第6講義

低温型燃料電池と炭素材

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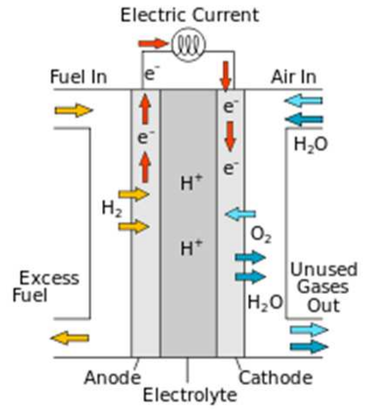
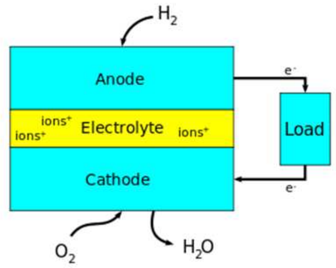
燃料電池の仕組み



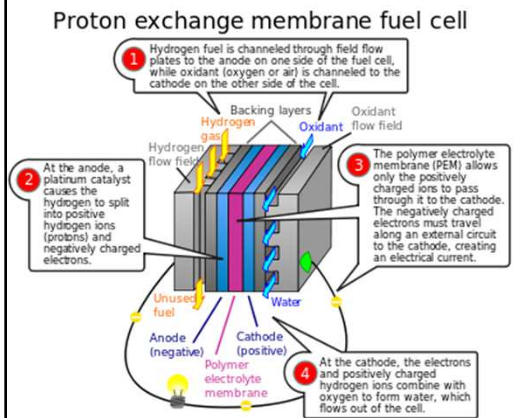
燃料電池のプロトン伝導性のスキーム

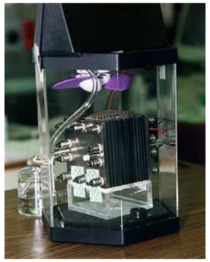


燃料電池のブロック図

高効率
低CO_2排出

水素燃料電池

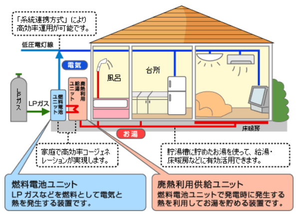




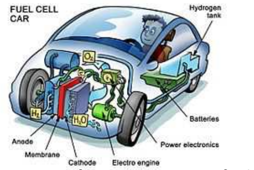
ダイレクトメタノール型燃料電池の実証モデル

高温の建設PEMFC：バイポーラプレートなどの電極導電性から製造に粉砕されたガス流路構造を有する複合材料（で強化グラファイト、カーボンブラック、炭素繊維、及び/又はカーボンナノチューブより伝導率のために）; [12] ポーラスカーボンペーパーであり、通常で反応層、ポリマー膜が適用され、高分子膜

燃料電池の商業化



家庭用燃料電池設置画像



Configuration of components in a fuel cell car

自立運転機能付き**家庭用燃料電池**
「エネファーム」

Toyota FCHV PEM FC fuel cell vehicle

代表的低温型燃料電池の電極反応

AFCとPEFCの電極反応

アノード：$H_2 + OH^- \rightarrow 2H_2O + 2e$

カソード：$O_2 + 2H2O + 4e \rightarrow 4OH^-$

DMFCの電極反応

アノード：$CH_3OH + H_2O \rightarrow 6H^+ + CO_2 + 6e$

カソード：$6H^+ + 3/2O_2 + 6e \rightarrow 3H_2O$

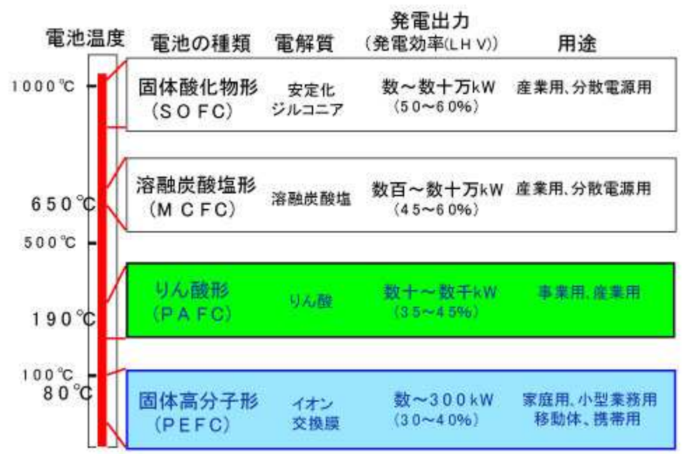
PAFCとPEFCの電極反応

アノード（燃料極）： $H_2 \rightarrow 2H^+ + 2e$

カソード（空気極）： $1/2O_2 + 2H^+ + 2e \rightarrow H_2O$

燃料電池タイプの比較

燃料電池の名前	電解質	修飾電力（W）	作業温度（℃）	効率（セル）	効率性（システム）	ステータス	コスト（米ドル/kW）の
空気亜鉛電池	アルカリ水溶液					量産	
再生燃料電池	高分子膜（アイオノマー）					商用/研究	
アルカリ型燃料電池	アルカリ水溶液	10 – 100キロワット		から70パーセント	62パーセント	商用/研究	
ダイレクトメタノール型燃料電池	高分子膜（アイオノマー）	100 MW – キロワット	から120	から30パーセント	から20パーセント	商用/研究	125
直接エタノール燃料電池	高分子膜（アイオノマー）	MW / cm²の	25 ? 90から120			研究	
プロトン交換膜燃料電池	高分子膜（アイオノマー）	100W – 500kWの	から120（ナフィオン） 125から220（PBI）	から70パーセント	から50パーセント	商用/研究	50から100
りん酸形燃料電池	溶融したリン酸（H_3PO_4）	メガワット	から200	55パーセント	パーセント CO-GEN：90%	商用/研究	4から4.50
溶融炭酸塩型燃料電池	溶融アルカリ炭酸塩	メガワット	から650	55パーセント	47パーセント	商用/研究	
管状の固体酸化物形燃料電池（TSOFC）	O^{2-}セラミック伝導酸化物を	メガワット	から1100	から65パーセント	から60パーセント	商用/研究	
プロトン性セラミック燃料電池	H^+伝導性セラミックス酸化物		700			研究	
ダイレクトカーボン燃料電池	いくつかの異なる		から850	80パーセント	70パーセント	商用/研究	



U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

FUEL CELL TECHNOLOGIES PROGRAM

Comparison of Fuel Cell Technologies

Fuel Cell Type	Common Electrolyte	Operating Temperature	Typical Stack Size	Efficiency	Applications	Advantages	Disadvantages
Polymer Electrolyte Membrane (PEM)	Perfluoro sulfonic acid	50-100°C 122-212° typically 80°C	<1kW-100kW	60% transportation 35% stationary	• Backup power • Portable power • Distributed generation • Transporation • Specialty vehicles	• Solid electrolyte reduces corrosion & electrolyte management problems • Low temperature • Quick start-up	• Expensive catalysts • Sensitive to fuel impurities • Low temperature waste heat
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90-100°C 194-212°F	10-100 kW	60%	• Military • Space	• Cathode reaction faster in alkaline electrolyte, leads to high performance • Low cost components	• Sensitive to CO_2 in fuel and air • Electrolyte management
Phosphoric Acid (PAFC)	Phosphoric acid soaked in a matrix	150-200°C 302-392°F	400 kW 100 kW module	40%	• Distributed generation	• Higher temperature enables CHP • Increased tolerance to fuel impurities	• Pt catalyst • Long start up time • Low current and power
Molten Carbonate (MCFC)	Solution of lithium, sodium, and/or potassium carbonates, soaked in a matrix	600-700°C 1112-1292°F	300 kW-3 MW 300 kW module	45-50%	• Electric utility • Distributed generation	• High efficiency • Fuel flexibility • Can use a variety of catalysts • Suitable for CHP	• High temperature corrosion and breakdown of cell components • Long start up time • Low power density
Solid Oxide (SOFC)	Yttria stabilized zirconia	700-1000°C 1202-1832°F	1 kW-2 MW	60%	• Auxiliary power • Electric utility • Distributed generation	• High efficiency • Fuel flexibility • Can use a variety of catalysts • Solid electrolyte • Suitable for CHP & CHHP • Hybrid/GT cycle	• High temperature corrosion and breakdown of cell components • High temperature operation requires long start up time and limits

For More Information

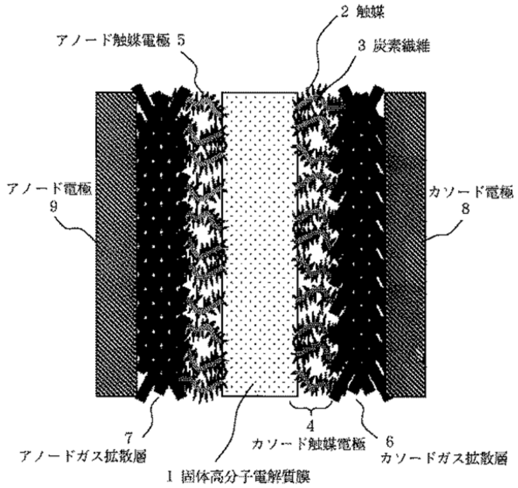
More information on the Fuel Cell Technologies Program is available at http://www.hydrogenandfuelcells.energy.gov.

