

炭素の合成 (機能性炭素材の製造法)

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1. 炭素の種類

- 炭素質, 炭素, 黒鉛
- 易黒鉛性及び難黒鉛化性炭素

2. 気相, 液相および固相炭素化

3. 液相炭素化

- ピッチおよび等方性コークス
- 液相ピッチおよびニードルコークス

4. 気相炭素化

- 炭素ナノ繊維の調製

5. 固相炭素化

- バイオマスを用いたLi-ion電池負極材の調製

6. まとめ

炭素材料

炭素材料: 90%以上炭素によって構成された材料

人造炭素材料



天然黒鉛



人造黒鉛



ガラス状炭素



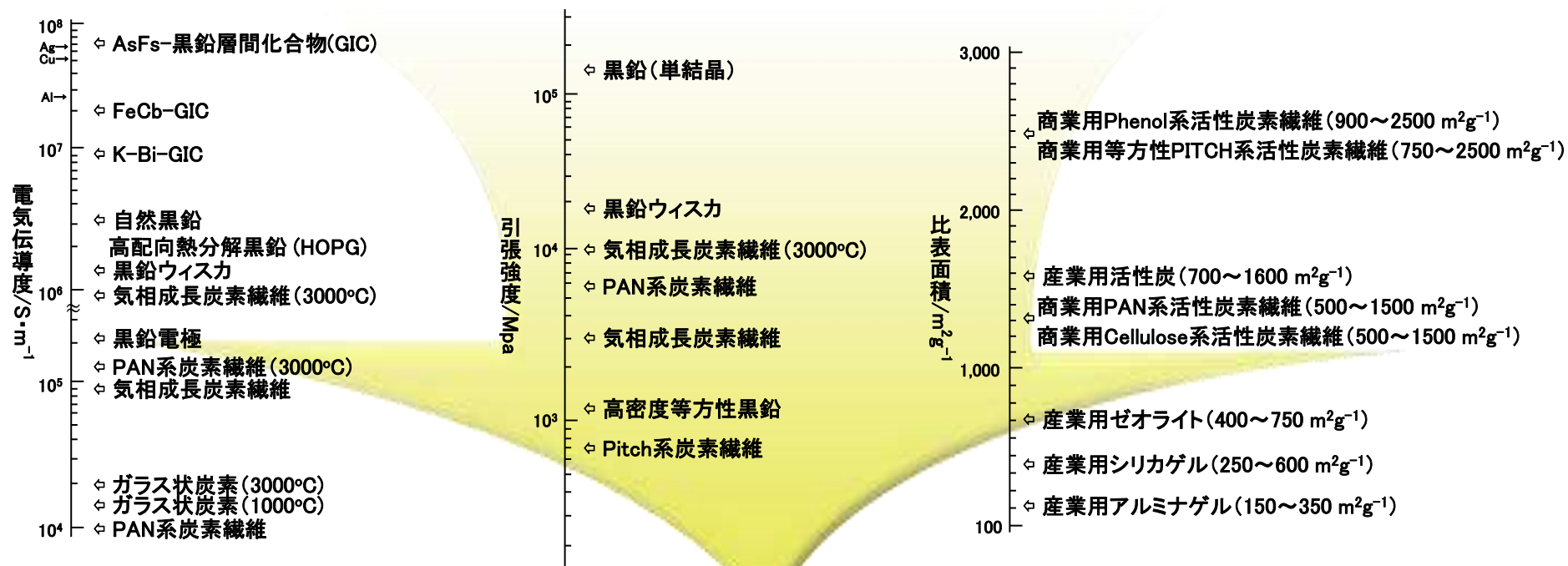
炭素繊維



活性炭素繊維



活性炭



黒鉛電極



電極材



複合材



スポーツ用材料



キャパシタ



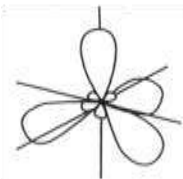
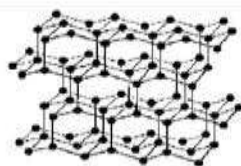
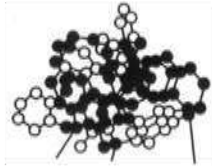
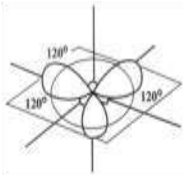
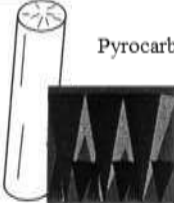
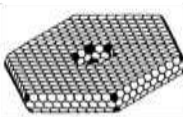
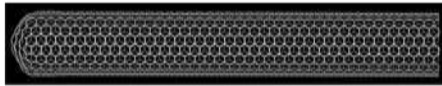
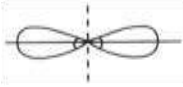
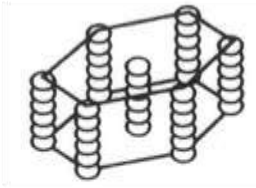
吸着材

1.炭素の種類

- 炭素質，炭素，黒鉛
- 易黒鉛性及び難黒鉛化性炭素

炭素基礎(多様な炭素同素体)

4

Bonding Hybridization	Allotropes	Derived and Defective Forms
 SP³	 Cubic diamond	 Diamond-like Carbon
 SP²	 Hexagonal graphite	     Poly-crystalline Graphite Carbon Black Cokes and Activated Carbons Carbon Fibers
 SP^{2+ε} rehybridization	 Fullerene	   Bucky Onions Toroidal Structures Acetylene Blacks  Nanotubes
 SP¹	 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.

Carbon Allotropes

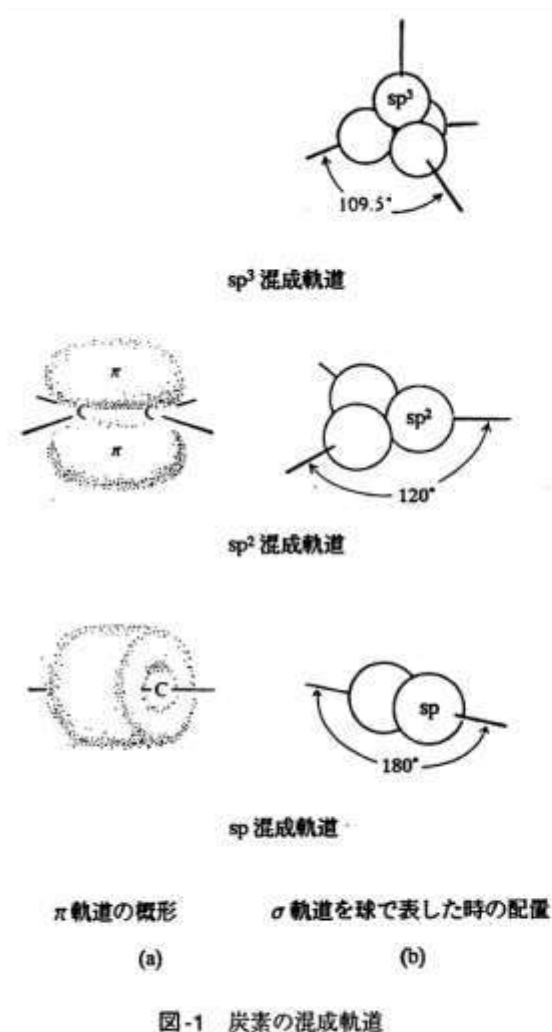


表-1 各種炭素-炭素結合の結合解離エネルギーと結合距離¹⁾

化合物	結合解離エネルギー (kcal/mol)	結合距離 (Å)
H ₃ C-C ₃ H	88	1.53
H ₂ C=C ₂ H	163	1.34
HC≡CH	198	1.21

表-2 炭素同素体の種類³⁾

結合の種類	配位数	炭素同素体
sp	2	カルビン (ポリイン, クムレン)
sp ²	3	グラファイト (六方晶, 菱面体晶) フラーレン (C ₆₀ , C ₇₀ , バックイチューブなど)
sp ³	4	ダイヤモンド (立方晶, 六方晶, 菱面体晶*) ダイヤモンド多形体 (6H, bc-8*など) ダイヤモンドライクカーボン (DLC), i-カーボン
イオンまたは 金属的	6	単純立方晶*, β-スズ型*
	8	体心立方晶*
	12	面心立方晶*, 六方最密充填*

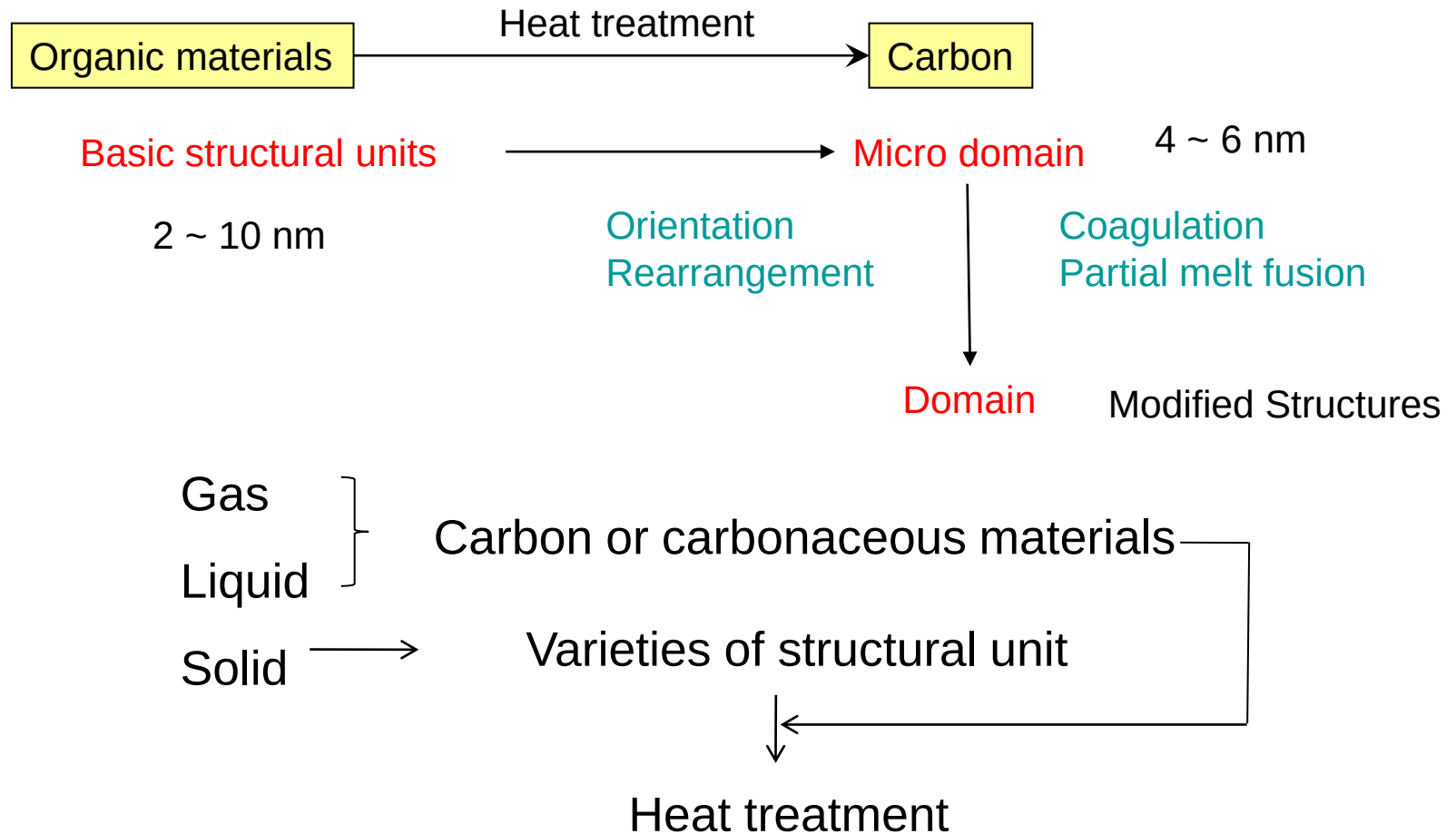
* 実!

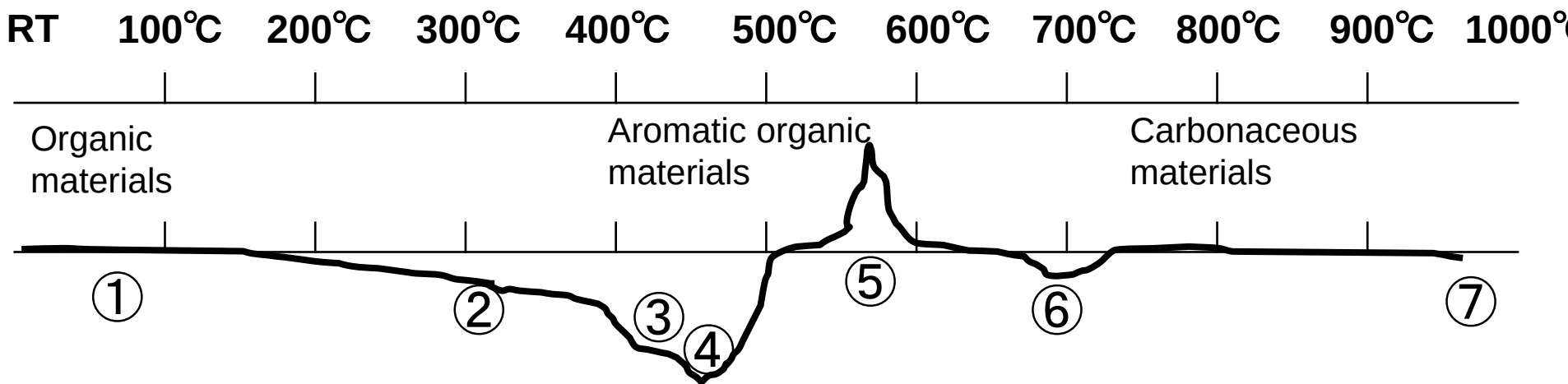
表-4 IV族 sp³ 立方晶体の性質⁶⁾

性 質	ダイヤモンド	β-SiC	Si
格子定数 (Å)	3.567	4.358	5.430
密度 (g/cm ³)	3.515	3.216	2.328
熱膨張率 (×10 ⁻⁶ /℃)	1.1	4.7	2.6
融点 (℃)	4000	2540	1420
バンドギャップ (eV)	5.45	3.0	1.1
キャリア移動度 (cm ² /(V · S))			
電 子	2200	400	1500
ホール	1600	50	600
熱伝導率 (W/(cm · K))	20	5	1.5
硬度 (kg/mm ²)	10000	3500	1000

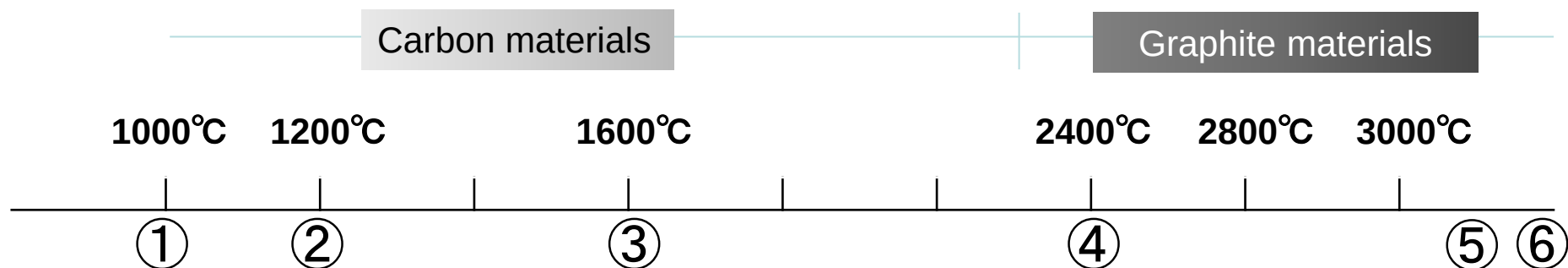
What is the synthetic carbon!

Origin of Structural Units And Crystalline Defects



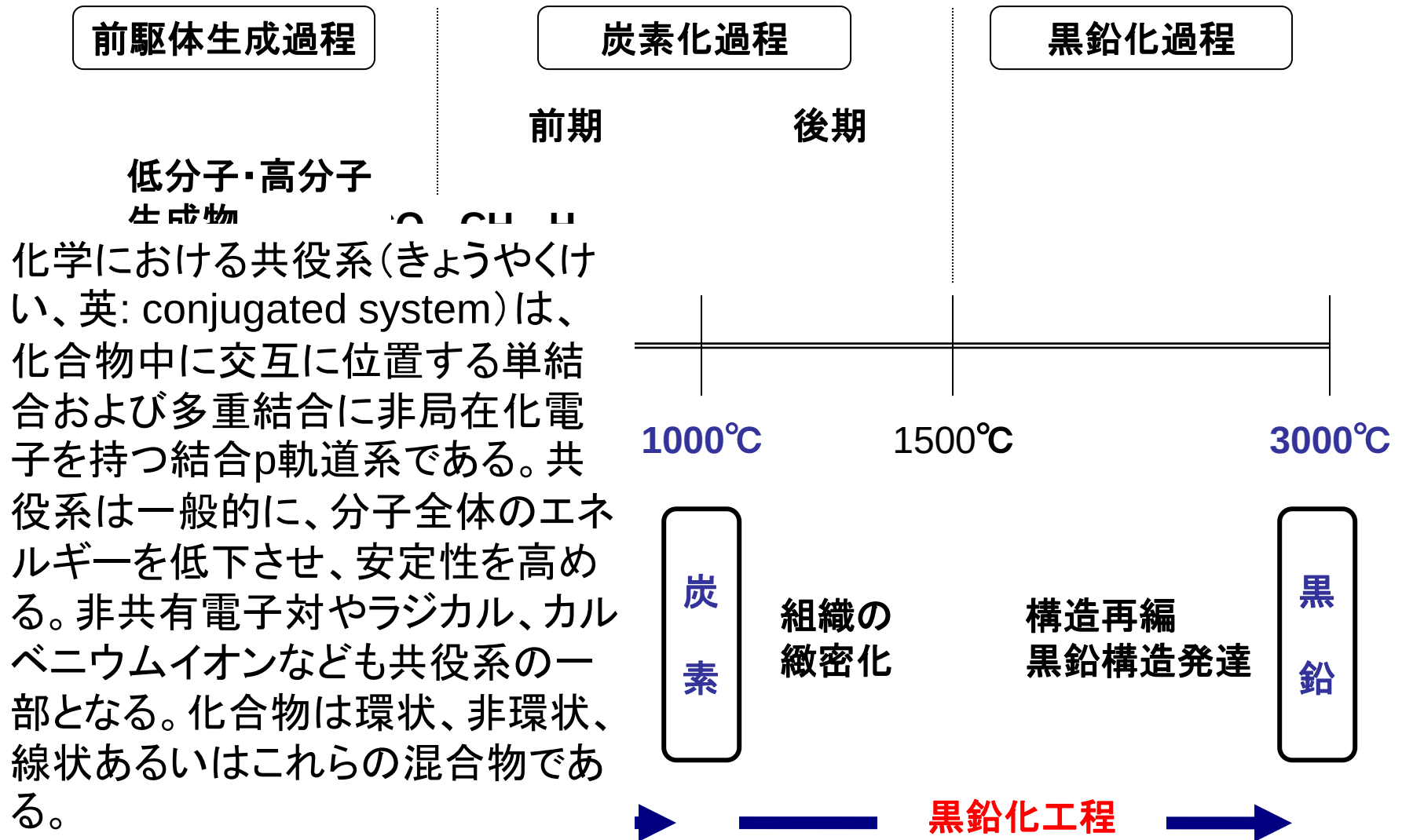


	ΔH	Reactions
①	+	Removals of water and VMs
②	+	Dissociation and removals of light organics
③	+	Dissociation and polymerization of organics
④	+	Polycondensation of organics, dealkylation
⑤	+	Coking
⑥	-?	Dehydration and dehydrogenation, CO removal
⑤~ ⑥	+	Removal of sp^3 bridged bonds
⑥~ ⑦	+?	Completion of polycondensation of intra-cluster units (Dehydrogenation), Removal of alkyl groups, Removal of ultramicroporosity

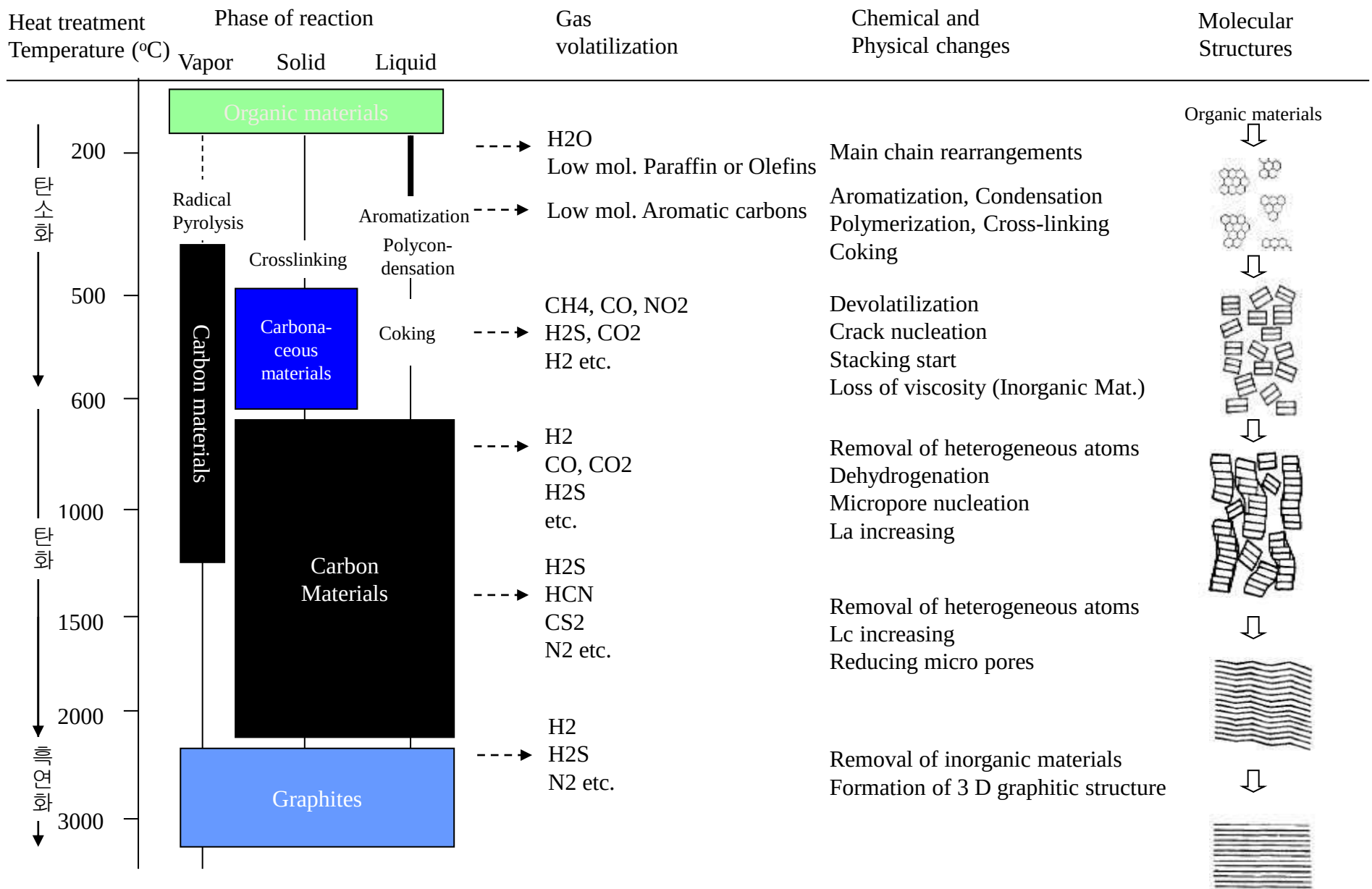


	ΔH	Reactions
①~②	- ?	Start of linkage with inter-clusters
②~③	- ?	Linkage with inter-clusters, Removal of edge phase, almost removal of microporosity
③~④	-	?
④~⑤	- ?	Construction of 3D structure maintaining domain structure, Complete removal of micro-porosity
⑤~⑥	- ?	Completion of graphitic structure with removal of domain structure, HOPG forming temperature

有機物の加熱による変化







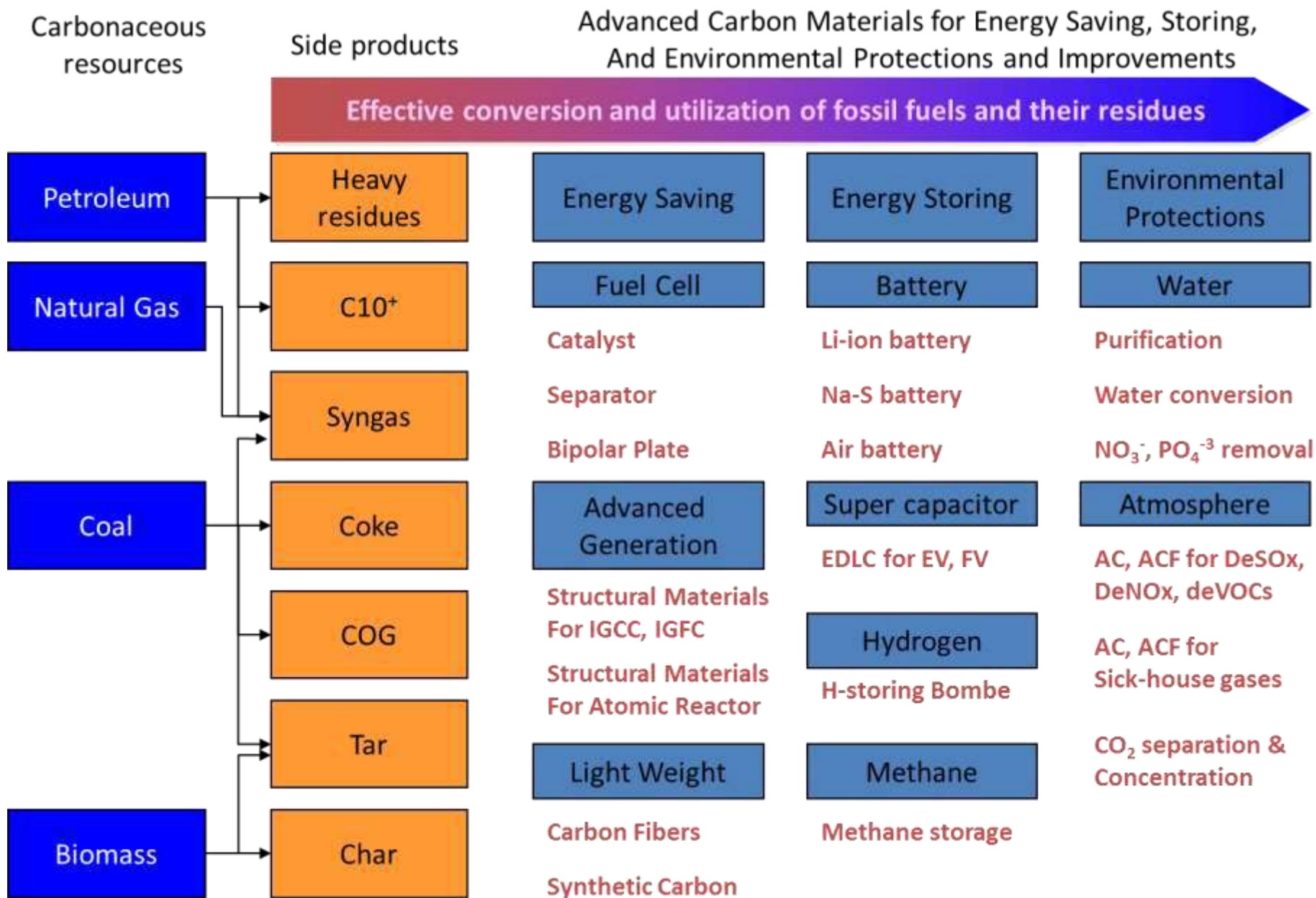
탄소화

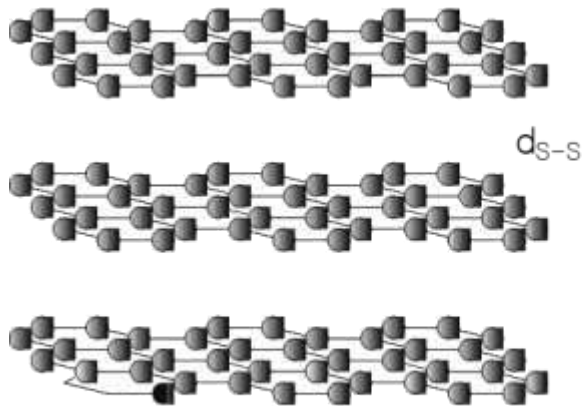
탄화

흑연화

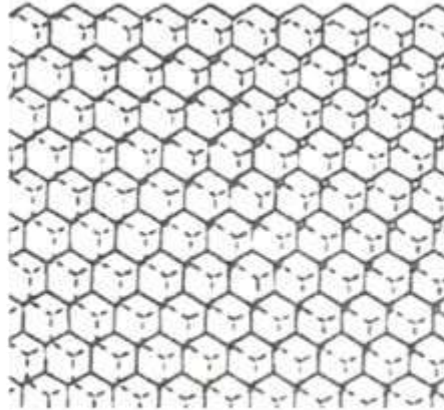


From fossil fuel to functional carbons

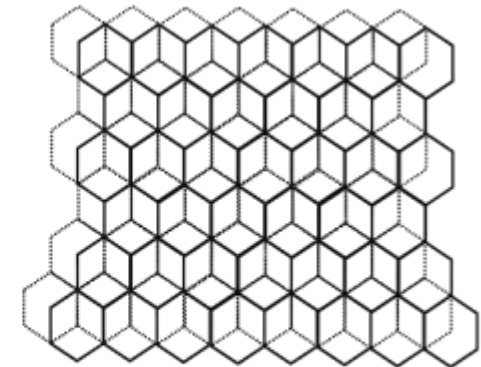




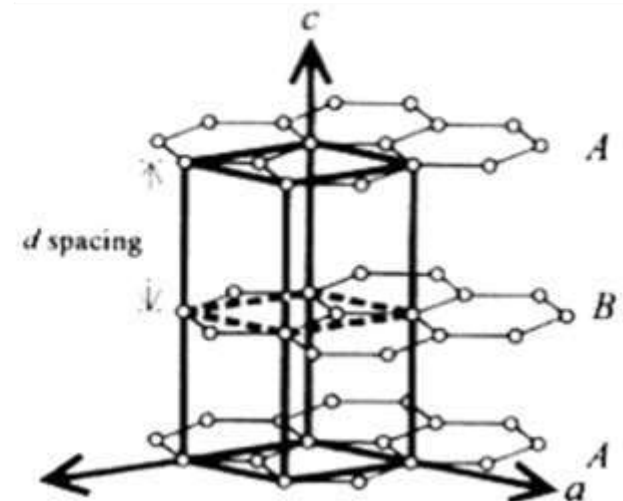
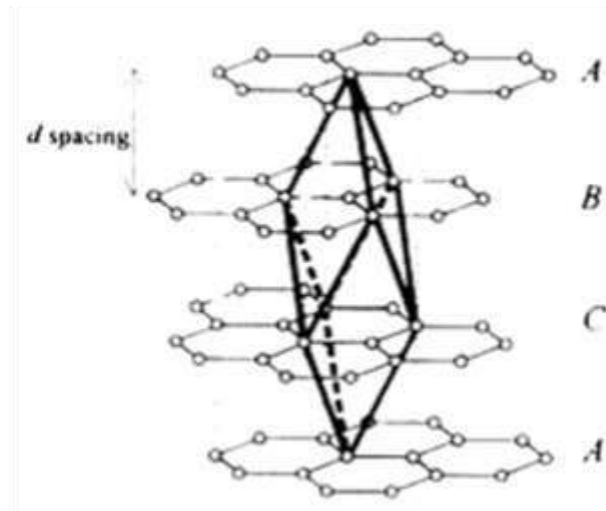
(a) Basic Structure of Graphite



(b) Turbostratic structure (low crystallinity)

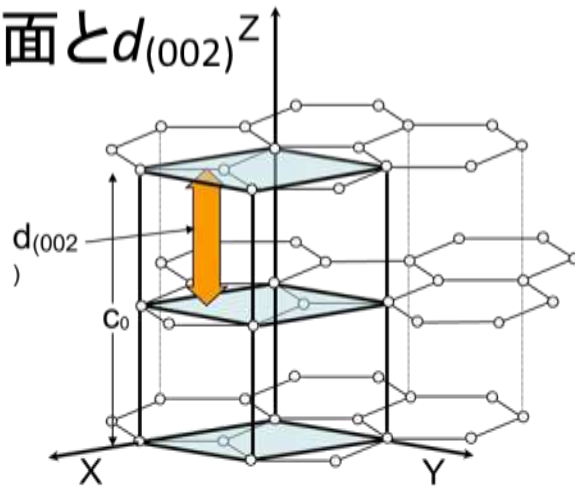


(c) Graphitic structure (high crystallinity)

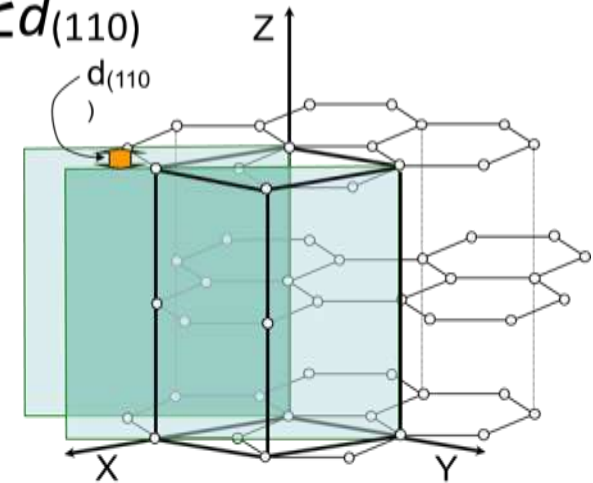


結晶面と面間隔の関係

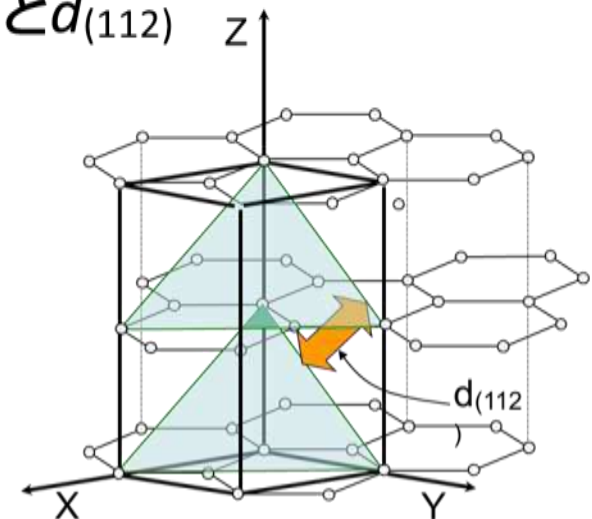
(002)面と $d_{(002)}$



(110)面と $d_{(110)}$



(112)面と $d_{(112)}$



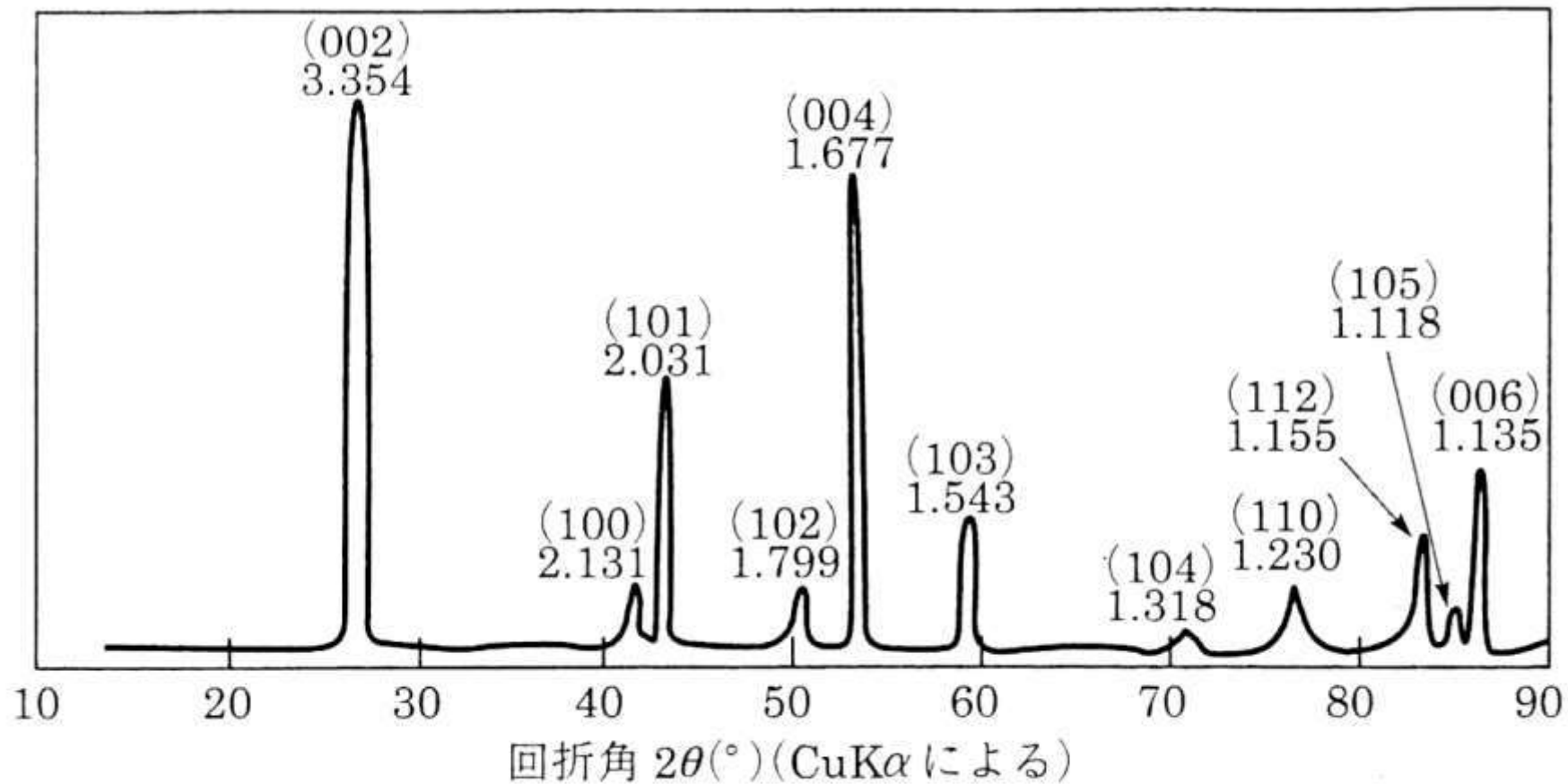
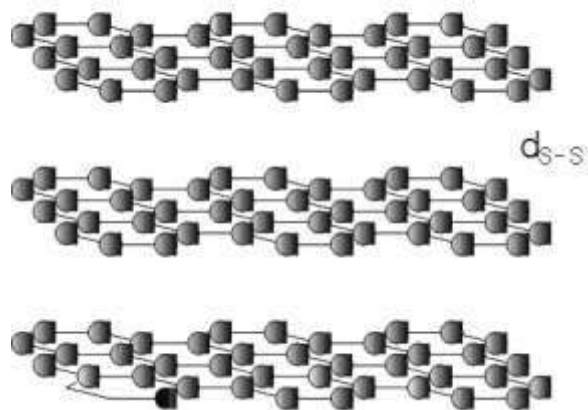
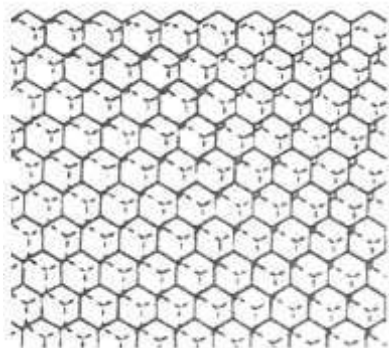


