

第5講義
表面利用

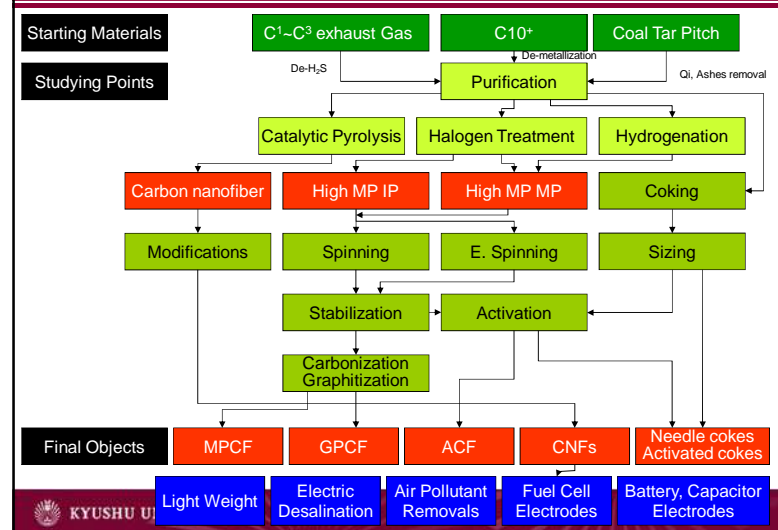
活性炭の応用

Professor Seong-Ho Yoon

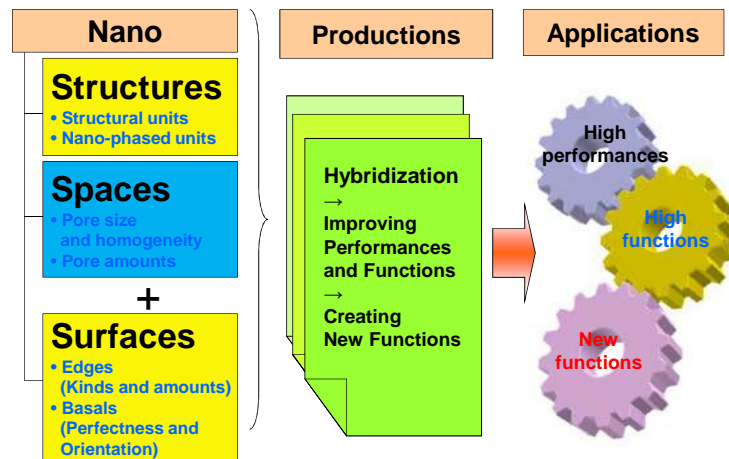
IMCE, Kyushu University
Kasuga, Fukuoka, Japan



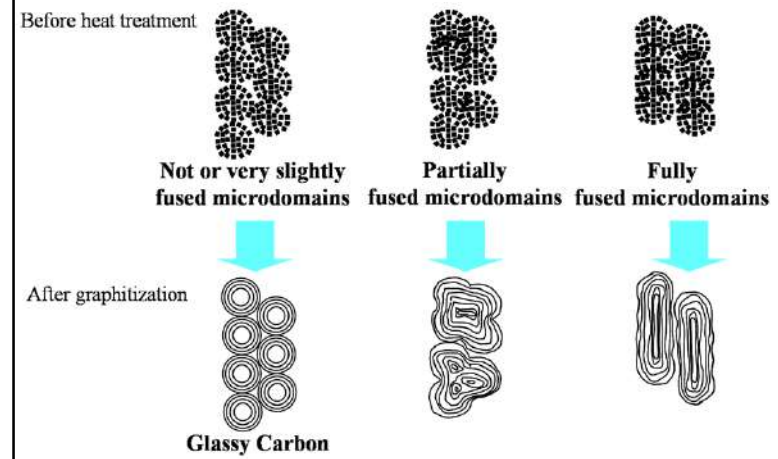
More concrete connections with raw materials to FCs



Understanding carbon structures: Carbon nano-world

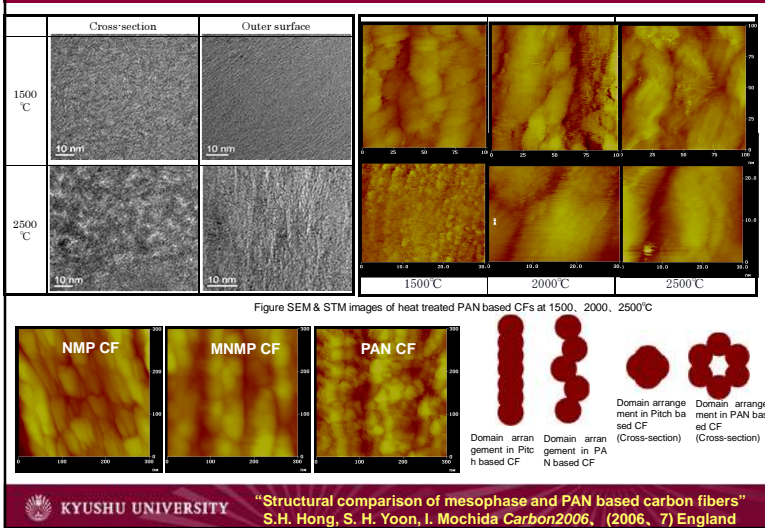


Basic structure and structural control of carbon



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

Nanoscopic Structure of PAN Based CF



Key Materials for Energy and Environmental Devices

Carbon is an Indispensable Material for Energy related Devices

Best Structure for Best Performance

Best Selection

Best Selection

Scientific Cycle

- Structural Understanding
- Structure Preparation
- Working Mechanism
 - Molecular Level
 - Electrochemical
 - Catalytic / Kinetics
 - Molecular / Heat Transfer

Carbon

KYUSHU UNIVERSITY

Preparation of 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

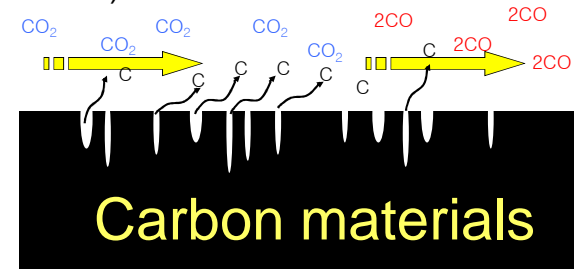
- CO_2 , H_2O
- Alkali Hydroxides / Carbonates; More Research
- Selective Catalytic Gasification ; Catalyst Control

- ❖ Very Large Surface Area > 3000 m^2/g
- ❖ Adequate Pore And Wall

KYUSHU UNIVERSITY

7

Activation (Making small pores in the carbon materials)

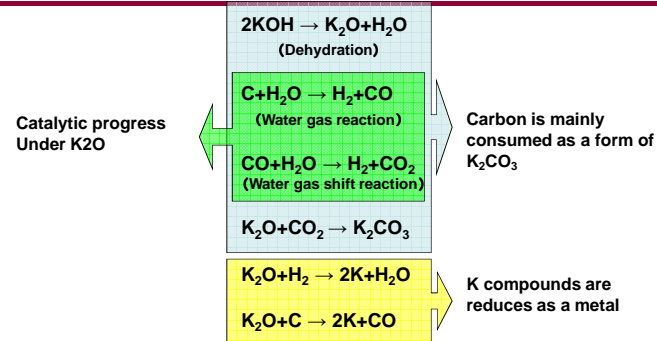


Activation reagents

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

KYUSHU UNIVERSITY

KOH Activation



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

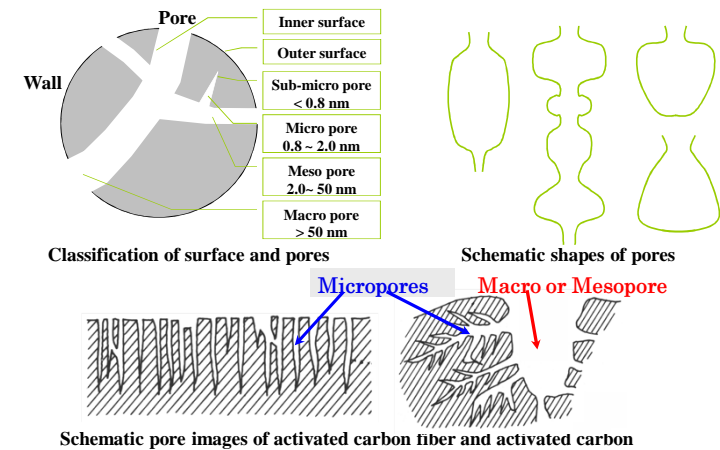
KOH
MP: 380°C
BP: 1324°C

K₂O
MP: 490°C (350°C, KO and K)