U.S. DEPARTMENT OF ENERGY
Energy Efficiency & Renewable Energy

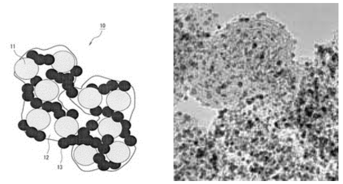
EERE Information Center
1-877-EERE-INFO (1-877-337-3463)
www.eere.energy.gov/informationcenter

February 2011

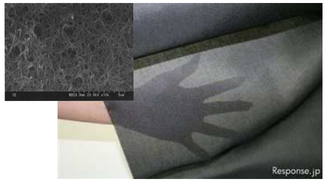
PEMFCの構造



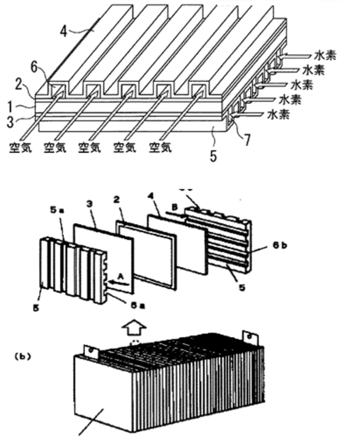
PEMFCに使用する炭素材



低温型燃料電池用触媒



低温型燃料電池用触媒支持体



低温型燃料電池用セパレータ

PEMFCに使用される炭素材の問題点

炭素材の種類	問題点	研究傾向
触媒(担体)	• 低活性 • 白金(高コスト)	• 担体の開発→CNT, CNF, Mesoporous carbon, etc. • 窒素含有カーボン • Fe-Co-Ni
触媒支持体	• 高電導度 • コスト	• CF-CNT/CNFの複合体 • ピッチ系炭素繊維 • その他
Separator	• 伝導性(電気・熱) • 腐食性 • 高コスト • 厚い	• 黒鉛・高分子複合体 • CNT/高分子複合体 • 鉄板(厚さ) • その他

Application and Optimization of CNF as a Catalyst Support for DMFC and PEMFC

Background

1. Carbon Black as catalytic supports for DMFC and PEMFC

CB has advantageous characteristics of high electric conductivity, high surface area, developed surface and proper kinds and amounts of functional groups, which are very suitable for the well-dispersion of precious metal. As CB has already attained the limitation for improving the catalytic activity, novel support material for higher catalytic activity should be necessary.

2. Nano-carbon as catalytic supports for DMFC and PEMFC

Carbon nanotube (CNT) and Carbon nanofiber (CNF) have been extensively studied as novel catalytic supports during last 2 decades.

3. CNF as a catalytic support for DMFC and PEMFC

Advantage and disadvantage of CNF
➢ Advantage : Various structures and surface, higher crystallinity, Higher electric conductivity, Surface edges
➢ Disadvantage : Low surface area, low dispersion property, small functional groups

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Objective

Research Objective

Optimized application of CNF as high performance catalytic supports for DMFC and PEMFC

- ➠ 2 Examination of various CNFs as catalyst supports for DMFC
- ➠ 3 Introduction mesopores to CNF for improving the catalytic activity for DMFC
- ➠ 4 Improving the dispersion of small CNFs for improving catalytic activity of DMFC using nano-dispersion machine
- ➠ 5 CNF compositeness on the surface of CB for improving the catalytic activity of DMFC
- ➠ 6 Hybridization of CNF and CB for obtaining the catalytic activity of PEMFC

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Catalysis for Sustainable Energy Production
Chapter 3. Selective Synthesis of Carbon Nanofibers as Better Catalyst Supports for Low-Temperature Fuel Cells,
S. Hong, M. Jun, I. Mochida, S. Yoon, Wiley-VCH, pp. 71-87, 2009

2. Application of CNFs for the catalytic supports of DMFC

✓ Examination of the effect of CNF structure on the catalytic activity for DMFC

Ref.) Seong-Ho Yoon et al. Carbon, 43, (2005), 1828–1838.

Preparation conditions	Tubular CNF	Platelet CNF	Herringbone CNF	
			Thick H-CNF	Thin H-CNF
Catalyst	Fe-Ni	Fe	Cu-Ni	Ni-MgO
Temp.(°C)	630	600	580	590
Gases	Co/H_2	Co/H_2	C_2H_4/H_2	C_2H_4/H_2

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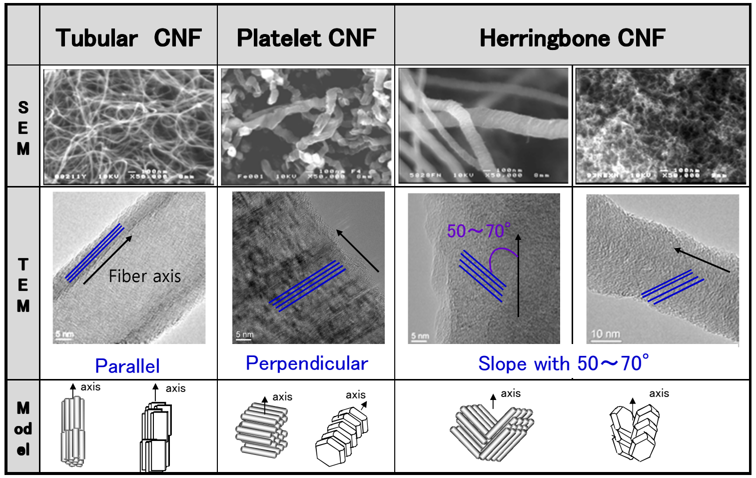
SEM and TEM images of various CNFs



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Characteristics of various CNFs

Structure		Tubular CNF	Platelet CNF	Herringbone CNF	
Code		T-CNF	P-CNF	Thick H-CNF	Thin H-CNF
Diameter (nm)		40-60	100-250	150-350	10-60
XRD	Lc (002) (nm)	13	30	3	7
	d_{002} (Å)	3.37	3.36	3.45	3.42
N_2-BET SA (m^2/g)		90	90	250	98

Thick H-CNF showed largest surface area。

Preparations of catalyst and electrode for DMFC

Reference for catalyst preparation

①Adams and Schriner method (J. Am. Chem. Soc, 45, 2171-2179, (1923).)
Red: $NaNO_3$、Temperature: 300℃

②Ethylene glycol reduction method (J. Am. Chem. Soc, 126, 8028-8037, (2004).)
Red: $HOCH_2CH_2OH$、Temperature: 160℃

③Formaldehyde reduction method (Catalysis Today, 93-95, 523-528, (2004).)
Red: HCHO、Temperature: 90℃

④Borohydride method (2000 Fuel Cell Seminar, 167, (2000).)
Red: $NaBH_4$、Temperature: 25℃

Preparation of catalyst and electrode

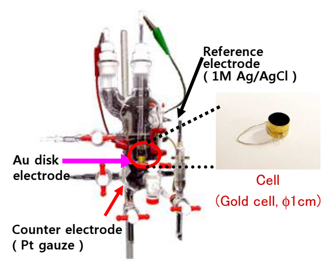
- CNF + H_2O
  - ← $RuCl_3$-xH_2O + H_2O
  - ← H_2PtCl_6-6H_2O + H_2O
  - ← 0.25M $NaBH_4$
- Washing and Filtering
- Drying at 80℃
  - ← Nafion Ionomer + H_2O
- Brushing on Carbon Paper
- Preparation of MEA

MEA : Membrane Electrode Assembly

Half and single cell tests

Methanol oxidation activity of catalysts

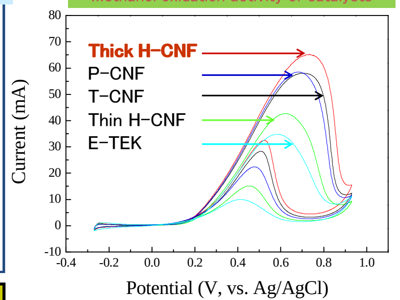
Composition of half cell



Pt-Ru amounts	Pt	Ru	C
40wt% 0.3mg Slurry	0.08	0.04	0.18
60wt% 0.3mg Slurry	0.12	0.06	0.1

