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Exfoliation of carbon fibers and its applications

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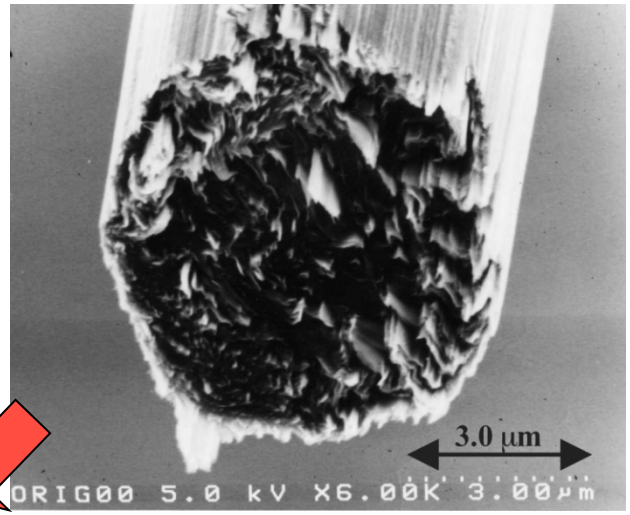
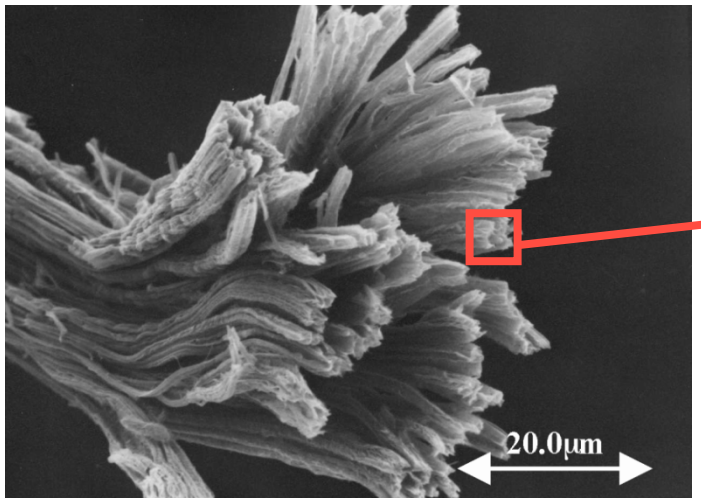
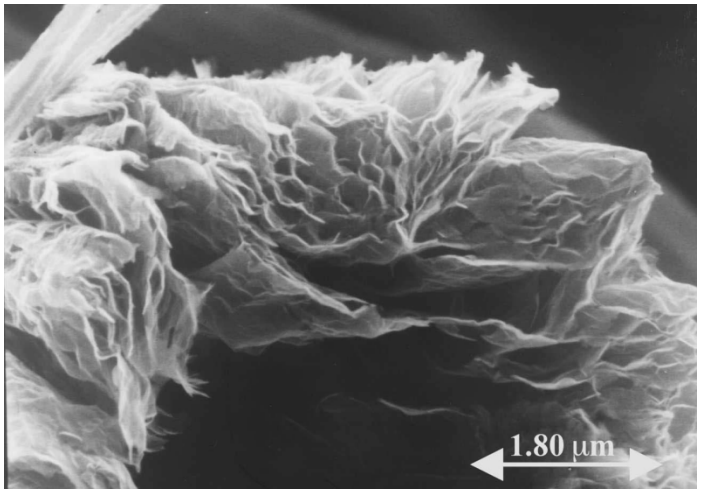
What is “Exfoliation of Carbon Fibers” ??

What is the exfoliated carbon fibers (ExCFs) !!







After exfoliation of carbon fibers through electrolysis by nitric acid electrolyte

Graphite particles can be exfoliated through chemical processing such as dipping of graphite particles in H_2SO_4 solution with HNO_3..

➡ Exfoliation of graphite particles (Exfoliated Graphite)

Exfoliation of carbon fibers via intercalation compounds is known to be limited except for well-graphitized vapor grown carbon fibers (VGCF) [1] .

[1] Yoshida A., Hishyama Y, and Inagaki M, Carbon, 28 (1990) 539.

And then a few exfoliation of carbon fibers through their intercalation compounds are referred; $SbCl_5$ into benzene-derived carbon fibers [2].

[2] Jimenez-Gonzalez H, Speck JS, Roth G. Dresselhaus MS, Endo M, *Carbon*, 1986; 24: 627-633.

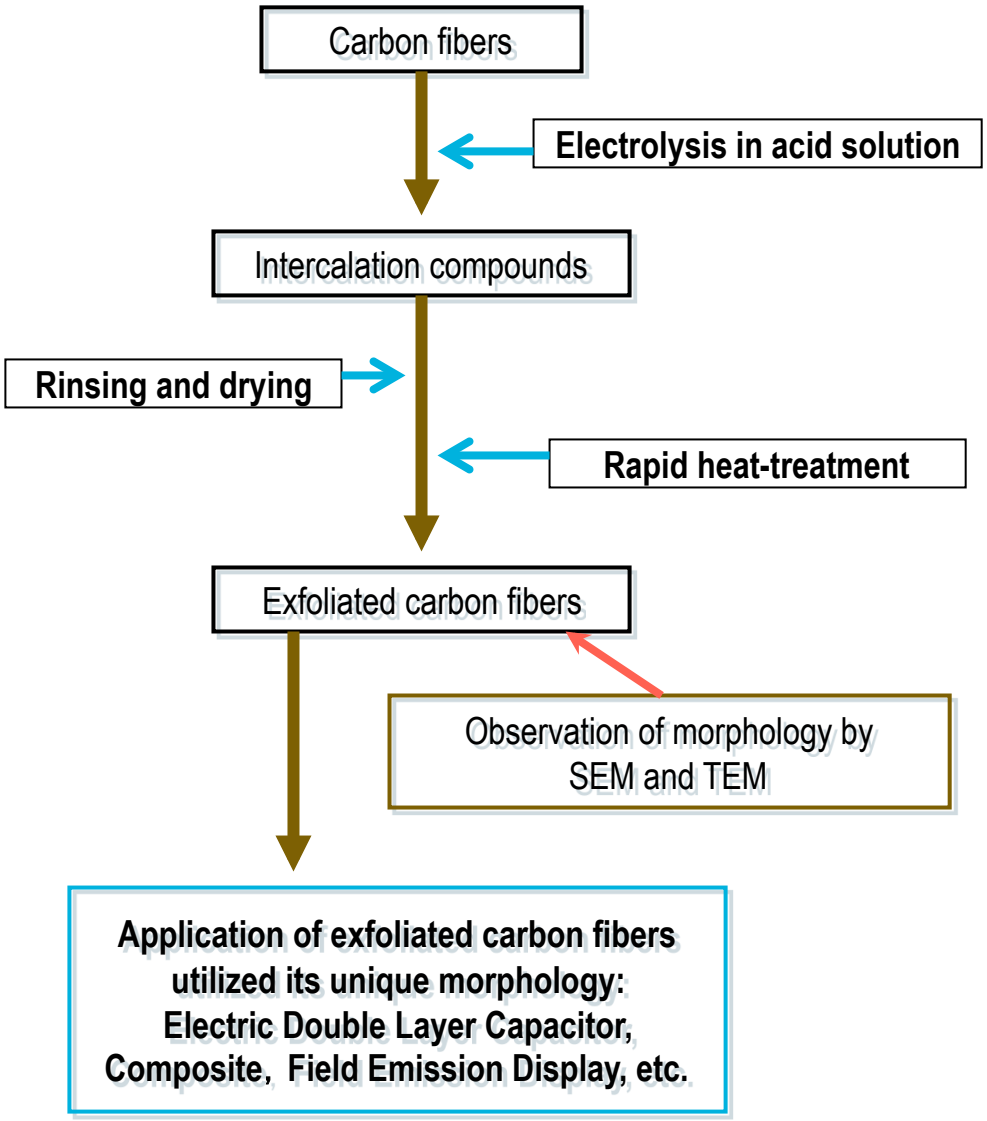
On the other hand, no detailed study on exfoliation process and structural change was performed.

Exfoliation of pitch- based carbon fibers heat-treated at a high temperature was firstly reported by Anderson and Chung [4]. However, from their SEM micrographs marked exfoliation as observed in natural graphite flakes and vapor-grown carbon fibers ***was not recognized on its carbon fibers.***

[4] Anderson S. H, and Chung D. D. L, *Synth. Met.*, 8, (1983) 343.

I succeeded in the formation of intercalation compounds of various carbon fibers by electrochemical methods in acid electrolyte, and also in marked exfoliation of them by heat-treatment. Exfoliated carbon fibers are bundle of nano-filaments.

