

先端炭素材の調製と応用

1. バインダー、ニードルコークス
2. Li-ion電池用負極材
3. ピッチ系炭素繊維
4. 活性炭及び活性炭素繊維

九州大学先導物質化学研究所、教授

尹 聖昊

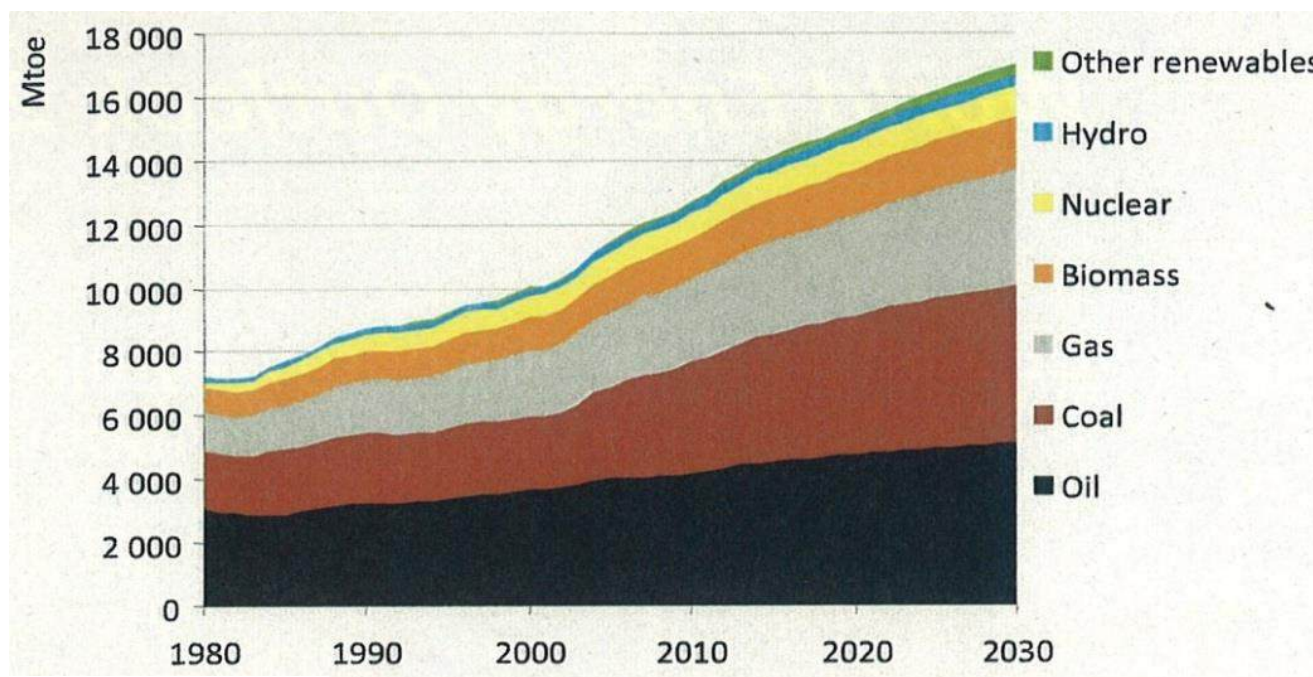
2013年9月27日



九州大学

先端炭素材開発のNeedsとSeeds

1



	1980	2000	2006	2015	2030	Annual average increase rate 2006-30
Coal	1788	2295	3053	4023	4908	2.0%
(US)			551	580	633	0.6%
(China)			1214	1898	2441	4.0%
(India)			223	315	579	6.0%
Petroleum Oil	3107	3649	4029	4525	5109	1.0%
Gas	1235	2088	2407	2903	3670	1.8%
Nuclear Power	186	675	728	817	901	0.9%
Hydraulic Power	148	225	261	321	414	1.9%
Biomass	748	1045	1186	1375	1662	1.4%
Other Renewables	12	55	66	158	350	7.2%
Total	7223	10034	11730	14121	17014	1.6%

Approx. 45% increase

Three countries - U.S., China, and India - account for 75% in 2030



•Marked Increase of Energy Demand in Asia and Africa in 21st Century

- ❖ Population x Demand/Head
- ❖ Three to Four Times of Current Demands of Fossil Fuels ⇒ Increasing By-products of Fossil Fuels

Issues

- ▣ Supply
- ▣ CO₂ Emission Enhances Global Warming
- ▣ Effective utilization of by-products of fossil fuels

Raw materials and precursors for carbons

Raw materials

Coal tar

Polymer: Thermosetting and thermoplastic

Heavy oil and residues

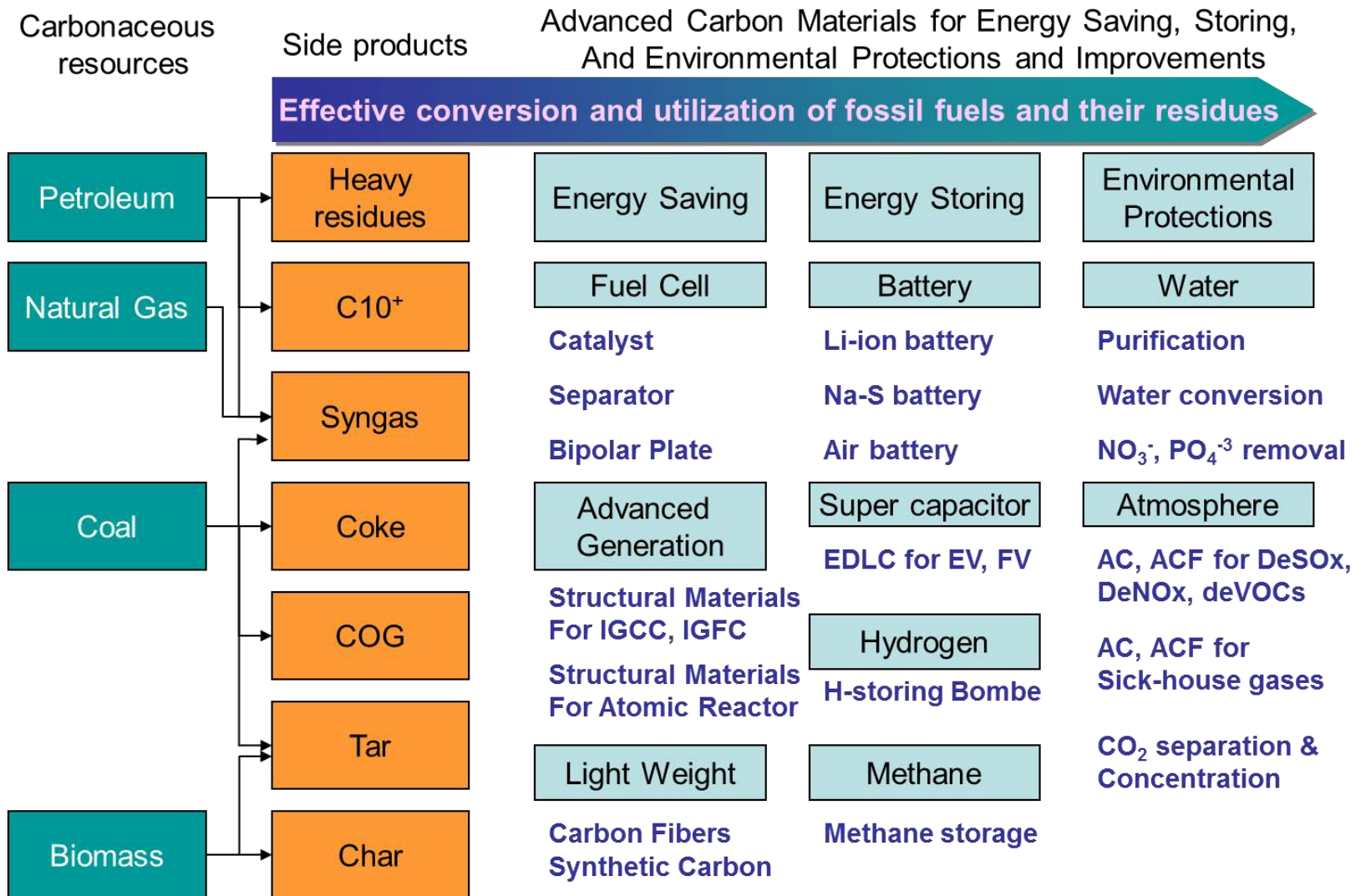
Biomass

Precursor

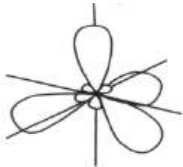
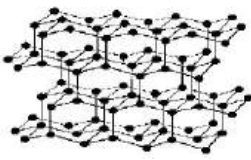
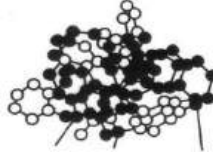
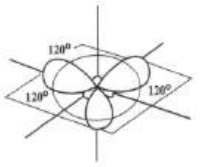
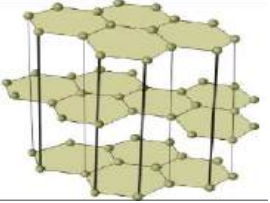
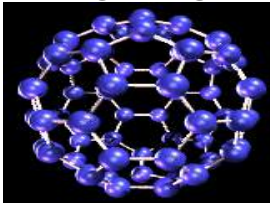
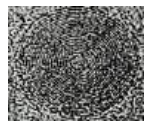
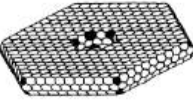
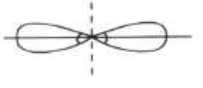
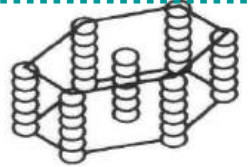
- Pitches: CF, ACF, MCMB, Ball type AC, Binder pitch, Additives
- Polymer: AC, ACF, Glassy carbon, CF
- Cokes: Electrode, Capacitor, Battery anode, AC, Additives
- Char: AC, Additives, Reducer for Solar cell



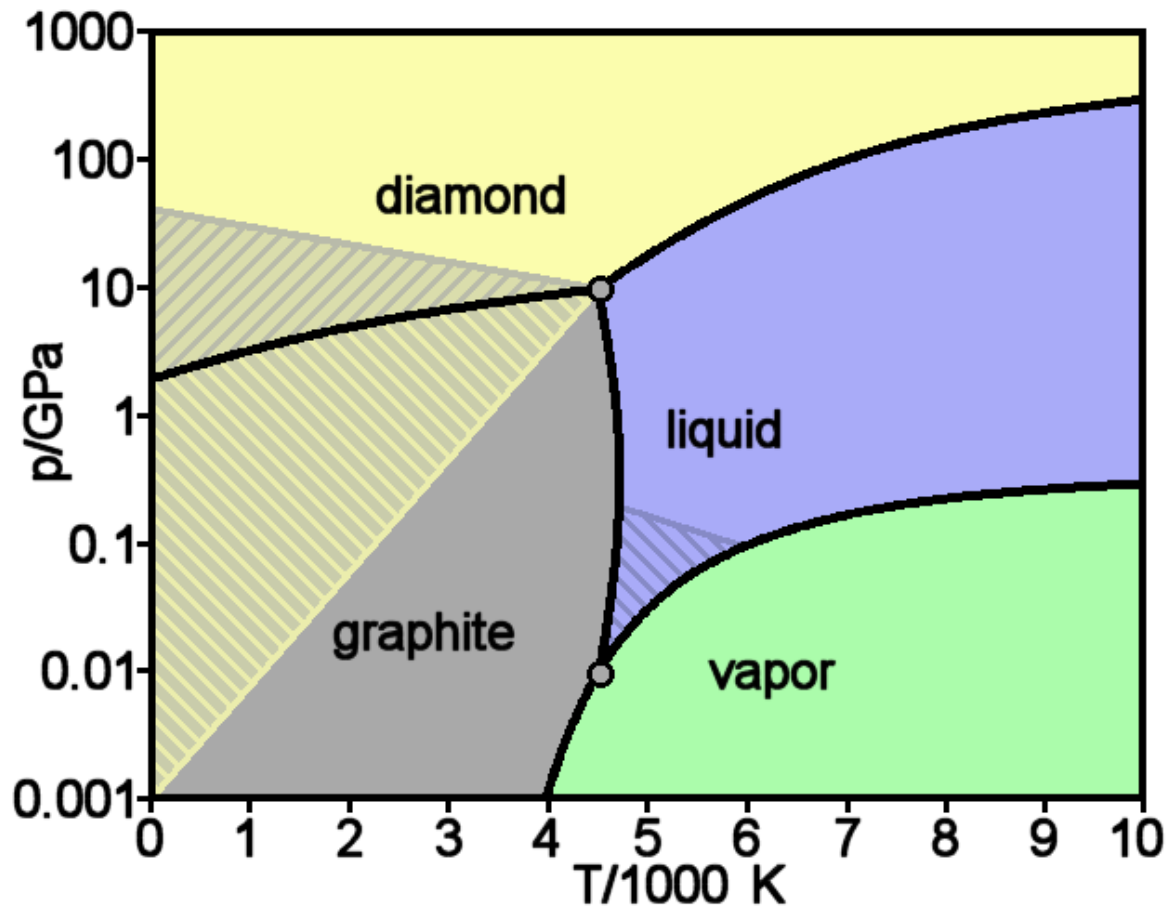
From fossil fuel to functional carbons



Carbon Isotopes

Bonding Hybridization	Allotropes	Derived and Defective Forms
 sp^3	 Cubic diamond	 Diamond-like Carbon
 sp^2	 Hexagonal graphite	 Poly-crystallin  Carbon Black  Activated Carbons  Cokes  Carbon Fibers
 $sp^{2+\epsilon}$ rehybridization	 Fullerene	 Bucky Onions  Toroidal Structures  Acetylene Blacks  Nanotubes
 sp^1	 Carbyne	Ref.) Bourrat, X. Structure in Carbons and Carbon Artifacts. In: <i>Sciences of Carbon Materials</i> . Marsh, H.; Rodriguez-Reinoso, F., Eds., Universidad de Alicante, 2000. pp1-97.

炭素の状態図



0.001GPは10気圧に相当する

炭素の物理特性

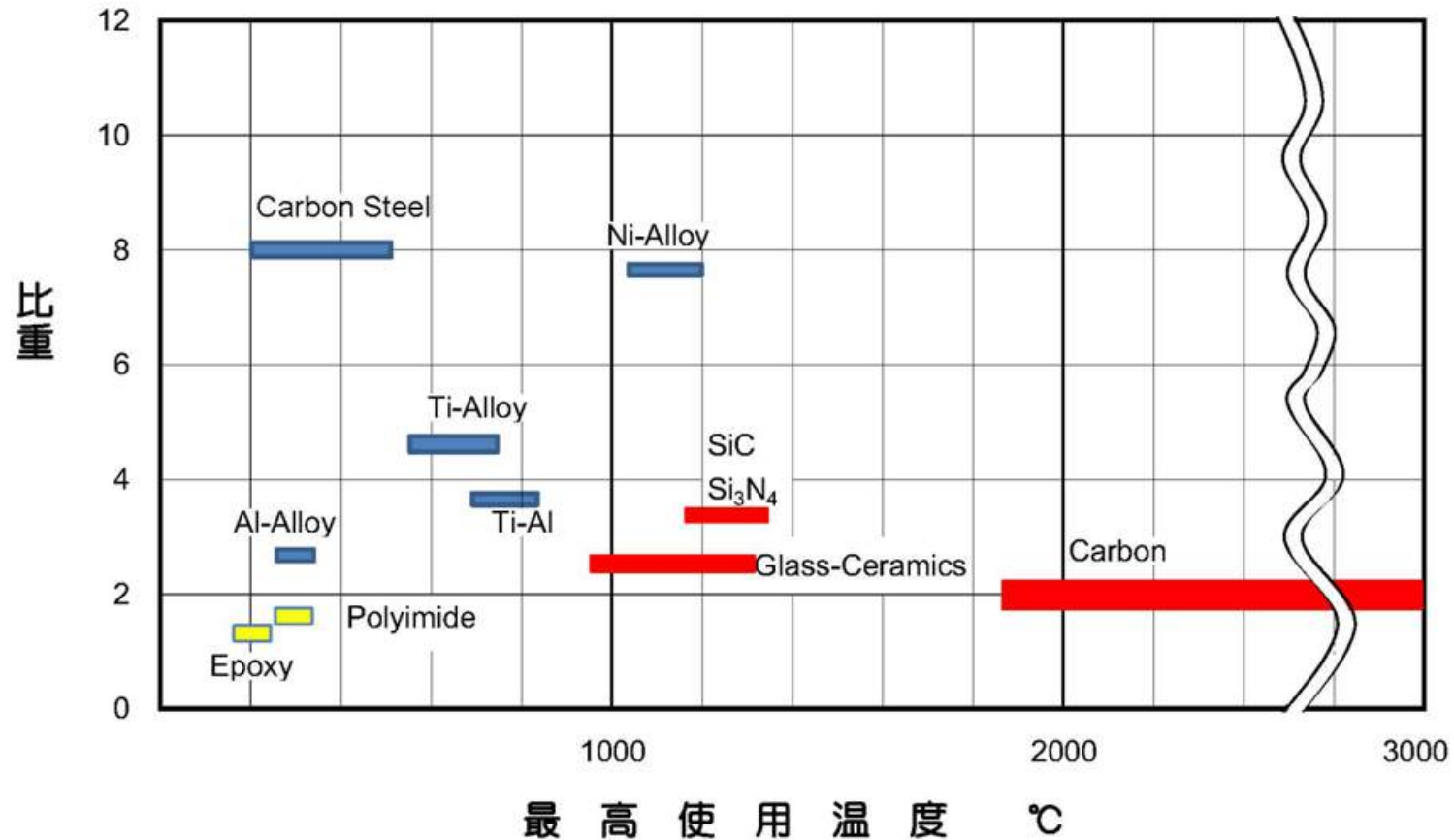
<u>相</u>	<u>固体</u>
<u>融点</u>	3823 <u>K</u> (3550 °C)
<u>沸点</u>	5073 K (4800 °C)
<u>気化熱</u>	355.8 kJ · mol ⁻¹
<u>音の伝わる速さ</u>	18350 <u>m · s⁻¹</u> (293.15 K)



黒鉛の化学反応性

雰囲気又は反応対象物	反応温度 (°C)	反応生成物
大気中	400	酸化
水蒸気中	700	酸化
水素ガス中	1,100	CH ₄ ガス
真空中	2,200	気化
窒素ガス中	2,500	C ₂ N ₂
Al	800	Al ₄ C ₃
B	1,600	B ₄ C
Fe	600-800	Fe ₃ C
W	1,400	W ₂ C, WC (水素中)

各種材料の耐熱性と比重

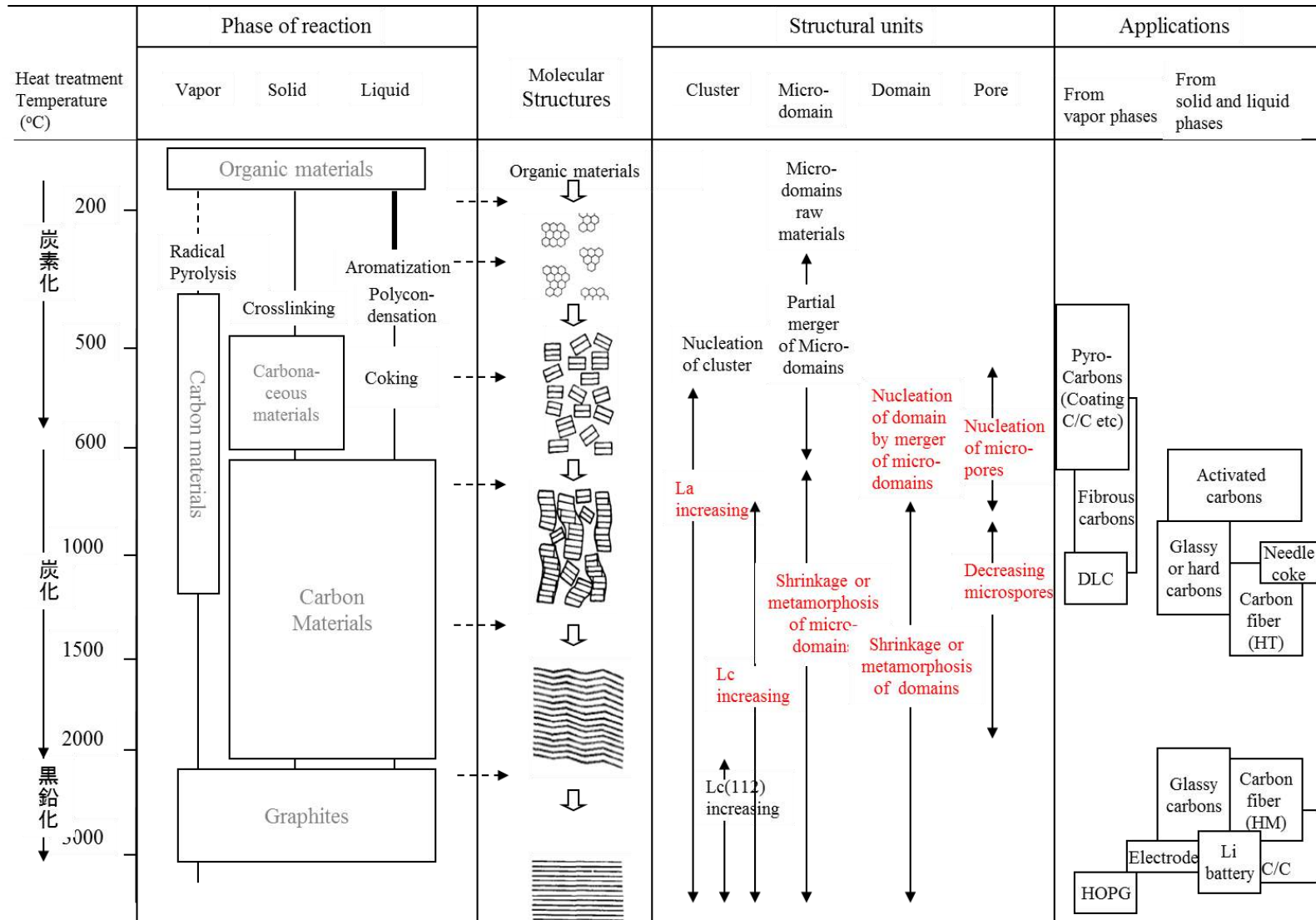


炭素化反応

炭素の生成反応



炭素の生成(固・液相)

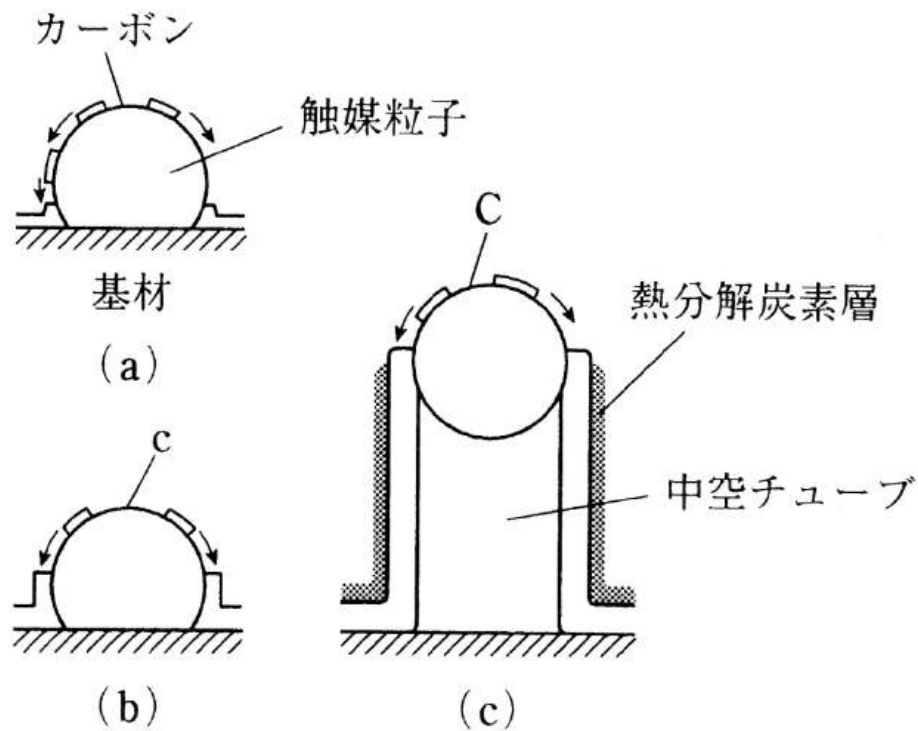


炭素化プロセスと特徴

プロセス	原料	炭素材料	特徴
気相炭化	揮発性有機物	カーボンブラック 熱分解炭素 カーボンホイスカー	超微粒 高配向性 高強度、高電導性、 高弾性
液相炭化	溶融溶解性有機物、溶融性石炭	コークス 人造黒鉛 高密度等方性黒鉛	高異方性 高異方性、高電導性 等方性、高密度
固相炭化	不融性繊維状有機物 熱硬化性高分子 木材、非溶融性石炭	炭素繊維 ガラス状炭素 活性炭 モレキュラーシーブ カーボン	高強度、高弾性 高強度、ガス不適過 多孔性、吸着 分子ふるい