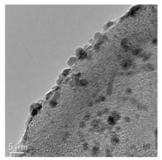
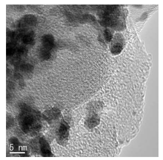
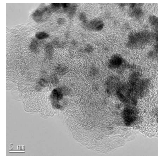
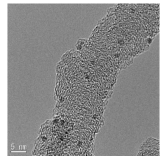
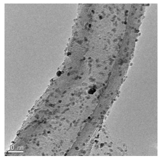
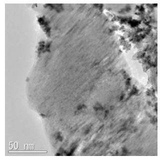
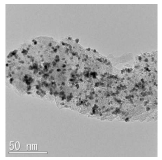
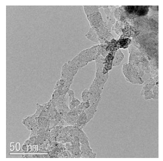
✓ Pt:Ru (1mol:1mol)
✓ Total catalyst amount for whole electrodes

Methanol oxidation activity of catalysts



1 Catalyst
-40wt%Pt-Ru/CNF
-Reference (E-TEK): 60wt%Pt-Ru/C
2 Electrolyte
-1mol MeOH + 1mol H_2SO_4
3. Temperature: 25℃

TEM images of catalysts (40wt%PtRu)

T-CNF (40wt%)	P-CNF (40wt%)	Thick H-CNF (40wt%)	Thin H-CNF (40wt%)
			
			

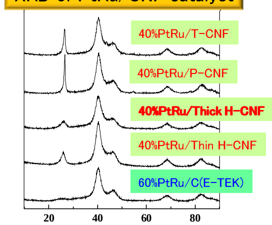
T-CNF and Thick H-CNF showed higher dispersion compared to P-CNF and thin H-CNF

Measurement conditions for half cell

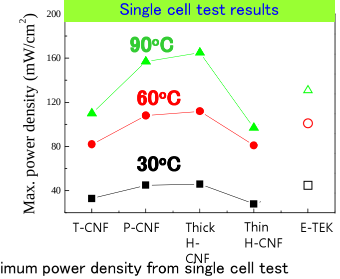
	Containing amounts of precious metals	Slurry amounts (mg/cm²)	Pt	Ru	C
			(mg/cm²)		
Catalyst amount	−Reference catalyst− Commercial **60%PtRu/C** ✓E-TEK **(E-TEK)** ✓Johnson Matthey **(JM)**	5	2	1	2
	−Catalyst− **40% PtRu/CNF**	5	1.33	0.67	3
Electrode size	2.5×2.5 cm²				
MEA	Electrolyte membrane	Nafion 115			
	Pressure	100 kg/cm²			
	Temperature	135℃、10分			
Flow rate	Anode : 2M メタノール (2 ml/min)				
	Cathode Oxygen (200 ml/min)				

XRD analysis and single cell test of catalyst

XRD of PtRu/CNF catalyst



Single cell test results



➢ PtRu particle size from XRD and maximum power density from single cell test

	PtRu particle サイズ (nm)	Maximum power density (mW/cm²)		
		30°C	60°C	90°C
40%PtRu/T-CNF	3.46	33	82	112
40%PtRu/P-CNF	3.35	52	108	157
40%PtRu/Thick H-CNF	**3.29**	**46**	**116**	**165**
40%PtRu/Thin H-CNF	3.42	28	81	98
60%PtRu/C(E-TEK)	2.96	41	112	140

Short summary

1. Thick H-CNF with many edges showed highest activity among the catalysts。

Higher surface area of H-CNF is needed for improving the catalytic activity

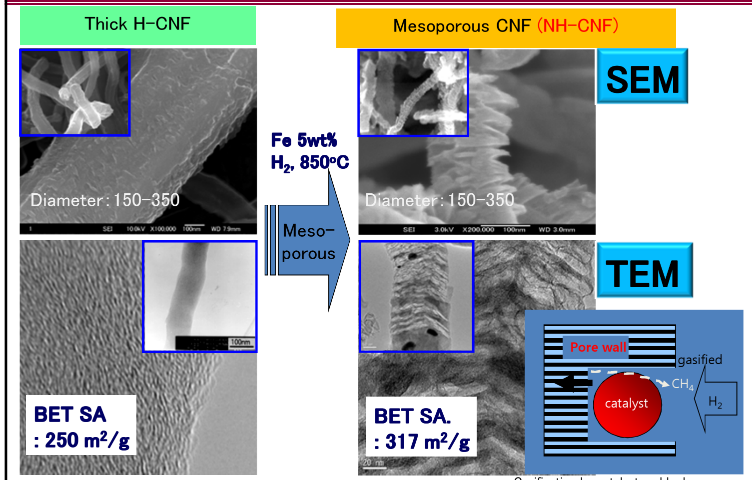
Increasing Surface area → Introduction of mesopores

Mesoporous CNF as a catalytic support for DMFC and PEMFC

✓ To improve the low surface area of CNF: introduction of mesopores to CNF

"Carbon nanofibers with radially oriented channels",
Lim S, Hong SH, Qiao WM, Whitehurst DD, Yoon SH, Mochida I, An B, Yokogawa K,
CARBON 45 (1): 173-179 JAN 2007.

SEM and TEM images of mesoporous CNF (NH-CNF)



Gasification by catalyst and hydrogen

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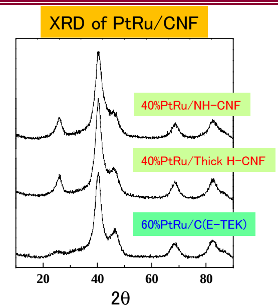
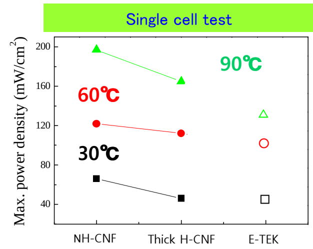
XRD analysis and single cell test





➢ PtRu particle size from XRD and maximum power density from single cell test

	PtRu particle size(nm)	Maximum power density (mW/cm²)		
		30°C	60°C	90°C
40%PtRu/ **(NH-CNF)**	3.13	66	122	197
40%PtRu/Thick H-CNF	3.39	46	112	165
60%PtRu/C(E-TEK)	2.96	45	102	113

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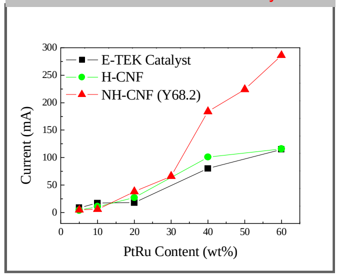
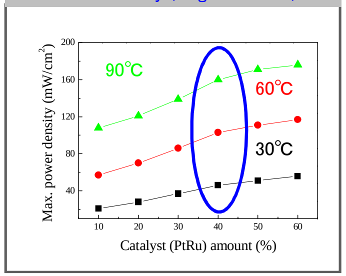
Effect of catalyst supporting amount

Methanol oxidation activity



Power density (single cell test)



Half cell tester

➢ Catalyst activity is saturated at 40 wt % supported。

➢ 40wt % supporting is settled.

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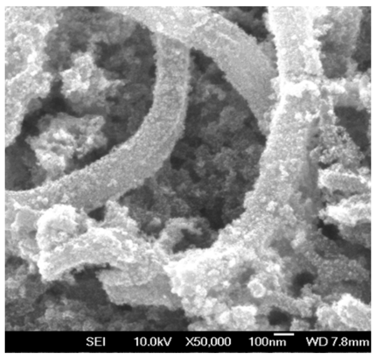
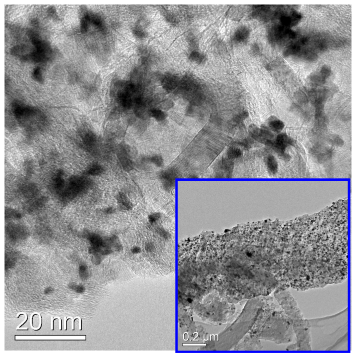
SEM and TEM images of PtRu40% supported NH-CNF

SEM



TEM



40% of catalysts are well dispersed on the surface of NH-CNF

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Short summary

1. NH-CNF was successfully obtained through the partial gasification of Thick H-CNF. NH-CNF showed higher surface area compared to thick H-CNF.

2. PtRu/NH-CNF showed higher oxidation activity of methanol compared to that of PtRu/thick H-CNF.

3. 40wt% of PtRu supporting is determined as most adequate for NH-CNF.

