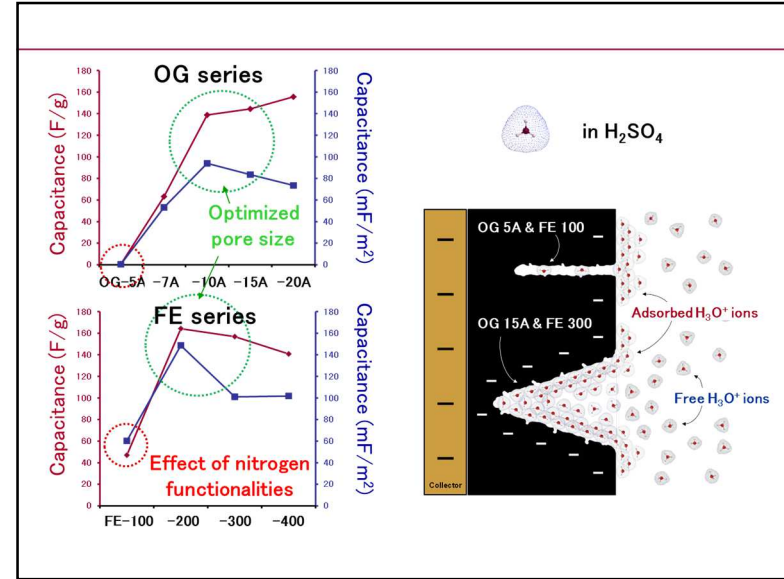
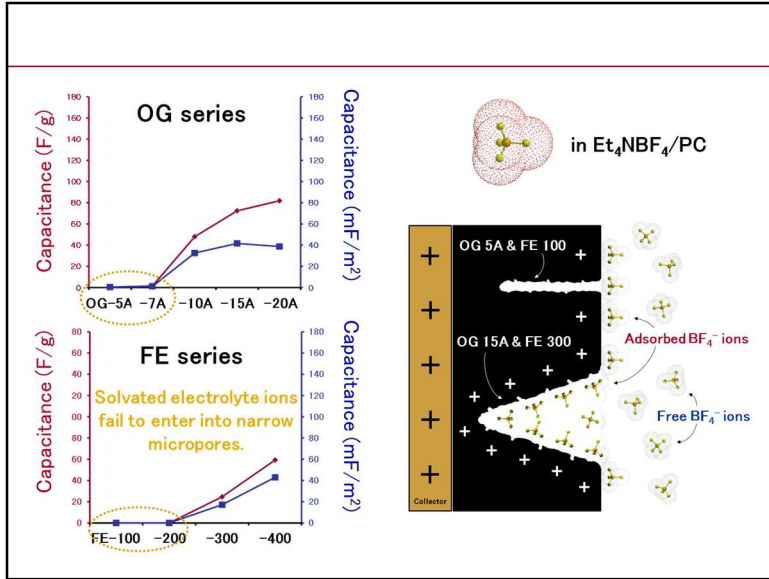
Model of micropores of OG and FE series