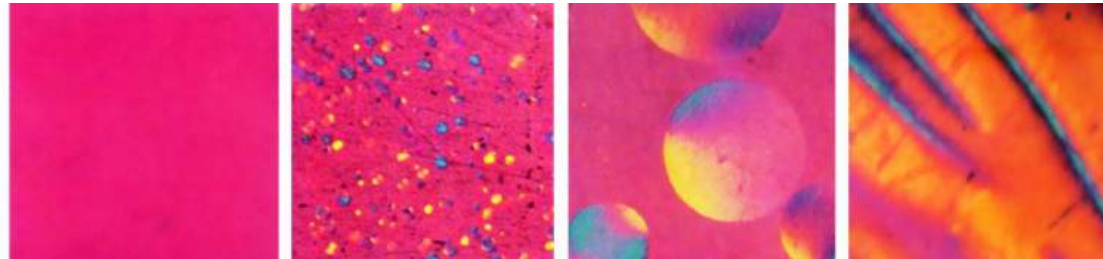
VGCF、CNTの成長モデル



T. Bairdモデル; (a)→(b)→(c)の順に成長

典型的な液相炭化反応の様相

低 熱処理温度 高
短 熱処理時間 長

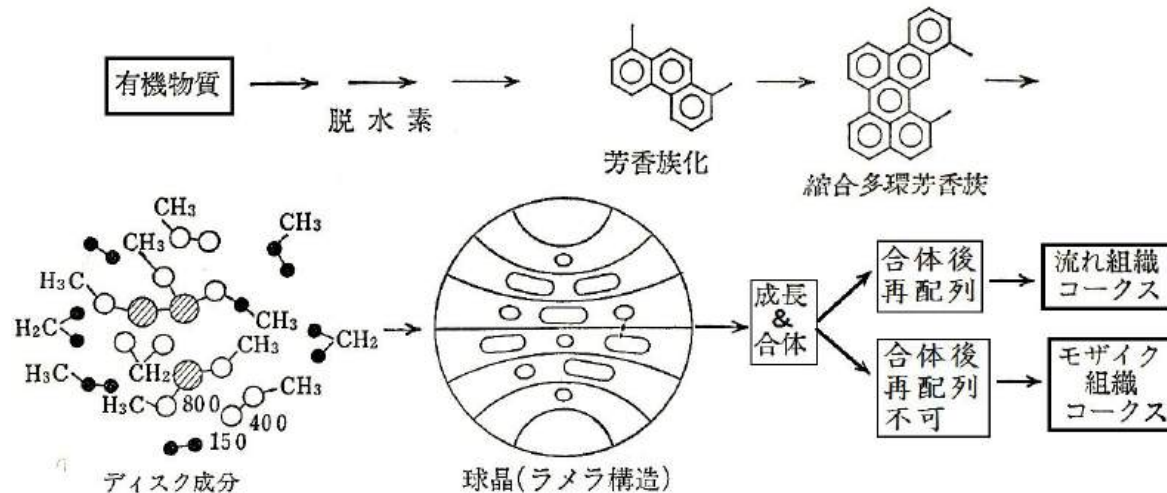


原料ピッチ

メソフェーズ
球晶発生

メソフェーズ
球晶成長

球晶成長・合体
バルクメソフェーズ

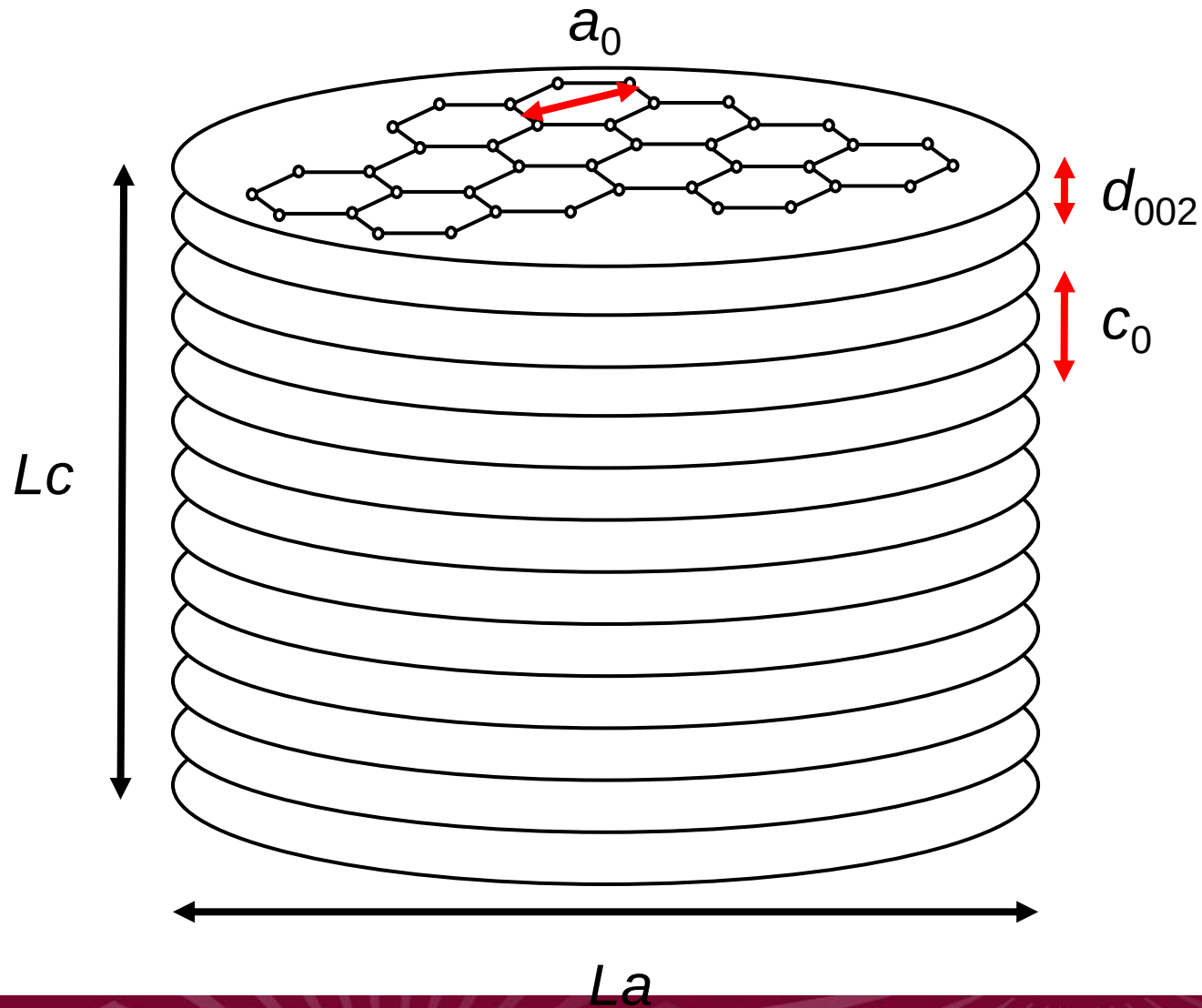


固相炭化の原料となる高分子

分類		高分子	通常の炭化相	用途
天然	不融	セルロース $\left[\text{O} - \begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{C} \\ \\ \text{OH} \end{array} - \text{O} - \begin{array}{c} \text{OH} \\ \\ \text{C} \\ \\ \text{CH}_2\text{OH} \end{array} - \text{O} \right]_n$	固相	ガラス状炭素 炭素繊維 モレキュラーシーブカーボン
		フェノール-ホルムアルデヒド樹脂 $\left(\begin{array}{c} \text{C}_6\text{H}_4 \\ \\ \text{OH} \end{array} \right)_n$ フルフリルアルコール樹脂 $\left(\begin{array}{c} \text{C}_5\text{H}_6\text{O} \\ \\ \text{OH} \end{array} \right)_n$ フェノール-フラン系樹脂 架橋状ポリスチレン	固相 固相 固相	ガラス状炭素 ガラス状炭素 ガラス状炭素繊維 微小球粉体
合成	熱可塑性	ポリスチレン $\left(\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{C}-\text{C} \end{array} \right)_n$	分解	
		ポリアミド $\left[(\text{CH}_2)_n - \text{CONH} \right]_n$ ポリアクリロニトリル (PAN) $\left[\text{C}-\text{C} \cdot \text{CN} \right]_n$ ポリ塩化ビニリデン (PVDC) $\left[\text{C}-\text{C} \cdot \text{Cl}_2 \right]_n$ ポリ塩化ビニル (PVC) $\left[\text{C}-\text{C} \cdot \text{Cl} \right]_n$ ポリビニルアルコール (PVA) $\left[\text{C}-\text{C} \cdot \text{OH} \right]_n$	固相 固相 (耐炎処理) 固相 液相 HClガス下ピッチ化	炭素繊維 炭素繊維 モレキュラーシーブカーボン 炭素繊維 炭素繊維
ピッチ	可融	ピッチ	不融化処理後固相	炭素繊維

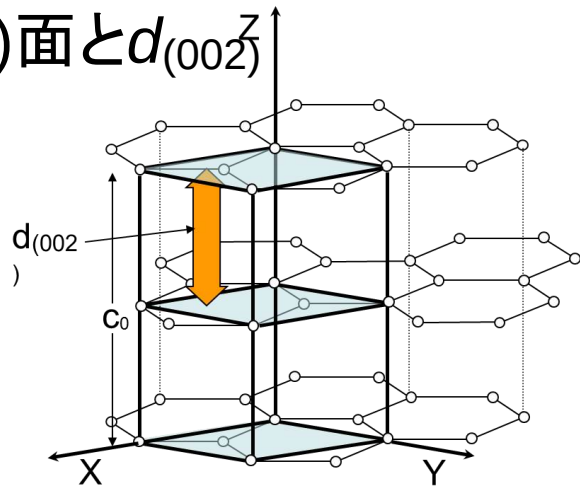
炭素の構造



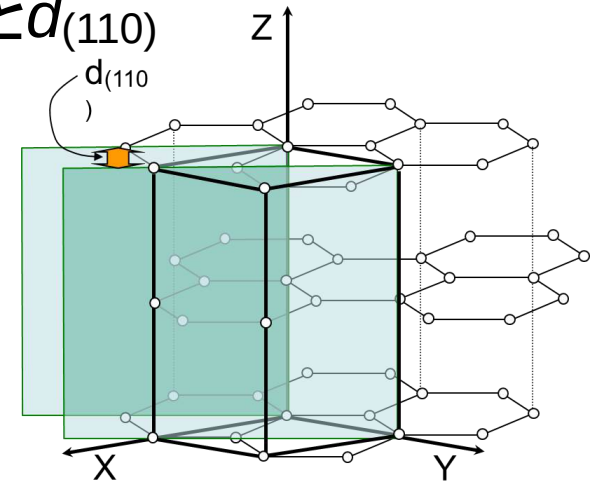


結晶面と面間隔の関係

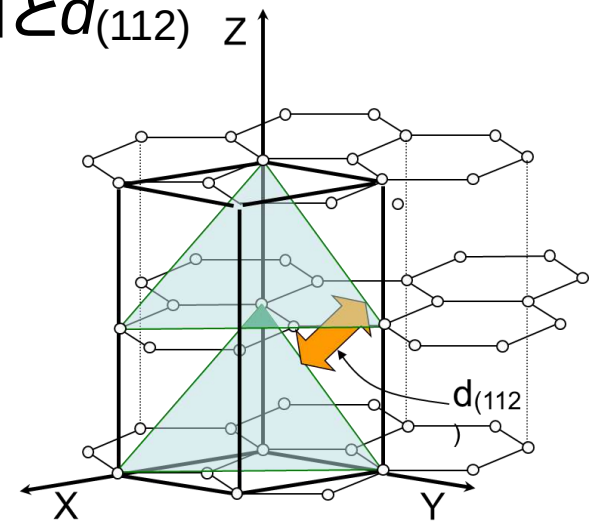
(002)面と $d_{(002)}$



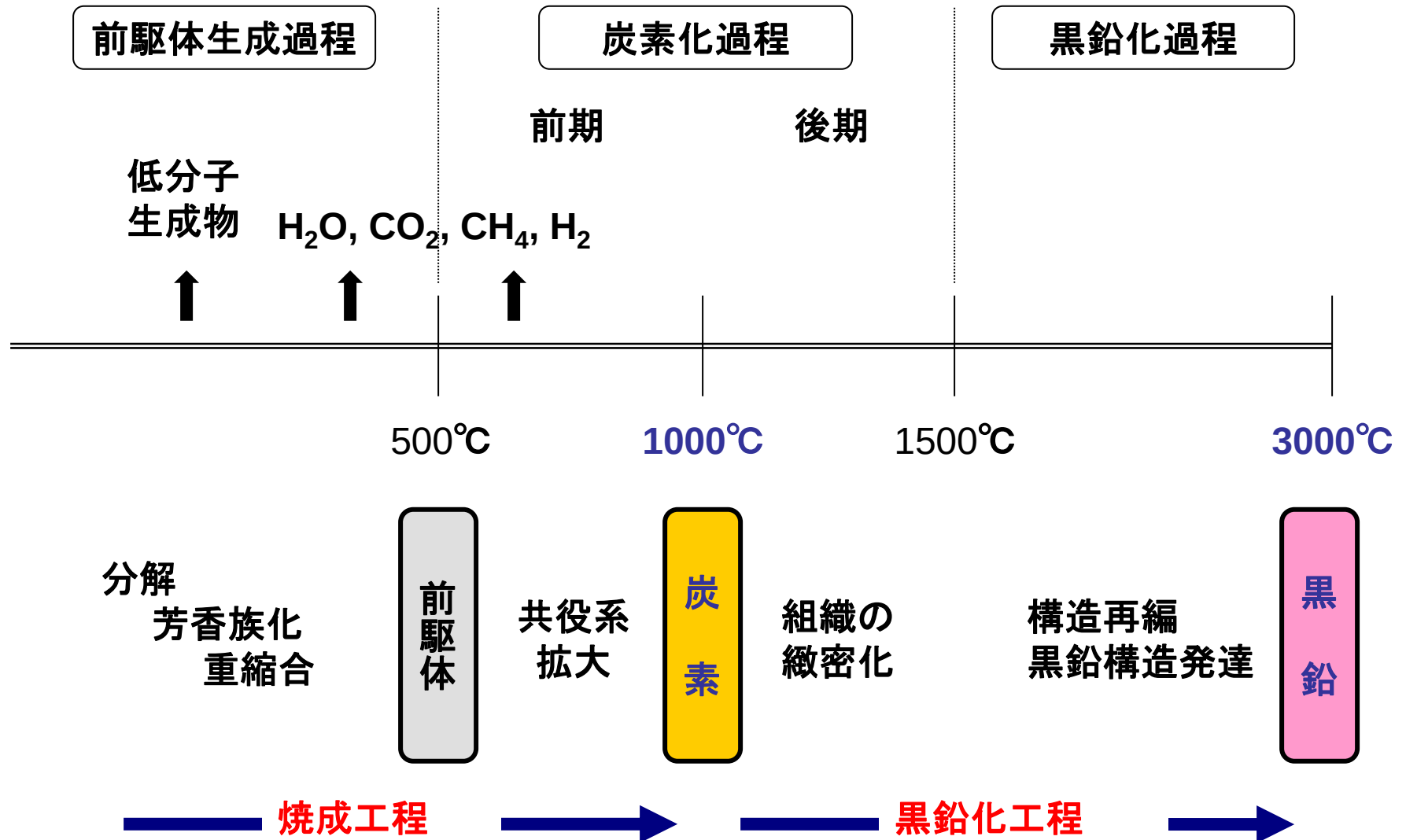
(110)面と $d_{(110)}$



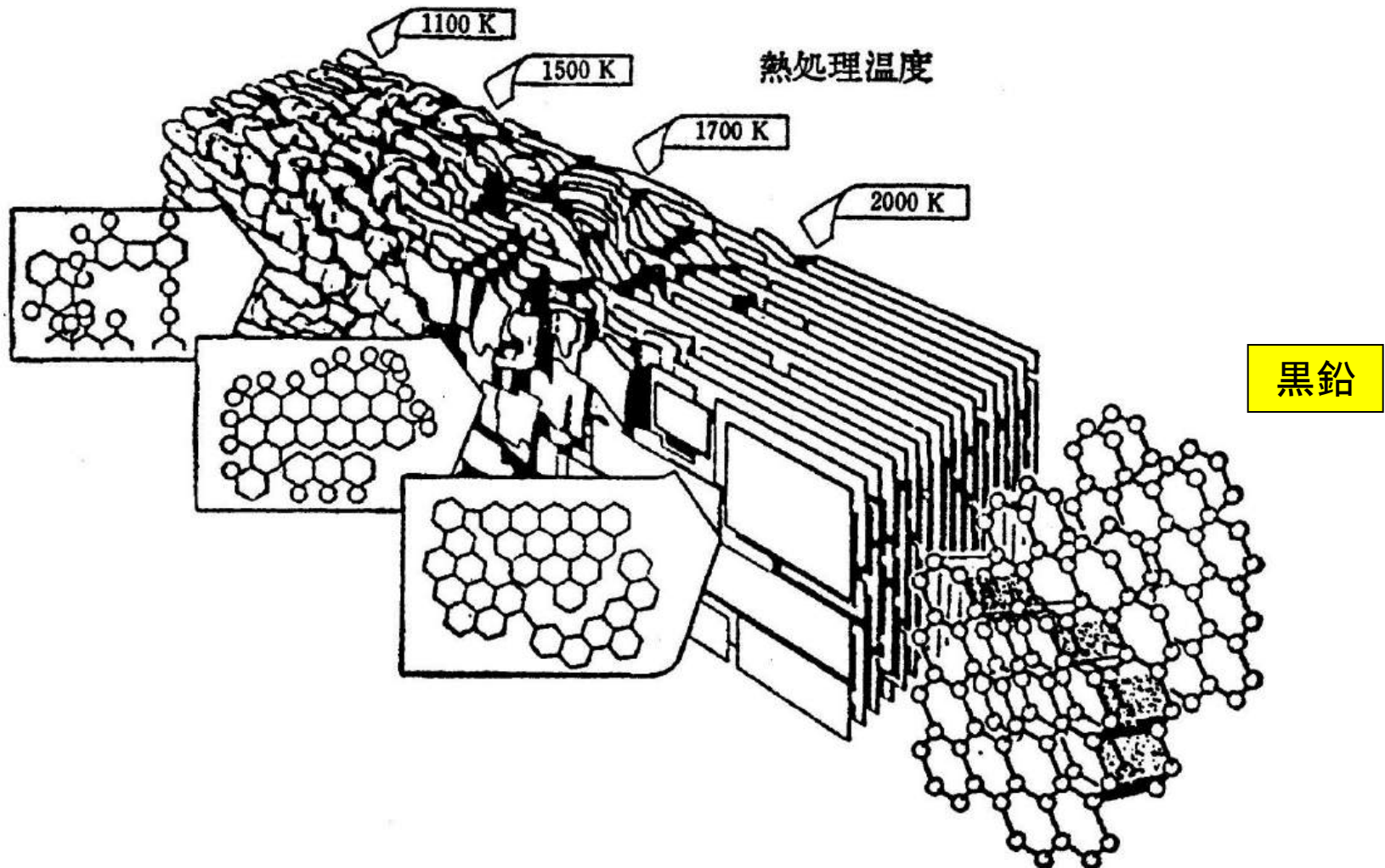
(112)面と $d_{(112)}$



有機物の加熱による変化



熱処理温度による結晶構造変化



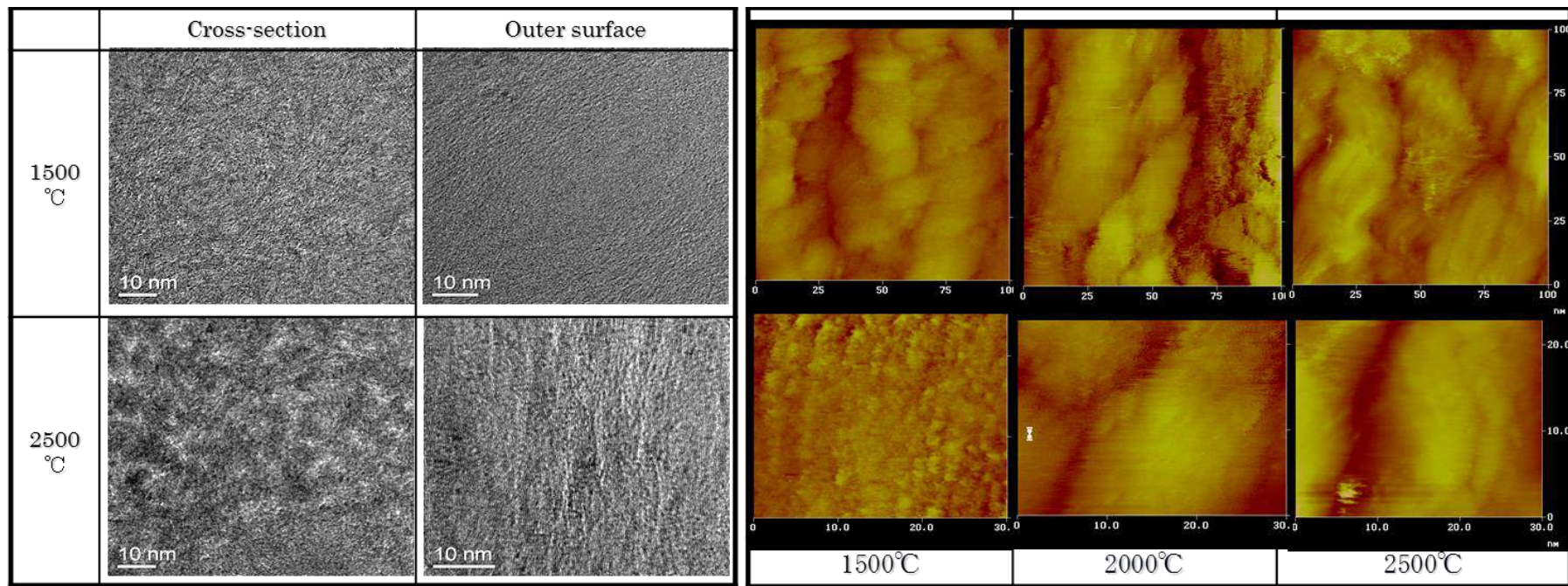
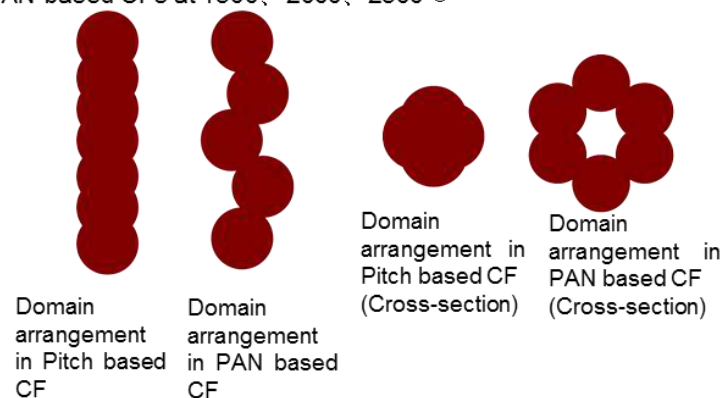
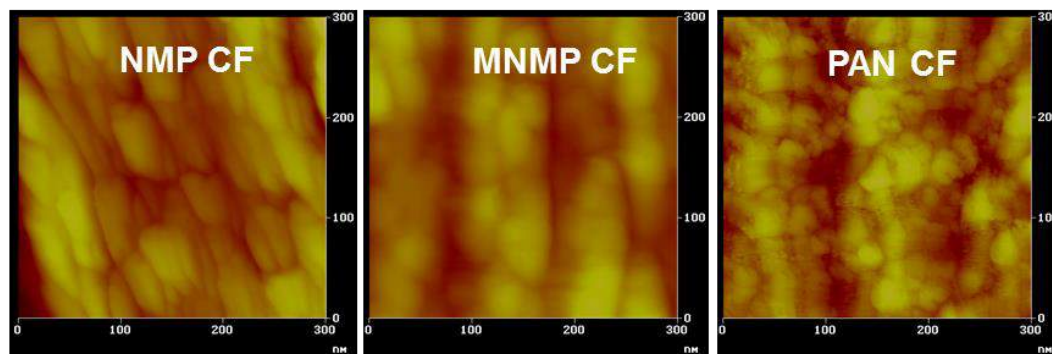


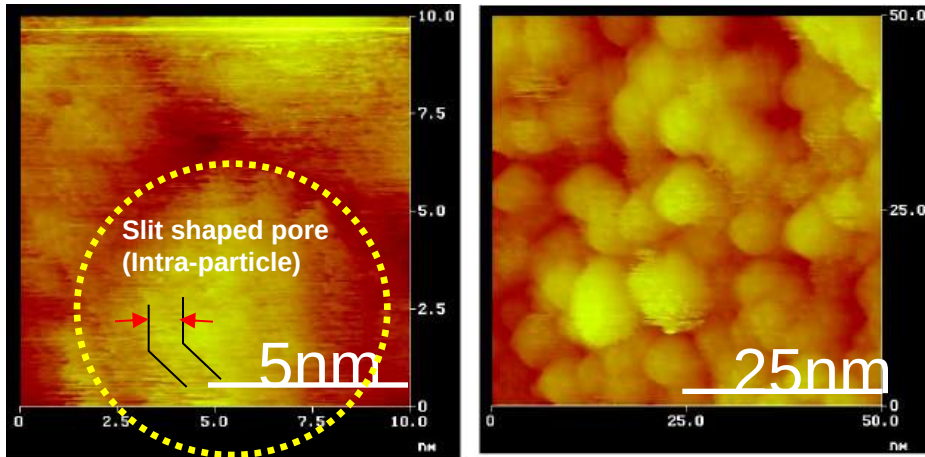
Figure SEM & STM images of heat treated PAN based CFs at 1500、2000、2500°C



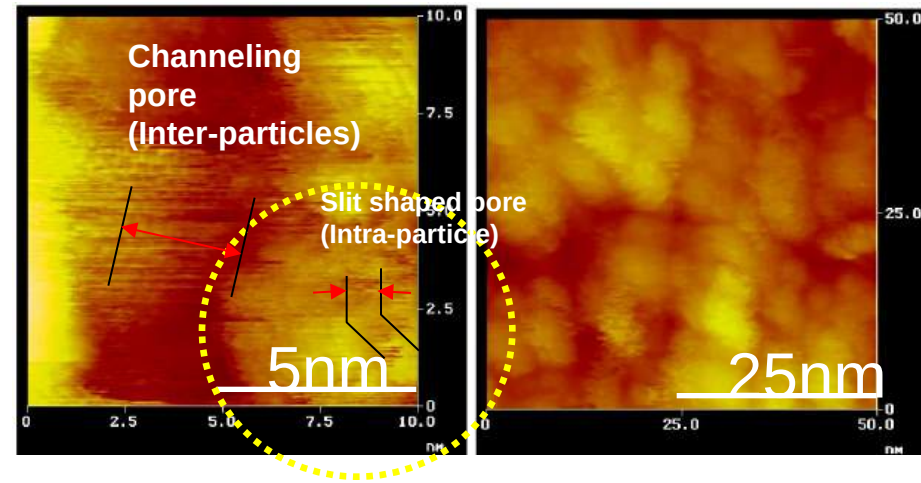
STM images of ACFs

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

OG7A-800H



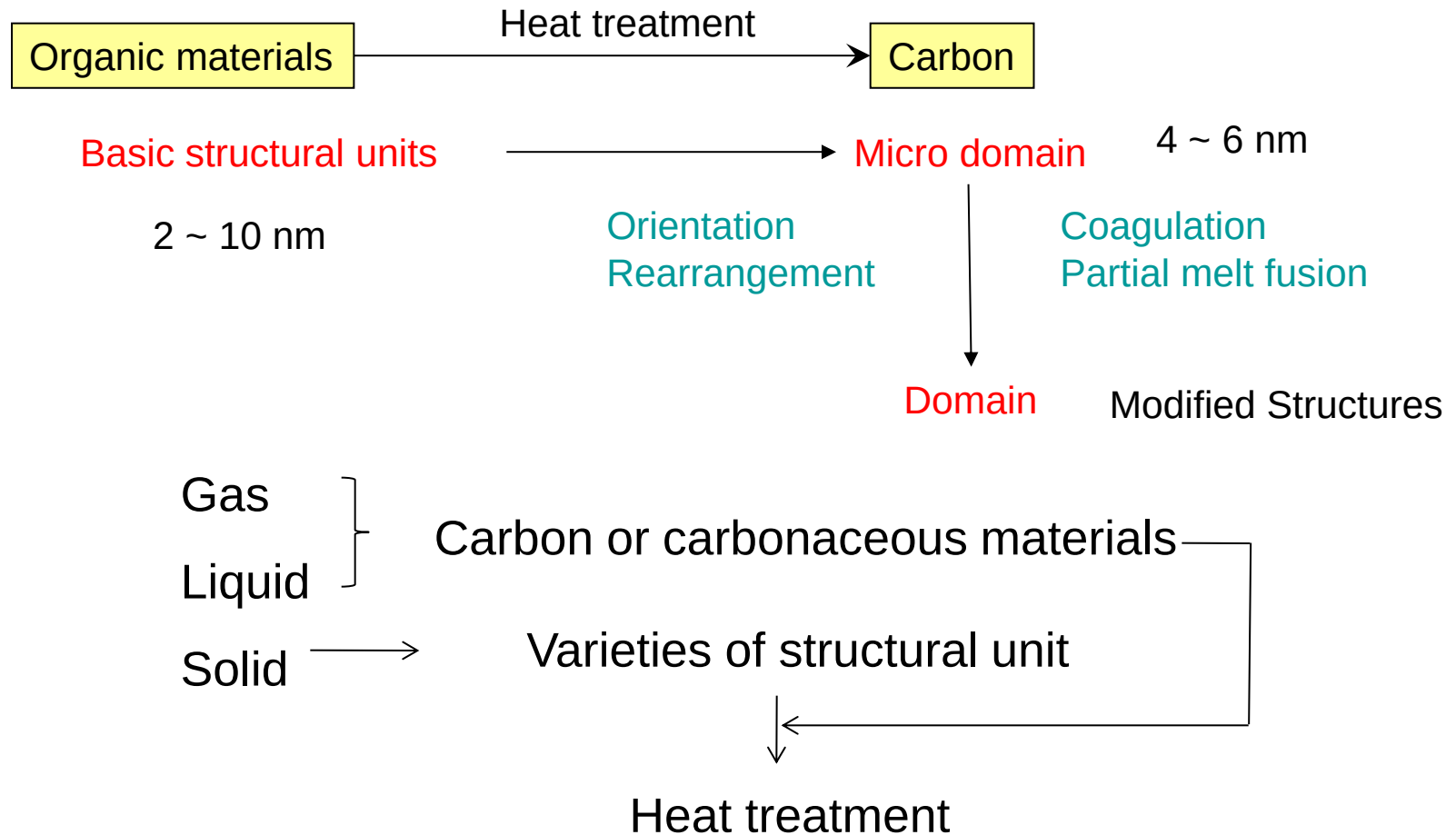
OG20A-800H



- ♣ 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.

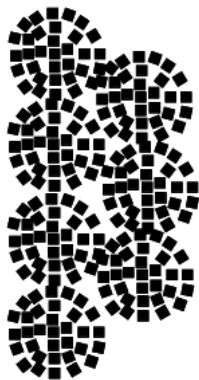
What is the synthetic carbon!