Flow diagram of preparation of exfoliated carbon fibers



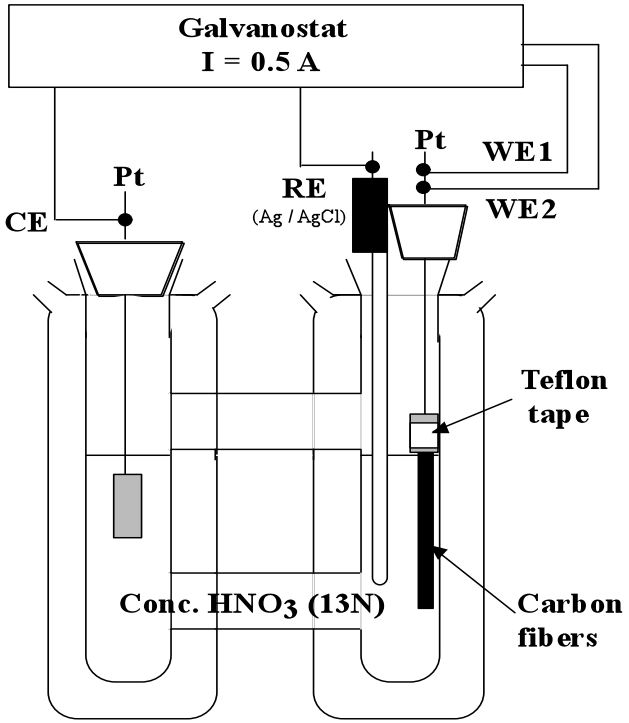


Fig. Equipment of electrolysis

Experimental Conditions

Pristine carbon fiber used

Carbon fiber used	Cross sectional texture	Heat-treatment temperature / °C
Mesophase-pitch-based carbon fibers	Straight Radial, Corrugate Radial, Flat Layer,	3000 °C, 2500 °C, 2000 °C, 1500 °C, 1150 °C
PAN-based carbon fibers		2600 °C, 2000 °C

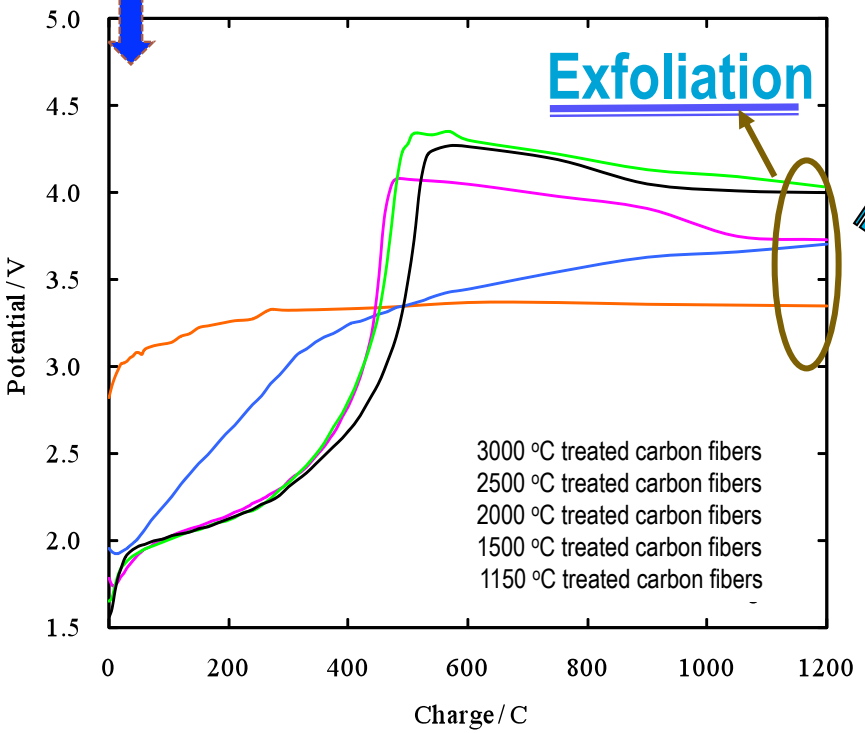
Intercalation condition

Electrolyte	Concentration of Electrolyte / mol/dm^3	Applied current / A
Nitric acid Formic acid	13.0, 5.0 and 1.0 mol/dm^3 50 %	0.5 A to 1.5 A

Exfoliation condition

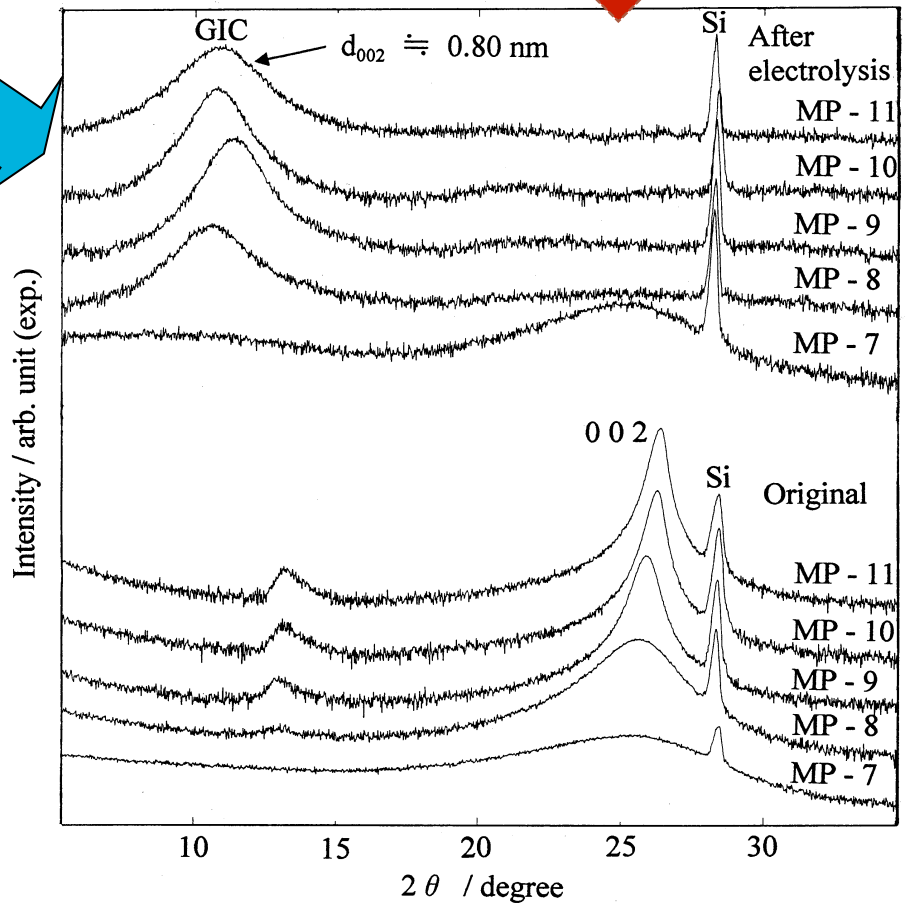
Heat-treatment temperature / °C	Holding time in a tubular furnace
1000 °C	5 sec

Behavior of the electrolysis in acid solution and behavior of formation of intercalation compounds of carbon fibers

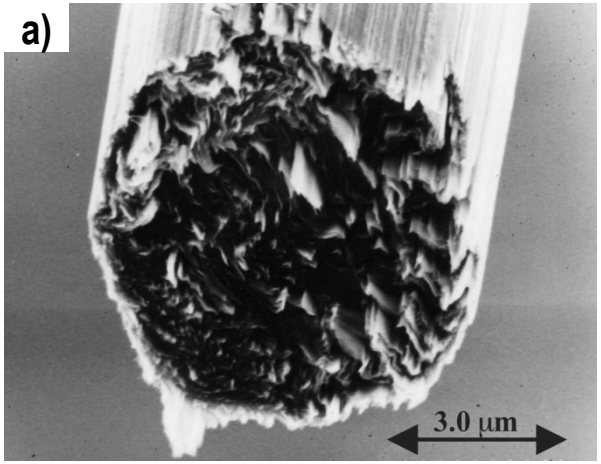


Changes in the anode potential for mesophase-pitch-based carbon fibers with heat-treatment temperature.

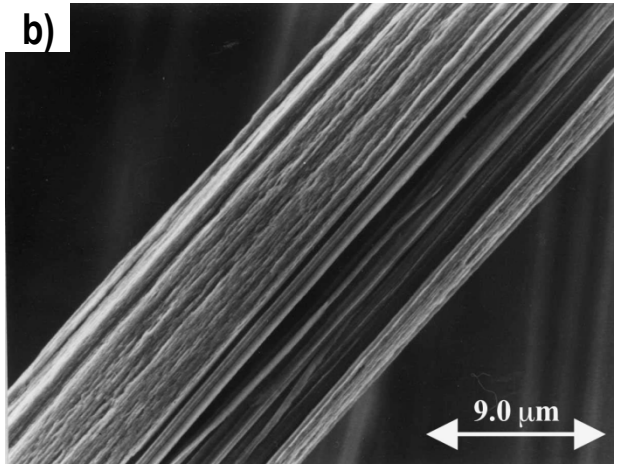
MP-11: 3000 °C treated carbon fibers
MP-10: 2500 °C treated carbon fibers
MP- 9: 2000 °C treated carbon fibers
MP- 8: 1500 °C treated carbon fibers
MP- 7: 1150 °C treated carbon fibers



Changes in XRD patterns of pristine carbon fibers to After electrolysis of carbon fibers