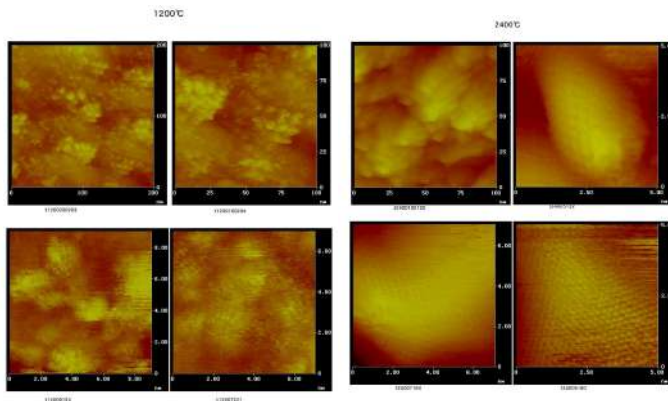
K₂CO₃
MP: 891°C

K
MP: 64°C
BP: 774°C

Activated carbon : Images of pores



Glassy carbons from Novolak resin



Structure 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

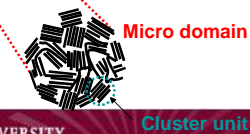
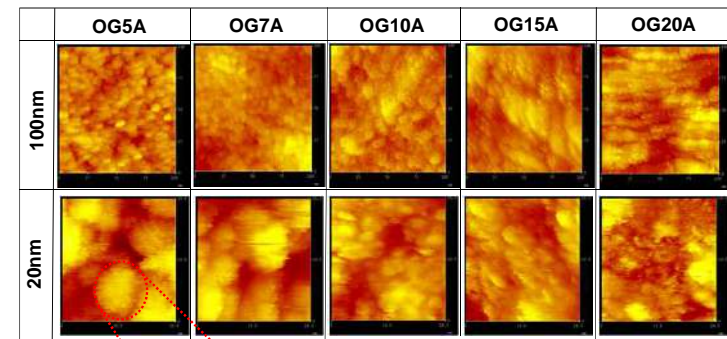
Some properties of pitch based ACFs

- ◆ Pitch-based activated carbon fibers (ACFs) used in this study.
OG5A, OG7A, OG10A, OG15A and OG20A were provided by Osaka Gas Co.

Some physical properties of ACFs given by Osaka Gas Co.

	OG5A	OG7A	OG10A	OG15A	OG20A
Specific surface area (m ² /g)	480	850	1300	1725	2000
Average pore size (nm)	1.4	1.6	1.8	1.9	2.2
Average pore volume (cm ³ /g)	–	0.38	0.54	0.81	1.13

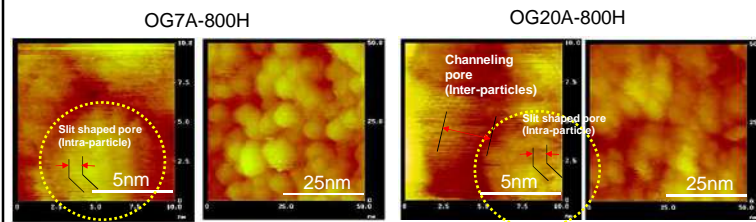
STM images of ACFs



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

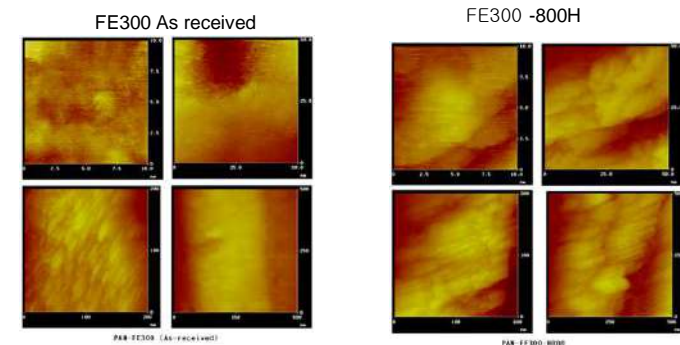
STM images of ACFs

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.

STM images of PAN Based ACFs



- ♣ FE300 is also composed of micro-domain structures.
- ♣ Basic structural units of PAN based ACF are more difficult to observe because of high heterogeneous effects of surface heterogeneous atoms and many defects.

Activation of carbons

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

Structural factor should be considered for the better understanding of activated carbons and their applications.

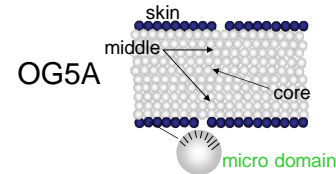
Size and arrangement of BSU
Etching and diffusion of oxidative agent against BSU

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

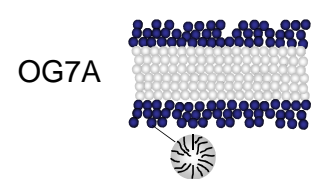
Pores from interparticles (Channeled shaped having wider pore size distributions (0.2 ~ 50 nm))

Mechanism of the pore formations in ACFs

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.

Mechanism of the pore formation in ACFs

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.

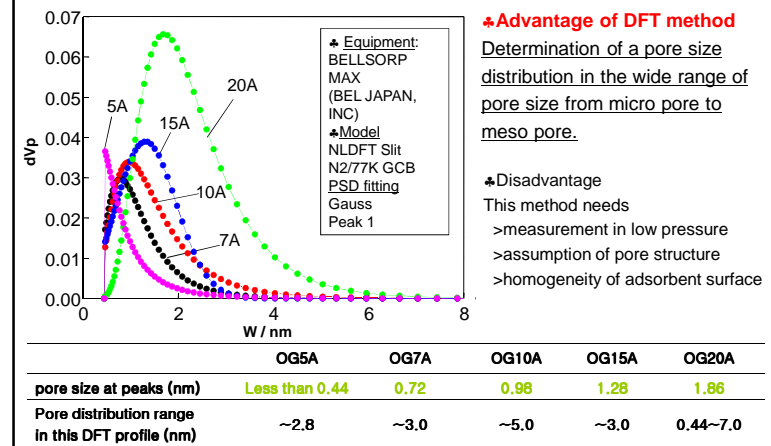
More homogeneous pore distribution than that of OG10A

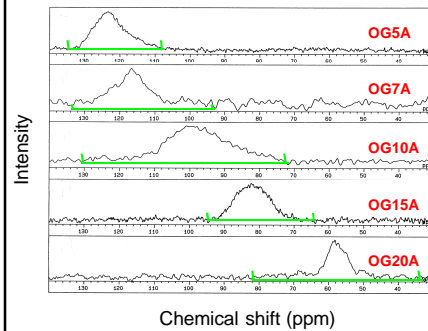
OG20A

- 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.