Origin of Structural Units And Crystalline Defects



Basic structure and structural control of carbon

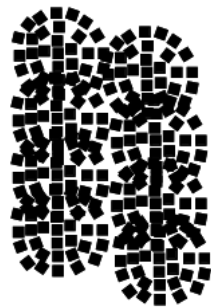
Before heat treatment



**Not or very slightly
fused microdomains**



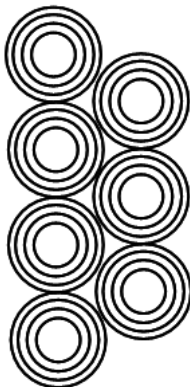
**Partially
fused microdomains**



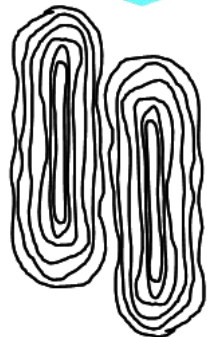
**Fully
fused microdomains**



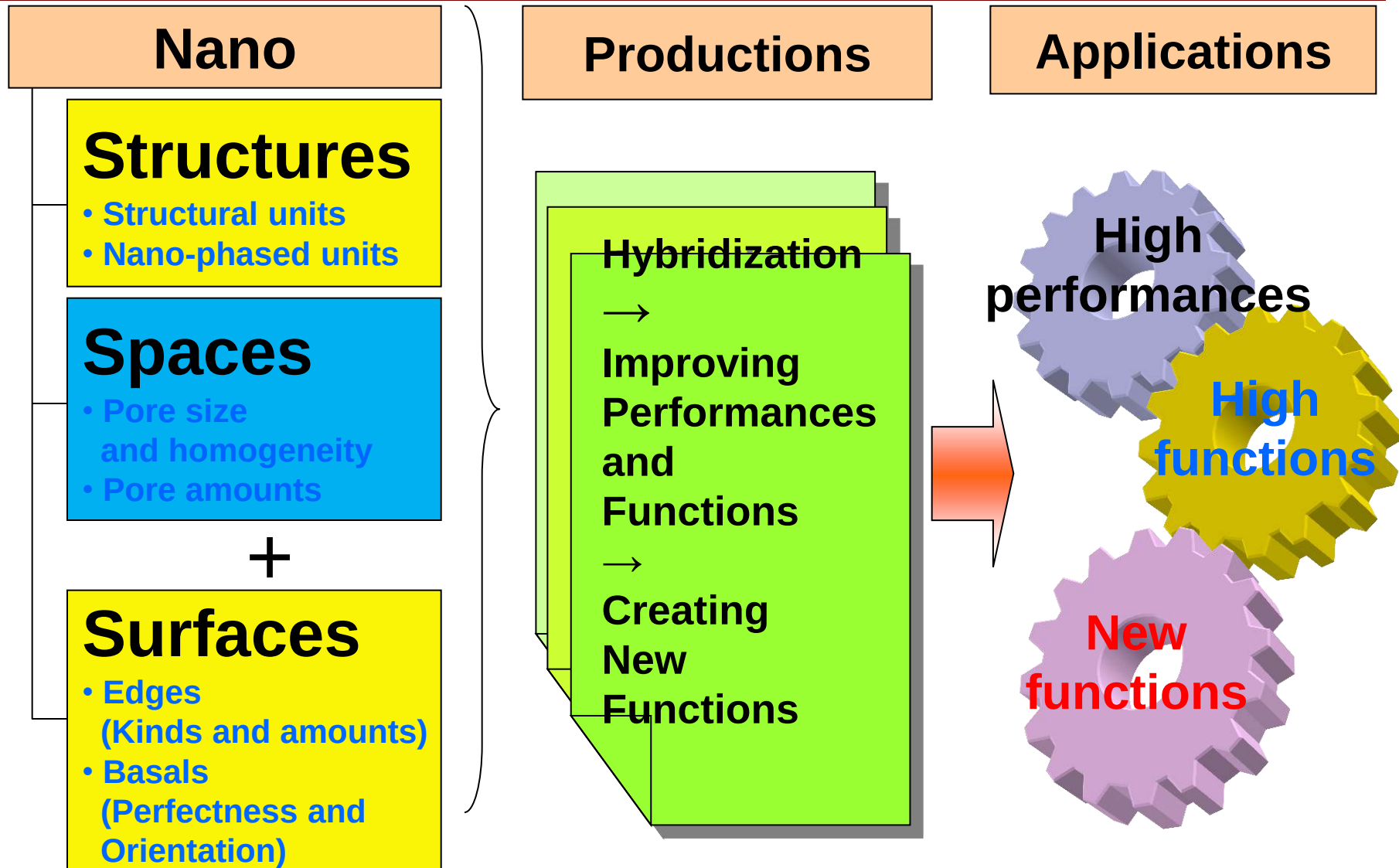
After graphitization

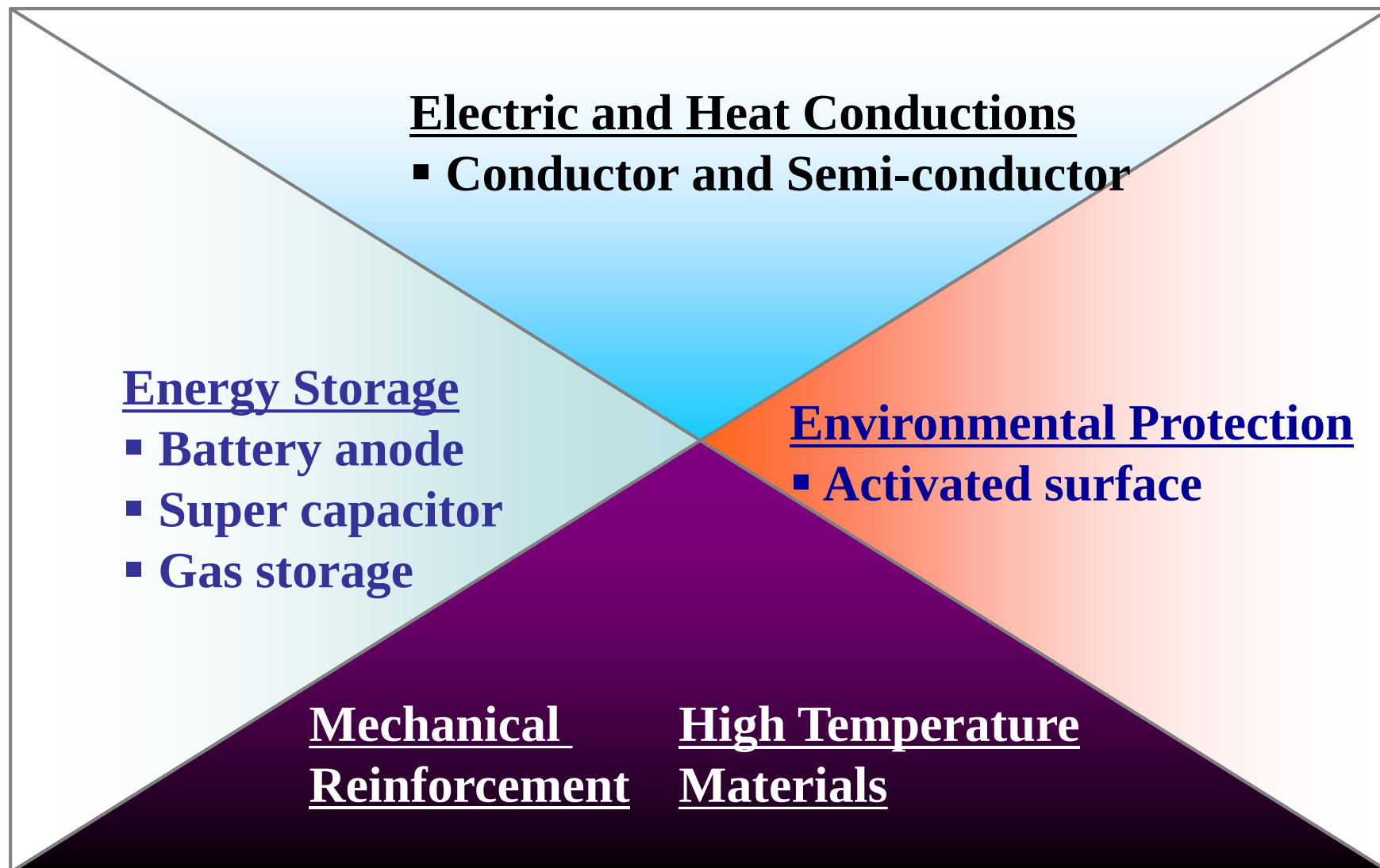


Glassy Carbon

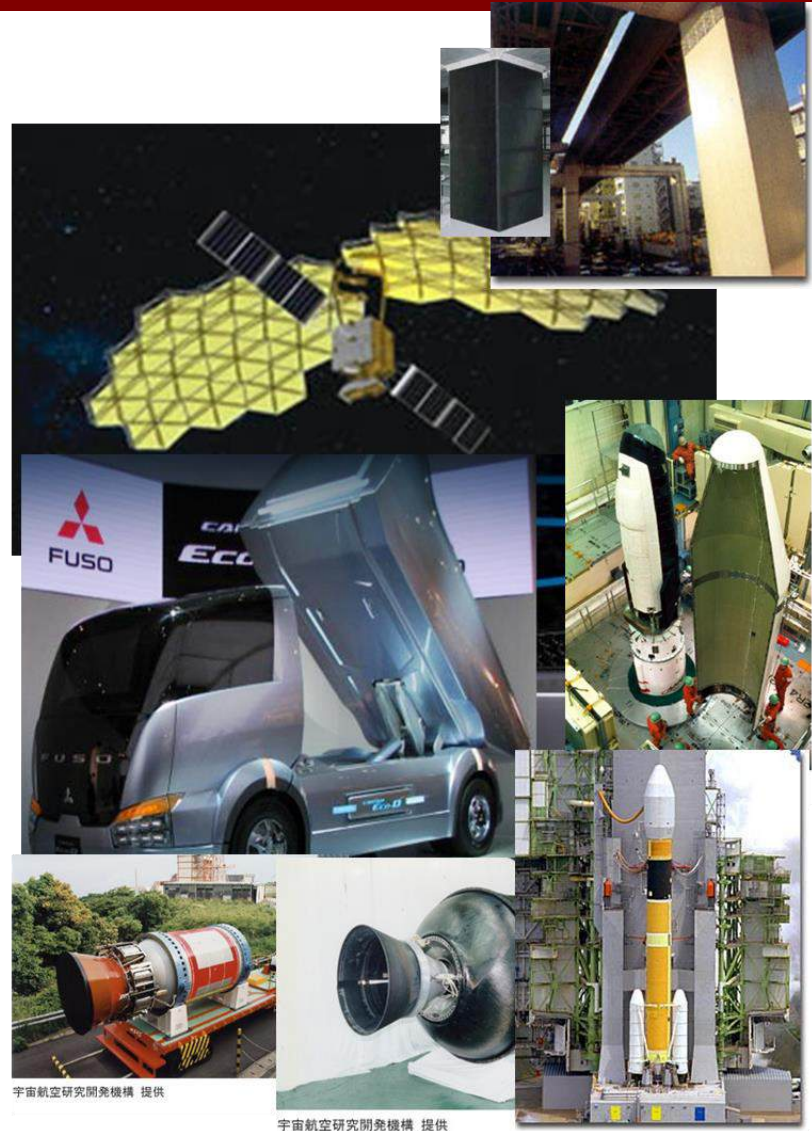
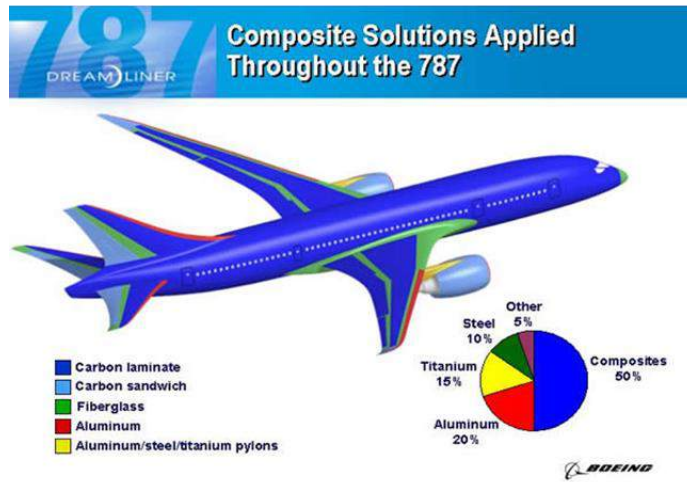
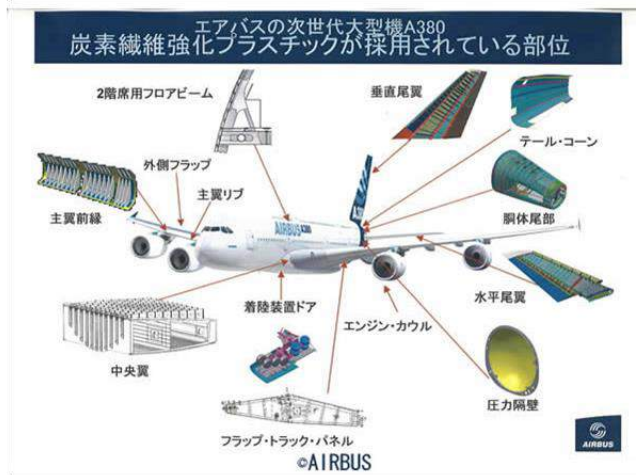


Understanding carbon structures: Carbon nano-world

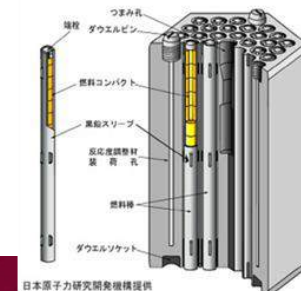
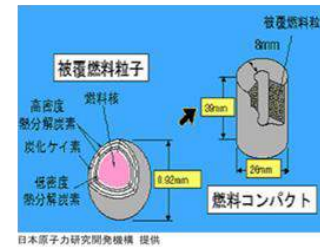
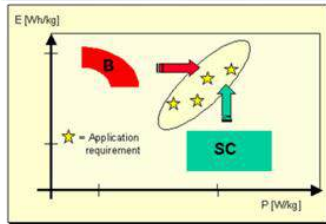
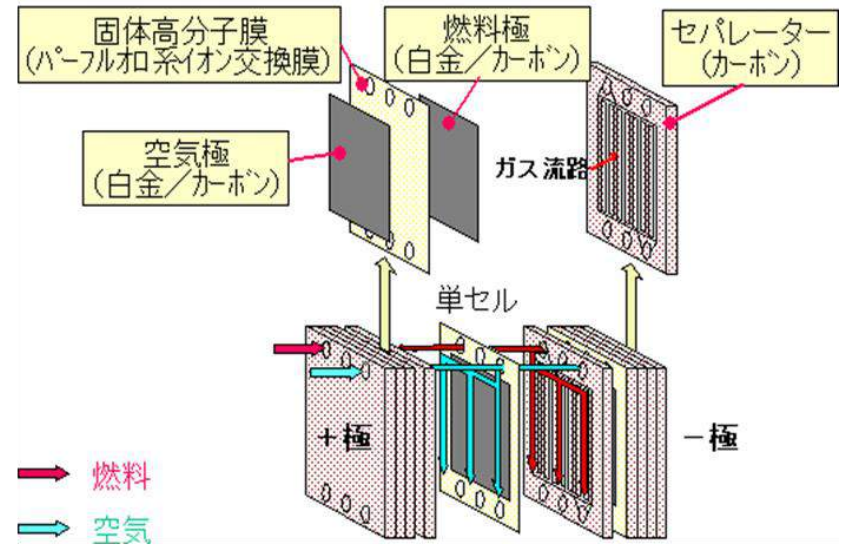
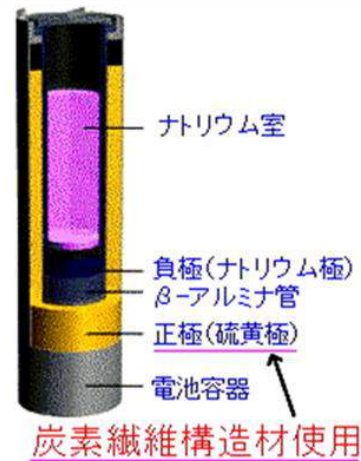
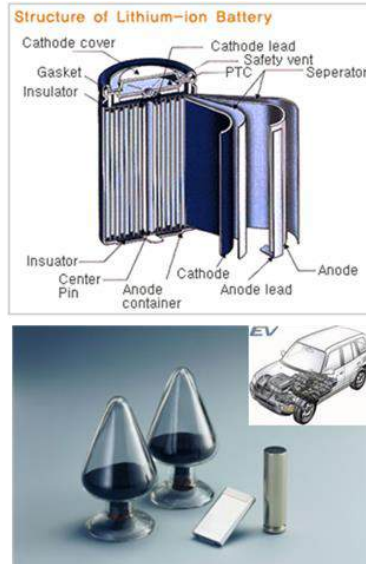




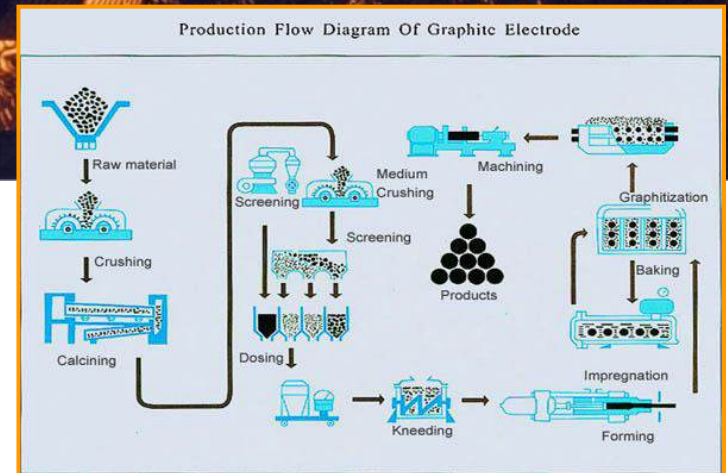
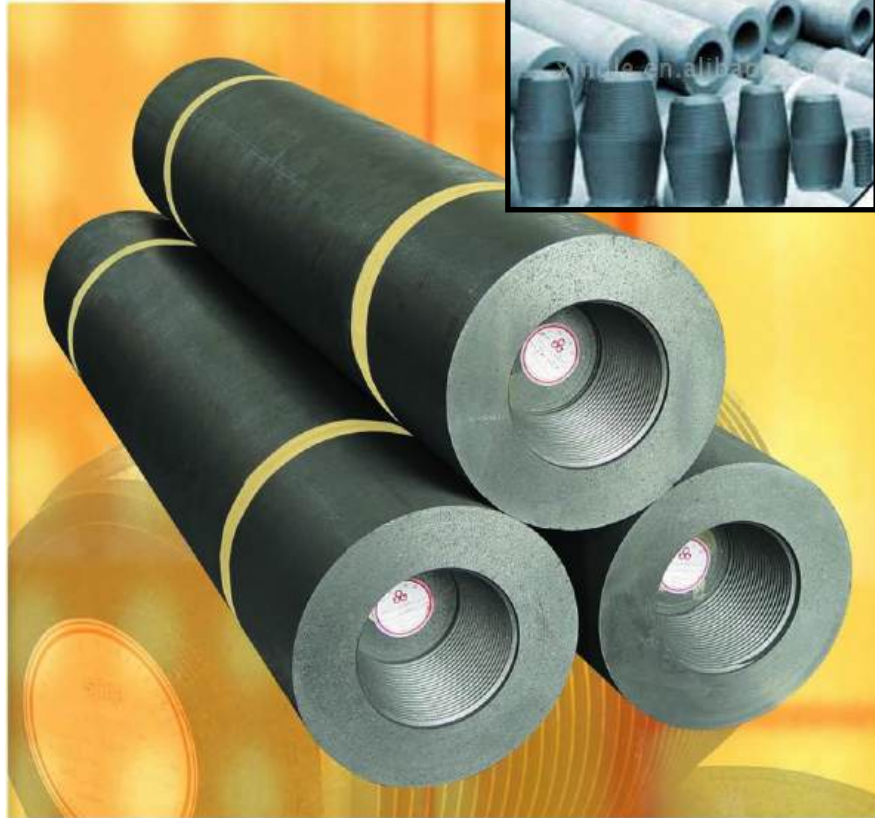
Carbon Fiber



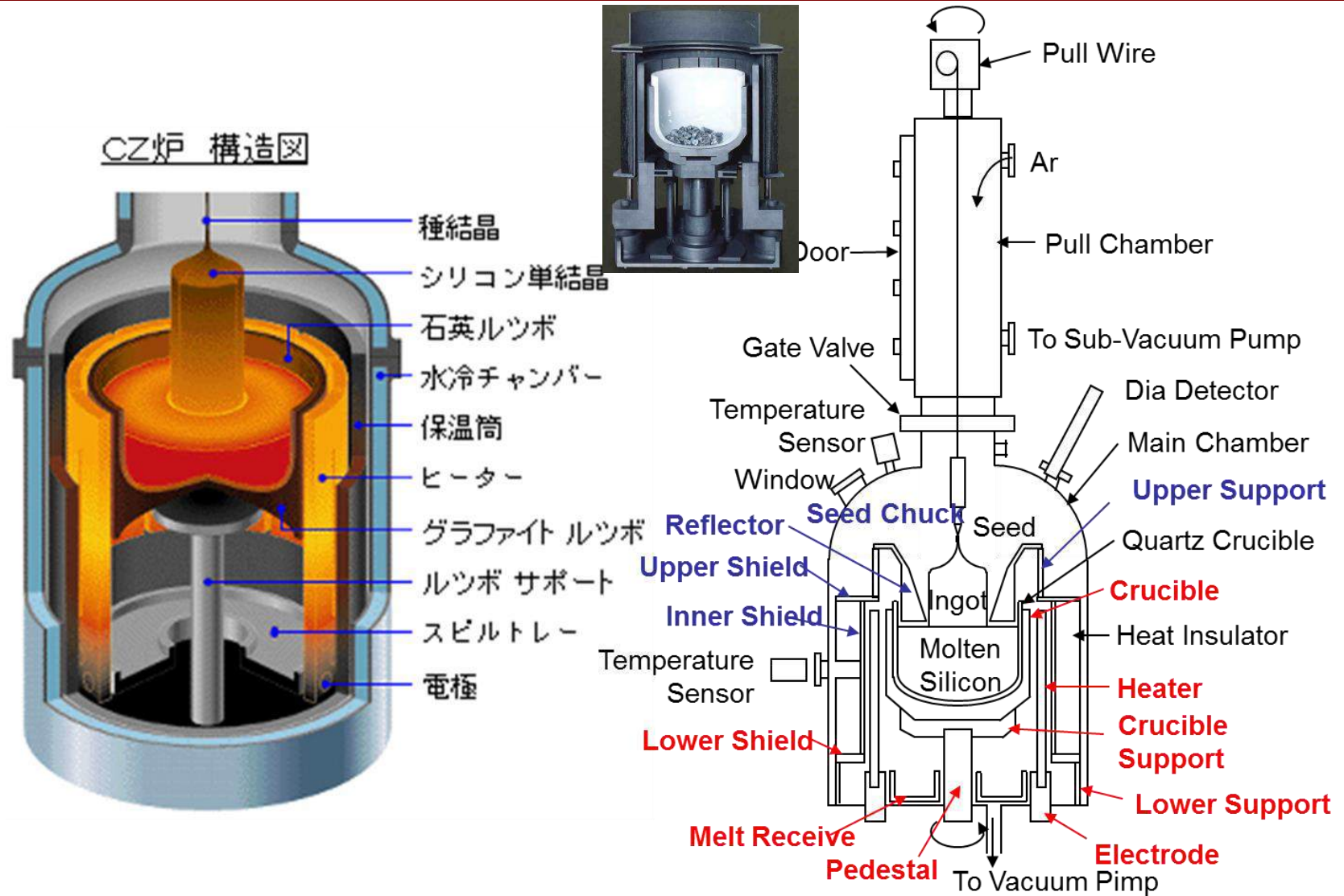
Battery, Capacitor, Atomic and Coal Power Plants



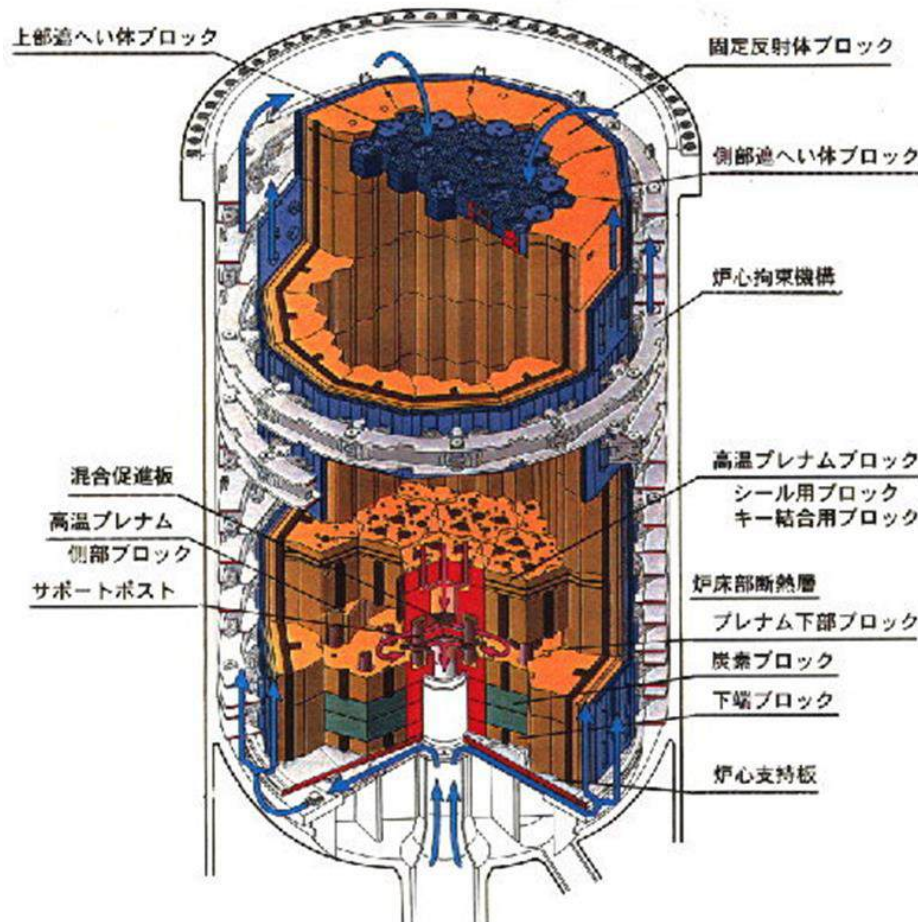
Graphite Electrode



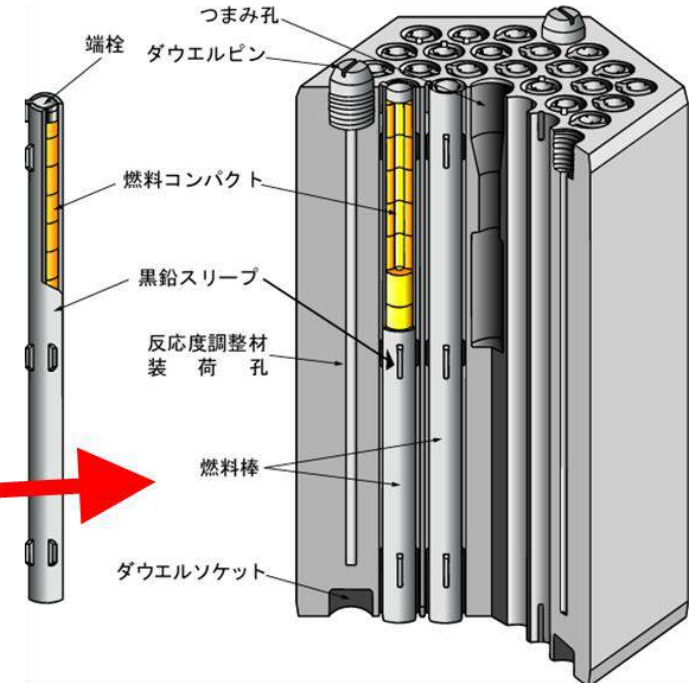
単結晶シリコン引き上げ用CZ炉



高温工学試験研究炉 (HTTR)



炉心構造体

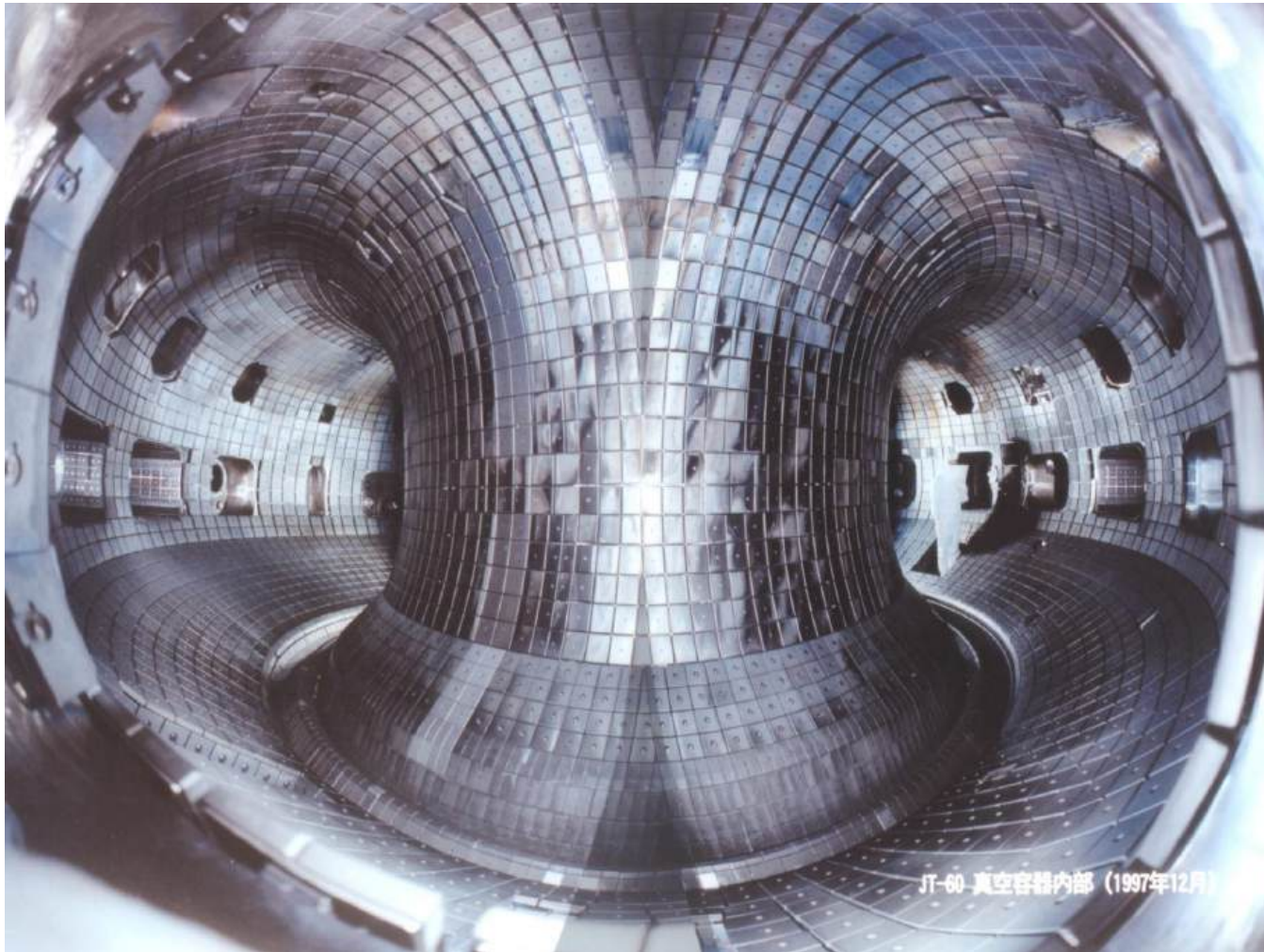


黒鉛プレナムブロック

燃料棒が収納される

出典: 日本原子力研究開発機構 HP

臨界プラズマ(核融合)試験装置JT-60



JT-60 真空容器内部 (1997年12月)