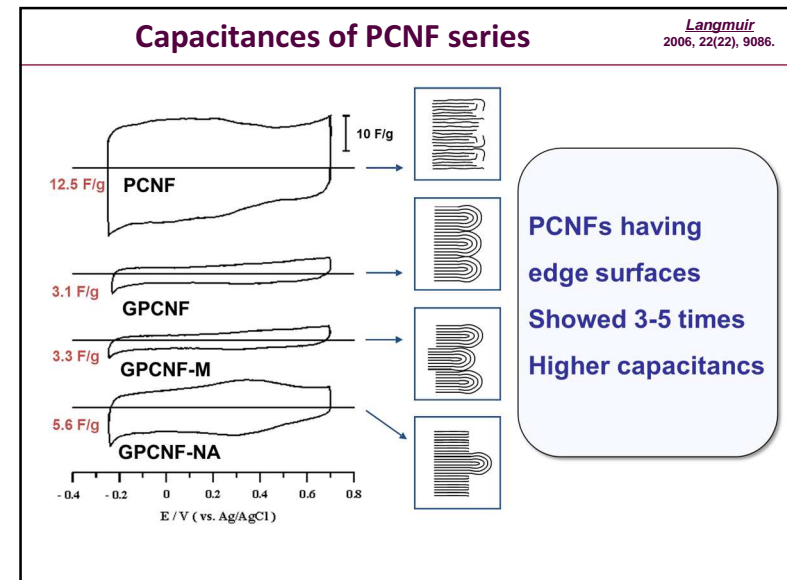
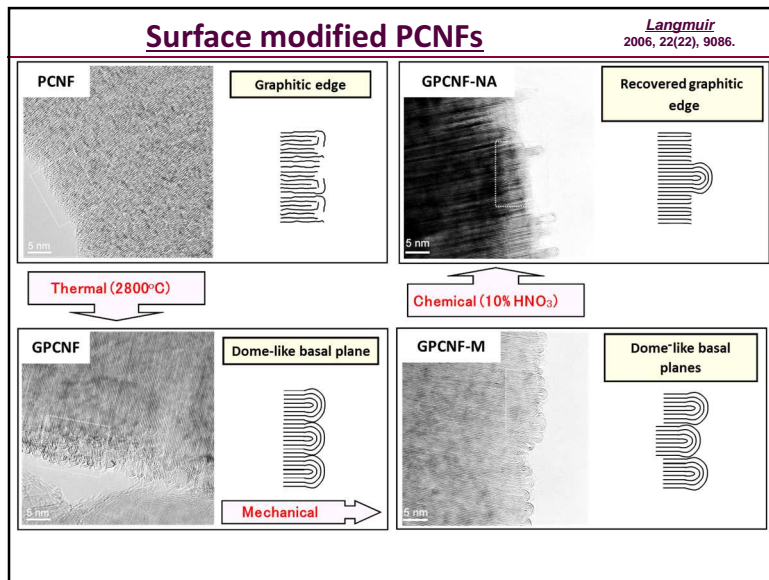
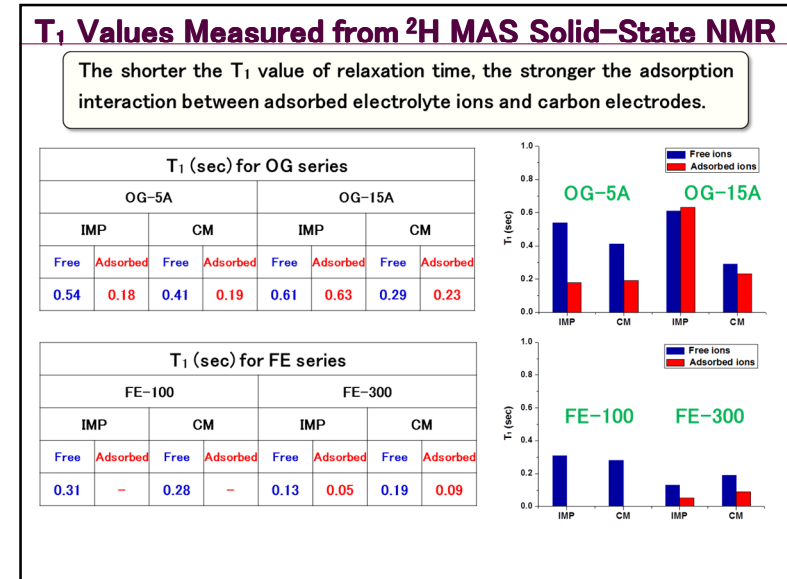
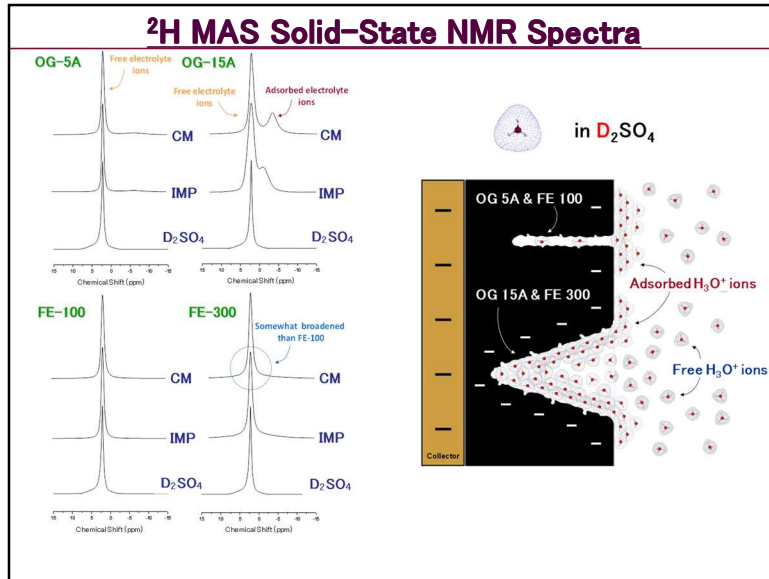
OG-5A FE-100 OG-15A FE-300

Aqueous and non-aqueous electrolytes with different ion sizes

H_3O^+ in H_2SO_4/H_2O BF_4^- in Et_4NBF_4/PC







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 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
- 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)