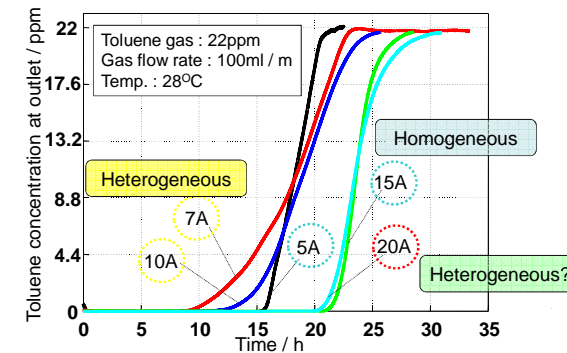
Pore distribution using NLDFT method



^{129}Xe -NMR spectrum of ACFs

	pore size at peak (nm)	Pore distribution width (nm)
OG5A	0.84	0.81~0.98
OG7A	0.89	0.79~1.15
OG10A	1.04	0.82~1.50
OG15A	1.23	1.15~1.55
OG20A	1.49	1.32~3.84

- ◆ Chemical shift at highest intensity, corresponding to pore size, increased in the order of OG5A < 7A < 10A < 15A < 20A.
- ◆ 5A and 15A exhibited narrow peaks. → relatively **homogeneous pore size**
- ◆ Peak broadening can be seen for 7A, 10A and 20A. → **heterogeneous pore size**

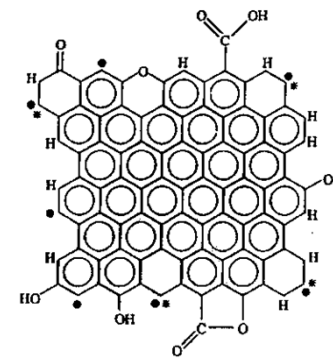
Toluene adsorption characteristics of ACFs

- ◆ 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.

Some Properties of ACFs

Pitch based ACF	BET (m ² / g)	Elemental analysis (wt %)					N / C
		C	H	N	O		
OG5A	563	92.4	0.6	0.7	6.0		0.007
OG7A	901	93.0	0.6	0.8	5.4		0.007
OG10A	1085	95.3	0.6	0.5	3.4		0.004
OG15A	1606	95.2	0.6	0.3	3.4		0.003
OG20A	1924	94.1	0.6	0.4	4.8		0.003

PAN based ACF	BET (m ² / g)	Elemental analysis (wt %)					N / C
		C	H	N	O		
FE100	450	70.9	2.0	8.4	17.3		0.102
FE200	650	72.5	1.8	4.8	17.9		0.057
FE300	880	74.3	1.6	3.3	17.2		0.038
FE400	1020	76.8	1.6	2.3	19.4		0.026

Surface Oxygen Functional Groups of ACF

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

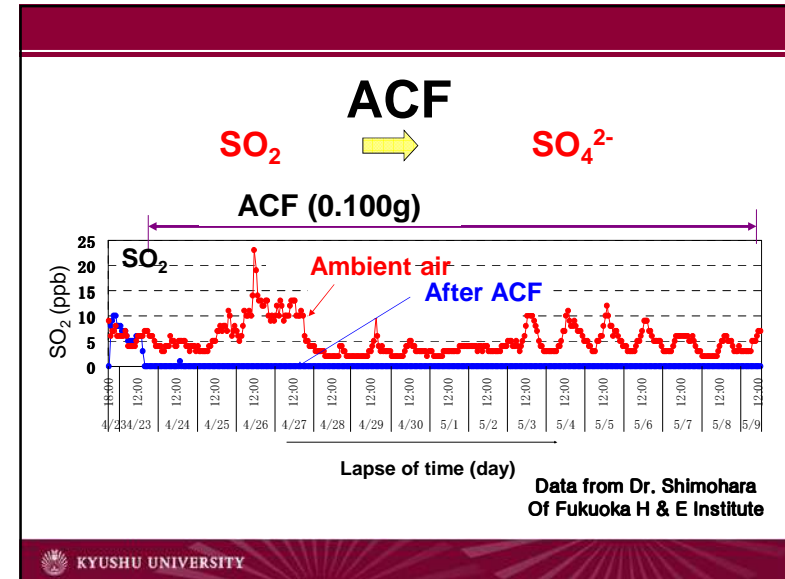
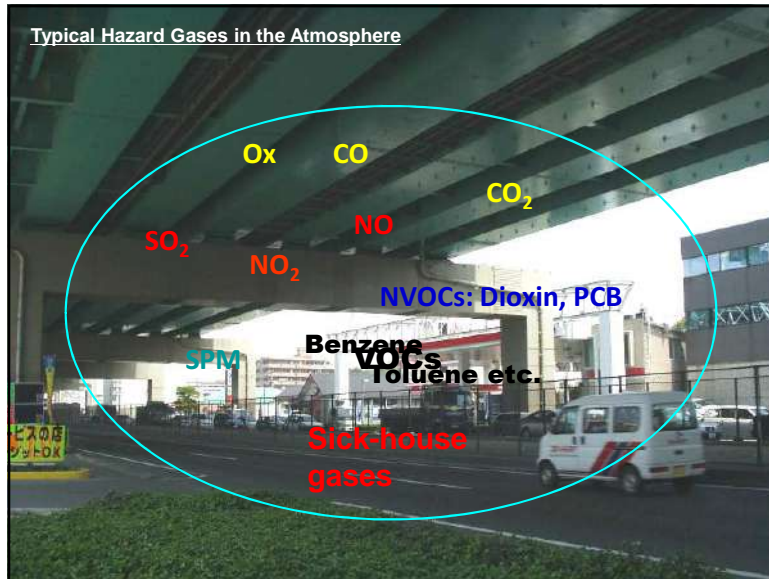
Some Properties of ACFs

Pitch based ACF	BET (m ² / g)	Elemental analysis (wt %)				N / C
		C	H	N	O	
OG5A	563	92.4	0.6	0.7	6.0	0.007
OG7A	901	93.0	0.6	0.8	5.4	0.007
OG10A	1085	95.3	0.6	0.5	3.4	0.004
OG15A	1606	95.2	0.6	0.3	3.4	0.003
OG20A	1924	94.1	0.6	0.4	4.8	0.003

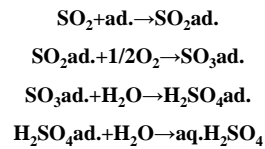
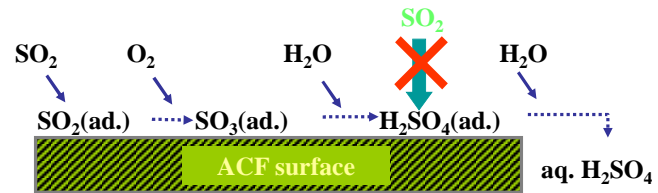
PAN based ACF	BET (m ² / g)	Elemental analysis (wt %)				N / C
		C	H	N	O	
FE100	450	70.9	2.0	8.4	17.3	0.102
FE200	650	72.5	1.8	4.8	17.9	0.057
FE300	880	74.3	1.6	3.3	17.2	0.038
FE400	1020	76.8	1.6	2.3	19.4	0.026

Removal of SO_x and NO_x Using ACFs

Typical Hazard Gases in the Atmosphere



DeSOx mechanism using ACF



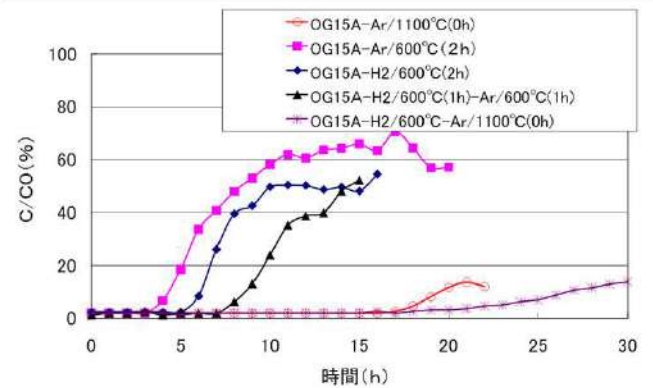
Active Sites on Carbon Surface

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 SO₂ Removal

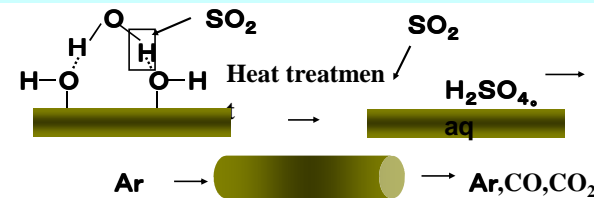
Optimum Post-Heat treatment with Reductive Oxygen Removal