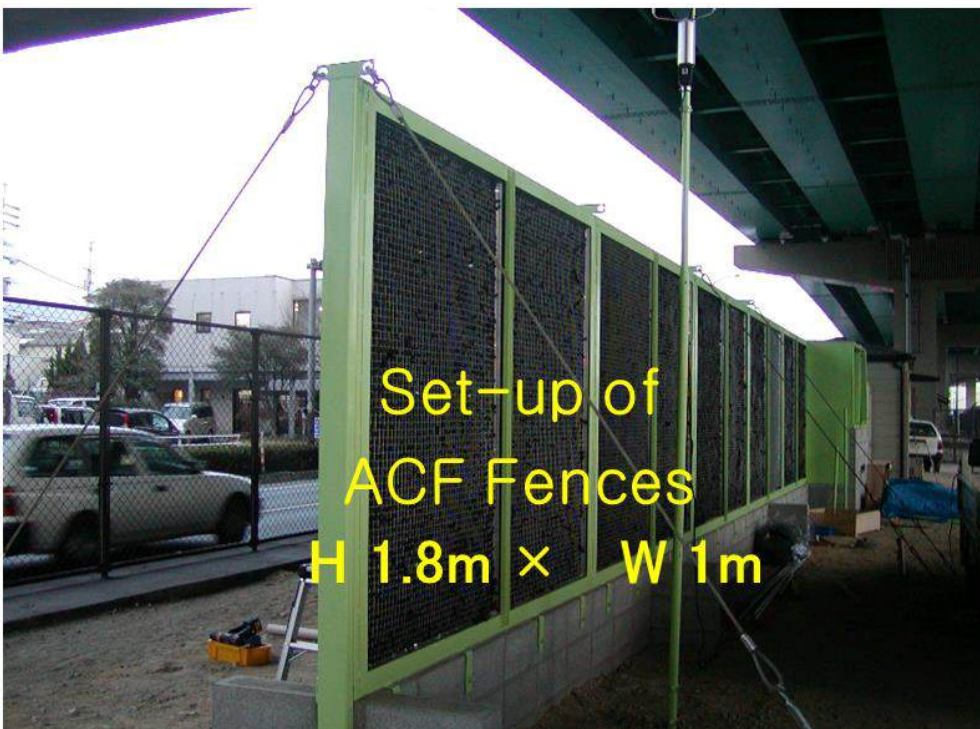
提供: 日本原子力研究開発機構





Air Purification Using ACF (Remote Watching System)

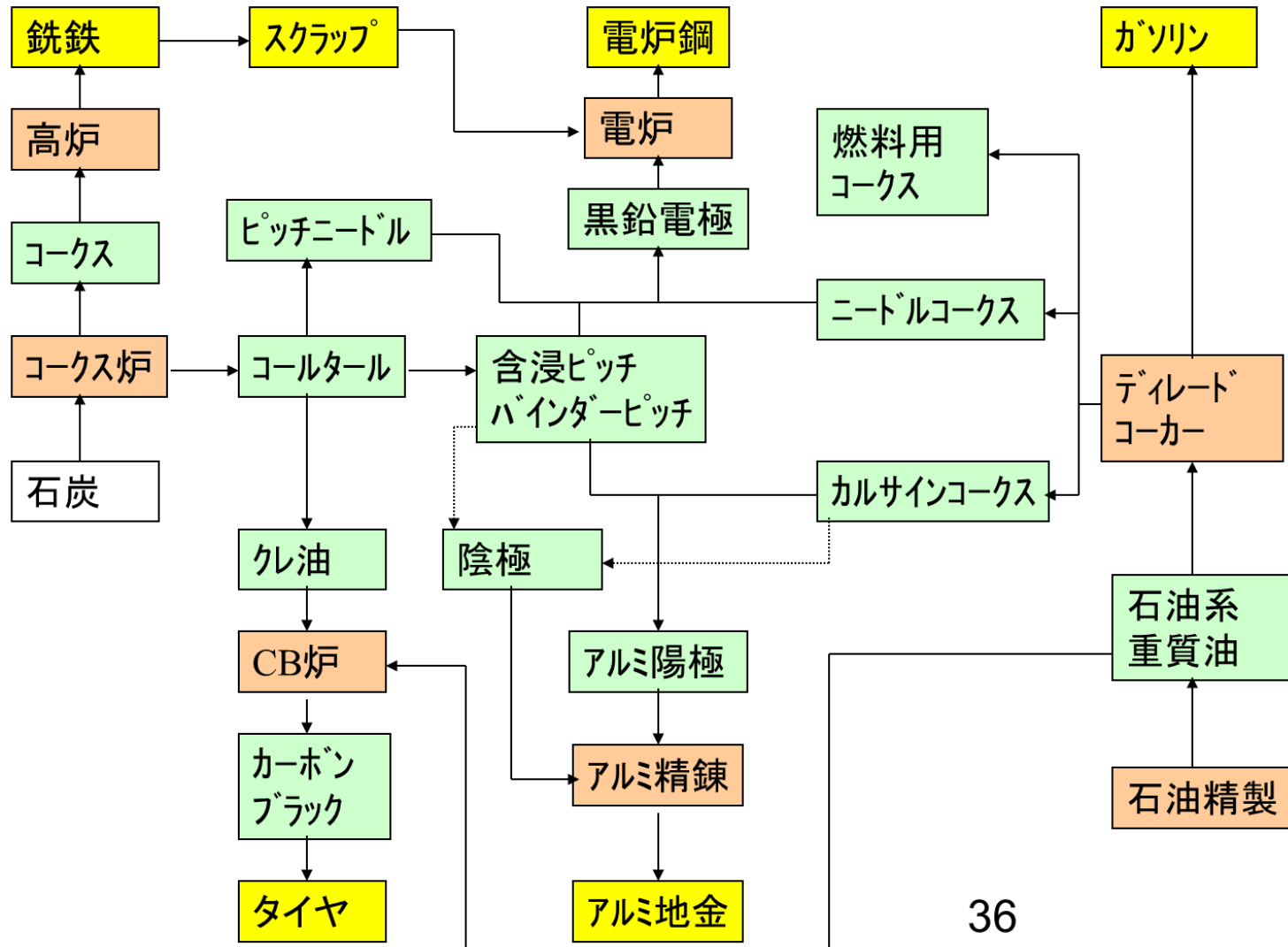
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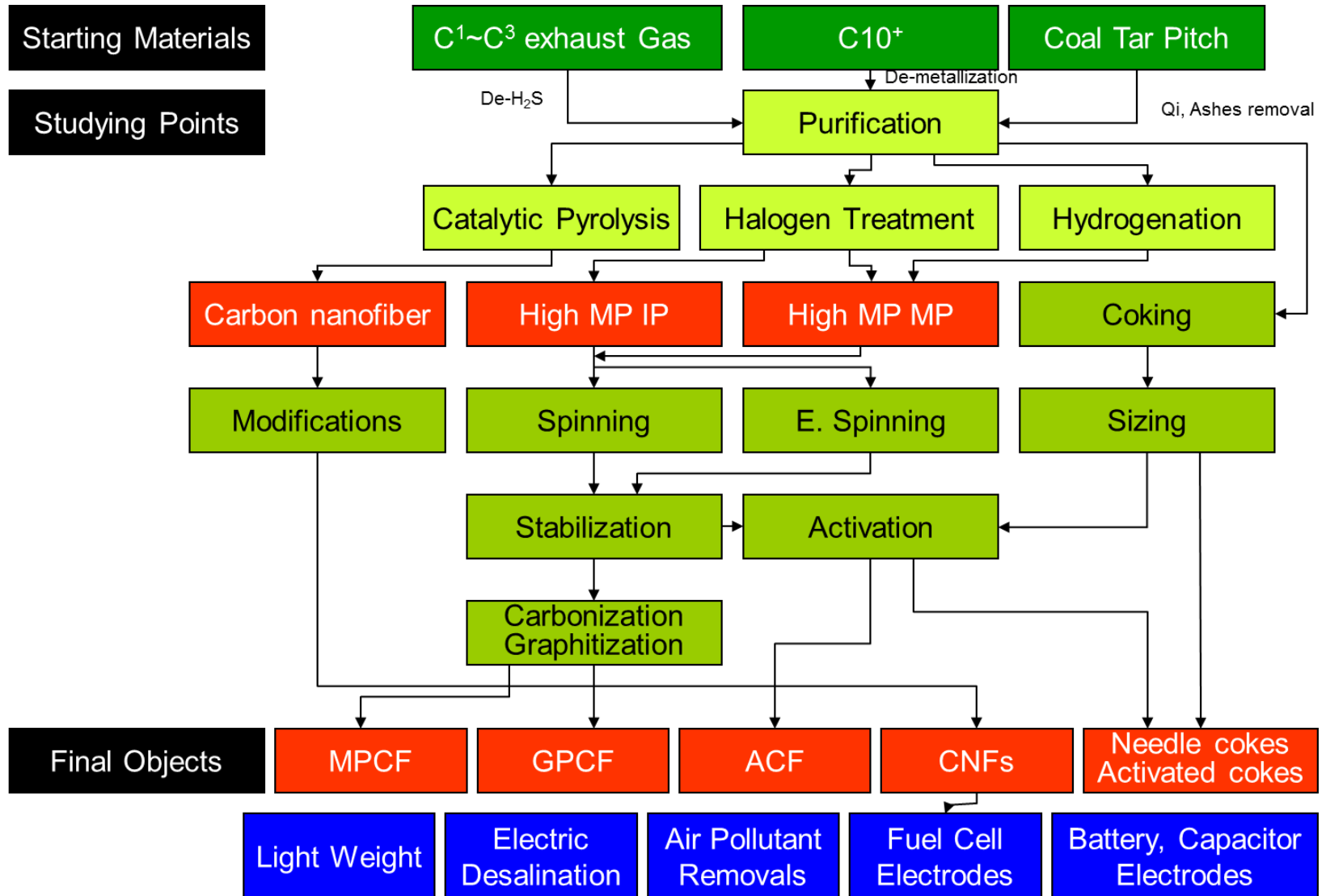
炭素材の製造

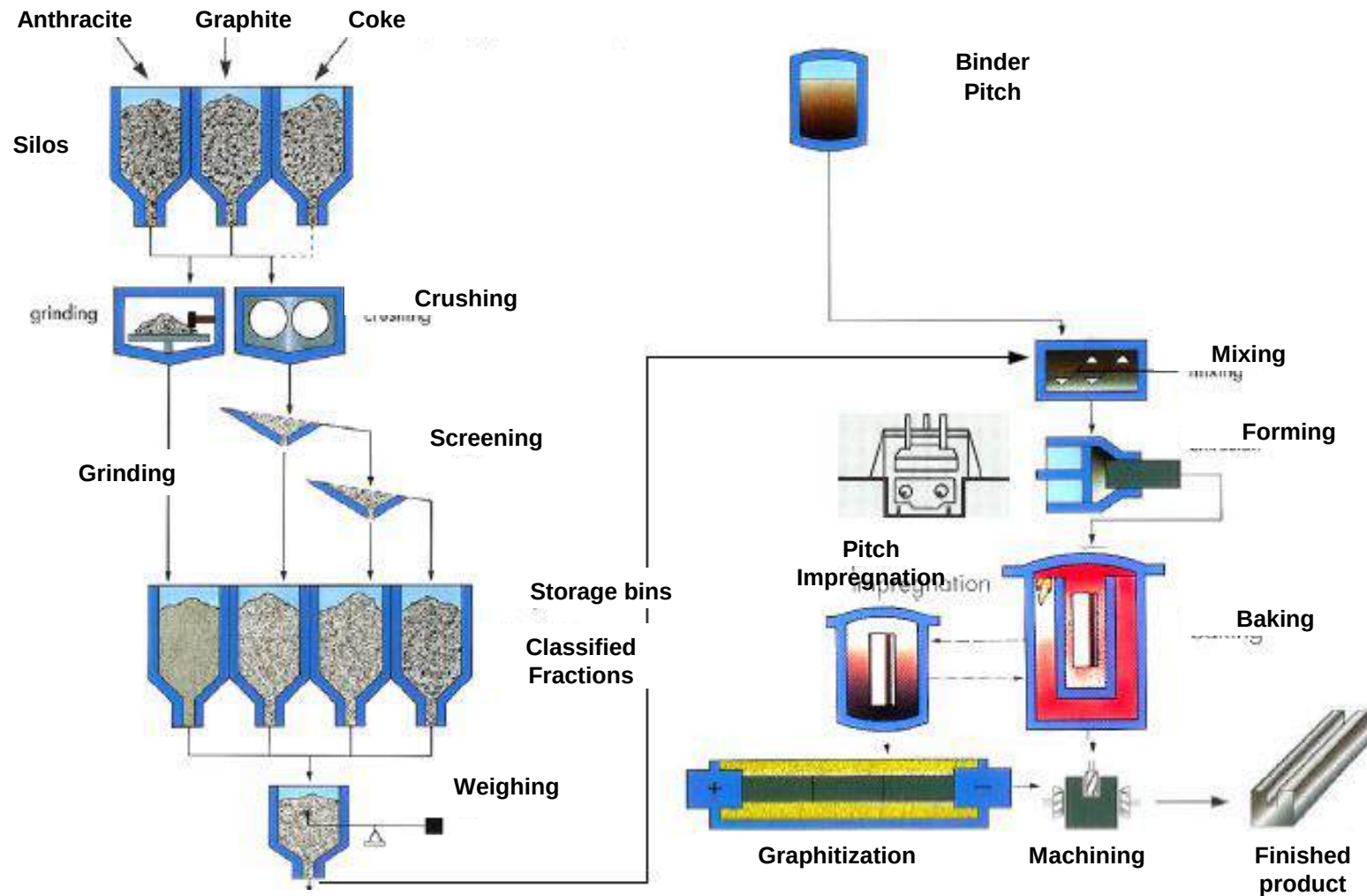
重質油を用いたカーボンサークル



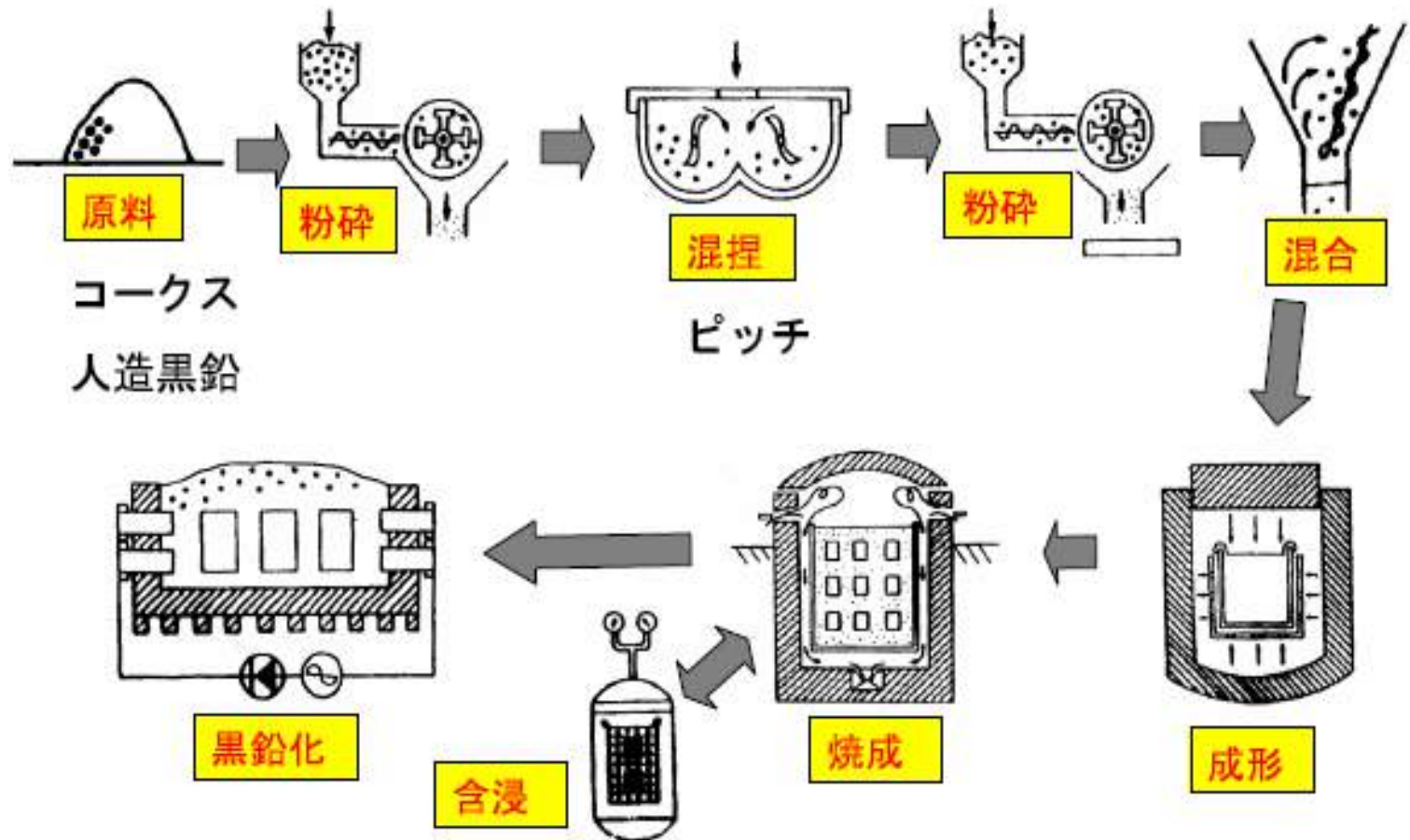
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重質油又は石炭残渣を用いた炭素材の製造模式図





等方性黒鉛の製造工程(二元系原料)



先端炭素材の製造におけるポイント

High performance pitch based carbon fibers: less than 50 ppm

Capacitor : less than 500 ppm

High performance needle coke : 500 ppm

Carbon medicines: less than 300 ppm?

Carbon anode for LIB: less than 100 ppm

...



コールタールピッチのQI 除去

Method	Principle	Advantage	Disadvantage
① Filtering (Heat, Solvent)	Decreasing viscosity by heating or solution Mesh filtering of QI	Only QI Removal No heavy fraction removal	Large equipment X
② Centrifuging (Heat, Solvent)	Decreasing viscosity by heating or solution Centrifugal condensing of QI	Only QI Removal No heavy fraction removal	Large equipment X
③ Solvent - Precipitation	Mixing of miscible solvents Precipitation removal of QI		Low productivity
④ Non-solvent Precipitation	Mixing of non-miscible solvents Precipitation removal of QI	Large equipment OK	Heavy fraction removal

- It is relatively easy to remove QI in lab scale.
- QI removal in the industrial scale
 - Very difficult to remove finely dispersed QI from large amount of viscous liquid
 - Only success in Japan
Japan several ten thousands ~ hundreds tons/year scale



ピッチ系炭素繊維

Needs and Seeds of Carbon Fiber

- High Performance Carbon Fiber(HPCF) : CF with TS over 3500MPa
 - CFRP for lightening :
 - Transportation: Aerospace (B787, A380,...), Military, EV (EV, HEV, FEV: Parts need special properties/performances)
 - Sports, Robotics, ...
 - Energy Devices: Windmill, ...
 - Construction: CFRC, Supplement
- Middle Performance Carbon Fiber(MPCF) : CF with TS of 1500~3500MPa
 - CFRP Application: CF with TS of 1500~3500MPa, Long Fiber
 - Transportation: Main Body for EV (EV, HEV, FEV)
 - Construction (Short Fiber ⇒ CFRC)
- Low Performance Carbon Fiber(LPCF) : CF with TS Less Than 1200 MPa
 - Refractory Materials for High Temperature Devices (Short Fiber)
 - ACF for Environmental Protections

⇒ Strong demand of MPCF with appropriate mechanical properties and production cost for broadening novel market;
Pitch Based Carbon Fiber Can Meet of the Carbon Fiber.



Production Capacity of PAN CF in the world

Company	T/Y
Toray	17,600
Toho TENAX	13,900
Mitsubishi Rayon	7,400
etc.	16,400
Total	55,300

* Capacity for less than 24K, 2010



Current State Production Capacity of Pitch Based CF

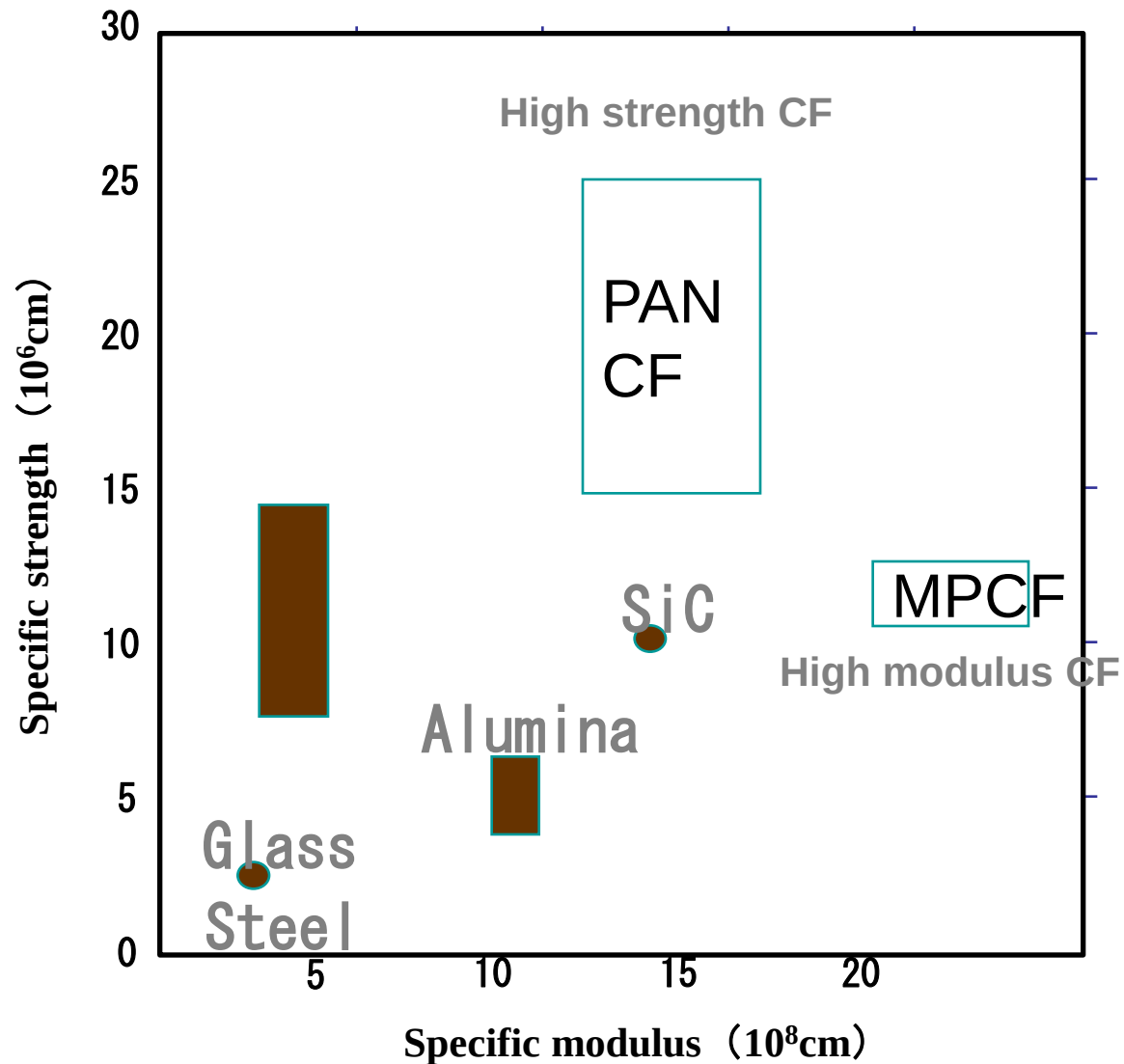
45

Company	T/Y	Type	Precursor Pitch
Kureha	1450	Short	Isotropic
Osaka Gas Chemical	600	Short	Isotropic
Mitsubishi Chemical	1000	Long	Mesophase
Japan Graphite Fiber	180	Long	Mesophase
CYTEC	230	Long	Mesophase
Total	3460		

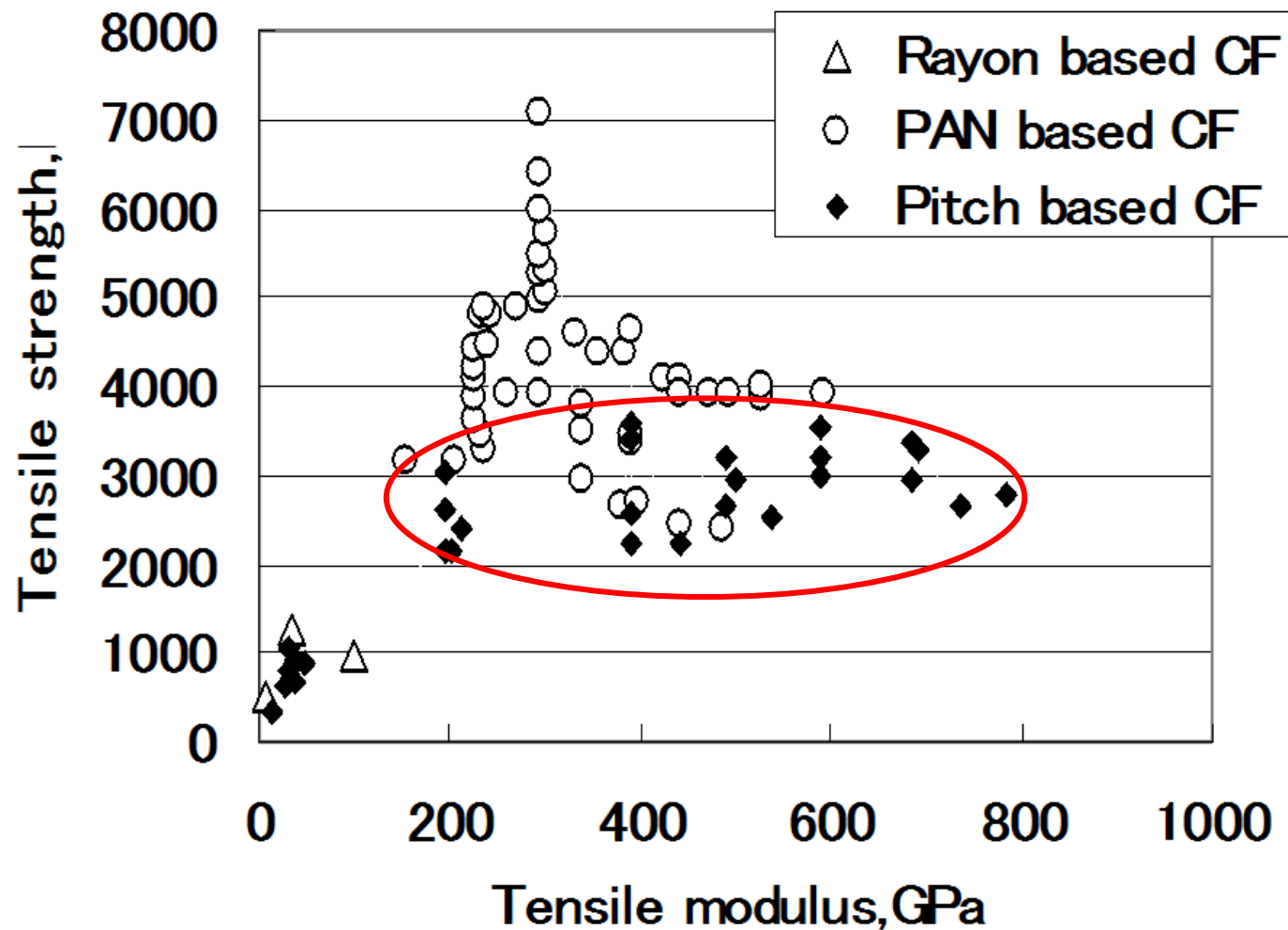
* 2010, (From HP Information, China: 200T/Y, Isotropic)



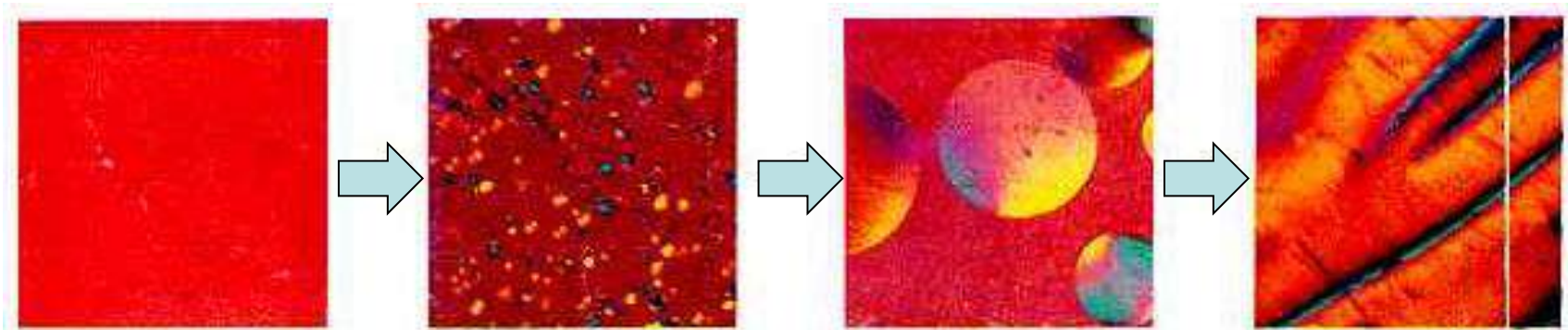
Specific tensile strength and modulus of various reinforcing fibers 46