Increase of outer SA → Adoption of thin CNF

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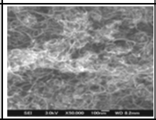
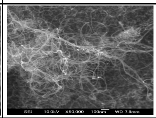
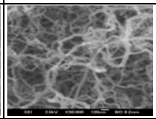
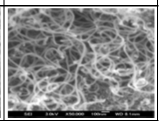
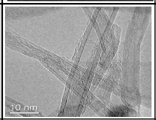
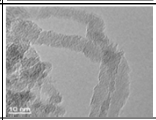
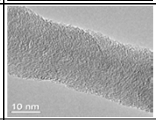
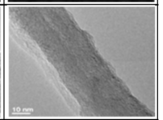
Thin CNF as a catalytic support for DMFC

- ✓ Smaller CNF (5-50nm) shows larger outer surface area, but small CNF shows agglomerated state which can be very difficult to disperse.
- ✓ Nano-dispersion machine was applied to disperse small CNF at first.
- ✓ Small CNF was used as catalyst support for DMFC

"Selective synthesis of thin carbon nanofibers: I. Over nickel-iron alloys supported on carbon black"
Carbon, 42, 1765-1781, 2004
Seongyop Lim, Seong-Ho Yoon, Yozo Korai and Isao Mochida
57. "Selective synthesis of thin carbon nanofibers: II. Over nickel-iron of nanoparticles prepared through burning of support", CARBON 42 (8-9): 1773-1781 2004, Lim S, Yoon SH, Mochida I

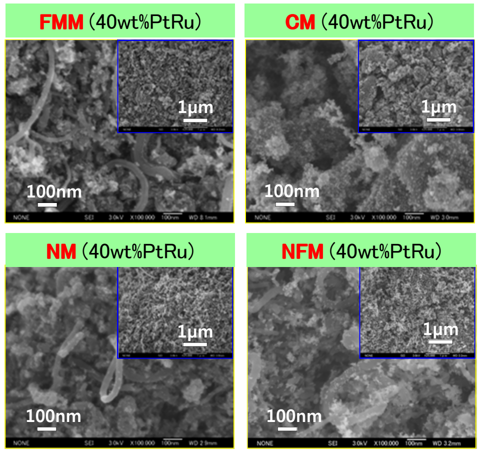
30

SEM and TEM images of various small CNFs

	FMM	CM	NM	NFM
Catalyst	Fe: Mo: MgO	Co: MgO	Ni: MgO	Ni: Fe: MgO
Diameter (nm)	5-15	7-20	10-60	20-50
SEM				
TEM				
Structure	**Tubular**	**Herringbone**	**Herringbone**	**Herringbone**
N_2-BET SA(m^2/g)	**275**	**247**	**98**	**111**

31

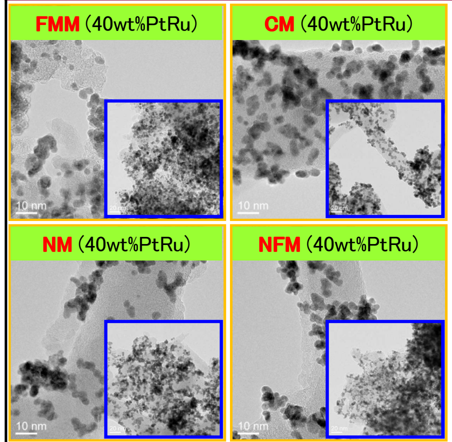
SEM images of PtRu supported various small CNFs



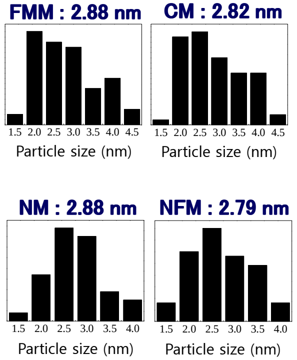
CM shows better dispersed state of PtRu compared to other CNFs

32

TEM images of PtRu supported various small CNFs



Particle size of PtRu



CM showed better dispersion of PtRu compared to other small CNFs and the particle size of PtRu was estimated by 2.79-2.88 nm.

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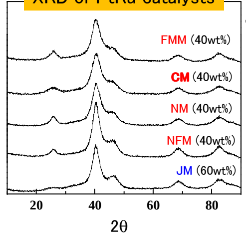
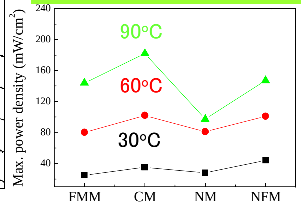
Activity evaluation of PtRu/small CNFs (Non-dispersed states)

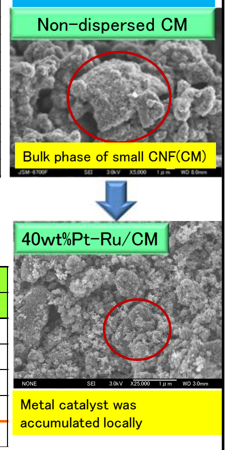
XRD of PtRu catalysts



Single cell test



SEM



➢ XRD analysis and maximum power density of PtRu/small CNFs (Non-dispersed states)

Sample (PtRu %)	PtRu particle size (nm)	Maximum power density (mW/cm²)		
		30°C	60°C	90°C
FMM (40wt%)	2.64	25	80	144
CM (40wt%)	2.63	**35**	**102**	**182**
NM (40wt%)	2.64	28	81	97
NFM (40wt%)	2.60	44	101	147
Jonson Matthey (60wt%)	2.80	55	121	162

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Improvement of dispersion state of small CNF by Nano-disperser

Problem of small CNF

➢ Small CNF has agglomerated state like a bulk phase which can not afford enough outer surface for the effective dispersion of PtRU.

Solution of problem

➢ Nano-dispersion machine is used for obtaining better dispersed state of small CNFs

Nano-disperser

✓Premix T.K.FILMICS 56-50 type

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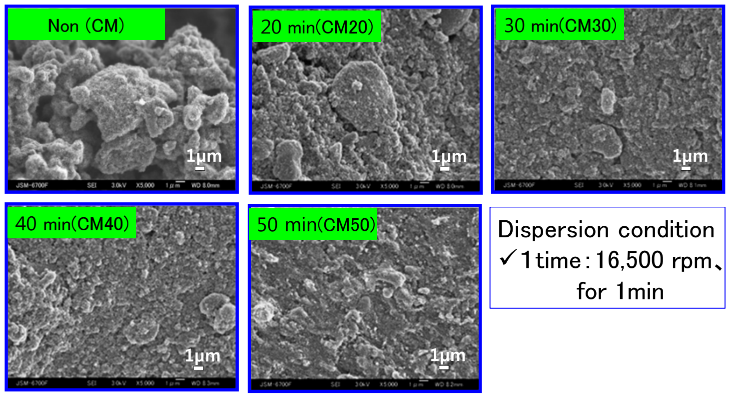
Dispersion effect of small CNF by nano-dispersion machine



Dispersion condition
✓1time : 16,500 rpm, for 1min

✓ Agglomerated size decreased with increasing the time of dispersion

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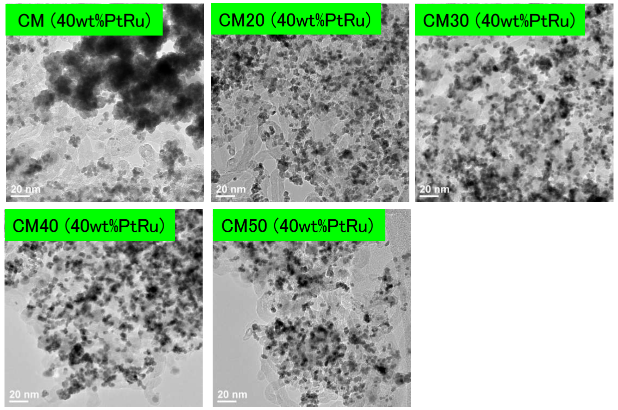
TEM images of PtRu/small CNF (Dispersed state)



Better PtRu dispersed state can be obtained with increasing CNF dispersion.