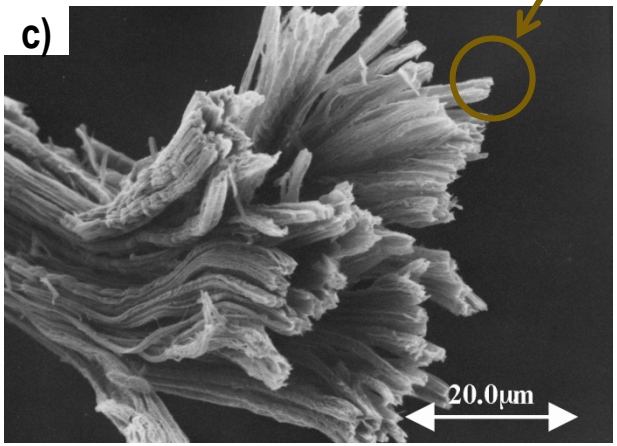


Original single fiber



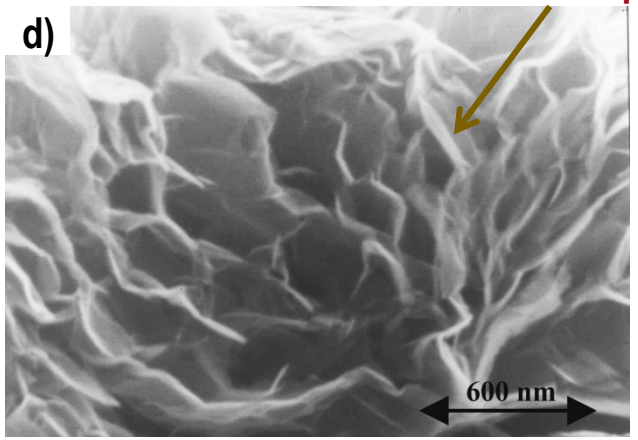
After intercalation of nitric acid

Thin filament



After exfoliation of carbon fiber

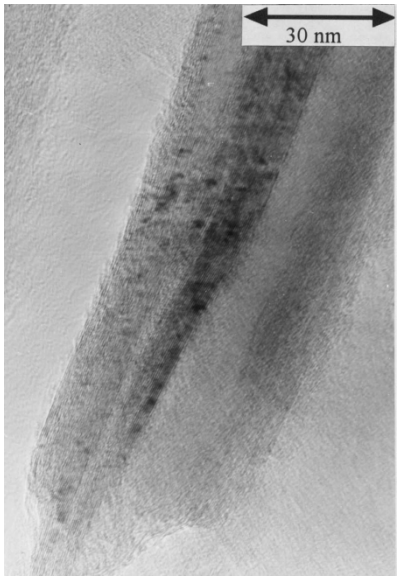
Nano space



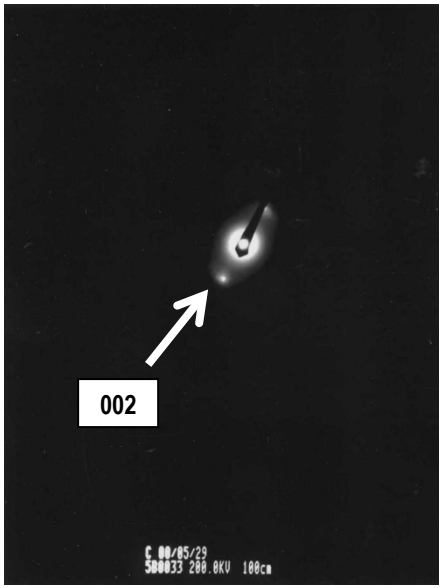
Micro observation in cross-section after exfoliation

After exfoliation of carbon fibers through electrolysis by nitric acid electrolyte

Low magnification

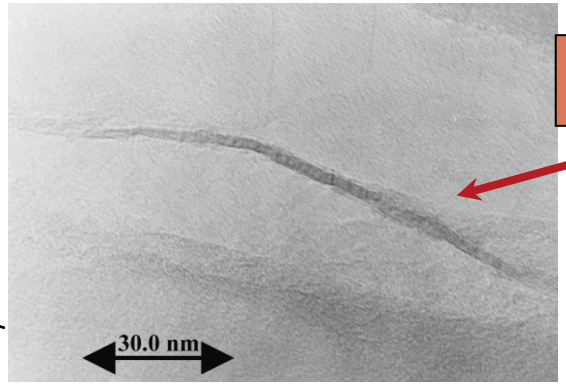


002 lattice image



Selected area electron diffraction

Each fibrils are keeping the graphite layer even though after exfoliation

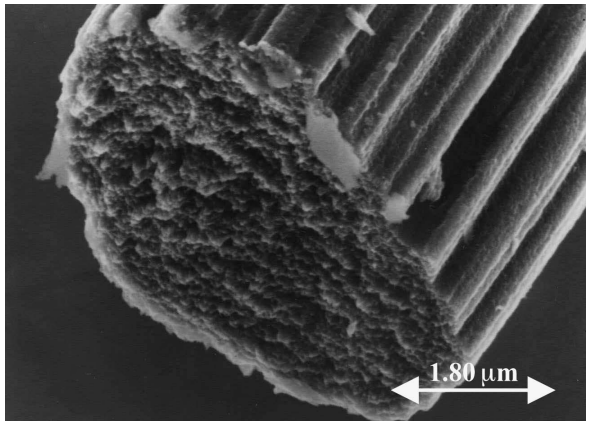


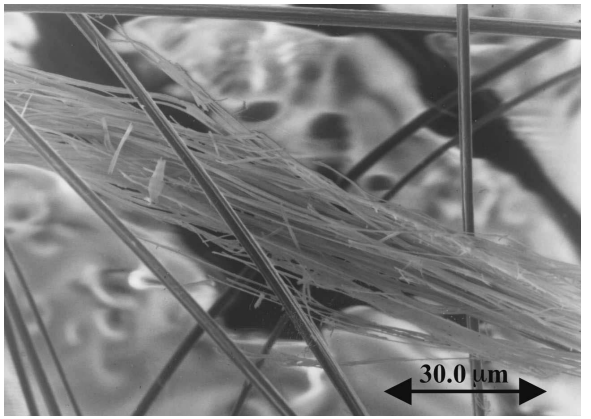
lattice image

Nano meter Sized thin filament

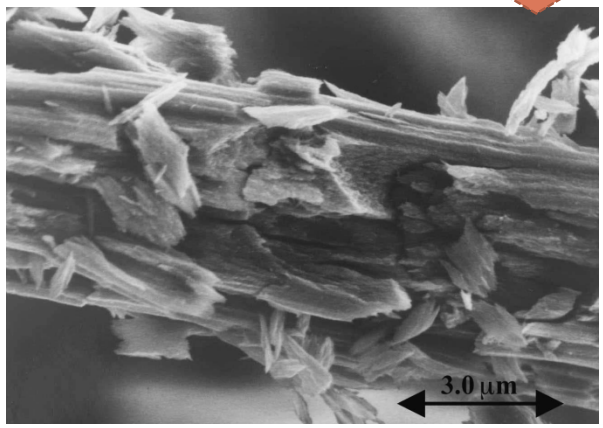
TEM micrographs of filaments obtained by exfoliation of mesophase-pitch-based carbon fiber heat-treated at 3000 °C. 002 lattice image and selected-area electron diffraction pattern

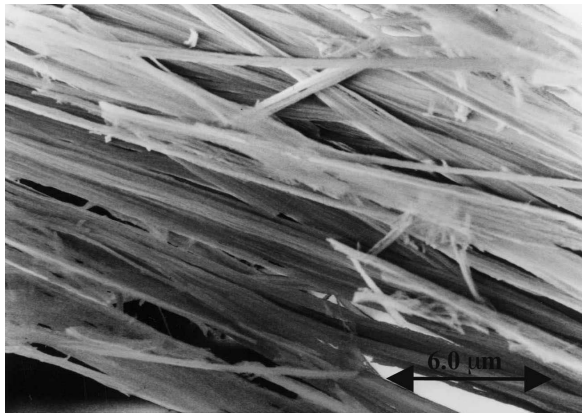
After exfoliation of PAN based carbon fibers and 1500 °C treated pitch-based carbon fibers through electrolysis in nitric acid electrolyte