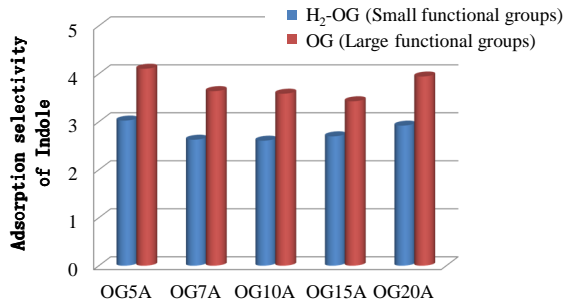
Ball type activated carbons

Ball type activated carbons with diameters of 100~300 μm

- Surface area and pore
- Surface property

Pore size (nm)	SA (m ² /g)	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	Semep	SACmir
		A micro	646	982	1283	1688	1928	728	1247	1305	1548	1802	1254	1585	570
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	
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



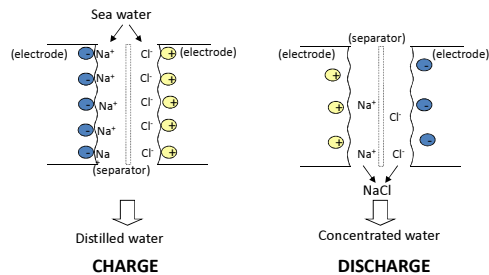
Removal ratio of Indole (%)	OG5A	OG7A	OG10A	OG15A	OG20A
Small functional groups	49.9	70.1	69.3	70.9	72.1
Large functional groups	43.1	63.3	63.8	69.9	68.6

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)

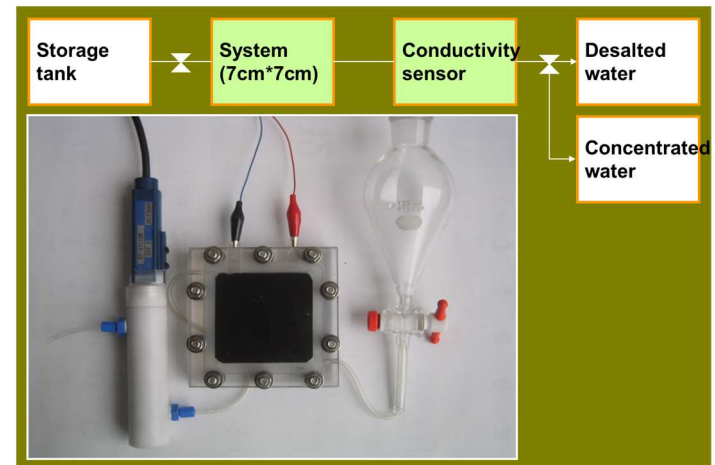
70

Principle of electrical desalination

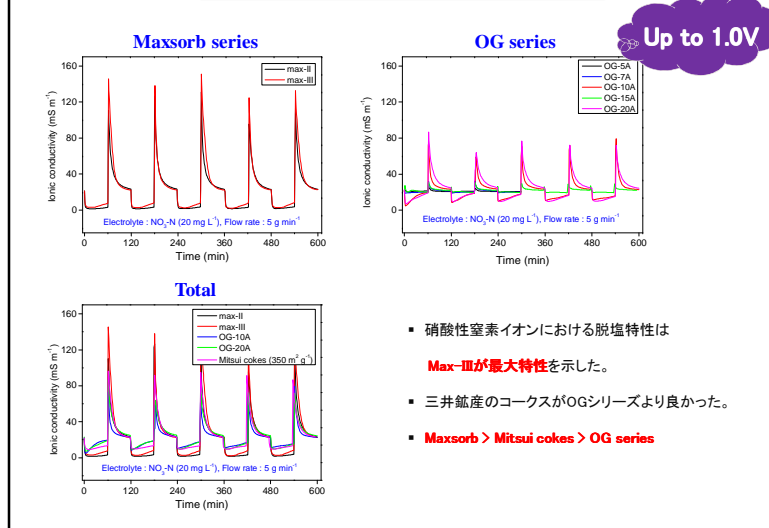


- Diffusion of ions inside of pores
 - Rapid electrochemical adsorption and desorption