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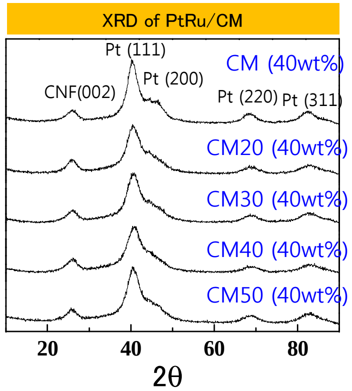
XRD analysis of PtRu/CM (Dispersed state)



➢Particle size of PtRu by XRD

Sample (PtRu %)	PtRu particle size (nm)
CM (40wt%)	2.63
CM 20 (40wt%)	2.14
CM 30 (40wt%)	2.28
CM 40 (40wt%)	2.16
CM 50 (40wt%)	2.29

Particle size of PtRu supported on the dispersed CM is smaller than non-dispersed CM

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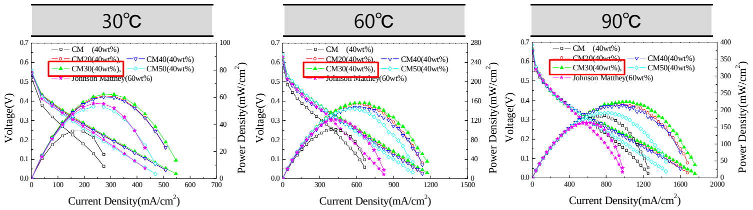
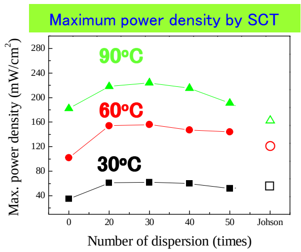
Single cell test of PtRu/CM (Dispersed state)





➢Maximum power density of PtRu/CM (dispersed state)

サンプル (PtRu%)	最大電力密度 (mW/cm²)		
	30℃	60℃	90℃
CM (40wt%)	35	102	182
CM 20 (40wt%)	61	154	218
CM 30 (40wt%)	**62**	**156**	**224**
CM 40 (40wt%)	60	147	215
CM 50 (40wt%)	52	144	191
Johnson Matthey (60wt%)	55	121	162

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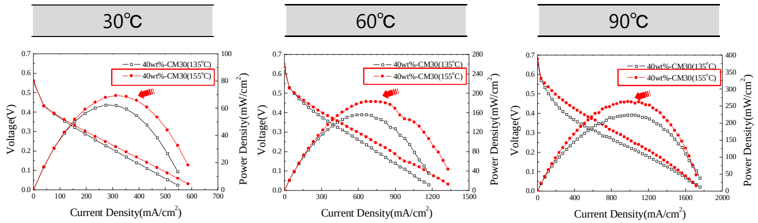
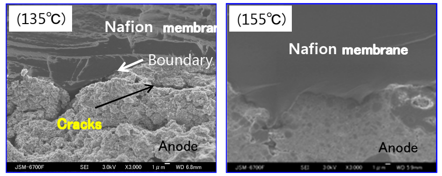
Improvement of MEA state of CM30(40wt% PtRu)



➢Maximum power density of CM30

➢(Effect of MEA preparation temperature

MEA temperature	Max. power density (mW/cm²)		
	30°C	60°C	90°C
135°C	62	156	224
155°C	69	183	262



MEA prepared at 135℃ showed cracks and defects in the boundary layers of catalyst and membrane, which can increase the resistance.

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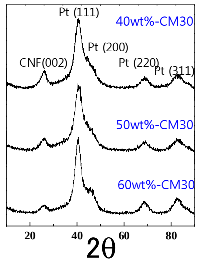
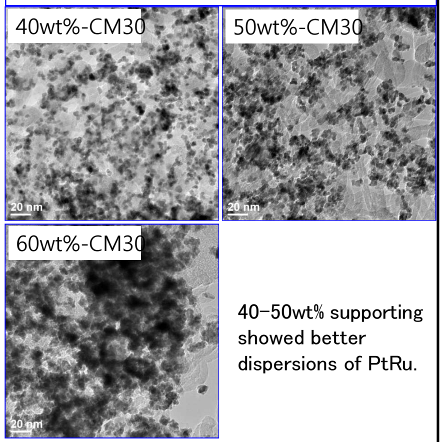
TEM images and XRD of CM30 catalysts

XRD of PtRu/CM30



TEM

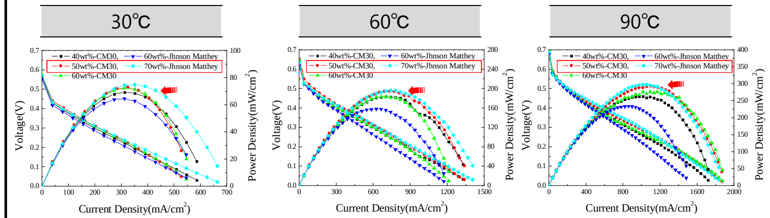


➢PtRu particle size of CM30 catalysts

PtRu %-CM 30	PtRu particle size (nm)
40wt%-CM 30	2.28
50wt%-CM 30	2.25
60wt%-CM 30	2.63

40–50wt% supporting showed better dispersions of PtRu.

Single cell test of PtRu/CM30



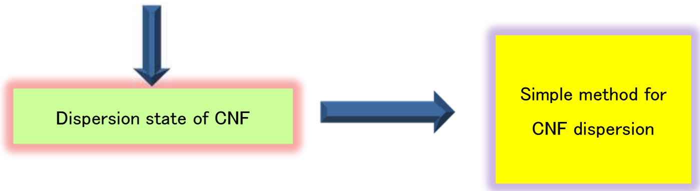
Maximum power density by single cell test

PtRuwt%	Maximum power density (mW/cm²)		
	30°C	60°C	90°C
40wt%-CM30	69	183	262
50wt%-CM30	72	194	292
60wt%-CM30	72	183	276
60wt%-Johnson Matthey	64	157	233
70wt%-Johnson Matthey	74	196	297

PtRu50%/CM showed the highest maximum power density which is very similar with commercial 70% JM catalyst.

Short summary

1. Various small CNFs were successfully prepared。
2. CM which showed relatively independent fiber coagulum has higher catalytic activity compared to FMM, NM and NFM.
3. The proper dispersion of CM (30) using nano-disperser improved the catalytic activity compared to non-dispersed state of CM.
4. CM(30) showed maximum power density of 72、194、292 mW/cm² at 30, 60, and 90℃, respectively.



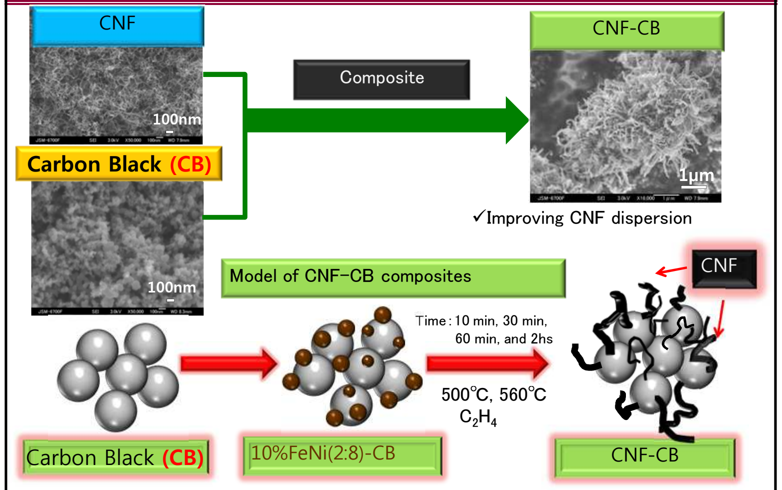
CNF composite as a catalytic support for DMFC

✓ The proper dispersion of small CNF was very effective to improve the catalytic activity using special type of nano-disperser.

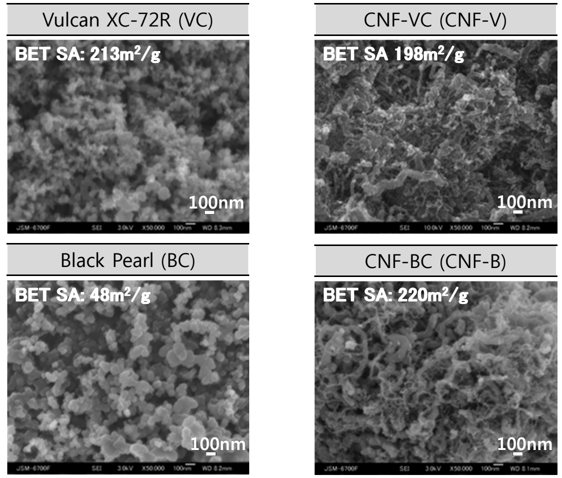
✓ Simple method to obtain well dispersed state of small CNF was tried through the introduction of CNF-CB compositeness

Electro catalytic Activity Enhancement of Fuel Cell Catalyst Supported by Carbon Nanofiber/Carbon Black Hierarchical Nanostructures, Mun-Suk Jun[1,2], Ruitao Lv[2,3], Jin Miyawaki[2], Isao Mochida[2], Feiyu Kang[3], Seong-Ho Yoon[2,*] paper submitted.