Scale like morphology

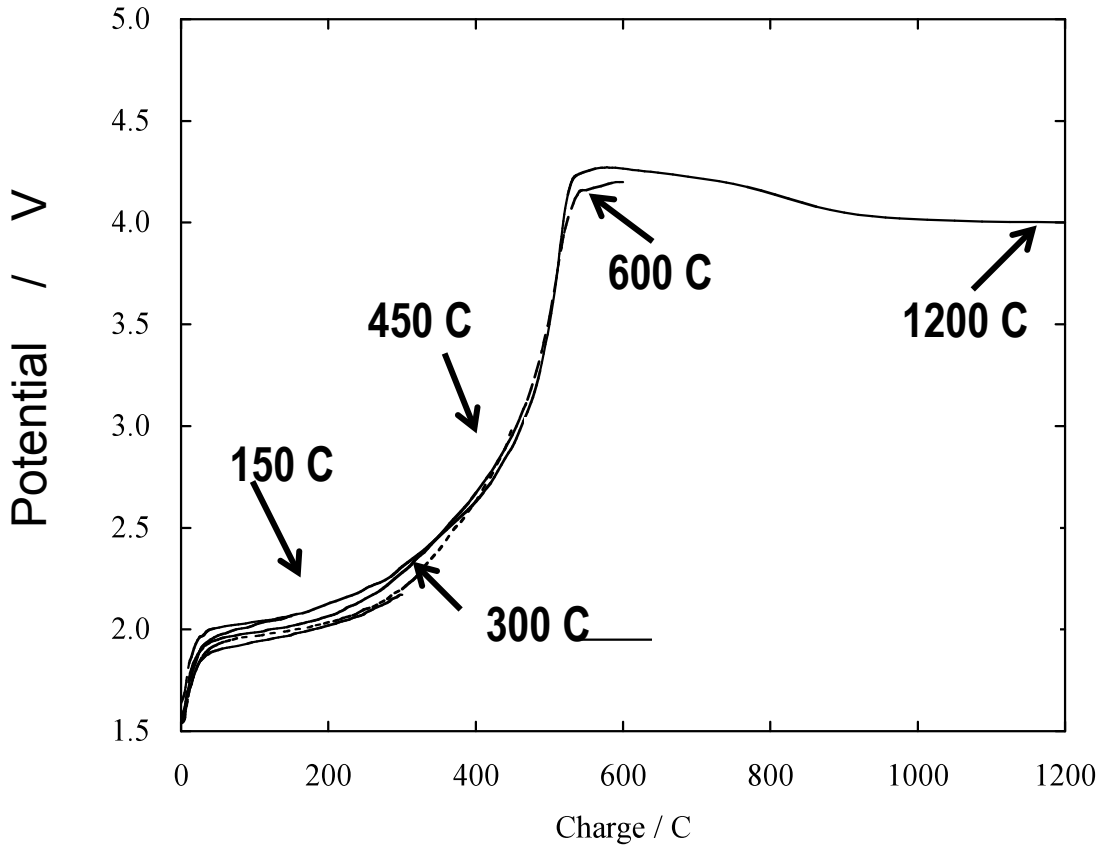




PAN based carbon fibers

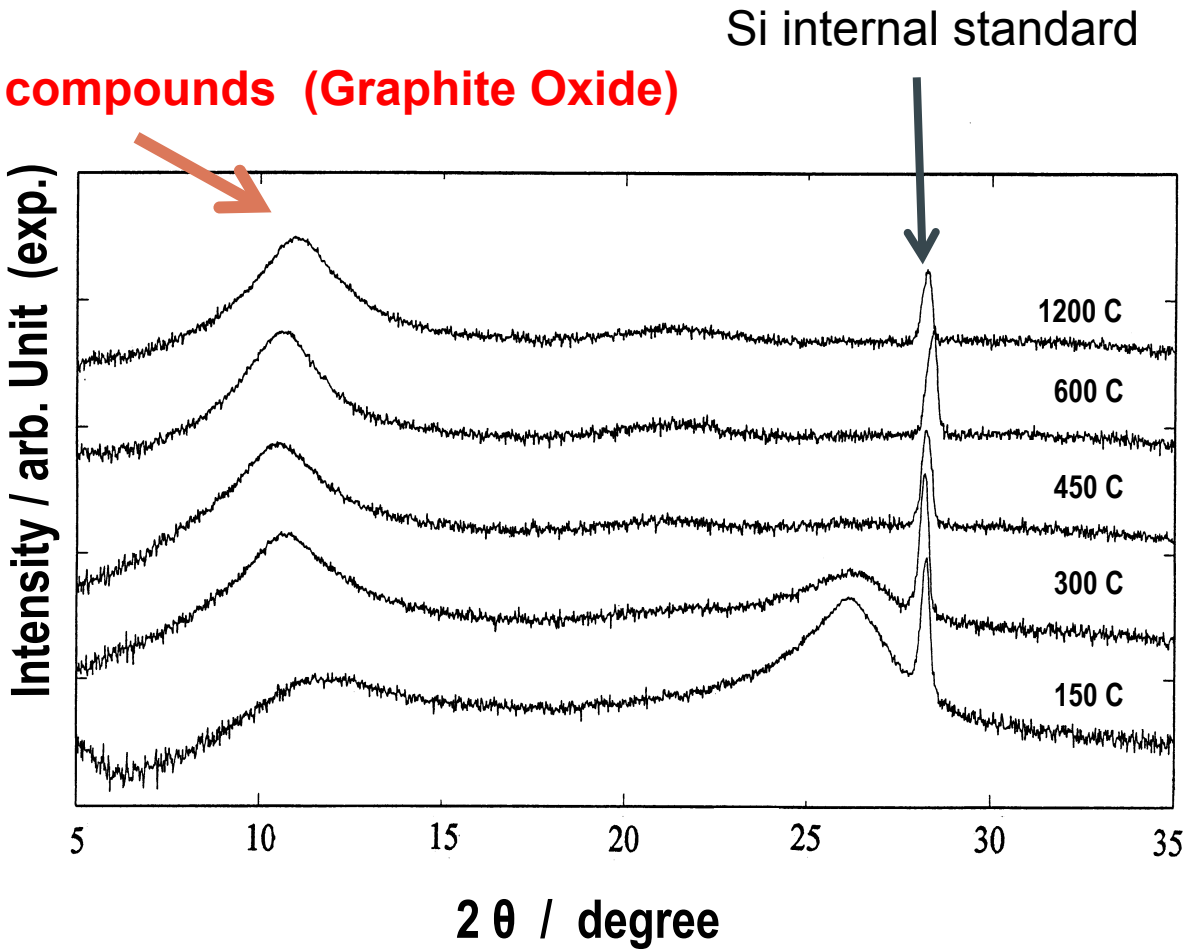
1500 °C treated pitch-based carbon fibers

How does Formation of the intercalation compound progress ?



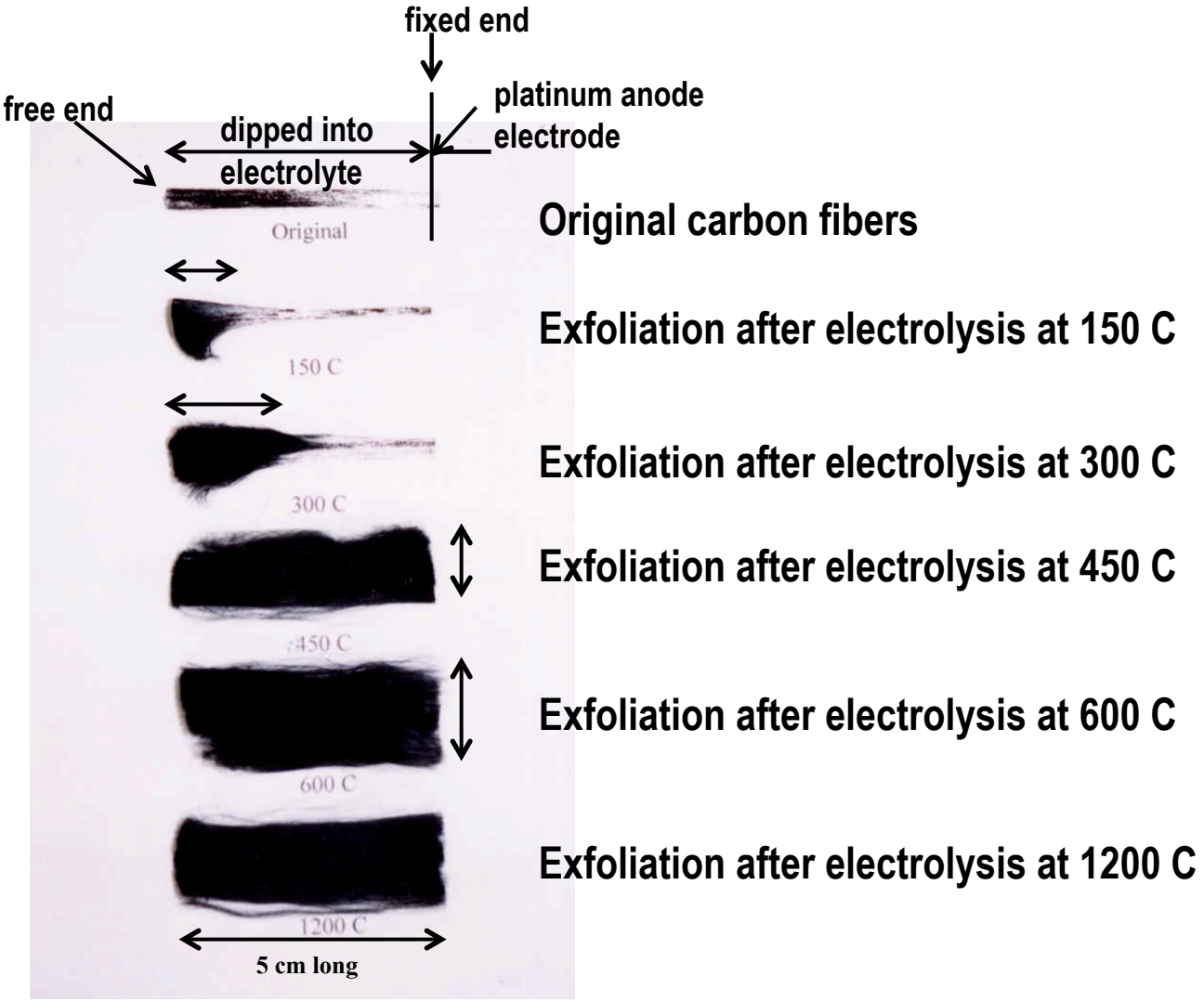
Potential curves during the electrolysis of mesophase-pitchbased carbon fibers treated at 3000 °C

Intercalation compounds (Graphite Oxide)



XRD patterns of electrolyzed carbon fibers with different electrical charge applied