Relationship between TS & YM before Improving⁴⁷



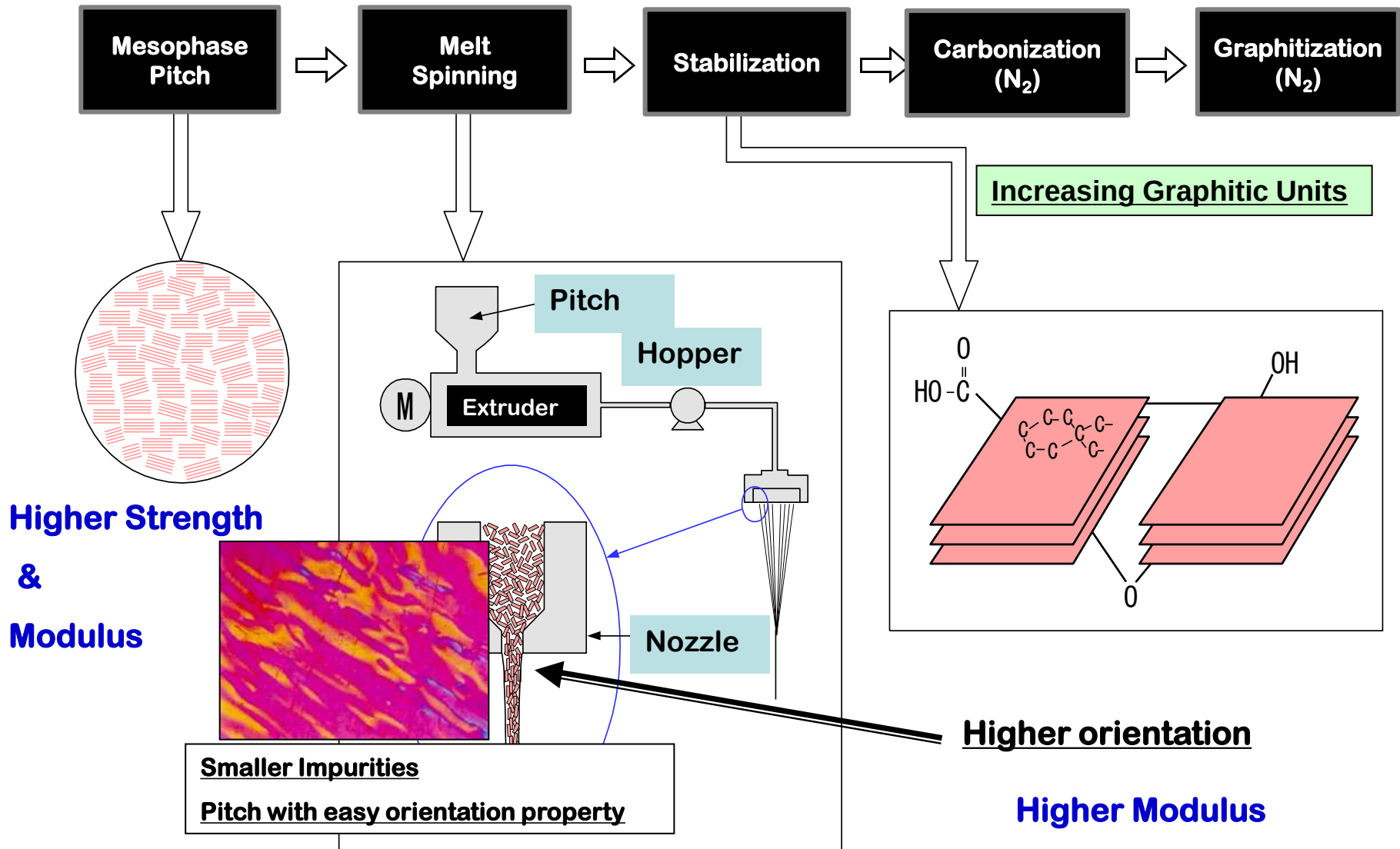
Raw Material	Before treatment and transferring to mesophase
DO	De-ash → Thermal Polycondensation → Thermal Transferring to Mesophase → Mesophase pitch
Coal tar	De-ash → Hydrogenation → Thermal Polycondensation (Mesophase) → Mesophase Pitch
Naphthalene	Polycondensation (HF/BF_3) → Removal of light Matters → Mesophase Pitch



Isotropic pitch
Formation of
mesophase

Growth of
mesophase

Bulky
mesophase



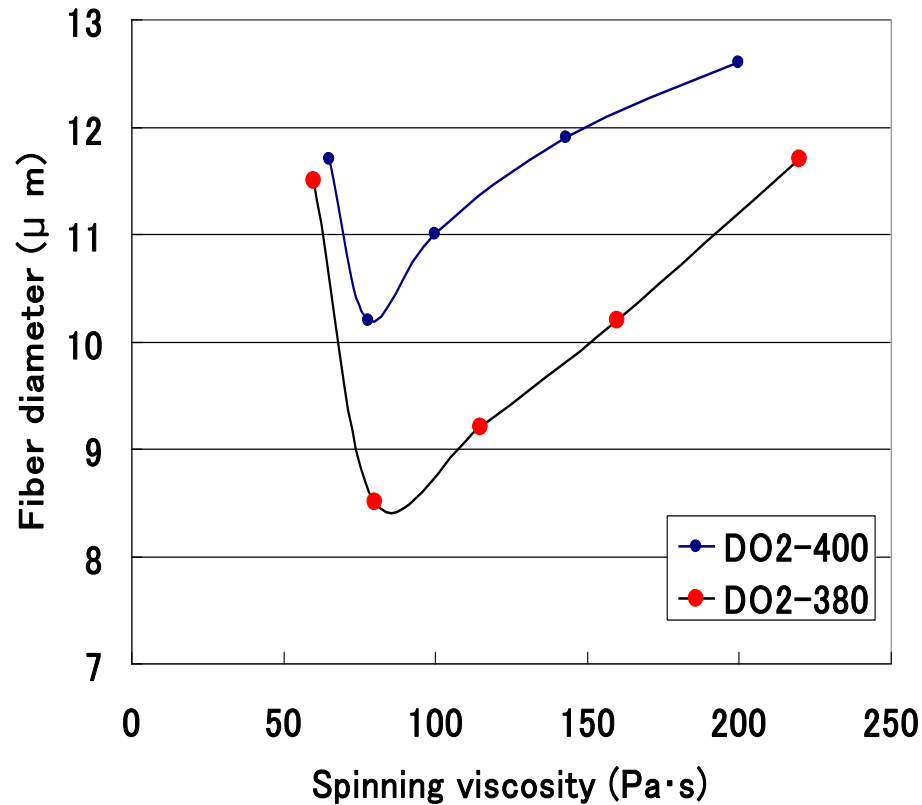


Fig. Correlation between fiber diameter and spinning viscosity

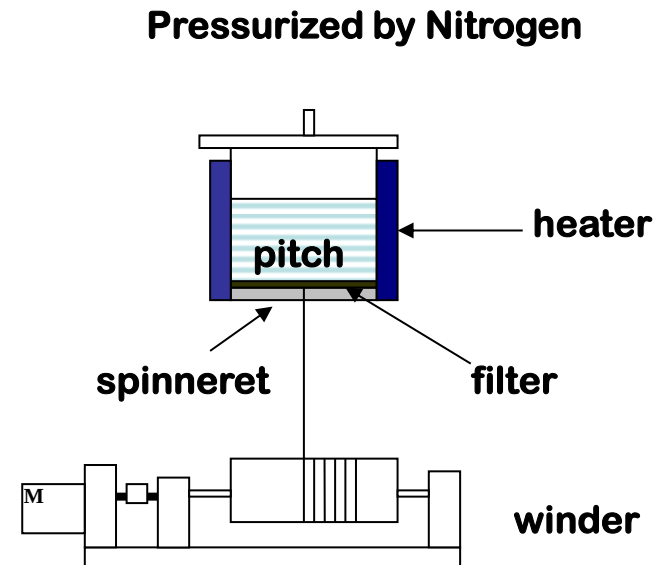
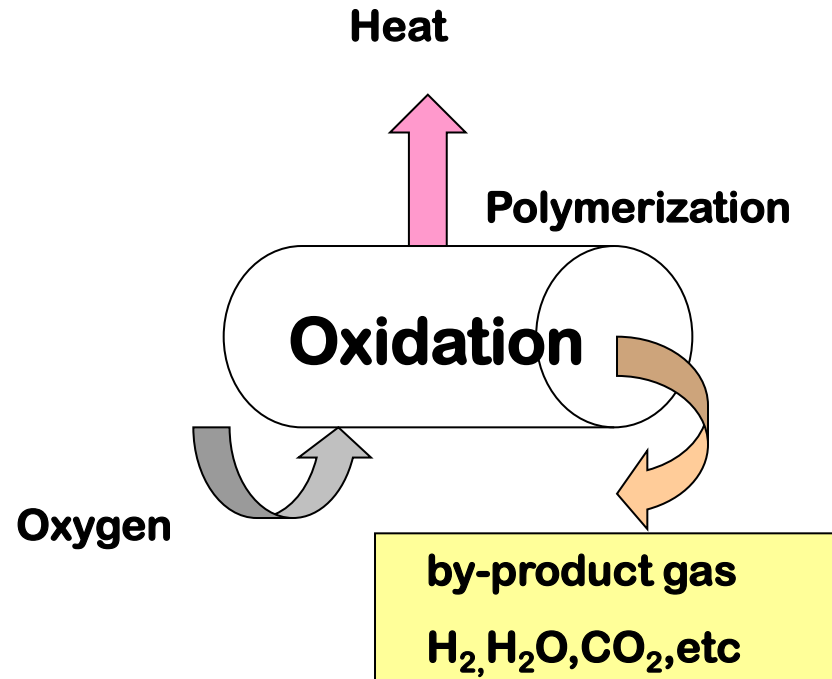
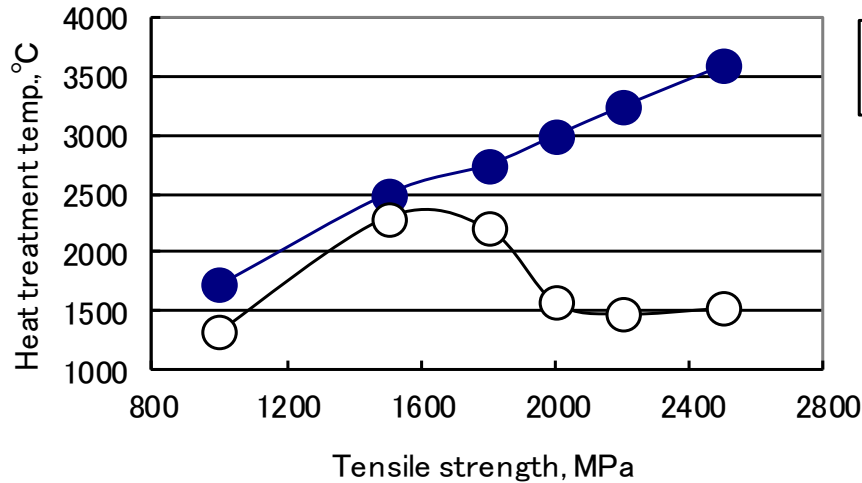


Fig. Spinning apparatus

Stabilization of Pitch Fibers

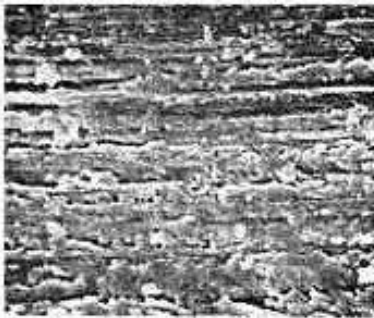


Increasing Tensile Strength by Removal of Inorganic Impurities



$\text{SiO}_2 + \text{C} \rightarrow \text{SiC} + \text{CO}_2$
 Over 1250 °C
 $\text{SiC} \rightarrow \text{Si} + \text{C}$
 Nucleation of voids
 Over 1800 °C

Fig. Relationship between the tensile strength and heat treatment temperature



30ppm



270ppm

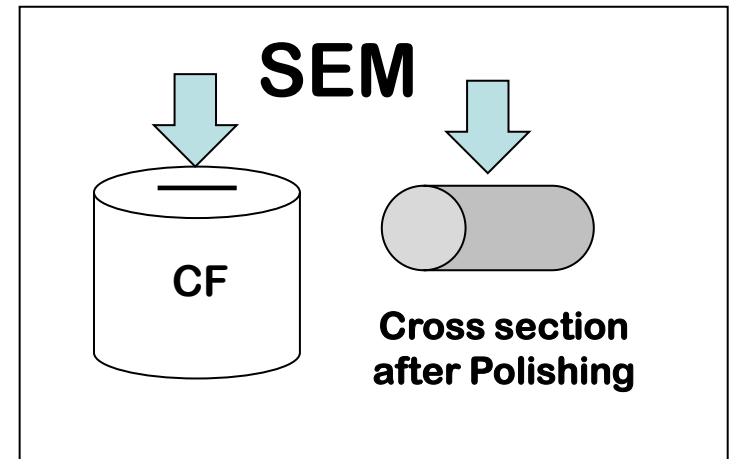
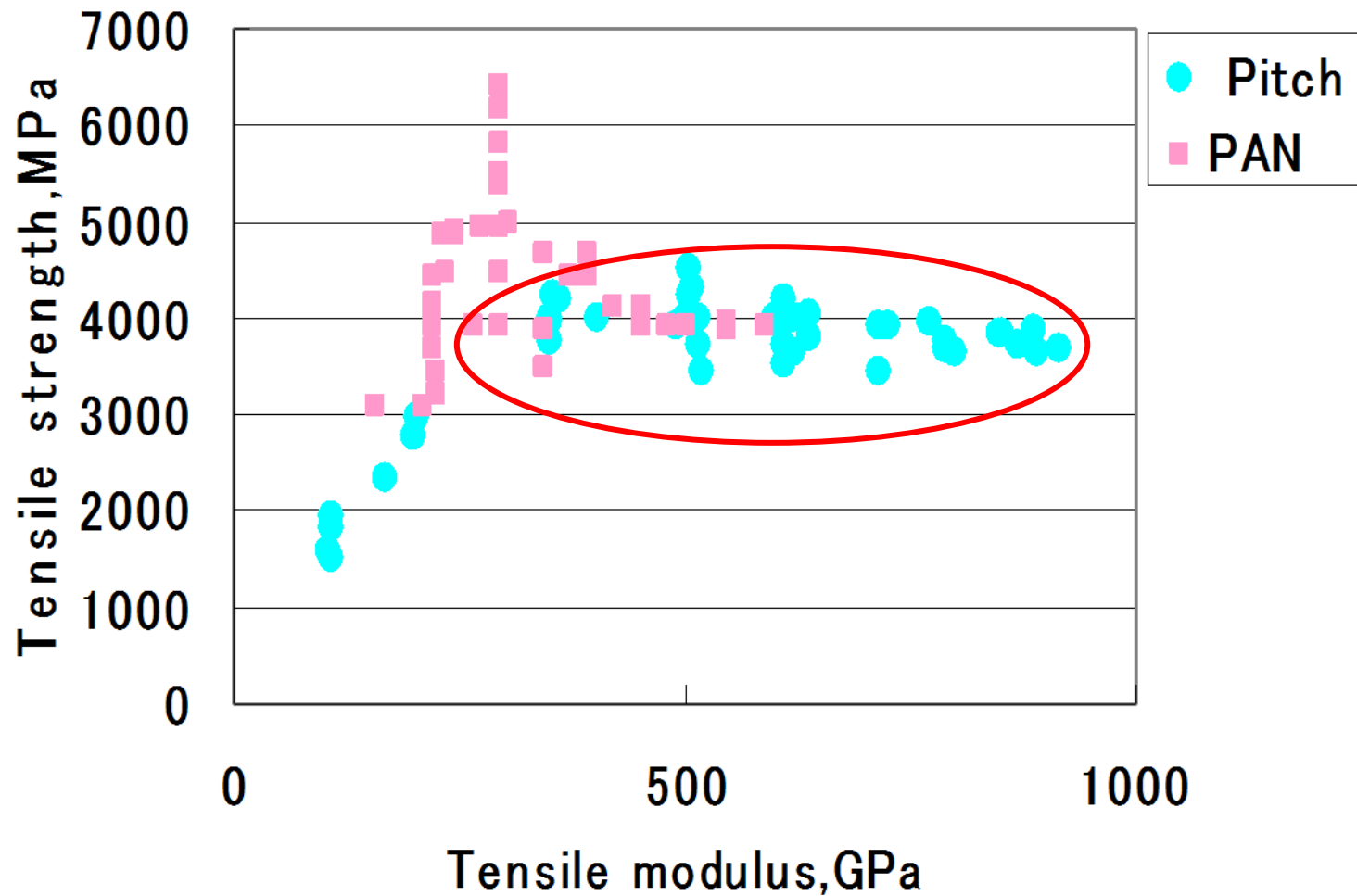
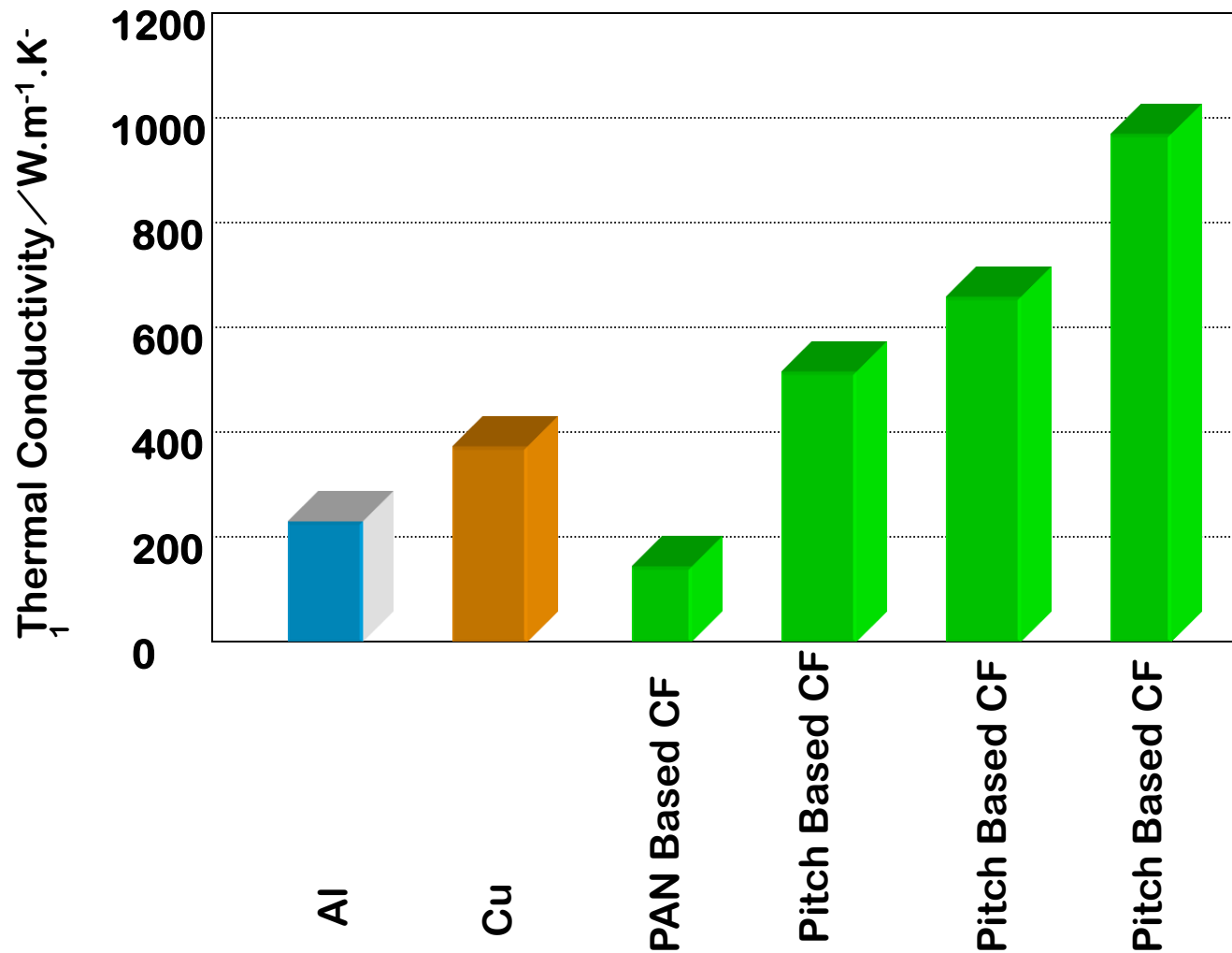


Fig. Observation of void defect

Relationship between TS & YM of Recent CFs



Thermal Conductivity of CF



How to Achieve Pitch Based MPCF

- **Cost : Yields of Pitch and Fiber, High Productivity Fiber**
- **Required Characteristics**

Tensile Strength	800~1100 MPa $\Rightarrow$ 1500~3500 MPa
Elongation Property	1.5 % $\Rightarrow$ 2.0~2.5%
Fiber Shape	Diameter: Less than 10 μm, Long Fiber

- **How to Achieve?**

Precursor	Low Cost, Linear, high MW highly polymeric molecular compositions $\Rightarrow$ Introduction of Molecular Orientation, High Purity
Spinning	Less than 10 μm and Control of microstructure
Stabilization	Low Defect (Low Heat Value), Homogeneous Oxidation
Carbonization	High Carbonization Yield, Low Defects





電池材料

Carbon is key element for Batteries !!

57

① Li-ion



[High capacity]

(+) : LiCoO_2

(-) : **Carbon(Graphite)**

Conductor : **Carbon**

② Dry Battery



[Cheap]

[Easy Available]

(+) : MnO_2

(-) : Zn

Conductor : **Carbon**

③ Ni-MH



[High power]

[Total balance]

(+) : $(\text{Ni-Co})(\text{OH})_2$

(-) : $\text{Mm}(\text{Ni-Mn-Al-Co})_5$

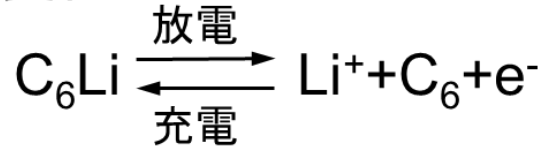
substrate: Nickel and **Carbon**

23/24

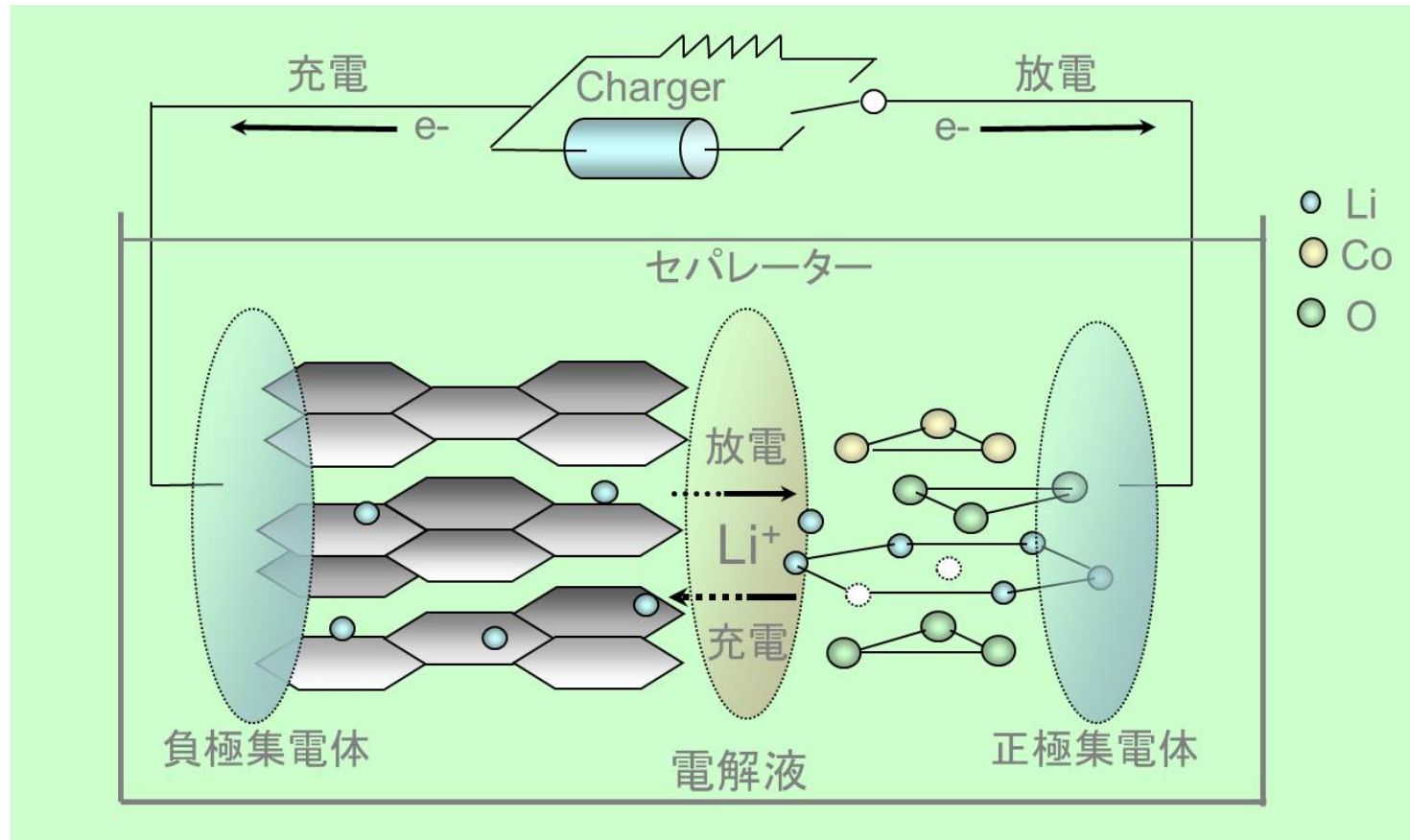
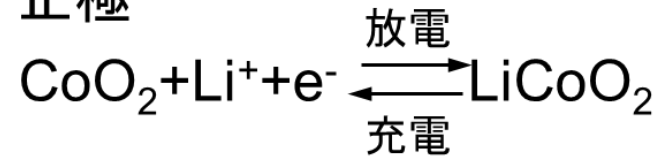


リチウムイオン二次電池の動作原理

負極



正極

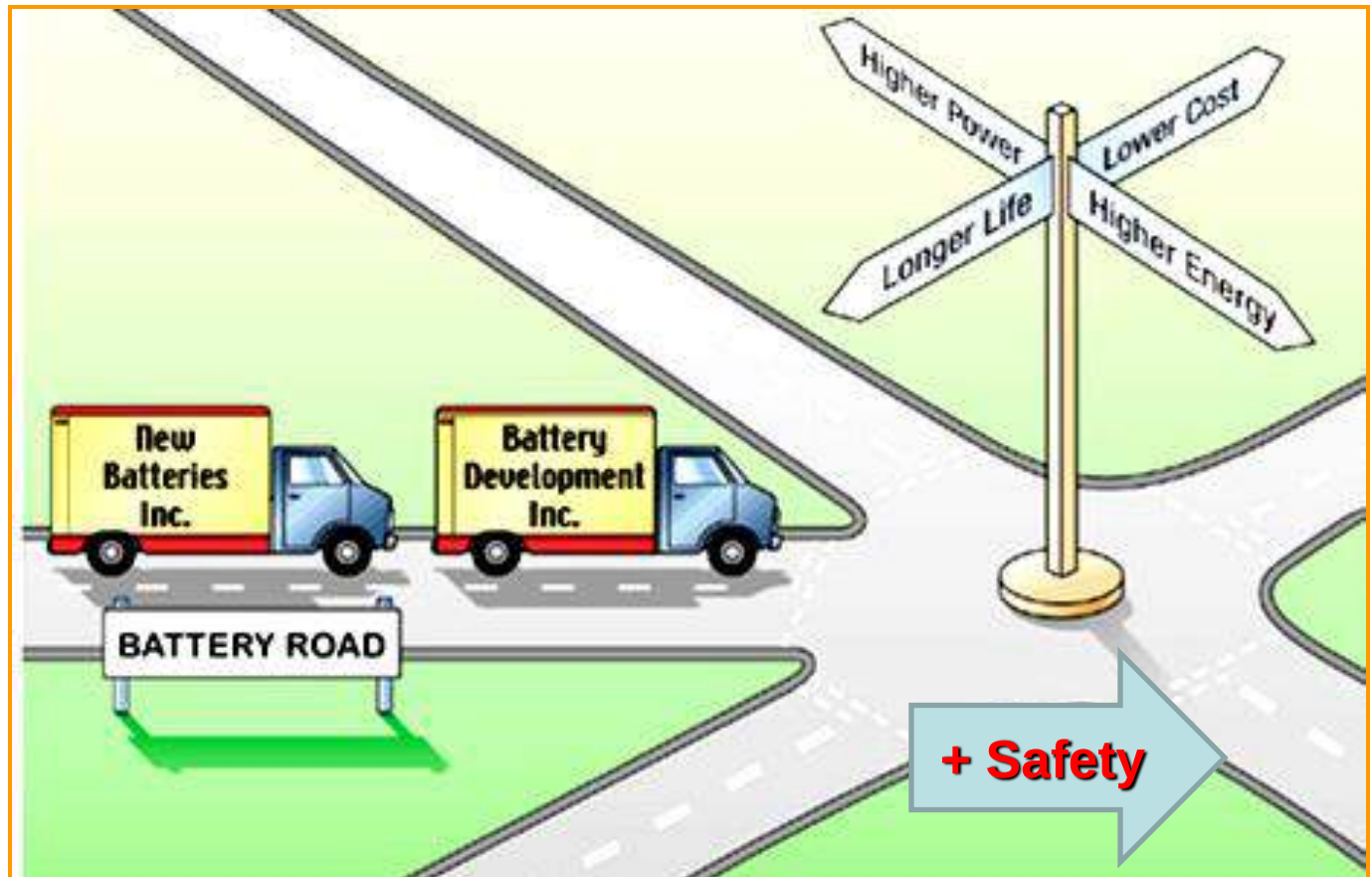


Electrode Materials for Lithium Secondary Battery

Different materials for different applications

A spectacularly reactive cathode

Nature Materials 2, 705–706 (2003)