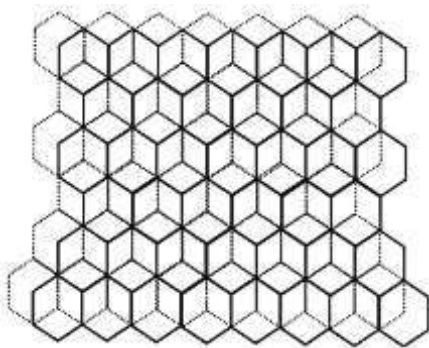
図4.4 グラファイトのX線回折パターン



黒鉛の基本構造

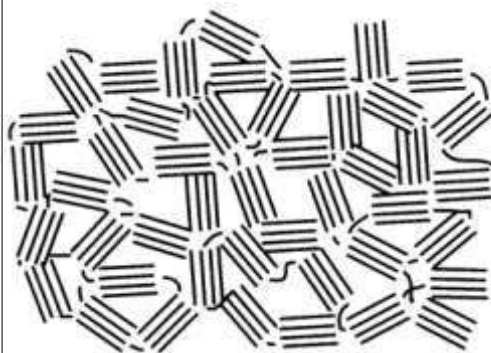


Turbostratic-構造
低結晶度

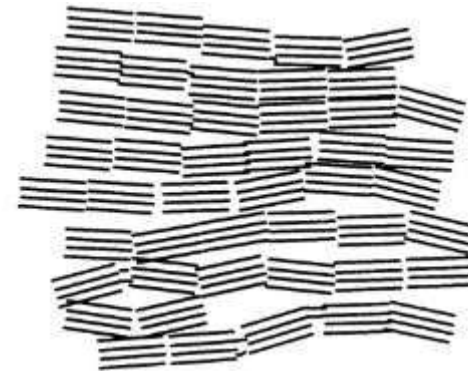


Graphitic-構造
高結晶度

炭素六角網面積層の配列



難黒鉛化性



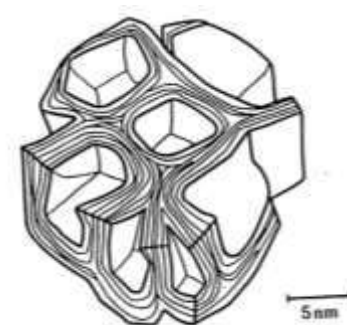
易黒鉛化性

Franklin モデル^[1]

XRDから 2次元



リボンモデル^[2]



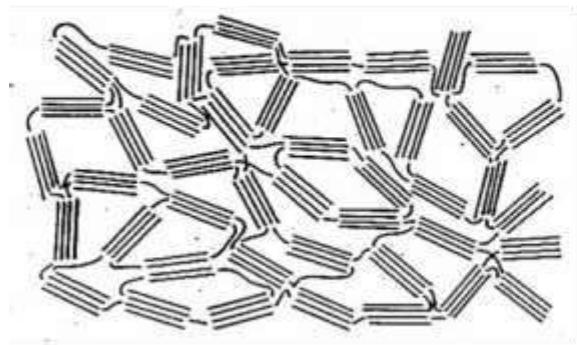
シェルモデル^[3]

TEMから 3次元

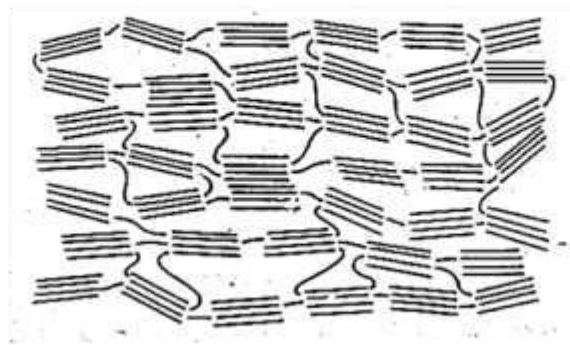
[1] Franklin R E. Proc. Roy. Soc. London A, 1951, 209: 196

[2] Johnson G M. Kawamura K, Nature, 1971, 231: 175

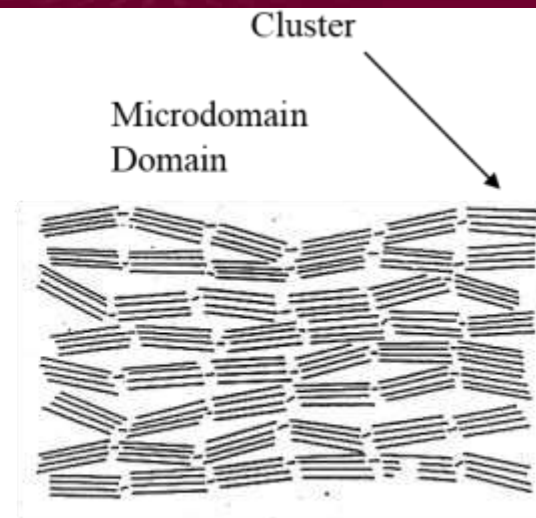
[3] Shiraishi M, Kaitei Tansozairyou Nyuumon, 1984, 29



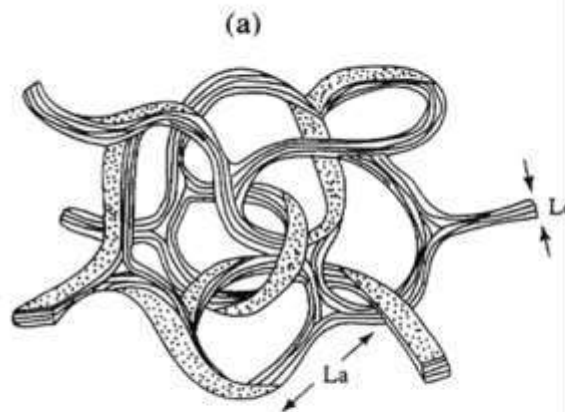
(a) Non-Graphitizing (Isotropic)



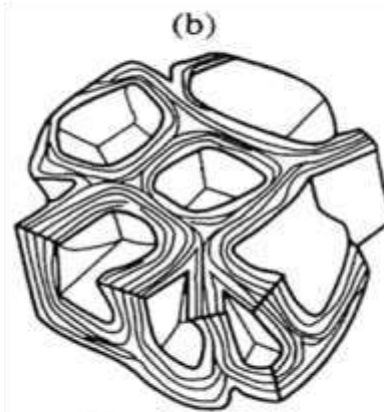
(b) Partially Graphitizing



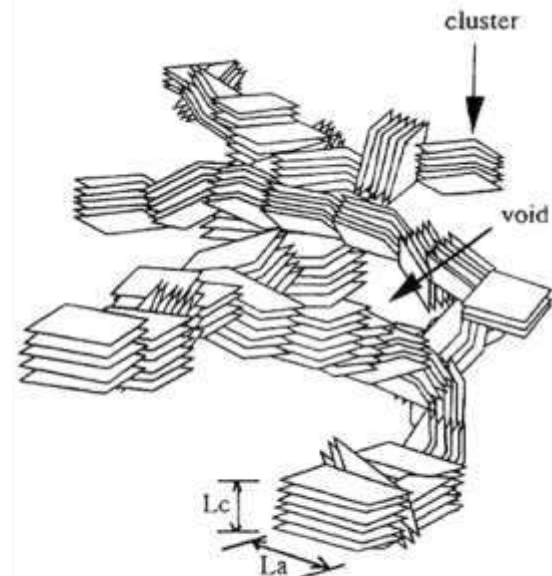
(c) Graphitizing



La: Crystallite size
Lc: Crystallite thickness
Jenkins-Kawamura model

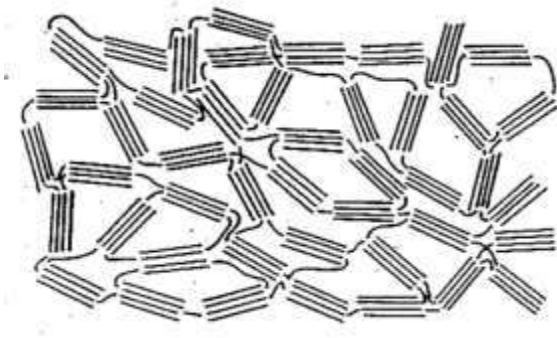


5 μm
Shiraishi model

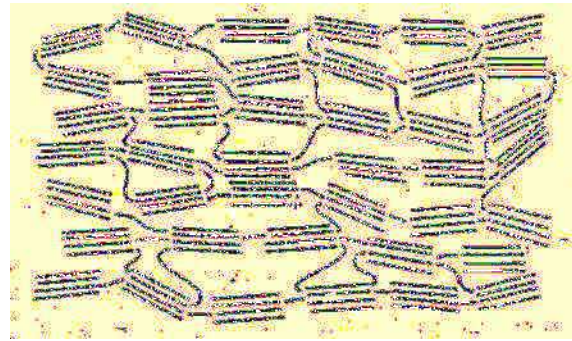


Mochida model

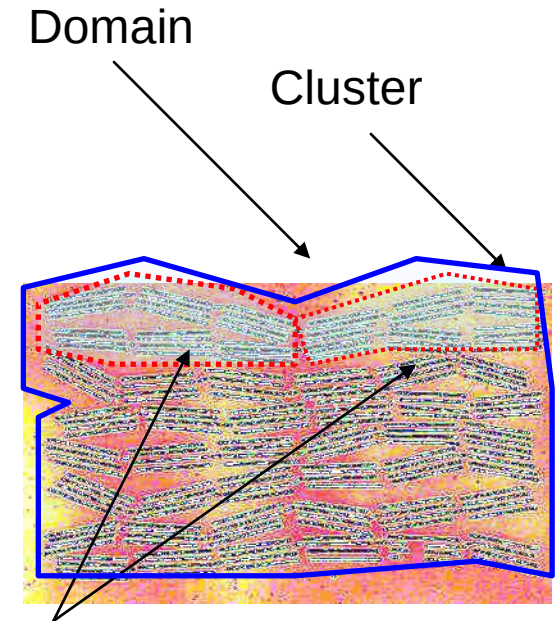
ドメイン構造との連携



(a) Non-Graphitizing (Isotropic)



(b) Partially Graphitizing



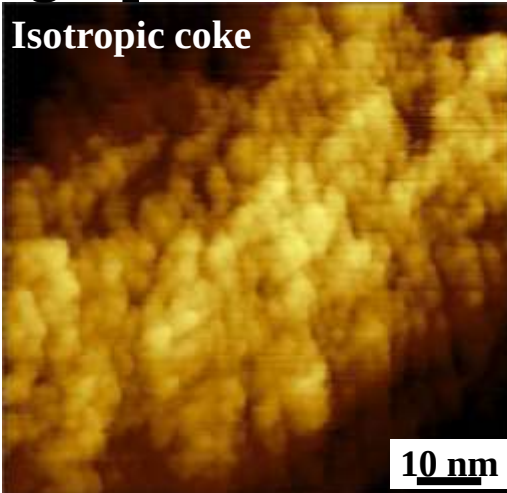
Microdomain

(c) Graphitizing

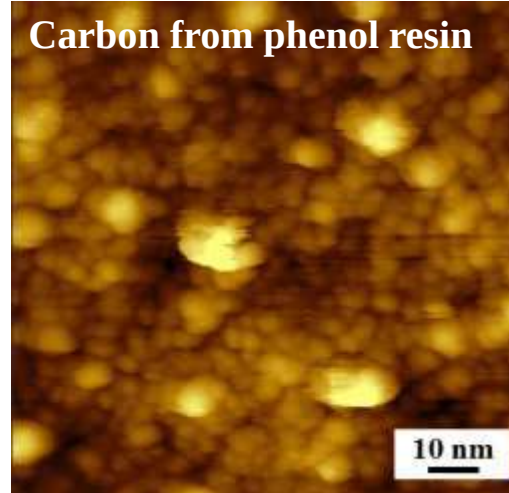
炭素の基礎(易黒鉛化性炭素と難黒鉛化性炭素)²⁰

Non-graphitizable

Isotropic coke



Carbon from phenol resin

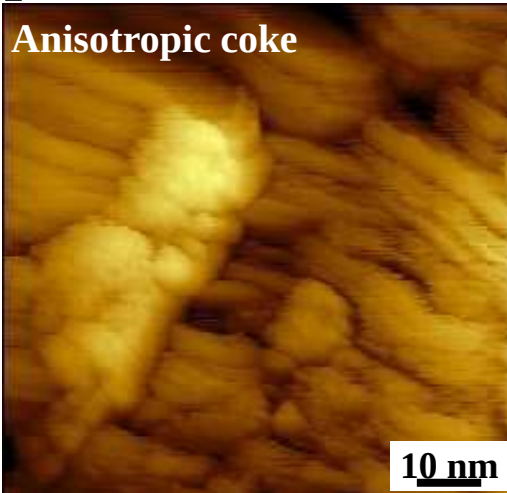


Feature

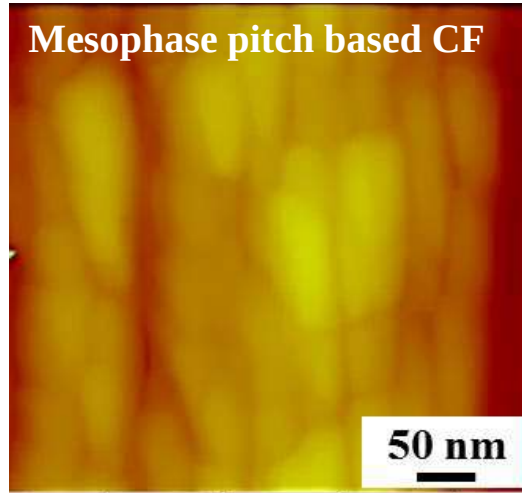
- Non-graphitizable
- Ball shaped domain
- Domain $\approx$ Micro-domain

Graphitizable

Anisotropic coke



Mesophase pitch based CF



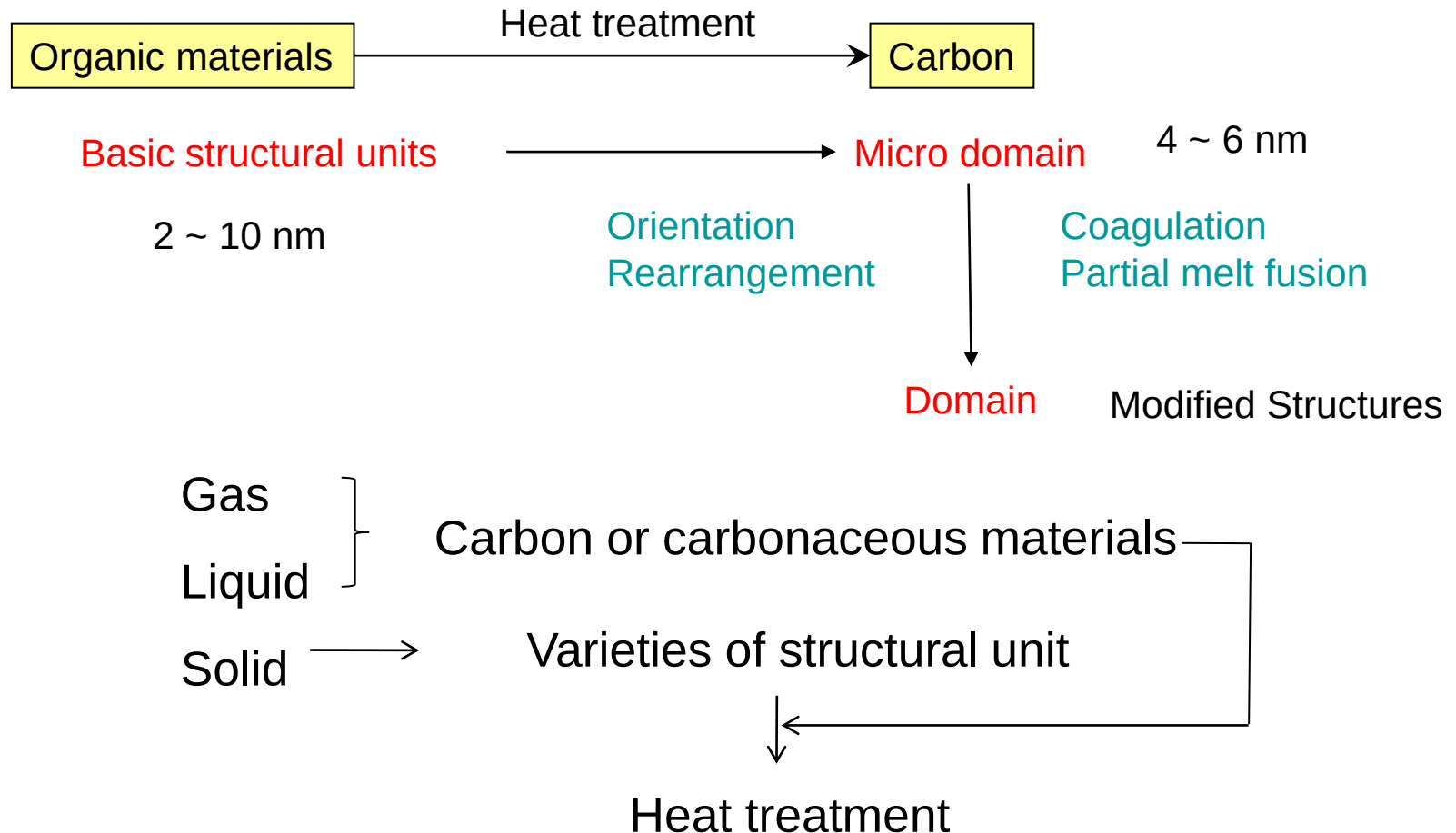
Feature

- Graphitizable
- Linear shaped domain
- Domain $>$ Micro-domain

Domain of NGC has similar size and shape of micro-domain, whereas GC does larger and much linear shaped domain than that of NGC

What is the synthetic carbon!

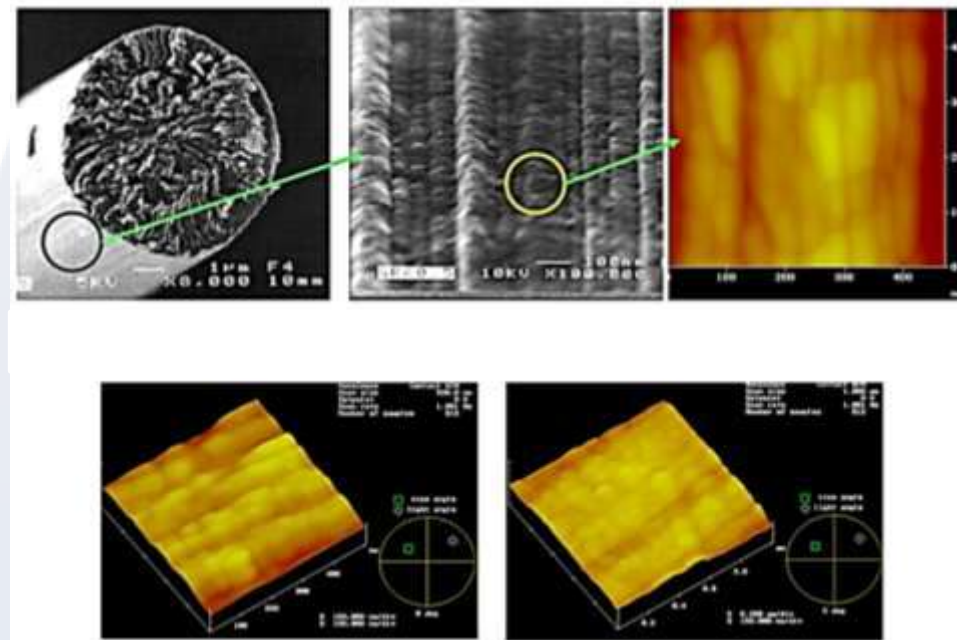
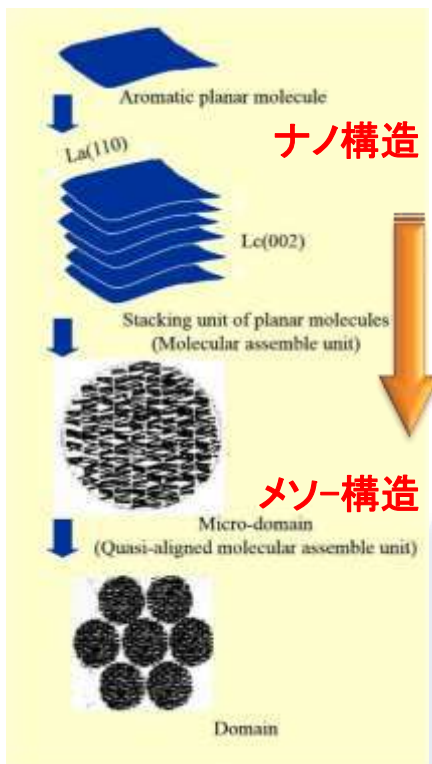
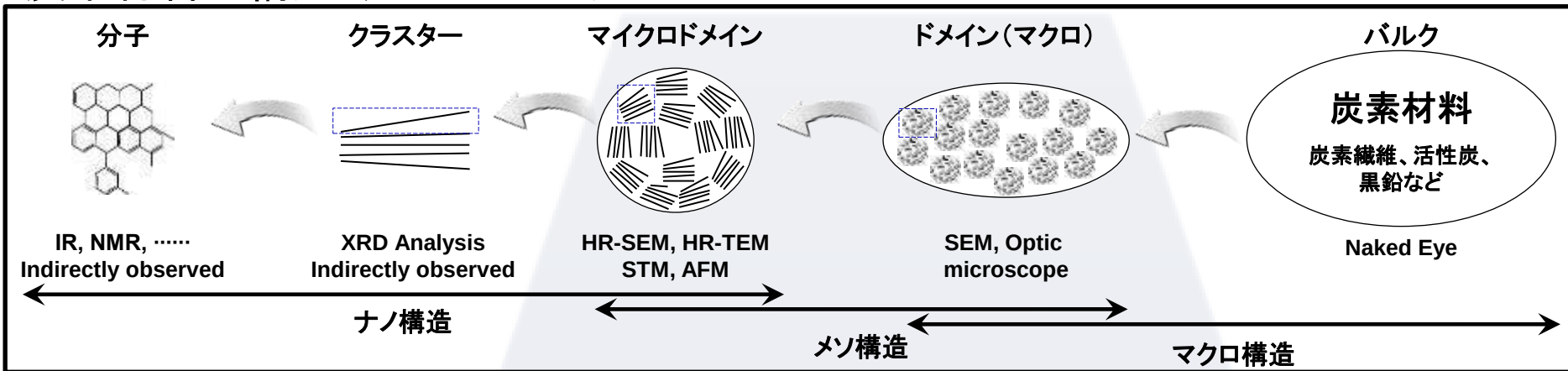
Origin of Structural Units And Crystalline Defects



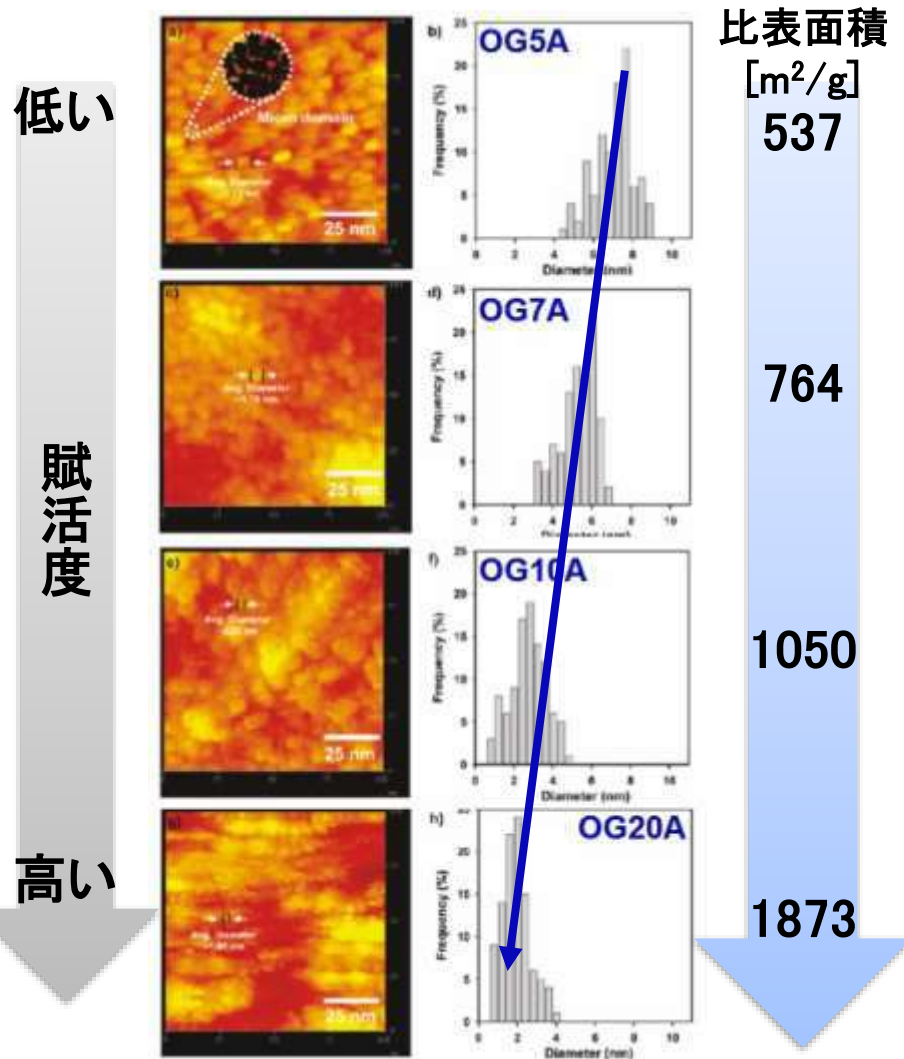
ドメインモデル

炭素材料の構造: 分子～バルク

I. Mochida, et al., TANSO, 215, 274-284 (2004).



図。マイクロドメインとドメインモデルからメソフェーズピッチ系黒鉛繊維の構造ヒエラルキー



賦活度が高くなるにつれて

1. ドメインサイズが減少
2. 表面外側から酸化
3. 細孔の生成進む



ドメインとマクロ構造特性が
密接な関係を確認した。

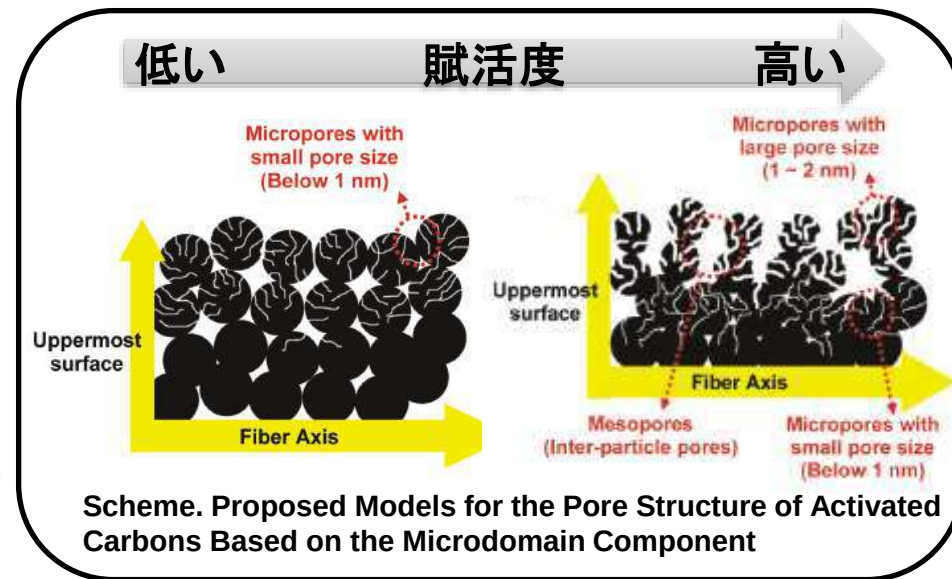
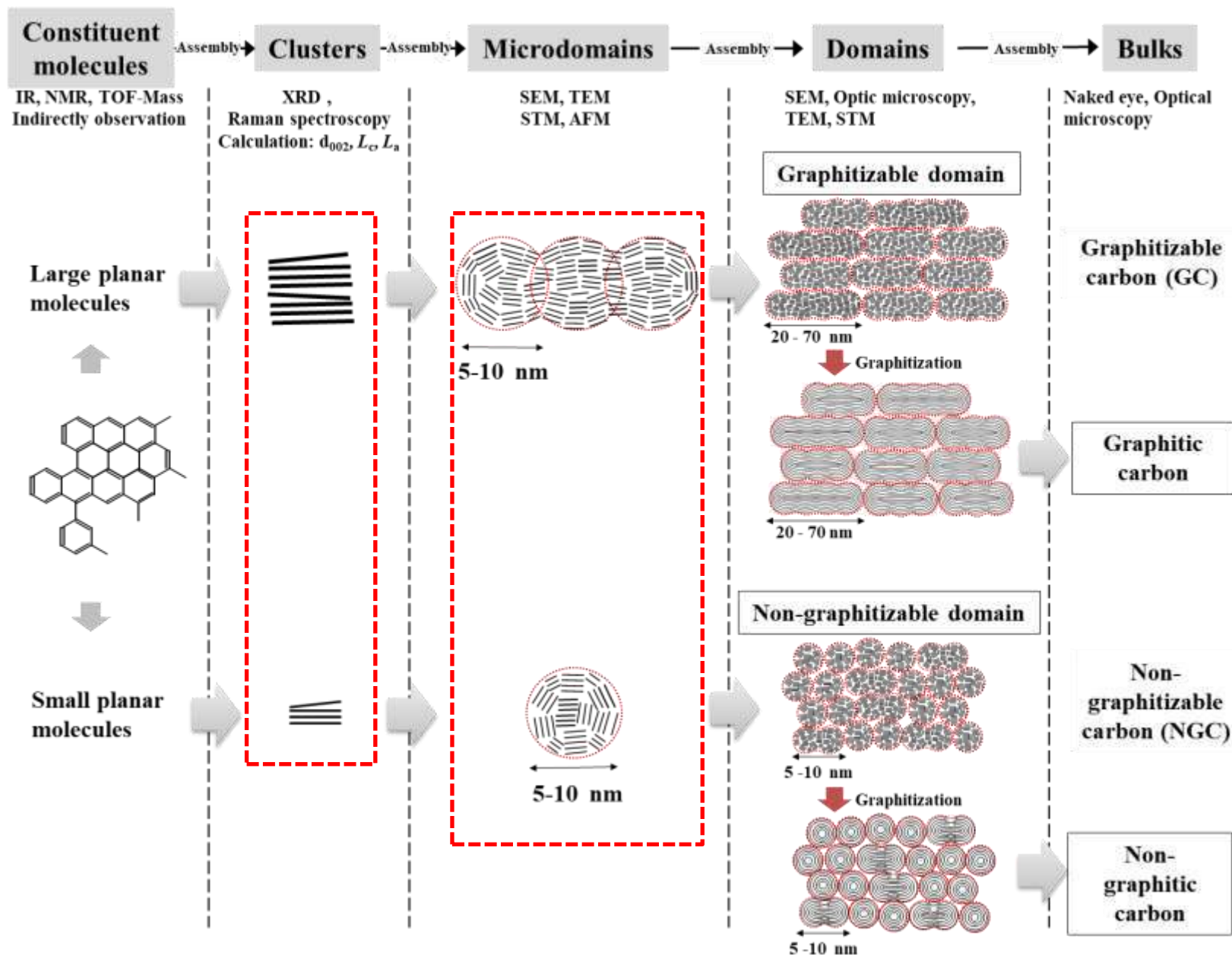


Fig. STM images of (a) OG5A, (c)OG7A, (e)OG10A, and (g) OG20A
Pitch-based activated carbon fiber

マイクロドメイン構造モデルに基づいて、賦活度に応じた細孔構造を説明した。



2. 気相，液相および固相炭素化

種々の炭素材料の炭素化過程, 前駆体, 特徴

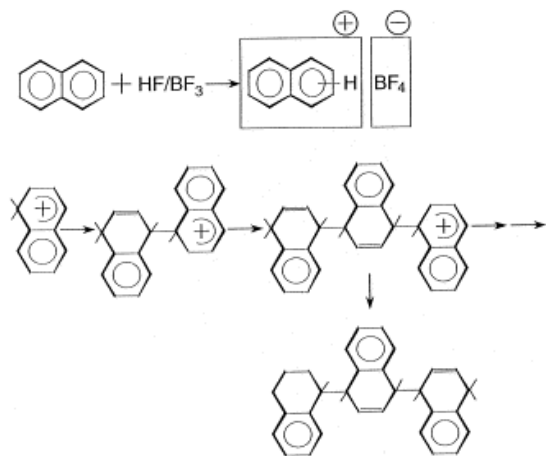
炭素化過程	原料 (前駆体)	炭素材料	特 徴
気相炭素化	炭化水素ガス (空間中で分解)	カーボンブラック	微粒子, ストラクチャー (連鎖構造)
	炭化水素ガス (基盤上に析出)	熱分解炭素	多様な組織 (基盤上に析出)
	炭化水素ガス (金属触媒あり)	気相成長炭素繊維 カーボンナノファイバー	繊維状状態 多様なナノ組織
	炭化水素ガス (触媒なし)	ダイヤモンド状炭素	薄片フィルム sp ³ 炭素, 非晶質構造
	炭素蒸気	カーボンナノチューブ	チューブ状, 単層および多層構造
	炭素蒸気	フラーレン	球状, 分子性
固相炭素化	植物, 石炭, ピッチ	活性炭	高い多孔質吸着特性
	フルフリルアルコール樹脂, フェノール樹脂, セルロース など	ガラス状炭素	非晶質構造, 貝殻状破面 気体不透過性
	ポリアクリロニトリル, ピッチ セルロース, フェノール樹脂	カーボンファイバー	繊維状形態, 高い機械特性
	ポリイミドフィルム	カーボンフィルム 高配向黒鉛	フィルム状, 広範な黒鉛化性
液相炭素化	ピッチ, コールタール	コークス, メソフェーズ小 球体	多孔質塊, 球状粒子
	ピッチ混練コークス	多結晶黒鉛ブロック (高密度等方性黒鉛を含む)	広範な密度, 広範な配向性

炭素材の製造例

3. 液相炭素化:

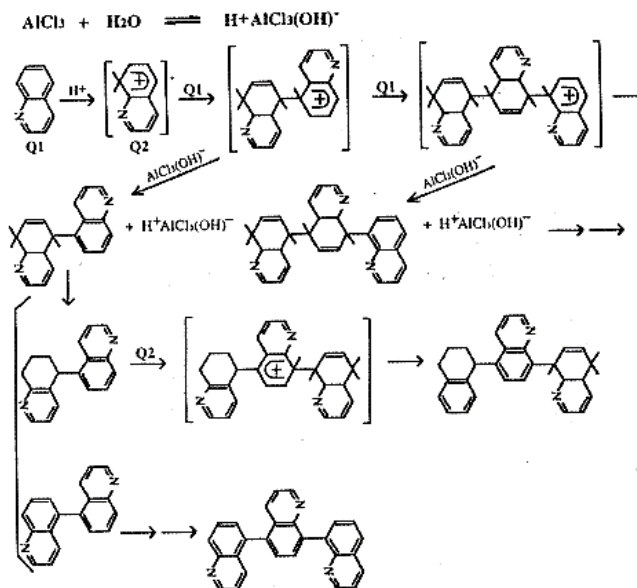
- 等方性ピッチおよび液相ピッチ
- ニードルコークス

- 液相炭素化 (Liquid phase carbonization): 液相を経由する炭素化. 炭素化反応が液相中で進行するため, 分子の移動や配向が起こり易い. 熱溶融性の有機物前駆体を, 常圧下300~500°C程度に熱処理して得られる生コークスのほとんどは易黒鉛化性炭素である. 液相炭素化する前駆体としては, 石油や石炭タールの精製残渣としての重質油やピッチ, ポリ塩化ビニル等の熱可塑性高分子, アセナフチレン, デカシクレンなどがある. これらの前駆体は一般には炭素化反応中に極めて高分子量の平面性芳香族化合物を生じ, それらを構成成分としてメソフェーズを生成する. メソフェーズの組織や発達程度によって, 高温処理後の炭素材料の黒鉛化度が支配される. そのため, この段階におけるメソフェーズの制御が重要で, 前駆体の選択やフリーカーボンの除去, 炭素化条件などが工夫されている.
- 縮合:
 - 脱水素縮合 (Dehydrogenative condensation): パラフィンの脱水素環化芳香族と芳香族化合物の縮合は通常, 脱水素を伴って進行する. これによって炭素化収率, 軟化点が向上する. 熱的に加えて接触的, 炭素化的な脱水素縮合も進行し, 工学的にも応用されている. エアブローは酸化的脱水素縮合の代表例で, 舗装用アスファルトや活性炭素繊維や粒子の原料ピッチ製造に応用されている. このほか, アルカリ金属, ヨウ素, 遷移金属塩化物, 酸化物等の脱水素複合剤も知られている.
 - 非脱水素的縮合 (Non-dehydrogenative condensation): 分子量の小さい成分や重質油は, 縮合反応によって重質化されることにより炭素化性を変えることができるが, この際, 水素を脱離しない場合を非脱水素的縮合という. 例えば, AlCl_3 を用いるとその低温での縮重合促進効果は, コークス収率を上げることからも明らかであるが, 減圧残油の軟化点を比較的に低く押さえることもできる. これは水素を脱離せずに芳香族の縮合が進み, 縮合と同時にナフテン環を形成することによると推定できる. HF/BF_3 は金属腐食性の超強酸であるが, 回収の容易な極めて強力な酸としてナフタレン等の種々の芳香族化合物を200~300°Cの温度で非脱水素的縮合化を進め, 高純度のメソフェーズピッチの直接合成に利用できる.

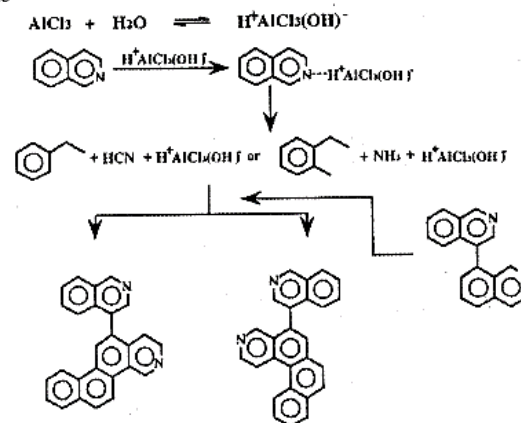


Catalytic condensation of aromatic hydrocarbon with HF/BF_3

quinoline



isoquinoline



Scheme of catalytic polymerization of quinoline and isoquinoline with AlCl_3

ピッチ(Pitch):木材, 石炭などの乾留の際に得られる液状タール, オイルサンドから得られるビチューメン, オイルシェールの乾留によって得られる油分, 原油の蒸留による残渣油, 石油留分のクラッキングによって生成するタールなどを熱処理, 重合して得られる常温で固体状のものの総称. 工業的には石炭系ピッチ, 石油系ピッチが重要である. 最近ナフタレンなどの芳香族化合物を重合した合成ピッチも製造されるようになった. ピッチは化学的には無数の縮合多環芳香族化合物の混合物で, 平均分子量は300~1000程度の範囲にある. 350~450°C程度の温度で熱処理すると光学的異方性組織(メソフェーズ)の炭素質液晶が発達する. メソフェーズの組織構造(テキスチャー)はコークス, 炭素材料の特性をほぼ決定してしまうので, ピッチの化学構造, 熱分解ならびに重合挙動を知っておくことはきわめて重要である. 分子量, 分子量分布ならびにNMR, IRから求められる化学構造指数(例えば芳香族炭素分率, 縮合環数など), 粘度などが測定される.