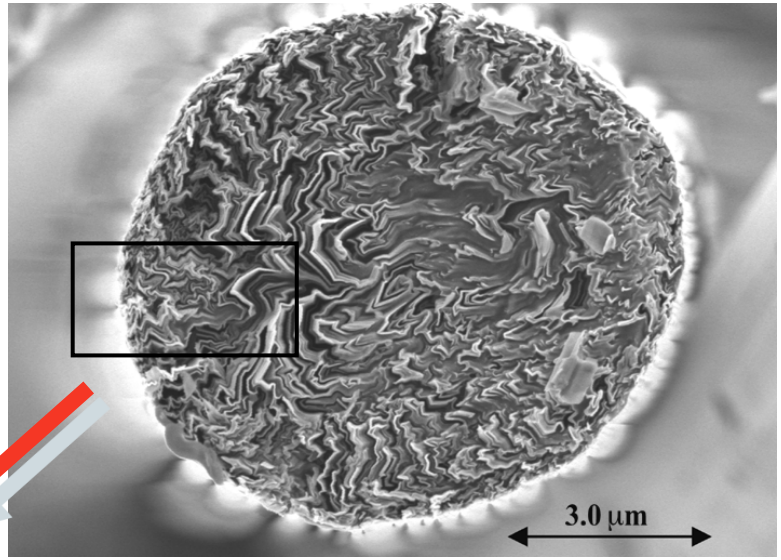
Morphology change after exfoliation



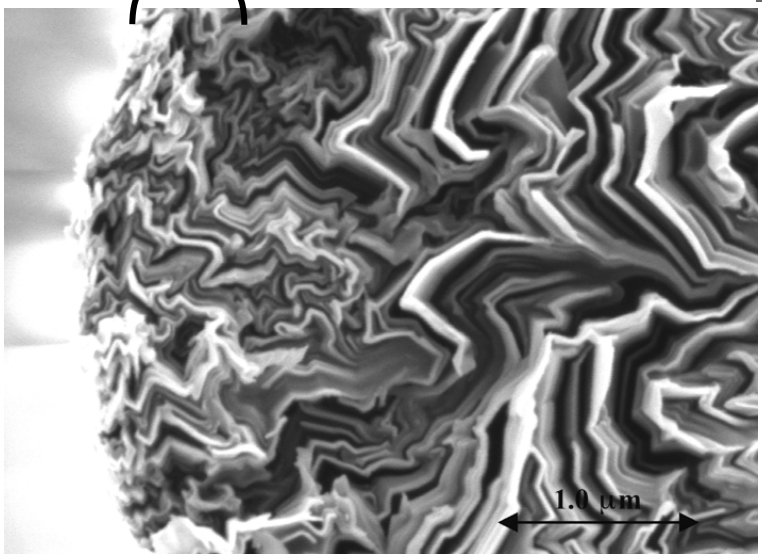
Appearance of carbon fibers after exfoliation which were obtained by interruption of electrolysis at different charges

What is the restriction of the intercalation (exfoliation) ?

In the carbon fiber, the strong restriction force for maintaining the fiber-form works.



Closed packed surface area

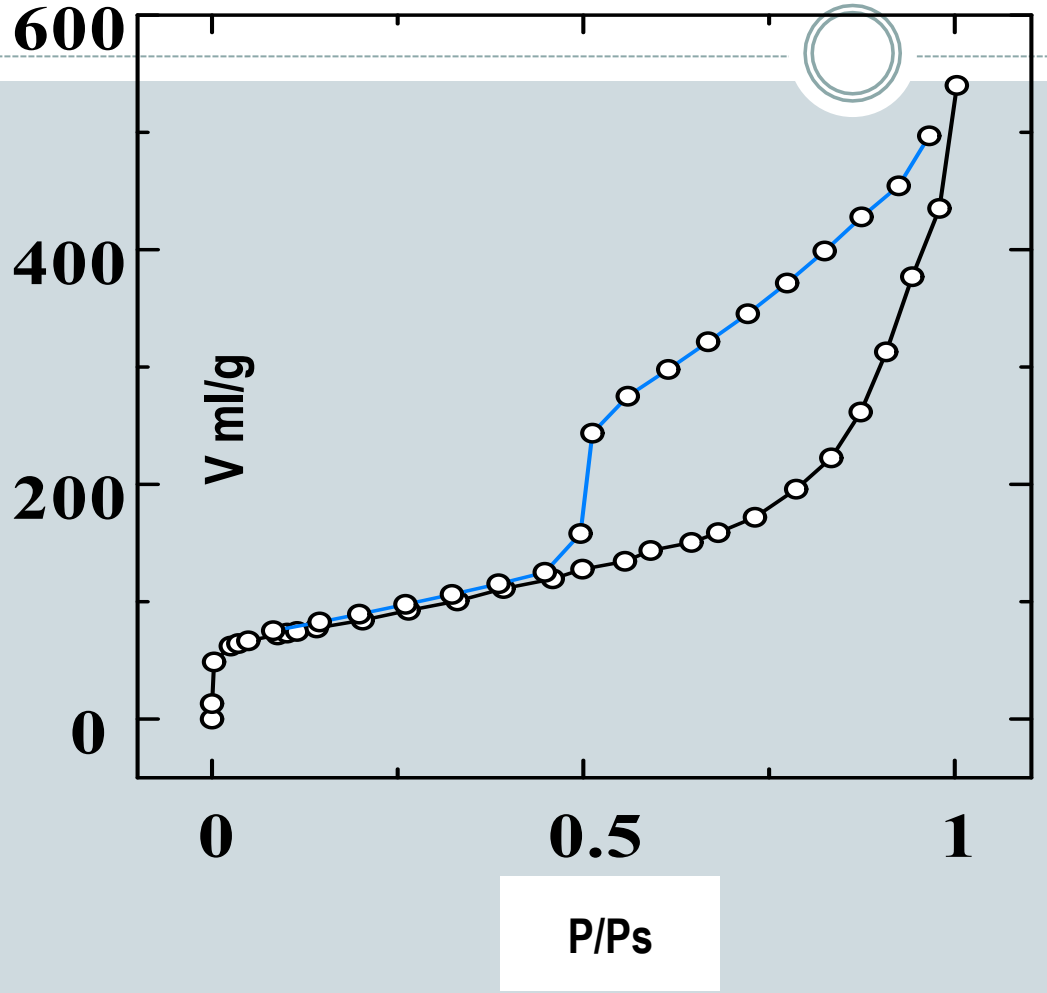


Closed packed surface area of original carbon fiber was hindered that the intercalate inserted into surface area of carbon fiber.

SEM micrograph of cross section morphology of carbon fiber

Prsented by Dr. Yoshida.

Surface characteristics of exfoilated pitch-based carbon fibers



Equipment: Autosorb-3-MP

Adsorbate: Nitrogen

Bath Temperature: 77K

ExCF (HTT3000)
13M HNO_3-1200*C*

BET: 292 m^2/g

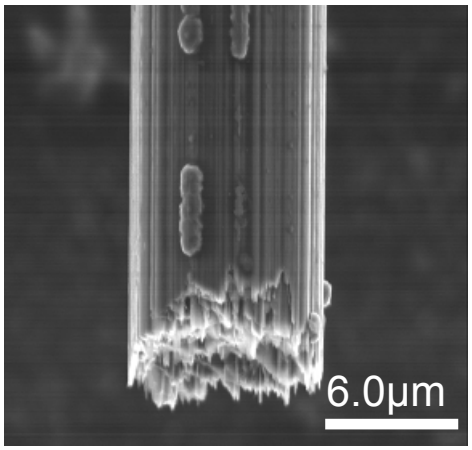
total cumulative volume: 10ml/g
(Hg porosimetory)

N_2 adsorption isotherm at 77K fot the ExCFs derived pitch-based carbon fibers

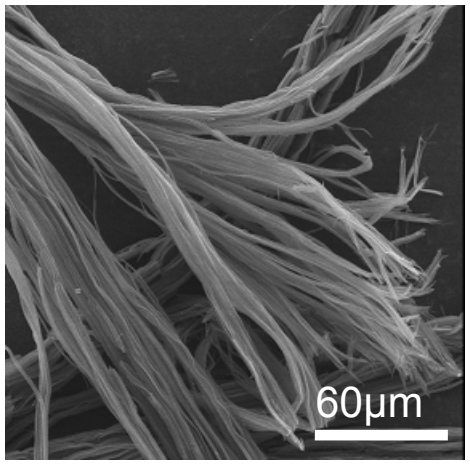
Application of ExCFs

- Electrode for capacitor
  - **Electric Double Layer Capacitor**
  - Li ion Battery
- Conductive materials
  - **Assistant materialsfor conductor**
- Base Material for composite
  - **Composite with plastics**
- **Support of medical materials**
- **etc..**

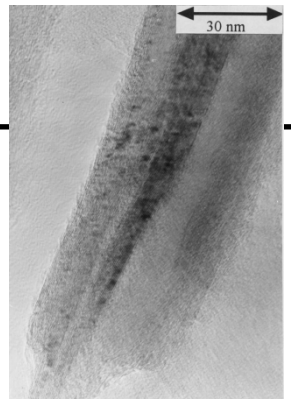
(Exfoliated Carbon Fibers : ExCFs)

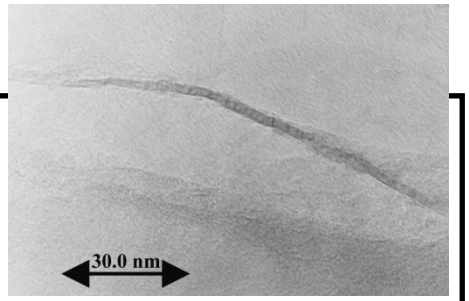


Morphology of CF monofilament



Morphology of ExCFs bundle of filament





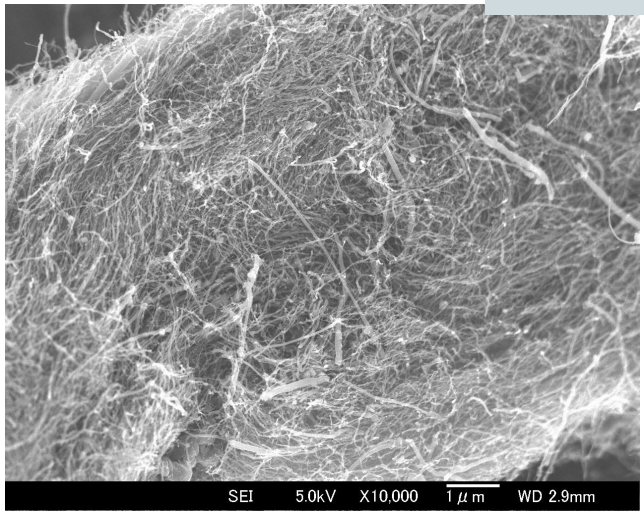
Advantages of ExCFs

- High conductivity
- Non-contamination
- High aspect ratio
- Dispersion is possible for the nanometer size
- Graphitization degree of the starting carbon fiber is maintained.