Anodic Electrode to Hold Reduced Li-ion

Intercalation → Graphite

Surface Electron Transfer into Sealed Void
→ Hard or Low Temperature
Calcined Carbon

Electron Conductive Material

Anodic Carbon and Cathode Material

Expansion Moderator

Holding and Release of Ion Is Accompanied with
Volumetric Charge

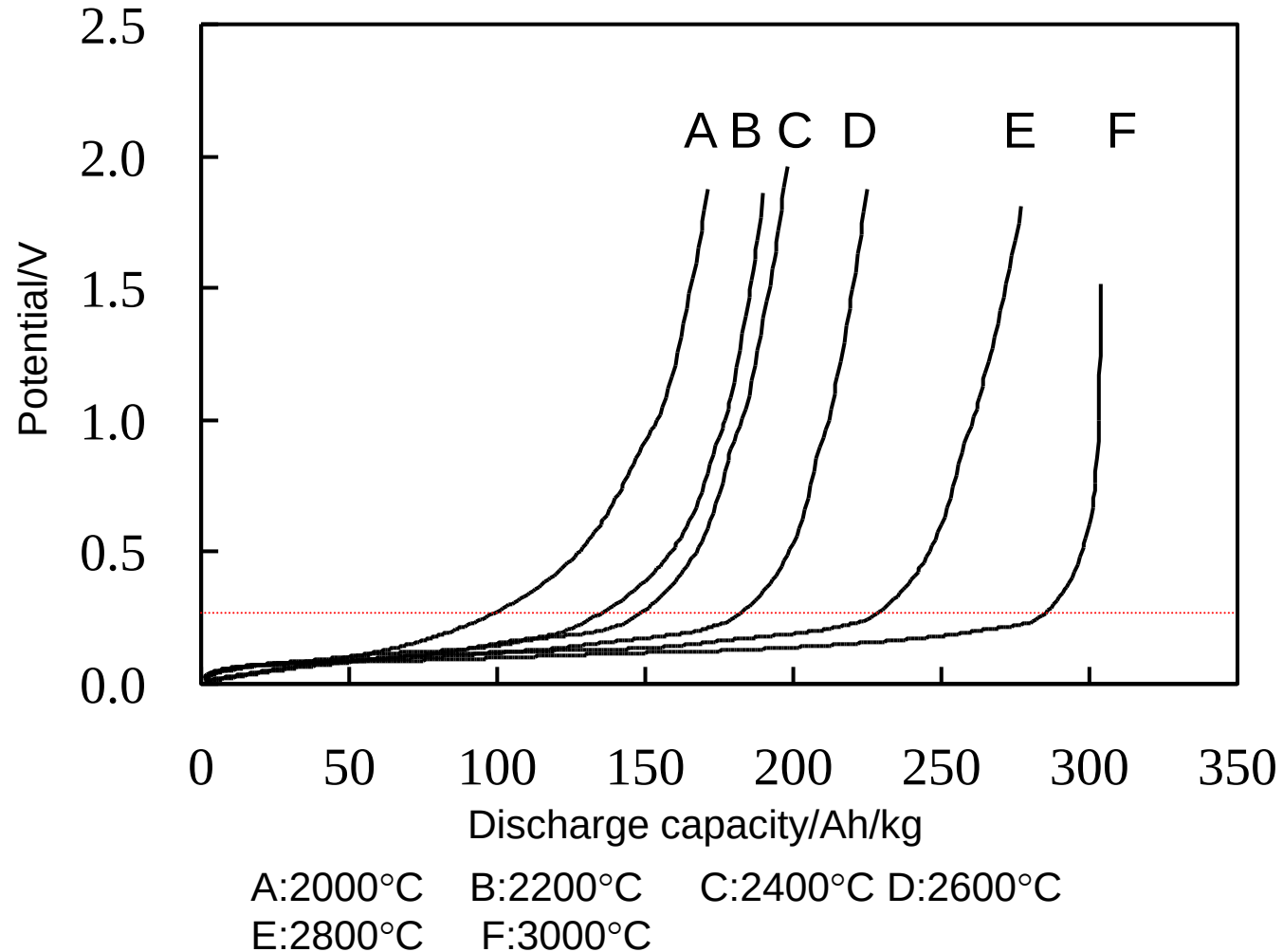
Larger Capacity per Volume → Larger Expansion

Moderation and Control of SEI

Irreversible Charge → Surface Coating, Composite
Structure

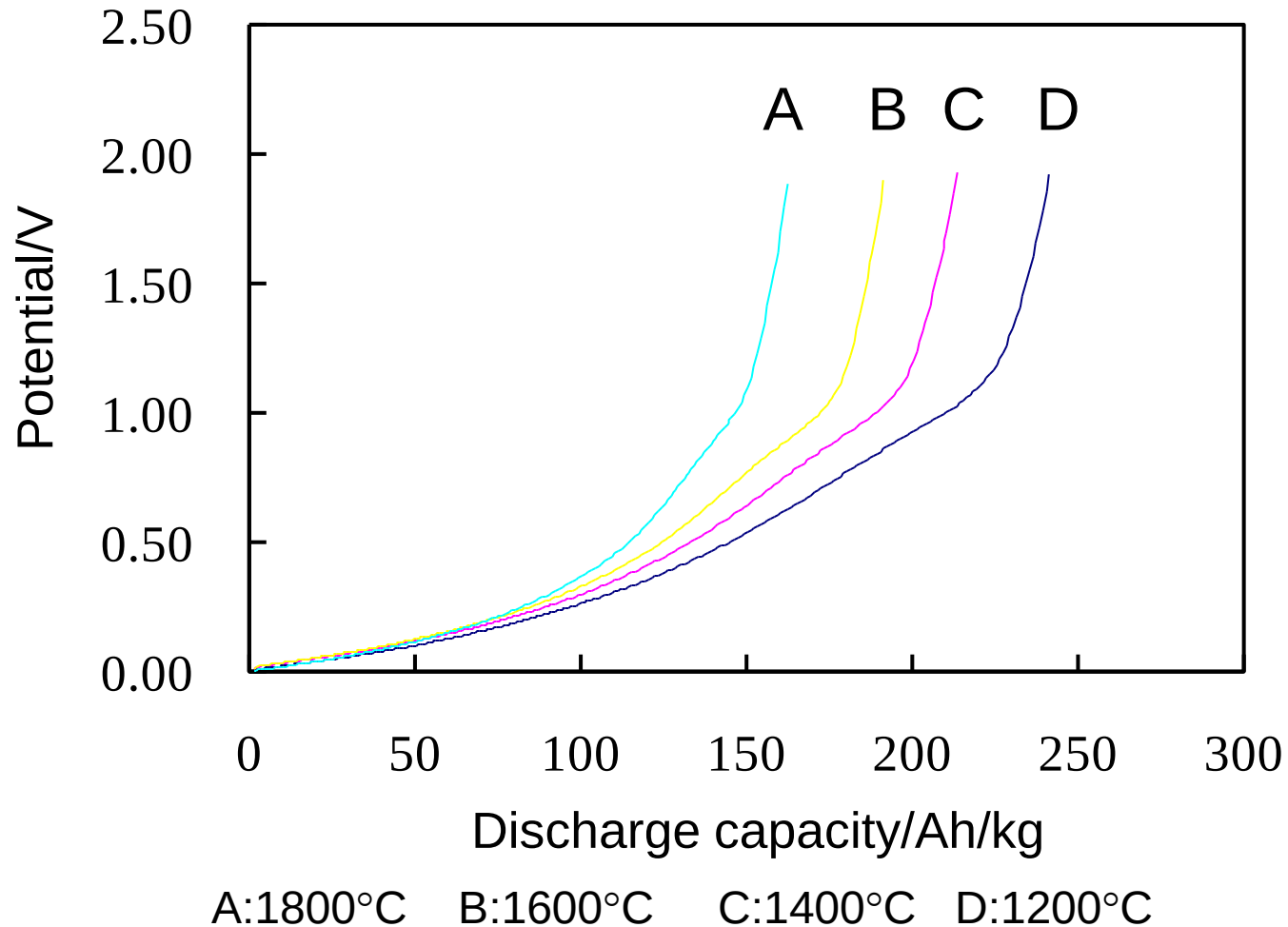
黒鉛系材料

炭素化温度と放電曲線の関係

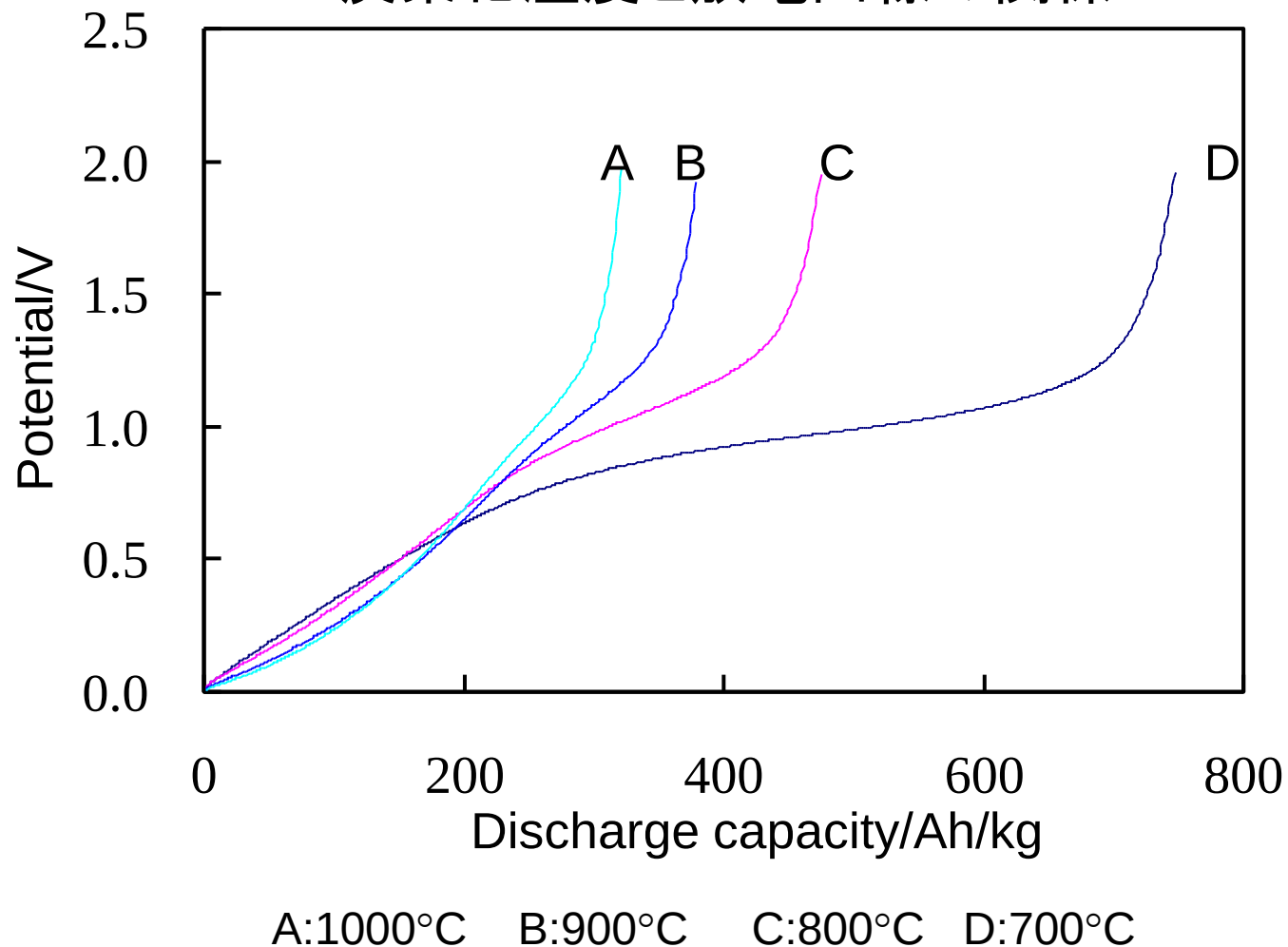


コークス系材料

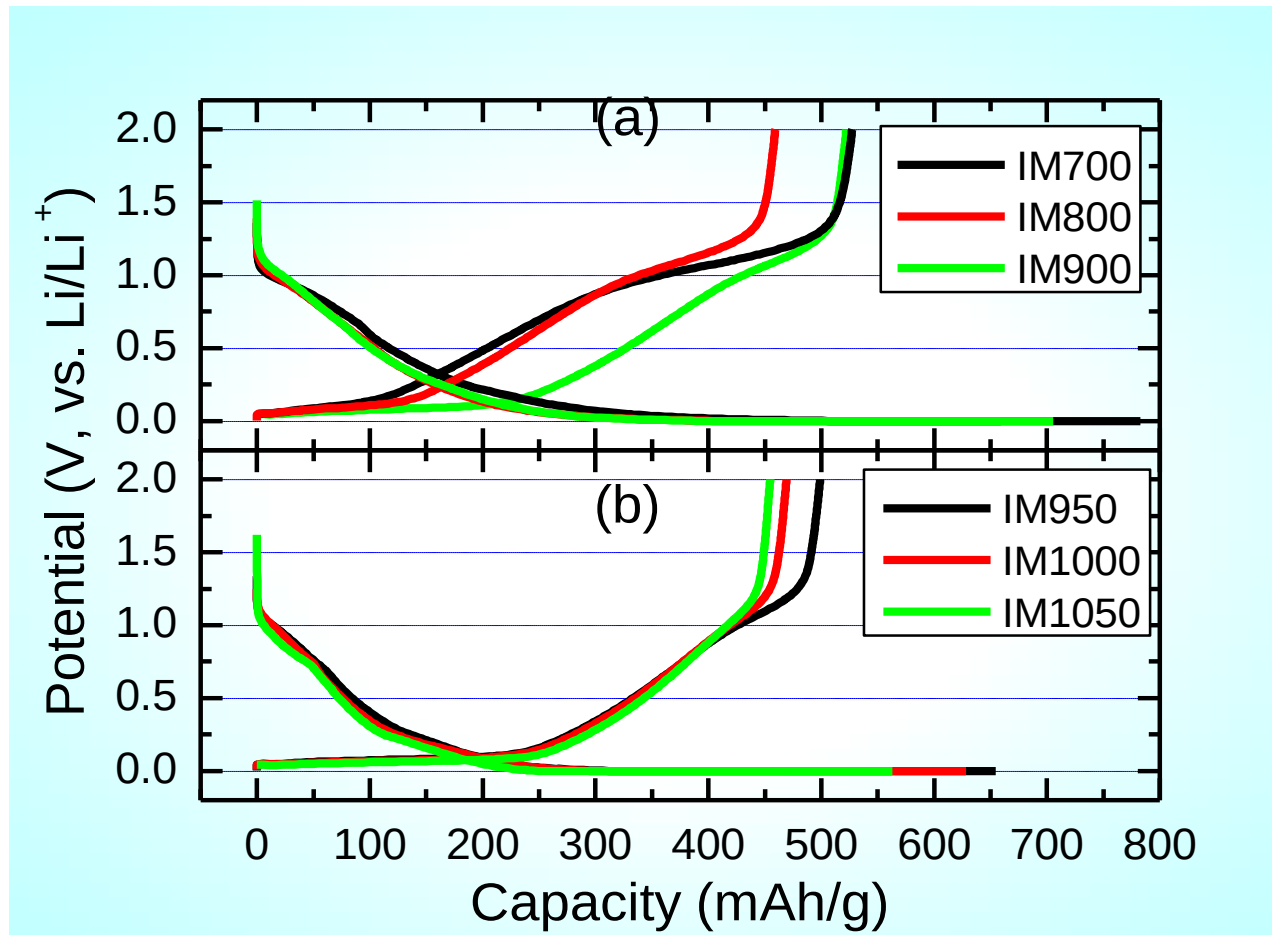
炭素化温度と放電曲線の関係



炭素化温度と放電曲線の関係



バイオ由来のハードカーボン



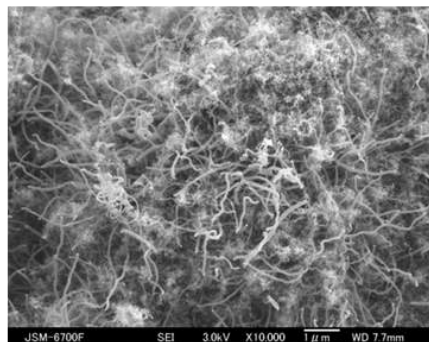
IM is heat treated under Ar atmosphere with the heating rate of 10°C/min



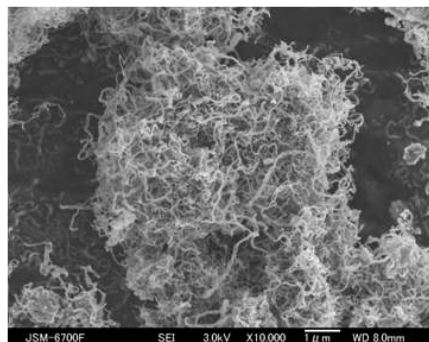
Preparation and Analysis of SiO-CNF Composites

65

SEM



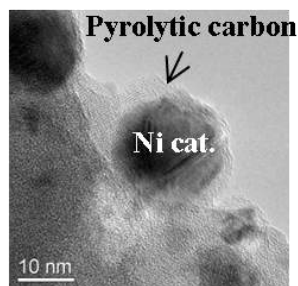
Ni cat. (500°C, H-CNF)



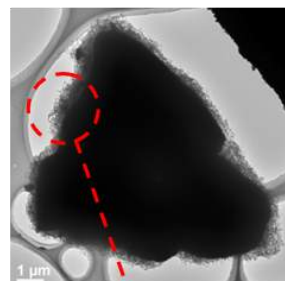
Fe cat. (600°C, P-CNF)

Ref: Yoon et al., Carbon 43 (9)
(2005),1828-1838

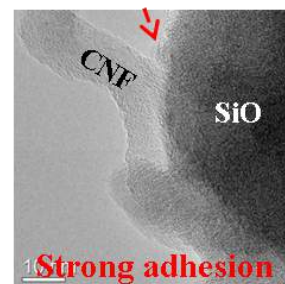
TEM



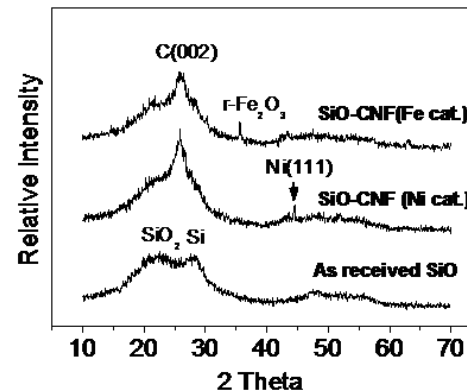
Reaction time (10s)



SiO-CNF composite



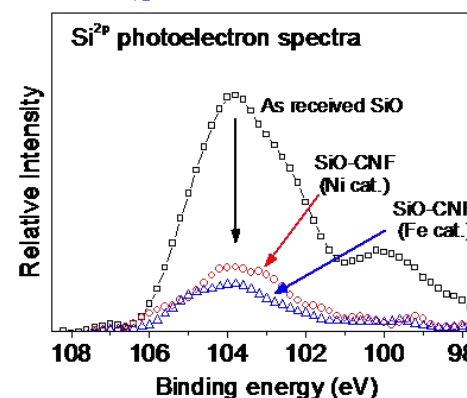
XRD



SiO showed amorphous structure

C(002) peak was observed by CNF growth

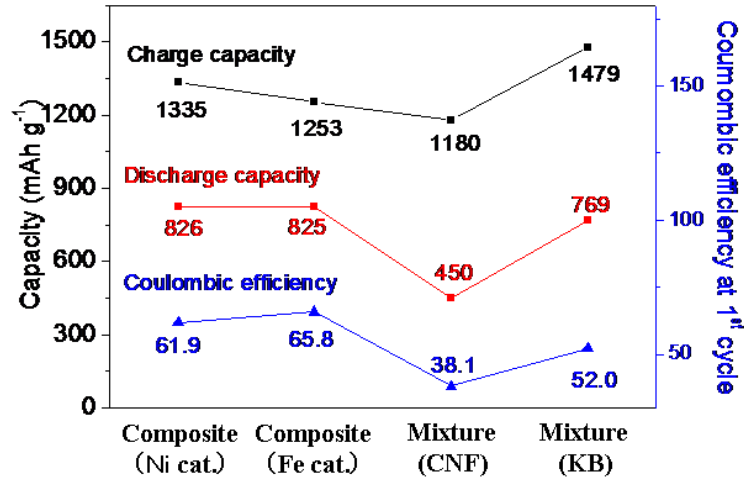
XPS



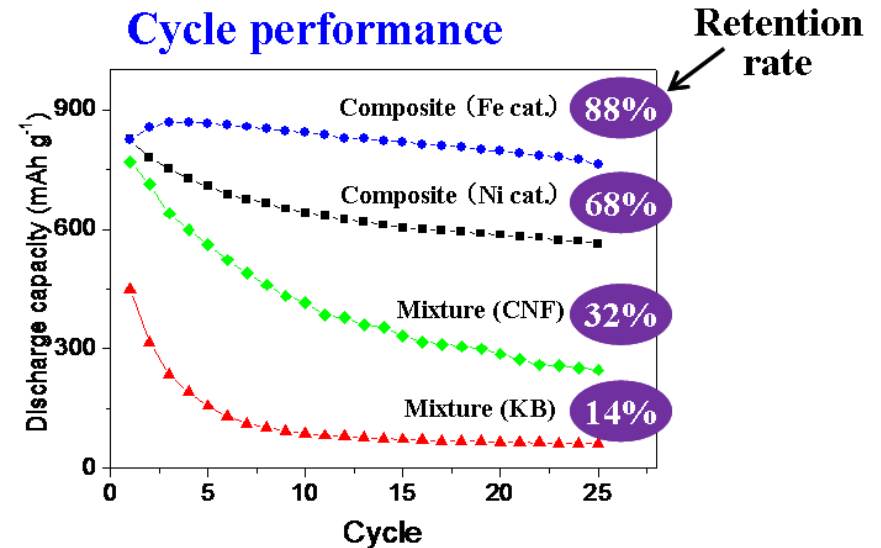
CNF growth decreases Si exposure.

Comparison *bet.* Composite *and* Mixture

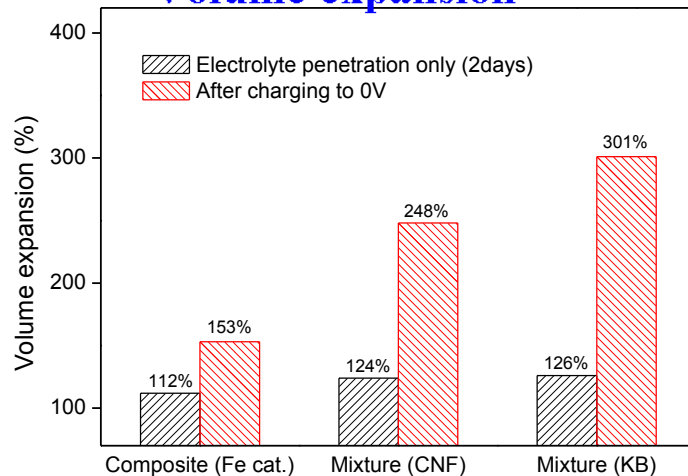
At 1st cycle



Cycle performance



Volume expansion



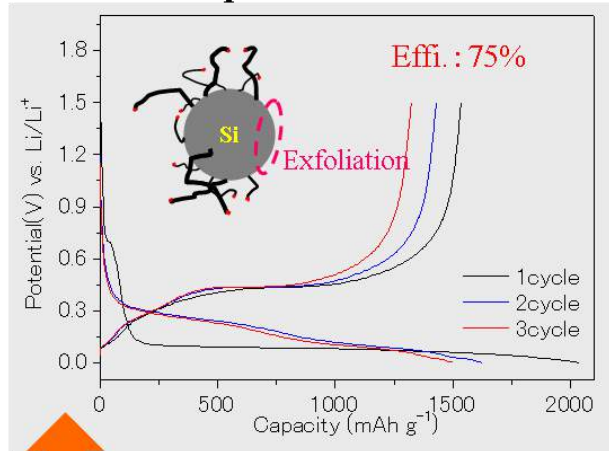
Superiority of the CNF composite

- High discharge capacity and coulombic efficiency at 1st cycle
- Excellent cycle performance
- Lower volume expansion

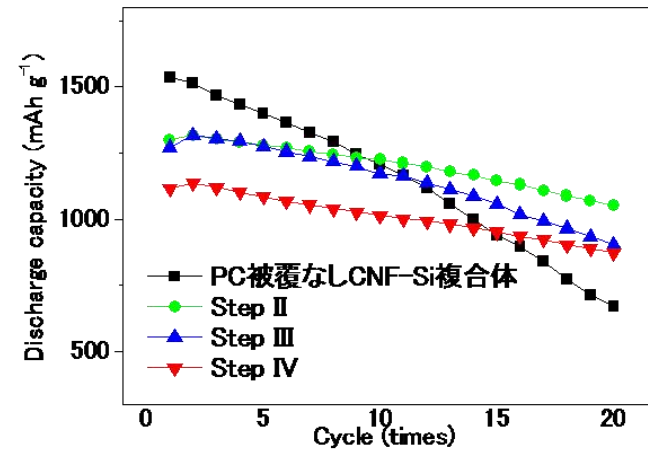
⇒ CNF growth provides spaces to relieve volume expansion and conductivities to improve performances

Cycle performances of PCSi-CNF composite

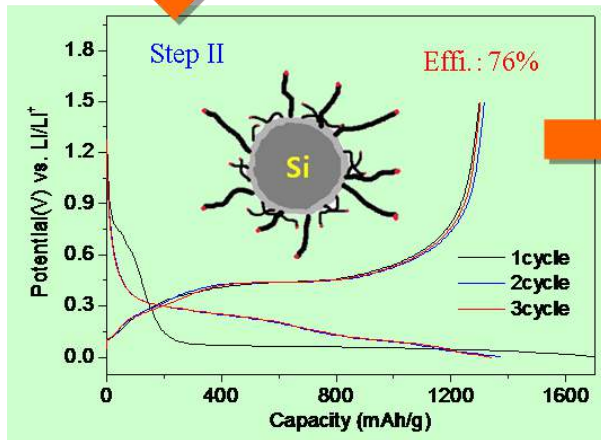
Si-CNF composite



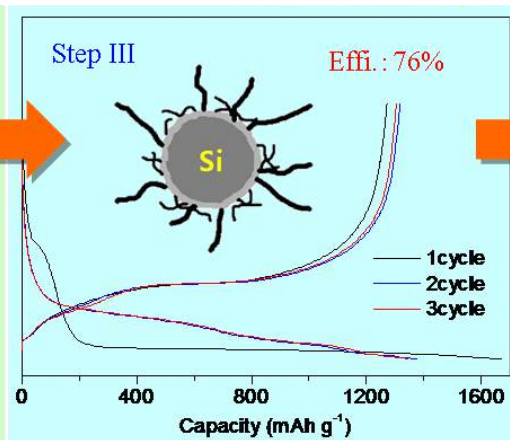
Cycle performance



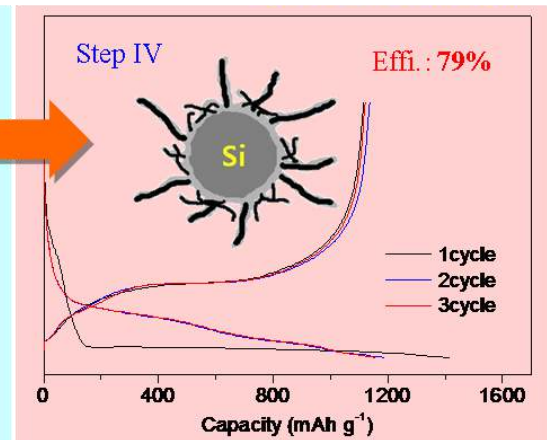
PCSi-CNF



PCSi -CNF (Fe removal)



PCSi -CNF (PC re-coating)