Experimental setup

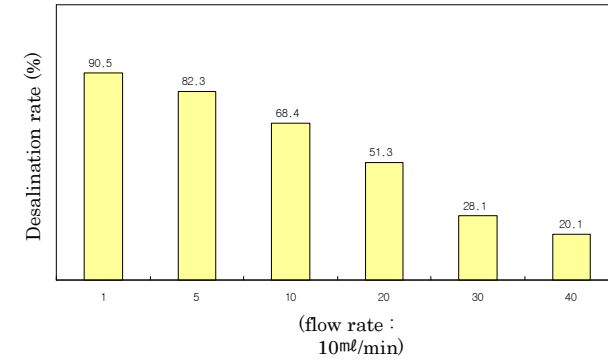


Nitric ion removal behaviors



Cl⁻ ions in the city water

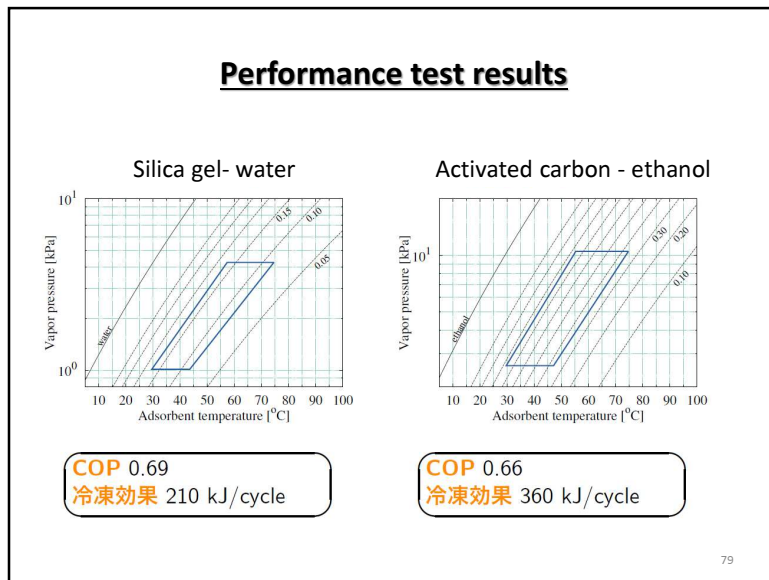
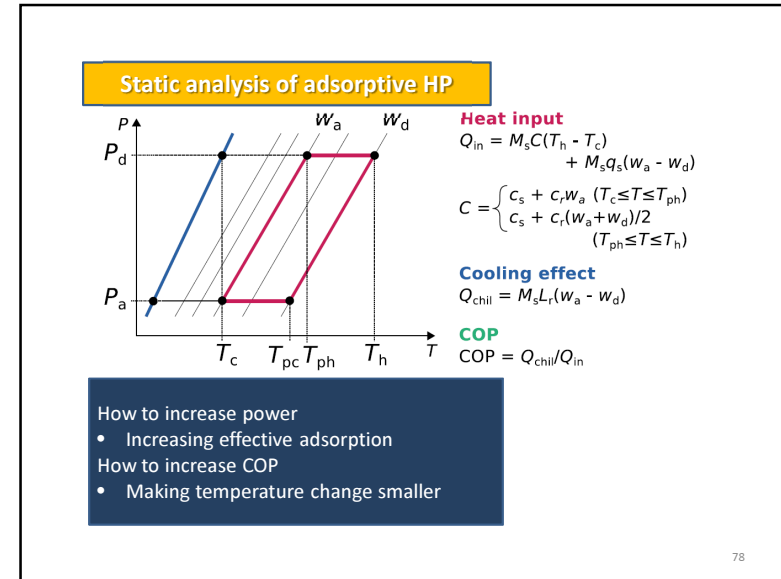
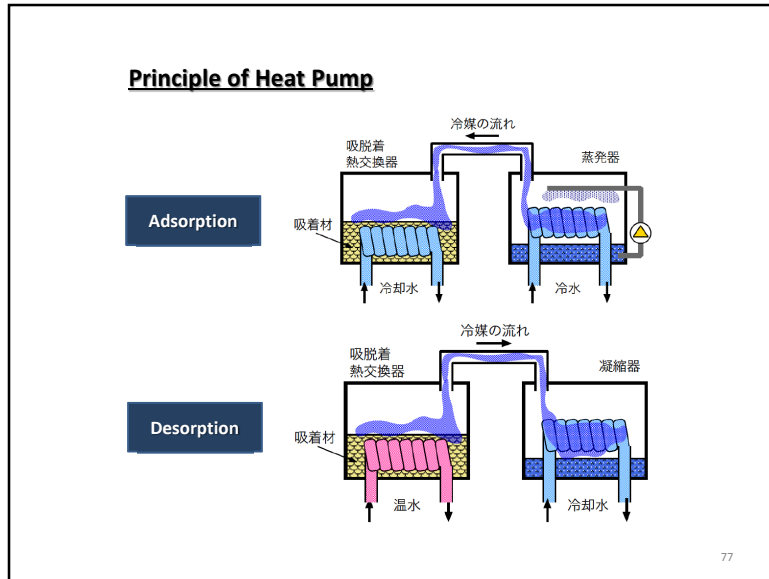
Effect of flow rate



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**



- ### 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