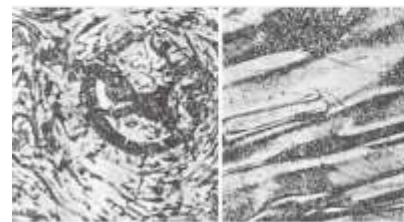
ピッチの高分子やオリゴマー等の有機化合物との違い

1. 多環芳香族の混合体: 5000種以上の多環芳香族物質が混在
2. 軟化点が高くなるにつれ, 溶媒に溶けない成分がある.
3. 炭素繊維前駆体ピッチなどの可溶性高軟化点ピッチは, ピッチの中で溶媒不溶成分と溶媒可溶成分が混在 → 溶媒成分の役割をする成分がある.
4. すでにある程度積層クラスター構造を形成している.
5. 軟化点以上になれば, 溶媒成分の積層は解体され, 溶質成分を分散させる. 液晶ピッチは可溶状態でも積層クラスターをもつ.

- 等方性ピッチ (Isotropic pitch): 縮合芳香族化合物を主成分とする石炭系, 石油系のタールピッチ, ナフタレンのような化合物から合成されたピッチは, 分子または分子の集団 (ラメラ) が無秩序に配向しているために偏光顕微鏡で観察しても光学的に等方性である. このようなピッチを加熱処理すると光学的異方性を示すメソフェーズが生成する.
- メソフェーズピッチ (Mesophase pitch): メソフェーズを含むピッチ. メソフェーズは偏光顕微鏡により光学的異方性を示す組織として観察されることから, メソフェーズピッチは異方性ピッチとも言われる. 異方性部分の分子配向に起因して, 高温熱処理により容易に黒鉛化が進行する典型的な易黒鉛化性炭素で, 重要な炭素原料の一つである. 特に, 繊維軸方向に沿って炭素網面が配向したピッチ系高弾性率炭素繊維の原料としての研究が進展した結果, メソフェーズピッチの調製や評価の技術が飛躍的に発展した. 炭素繊維用メソフェーズピッチは, 石炭系あるいは石油系タールピッチを適当な条件下で熱処理し, これに溶剤抽出, 水素添加を組み合わせる調製される. 超強酸を用いてナフタレンやメチルナフタレンなどを重縮合させる調製法も開発された.
- ニードルコークス (Needle coke): 針状コークスと同意語で, 1940年代にアメリカで製造された石油コークスがたまたま金属光沢を有し, 外観上細長く針状 (Needle like) を呈していたことに由来する. 別名No. 1コークスあるいはプレミアムコークスと称され熱膨張係数 (CTE) 値が低く強い異方性を有する点に特徴がある. 顕微鏡観察によると配向繊維状組織 (Fibrous texture) を示し, 流れ模様にそって炭素六角網面構造がよく発達して黒鉛化し易い特性も有している



(a) 外観



(b) 偏光顕微鏡像



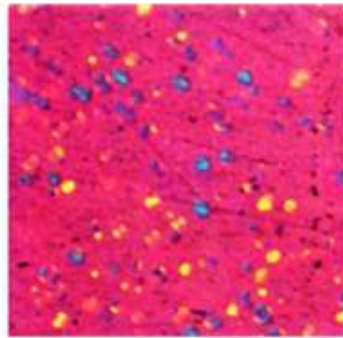
(c) 構造モデル

ニードルコークスの外観(a), 組織(b), 構造モデル(c) (持田勲: 炭素材の化学と工学, 朝倉書店(1990)p.231.)

光学的等方性ピッチを熱処理する際、異方性ピッチ化される過程



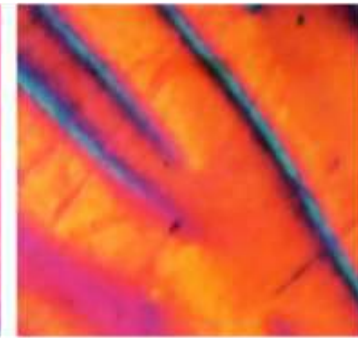
Raw pitch



Nucleation
of MCMB



Growth of
MCMB



Growth &
Merging of MCMBs
→ Mesophase

Low

Heating temperature

High



Short

Heating time

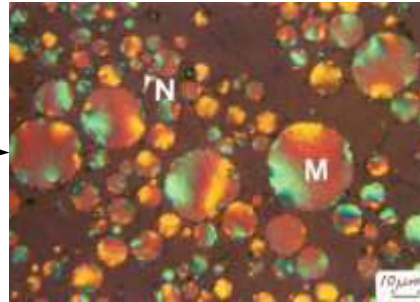
Long

ピッチへの積層構造

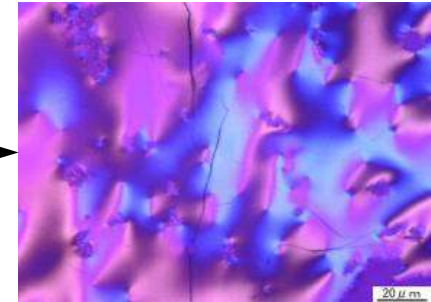
原料



球晶生成

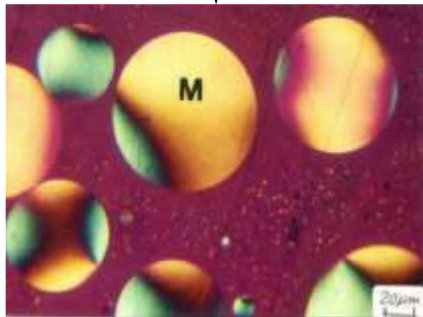


バルクメソフェース

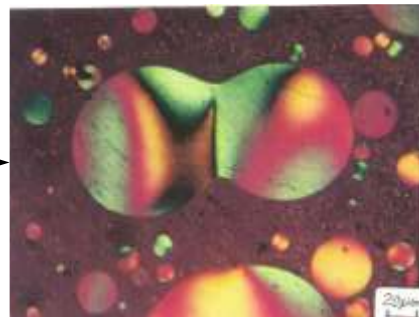


脱QI

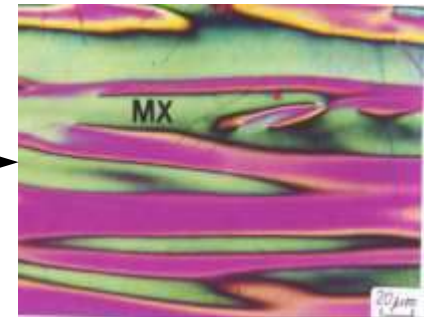
加熱



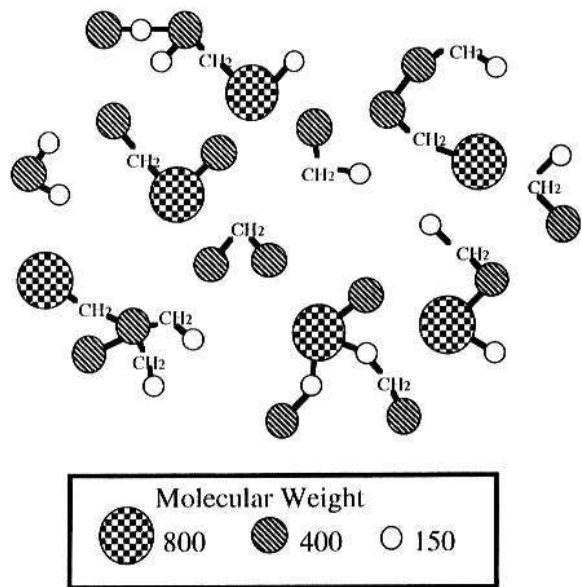
球晶生成



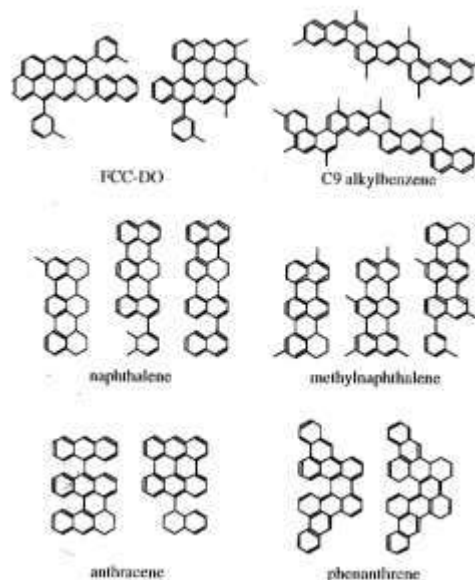
球晶成長・合体



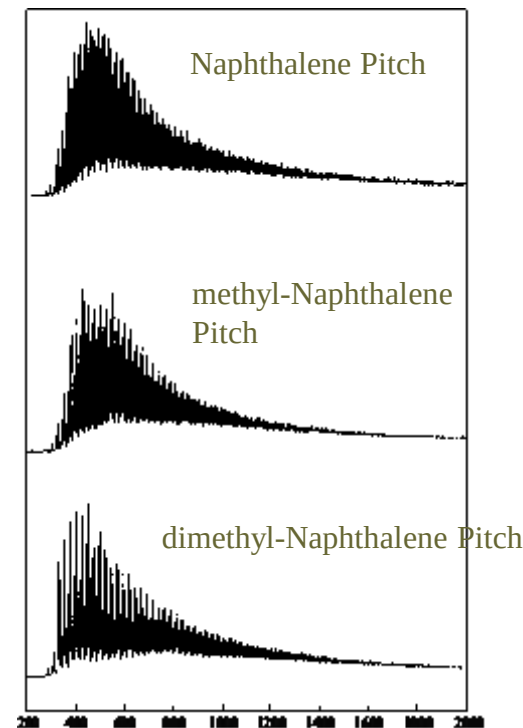
バルクメソフェース



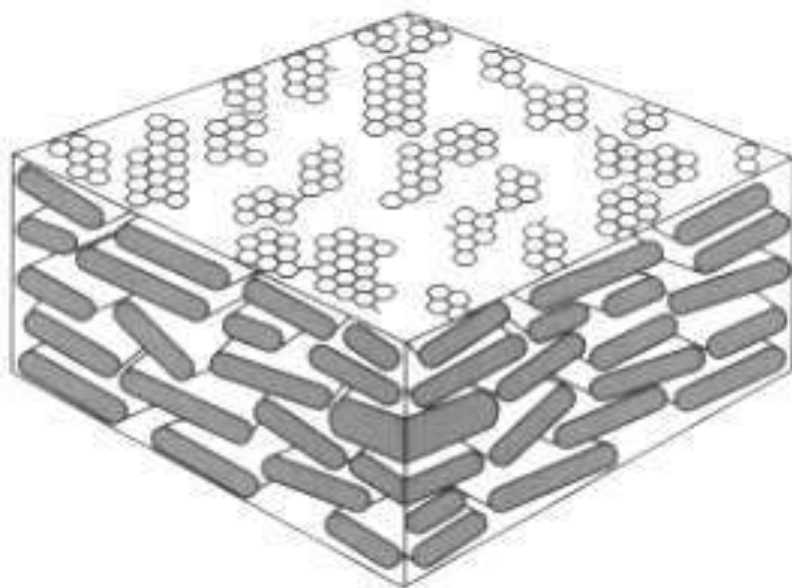
Models of mesophase constituent molecules



Typical mesogen units in various mesophase pitches
 (Mochida et al. Carbon 1990, 28, 311)

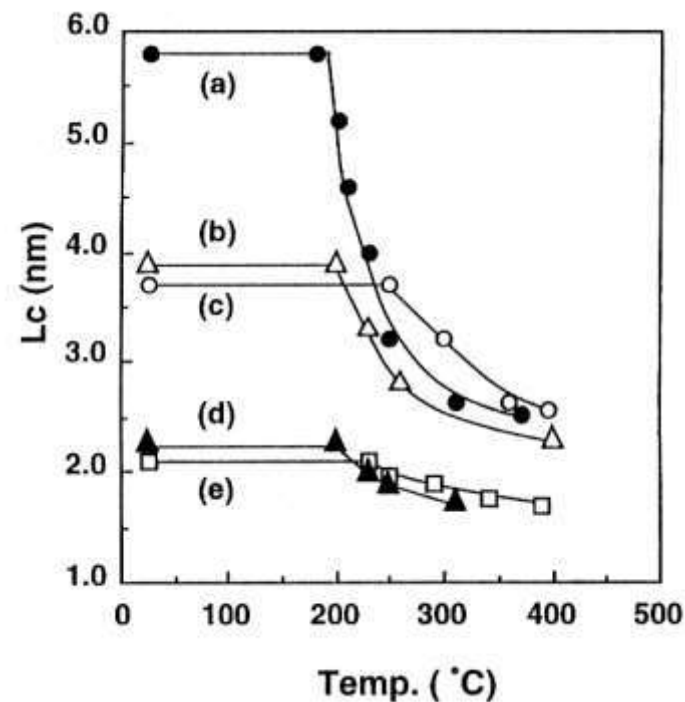


TOF-MS spectra of synthetic mesophase pitches



Molecular Models

Spider Wedge Stacking of mesophase pitch
(Zimmer et al. *Advances in Liquid Crystal*, New York, 1982, 5)



Melt-XRD analysis

Change in Lc of mesophase pitch at higher temperature; (a) methyl naphthalene-derived pitch; (b) petroleum-derived mesophase pitch; (c); coal tar derived-mesophase pitch; (d) naphthalene-derived mesophase pitch; (e) anthracene-derived mesophase pitch
(Korai et al. *Carbon*, 1992, 30, 1019)

Carbon Industry – Chain Industry

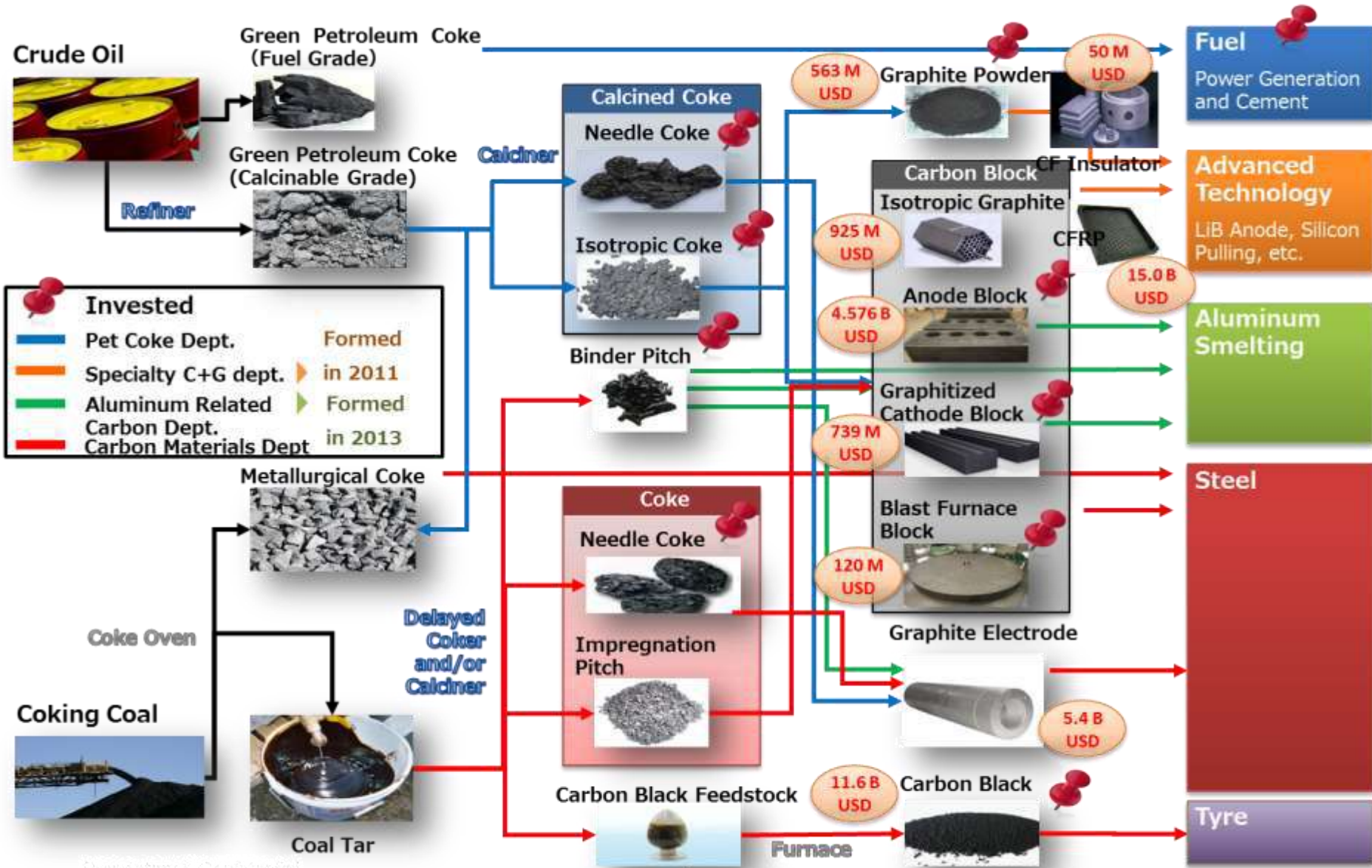


表-3 ピッチの特性値

種 類	用 途	軟化点 (℃)	固定炭素 (wt%)	比重	溶剤分別		元素分析				文献
					BI	QI	C	H	N	S	
石油系	含浸用	170F	36.3	1.185	2.5	0	91.8	5.98	0.66	1.8	35
石油系	電極用	92	53.7	1.246	32.5	5.5	92.0	5.65	0.1	1.0	37
石油系	製鉄コークス用	215	60.0	1.25	56.0	21.5	85.0	5.95	1.01	7.95	33
石炭系	(ストレート品)	67	50.5	1.29	16.1	3.9	91.9	4.7	1.4	0.3	36
石炭系	電極用	86	55.1	1.31	31.2	5.1	92.8	4.5	1.4	0.2	36

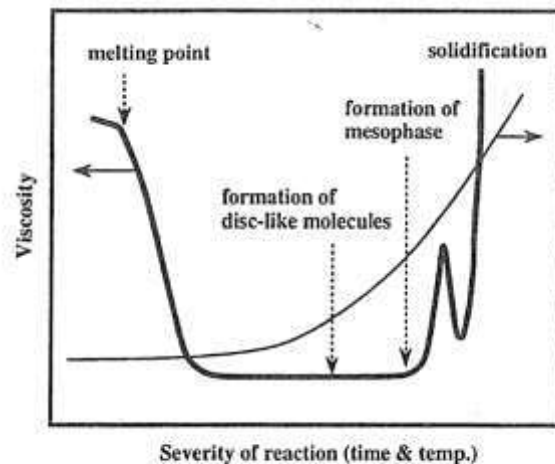


図-2 炭素化反応の苛酷度と構成分子の粘度、平均分子量の変化

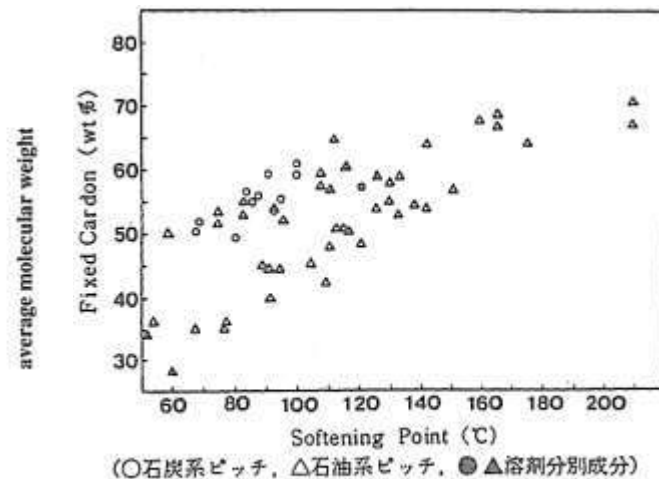


図-6 各種ピッチの軟化点と固定炭素の相関⁴¹⁾

表-1 光学組織の形状と寸法の分類

Optical texture	Abbreviation	Size (mm)
Isotropy	I	—
Anisotropic		
Spherical unit		
ultrafine mozaic	UMf	<0.5
very fine mozaic	Mvf	0.5~1.0
fine mozaic	Mf	1.0~2.5
medium mozaic	Mm	2.5~5.0
coarse mozaic	Mm	5.0~10.0
small domain	SD	10~60
domain	D	>60
Elongated unit		
elogated mozaic	EM	10~20
flow	F	20~60
flow domain	FD	>60

表-1 生コークスの性状

種 類	揮発分 (wt%)	灰分 (wt%)	真比重 (g/cm ³)	元素分析 (wt%)				備 考	文 献
				C	H	N	S		
石油系レギュラーコークス	8.2	0.08	1.39	93.5	3.4	1.6	0.48	デイルト・ユカー	27
石油系ニードルコークス	7.6	0.05	1.39	93.8	3.3	1.1	0.73	デイルト・ユカー	27
石油系高硫黄コークス	10.6	0.08	1.38	89.0	3.2	1.1	5.7	デイルト・ユカー	27
石油系高灰分コークス	16.1	1.22	1.35	92.0	4.2	1.3	0.36	—	27
石炭系コークス	7.8	0.11	1.41	94.6	2.8	0.8	0.29	デイルト・ユカー	27

表-2 か焼コークスの性状

種 類	硫黄分 (wt%)	灰分 (wt%)	真比重 (g/cm ³)	CTE*) ($\times 10^{-6}/K$)	文 献
石油系レギュラーコークス	1.1	0.35	2.07	3.1	28
石油系ニードルコークス	0.6	—	2.12	1.1	28
石油系ニードルコークス	0.5	0.20	2.08	1.2	28
石油系ニードルコークス	0.2	0.10	2.12	1.1	28
石炭系スポンジコークス	0.3	0.2	2.00	3	30
石炭系ニードルコークス	0.3	0.09	2.11	1.2	31

*) 熱膨張計数

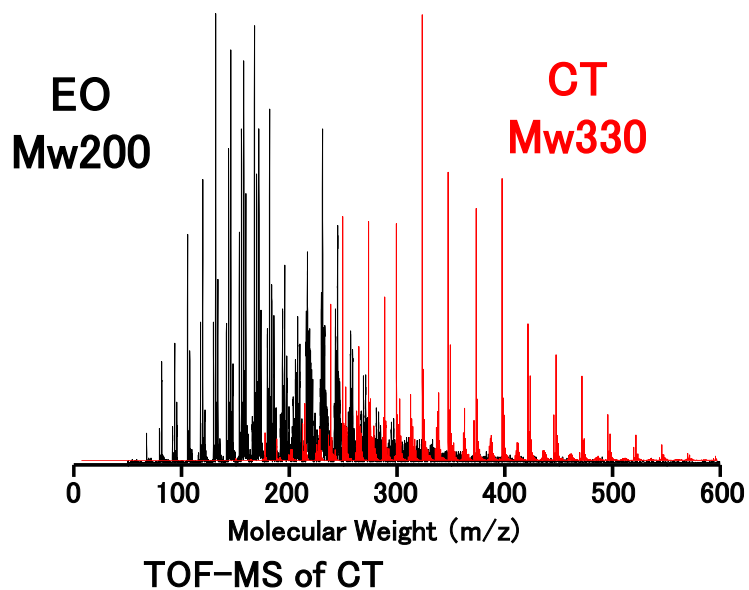
EOとCTの元素分析, ^{13}C -NMRおよびTOF-Mass分析

Elemental analyses

Raw material	C (wt%)	H (wt%)	H/C	N (wt%)	S (wt%)
EO	92.30	7.41	0.96	0.00	0.14
CT	92.58	5.96	0.77	0.84	0.62

^{13}C NMR analyses

	Aliphatic (%)			Aromatic (%)					fa
				C _{ar1,3}		C _{ar1,2}		C _{ar3} /C _{ar2}	
	CH ₃	CH ₂	C _{chain}	CH _{ar}	C _{ar3}	C ^s _{ar}	C _{ar2}		
	EO	9.0	10.2	6.4	19.3	9.7	7.8		
CT	1.1	10.6	1.9	1.3	24.3	2.1	58.7	0.41	0.86

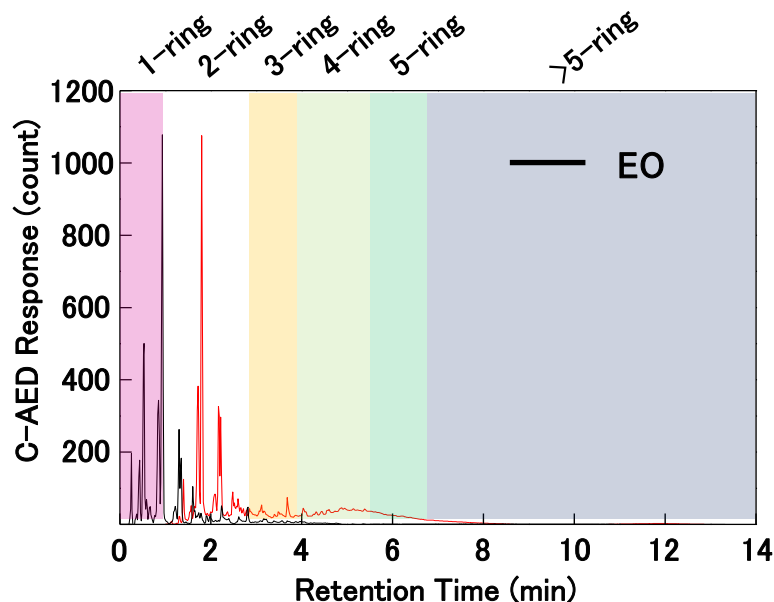


✓CT has more heterogeneous atomic compounds than EO

✓fa: 0.86

✓Mw: 200~500 (300~400)

GC-AEDを用いたEOの環数分布



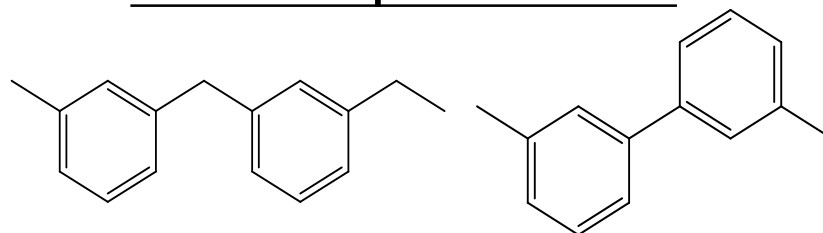
Molecular compositions of raw materials

Ring number	EO
1-Ring	46.7
2-Ring	43.9
3-Ring	5.5
4-Ring	3.5
5-Ring	0.4
>5-Ring	0.0

GC-AED

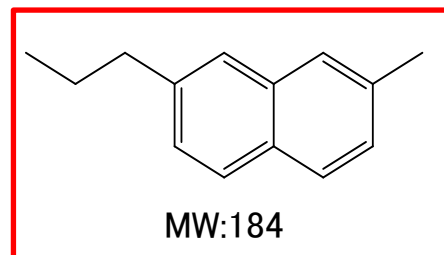
- ✓ EO: 90% of 1~2 six membered rings
- Many Alkyl Naphthalene

Model compounds of EO

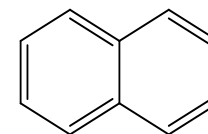


MW:210

MW:182

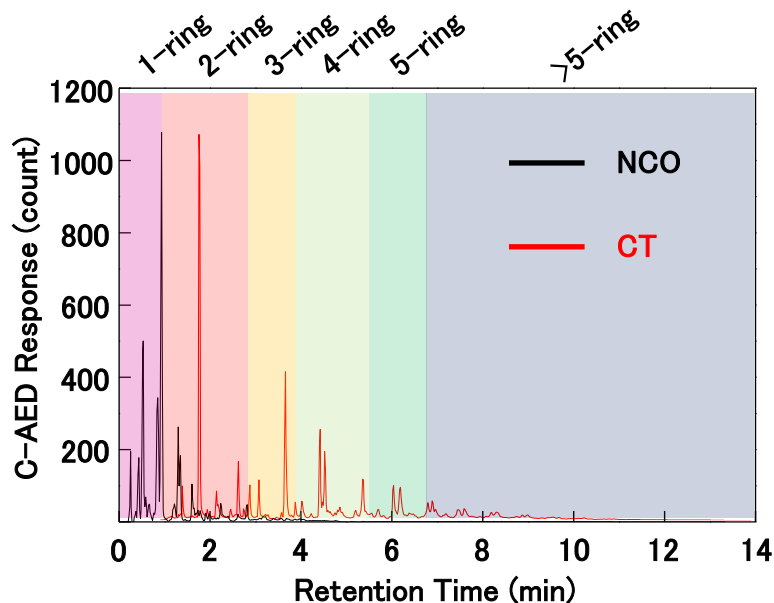


MW:184



MW:128

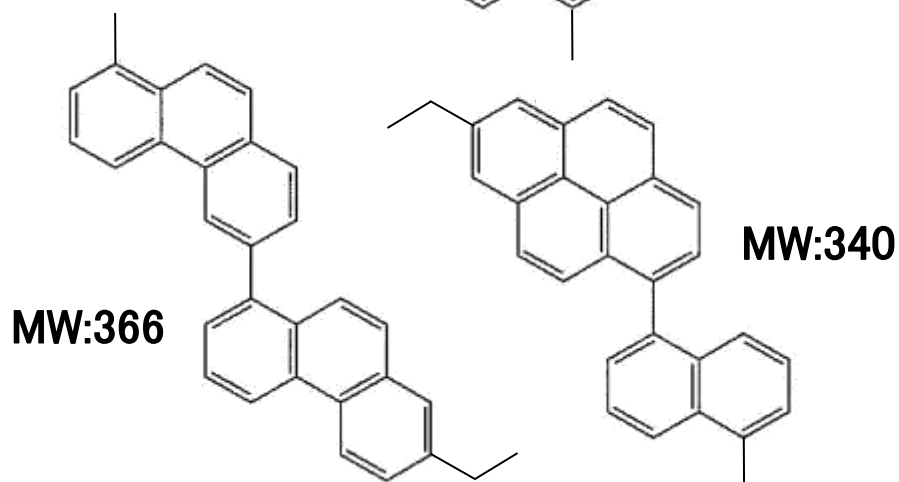
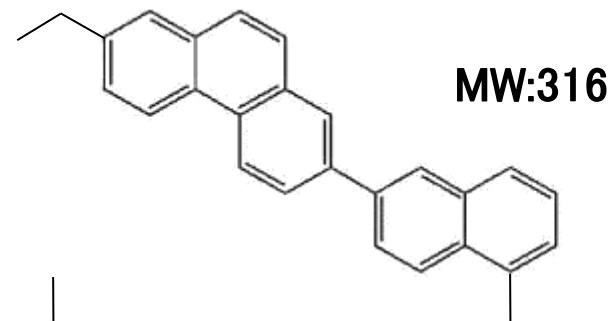
GC-AEDを用いたCTの環数分布



GC-AED

- ✓ CT: 2~4 six membered rings
- ✓ Almost 2 and 3 membered rings

Model compounds of CT



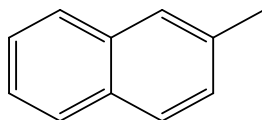
Ring compositions of CT

Ring number	NCO	CT
1-Ring	46.7	0.0
2-Ring	43.9	31.3
3-Ring	5.5	27.3
4-Ring	3.5	22.2
5-Ring	0.4	5.2
>5-Ring	0.0	4.0

2-MNのBromination-dehydrobromination反応

Process

2-Methyl
naphthalene
(2-MN)



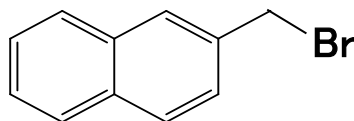
Halogenation

(Br₂: the same amount with 2-MN)

@30~180°C



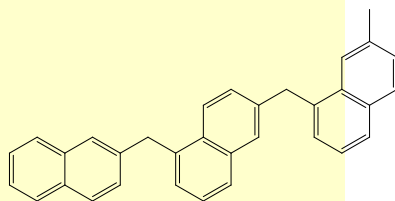
Bromination of
2-MN



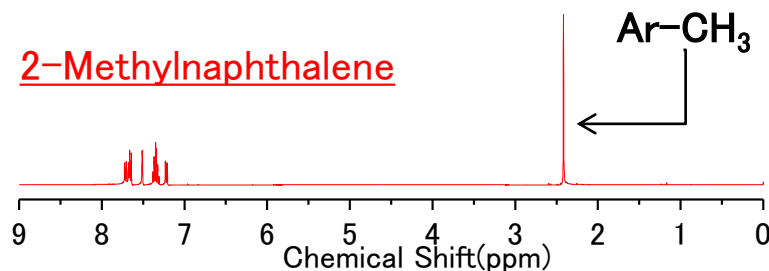
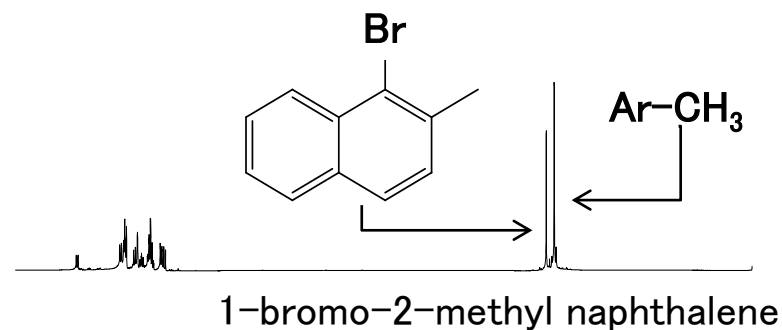
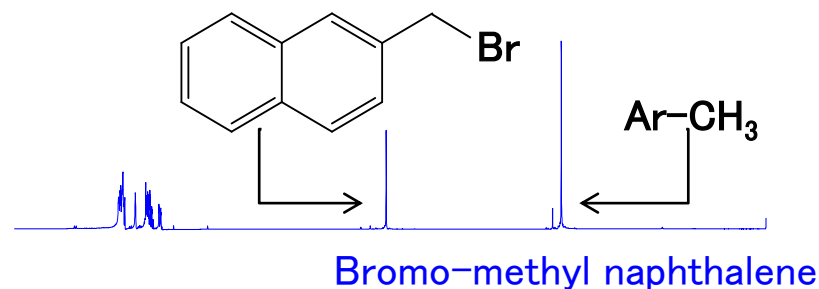
Aging

@320°C

Pitch

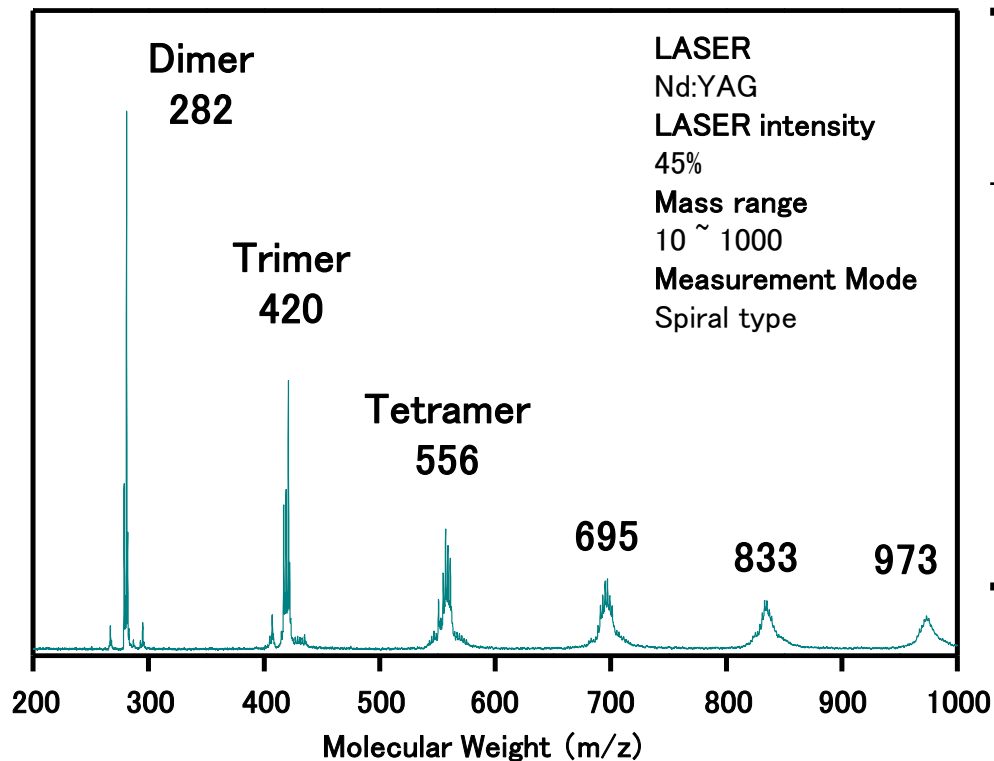


NMR analysis



合成したピッチの分子量と分子構造

TOF-MS



^{13}C NMR

pitch	Aromatic			Aliphatic		fa
	C ₁	C ₂	C ₃	C ₄	C ₅	
MN10	15.57	18.19	58.40	5.15	2.70	0.92
MN15	14.92	18.30	58.98	5.70	2.10	0.92
MN20	16.33	18.23	57.18	6.28	1.98	0.92
2MN	9.09	18.18	63.63	0.00	9.09	0.91

C₁: 132.5–149.2ppm, substituted carbon

C₂: 129.5–132.5 ppm, outer quaternary carbon

C₃: 115–129.5 ppm, unsubstituted carbon

C₄: 22–53 ppm, methylene carbon(methylene bridge)