SO₂ 1000ppm, O₂ 5vol.%, H₂O 10vol.%, N₂ balance, Flow rate: 100ml/min,
Temperature: 50°C

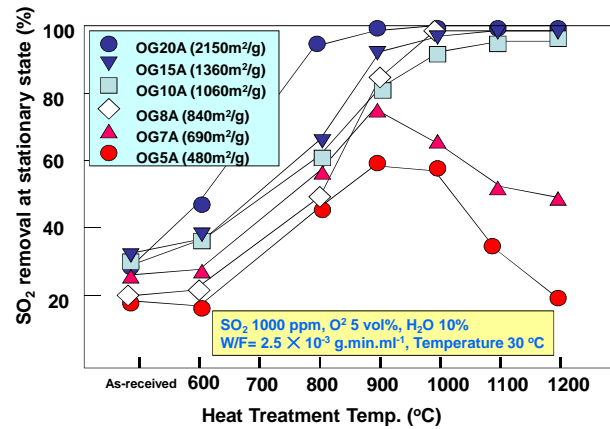
Effect of Heat Treatment

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

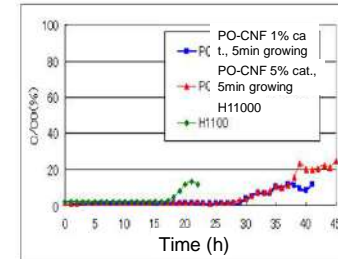
The Effect of Heat Treatment for SO₂ Removal



KYUSHU UNIVERSITY

DeSOx by ACF and CNF-ACF Composite

DeSOx Properties of ACF and ACF-CNF



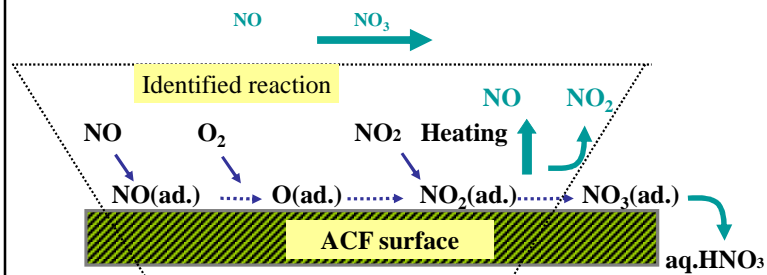
DeSOx condition: SO₂ 1000ppm, O₂ 5vol%, H₂O 10vol%, N₂ balance, Total flow rate: 100 ml/min, Reaction Temperature: 50 °C



PDU for SOx Removal by ACF

KYUSHU UNIVERSITY

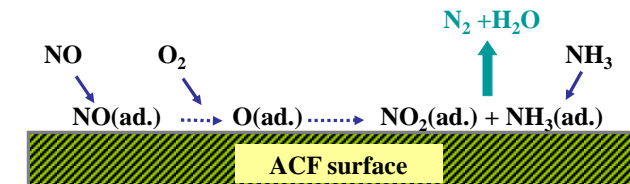
NO & NO₂ Oxidation over ACF



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

KYUSHU UNIVERSITY

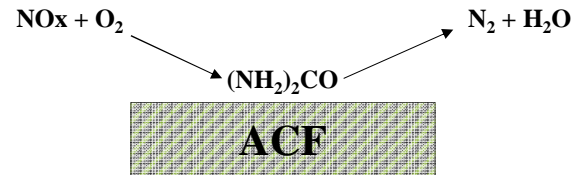
The Mechanism of NO Reductive Removal



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

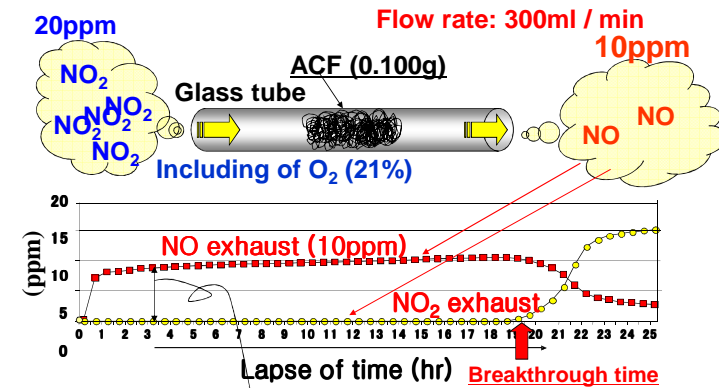
KYUSHU UNIVERSITY

NO_x Reduction at Room Temperature



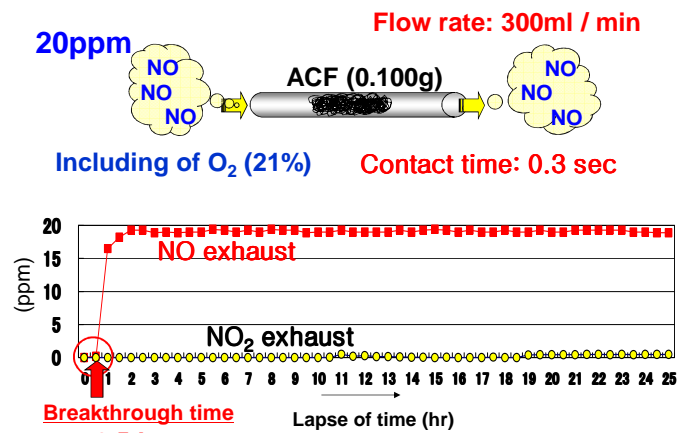
- NO_x oxidation
- Urea Activation
- NO_x in Environment
- Roles of ACF : More variety of ACF