Compositeness of CNF & Carbon Black

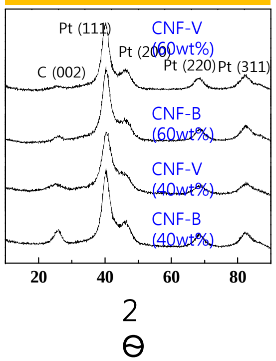


CNF-CB composites ➠ Preparation : 2hs, 500℃



XRD analysis of CNF-CB composites

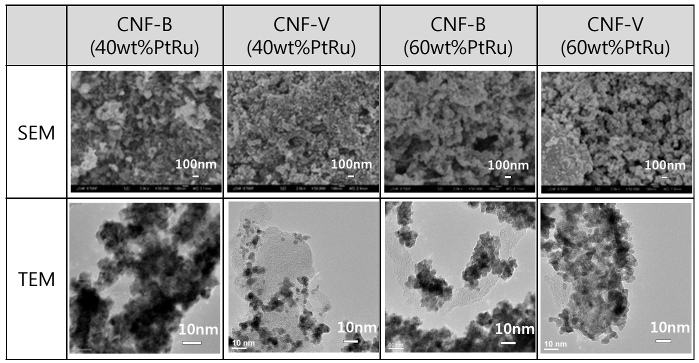
XRD of PtRu/CNF-CB



➢PtRu particle size of catalysts

サンプル (PtRu %)	PtRuの粒子サイズ (nm)
CNF-B (40wt%)	2.83
CNF-V (40wt%)	2.75
CNF-B (60wt%)	2.98
CNF-V (60wt%)	2.92

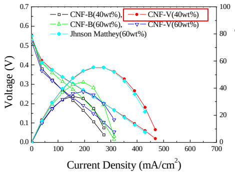
SEM & TEM images of PtRu/CNF-CB



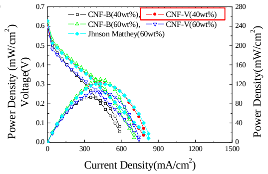
PtRu/CNF-CB showed many bulk phases in SEM images
PtRu/CNF-CB did not show well dispersed PtRu on the support surfaces.

Single cell test of PtRu/CNF–CB

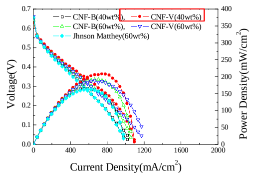
30℃



60℃



90℃

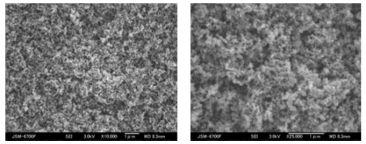


➢Maximum power density of PtRu/CNF–CB

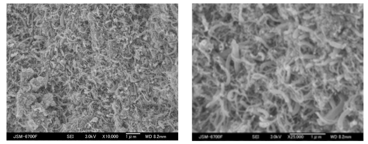
サンプル (PtRu %)	Maximum power density (mW/cm^2)		
	30°C	60°C	90°C
CNF–B (40wt%)	34	93	165
CNF–V (40wt%)	55	123	207
CNF–B (60wt%)	44	130	191
CNF–V (60wt%)	37	106	188
Johnson matthey (60wt%)	55	121	162

SEM images of CNF-VC composites

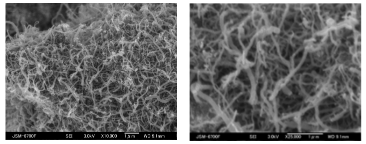
Vulcan XC–72R



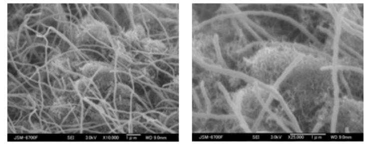
CNF growth time : **10 min**→CNF/VC=1/1 (w/w) **(CNF–V10)**



CNF growth time : **30min**→ CNF/VC=3/1 (w/w) **(CNF–V30)**



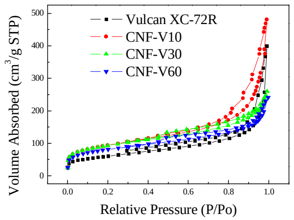
CNF growth time : **60 min**→ CNF/VC=5/1 (w/w) **(CNF–V60)**



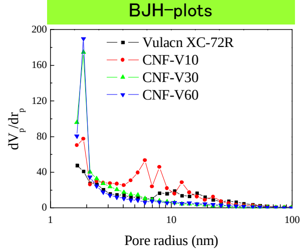
✓ CNF growth amount was successfully controlled by the control of growth time.
✓ Bulk phase of CNF showed after 60 min of the CNF growth time on CB surface.

SA and pore distribution of CNF–VC by N_2–BET

N_2 adsorption/desorption isotherms at 77K



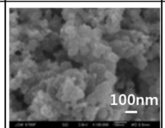
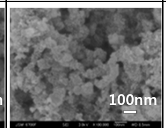
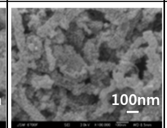
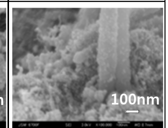
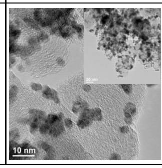
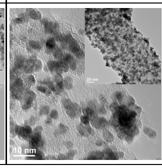
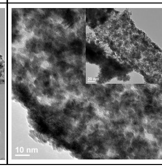
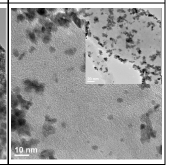
BJH-plots



CNF growth time	N_2-BET SA (m^2/g)	Total volume (cm^3/g)	Partial ratio of Pore volume	
			Mesopore (%)	Micropore (%)
Raw Vulcan XC-72R	213	0.61	87	13
CNF-V10	332	0.73	88	12
CNF-V30	328	0.39	74	26
CNF-V60	285	0.35	76	24

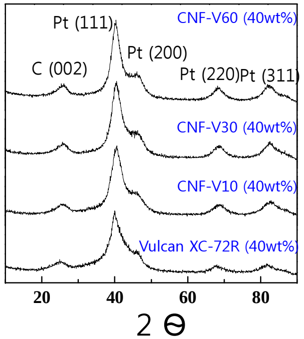
✓ Long CNF growth time triggered the bulk phase of CNFs

SEM & TEM images of CNF–V composites

	Vulcan XC-72R (40wt%PtRu)	CNF-V10 (40wt%PtRu)	CNF-V30 (40wt%PtRu)	CNF-V60 (40wt%PtRu)
SEM				
TEM				

XRD & TGA analyses of 40%PtRu/CNF-VC

XRD of PtRu/CNF-VC

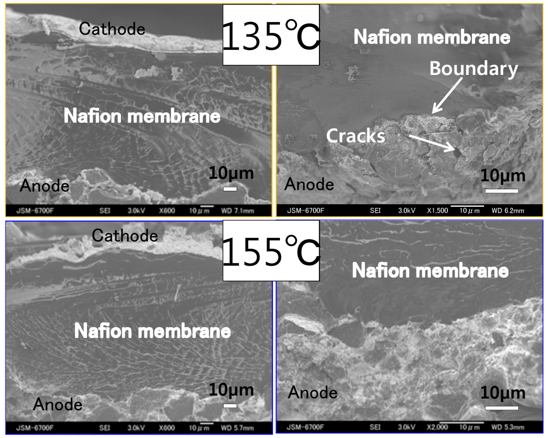


➢ Particle size of PtRu

サンプル (PtRu %)	PtRuの粒子サイズ (nm)
Vulcan XC-72R (40wt%)	2.97
CNF-V10 (40wt%)	2.33
CNF-V30 (40wt%)	2.77
CNF-V60 (40wt%)	2.91

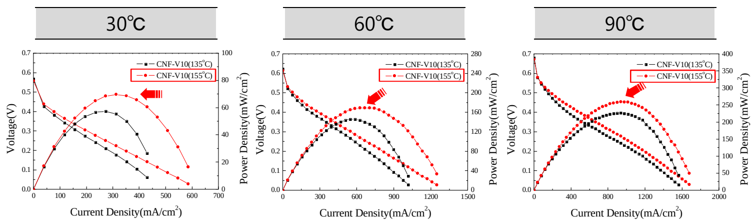
✓ The longer CNF growth time increased the particle size of PtRu

SEM images of MEA ➠ 40wt%PtRu/CNF-V10



MEA prepared at 135℃ showed some cracks in the layer boundary.