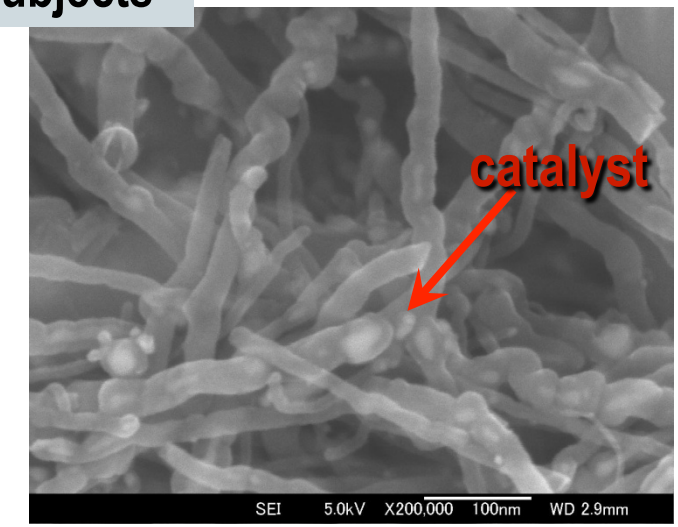
Nanometer sized carbon fibers (ExCFs and CNTs) reinforced plastics

CNTs have excellent mechanical properties. Therefore, it is possible to expect the advantage functional materials, when it was prepared with the plastics composite using excellent mechanical characteristic having CNT. However, it is difficult to perfectly disperse, because CNT are synthesized in the bundle state. And it is also impossible that CNT sufficiently demonstrates the effect compounded by the metal catalyst remaining after the synthesis.

Challenge subjects



Low maginification



High magnification

Morphology of carbon nano tubes

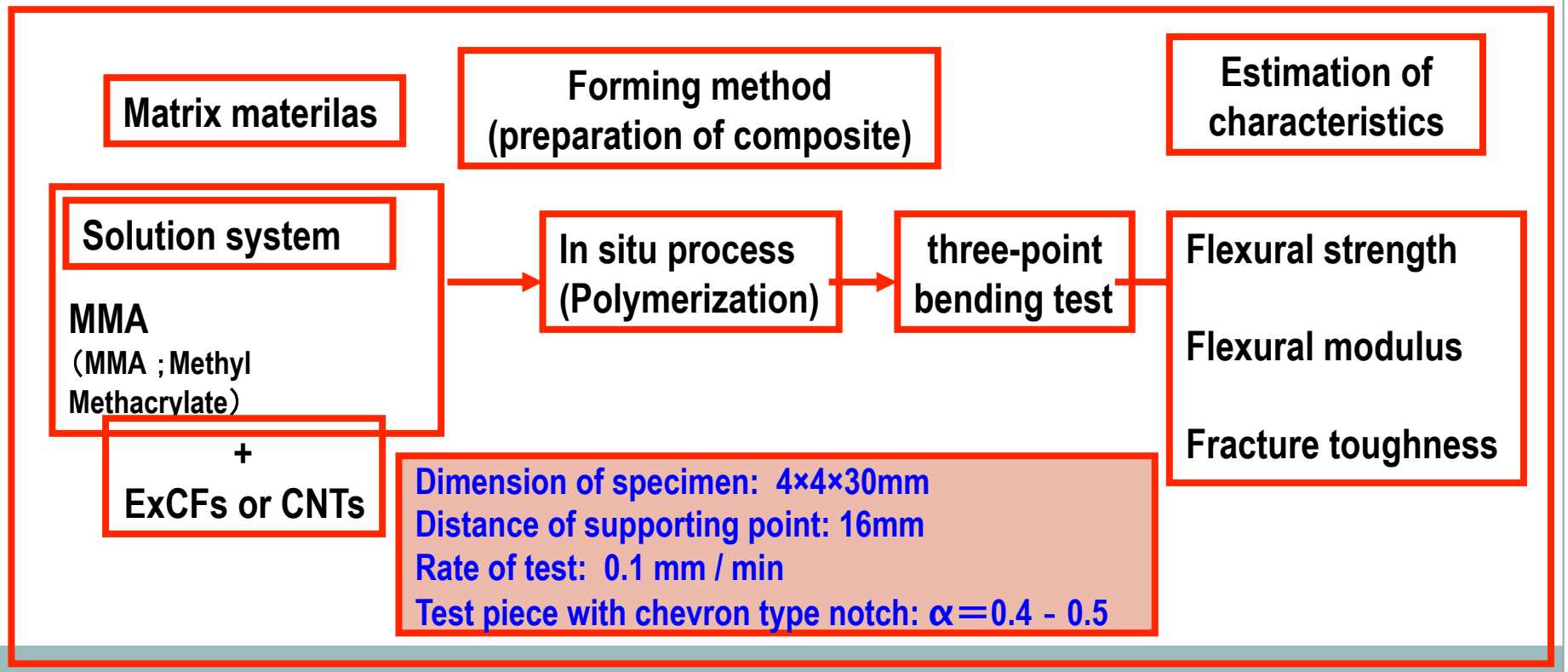
It is difficult to disperse to the monofilament, becasuse it is being synthesized in the bundle state.

The catalyst used for the synthesis becomes an impurity, and this removal and its operation is necessity.

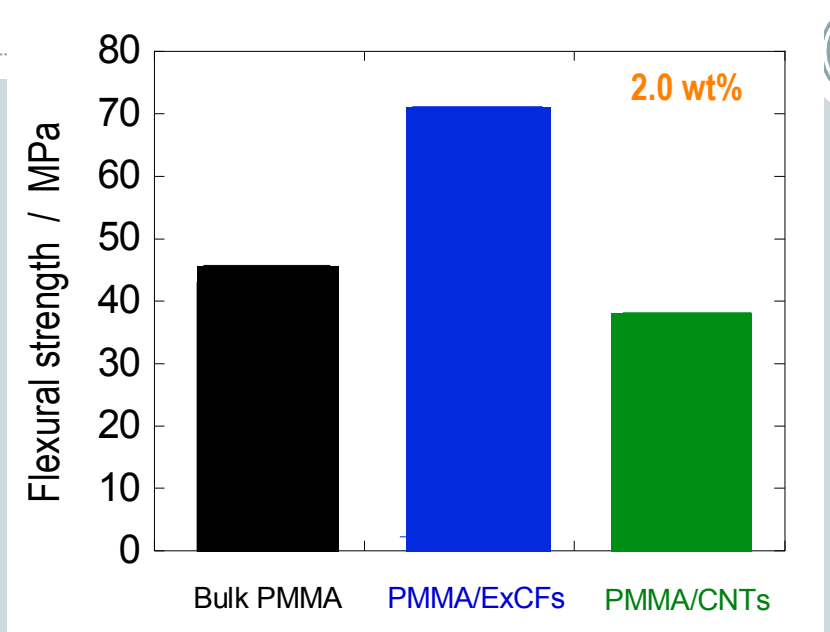
Purpose

1) Fabrication of exfoliated Carbon fibers rein forced plastics,
2) Investigation of mechanical properties and then possibility as a composite materials

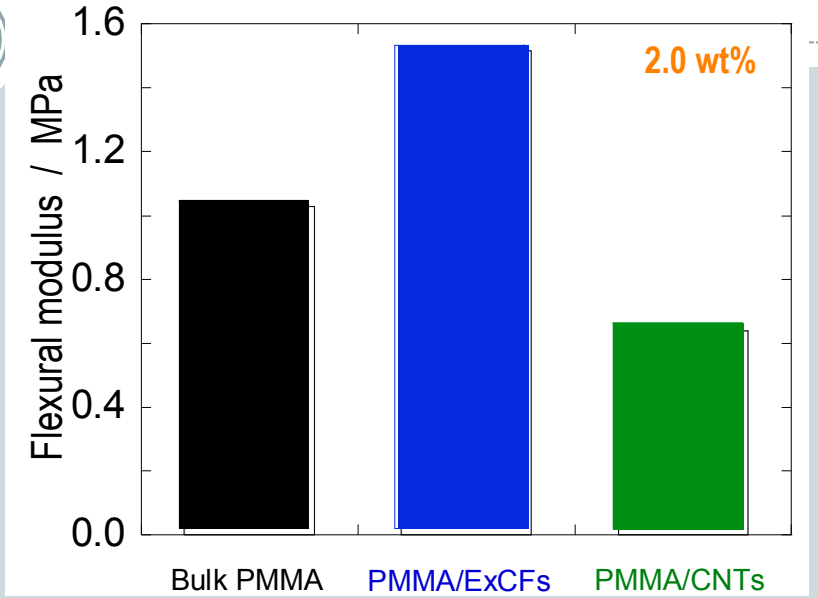
Experimental procedure



Effects of composite with ExCFs or CNTs



Comparison of flexural strength for Bulk PMMA, PMMA/ExCFs and PMMA/CNTs composites



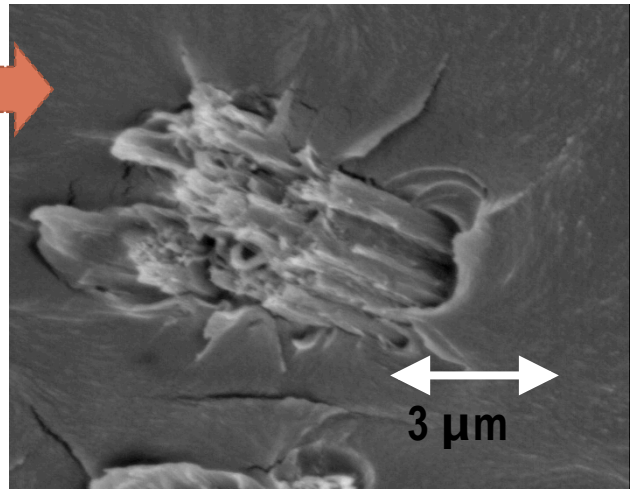
Comparison of flexural modulus for Bulk PMMA, PMMA/ExCFs and PMMA/CNTs composites

1) It was recognized that the flexural strength and modulus of PMMA were improved by addition of ExCFs.
2) Improvement of the flexural strength and modulus of PMMA by addition of CNTs could not be recognized and they were lowered.
3) The composite effect by the addition of CNTs were not obtained..