C₅: 22–11 ppm, methyl carbon(CH₃)

fa: carbon aromaticity

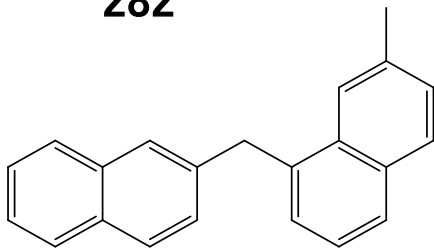
持田勲、炭素材の化学と工学、1990、p60

Diaz C, Blanco CG. Energy & Fuels, 17,(2003) 907

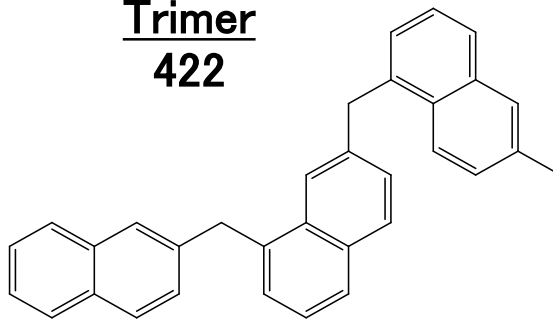


合成したピッチの代表的な分子構造

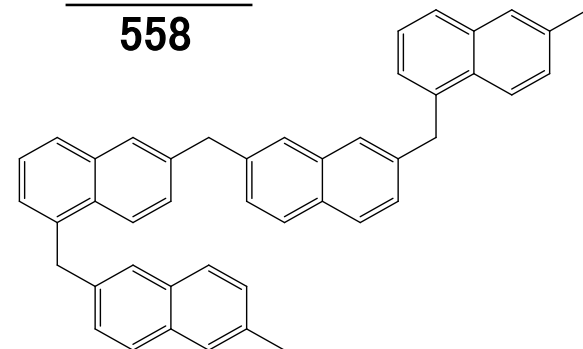
Dimer
282



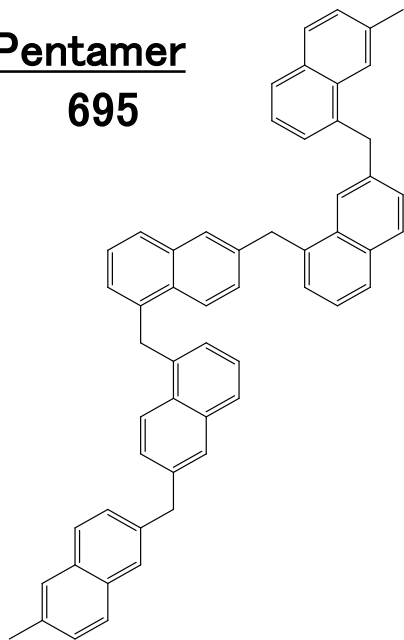
Trimer
422



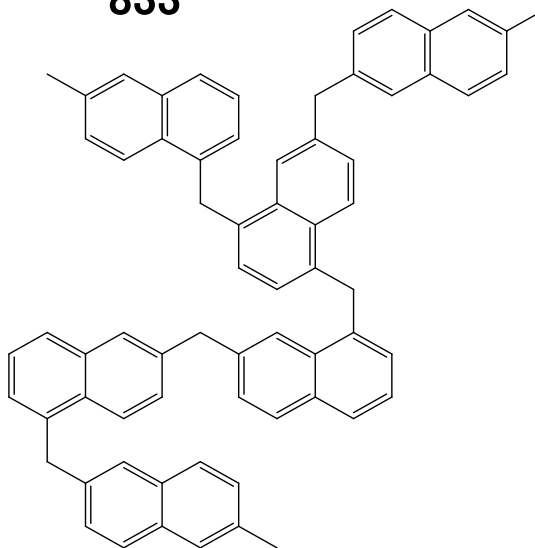
Tetramer
558



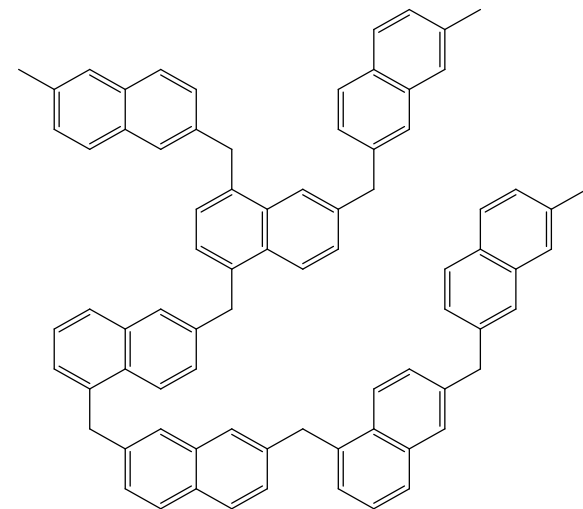
Pentamer
695



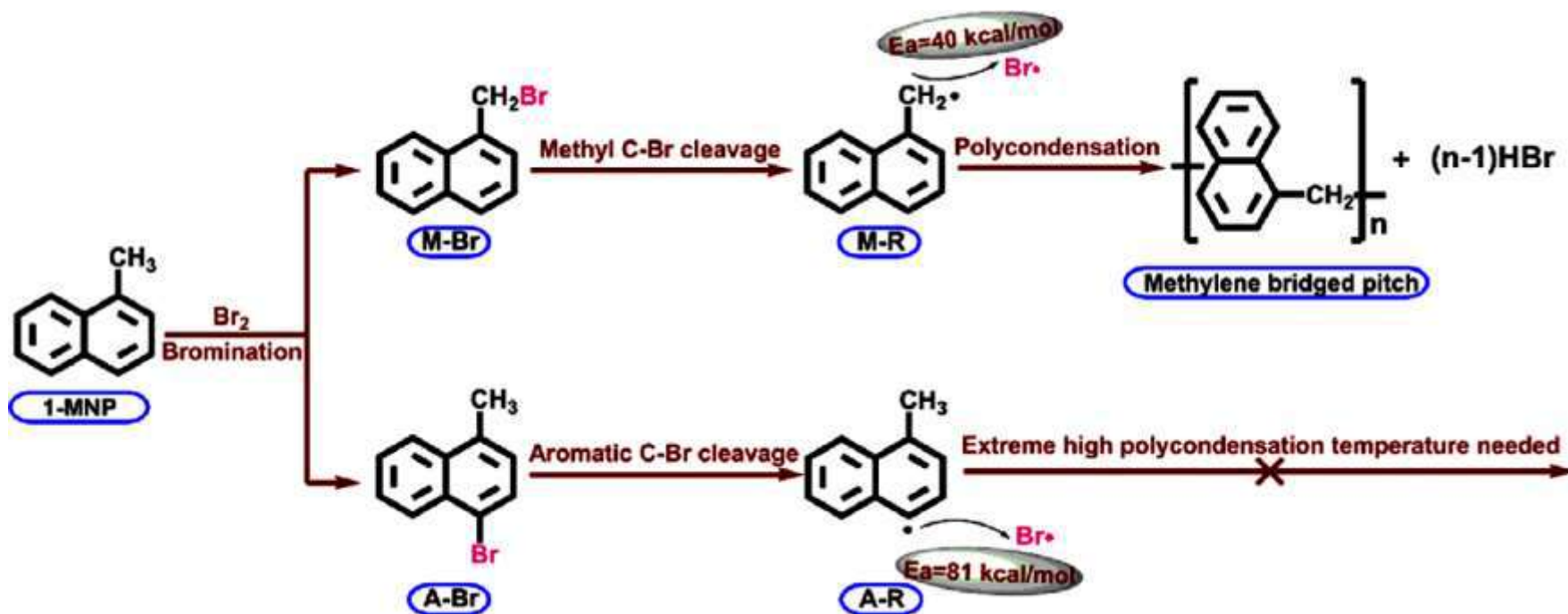
Hexamer
833



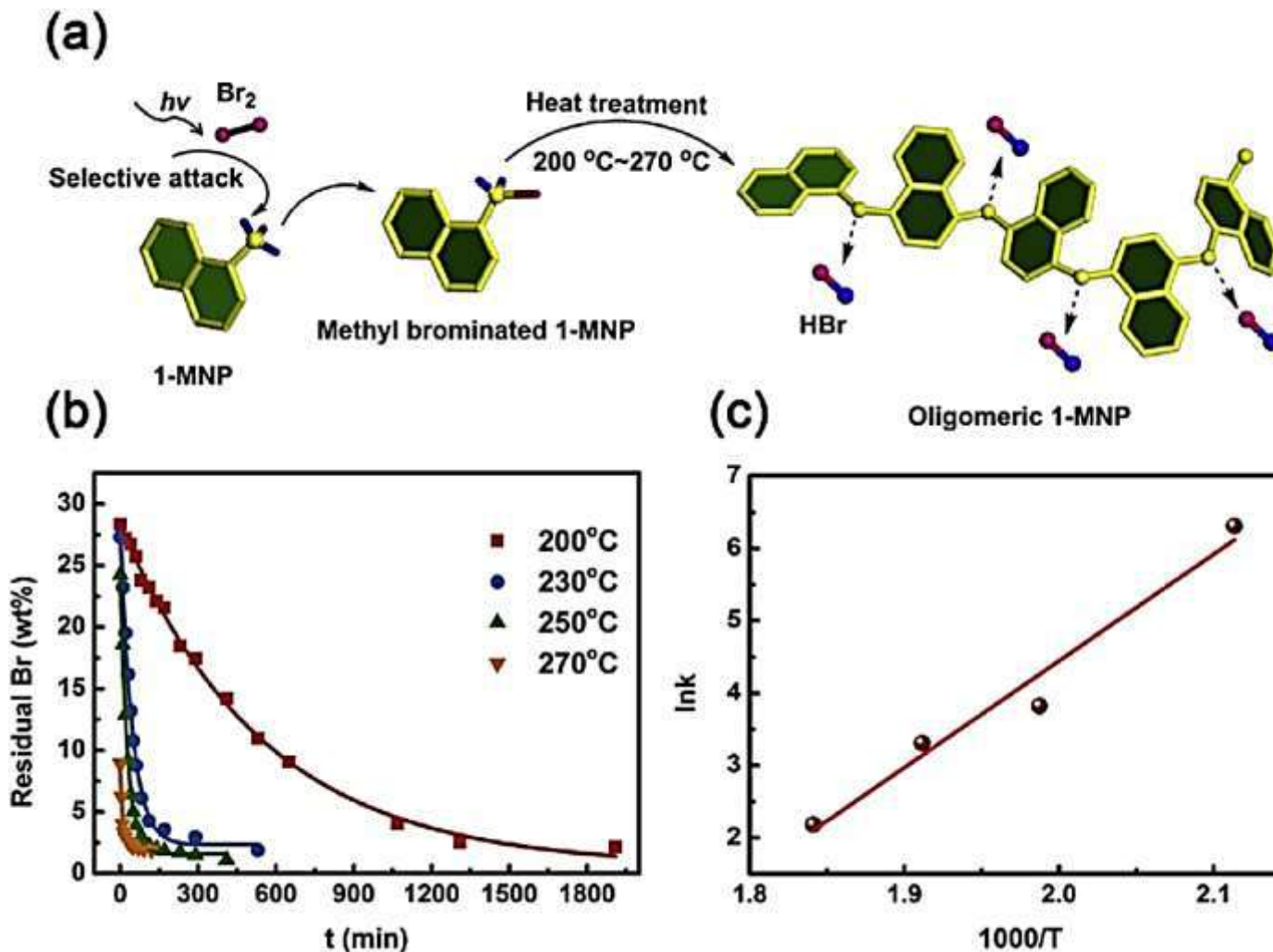
Heptamer
973



メチレン架橋による重合機構

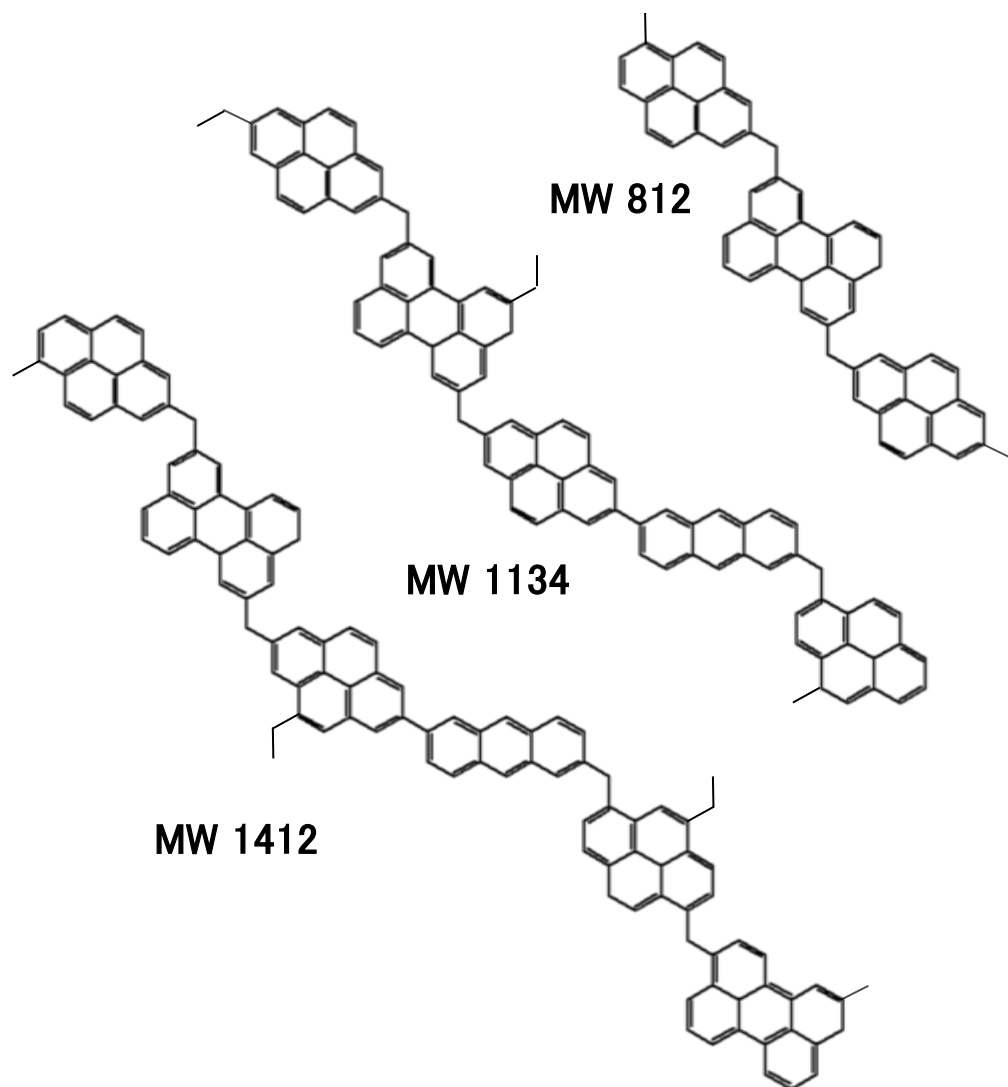


Dehydrobromination/polycondensationの際の (a) Scheme of dehydrobromination/polycondensation; (b) Isothermal dehydrobromination kinetic curves; (c) Arrhenius plots of $\ln k$ and $1/T$ for the thermal dehydrobromination of M-Br.

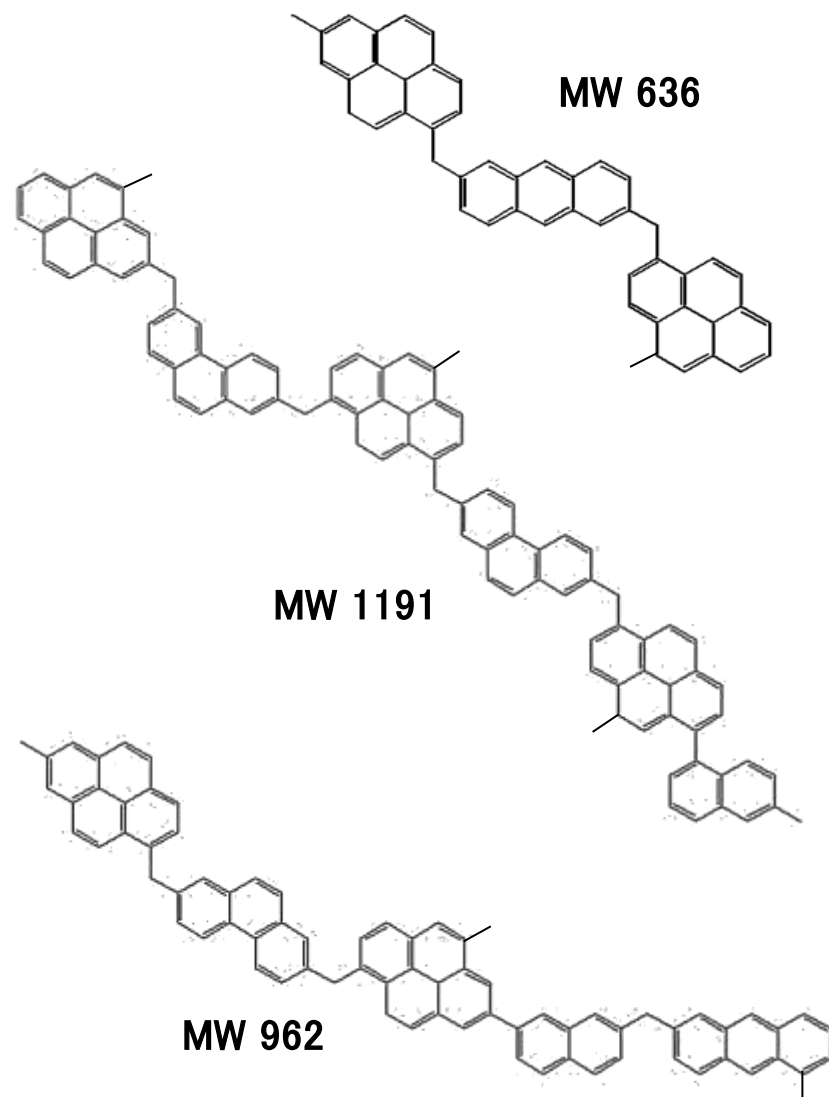


NCBとNBの代表的な分子構造

NCB



NB



Characteristics of needle coke

Graphite electrode

=

Needle coke + Binder pitch
Impregnation pitch

Prerequisite of Needle Coke

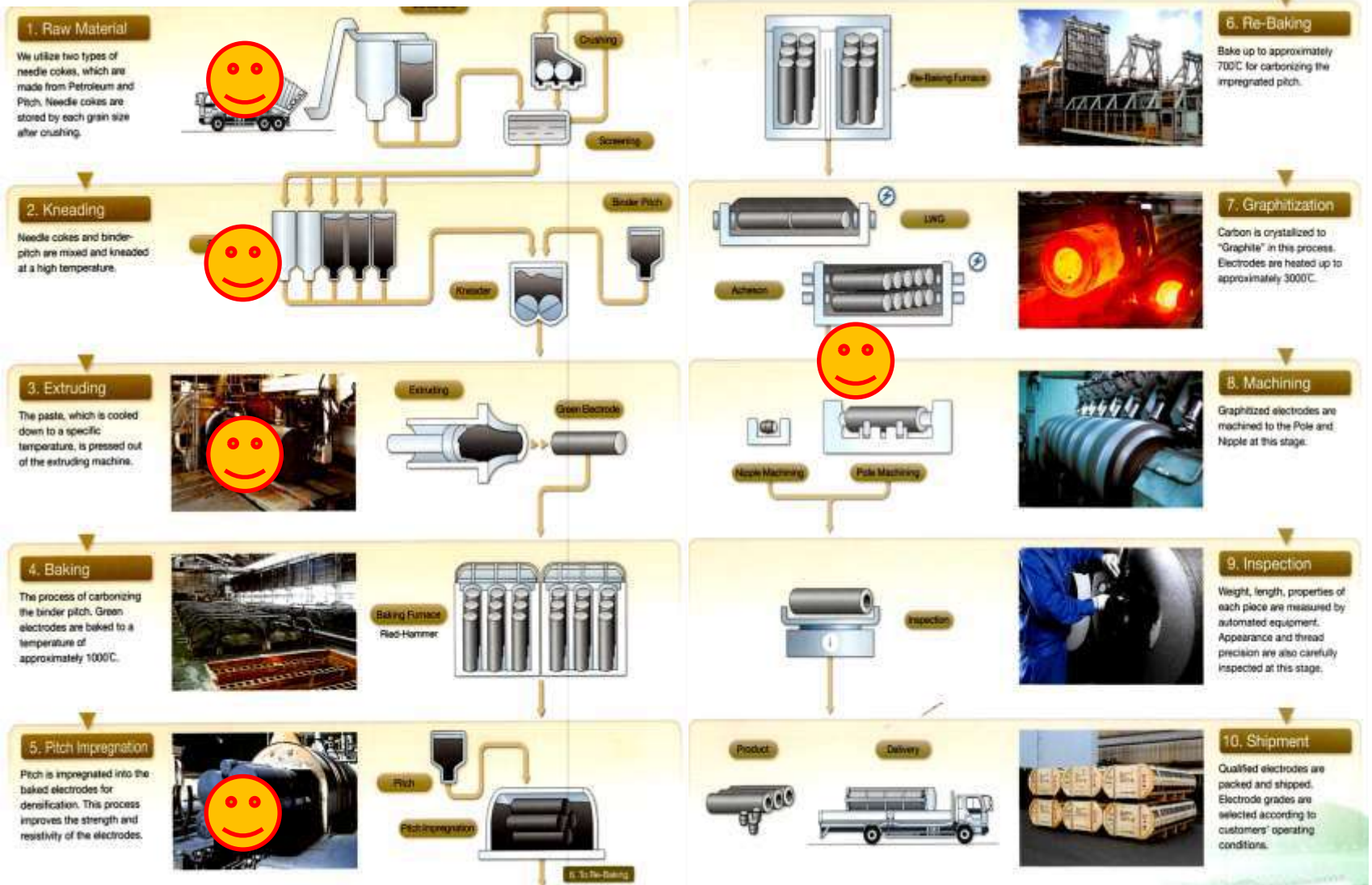
1. Low CTE
2. Low Puffing
3. High Strength of Grains
4. Good Wettability

⇒

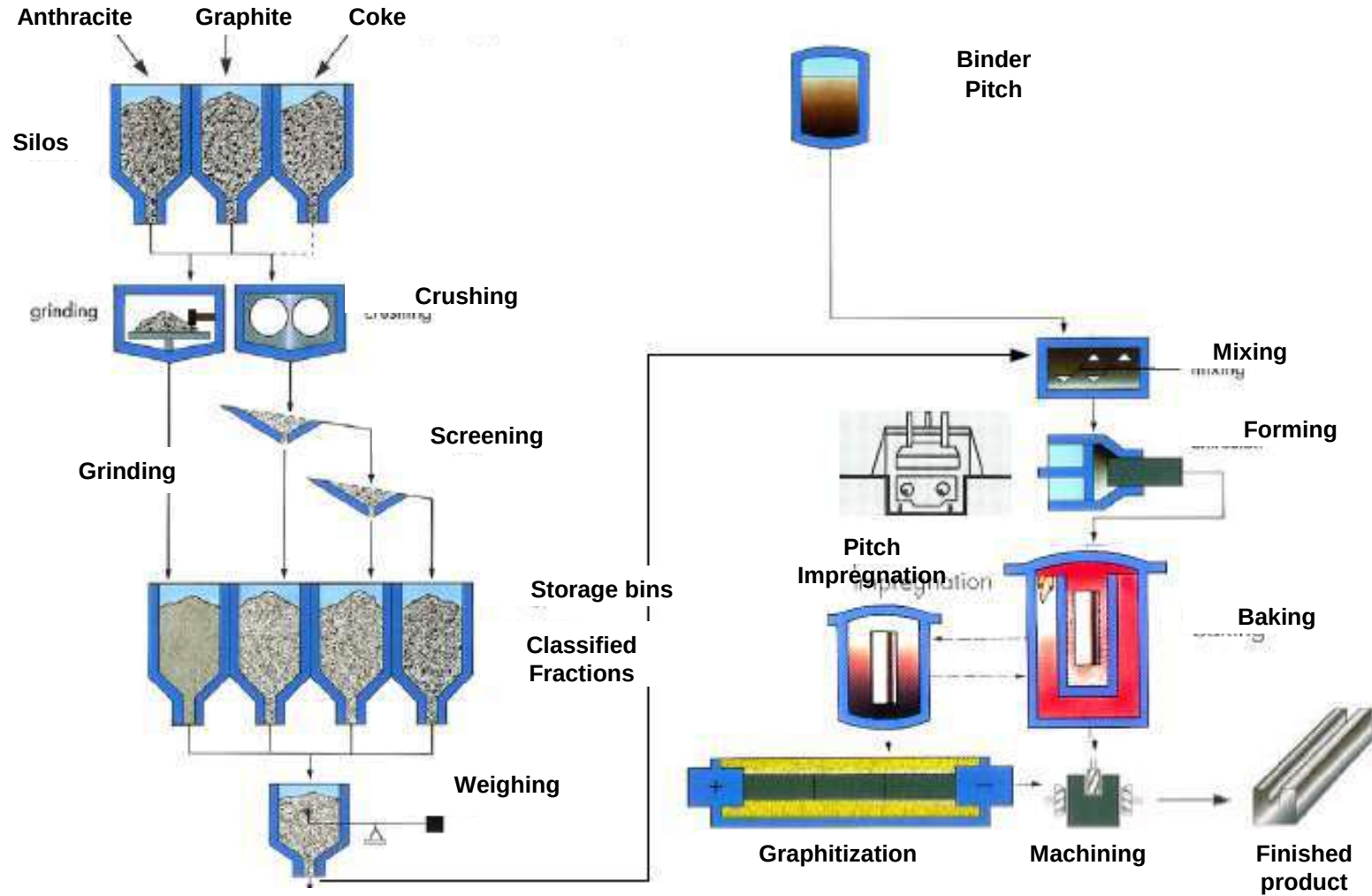
How to achieve above properties ?

Manufacturing Graphite Electrode

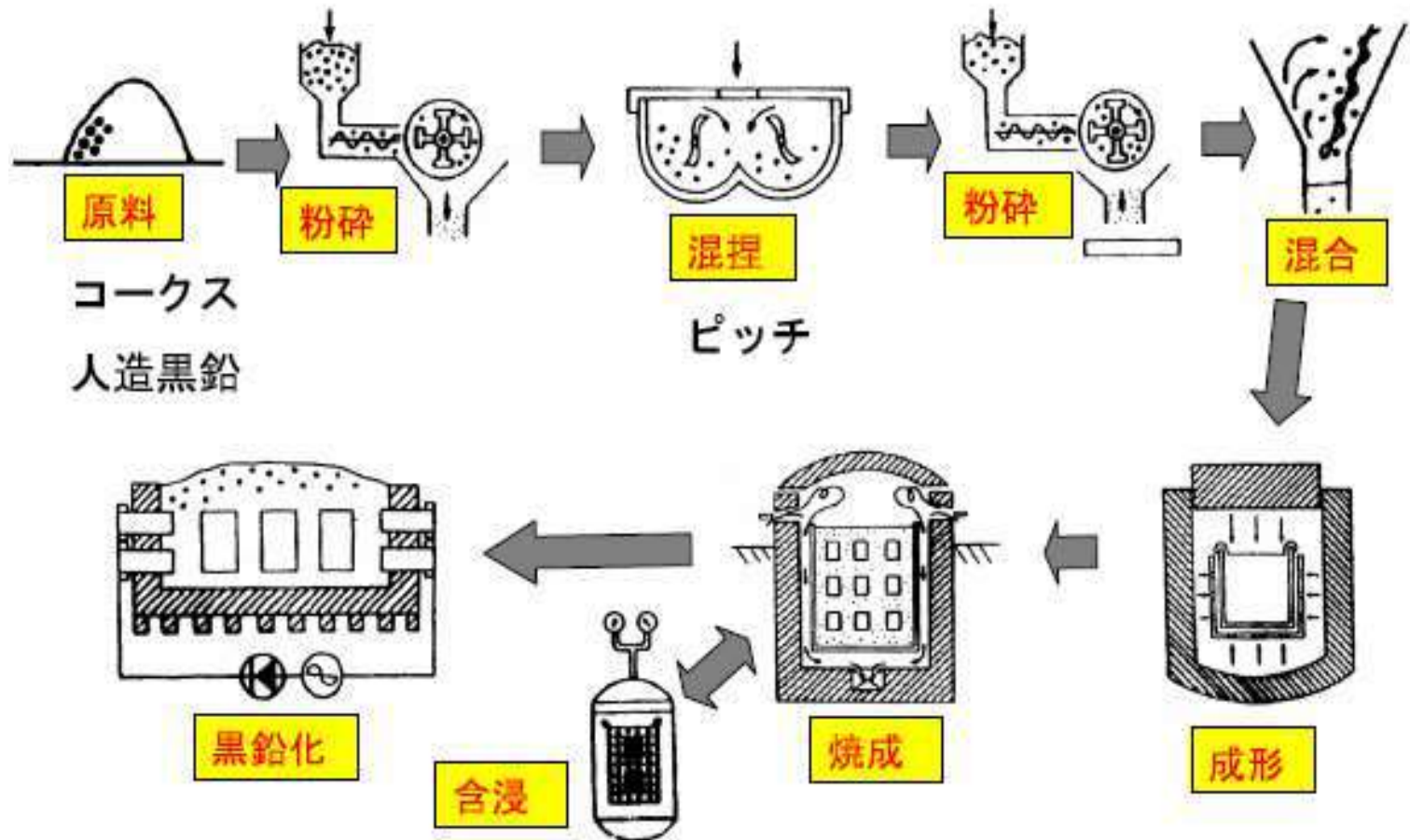
50



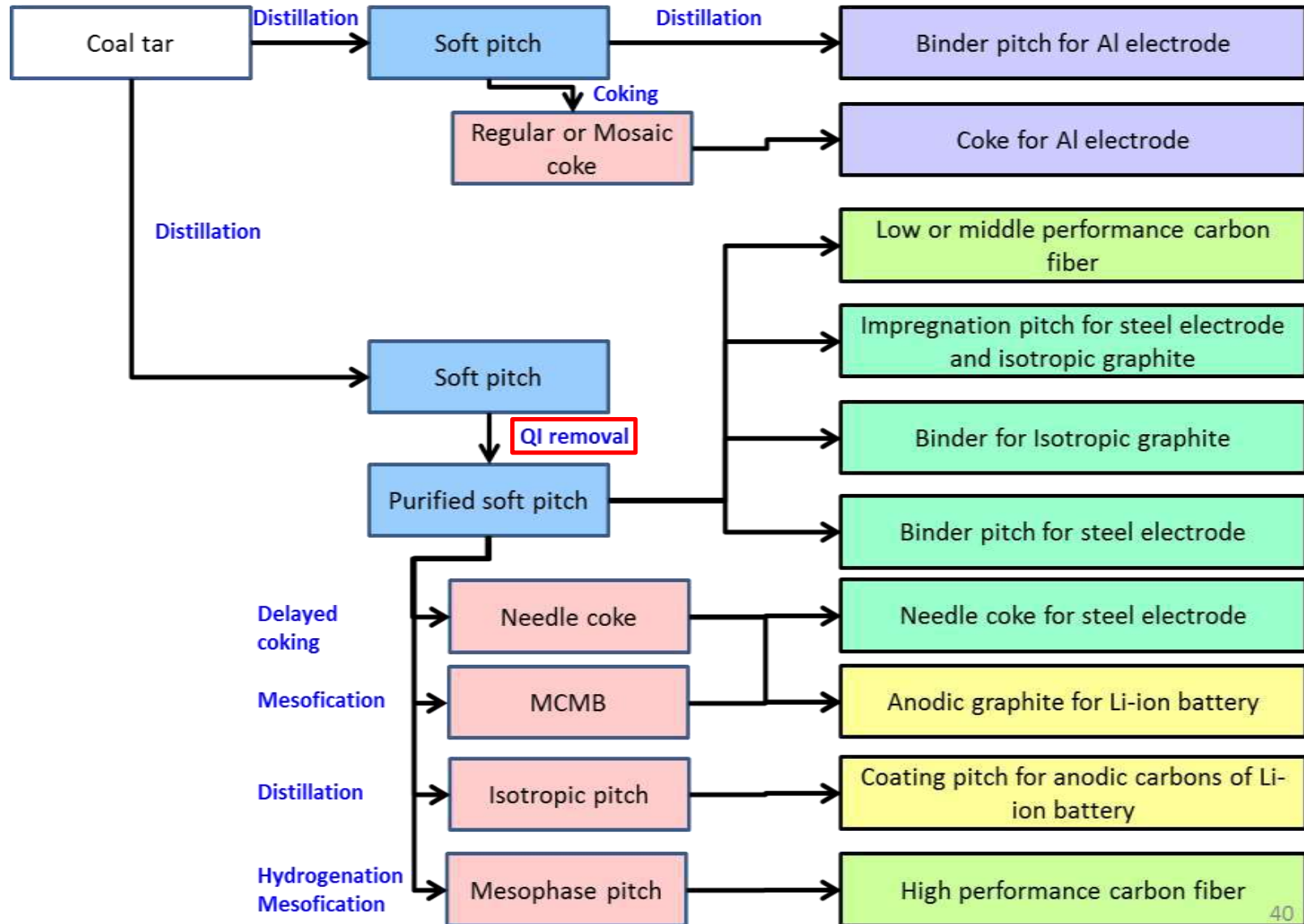
黒鉛電極の製造



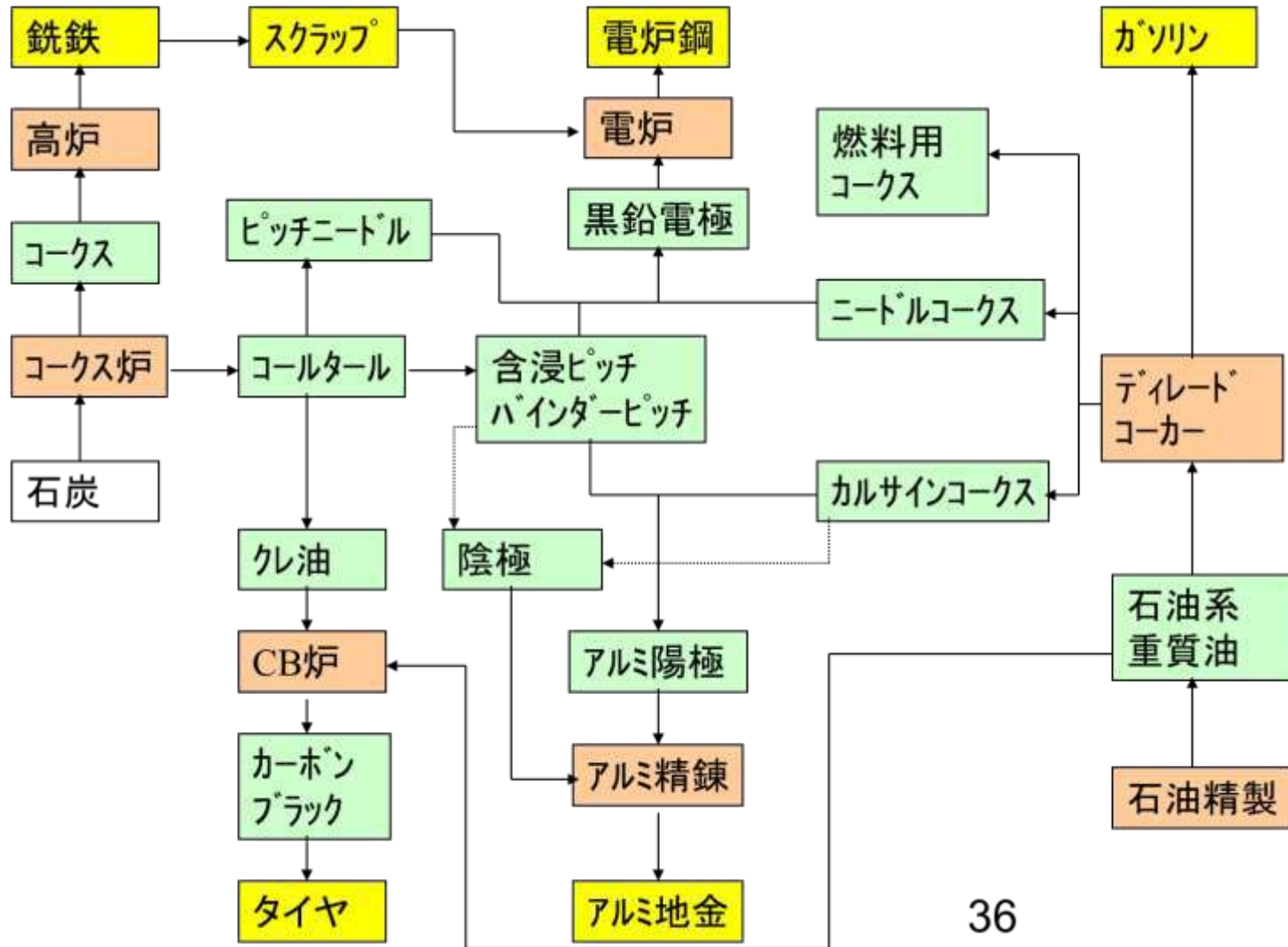
等方性黒鉛の製造工程(二元系原料)



Flow of coal tar related materials

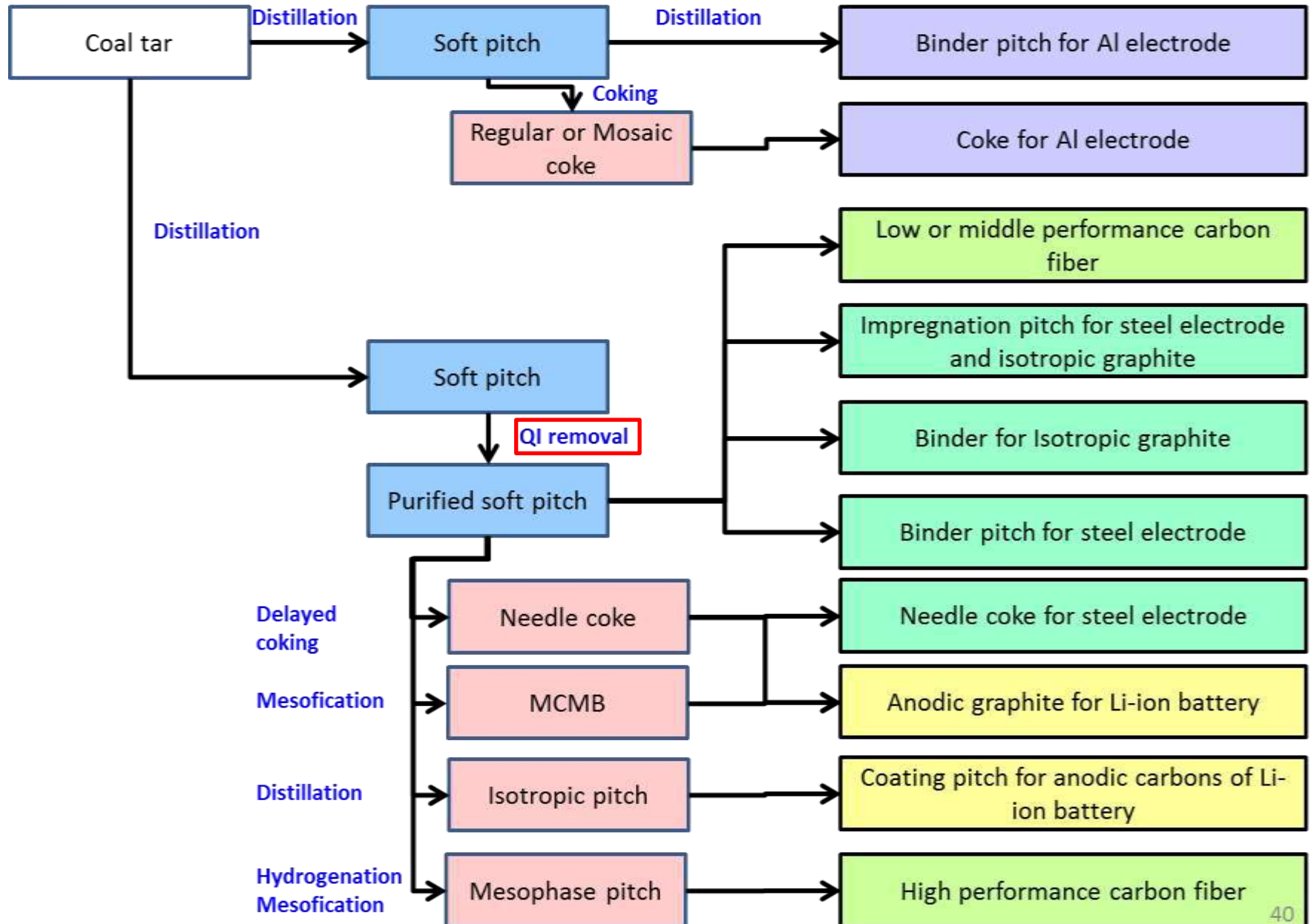


重質油を用いたカーボンサークル



36

Flow of coal tar related materials



Preparation of carbons

What is the most important for carbon manufacturing?