Single cell test ➠ 40wt%PtRu/CNF-V10



➢Maximum power density of PtRu/CNF-V10

MEA preparation	Max. power density(mW/cm²)		
	30°C	60°C	90°C
135°C	57	145	226
155°C	69	168	272

Short summary

1. CNF-CB composites were successfully prepared.
2. Too long CNF growth time caused bad effect to increase the CNF bulk phases, and resulted in increasing the catalyst particle size.
3. The optimization of CNF growth time improved the catalytic activity, and the CNF time of 10 min gave the maximum power density of 69, 168, 272 mW/cm² at 30, 60, and 90℃, respectively.

Mesoporous TCNF as a catalytic support for PEMFC

1. Very special type of mesoporous CNFs were produced by modified Hummer's method. Introduced mesopores can increase the surface area of basic CNF.
2. Catalytic activity of PEMFC was examined using such mesoporous CNFs

Meso-Channel Development in Graphitic Carbon Nanofibers with Various Structures, *Donghui Long[†,‡], Wei Li[†], Jin Miyawaki[†], Licheng Ling[‡], Isao Mochida[†], Seong-Ho Yoon[*,†], Paper is under review in ACS Nano*

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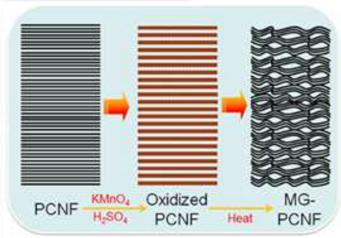
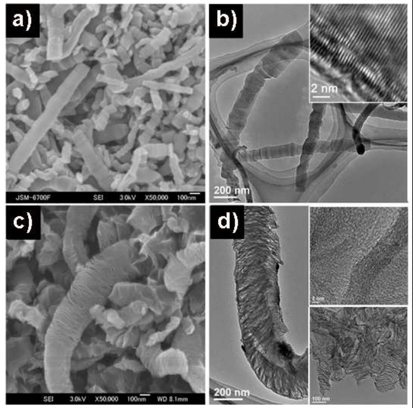
Development and control of mesopores in PCNFs

Introduction



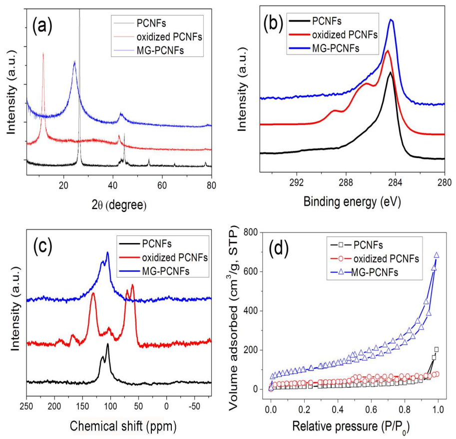


Objective

Developing a general method based on the oxidation and heat expansion to introduce the mesoporous channels into CNFs.

Development and control of mesopores in PCNFs

Structural evolution from PCNFs to mesoporous PCNFs

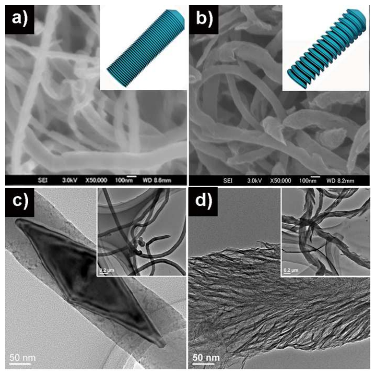


(1) Strong oxidation of CNFs caused large amounts of oxygen functional groups to be intercalated in the graphene layers, increasing the interlayer spacing.
(2) These intercalated components vaporized rapidly during the heat treatment, forcing apart adjacent graphene sheets and thus forming mesoporous channels.

(3) The porosity of mesoporous PCNFs could be adjusted by changing the oxidization degree of PCNFs. The BET surface areas and total pore volume were controlled in the range of 69-429 m2 g^{-1} and 0.2 to 1.35 cm^3 g^{-1}.

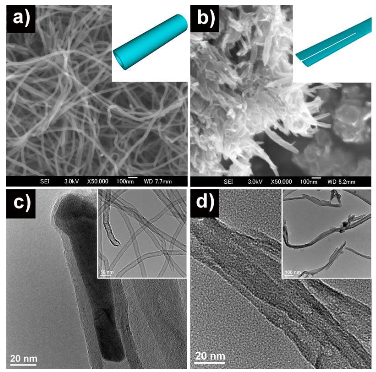
Development and control of mesopores in HCNFs and TCNFs

Mesoporous herringbone CNFs



BET surface area = 227 m^2 g^{-1}
total pore volume = 0.6 cm^3 g^{-1}

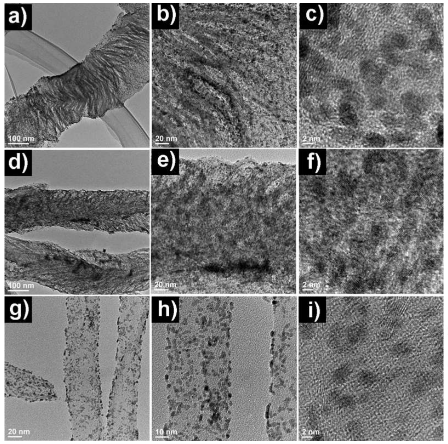
Mesoporous tubular CNFs

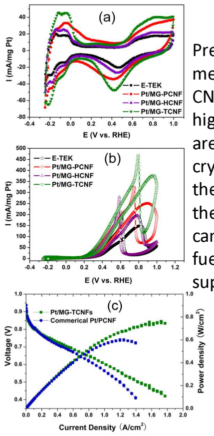


BET surface area = 168 m^2 g^{-1}
total pore volume = 0.35 cm^3 g^{-1}

Mesoporous CNFs as fuel cell supports

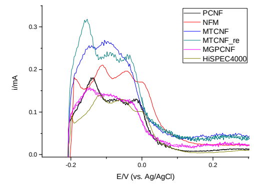
Mesoporous CNFs supported Pt nanoparticles as catalysts for fuel cell





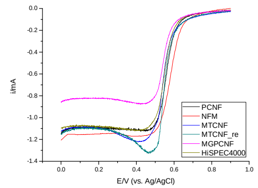
Prepared mesoporous CNFs exhibited high surface area and good crystallinity,so they will be the potential candidates for fuel cell catalyst supports.

Cyclovoltammometry and Oxygen Reduction Reaction



40% Pt	Pt 면적(m^2/g)
Pt/PCNF	71
Pt/NFM	95
Pt/MTCNF	129
Pt/MTCNF	120
Pt/MGPCNF	70
HiSPEC4000	64

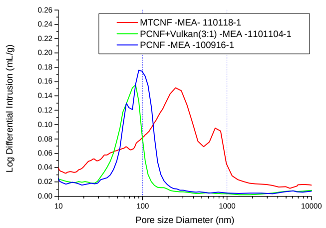
1) Preparation: Suntel, Polyol method (40%)
2) Pt surface increased very much.
3) Now under reproduction experiments

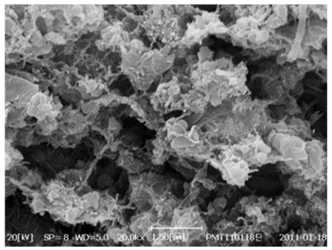


40% Pt	Onset (V)
Pt/PCNF	0.7048
Pt/NFM	0.7203
Pt/MTCNF	0.7109
Pt/MTCNF	0.7130
Pt/MGPCNF	0.6984
HiSPEC4000	0.6707

1) MGPCNF: large slope
2) Compared to Pt/NFM, Lower onset but large slope.

Pore distribution of MEA ➡ remains many improvement points





PCNF-CB hybridization as a catalytic support for PEMFC

1. Catalytic activity of PEMFC was examined using such mesoporous CNFs
2. Pt/(CNF+CB), Hybridization of CNF & CB was tried to optimize the pore distribution of MEA.