Adsorption of NO₂ in ACF

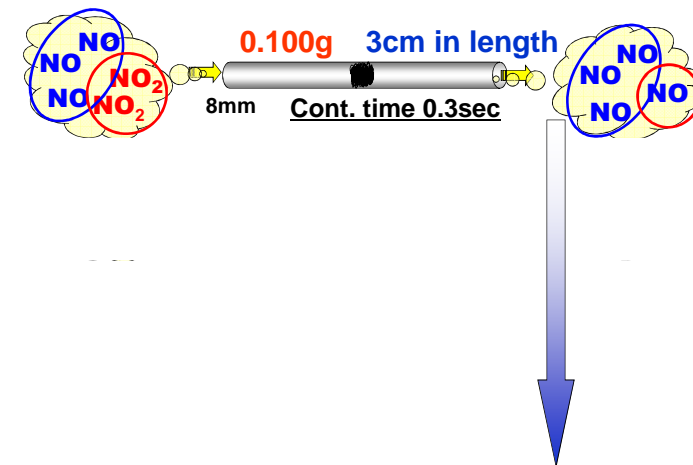


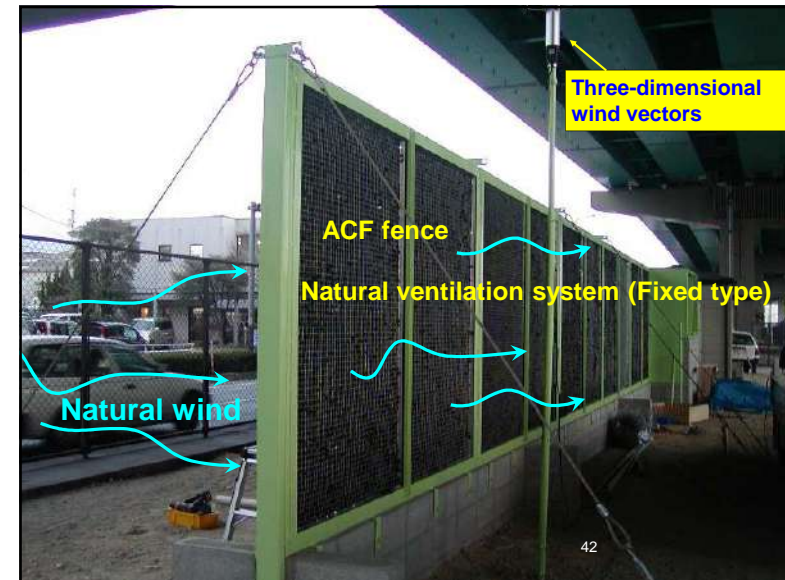
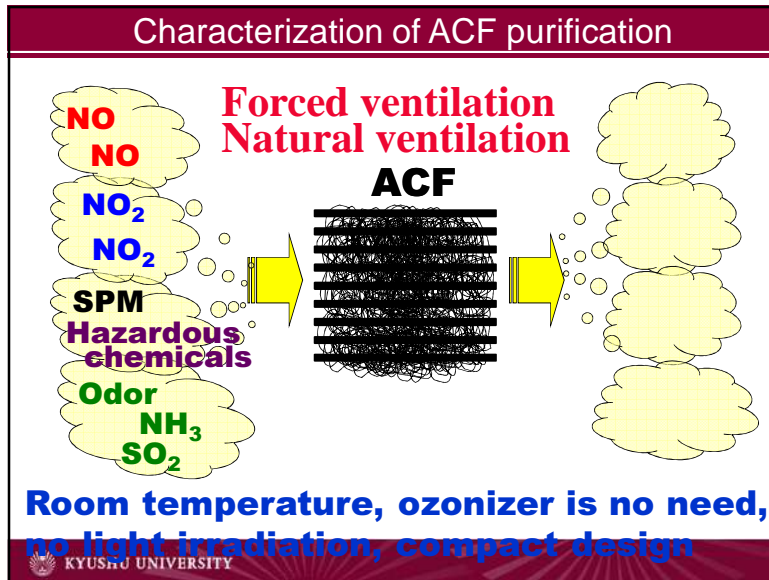
Half amount of adsorbed NO₂ is exhausted as NO.

Scavenging activities against NO



The characteristics of NO_x purification

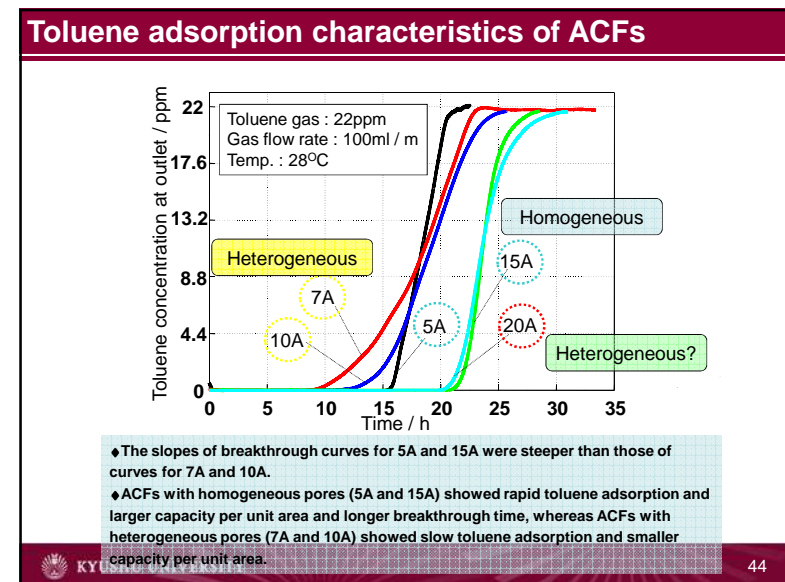




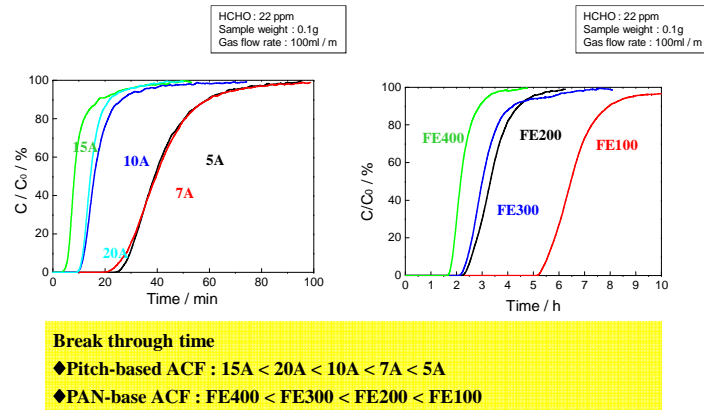
Removal of Sick-house gases using ACF/MnO₂

KYUSHU UNIVERSITY

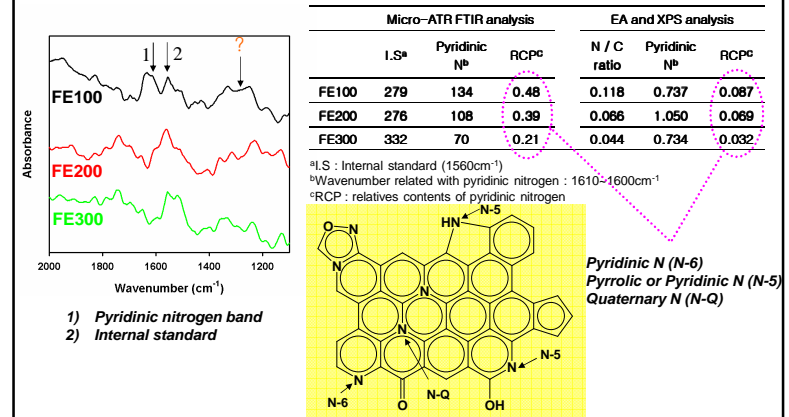
43



HCHO adsorption characteristics of ACFs



Micro ATR-FTIR spectrum of FE series



Micro-ATR FTIR analysis

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

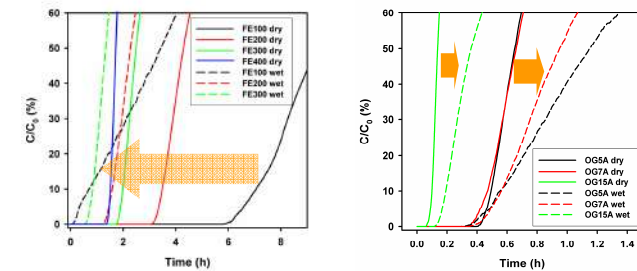
Sample	Internal Standard	Pyridinic N ^a	Internal Standard /Pyridinic N
FE100	279	134	0.48
FE200	276	108	0.39
FE300	332	70	0.21
FE400	330	64	0.19

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

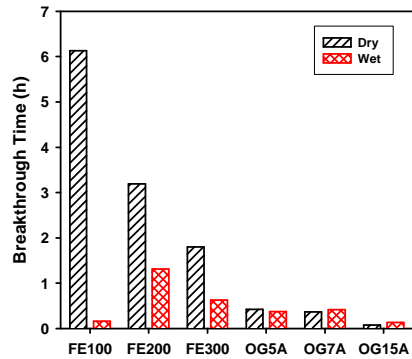
Breakthrough curves of formaldehyde adsorption