- Specific properties of target material.
ex) Carbon fiber
 - Tensile strength: impurity, surface property, molecular orientation
 - Modulus: molecular orientation, graphitization degree
 - Elongation property: selection of raw material, heat treatment temperature
 - Thermal conductivity: graphitization degree



- How to achieve such properties?
ex) Carbon fiber
 - Tensile strength: low impurity, amorphous surface property, high molecular orientation
 - Modulus: high molecular orientation, high graphitization degree
 - Elongation property: precursor control, low temperature heat treatment
 - Thermal conductivity: high graphitization degree

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

...



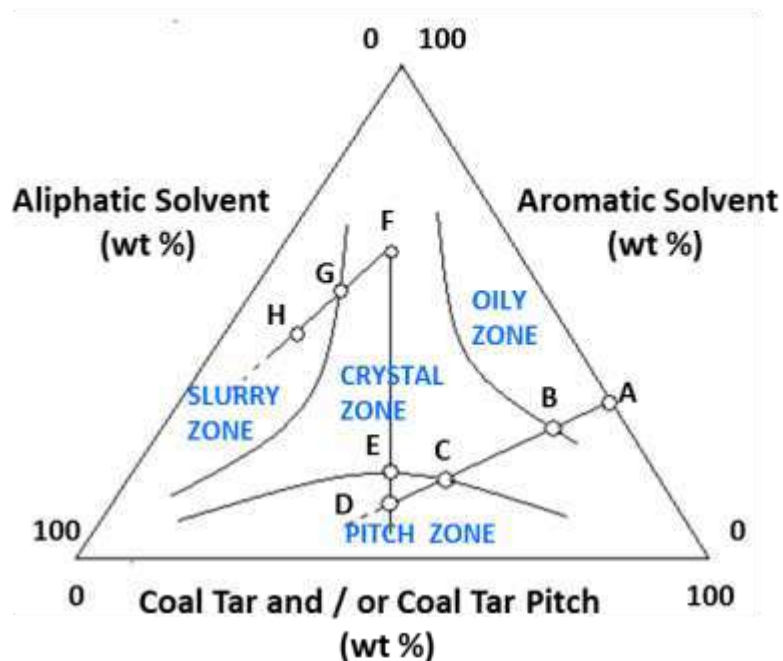
Purification of raw and precursor materials

- Advanced functional carbons always require higher than certain level of purification.
- Kinds of impurities are very dependent to the target materials.
 - In the case of needle coke: Sulfur and nitrogen compounds are important impurities.
- The purification of functional carbons almost rely on the purity of raw and precursor materials.
- The optimized purification method is very dependent to the raw materials, size of manufacturing and production cost.
 - Pitch-epoxy : Centrifugation method
 - Needle coke : Solvent-non solvent method
 - FCC-DO: High temperature centrifugation (several times)
- To find out the optimized purification method of raw or precursor materials is most important key technology in the functional carbon productions.

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

Stationary method



Experimental procedure

Coal Tar + Toluene

15min , 80°C

stirring treatment

n-Hexane

10~60min 80°C or
Room Temperature (RT)

stationary

Heavy oil precipitation

40min , 80°C

Filtration by Quinoline

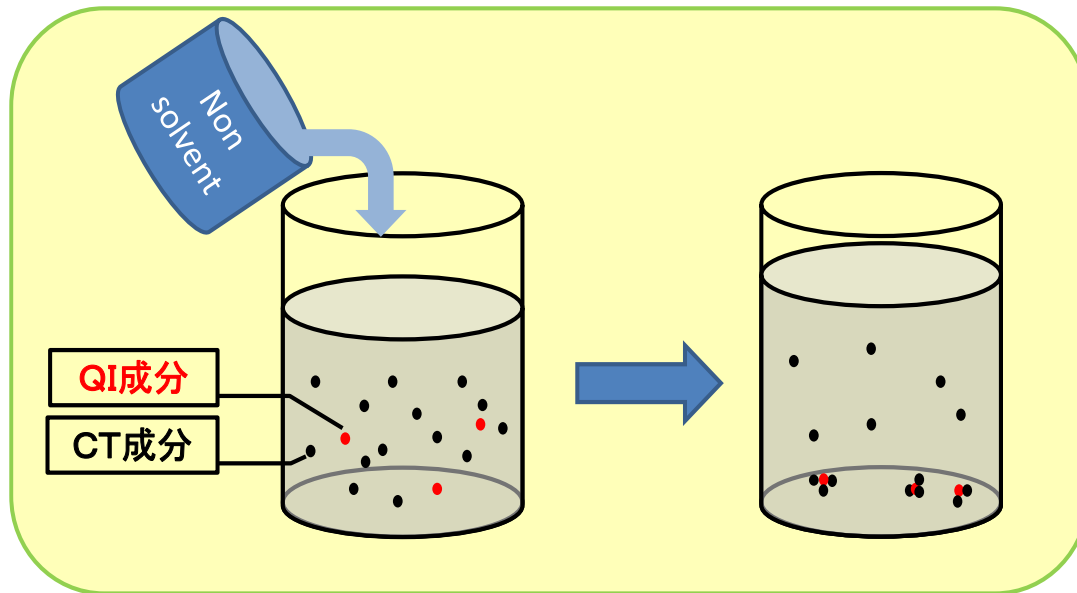
QI removal

The case using the general solvent(unit : wt %)

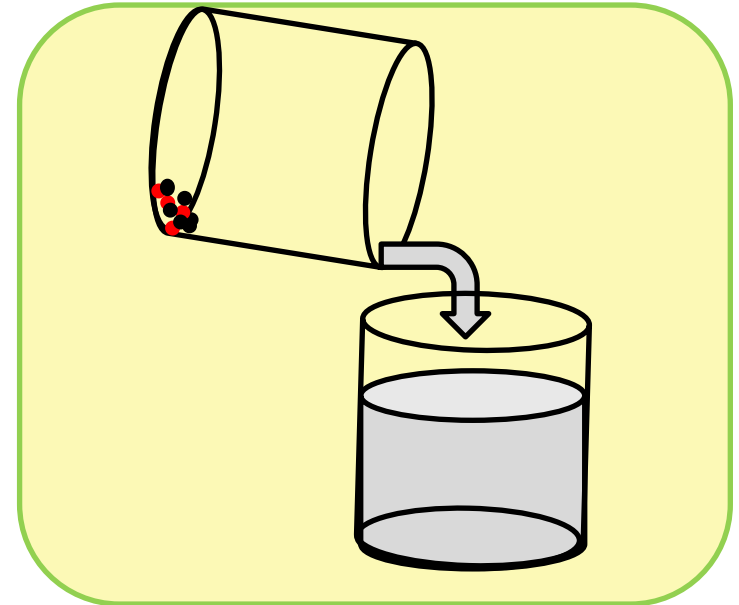
	Sample	Toluene	n-Hexane	Temperature
A	Coal Tar 50	50	0	80°C (→ RT)
B	Coal Tar 44	44	12	80°C (→ RT)
C	Coal Tar 36	36	18	80°C (→ RT)
D	Coal Tar 32	32	36	80°C (→ RT)
E	Coal Tar 28	40	32	80°C (→ RT)
F	Coal Tar 9	81	10	80°C (→ RT)
G	Coal Tar 7	67	26	80°C (→ RT)

QI removal from CT

Solvent-Non-solvent method



- (1) CT is dissolved into solvent
- (2) QI is precipitated by the addition of non-solvent
- (3) Pitch phased precipitate is removed.

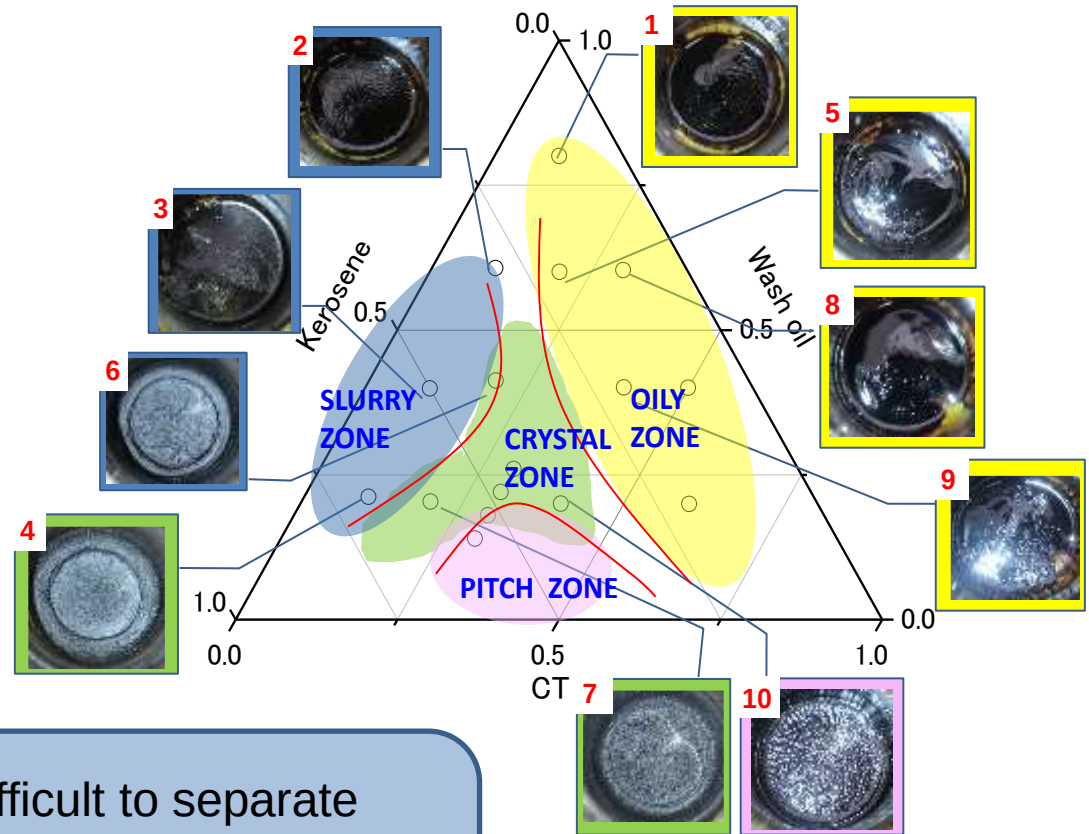


Solid – liquid separation by decantation *Time & Temperature

Phases of precipitate (QI+?)

Phase changes of precipitates

	CT w%	Wash oil w%	Kerocene w%	Precipitate w%
1	10	80	10	-
2	10	60	30	-
3	10	40	50	38.7
4	10	20	70	45.5
5	20	60	20	37.2
6	20	41	39	40.2
7	20	20	60	24.8
8	30	60	10	-
9	40	40	20	-
10	40	20	40	17.1
11	50	40	10	-
12	60	20	20	-



OILY ...No solid precipitate, difficult to separate
SLURRY ...Easy to separate but large amount of precipitate
CRYSTAL ...Difficult to separate
PITCH ...Small amount of precipitate, easy to separate

Adjustment of removal conditions



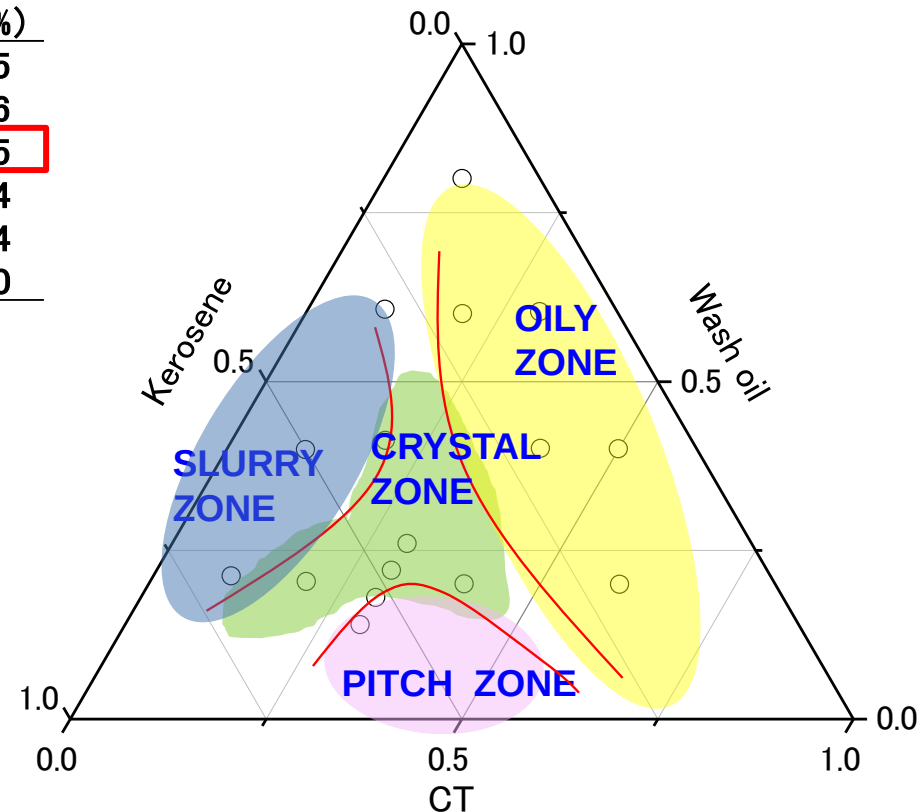
Changes of precipitate amounts of CT under various conditions

	CT	Wash oil	Kerocene	Precipitate (QI (%))	
①	30	26	44	①	23.6 2.15
②	30	24	46	②	23.6 2.16
③	30	22	48	③	10.36 2.35
④	30	18	52	④	11.5 2.64
⑤	30	16	54	⑤	18.2 2.54
⑥	30	14	56	⑥	30.1 2.50

Easiness of decatation

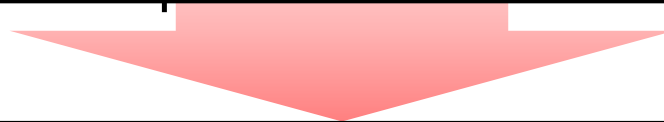
QI amount $\approx$ Precipitate amount

Kind of solvent, Mixing ratio
Temperature, and time



Understanding raw and precursor materials

- To select and design the target functional carbons, full understanding of raw and precursor materials are necessary.
- It is not still enough to understand the molecular structures of raw and precursor materials.



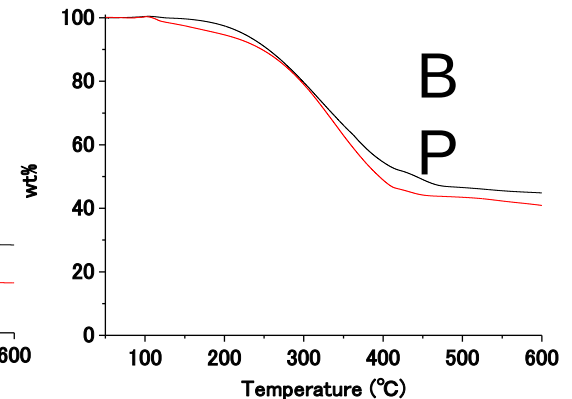
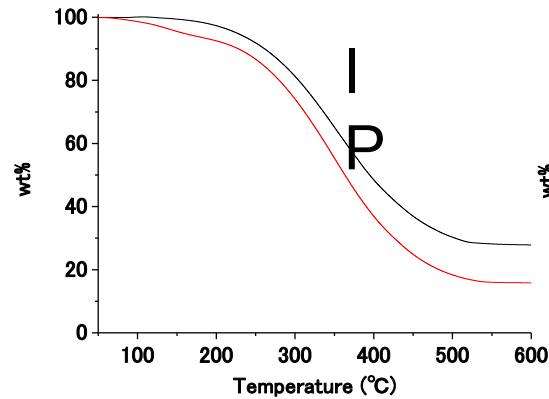
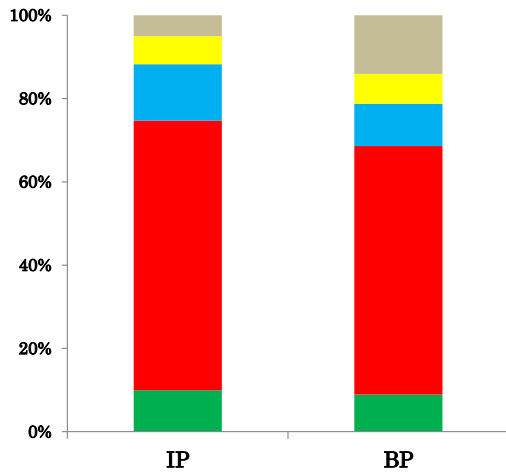
- It is strongly required that the novel analytical method to analyze the **detailed molecular structures of raw and precursor materials**.
- TOF-MASS, GC-GC (2D), **GC-AED**, etc.

- It is also strongly required that the novel analytical method to analyze the detailed **impurity structures** of raw and precursor materials.
- Chelated structures of Ni and V in DO materials, etc.

Properties of high performance binder materials

Property	Required level
Softening point (Ring & Ball method) (°C)	80 -110
Density (25 °C)	1.28 – 1.32
Coking value (%)	55-65
Benzene Insoluble (%)	30 – 35
Quinoline Insoluble (%)	10 -16
C/H (Atomic ratio)	1.70 – 1.85
Temperature appearing 500 cP (°C)	150 – 180

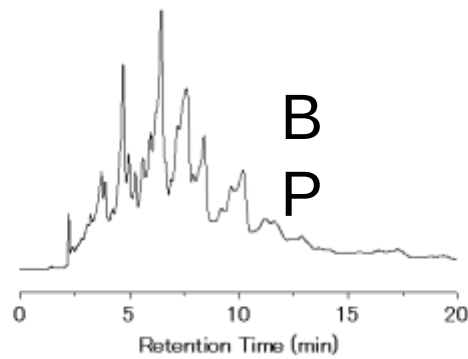
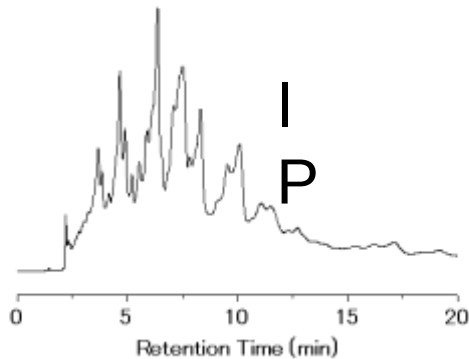
66 Some properties of binder and impregnation pitches



Solvent solubilities of impregnation and Binder pitches

TGA profiles of binder and impregnation pitches

* Black line: Pristine, Red line: HI-TS fraction of IP and BP

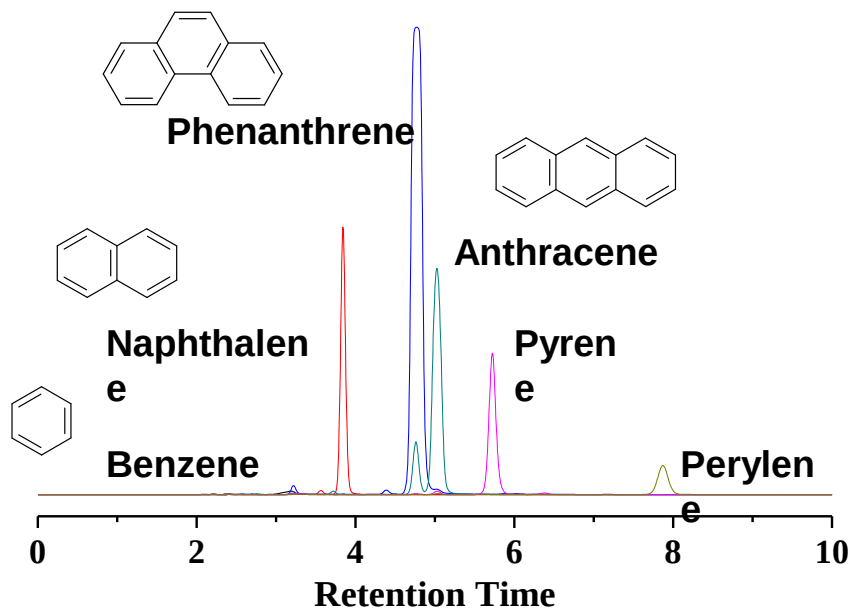


HPLC analyses of binder and impregnation pitches

Novel method for quantitation of aromaticity

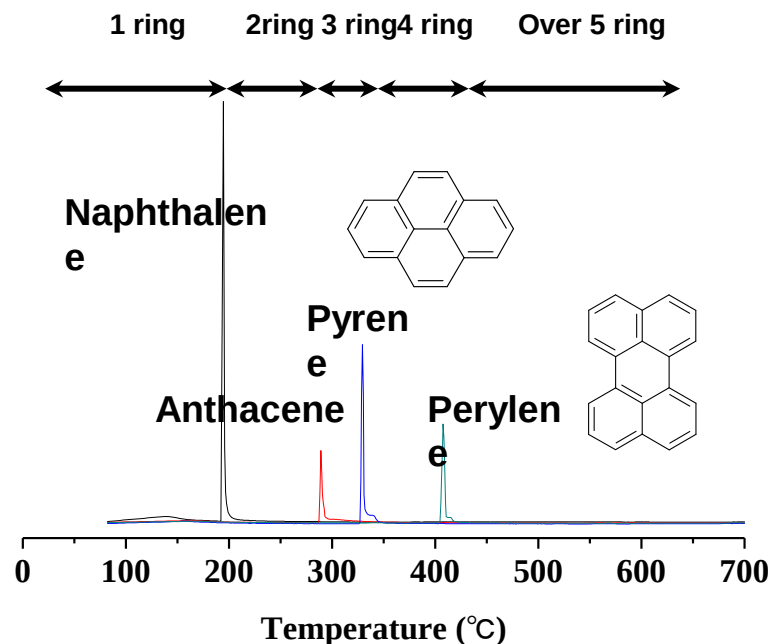
Standard materials

HPLC analysis



B : Benzene (1 ring, Retention Time : 3.18min)
 N : Naphthalene (2 ring, Retention Time : 3.84min)
 P : Phenanthrene (3 ring, Retention Time : 4.77min)
 A : Anthracene (3 ring, Retention Time : 5.03min)
 Py : Pyrene (4 ring, Retention Time : 5.72min)
 Pe : Perylene (5 ring, Retention Time : 7.87min)

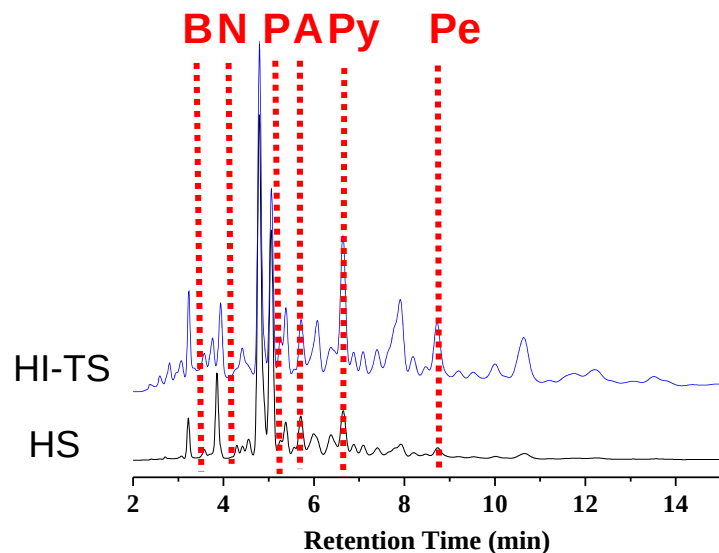
GC-AED analysis



N : Naphthalene (Temperature : 194.8°C)
 A : Anthracene (Temperature : 289.0°C)
 Py : Pyrene (Temperature : 329.3°C)
 Pe : Perylene (Temperature : 407.6°C)

Analyses of CT

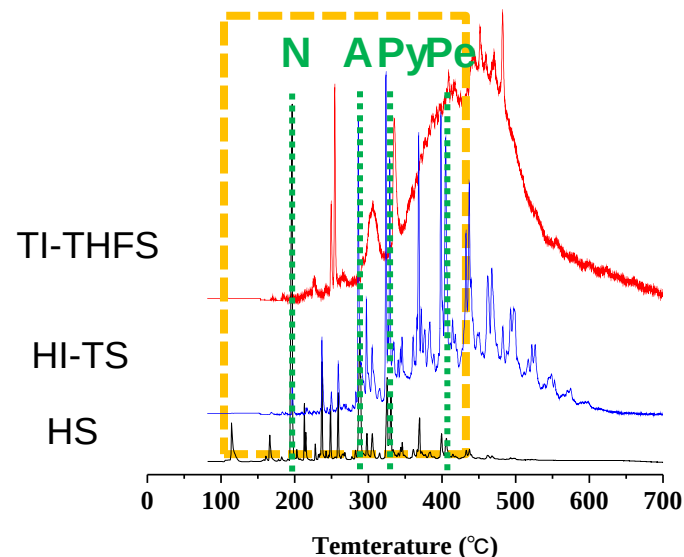
HPLC analysis



溶解度 (%)		芳香族環含有量-面積比 (%)				
		1環	2環	3環	4環	5環以上
HS	59	4.4	1.1	59	20	18
HI-TS	34	5.6	3.6	26	22	42
TS	92	4.2	2.0	47	21	27

HS: almost 3 membered rings
HI-TS: over 3 membered rings

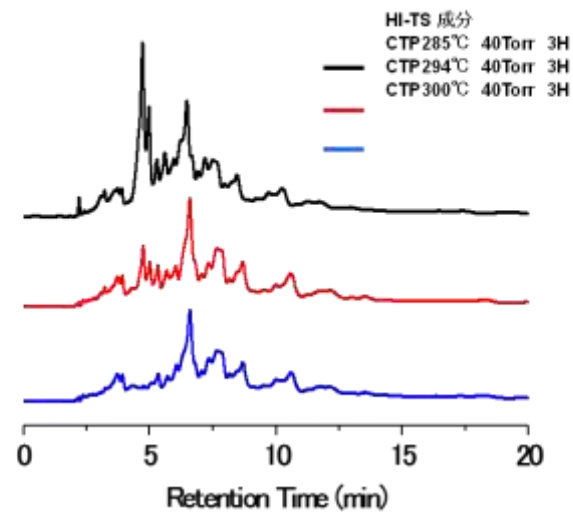
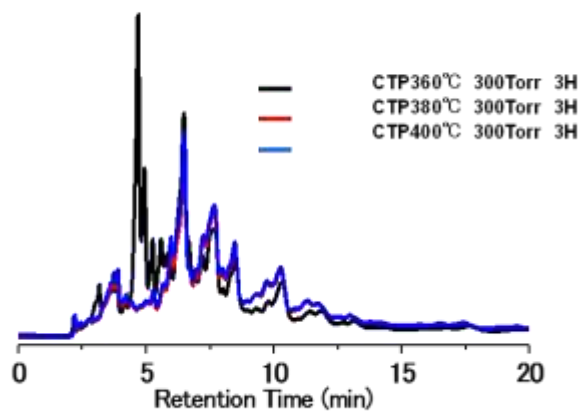
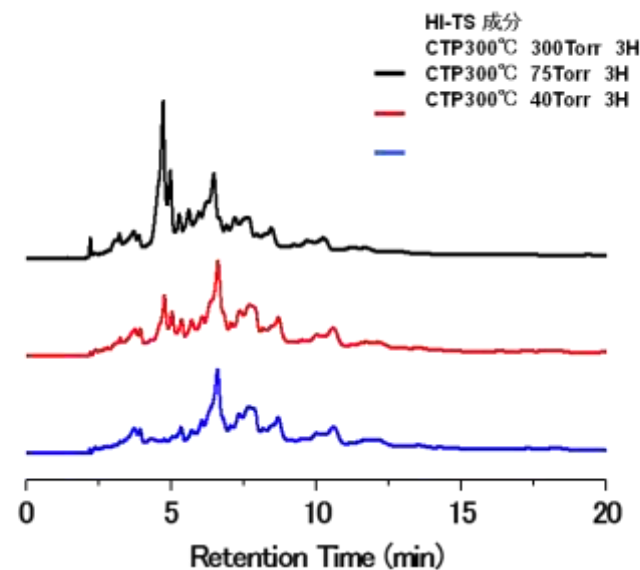
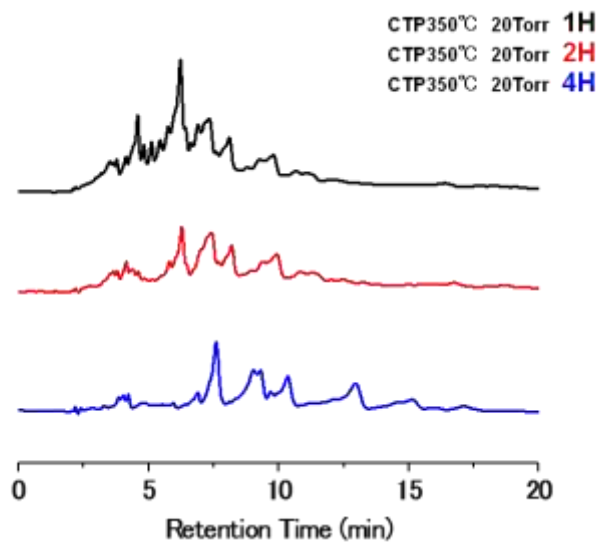
GC-AED analysis



溶解度 (%)		芳香族環含有量-面積比 (%)				
		1環	2環	3環	4環	5環以上
HS	59	6.3	38	24	18	15
HI-TS	34	0.09	2.5	14	30	53
TI-THFS	2.4	0.01	3.0	5.7	27	65
TS	92	4.0	25	20	22	28
THFS	95	3.9	24	20	23	30

HS: 2 – 4 membered rings
TI-THFS: Over 4 membered rings

HPLC analyses of CTP



70 Adjustment of molecular compositions of BP

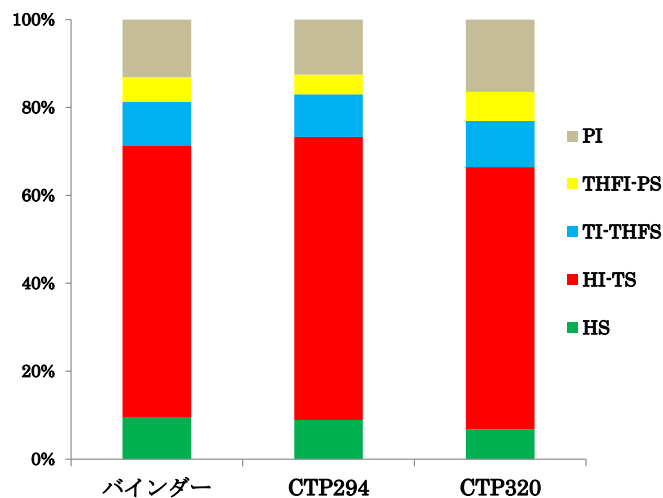


Fig 5.1 調製ピッチにおける各溶媒を用いた溶媒溶解度図
(バインダーピッチ, CTP294-40Torr, CTP320-40Torr)

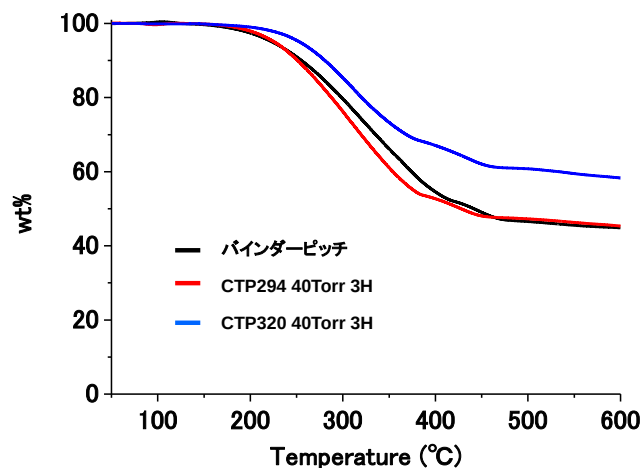


Fig 5.2 調製ピッチの N₂ 雰囲気下における蒸留温度別 TG 分析
(バインダーピッチ, CTP294-40Torr, CTP320-40Torr)

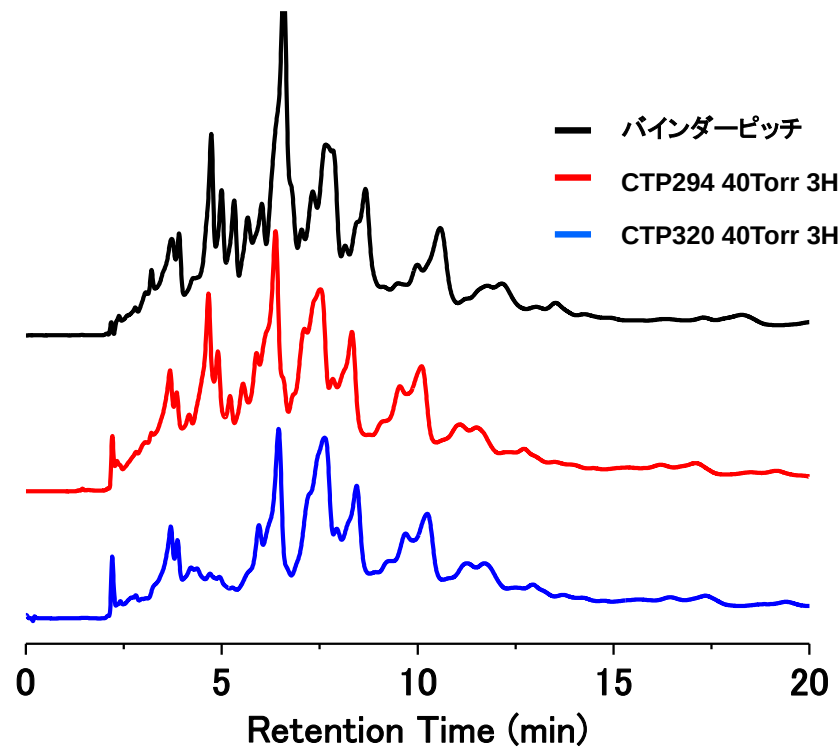


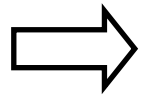
Fig 5.3 調製ピッチにおける HPLC 分析
(バインダーピッチ, CTP294-40Torr, CTP320-40Torr)

Mesophase pitch based high performance carbon fiber

- Heat treatment temperature: over 2200°C
- Tensile Strength: over 2500MPa
- Young's Modulus: over 450GPa
- Elongation: less than 0.7%
- Thermal conductivity: over 200 W/mK

Mesophase Pitch

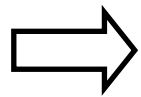
- Intermediate to Metallurgical and Needle Cokes
- Precursor for Carbon Fiber



Molecular Recognition
Controlled Syntheses

Nanoscopic Views

- Quantitative Recognition and Identification of Molecular Assembly
- Structural Hierarchy



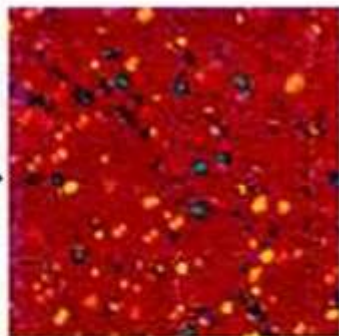
Further Development : Functionality
and Applications

Preparation of Mesophase Pitch

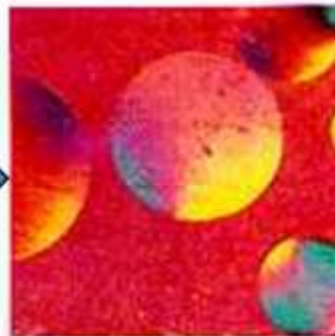
Raw Material	Before treatment and transferring to mesophase
DO	De-ash → Thermal Polycondensation → Thermal Transferring to Mesophase → Mesophase pitch
Coal tar	De-ash → Hydrogenation → Thermal Polycondensation (Mesophase) → Mesophase Pitch
Naphthalene	Polycondensation (HF/BF_3) → Removal of light Matters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



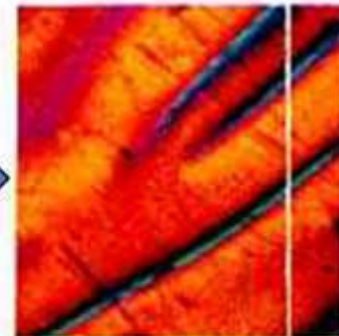
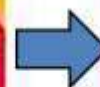
Isotropic pitch