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Development of PCNF+CB Hybrid catalyst

PCNF as a catalyst support for PEMFC
- Low performance of MEA (Low utilization catalyst)
- Large pore distribution and low porosity
  Too sensitive to humidity of the cell inside

CNF (activity) + CB (Homogeneous small porosity)

Increasing the utilization of catalyst

Prohibition of the flooding of cell inside

Preparation of catalyst

Ball mill mixing of PCNF+Carbon black

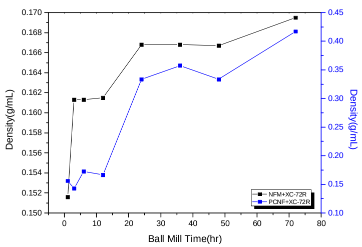
Mixing time control
- Tab density
- SEM
- Pore size and distribution
- Resistivity

Pt supporting
- Half cell, TEM

MEA Preparation and Test
- IV evaluation, Porosity

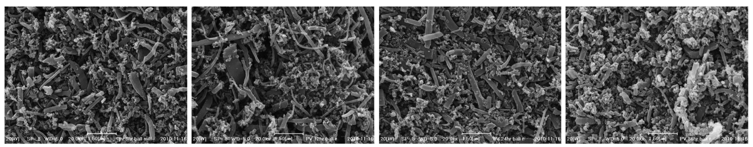
PCNF+CB Ball Mill Mixing

1) Tab density (5000 times, 3 time test)



Time	Tab density NFM+XC-72R	Tab density PCNF+XC-72R
1	0.1516	0.1563
3	0.1613	0.1429
6	0.1613	0.1726
12	0.1615	0.1667
24	0.1668	0.3336
36	0.1668	0.3576
48	0.1667	0.3337
72	0.1695	0.4173

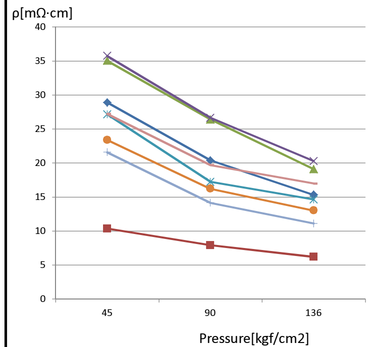
2) SEM

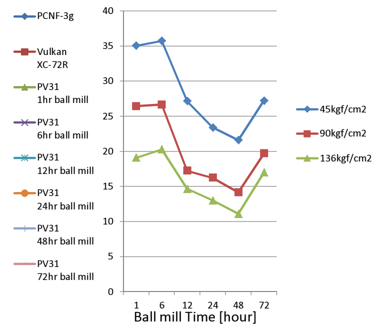


3hs **12hs** **24hs** **48hs**

PCNF+CB Ball Mill Mixing

3) Resistivity according to Pressure

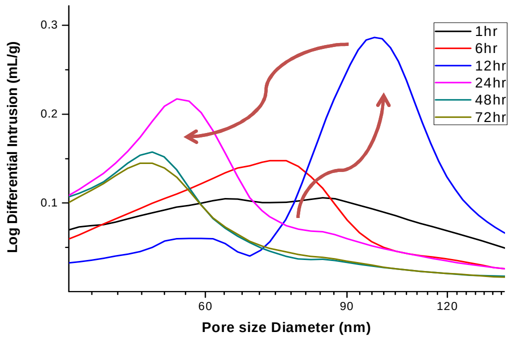




- **Resistivity was changed according to mixing time.**
- **12hs <Mixing time< 48hs (Optimized condition)**

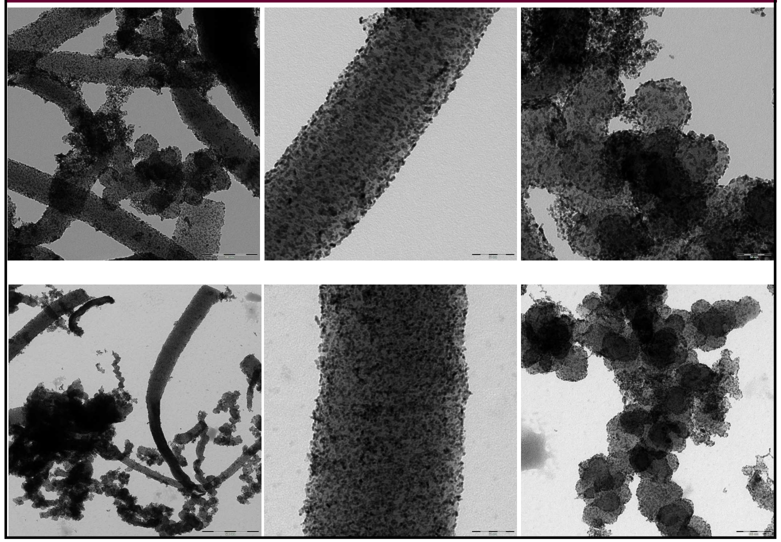
PCNF+CB Ball Mill Mixing

4) Porosity of electrode (Hg porosimeter)

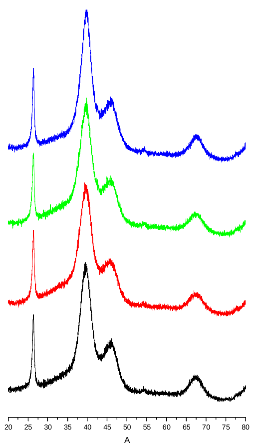


- **Porosity can control by the mixing time.**
- **12hs < Optimized porosity < 24hs**

TEM images of 40%Pt/PCNF+CB



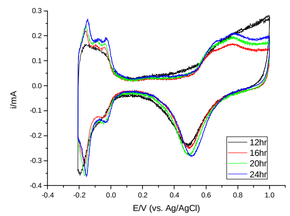
Preparation of 40%Pt/PCNF+CB

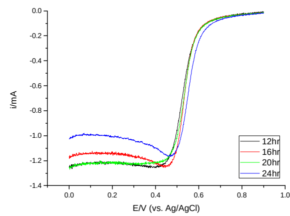


Sample Name	Size (XRD)	Size (TEM)
40% Pt on PV(12hr)_P110128 10g base	2.99	2.9
40% Pt on PV(16hr)_P110124-2 3g base	2.65	2.9
40% Pt on PV(20hr)_P110124-1 3g base	2.46	2.8
40% Pt on PV(24hr)_P101221-2 3g base	2.87	2.8

Preparation of 40%Pt/PCNF+CB

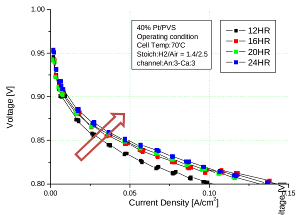
5) Half cell and single cell test(Mixing time: 16, 20 and 24hs)



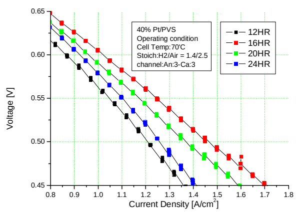


Mixing time	Pt SA [m2/g]	ORR(onset)	Comment
24 hs	107	0.7280 V	➢ TEM image ➢ The utilization of catalyst increased.
20 hs	95	0.7006 V	
16 hs	75	0.6976 V	
12 hs	72	0.6702V	

Evaluation of 40%Pt/PCNF+CB

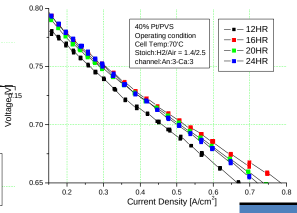


=> Catalytic activity



Time	Slope
24	-0.256
20	-0.242
16	-0.23
12	-0.259

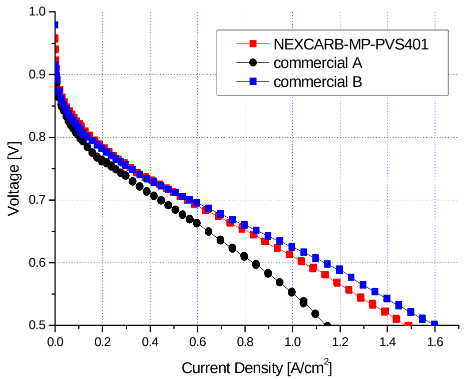
⇒Longer mixing time over 20 hs re-increased resistivity.



=> Resistivity reincreased over 20 h mixing

Time	Current Density	
	@0.7V	@0.6V
24	0.50	930
20	0.51	960
16	0.52	1.03
12	0.46	870

Evaluation of 40%Pt/PCNF+CB



Operating Condition

1) Cell Temp' : 70℃
2) Humidifier Temp'
   Anode / Cathode = 70 ℃ / 60 ℃
3) Flow H2/Air = ×1.4/×2.5
4) Ambient pressure
5) Electrode Size : 25㎠
6) Min flow : 400㎃/㎠

Very similar performance with Gore Japan MEA

Total summary

- CNF is the very promising support material for the catalysts of MCFC and PEMFC.
- Outer surface area with well-dispersed CNF is very effective.
  - Mesoporous CNF, small CNF
  - CNF-CB composites
- Hybridization of CNF with CB was very effective to optimize the MEA porosity.