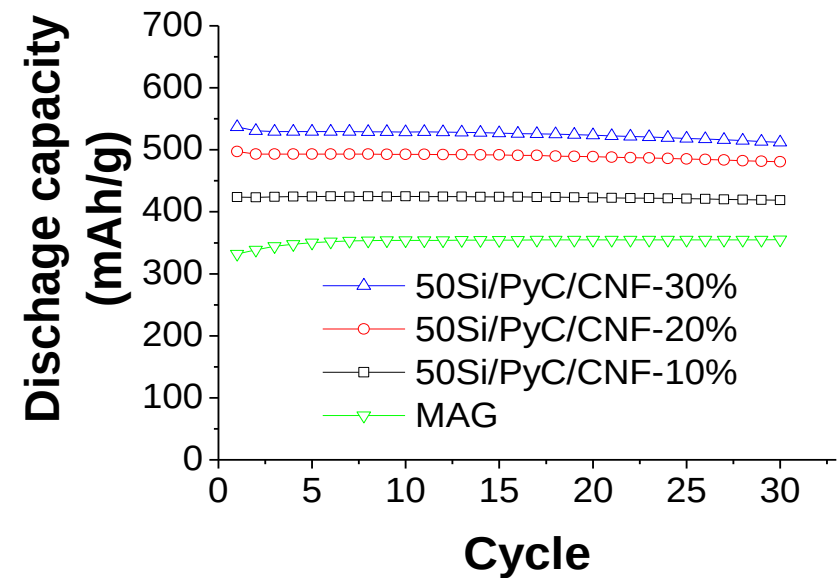
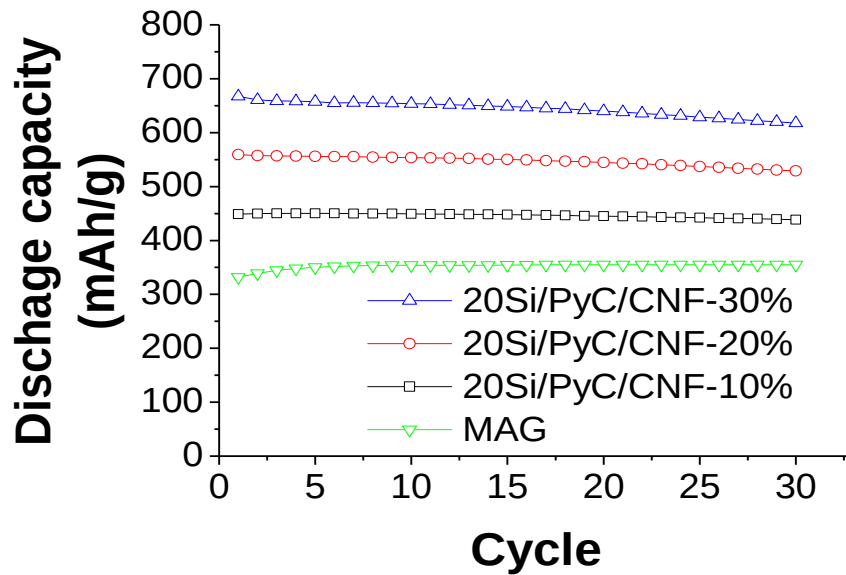


The decreased surface area

38



Si-CNF composite / Graphite Hybridization

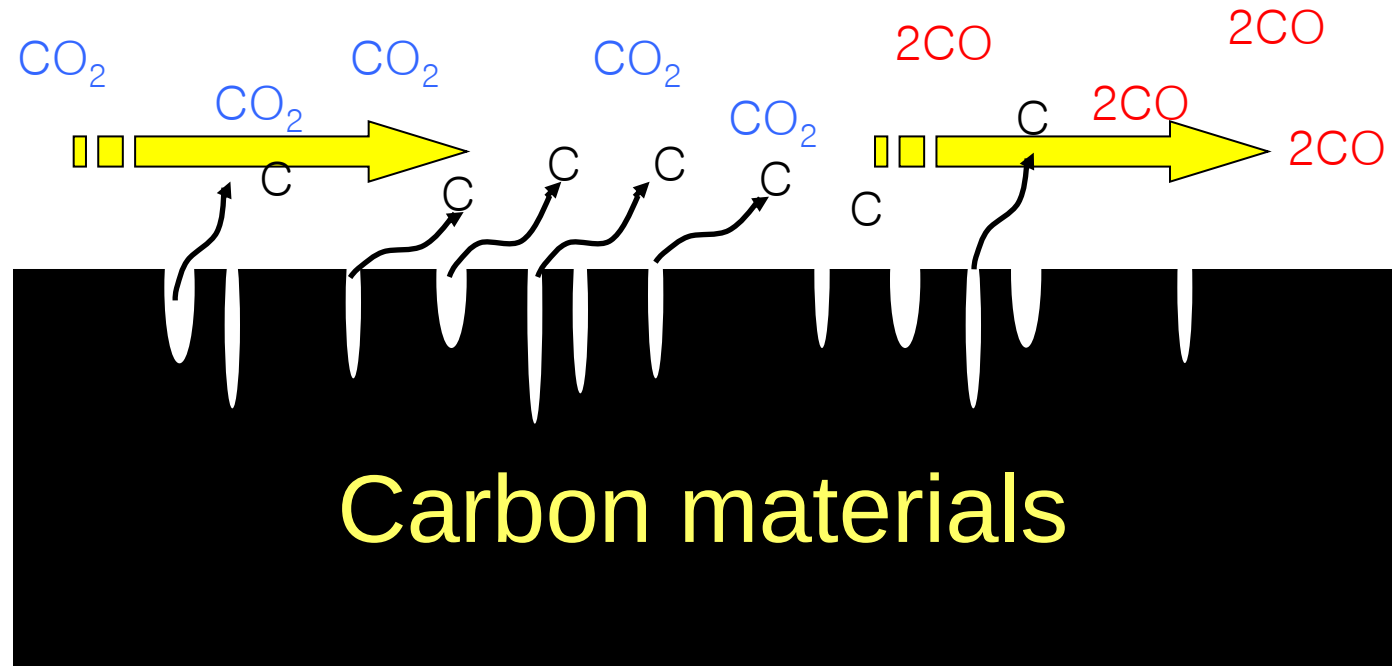


Activated Carbons for Energy and Environmental Devices



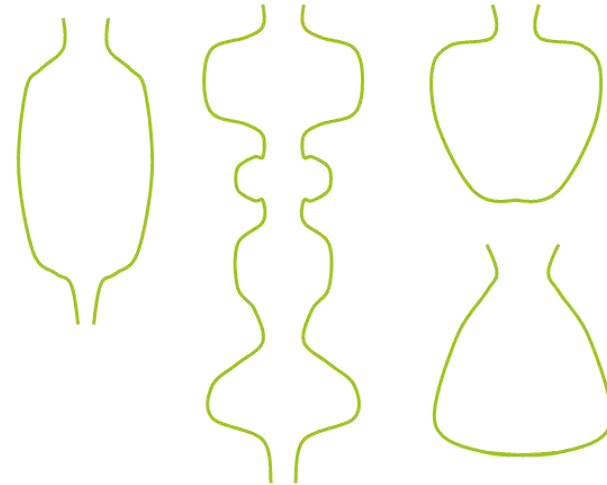
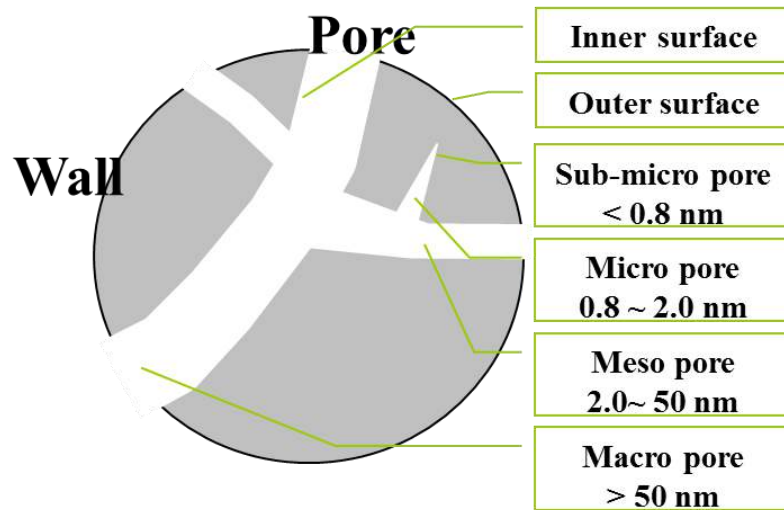
Activation (活性化)

(Making small pores in the carbon materials)



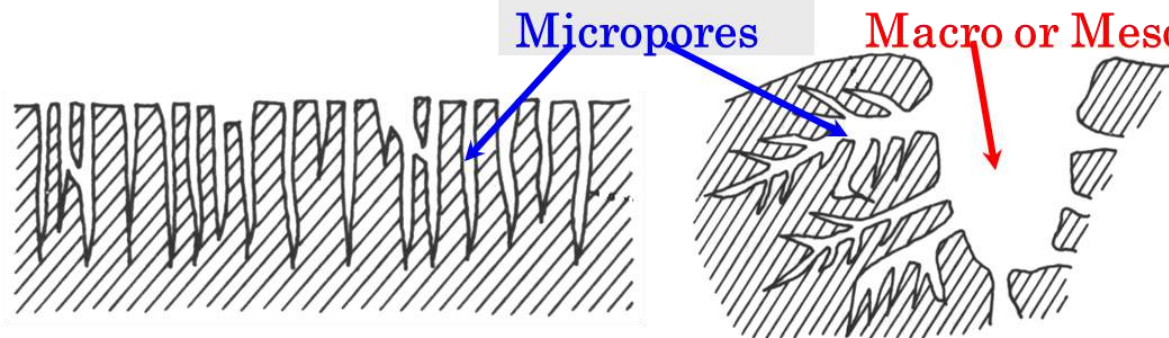
Activation reagents

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



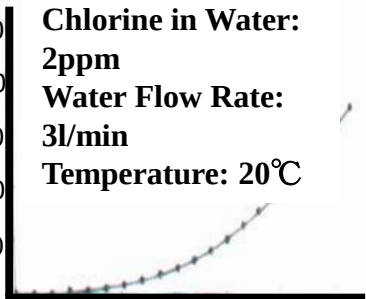
Classification of surface and pores

Schematic shapes of pores



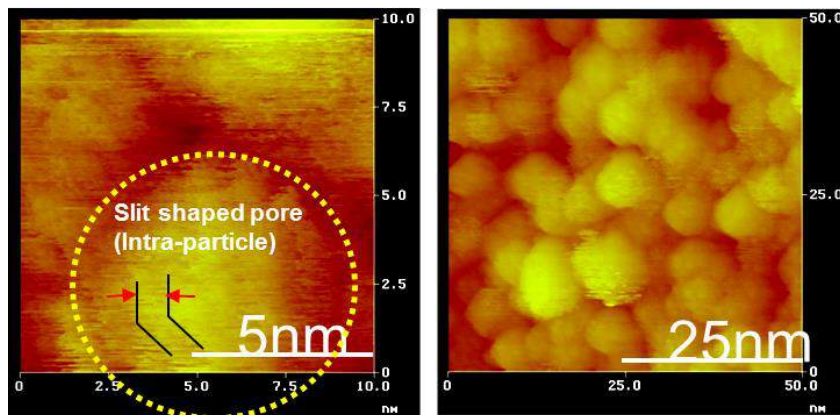
Schematic pore images of activated carbon fiber and activated carbon

ACF Products in Particular Forms

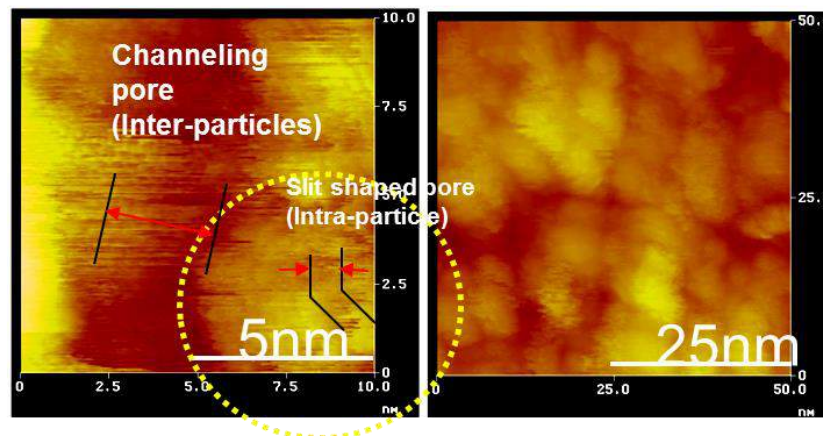
Felt	Paper	Manufacturing Products	
			
		Water Filter	Small Water filter
• Thickness 1~8 mm ACF Coat 60~100% • Mixing organic fibers to improve the strength and dimension stability. • Needle punched felt (FN type) heat-processed felt (FH type). • Selection according to the concentration and amount of the contaminant.	• Thickness 0.2~0.8 mm ACF Coat 60~70% • Anti-water • Anti-chemicals • Easy formation into any shapes	• Columnar • Low resistivity • Chlorine removal Chlorine in Water: 2ppm Water Flow Rate: 3l/min Temperature: 20°C 	

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

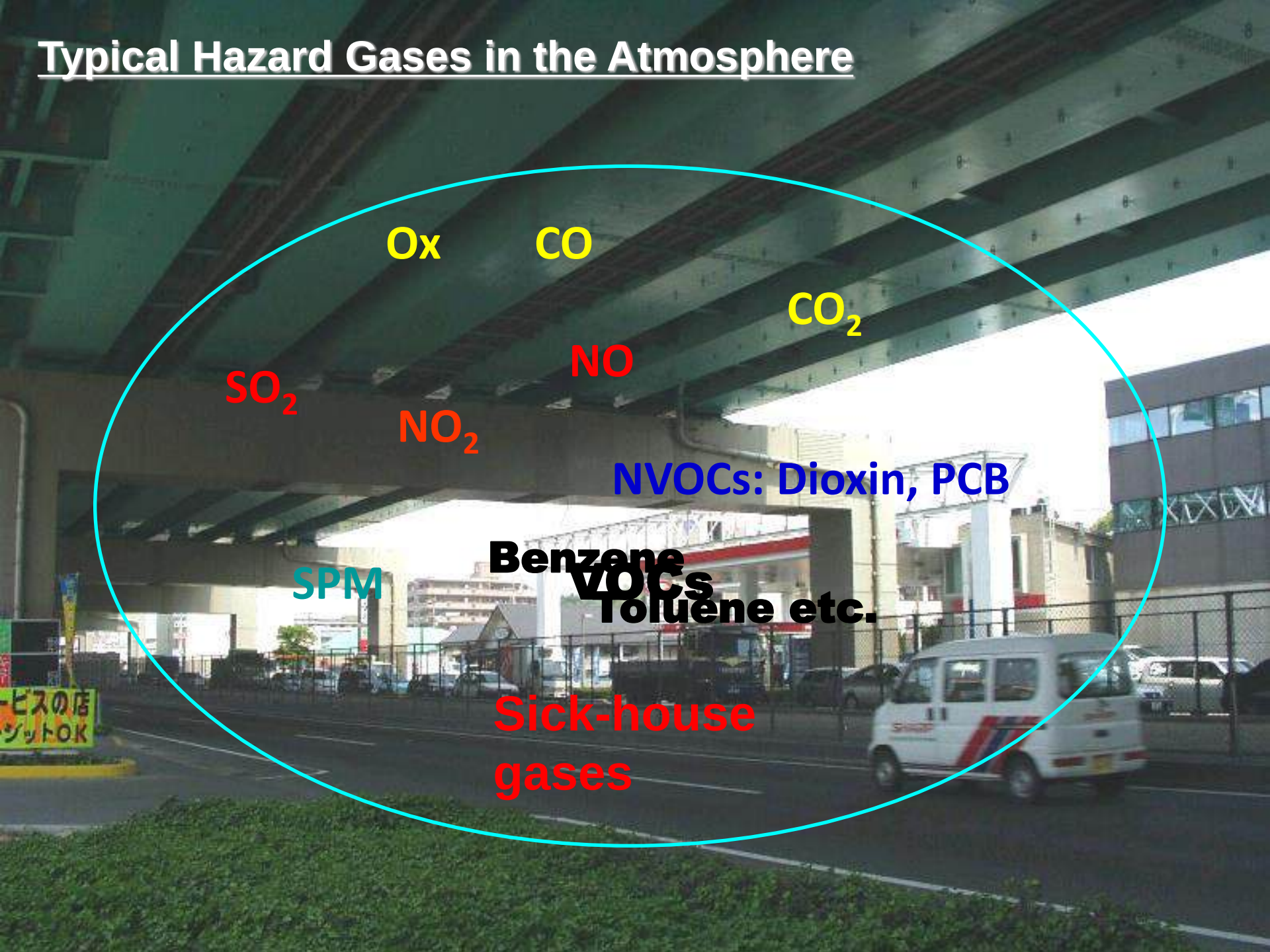


OG20A-800H



- ♣ 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.

Typical Hazard Gases in the Atmosphere



Ox

CO

CO₂

SO₂

NO

NO₂

NVOCs: Dioxin, PCB

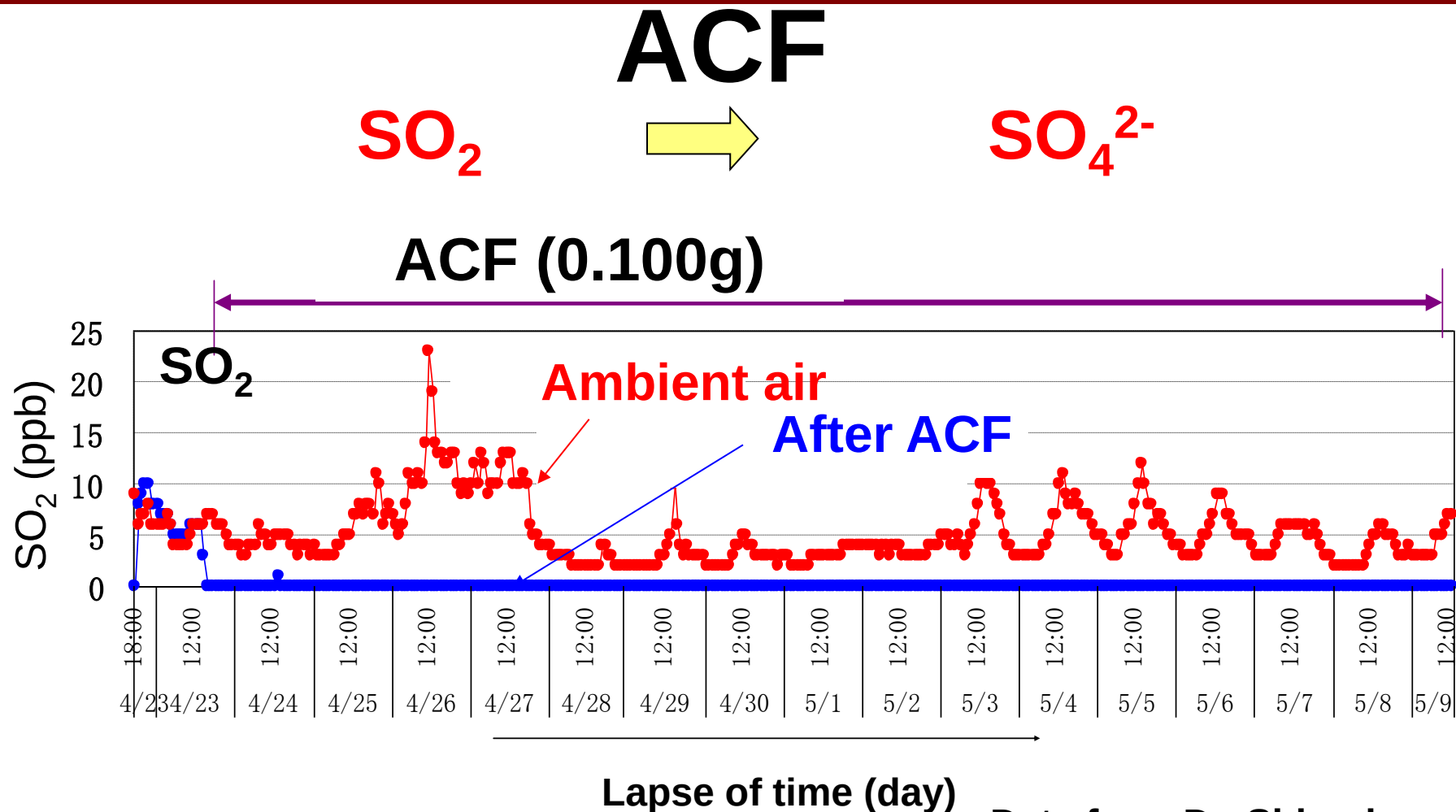
SPM

Benzene

VOCs

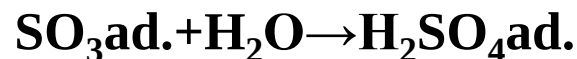
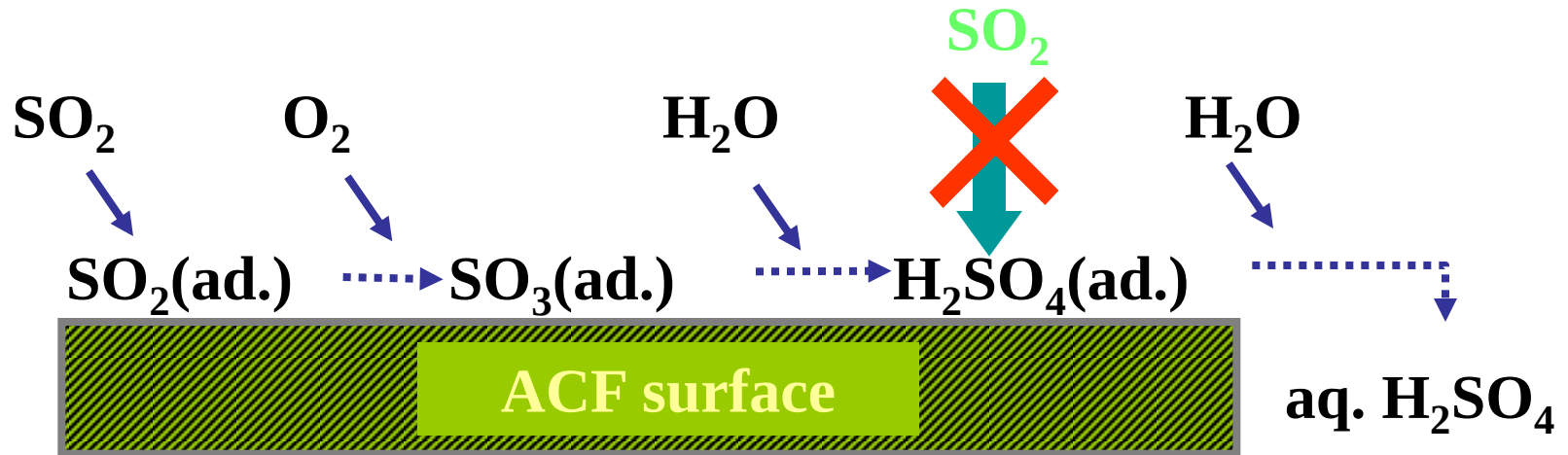
Toluene etc.

Sick-house
gases

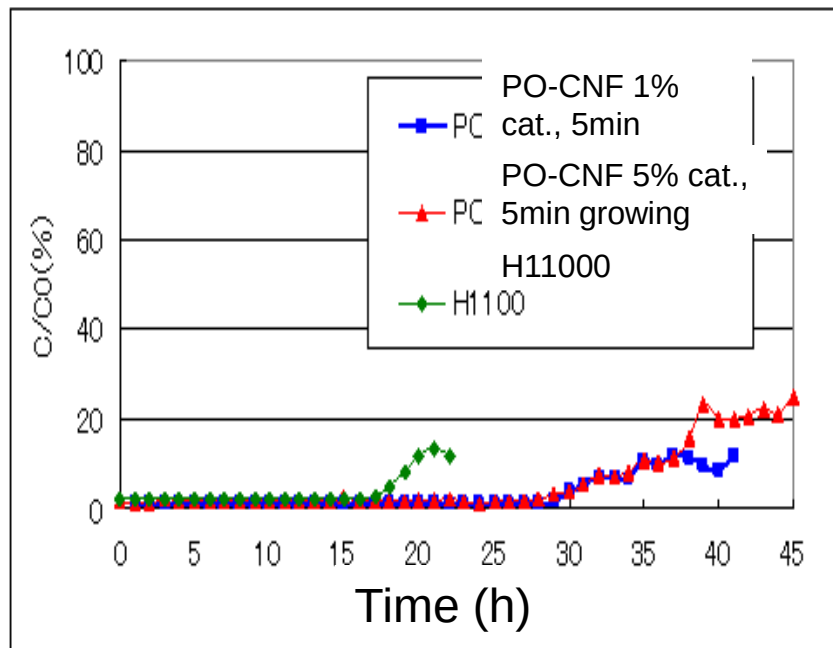


Data from Dr. Shimohara
Of Fukuoka H & E Institute

DeSOx mechanism using ACF



DeSOx Properties of ACF and ACF-CNF

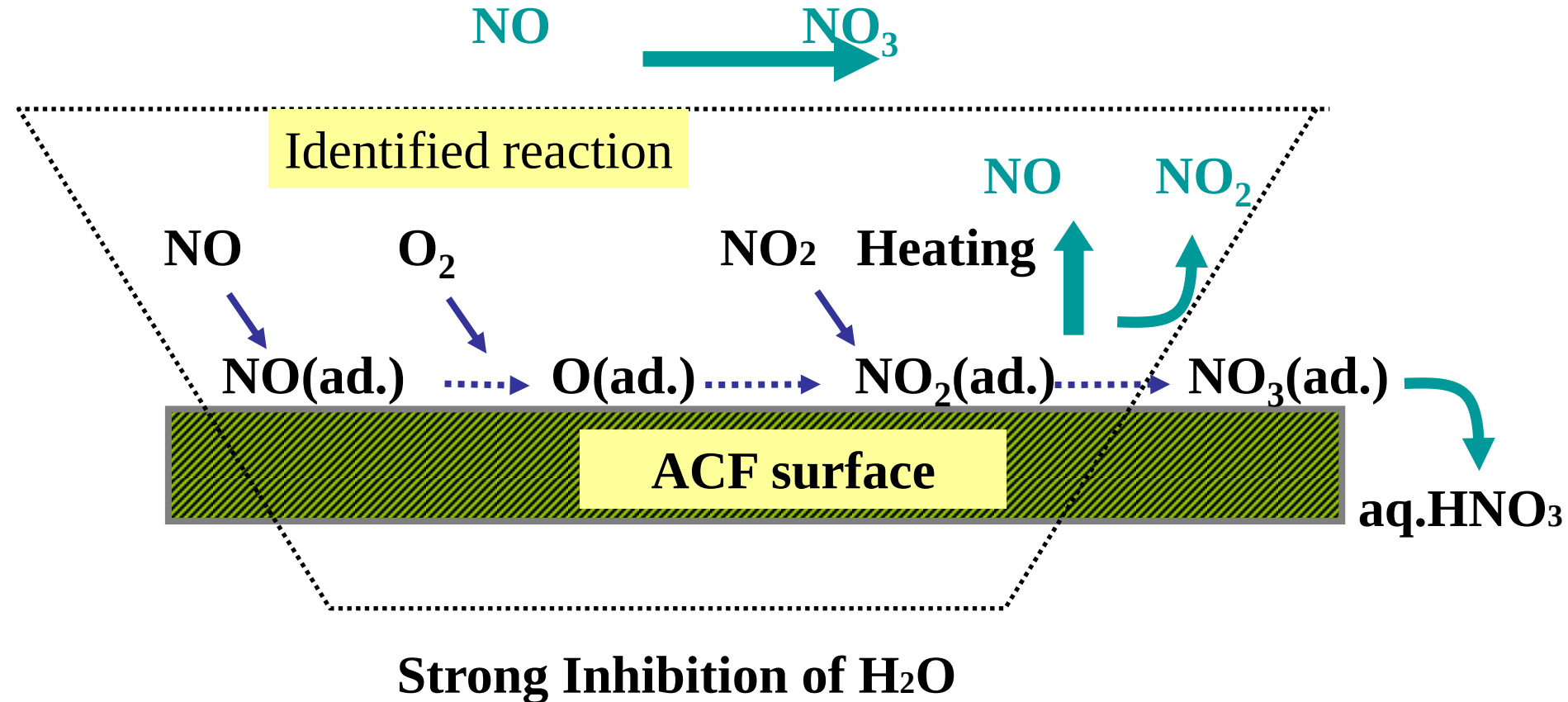


DeSOx condition: SO_2 1000ppm, O_2 5vol%,
 H_2O 10vol%,
 N_2 balance、Total flow rate: 100 ml/min
Reaction Temperature: 50 °C