Characteristics of ExCFs and its composite effect

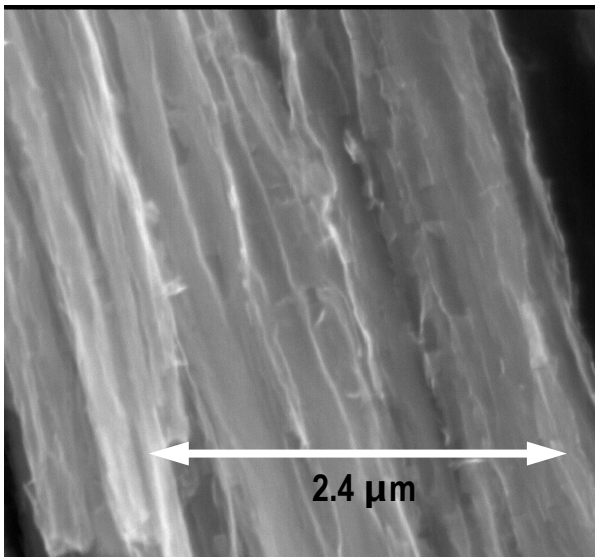
From observation of cross sectional morphology

Cross section with fracture of PMMA/ExCFs could not recognized pitfall.



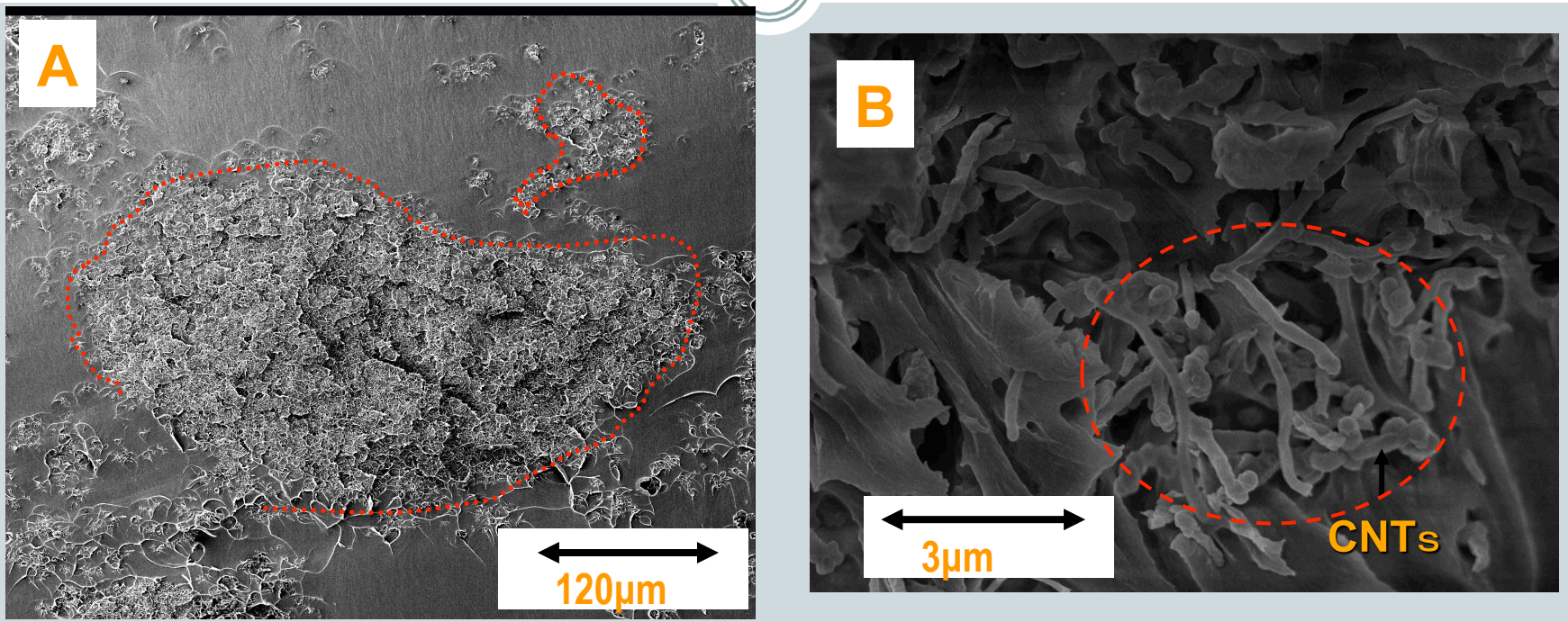
Cross sectional morphology of PMMA / ExCFs composite

It was judged that the surface area of ExCFs was around 300 m^2/g and its surface area is so rough, that is interface of fiber and matrix are so strong.



It was considered that large surface area of ExCFs and its unique surface morphology effectively reinforce the matrix.

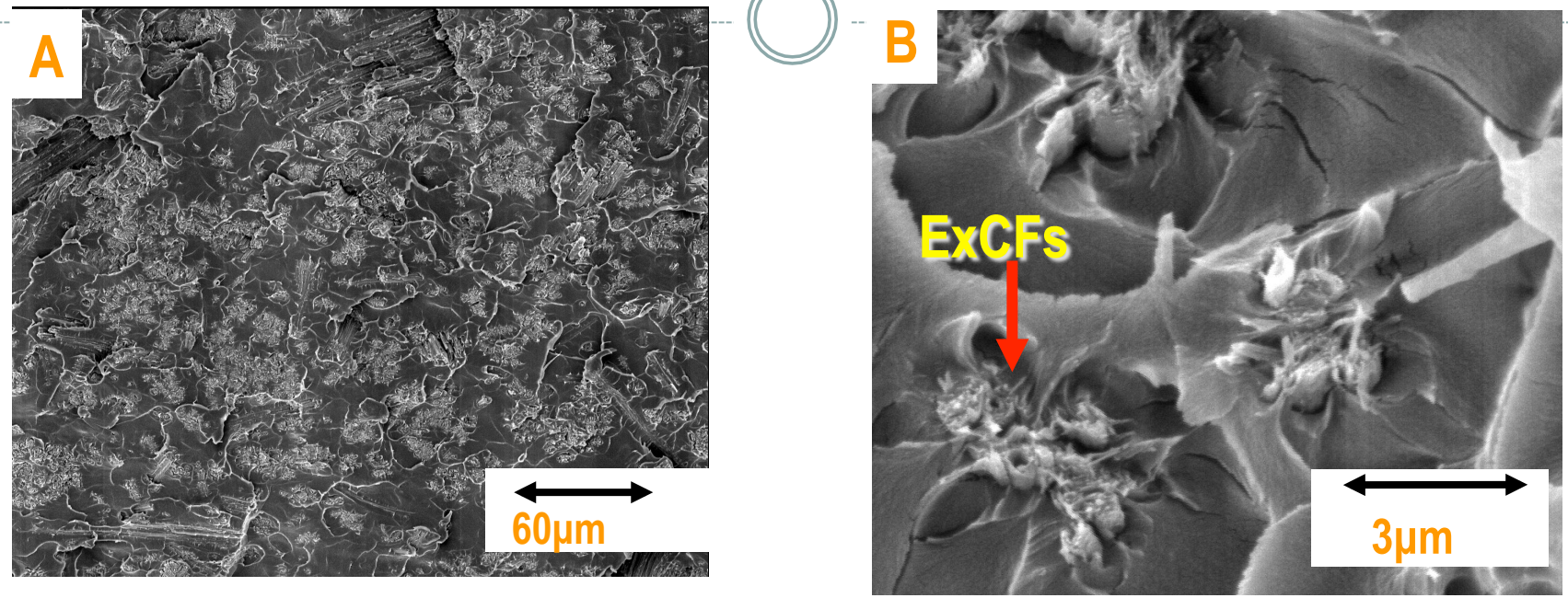
Cross sectional morphologies with fracture of PMMA/CNTs



Cross sectional morphology of PMMA / CNTs composite

Bundle structure having CNTs can not be easily released, therefore, the dispersion in monomer solution was impossible. Composite effect through addition of CNTs for PMMA could not be obtained, since aggregation of its fiber was generated. The stress is easy to concentrate in this void.

Cross sectional morphologies with fracture of PMMA/ExCFs



Cross sectional morphology of PMMA / ExCFs composite

Aggregation of ExCFs in PMMA could not be recognized in comparison with CNTs in it. The matrix was minutely being filled between ExCFs.

It was suggested that ExCFs is easy to be made to disperse further than CNTs, and the effect of reinforcement is also easy to be obtained.