Formation of mesophase

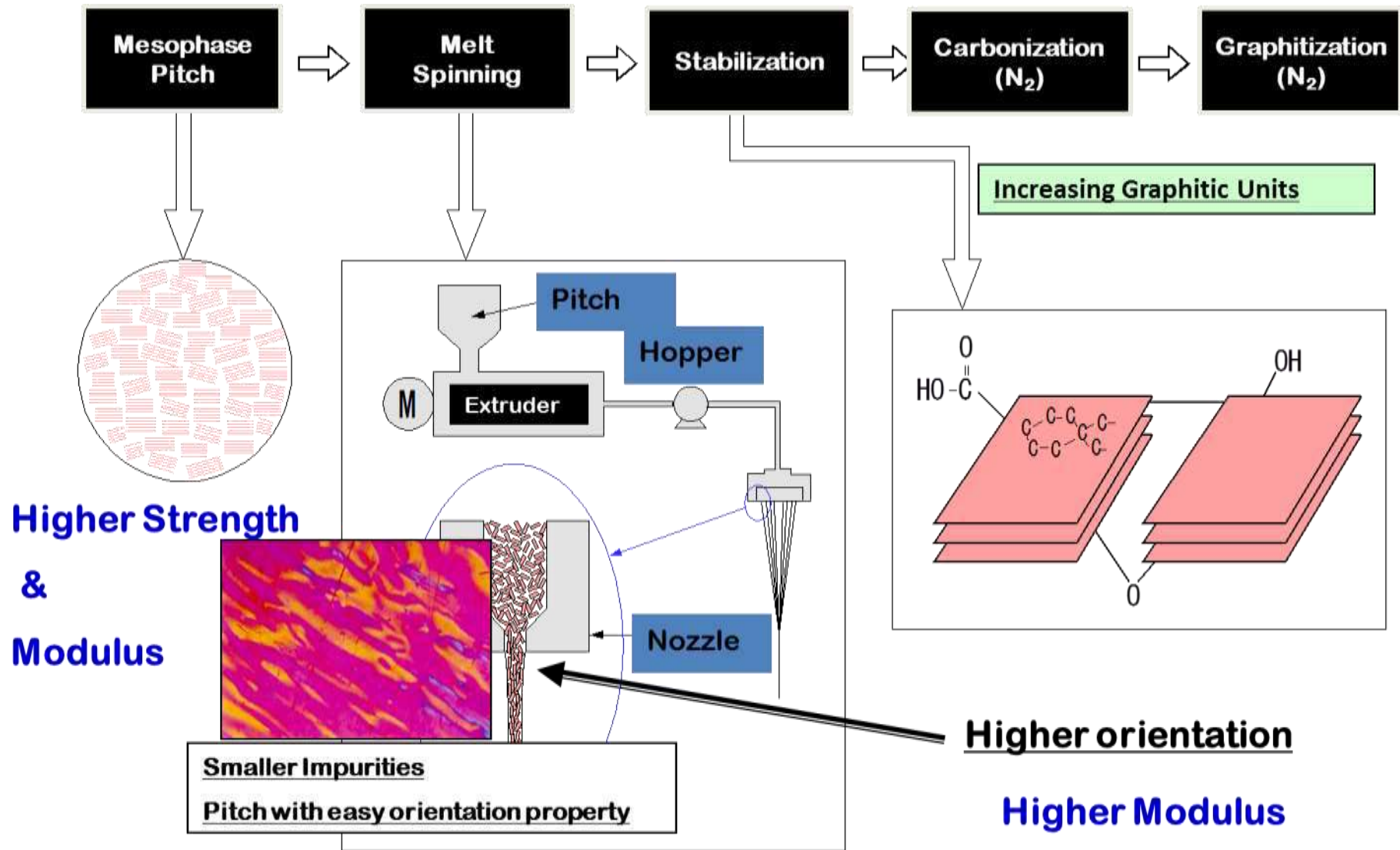


Growth of mesophase



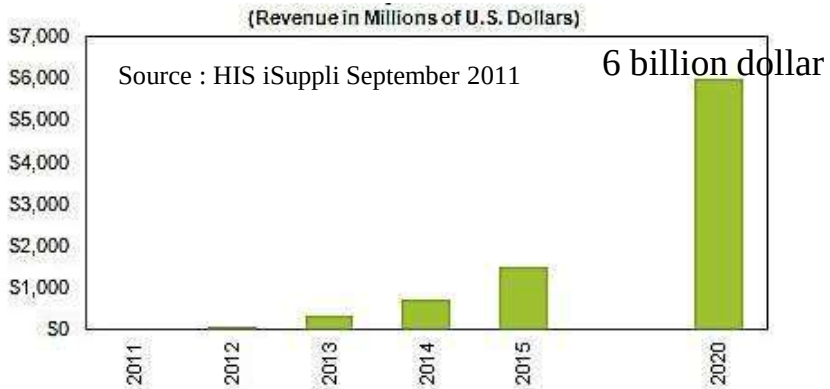
Bulky mesophase

MPCF Production Processes



Li-ion電池のマーケットと特性

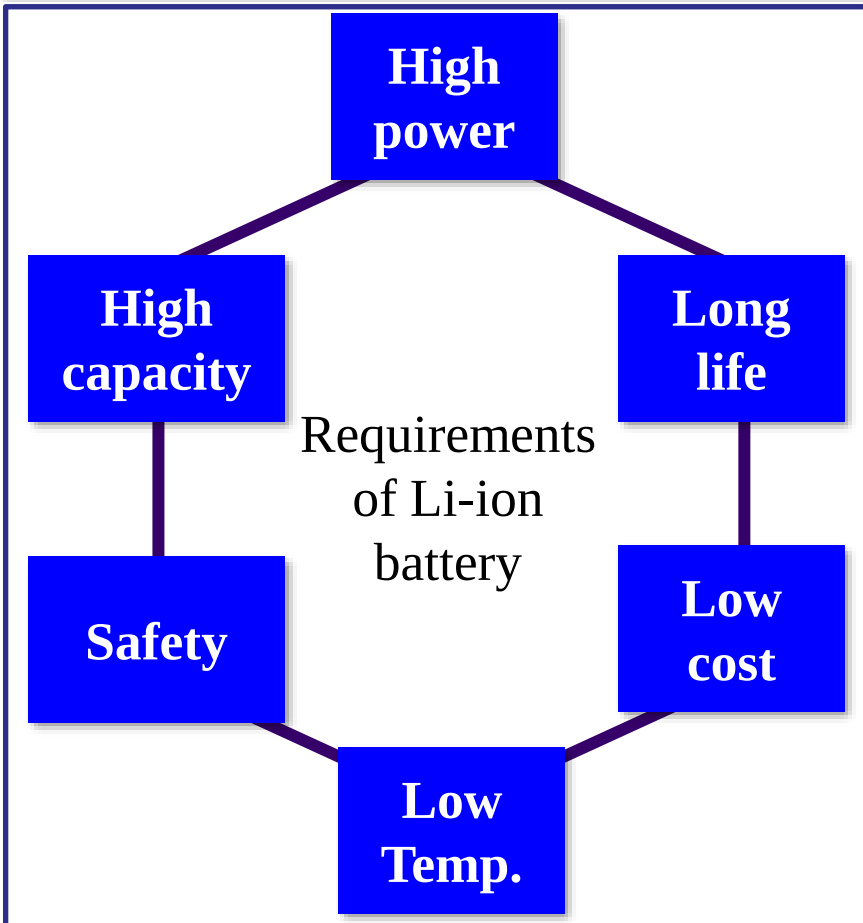
Global market of Li-ion battery in ESS



Global market of Li-ion battery in EV

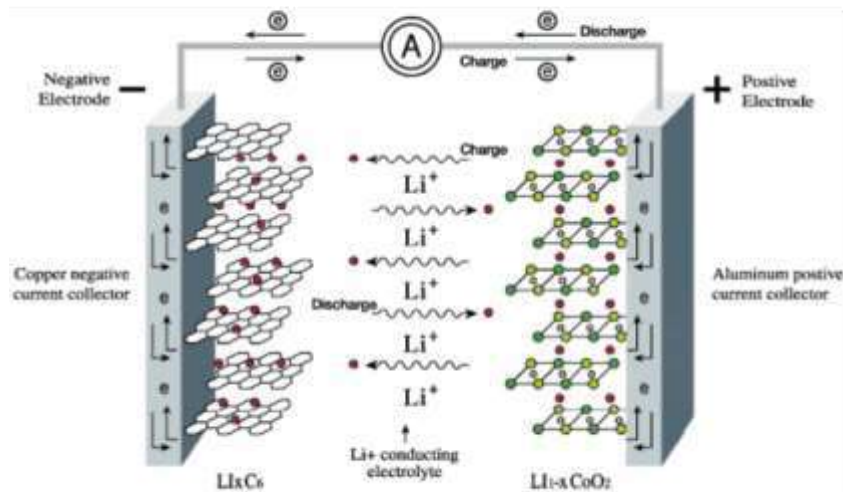


Requirements of Li-ion battery as power sources of **ESS and EV**



- Li metal anode: High reducing agent, Almost kinds of electrolyte would be reduced with Li-ion and nucleated as dendrite metal crystal ⇒ Moli energy (Canada): NTT mobile phone (short-accident in Tokyo), 1989
- Resin derived hard carbon was first selected as a safe anode for LIB: SONY, 1991
- Synthetic graphite (1989, Ashahi Kasei, Yoshida) (1993, Panasonic, C_6Li , 372 mAh/g) ⇒ Natural Graphite)

Ch./Dis. Principle of Li-ion 2nd Batteries



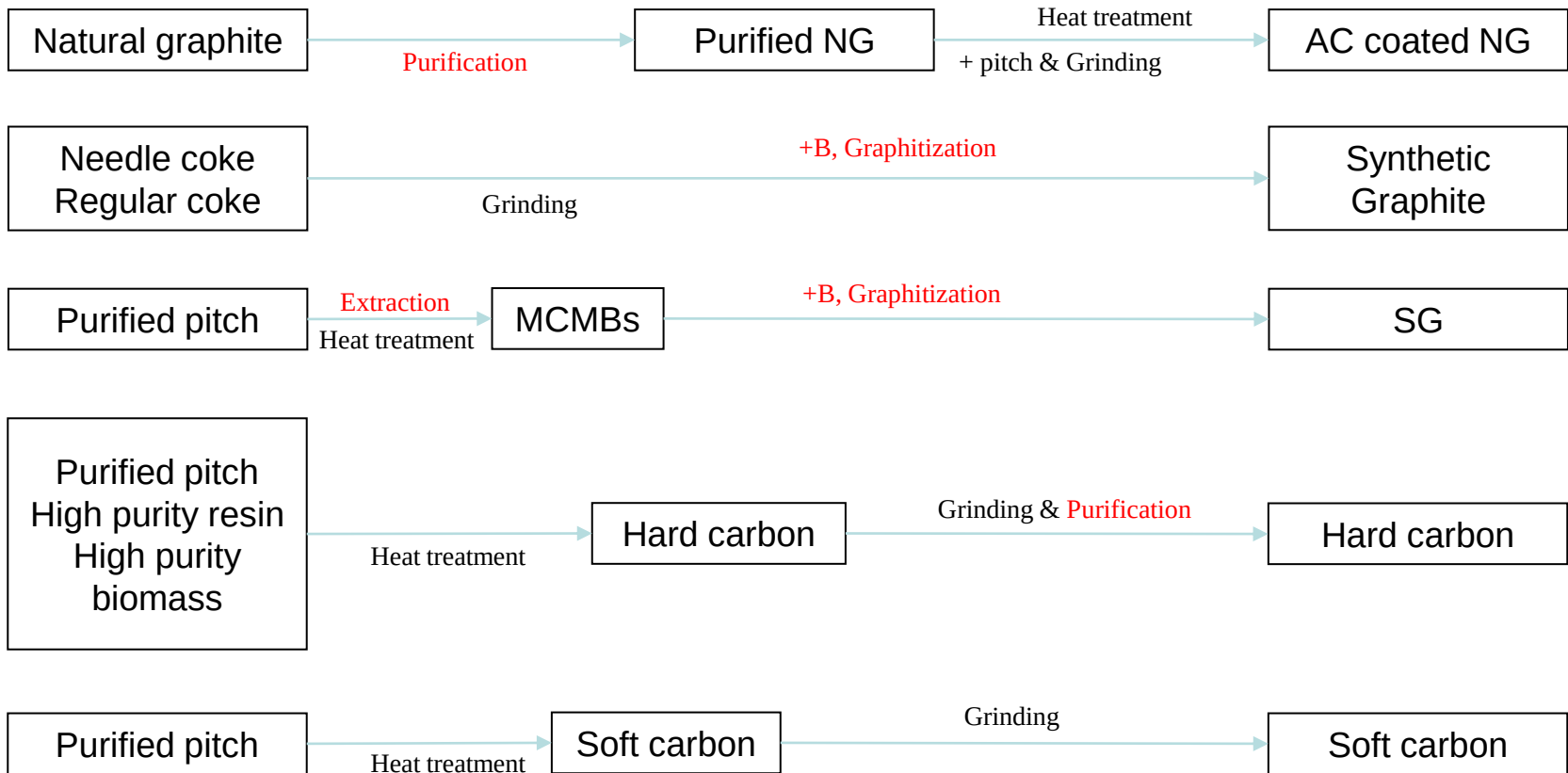
Anodic Materials for Li-ion 2nd Batteries

	Carbon	Si alloys	Li alloys
Theoretical Cap.(mAh/g)	372 (LiC_6)	4200 ($Li_{4.4}Si$)	3860
Present Stage	Commercialized	Developing	Developing
Merit	Low Cost Good Cycle Life Good Chemical Stability	High Capacity	High Capacity
De-merit	Low Rate Capability	High Volume Expansion ⇒ Bad Cycle	Strong Reaction ⇒ Bad Cycle & Thermal Stability
Materials	Graphite, Soft/Hard carbon	-	-
User	Sanyo, Matsushita, STC, A&T Battery, Shin-Kobe, GS, Moli, Mitsubishi, Sony, SDD, Hitachi Maxcel, LG Chem.	-	-

- Safety: $Li^+ \rightleftharpoons Li^0$
- C_6Li : Low potential similar with Li^0
- Carbon material: Chemically and Physically stable, Electrically and thermally conductive

- Graphite: Mainly Li⁺ intercalation & deintercalation
- Hard carbon: Mainly Li⁺ insertion & desertion (Doping & dedoping)
- Soft carbon: Mixing of intercalation and doping?

	Precursor	Advantages	Disadvantages
Graphite (over 2800°C)	Natural / Artificial graphite MCMB, Needle cokes VGCF	Low discharge potential ($\approx 0.2\text{V}$) Long cycle life	Low discharge capacity (372 mAh/g) Poor rate performance High cost
Soft Carbon Graphitizable carbon (600~800°C)	MCMB Meso phase pitch Green cokes	High capacity (700~1000mAh/g) Low cost	High discharge potential ($\approx 1.0\text{V}$) High irreversible capacity Poor cycle stability
Hard Carbon Non-graphitizable carbon (1000~1400°C)	Thermosetting polymer Glassy carbon, Coal Organic material Stabilized isotropic pitch	High capacity (400~700mAh/g) High rate performance Low discharge potential ($\approx 0.1\text{V}$) Low cost	Large irreversible capacity



Price of carbon anodes: Almost no room for technical modifications!

- Natural graphite: \$ 3-5/Kg, Synthetic graphite: \$ 3-10/Kg
- Hard carbon: \$ 3-5 Kg
- Soft carbon: \$ 3-5 Kg
- Conductive material: \$ 10-20/Kg

4. 気相炭素化:

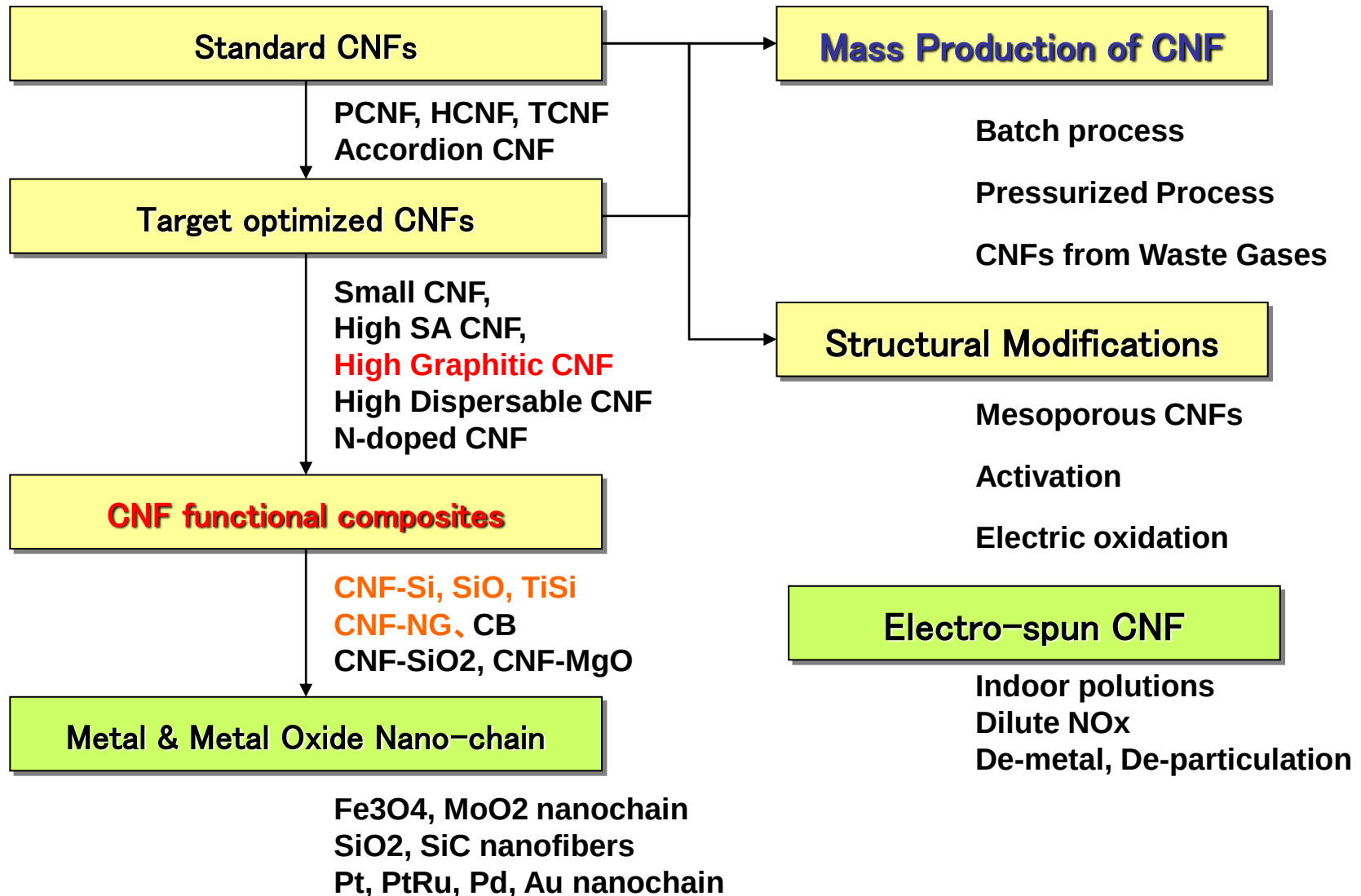
- 炭素ナノ繊維の調製



Fullerene	Zero dimension Basal surface Nano-size	High price Very limited application Mass-production (Frontier Carbon Tech.)
Graphene	Two dimension Basal surface Nano-size	Somewhat high price Broad application Mass-production
CNT	One dimension Basal surface Nano-size	Relatively high price Patent problems Mass-production (Showa Denko) Limited application
CNF	One dimension Various surfaces and structures Nano-size	Relatively low price Patent problems Mass-production (Mitsubishi Materials) Limited applications



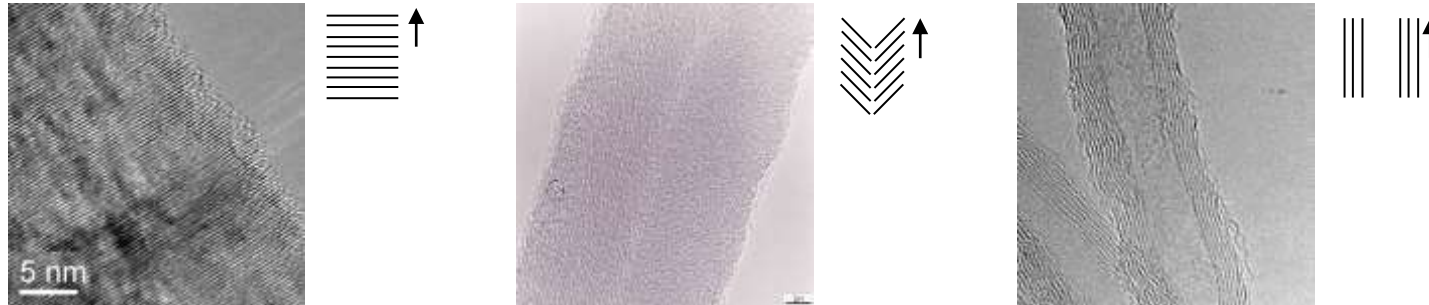
Selective Preparation of CNFs



Structural variety of CNFs

Typical classification of CNF Structure

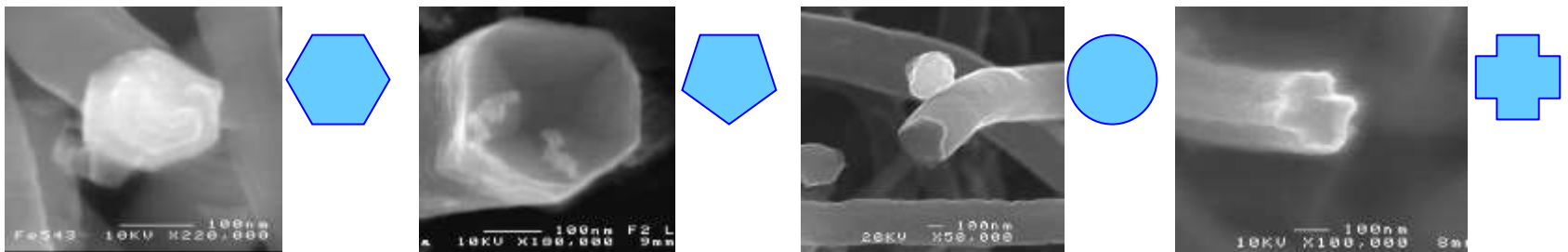
- graphene ((002) layers) alignment to the fiber axis, TEM observation



< Simple cases of CNF structure >

- However, complicated structure is often found.
- The morphological diversity confirmed simply by SEM observation cannot be neglected, considering possibly their different physical properties.

Various cross sections of CNFs



Polygonal

Circle

Cross

Different Surface Characteristics



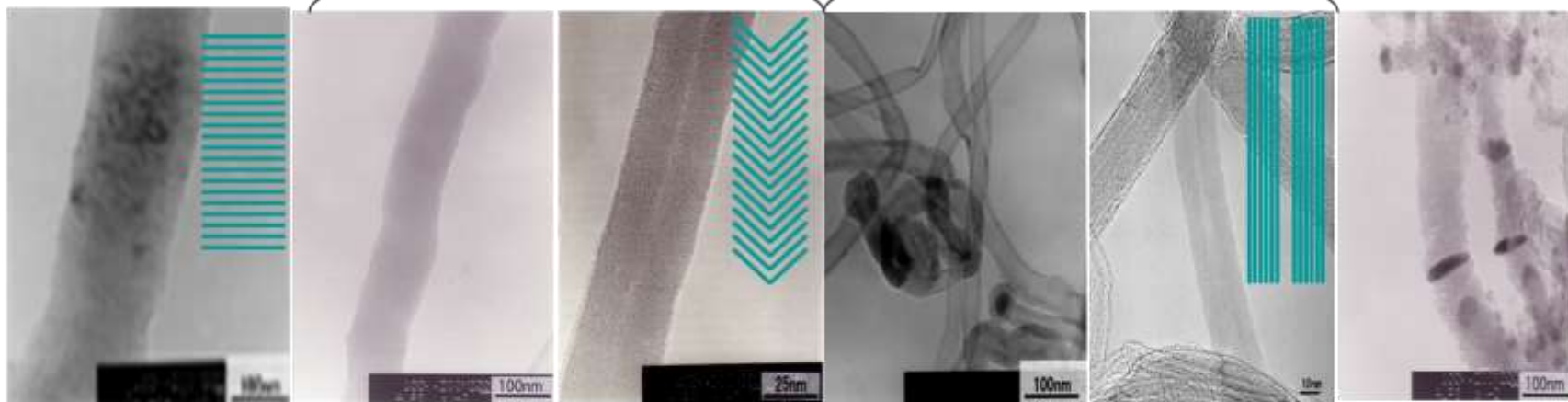
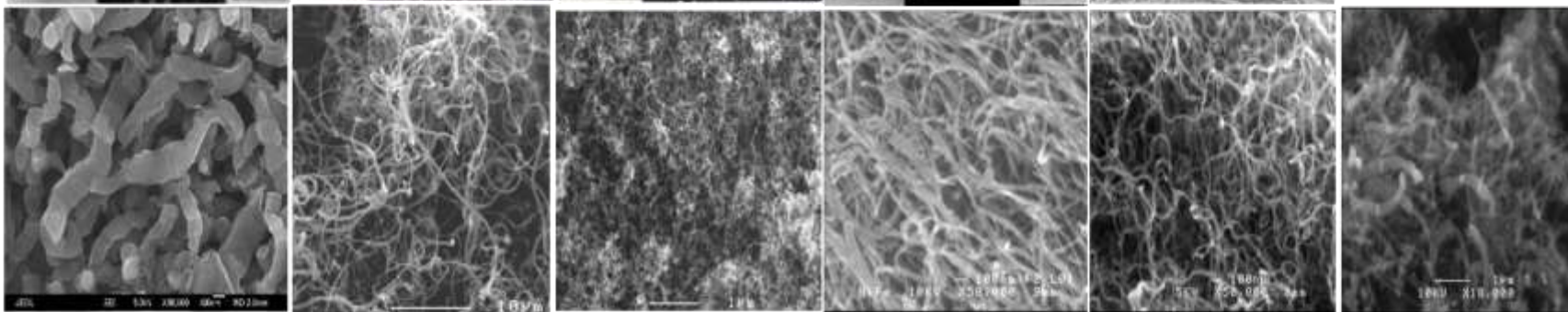
Structural varieties of CNFs

Platelet

Herringbone

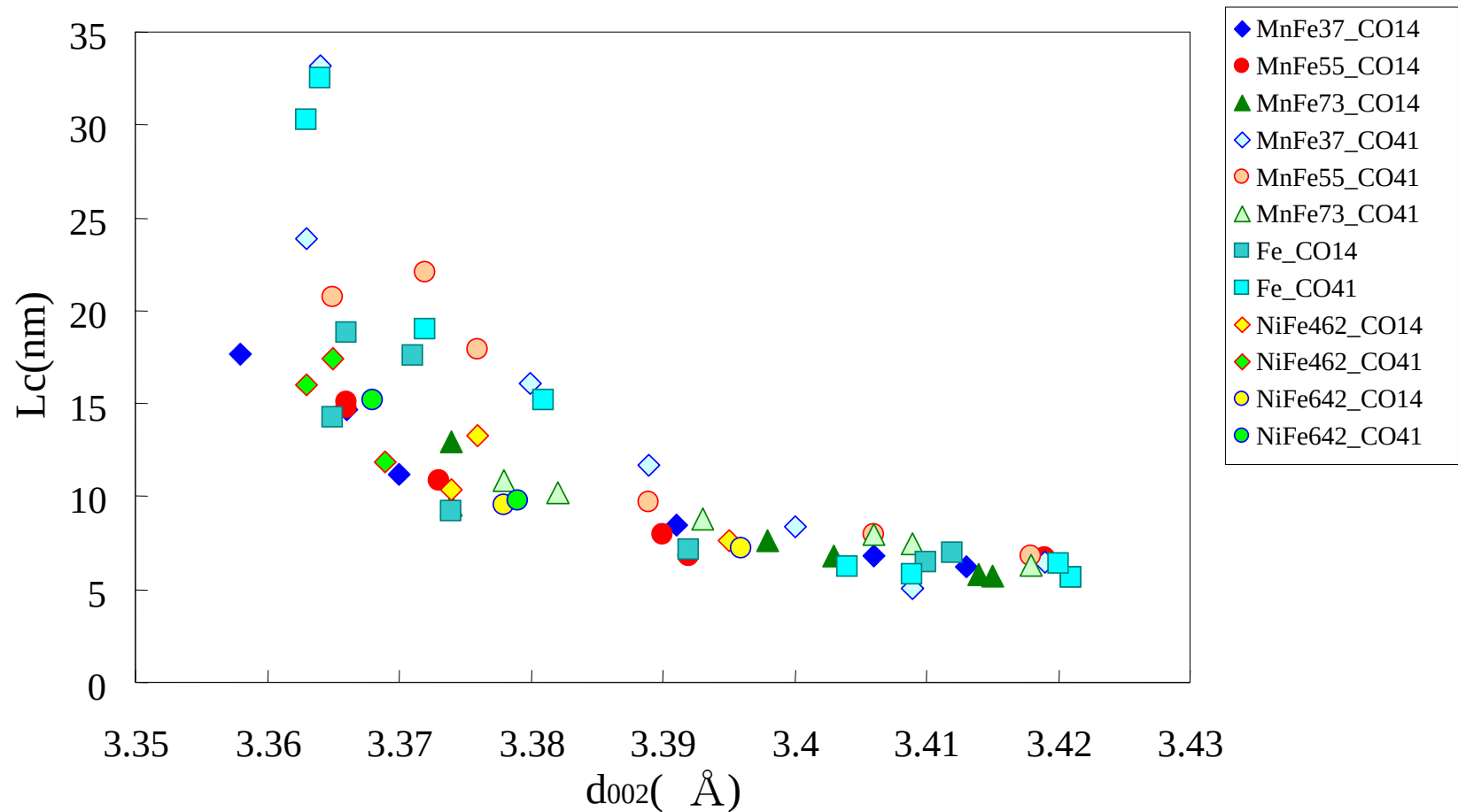
Tubular

Accordion

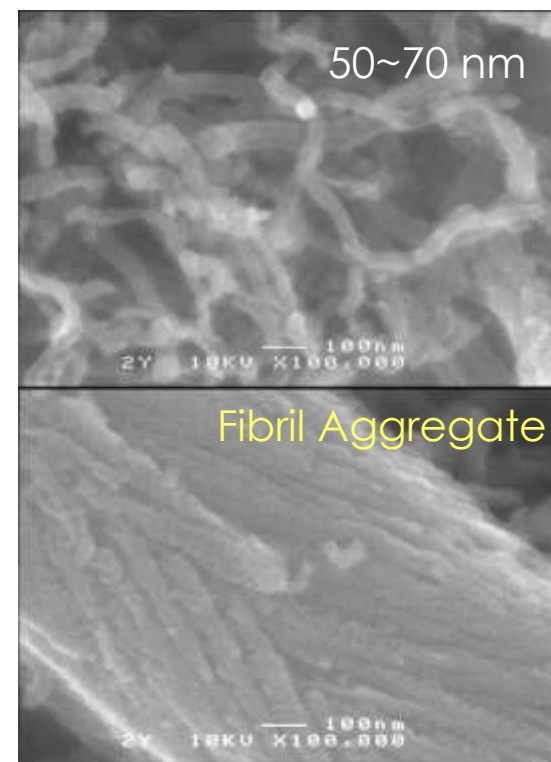
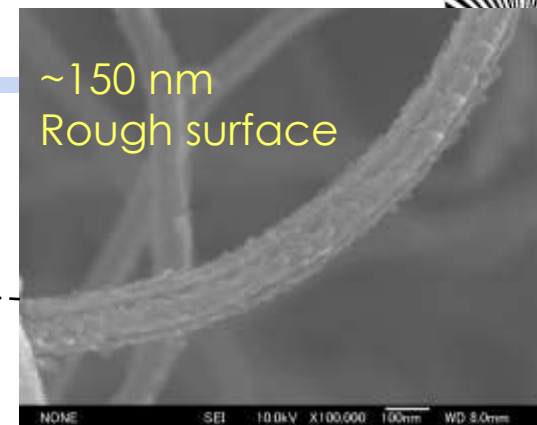
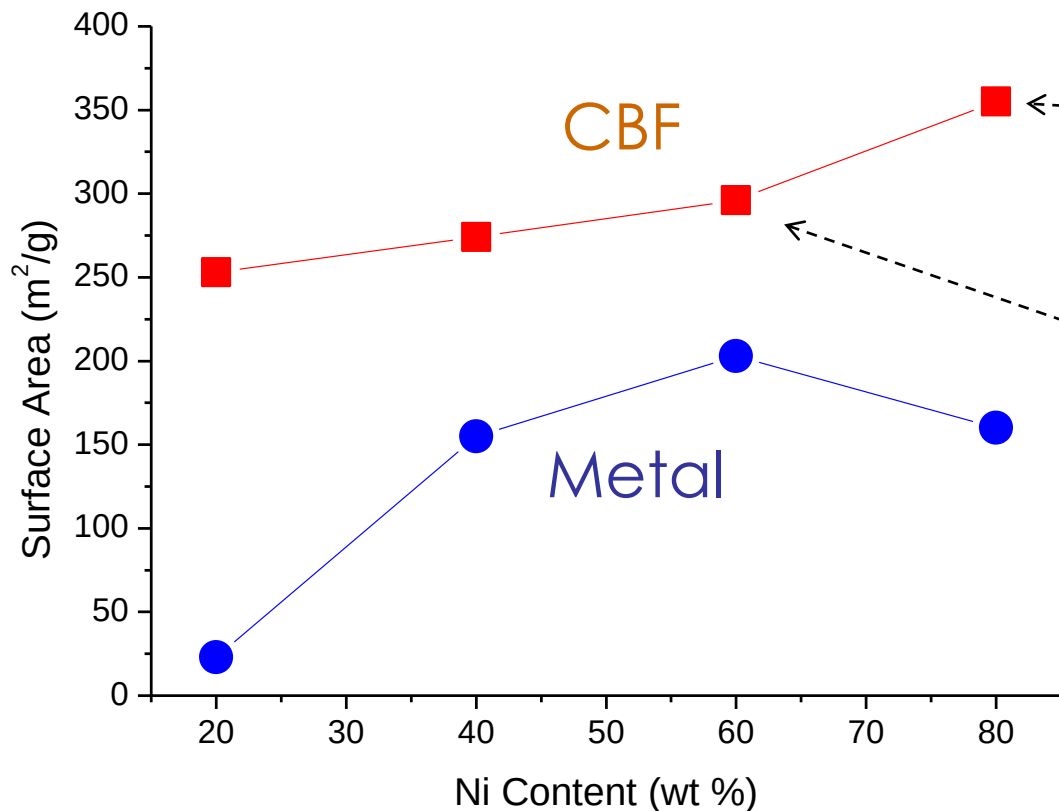
T
E
MS
E
M

- 1) Preparation of various CNFs that are best for the special applications
- 2) Lower price
- 3) Proper method for the mass production

Control of Graphitic Properties of TCNFs



Control of surface area

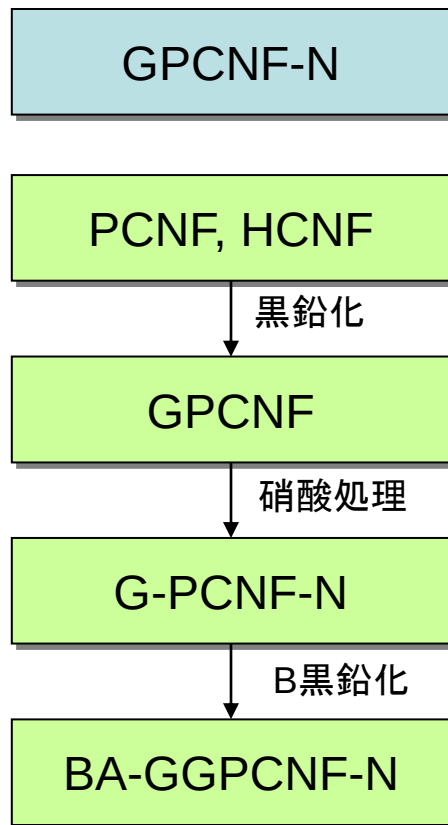


- CBF fibers 250 ~ 350m²/g, Metal fibers 20 ~ 200 m²/g
- CBF fibers shows 2~10 times higher SA than Metal fibers.
- SEM of CBF fibers with SA around 300 m²/g: small fibrils, fibril aggregate, and rough surface one like activated one.