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



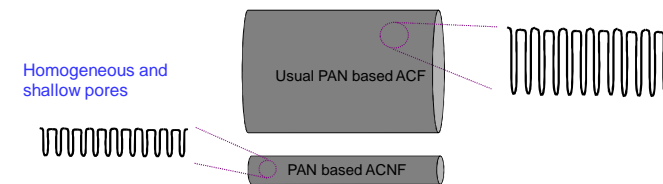
Comparison of formaldehyde adsorption in different ACFs between dry and wet condition



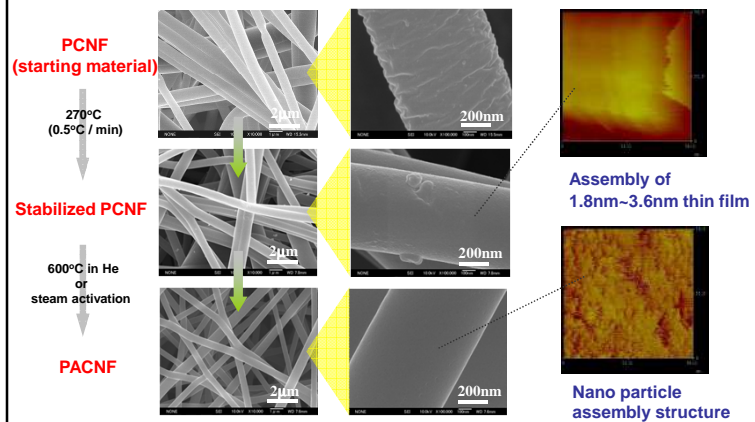
Selection of Precursor for ACF

- ◆ 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.

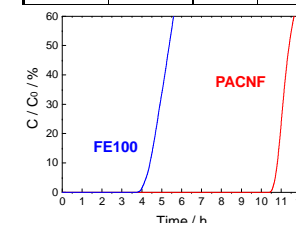


SEM images of PCNF, stabilized PCNF and PACNF

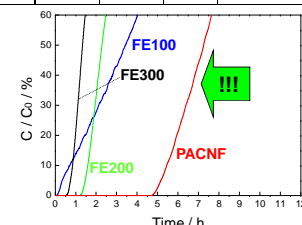


HCHO adsorption characteristics of PACNF in humidified atmosphere

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%



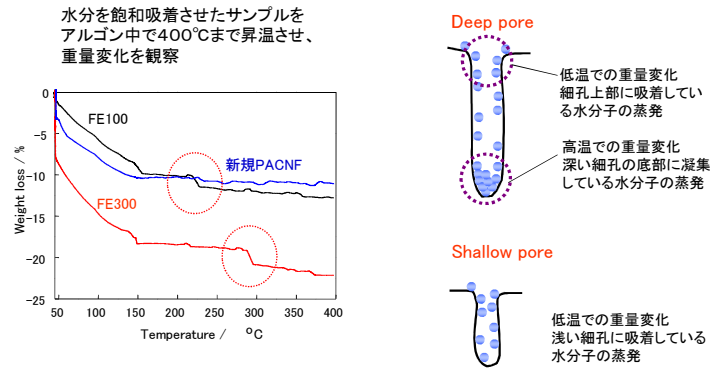
Experimental
HCHO : 11 ppm
Sample weight : 0.05g
Gas flow rate : 100ml / ml
Humidity of condition : 0%



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.

Water adsorption property

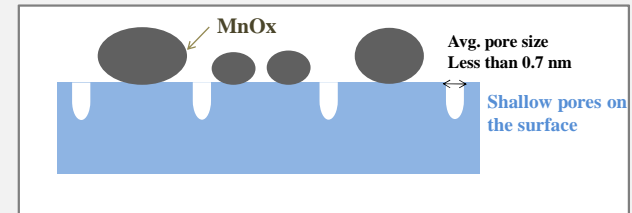


Concept of the newly designed MnOx/ACNF

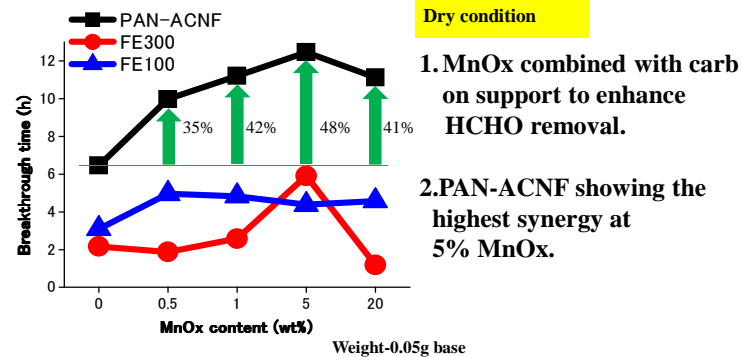
- ① Activated nano carbon fiber ② Catalytic decomposition of HCHO by MnOx into water and carbon dioxide

③ Clean removal into Water and Carbon dioxide
Lifetime prolonged

The conceptual model of MnOx-carbon catalyst



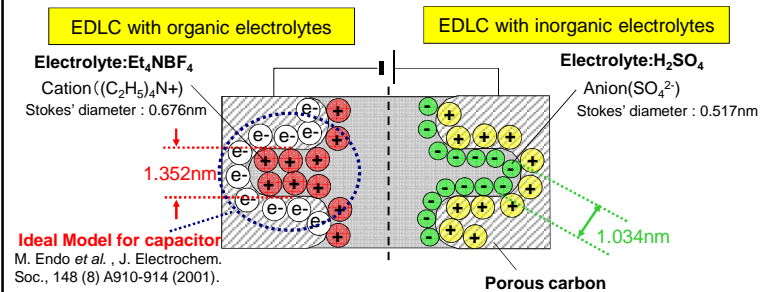
Influence of MnOx content on HCHO breakthrough time



Mn₃O₄ or MnO₂ alone breakthrough in less than an hour.

→ Deposition on carbon support improves catalytic activity of MnOx.

Conjecture of pore size using capacitance data



In using Et₄NBF₄ as an electrolyte, at least pore size larger than 1.3nm is necessary to have electric double layered capacitance.

In using H₂SO₄ as an electrolyte, pore size of about 1.0nm is enough to have electric double layered capacitance.

Samples

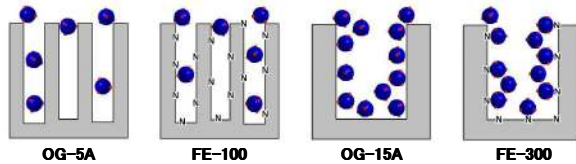
Pitch-based Activated Carbon Fibers (ACFs)

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

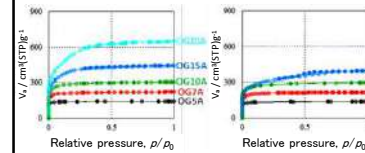


Aqueous and non-aqueous electrolytes with different ion sizes



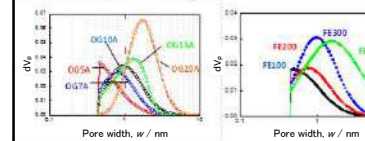
Properties of Activated Carbon

N_2 adsorption/desorption isotherms @77K



Pore size distributions

(calculated by NL-DFT method)

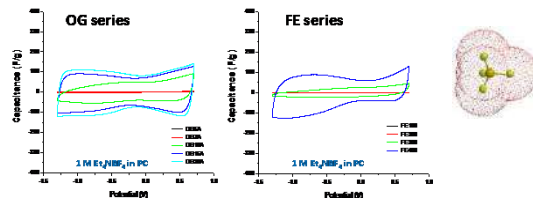


Pore structure parameters (calculated from *t*-plot method)