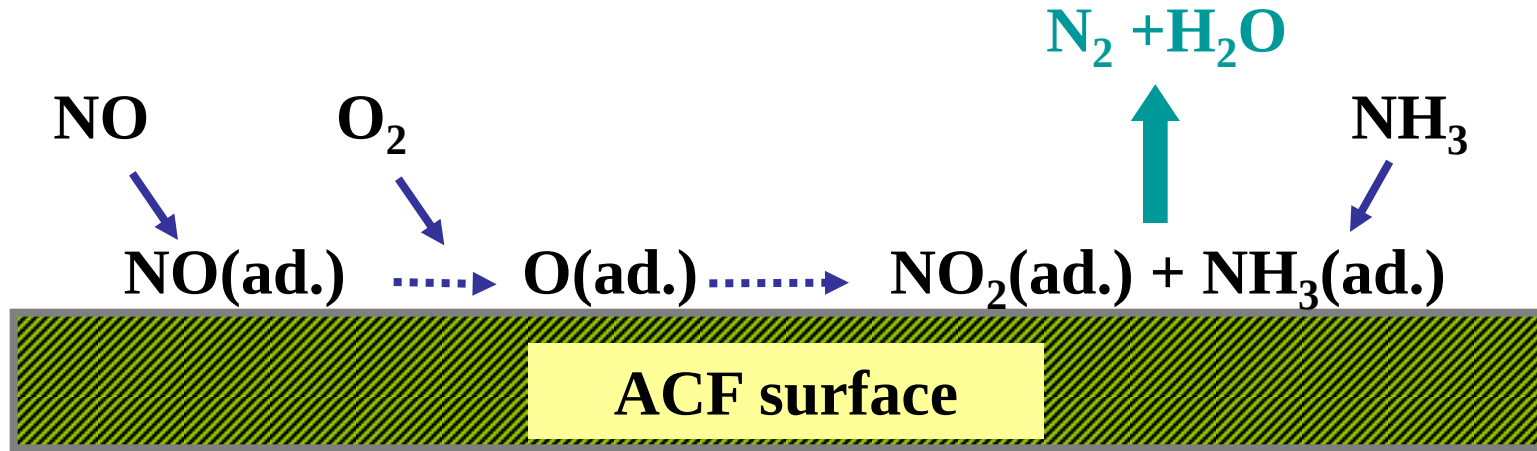
PDU for SOx Removal by ACF

NO & NO₂ Oxidation over ACF

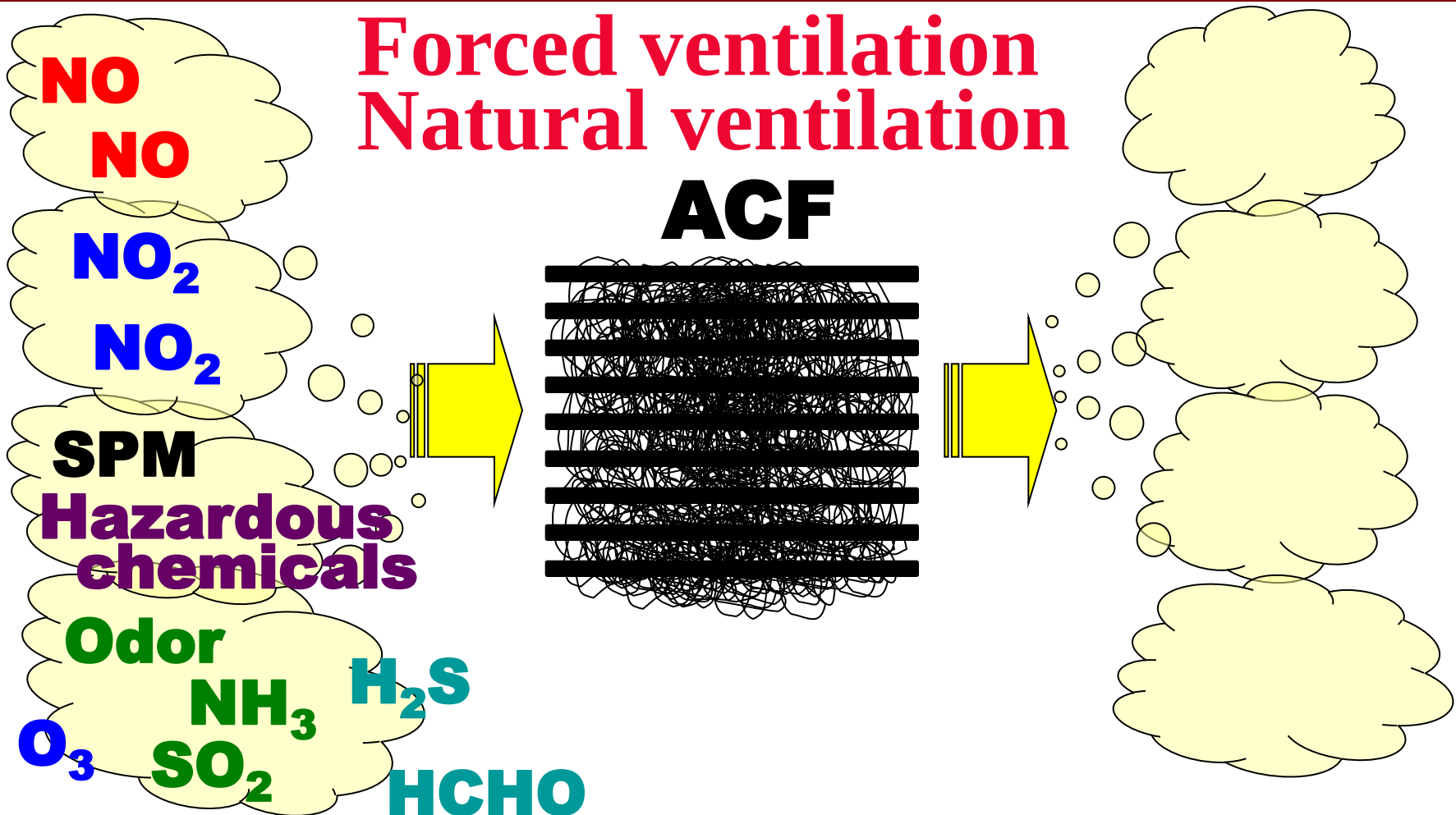


The oxidation of NO₂ always produces NO
And NO₃ through the disproportionation.

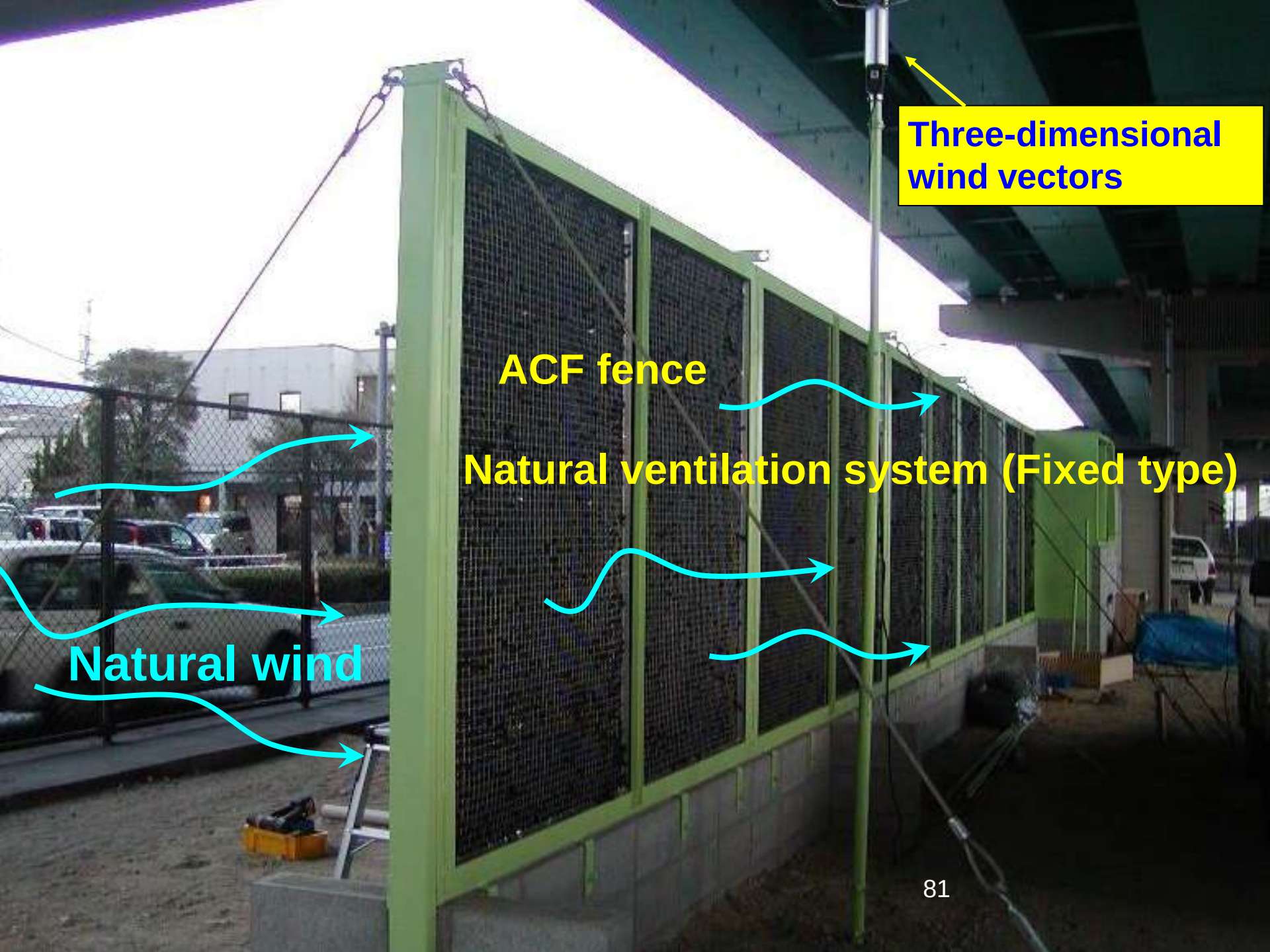
The Mechanism of NO Reductive Removal



The mechanism of NO removal consists of adsorption and oxidation of NO into NO_2 which is reduced with NH_3



Room temperature, ozonizer is no need, no light irradiation, compact design



Three-dimensional
wind vectors

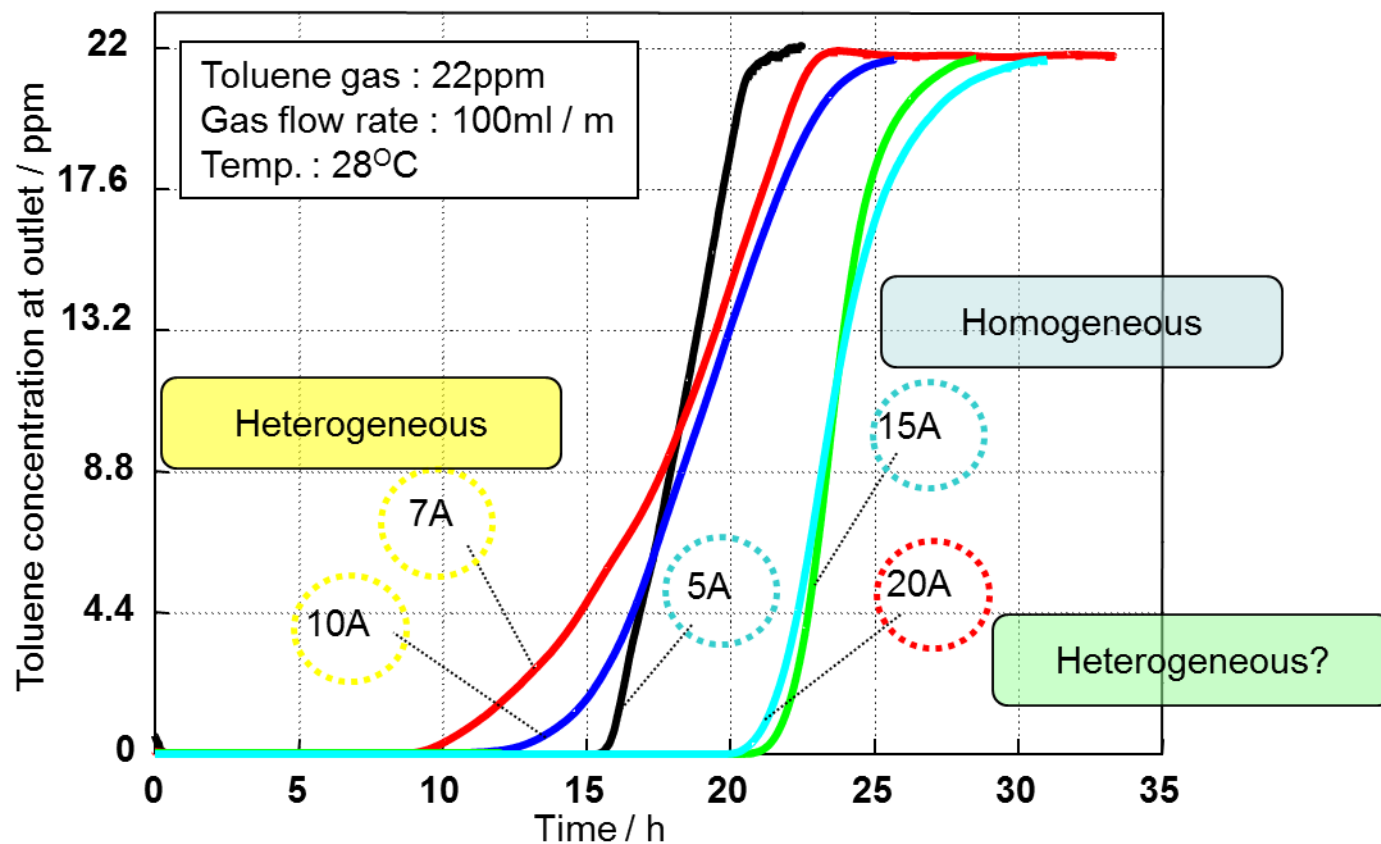
ACF fence

Natural ventilation system (Fixed type)

Natural wind

Toluene adsorption characteristics of ACFs

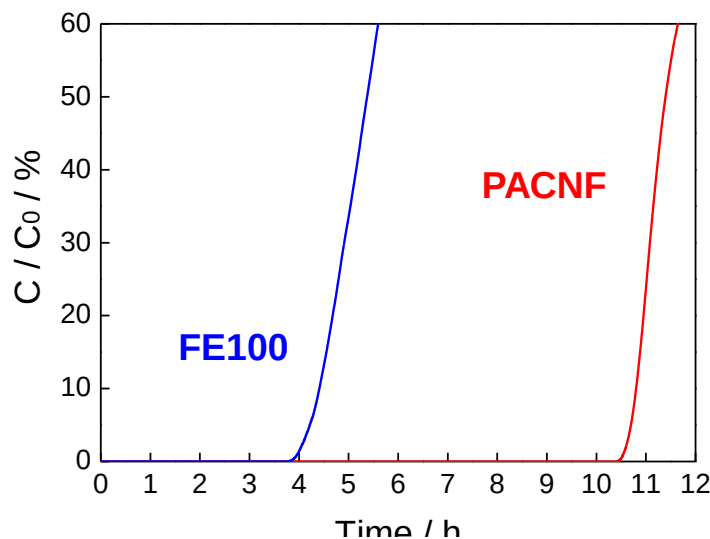
82



HCHO adsorption characteristics of PACNF in humidified atmosphere

83

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



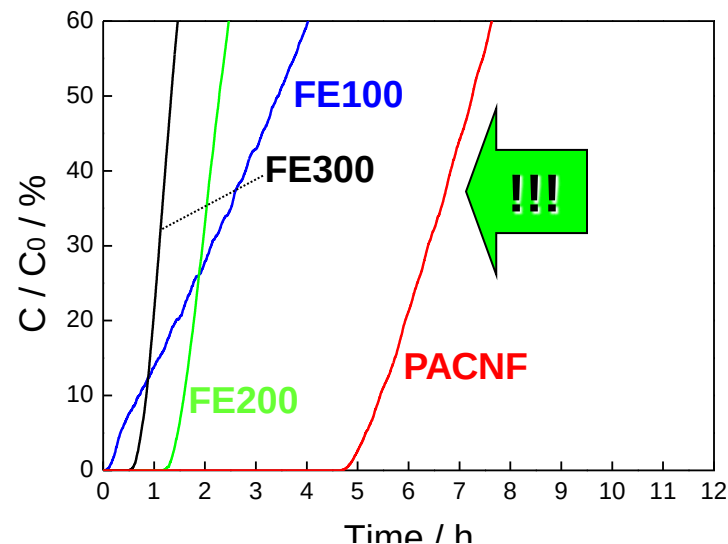
Experimental

HCHO : 11 ppm

Sample weight : 0.05g

Gas flow rate : 100ml / ml

Humidity of condition : 0%



Experimental

HCHO : 11 ppm

Sample weight : 0.05g

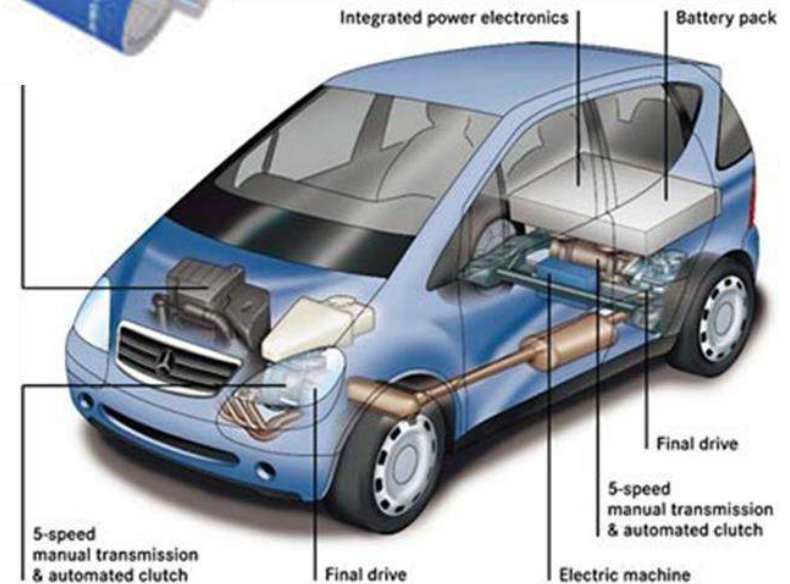
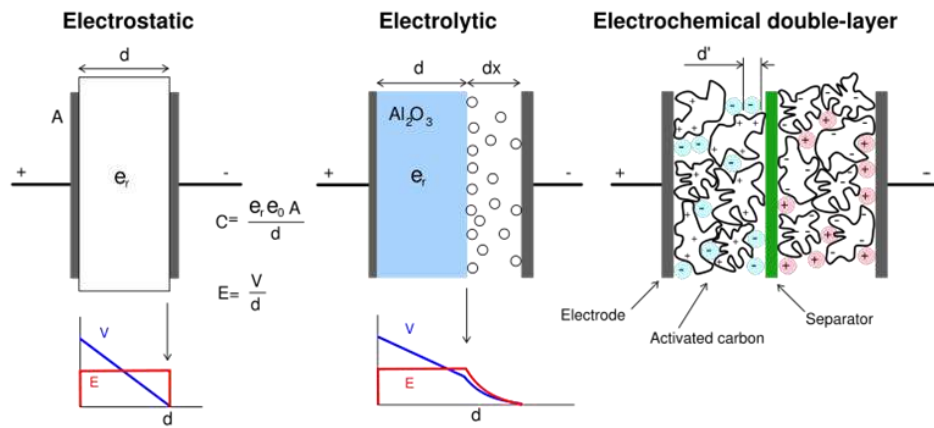
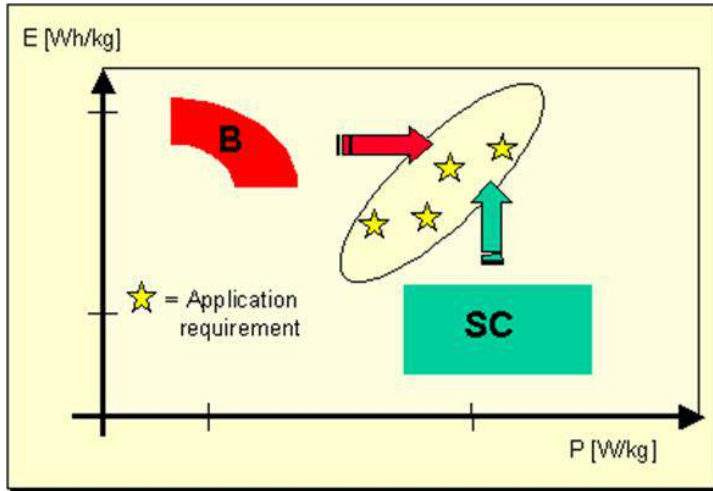
Gas flow rate : 100ml / ml

Humidity of condition : 50%

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



Carbons for Super Capacitor

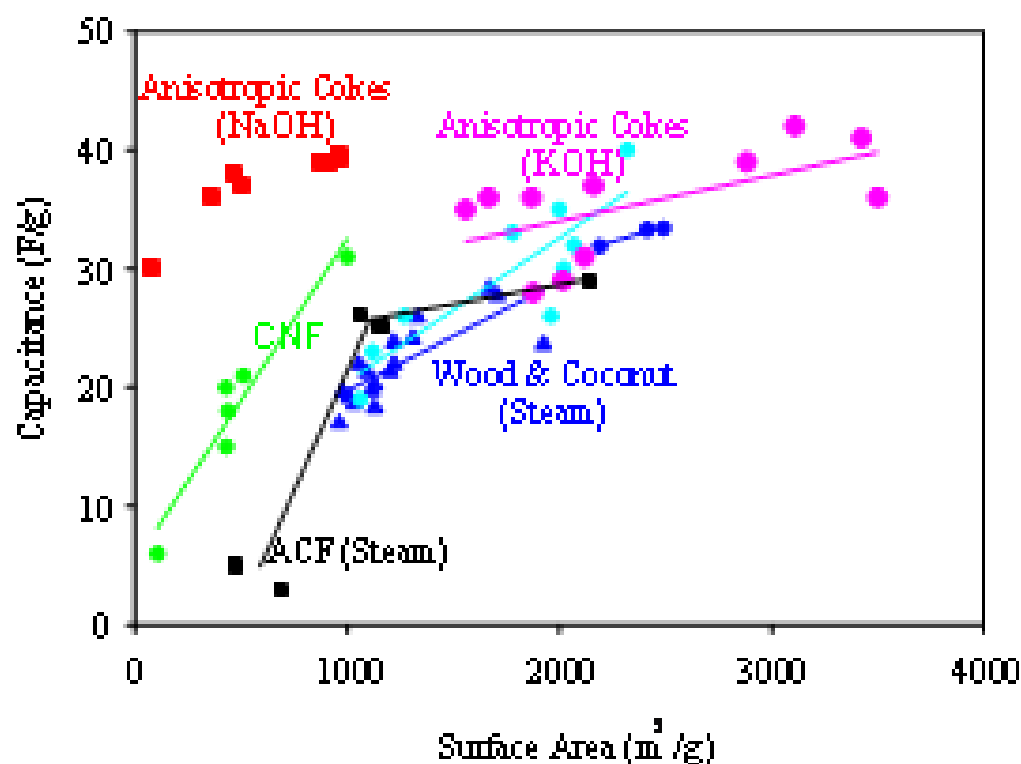


Relationship Between Organic Capacitance And Surface Area

85

1M Et₄NBF₄/PC, 2.7V, Capacitance per Volume

Surface Area vs. Capacitance Per Weight



Conjecture of pore size using capacitance data

86

EDLC with organic electrolytes

Electrolyte: Et_4NBF_4

Cation ($(\text{C}_2\text{H}_5)_4\text{N}^+$)

Stokes' diameter : 0.676nm

1.352nm

Ideal Model for capacitor

M. Endo *et al.*, J. Electrochem. Soc., 148 (8) A910-914 (2001).

EDLC with inorganic electrolytes

Electrolyte: H_2SO_4

Anion (SO_4^{2-})

Stokes' diameter : 0.517nm

1.034nm

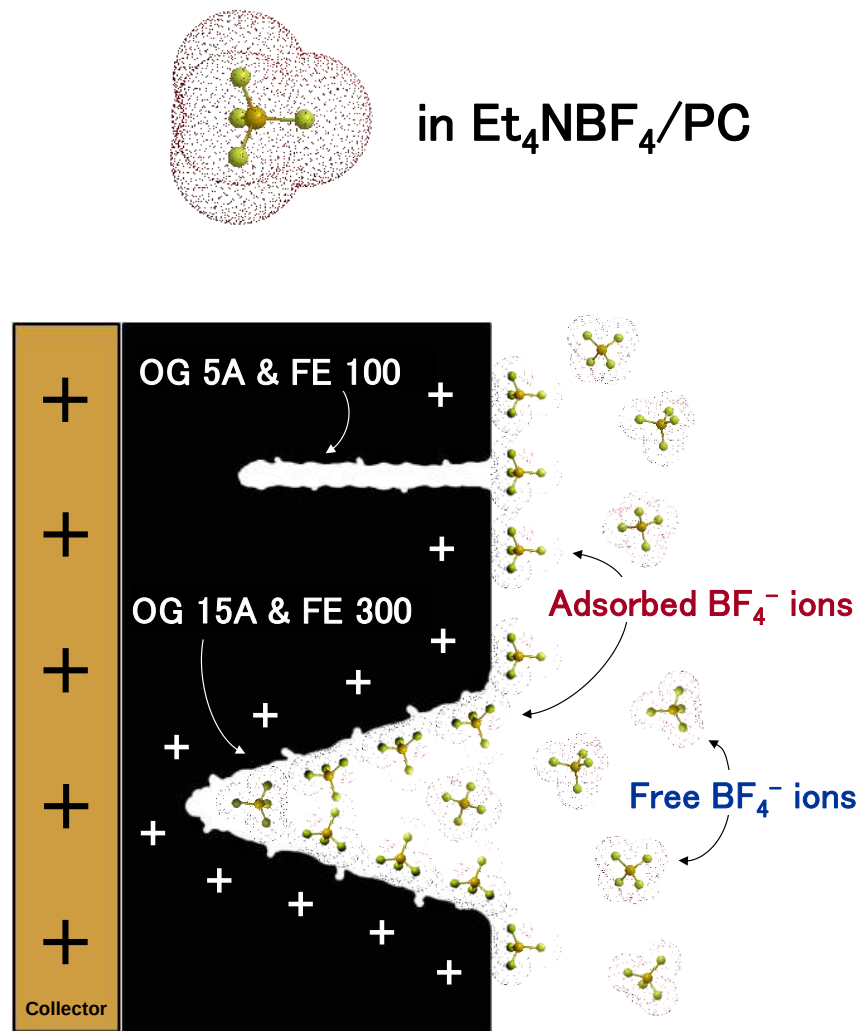
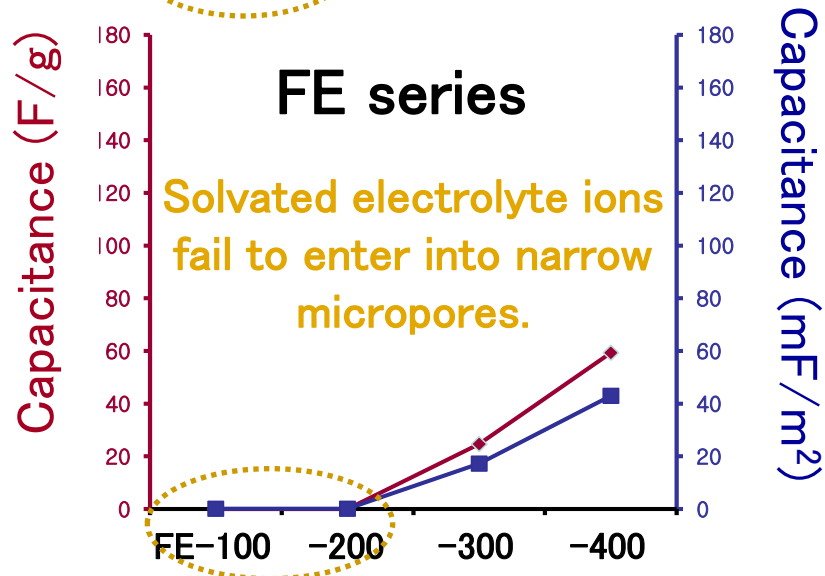
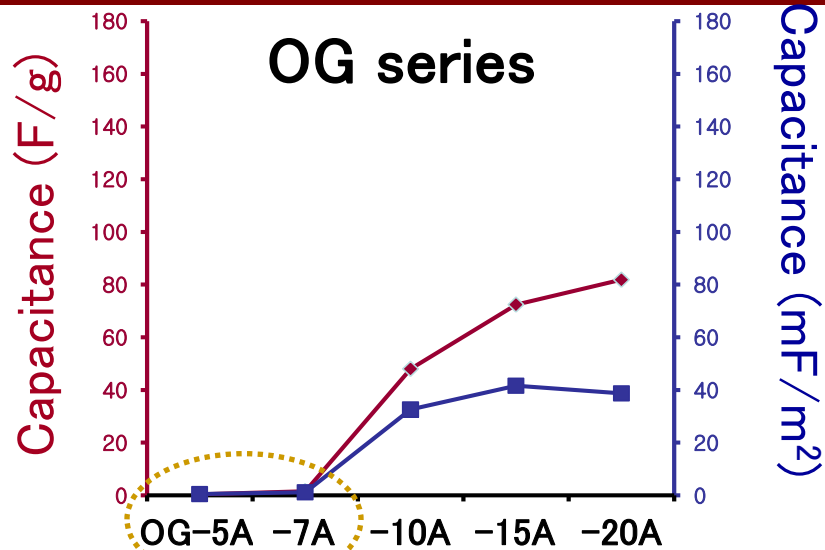
Porous carbon

In using Et_4NBF_4 as an electrolyte, at least pore size larger than 1.3nm is necessary to have electric double layered capacitance.

In using H_2SO_4 as an electrolyte, pore size of about 1.0nm is enough to have electric double layered capacitance.



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



Conclusion

- Carbon is a key material for energy and environmental devices.
- High Utilization of coal and petroleum residues as resources for advanced functional carbon is most necessary to develop the advanced energy and environmental devices.
- Full understanding of carbon structure is necessary for improving the performance and useful applications of carbons

University:

- ❖ Creation and leading of projects
- ❖ Manpower cultivation



Thank you for your attentions!