Highly graphitic CNFs

- CNF of similar graphitic properties with Natural Graphite
- CNT usually shows low graphitic properties
- Conductive materials or supports for heterogeneous catalysts



	Preparation conditions	d_{002} (nm)	$L_c(002)$ (nm)
PCNF	Fe catalyst, 620, CO/H ₂ : 4/1	0.3365	72
G-PCNF	2800°C heat treatment of PCNF	0.3364	83
G-PCNF-N	30% HNO ₃ treatment of GPCNF for 50°C, 8hs	0.3362	152
GG-PCNF-N	2800°C heat treatment of GPCNFN	0.3362	106
BA-G-PCNF	Boric acid added heat treatment of PCNF	0.3359	115
BA-GG-PCNF-N	30% HNO ₃ treatment of GPCNF for 50°C, 8hs Boric acid added heat treatment	0.3357	377
BC-G-PCNF	Boron carbide added heat treatment of PCNF	0.3354	178
BC-GG-PCNF-N	30% HNO ₃ treatment of GPCNF for 50°C, 8hs Boron carbide added heat treatment	0.3354	167

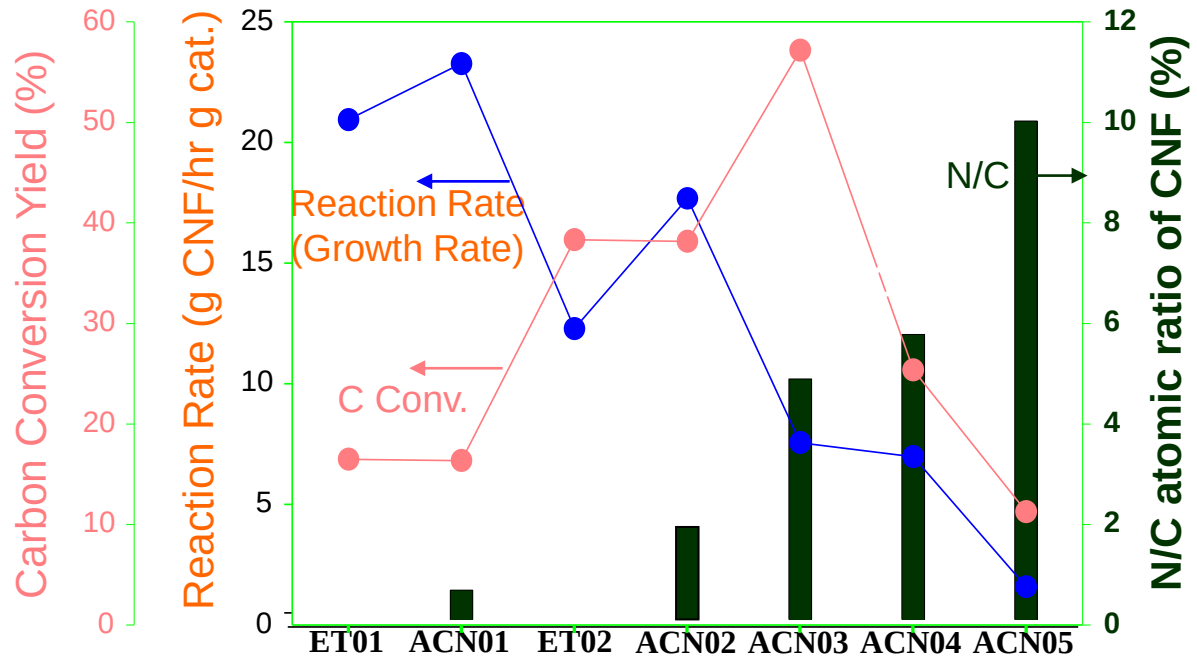


N-doped CNFs

N-Source
: Acetonitrile



Reaction Temp.
530°C



Ethylene		160	160	40	40	0	0	0	Total 200 ml/m
Hydrogen	ml/m (g)	40	40	40	40	40	40	0	
He		0	0	120	120	160	160	200	
Acetonitrile (liq.)	μl/m	0	35	0	35	35	70	35	
Input N/C	at. %	0	4.6	0	14.5	50	50	50	



Preparation of N-doped CNFs

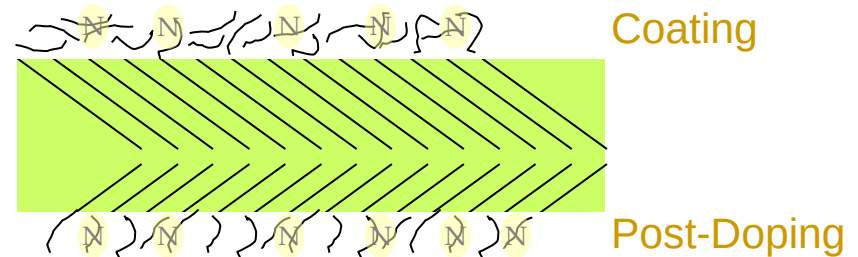
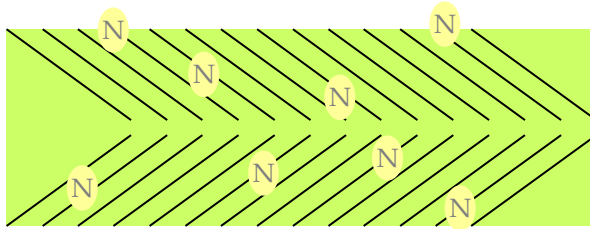
A. Direct Synthesis of Carbon Nanofibers with Nitrogen (the method of this study)

B. *Deposition of Nitrogen Components on Carbon Nanofibers (Post-synthesis)*

- Using Carbon Sources Containing Corresponding Heteroatoms
- Mixing General Carbon Sources with a Nitrogen Source (NH_3)

Expected features	
Route A	Route B
• One step synthesis • Graphitic structure • N both in-plane and at the surface (edge)	• Two step synthesis • Amorphous region at the surface (probably unstable) • N selectively at the surface (edge)

Direct Synthesis





TEM & SEM of SiO_x NFs

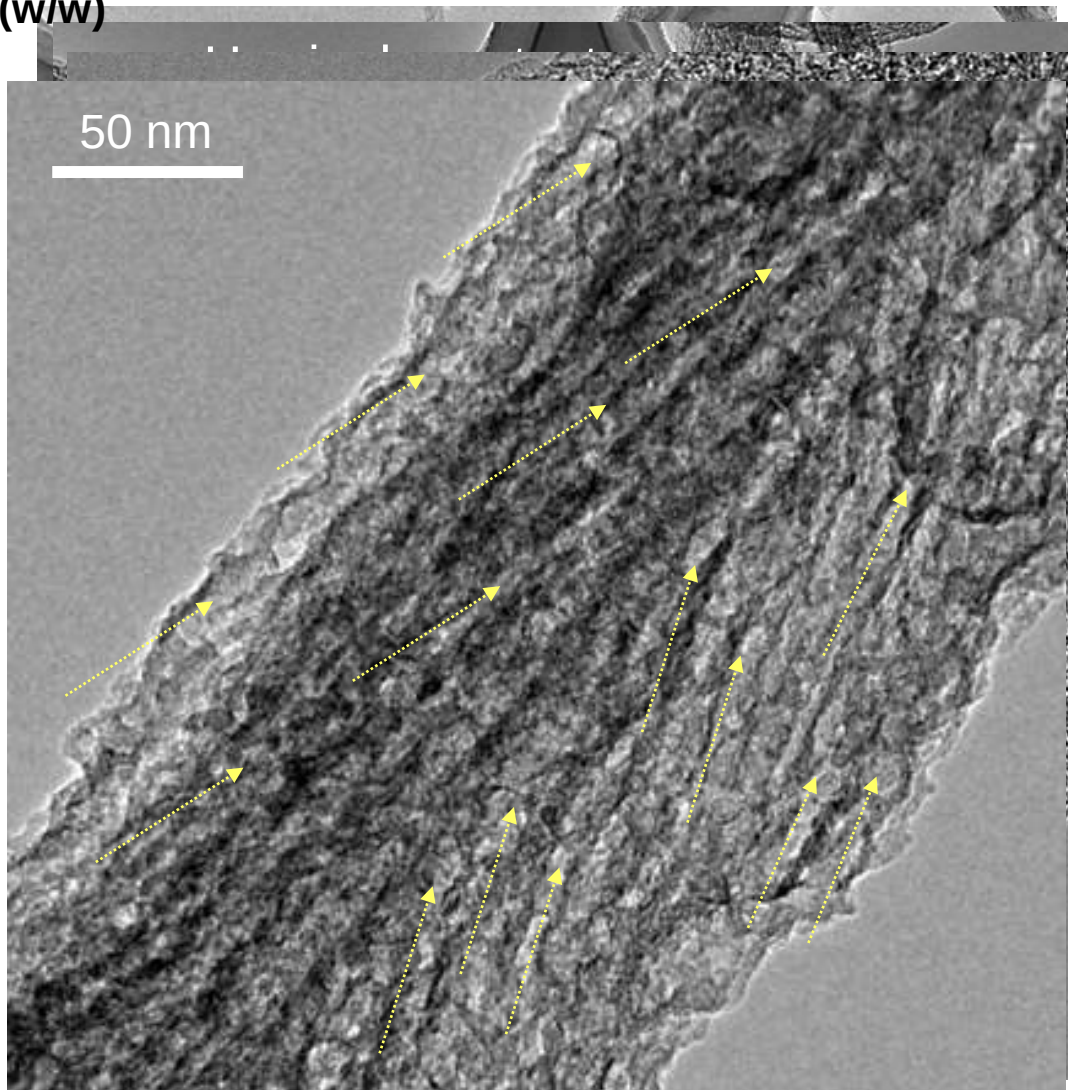
- **PS in Toluene**

- * completely soluble

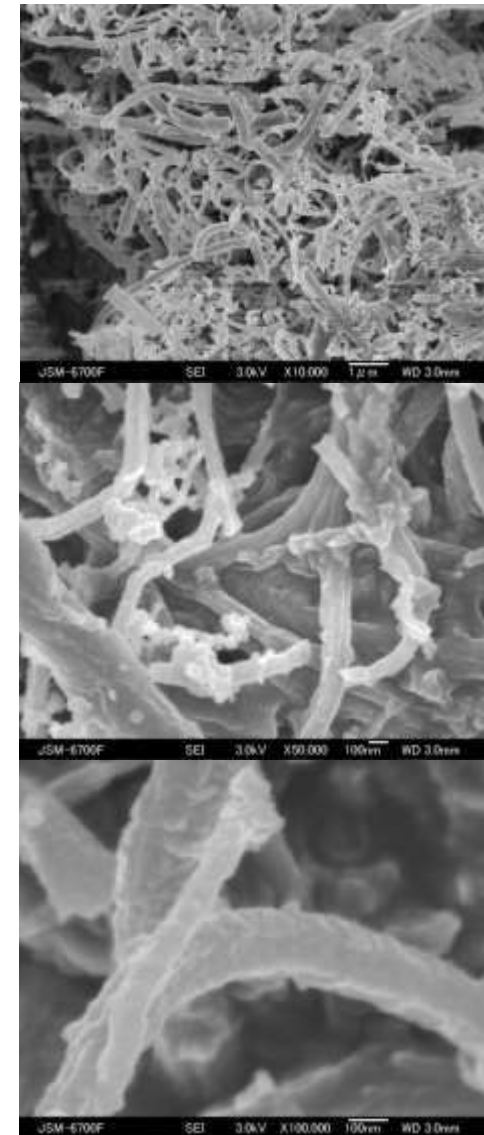
- **PS/HCNF 1/5 (w/w)**

- **450°C in Air**

TEM of SiO_x-NF



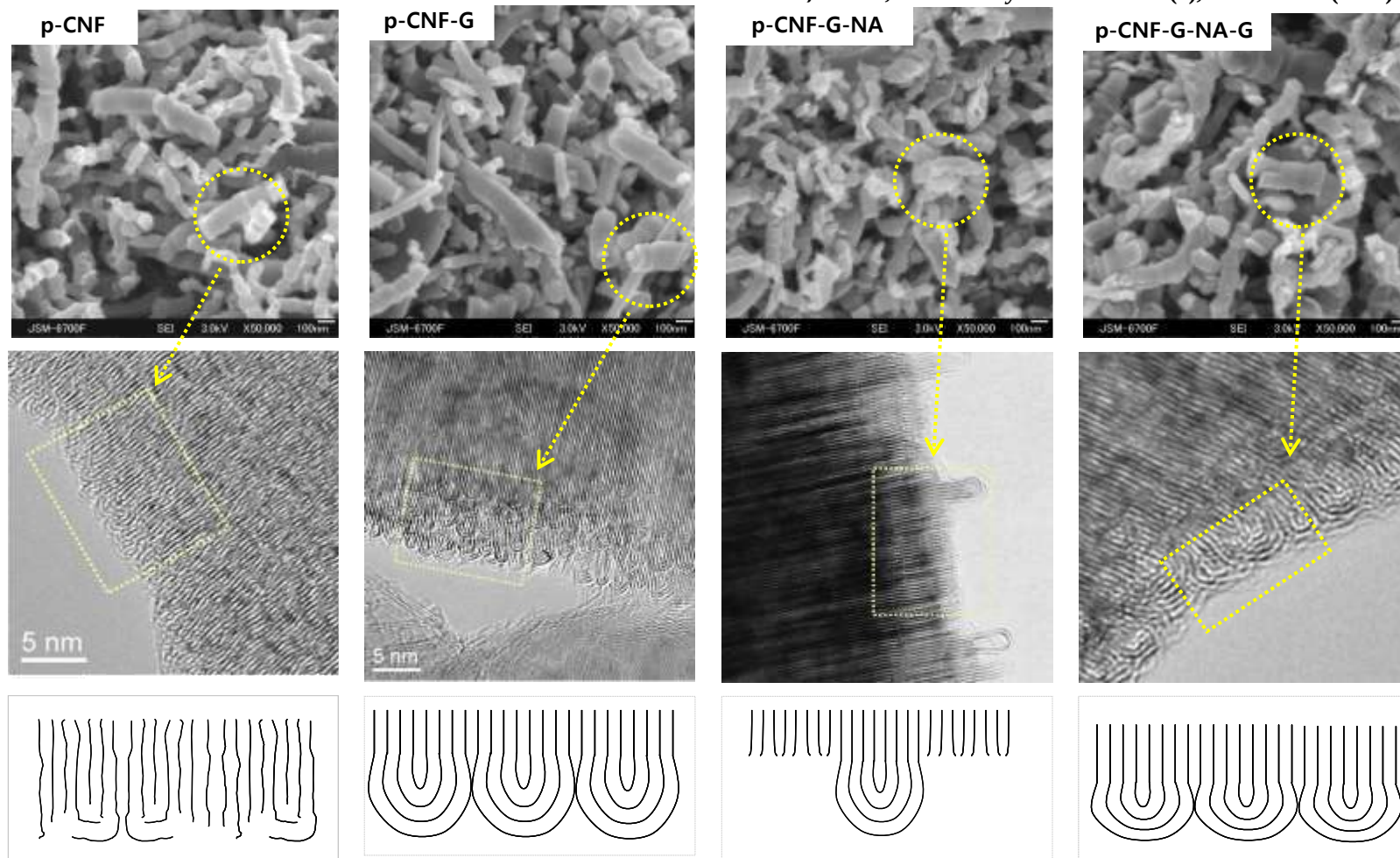
SEM of SiO_x-NF



Surfaces of PCNF



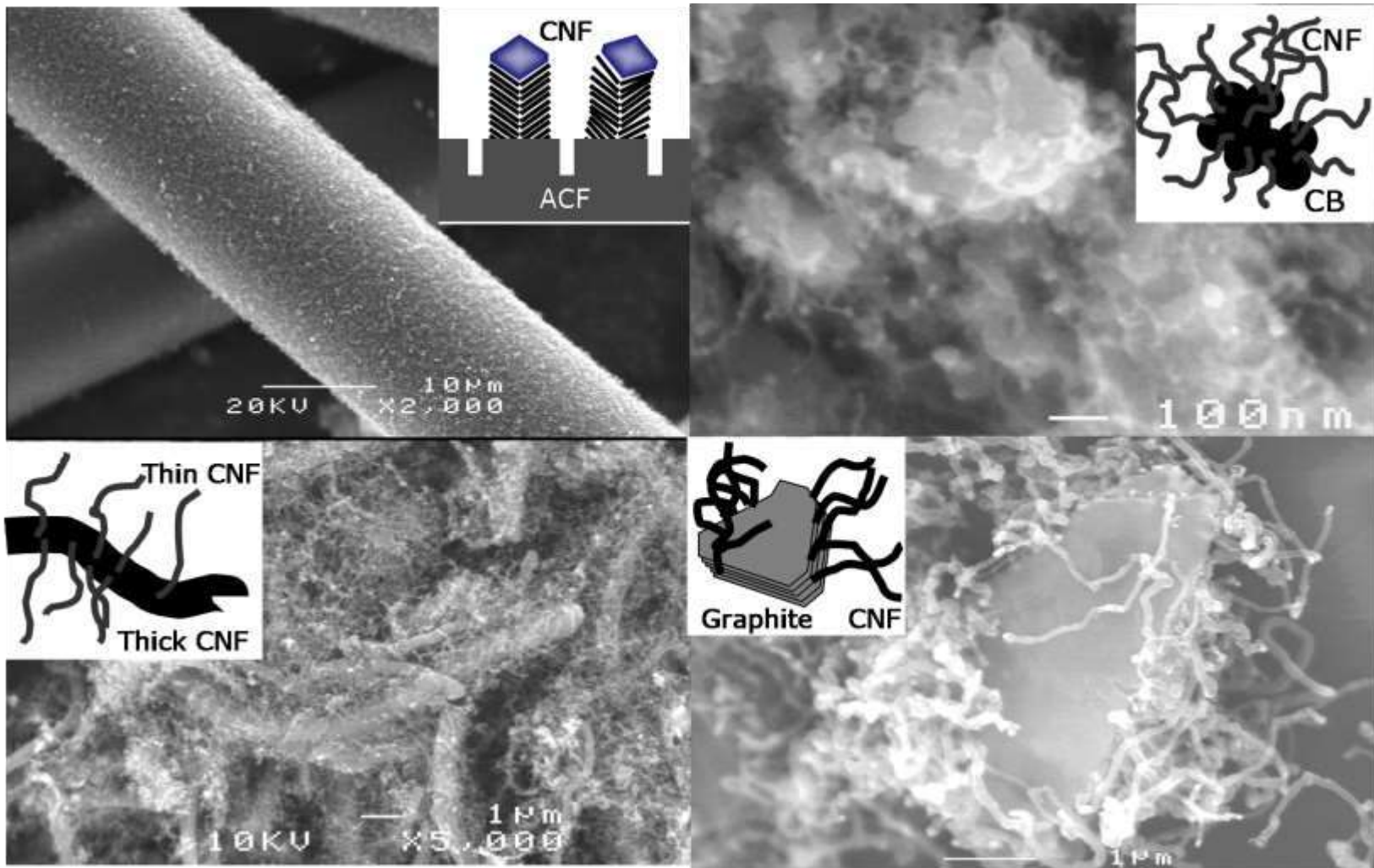
Ref.) S. Lim, et al., *J. Phys. Chem. B* 108 (5), 1533 – 1536 (2004)



**According to the graphitization degree,
we found some difference at edge plane by TEM analysis**



Various CNF composites



Magnifying the functions of basic materials: Silica, Alumina, Si, TiO_2 , Magnetites

Some problems of CNFs

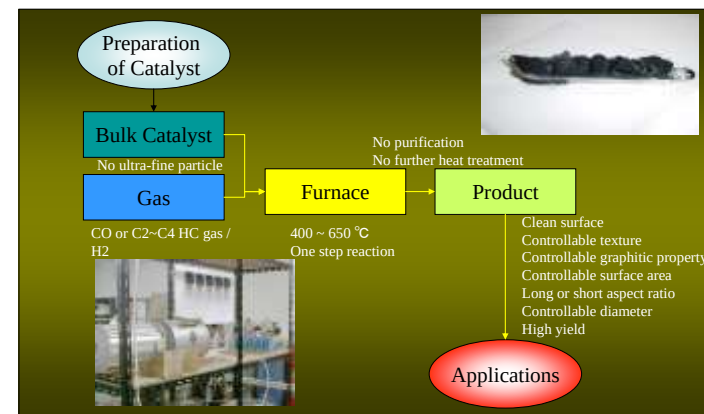
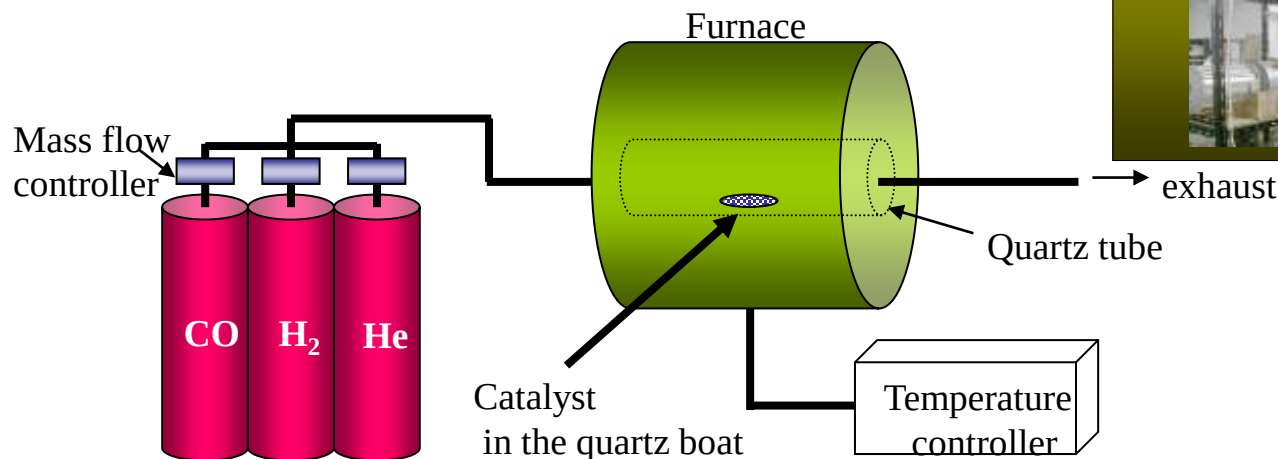


1. **Patents** : Relatively free but some application patents should be considered.
2. **Price** : ~10~200 \$ /kg
 - Effective process for mass-production
3. **Dimension & Uniformity control**
 - Diameter
 - Surface control; edge / functional groups
 - Linearity
 - Crystallinity, surface area
4. **Useful skills : Purification, Dispersion**



Objective of this study

Preparation (Fixed Bed Method)



Catalyst : Transition metals, Their alloys or supported catalyst

Catalyst preparation method : co-precipitation

1) Best, R. J. and Russell, W. W., J. Amer. Soc. 76, 838(1954)

2) Sinfelt, J. H., Carter, J. L. , and Yates, D. J. C., J. Catal. 24, 283(1972)

Reduction : H₂/He(1/9, 200sccm//4.5 cm diameter tubular furnace, 2h

Reaction : CO/H₂ (4/1 & 1/4v/v%), 200 sccm// 4.5 cm diameter tubular furnace

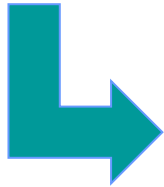
Reaction Time & temperature : 1 h, 540 ~ 675 °C

Mass Production of CNFs



Horizon type
Capacity: several grams

Capacity: H-, P-CNF 100g/1batch
T-CNF 20g/1batch

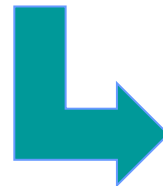


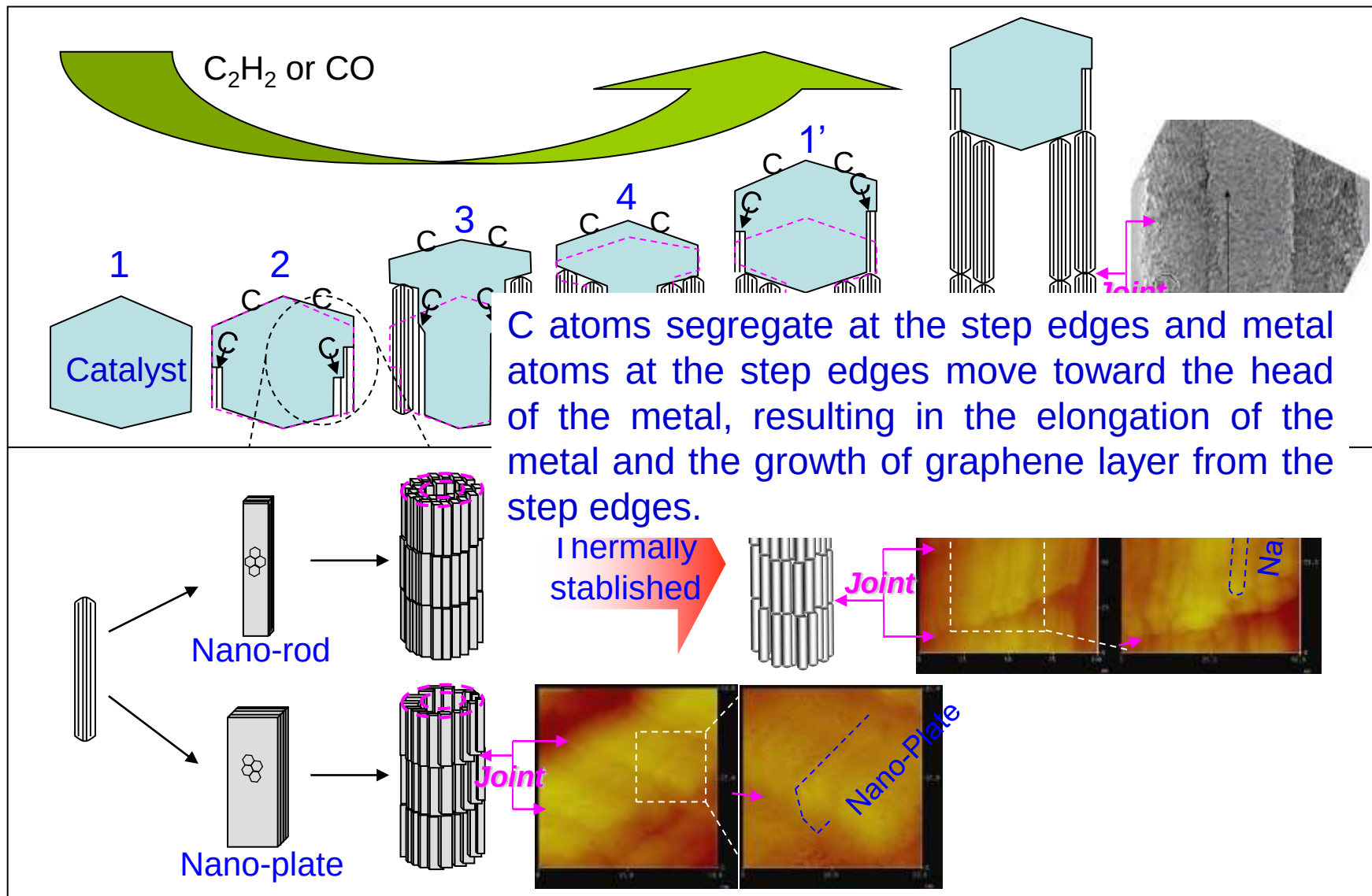
Scale up
Vertical type



Capacity: 500g/day

Scale up
Vertical type
Pressure







Catalysts for CNF Preparation

- Mono-metal
 - Fe, Co, Ni
 - Fe, Co, Ni / Supports
- Support: Alumina, Silica >>> MgO
- Bimetallic Catalyst
 - Fe, Co, Ni / Fe, Ni, Mn, Cu, .../Supports
- Trimetallic Catalyst
 - Fe, Co, Ni / Fe, Ni, Cu, Mn / Cr, Al, .../Supports

Functions of Second or Third Metals ?



Main Catalyst

2nd Catalyst

3rd Catalyst

Fe

Fe:Mg=8:2
収率: 1.2倍

Cr

Fe:Cr:Mg=6.4:1.6:2
収率: 4.6倍
繊維径: 40nm
Tubular

Mn

Fe:Mn:Mg=6:2:2
収率: 1.1倍

Cu

Fe:Cu:Mg=6:2:2
収率: 2.0倍

Ni

Mo

Fe:Cr:Mo:Mg=6:1:1:2
収率: 27.8倍
繊維径: 20nm
Tubular

Co

Fe:Mn:Co:Mg=4:2:2:2
収率: 11.6倍
繊維径: 50nm
不均一 CNF

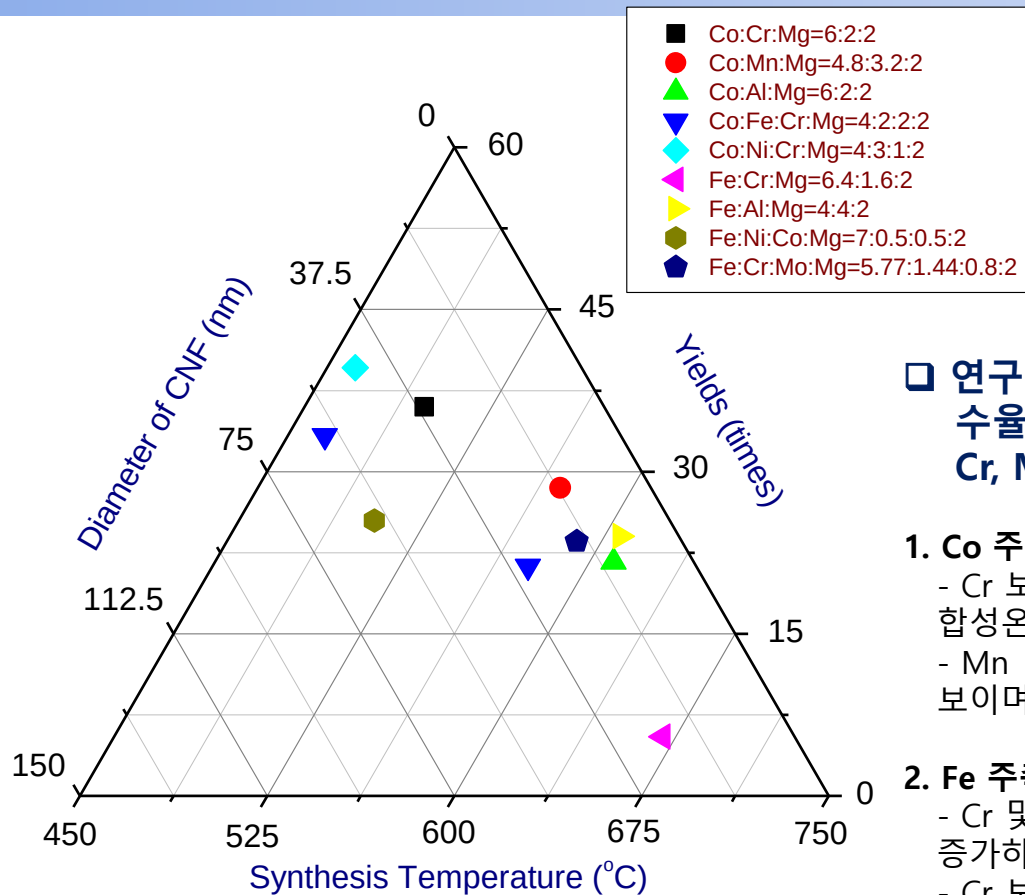
Co

Fe:Cu:Co:Mg=6:1:1:2
収率: 60.2倍
繊維径: 180nm
Herringbone CNF

Co

Fe:Ni:Co:Mg=7:0.5:0.5:2
収率: 60.2倍
繊維径: 120nm
Tubular

Tri Metallic Catalysts



□ 연구결과

수율, 섬경, 섬유의 구조 등에 영향을 줄 수 있는
Cr, Mn, Al 등의 새로운 보조촉매 발굴

1. Co 주촉매에 대한 보조촉매의 효과

- Cr 보조촉매는 낮은 합성온도에서 높은 촉매수율을 보이며, 합성온도가 낮아짐에 따라 Herringbone 구조의 섬유가 합성됨.
- Mn 및 Al 보조촉매는 높은 합성온도에서 높은 촉매수율을 보이며, 대부분 Tubular 구조의 섬유가 합성됨.

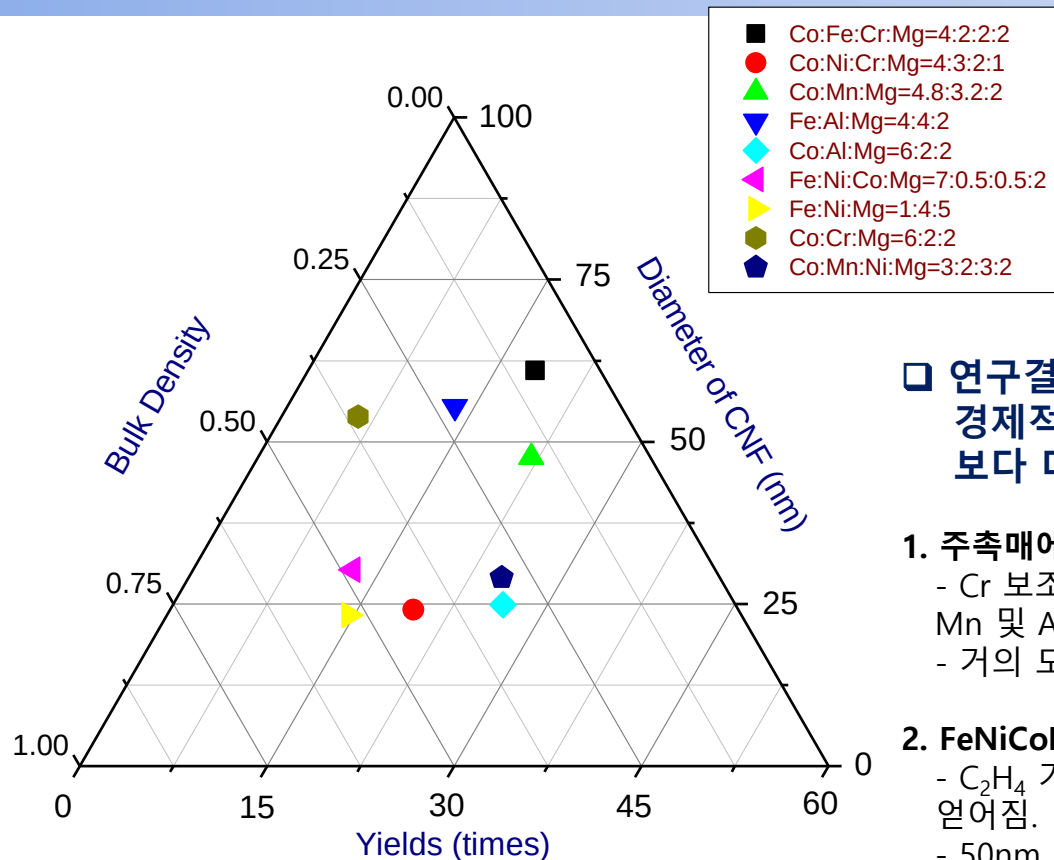
2. Fe 주촉매에 대한 보조촉매의 효과

- Cr 및 Al 보조촉매 모두 합성온도가 높을수록 촉매수율이 증가하는 경향을 보이며 Tubular 구조의 섬유가 합성됨.
- Cr 보조촉매의 경우에는 촉매수율이 매우 낮으나 반면 겔보기밀도가 매우 낮은 섬유가 합성됨.
- Cr 및 Mo 보조촉매를 같이 사용할 경우에는 30배 이상의 매우 높은 촉매수율을 얻을 수 있음.

3. FeNiCoMg 촉매

- 최대섬경 120nm 정도의 매우 굵은 Tubular 섬유를 합성할 수 있는 촉매시스템.
- Ni과 Co의 함량이 각각 0.5로 동일한 경우에 가장 높은 촉매수율 및 가장 균일한 섬유를 얻을 수 있음.

Tri Metallic Catalysts



□ 연구결과

경제적으로 저렴한 C_3H_8 가스를 이용하여 C_2H_4 가스보다 다소 높은 온도에서 CNF를 합성하였음

1. 주촉매에 대한 보조촉매의 효과

- Cr 보조촉매는 낮은 합성온도에서 높은 촉매수율을 보이며, Mn 및 Al 보조촉매는 높은 합성온도에서 높은 촉매수율을 보임.
- 거의 모든 촉매조성에서 Tubular 구조의 섬유가 합성됨.

2. FeNiCoMg 촉매

- C_2H_4 가스를 이용하여 합성했을 경우와는 전혀 다른 소재가 얻어짐.
- 50nm 정도의 섬유도 관찰되었으나 거의 대부분이 섬유형태가 아닌 카본덩어리였으며 겉보기밀도 또한 매우 높은 편임.

3. 향후 연구 방향

- 합성 후 배출되는 가스의 성분을 분석할 필요가 있음 → CH_4 , C_2H_2 , C_2H_4 등의 가스가 배출될 경우 이를 분리 수집하면 다른 CNF 소재의 합성에 이용가능할 것으로 예상됨.
- Ni를 주촉매로 이용할 경우 고온에서 Herringbone 구조의 CNF를 합성할 수 있을 것으로 예상됨.
- C_3H_8 가스를 이용한 CNF 합성에서의 반응 메커니즘 연구.

* 모든 CNF의 합성온도는 700°C임.
(Co:Ni:Cr:Mg=4:3:1:2, Fe:Ni:Mg=1:4:5 촉매는 600°C에서 합성한 결과임)

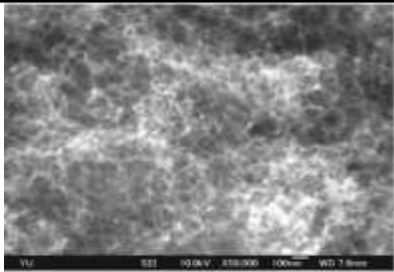
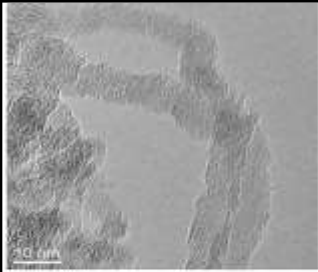
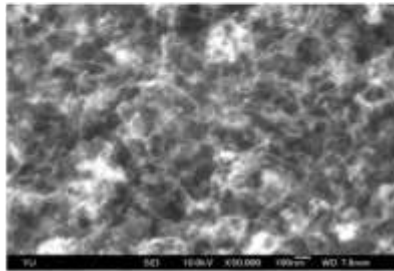
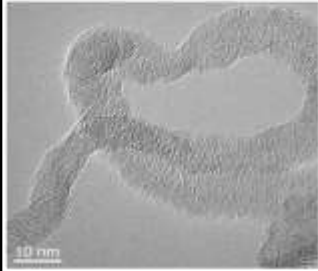
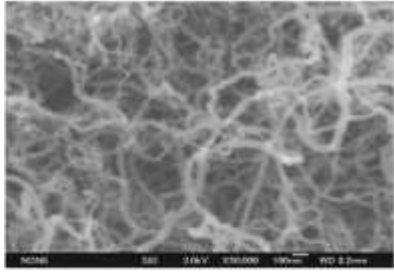
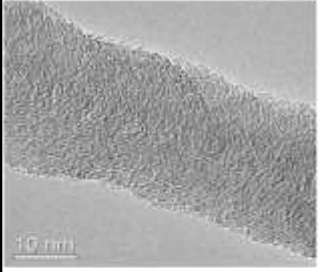
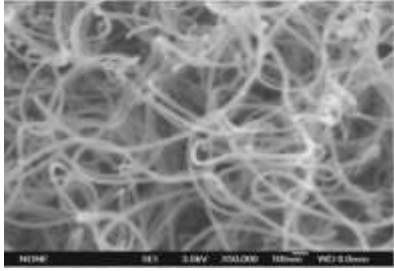
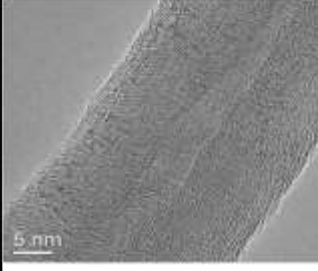


Standard CNFs

Sample #	SEM	TEM	Properties	Applications	Etc.
KNF-SPR Platelet Nano-rod			Platelet high graphit. deg. 80 ~ 400 nm, SA 90 m ² /g d ₀₀₂ 3.36Å, Lc(002) 30 nm	電池材料, 触媒担体, 触媒担体 例) 高活性水素化触媒Ru/PCNF	70 g/日
KNF-SH Herring-bone			Herringbone high surface area 70 ~ 500 nm, SA 150 m ² /g d ₀₀₂ 3.45Å, Lc(002) 3 nm	複合材料, ガス貯蔵, 吸着剤, 触媒担体, FED 例) DMFC用PtRu触媒担体	100 g/日
KNF-ST Tubular 高黒鉛化性			Tubular thin walls, open tips high graphit.deg. 20 ~ 50 nm, SA 90 m ² /g d ₀₀₂ 3.37Å, Lc(002) 13 nm	複合材料, 吸着剤, 触媒担体, 触媒	20 g/日
KNF-FM Tubular 小繊維径			tubular, hollow 5~15 nm, 4 -7 walls	複合材料、触媒担体、FED	20 g/日

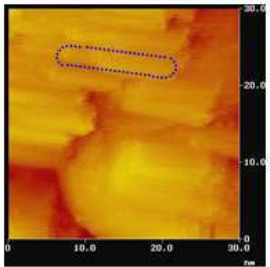
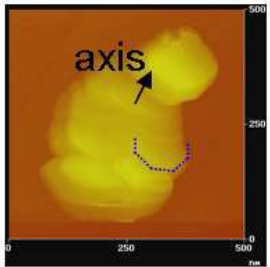
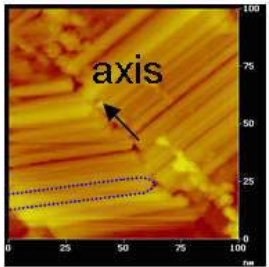
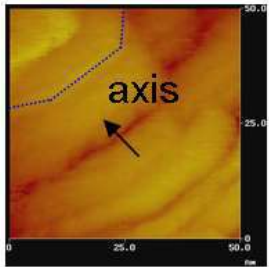
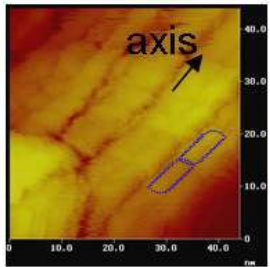
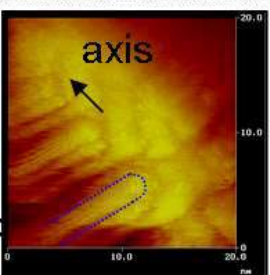
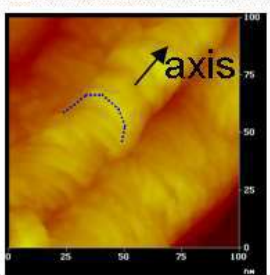
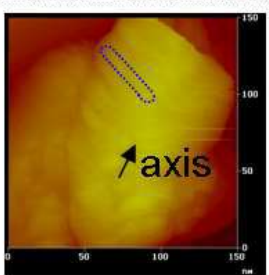
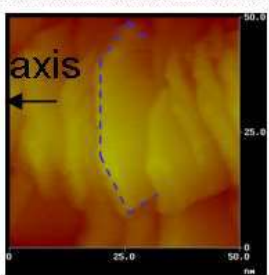
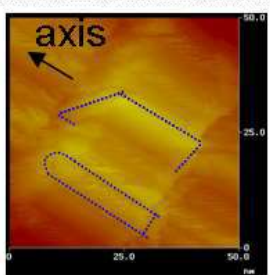
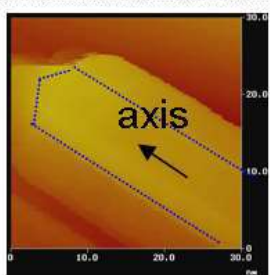
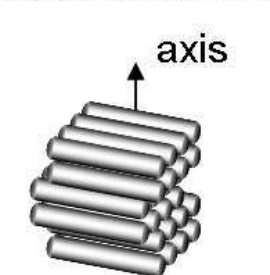
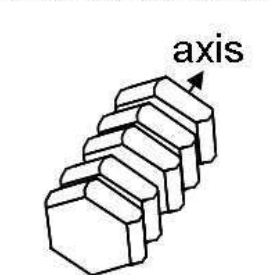
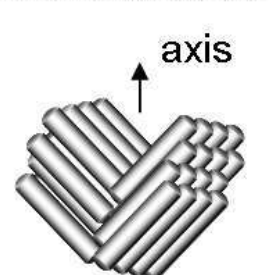
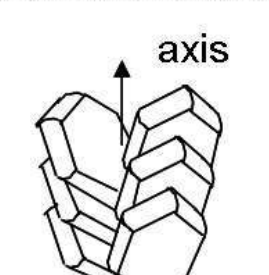
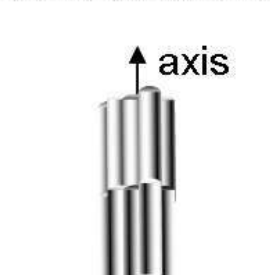
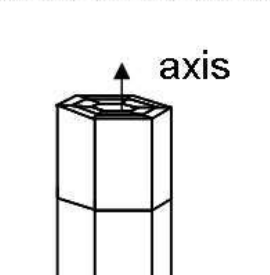
CNF (Small & Middle Diameters)

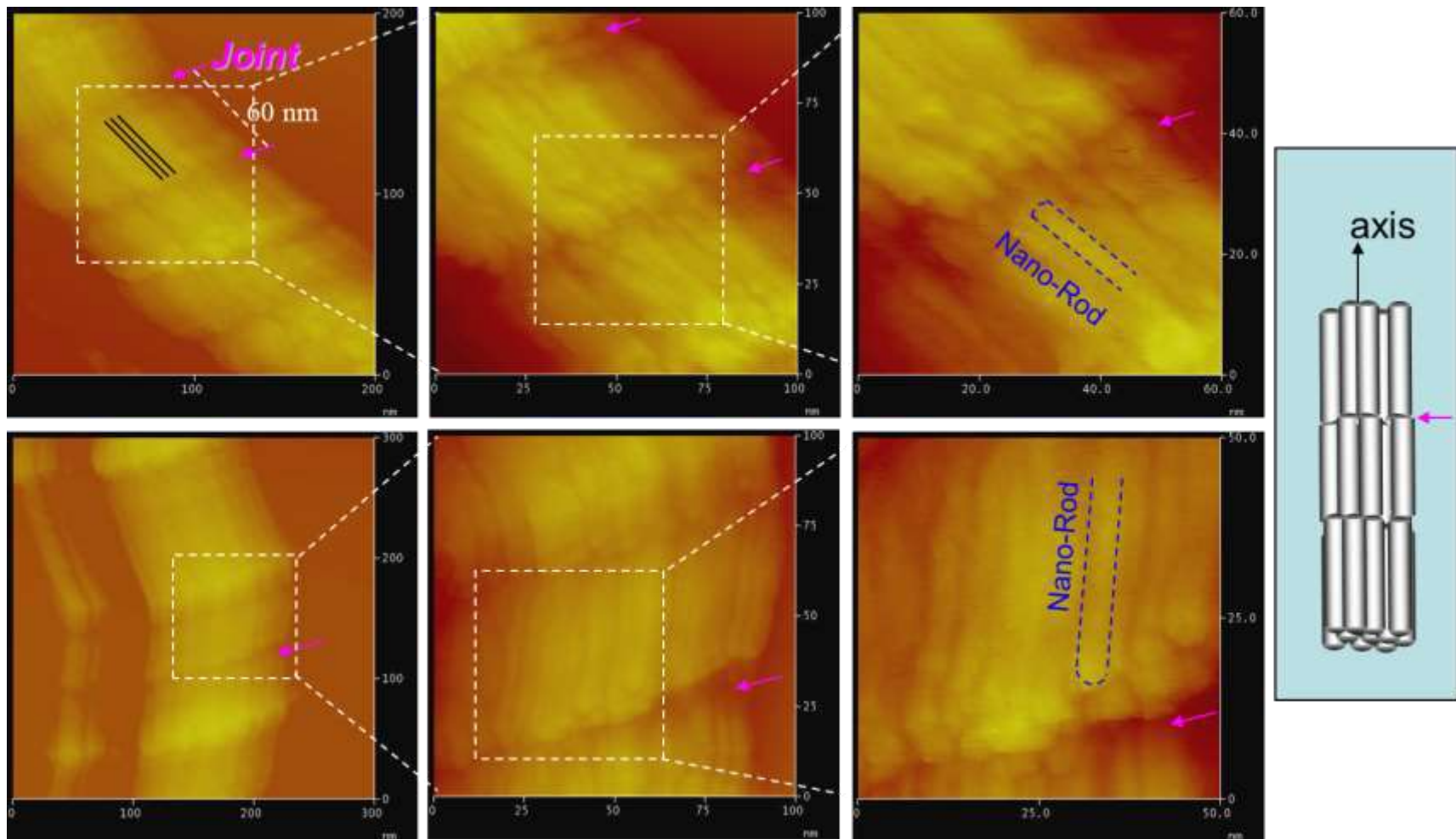


Sample #	SEM	TEM	Properties	Applications	Product
KNF-CM 小繊維径 高分散			Herringbone , hollow 7 ~ 20 nm	複合材料、吸着 剤、 触媒担体、FED	20-30 g/日
KNF-CC 小繊維径			Herringbone 7 ~ 15 nm	複合材料、吸着 剤、 触媒担体、FED	15-20 g/日
KNF-NM 中繊維径			Herringbone 10~60 nm (30~40)	複合材料、吸着 剤、 触媒担体	50-70 g/日
KNF-NF 中繊維径 直線性			Herringbone 20 ~ 50 nm Straightness	複合材料、吸着 剤、 触媒担体	50-70g/日



Structural Units of CNFs

		Platelet CNF		Herringbone CNF		Tubular CNF	
		Nano-Rod	Nano-Plate	Nano-Rod	Nano-Plate	Nano-Rod	Nano-Plate
STM images	As-prepared						
	Graphitize						
Models							



Structural units and their periodicity in carbon nanotubes, Long, D., An, B., Yokogawa, K., Ling, L., Miyawaki, J., Mochida, I., Yoon, S.-H., **Small** 6 (22), pp. 2526-2529 (2010).