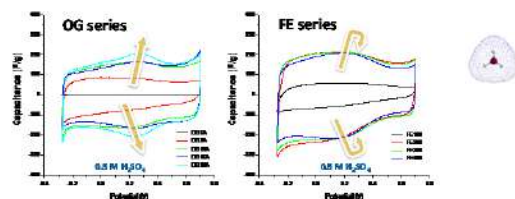
	Surface area (m²/g)				Pore volume (cm³/g)			Pore width (nm)	
	A _{total}	A _{external}	A _{micro}	A _{meso}	V _{total}	V _{micro}	V _{meso}	W _{micro}	W _{meso}
OG-5A	676.8	1.2	675.6	0	0.22	0.22	0	0.85	0.0
OG-7A	987.6	3.4	984.2	0	0.34	0.34	0	0.88	0.0
OG-10A	1211.7	5.4	1206.3	0	0.46	0.46	0	0.77	0.0
OG-15A	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	908.2	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

Cyclic Voltammograms in Aqueous/Non-Aqueous Electrolytes

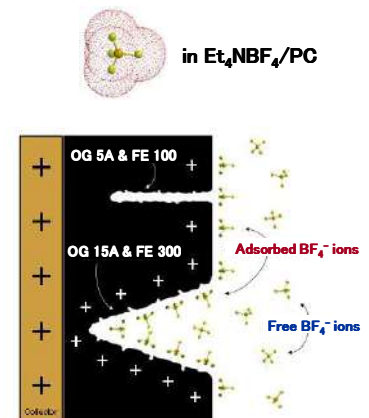
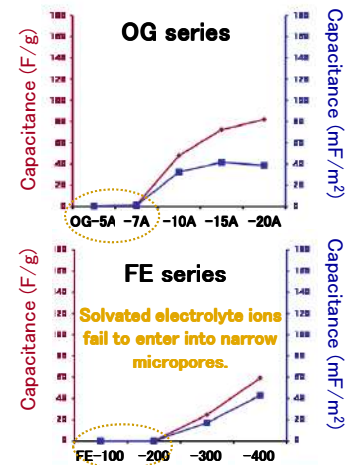
Cyclic voltammograms in 1 M $\text{Et}_4\text{NBF}_4/\text{PC}$

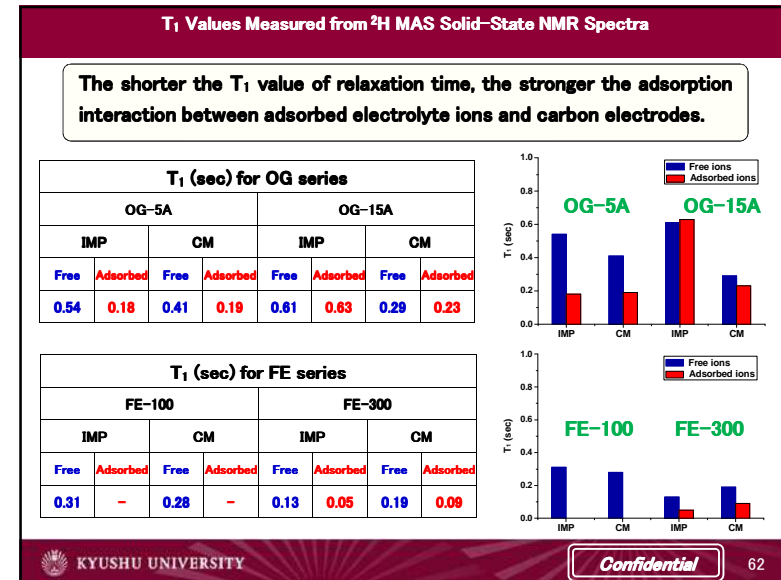
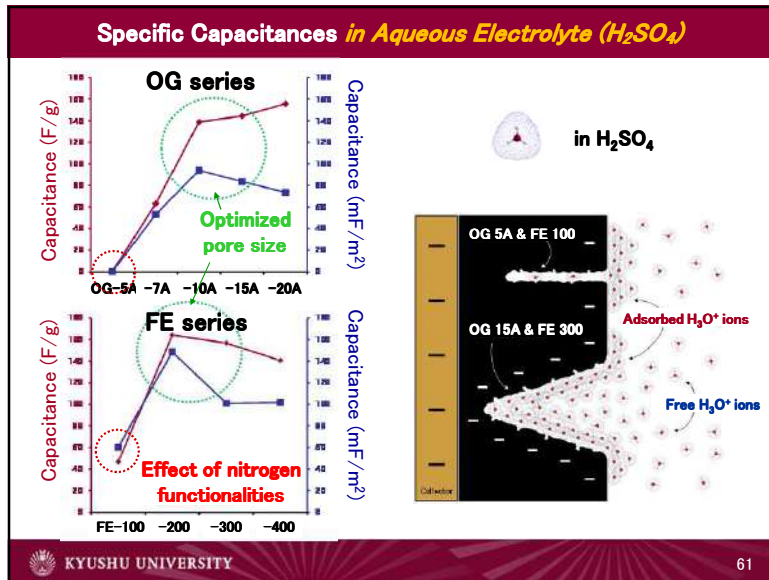


Cyclic voltammograms in 0.5 M H_2SO_4



Specific Capacitances in Non-Aqueous Electrolyte ($\text{Et}_4\text{NBF}_4/\text{PC}$)





Steam vs. Chemical Activations

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?