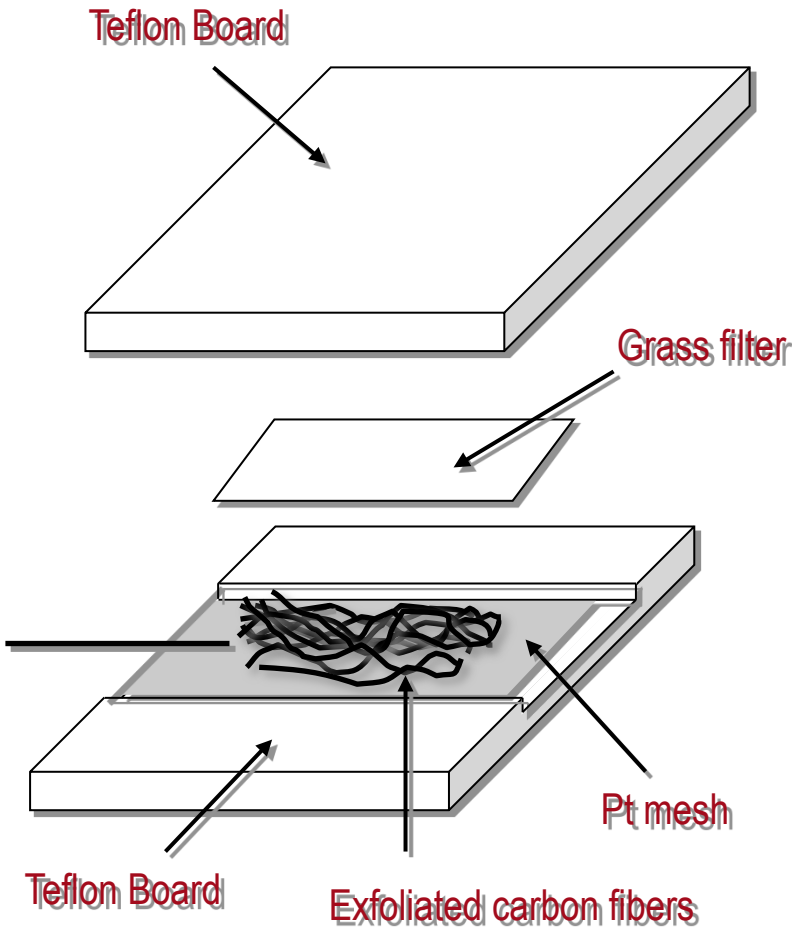
Possibility of composite by using ExCFs

- It is effective that ExCFs reinforces the matrix for the external stress.

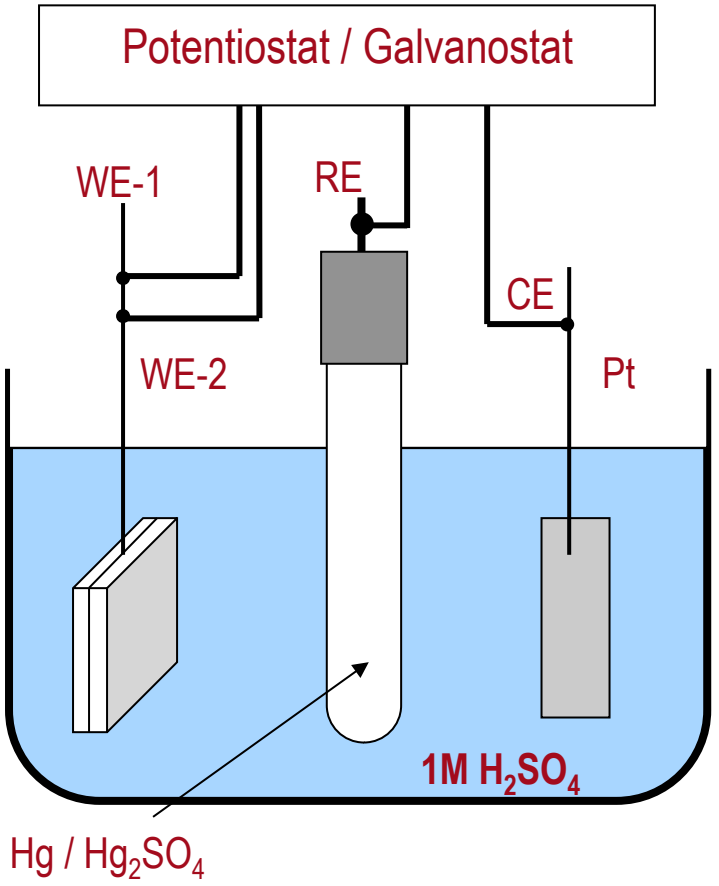
- It was considered that ExCFs is easy to be made to disperse in the matrix in comparison with CNTs, and reinforcement effect is easy to be obtained.

It is suggested that ExCFs might be used for the composite.

Application of the exfoliated carbon fibers for the electrode of Electric double layer capacitor (EDLC)



Fixation of carbon fibers with Pt mesh into PTFE jig



WE-1: Working Electrode 1 CE: Counter Electrode

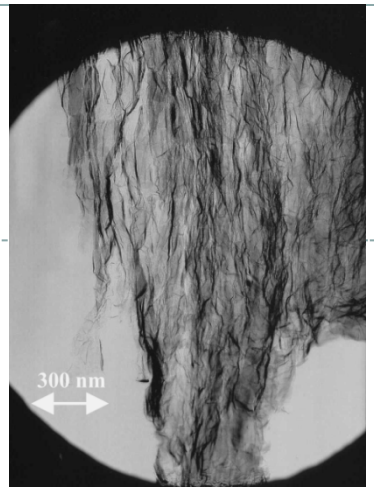
WE-2: Working Electrode 2 RE: Reference Electrode

Apparatus of cyclic voltamogram

Specific capacitance: Exfoliated Carbon Fibers (ExCFs), Activated Carbon (AC) and Activated Carbon Fibers (ACF)

	ExCFs	AC	ACF
S_{BET} [m^2/g]	295	1484	1950
C [F/g] in 1M H_2SO_4	117	80	143
C [F/g] in 18M H_2SO_4	555	146	186

Model of cyclic voltammogram of ExCFs in conc. H_2SO_4



Low magnification

Graphite layer observed by TEM

Intercalation

Electric double layer

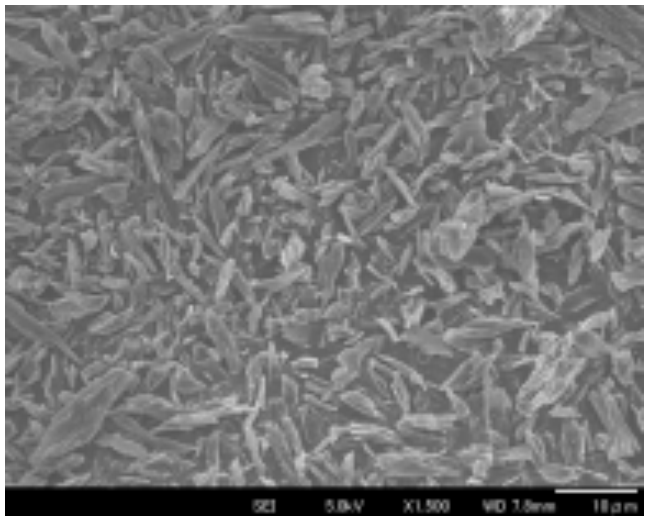
Current

-0.5

0.5

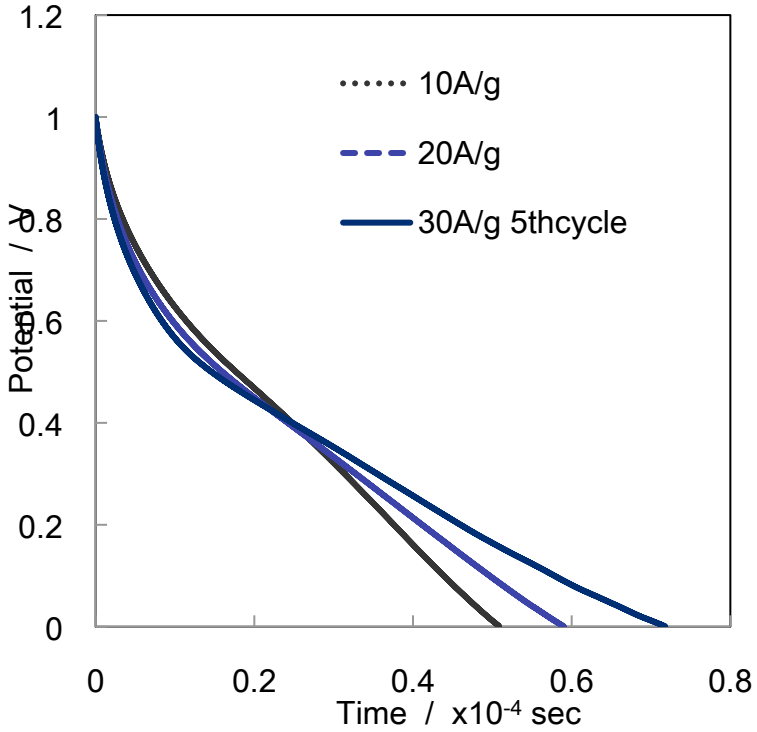
Potential

Application of the exfoliated carbon fibers for the Electric double layer capacitor (EDLC)



After exfoliation of the PAN-based carbon fibers

Capacitance = 500 F/g



Charge/discharge characteristics of exfoliated carbon fibers in 40% H_2SO_4 electrolyte with scan rate of 1mV/s

Conclusion

- Exfoliated carbon fibers derived from PAN-based carbon fibers have shown high specific capacitance for EDLC electrode such as 500 F/g in 40% H_2SO_4.

- Miniaturization and exfoliation of carbon fibers through electrochemical processing might be expected as an electrode materials to the energy storage and fiber rein forced plastics, though optimization is necessary.

- Thank you very much for your kind attentions

- Sagol

- This works partly supported bt Research and Development of Nanodevices for Practical Utilization of Nanotechnology Program in2008 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.