5. 固相炭素化

- バイオマスを用いたLi-ion電池負極材の調製

Hard carbon from Mangrove tree – the effect of preheat treatment on its electrochemical properties of Li-ion battery

✓ Objective

Development of biomass derived cheap hard carbon with relative high 1st cycle CE

✓ Contents

- Investigation of preheat treatment effect on the 1st cycle Coulombic efficiency in the preparation of hard carbon using biomass as raw material

❖ Yu-Jin Han, *et al.*, *IMPRESS*, 2013, **3**, 571.

“Influence of preparation conditions of biochar from raw biomass on initial Coulombic efficiency of biomass derived hard carbon in Li-ion batteries”

➤ Preparation of hard carbon from Mangrove char



(Mangrove char)

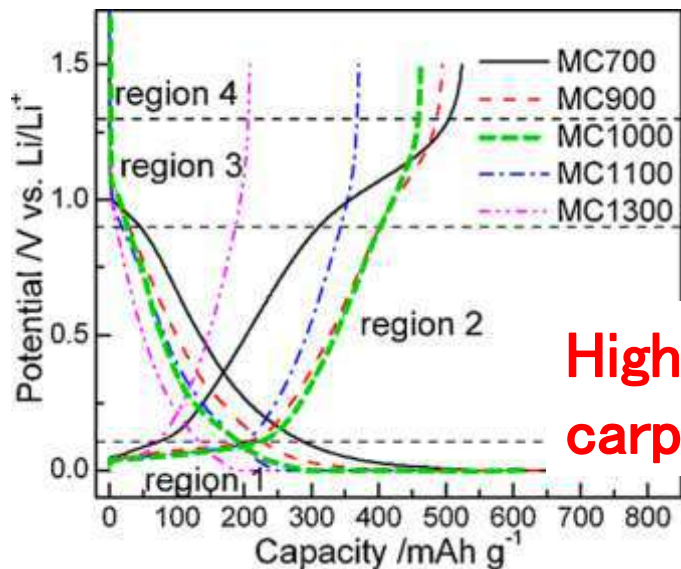
Milling
Particle size less
Than $45\ \mu\text{m}$

Heat treatment
at 1000°C



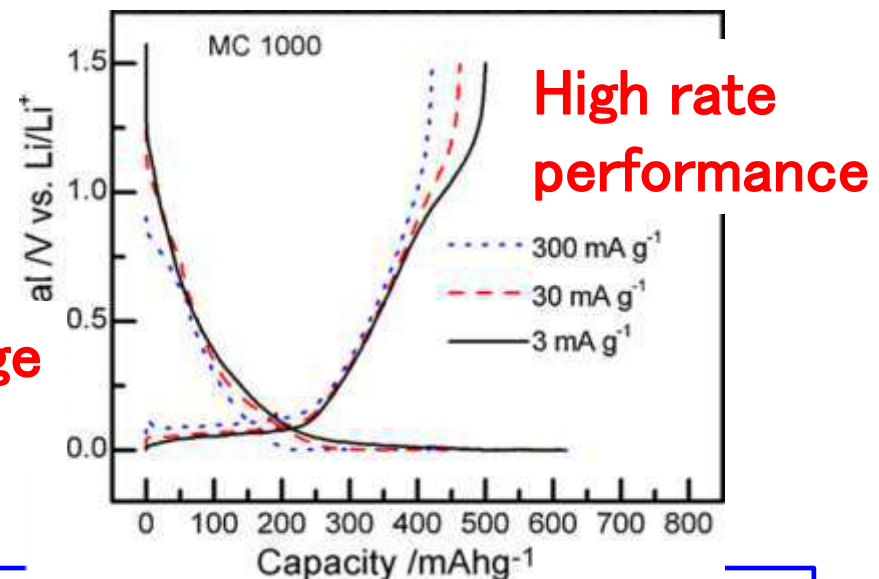
(Hard carbon)

• Charge-discharge properties



High discharge capacity

• Rate performance of biomass derived hard carbon



Cheap hard carbon with high discharge capacity can be prepared from biomass through suitable selection of raw material and heat treatment.

Status and distribution of mangrove forests of the world¹⁰⁷

< C. Giri et al., Global Ecology and Biogeography 20 (2011) 154 >



- **Total area of mangrove : 137,760 km² (2000年)**
 - Continent : Asia (42%), Africa (20%), North and Central America (15%), Oceania (12%), South Africa (11%)
 - Country : Indonesia (22.6%), Australia (7.1%), Brazil (7.0%), Mexico (5.4%)
- **Price of mangrove charcoal : US dollar 0.4-0.5/kg (Deal Indonesia CV)**
Price of natural graphite for battery : US dollar 0.8-2.0/ kg (Qingdao Caifeng Co. Ltd.)

Development of cheap hard carbon

- Investigation of structural effect of hard carbon on the electrochemical properties.
- Optimization of preheat treatment condition for hard carbon preparation

• Necessity of preheat treatment

(1) No preheat treatment



(Mangrove
Hard wood)

1st HT
(800°C)



2nd HT
(1000°C)



(Hard carbon)

(2) Pretreatment



(Mangrove
Hard wood)

Preheat treatment



(char)

1st HT
(800°C)

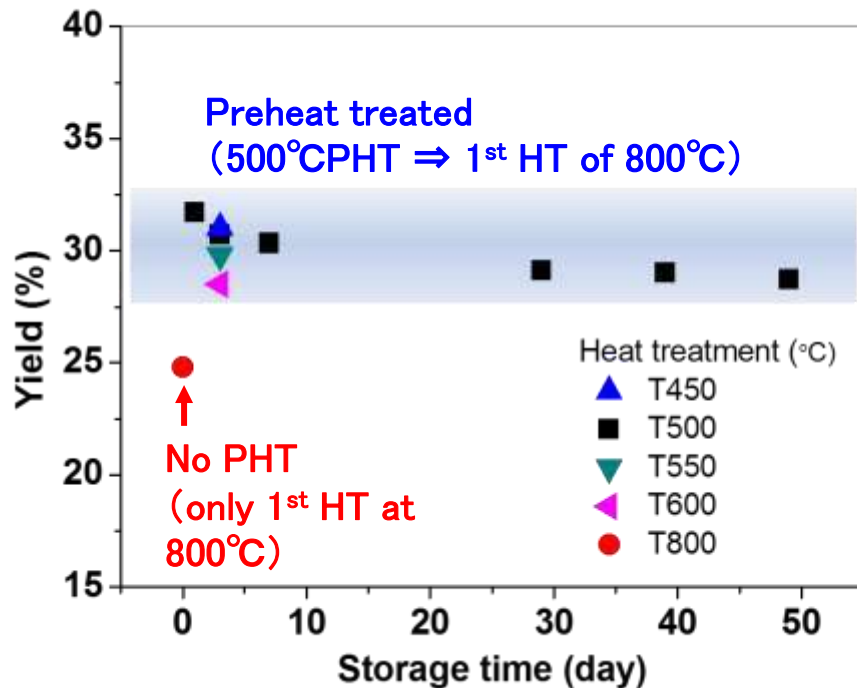


2nd HT
(1000°C)

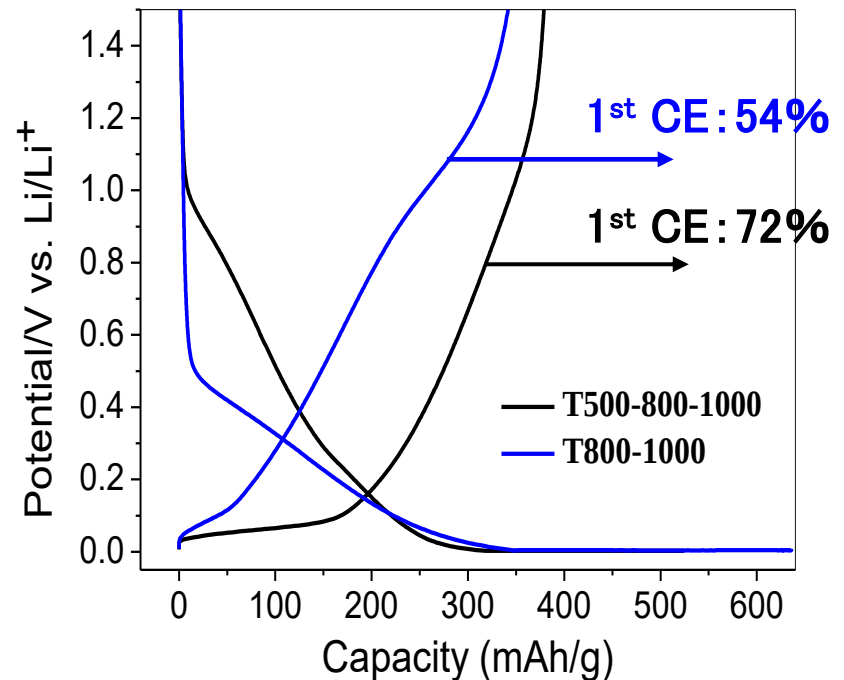


(hard carbon)

➤ Yield of 1st HT at 800°C



➤ Cha-discha properties of hard carbons



※ Hard carbon prepared at 1000°C from Mangrove tree

- Preparation yield and 1st cycle CE were improved through preheat treatment $\Rightarrow$ **PHT is necessary**

Preparation of hard carbon

➤ Preheat treatment

- Temp: 450、500、550、600°C
- Time: 1~49 days
- Pressure: 0.2、0.4、0.7 MPa

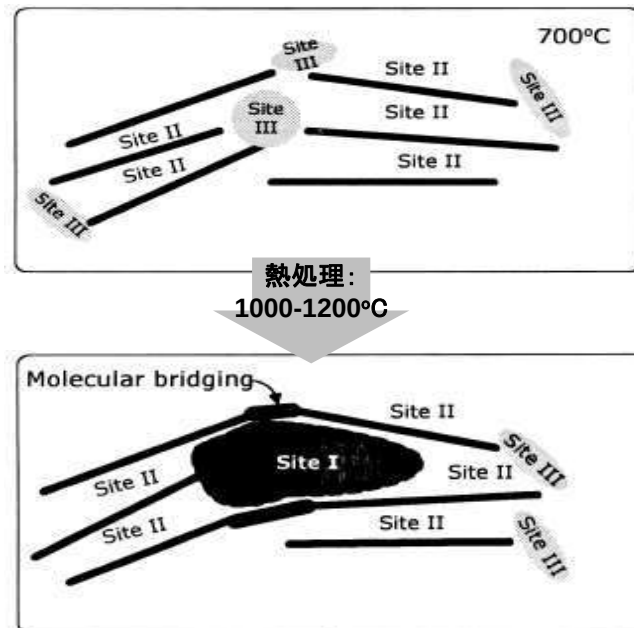
➤ Preparation of hard carbon

Charcoal
Milling less than 45 μm

Carbonization
1st HT: 800°C、30 min、Ar
2nd HT: 1000°C、1h、Vacuum

Evaluation of electrochemical property
Charge(CC/CV) : 30 mA/g、0.0~1.5 V、
To 3 mA/g
Discharge (CC): 30 mA/g、0.0~1.5 V

Li-ion storing sites



* Chul Wan Park, et al., *Carbon*, 2000, **38**, 995.

Site I (Potential range: 0.0—0.1 V)

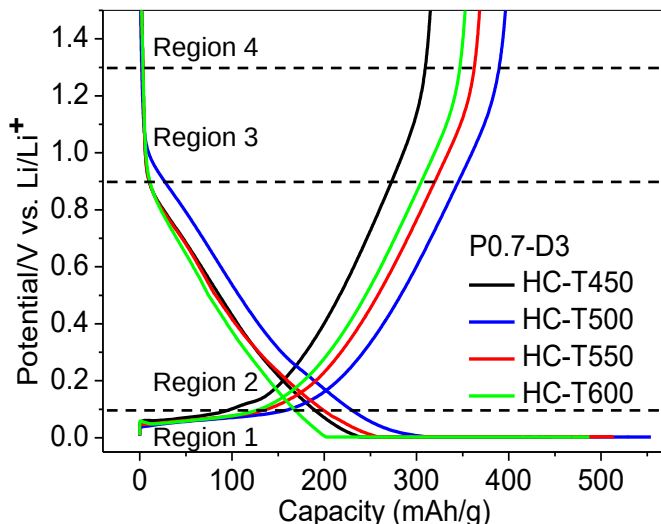
1000-1200°C heat treatment: Removal of heterogeneous atoms → formation of storing sites

Site II (Potential range: 0.1—0.9 V、1.3—1.5 V)
Between graphene sheets

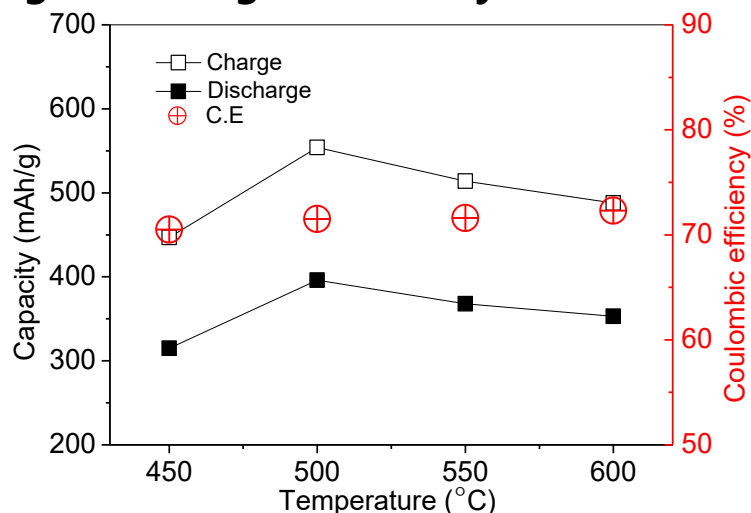
Site III (Potential range: 0.9—1.3 V)
Distortion of graphene sheet clusters

Charge-discharge properties

• Charge-discharge P: 0.7 MPa, D: 3 days



• Charge-discharge and 1st cycle CE



Discharge capacities

• Discharge capacity according to potential

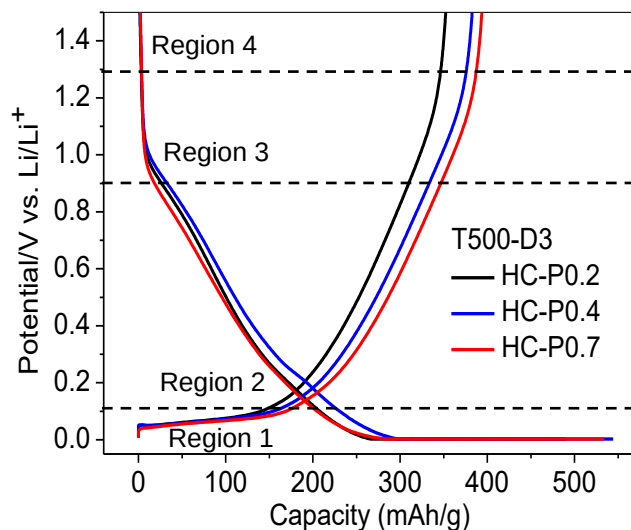
Samples	Total (0.0~ 1.5 V)	Discharge capacity (mAh g ⁻¹)			
		領域 1 (0.0~ 0.1 V)	領域 2 (0.1~ 0.9 V)	領域 3 (0.9~ 1.3 V)	領域 4 (1.3~ 1.5 V)
HC-T450	314	100	173	37	4
HC -T500	396	163	183	44	6
HC -T550	368	139	181	43	5
HC -T600	353	130	176	41	6

• Elemental analysis

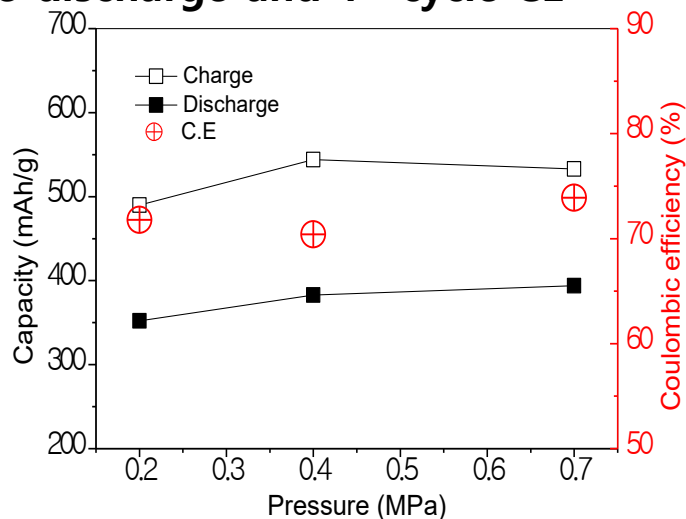
Samples	Atomic ratios (wt%)					Atomic ratios (%)	
	C	H	N	O _{diff.}	Ash	H/C	O/C
HC-T450	92.25	0.25	0.60	3.75	3.15	3.25	3.05
HC -T500	93.35	0.31	0.43	4.39	1.52	3.99	3.53
HC -T550	92.50	0.25	0.23	2.95	4.07	3.24	2.39
HC -T600	93.38	0.25	0.28	2.80	3.29	3.21	2.25

Charge-discharge properties

• Charge-discharge 温度: 500°C、P: 圧力、D: 3日間



• Charge-discharge and 1st cycle CE



Discharge capacities

• Discharge capacity according to potential

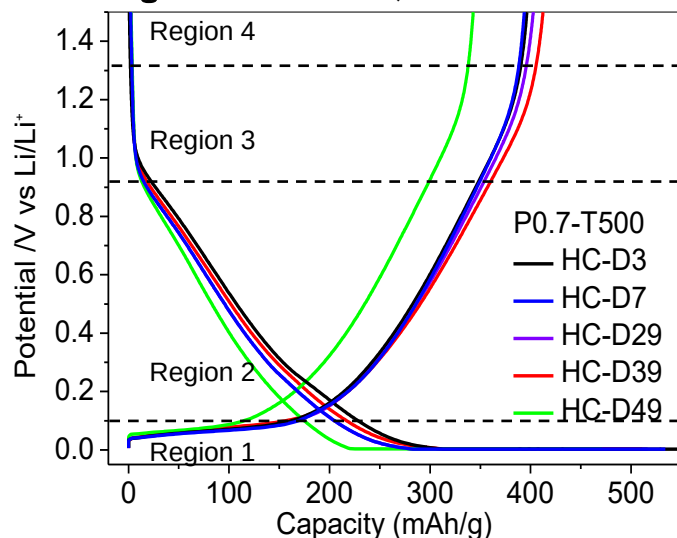
Samples	Total (0.0~ 1.5 V)	Discharge capacity (mAh g ⁻¹)			
		領域 1 (0.0~ 0.1 V)	領域 2 (0.1~ 0.9 V)	領域 3 (0.9~ 1.3 V)	領域 4 (1.3~ 1.5 V)
HC-P0.2	352	141	167	41	3
HC-P0.4	383	154	179	43	7
HC-P0.7	394	171	178	38	7

• Elemental analysis

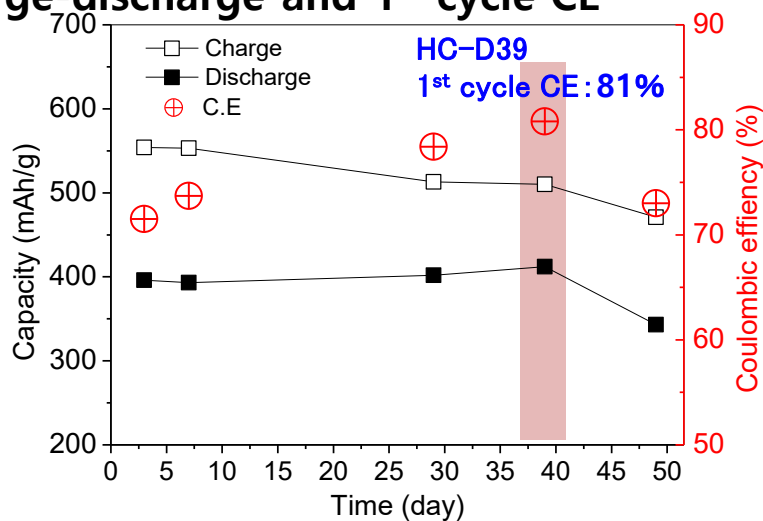
Samples	Atomic ratios (wt%)					Atomic ratios (%)	
	C	H	N	O _{diff.}	Ash	H/C	O/C
HC-P0.2	89.70	0.68	0.72	7.65	1.21	9.10	6.40
HC-P0.4	90.58	0.68	0.49	7.47	0.74	9.01	6.19
HC-P0.7	93.11	0.30	0.50	3.97	2.13	3.87	3.20

Charge-discharge properties

• Charge-discharge P: 0.7 MPa, T: 500°C



• Charge-discharge and 1st cycle CE



Discharge properties

• Discharge capacity according to potential

Samples	Total (0.0 V -1.5 V)	Discharge capacity (mAh g ⁻¹)			
		領域 1 (0.0 V -0.1 V)	領域 2 (0.1 V -0.9 V)	領域 3 (0.9 V -1.3 V)	領域 4 (1.3 V -1.5 V)
HC-D3	396	163	183	44	6
HC-D7	393	170	177	41	6
HC-D29	402	174	180	41	7
HC-D39	417	188	181	42	6
HC-D49	366	153	168	41	5

• Elemental analysis

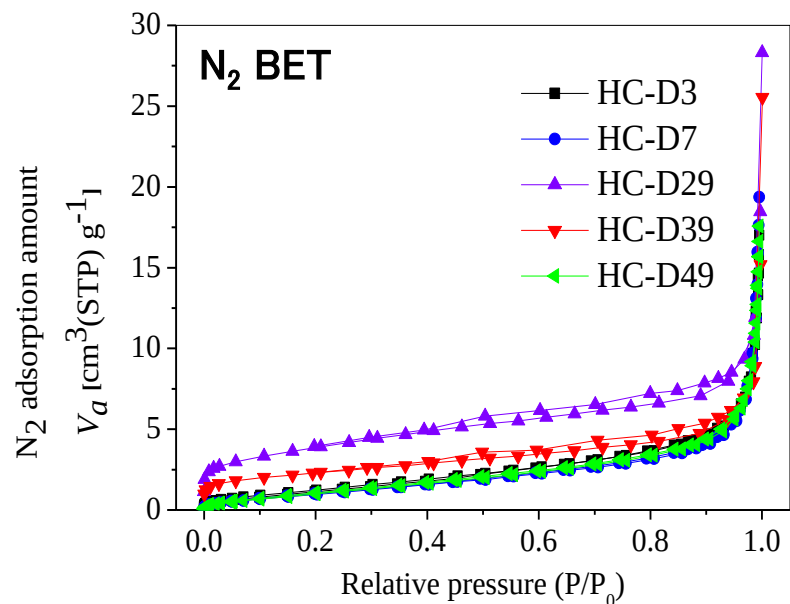
Samples	Atomic ratios (wt%)					Atomic ratios (%)	
	C	H	N	O _{diff.}	Ash	H/C	O/C
HC-D3	93.35	0.42	0.51	3.34	2.34	5.40	2.68
HC-D7	92.91	0.46	0.63	2.99	3.01	5.94	2.41
HC-D29	93.30	0.20	0.44	3.53	2.53	2.57	2.84
HC-D39	93.07	0.14	0.26	2.74	3.79	1.81	2.21
HC-D49	92.90	0.10	0.39	2.61	4.00	1.29	2.11

水素と酸素の含有量が減少

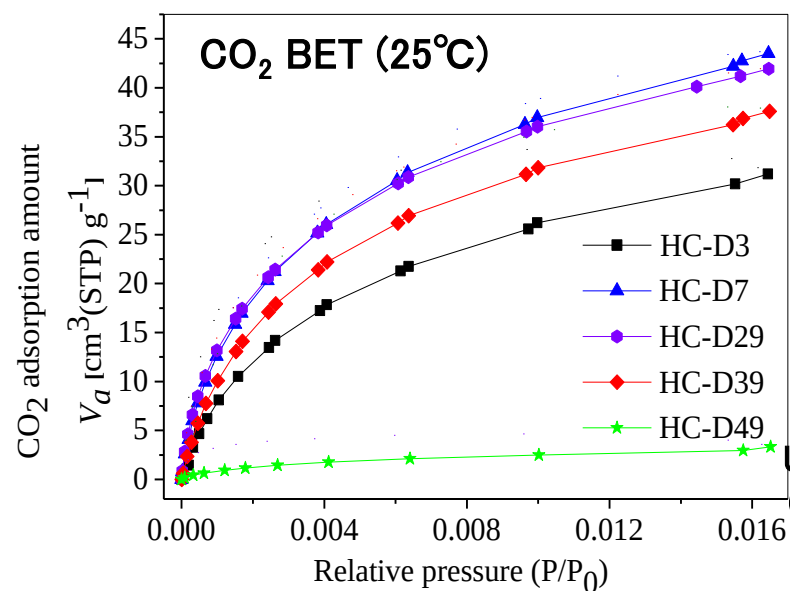
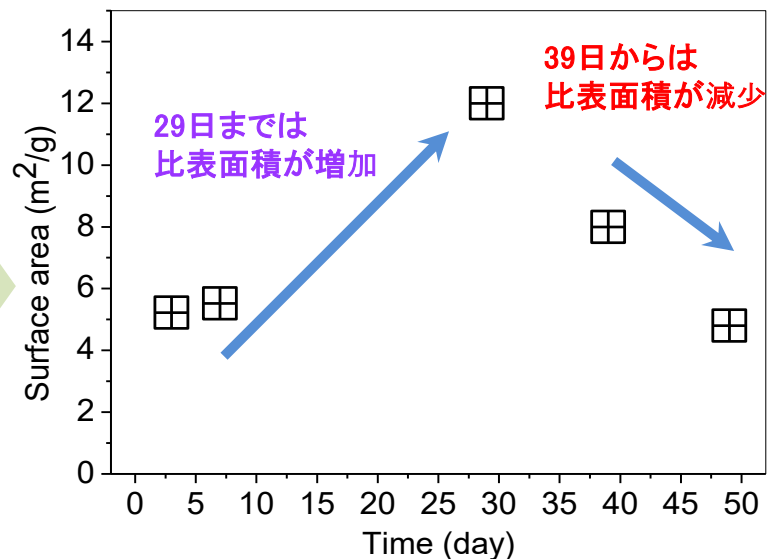
What is the factor to determine 1st cycle CE?

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➤ SA and Pore size distribution of hard carbons

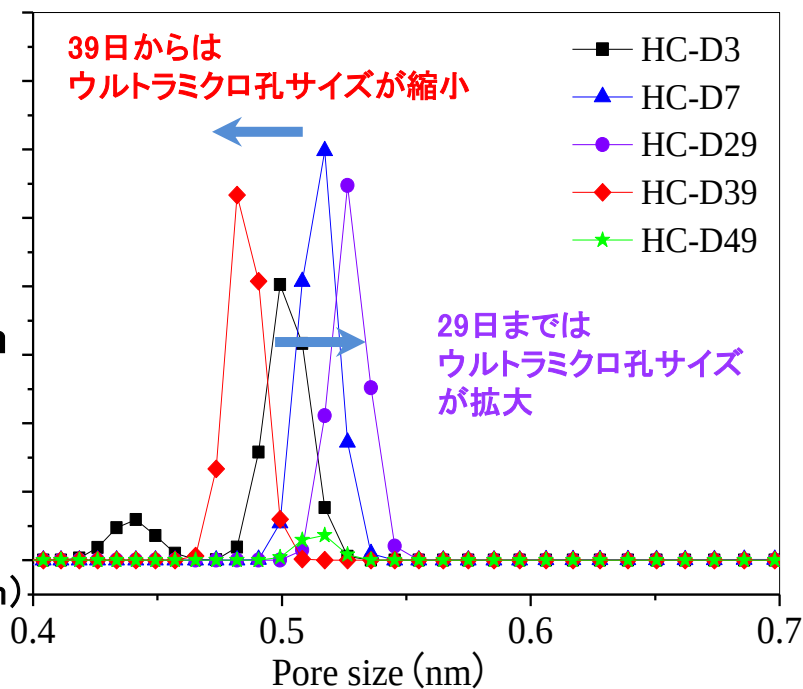


SA



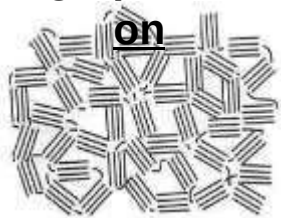
UMP
distribution

UMP
(Less than 0.7 nm)



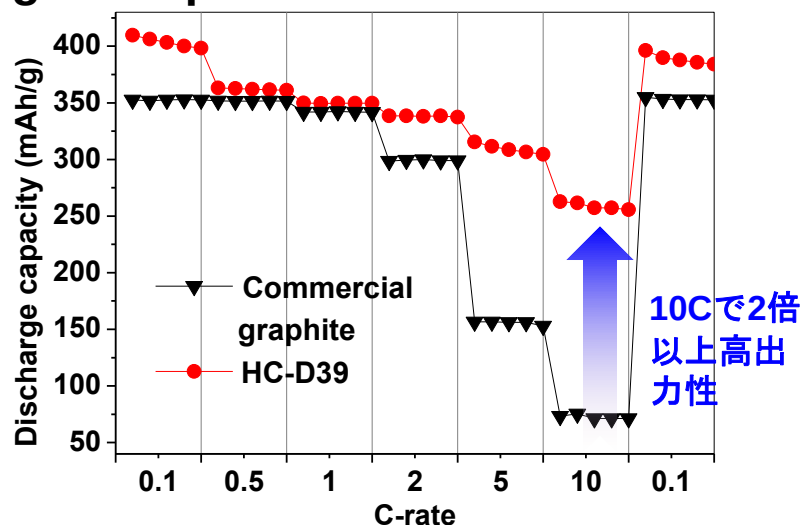
Characteristics of hard carbon

- Using nano-sized inner closed pores – not graphitized
- **Special properties**
 - Advantage : High cap., High rate
 - Disadvantage : Low 1st CCE, Low density
 - Raw material : Resin, coke, biomass



R.E. Franklin, *Proc. R. Soc. Lond.*, 1951, 209, 196.

- High rate performance of hard carbon



Approach of this study

- Optimization of hard carbon structure through controlling the low temperature pre-carbonization heat treatment

5

Development of biomass derived hard carbon:

Development of low cost hard carbon using Mangrove based biomass through simple heat treatments

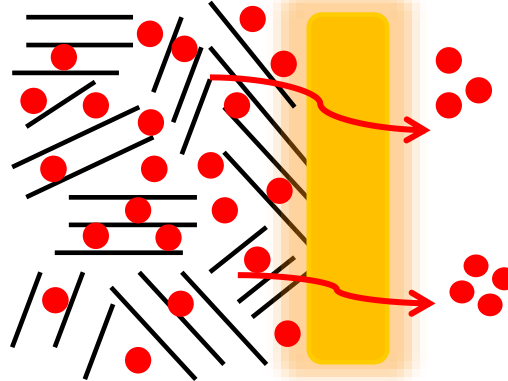
- **Price of raw materials**

- Price of mangrove char : US dollar 0.4-0.5/kg (Deal Indonesia CV)
- Natural graphite: US dollar 0.8-2.0/kg (Qingdao Caifeng Co. Ltd.)

1st cycle CE of hard carbon derived from Mangrove tree was improved through the optimization of preheat treatment conditions.

- Preheat treatment is closely related to the distribution of ultra micropores which might be related to the 1st cycle CE of hard carbon.
- Preheat treatment conditions of 500°C under 0.7 Mpa for 39 days can afford the cheap hard carbon which has discharge capacity of 417 mAh g⁻¹ with 80.5% of 1st cycle CE.

⇒ Hydrogen and oxygen amounts and UMP distribution might be important factors to determine the electrochemical properties of hard carbon.



1. 人造黒鉛材には易黒鉛化性炭素と難黒鉛化性炭素がある.
難黒鉛化性と易黒鉛化性炭素は積層単位の大きさの違いからドメインの構造が異なる.
2. 炭素材は気相, 液相, 固相炭素化で製造される. 95%以上の人造黒鉛は液相炭素化で製造される.
3. ナノ炭素中, フラーレン, CNTおよびCNFは気相炭素化で合成される.
一部易黒鉛化性炭素(VGCF, HOPG)は気相炭素化で製造される.
4. 易黒鉛化性炭素材は主に液相炭素化によって製造される.
5. バイオマスおよび熱硬化性樹脂を用いた炭素材は固相炭素化で製造される.
高分子を前駆体としたPAN系炭素繊維およびナノ炭素ナノ繊維は固相炭素化で製造される.
一部高分子を原料とした高熱伝導性炭素フィルムは固相炭素化で製造される.

- ピッチは、木材、石炭などの乾留の際に得られる液状タール、オイルサンドから得られるビチューメン、オイルシェールの乾留によって得られる油分、原油の蒸留による残渣油、石油留分のクラッキングによって生成するタールなどを熱処理、重合して得られる常温で固体状のものの総称。
- 工業的には石炭の乾留の際生成される石炭系ピッチ (Coal tar pitch) と石油の蒸留の残渣から製造できる石油系ピッチ (Petroleum pitch) が重要。 最近、ナフタレンなどの芳香族化合物を触媒重合した合成ピッチも製造されるようになった。
- ピッチは、化学的には無数の縮合多環芳香族化合物の混合物であり、平均分子量は300～1000程度の範囲の混合物ある。 こうしたピッチは通常は光学的に等方性である
- こうした等方性ピッチを350～450℃程度の温度で熱処理すると光学的異方性組織 (メソフェーズ) の炭素質液晶が発達
- メソフェースピッチのテキスチャーは、これを前駆体と用いて製造されるコークス等の機能性炭素材の化学・物理的特性をほぼ決定してしまうので、メソフェースピッチ合成の際、原料の化学構造、熱処理の際の熱分解ならびに重合挙動をよく知っておくことはきわめて重要。 液晶ピッチはネマティック液晶。
- 芳香族多環縮合構造のプレーナ分子が積層され、メゾゲン単位を高温熱処理過程で形成した後、こうしたメゾゲン単位の濃度が増加することによって球晶が生成、その後生成した球晶の合体によって100%の光学的異方性組織を持つメソフェースピッチが形成
- 液晶ピッチは、石炭の熱分解課程で最初発見された際は不溶のものと認識されたが、可溶・可融性が見つけられ、高性能ピッチ系炭素繊維の前駆体として利用。

重質油又は石炭残渣を用いた炭素材の製造模式図