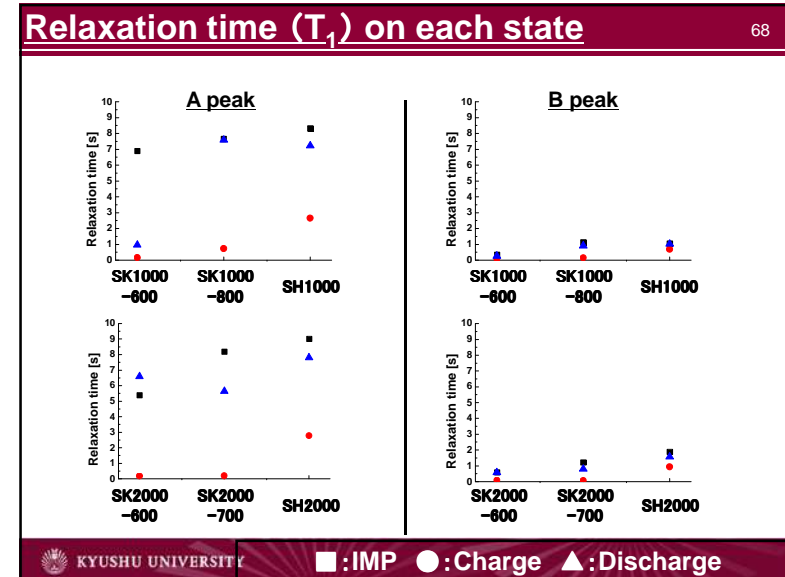
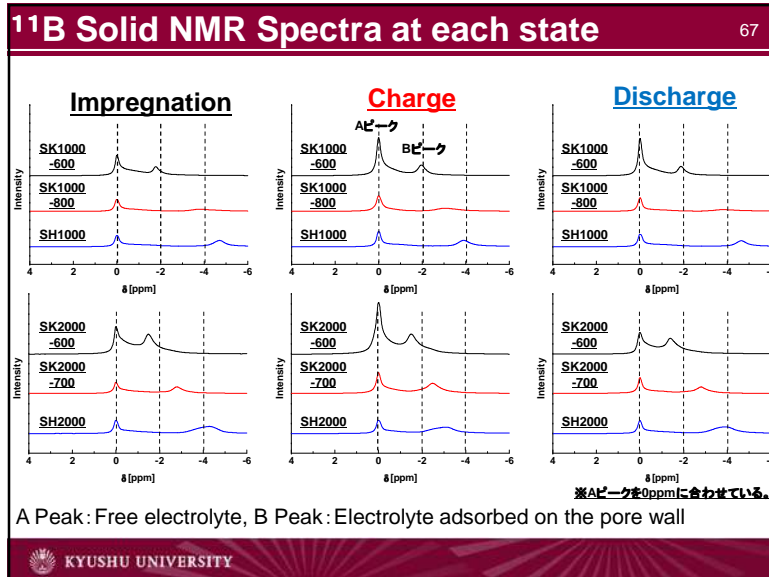
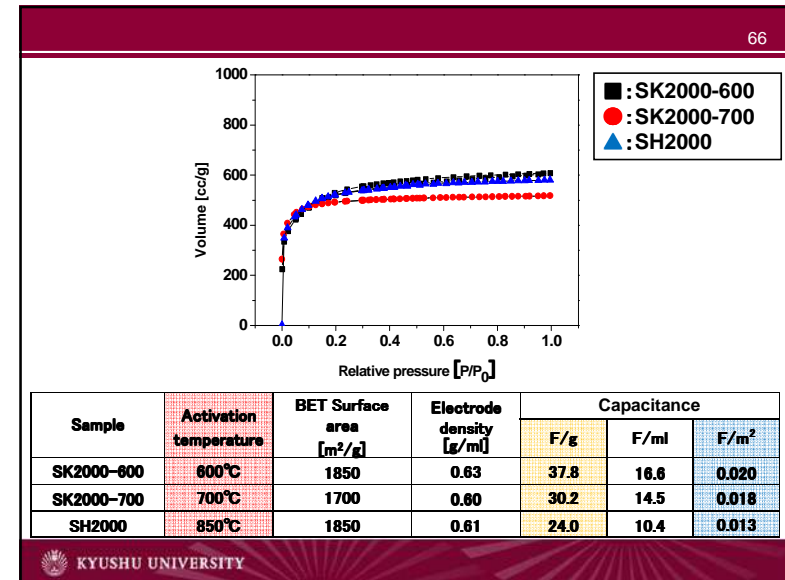
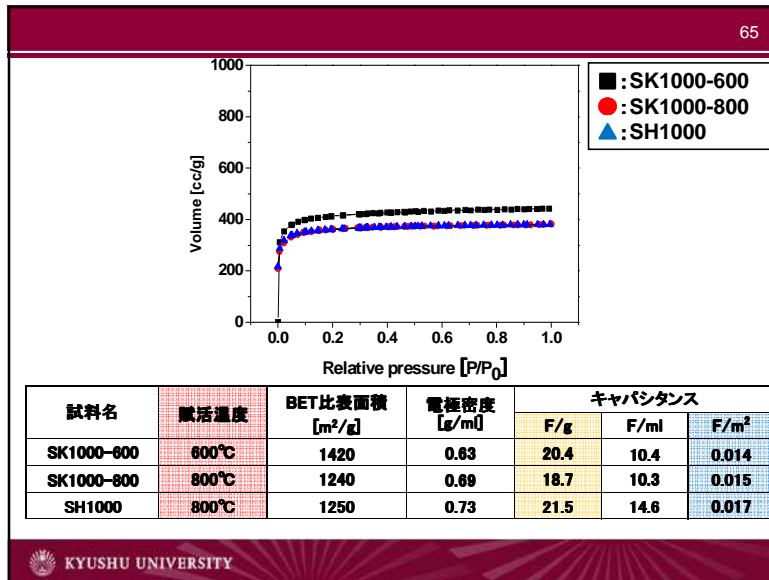
Structure of Activated Carbon

• Surface Area, Pore: Depth & Volume

Surface Structure
Surface Chemistry
Based and Edge Plane
Hetero atoms in Hexagon

• Carbon Structure of Wall

Nano, Micro, Macro Structure of Carbon Wall
-Graphitization Extent
-Domain Structure
→ Density, Reactivity (Activated Surface)
Precursor : Structure and Reactivity

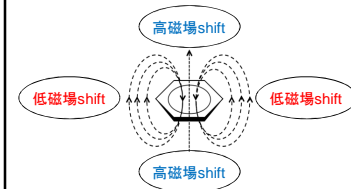


Discussion

69

Effect of wall surface

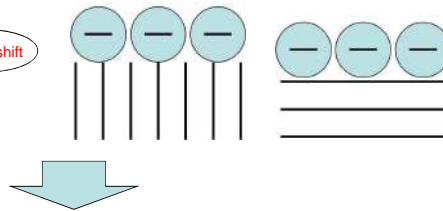
Contribution to chemical shift (Ring current effect)



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

KYUSHU UNIVERSITY

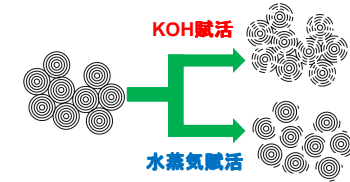
Discussion

70

Difference of chemical and steam activations

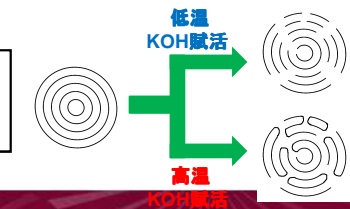
Methodological effect

KOH: Edge surface
 Steam: Basal surface



Conditional effect

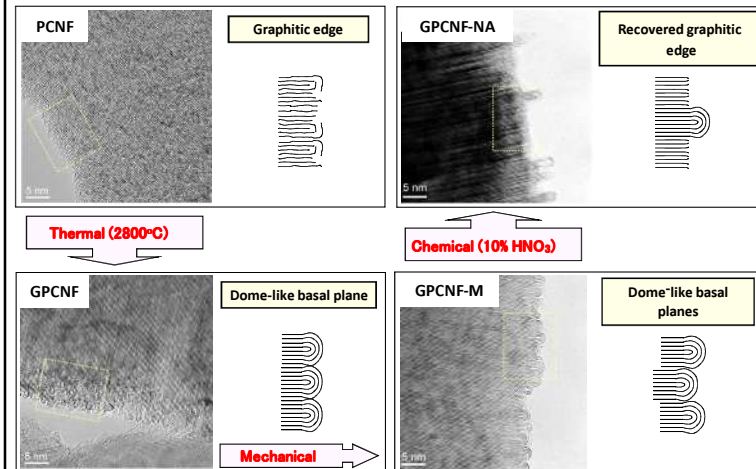
Less than 600°C:
 Most pore walls have edge
 containing surfaces



KYUSHU UNIVERSITY

Surface modified PCNFs

Langmuir
 2006, 22(22), 9086.

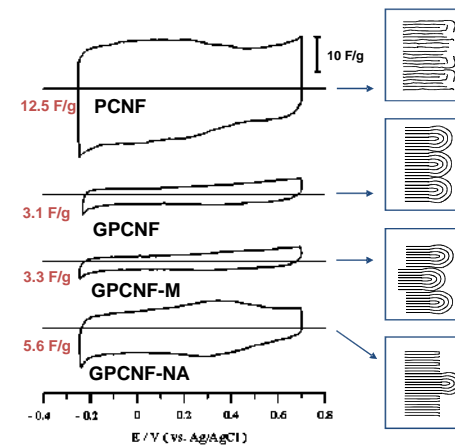


KYUSHU UNIVERSITY

71

Capacitances of PCNF series

Langmuir
 2006, 22(22), 9086.



PCNFs having
 edge surfaces
 Showed 3-5 times
 Higher capacitances

KYUSHU UNIVERSITY

72

Conclusion

- Carbon is a key material for energy and environmental devices.
- Full understanding of carbon structure is necessary for useful applications
- Korea has a lot of sources for carbon materials.
- No manpower and skill for carbon manufacturing.

University:

- ❖ Changing the consciousness
- ❖ Creation and leading of projects
- ❖ Manpower cultivation