Nano Material Applications in Fuel Cell

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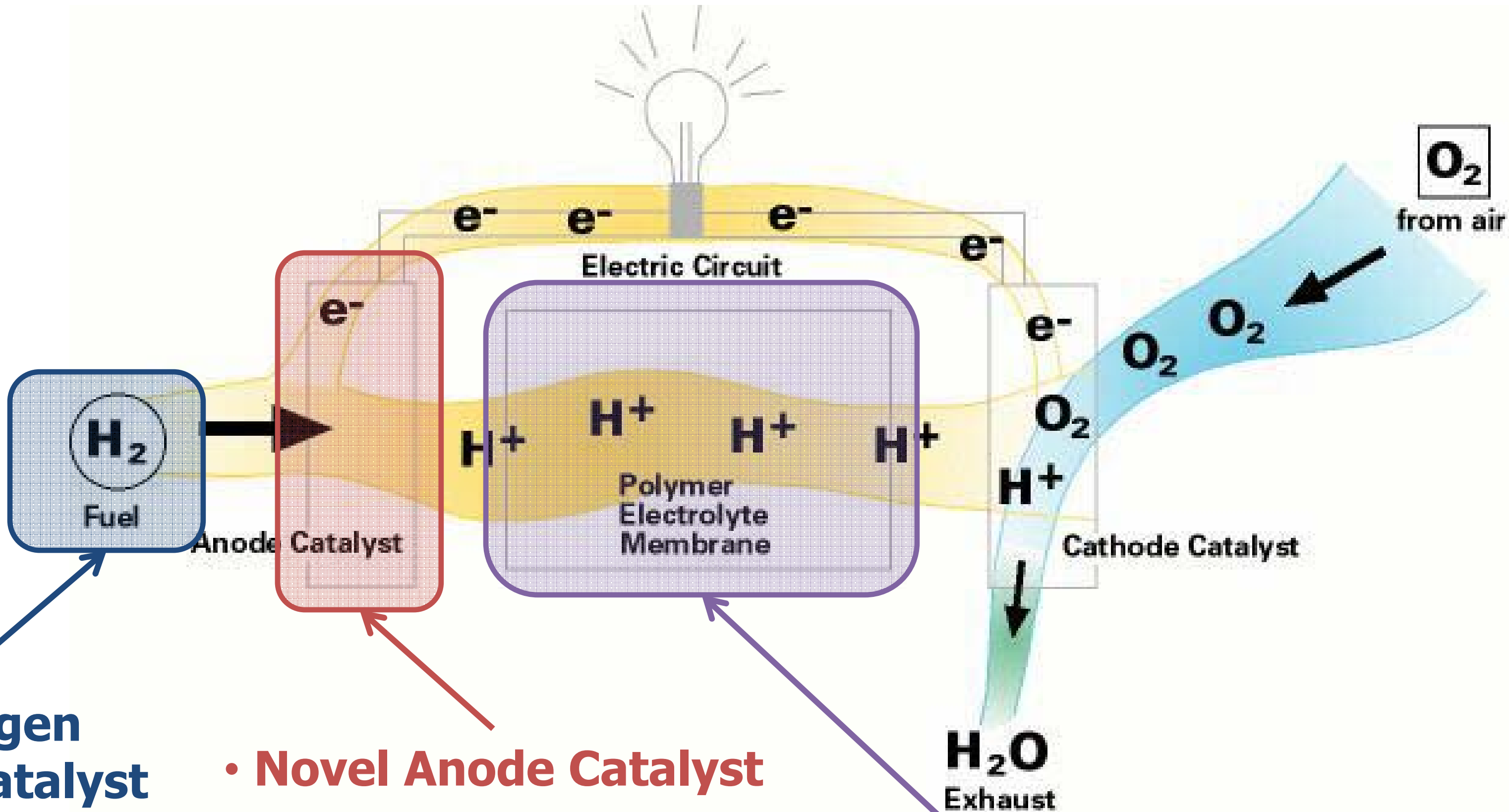
Nano Materials in Fuel Cell



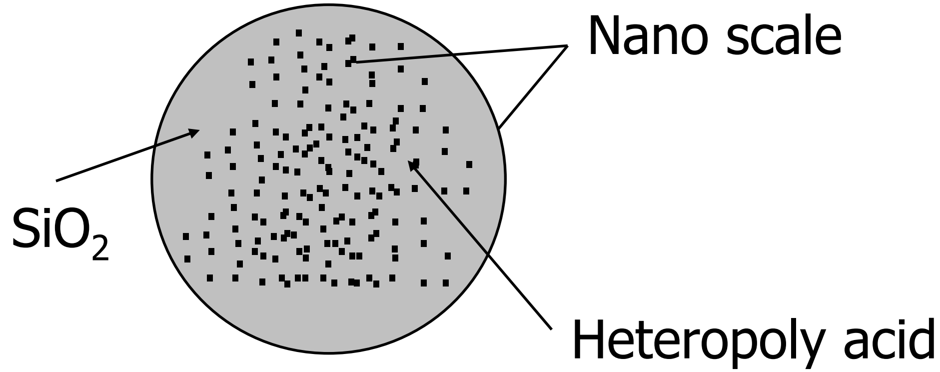
- **Hydrogen Release Catalyst**
- **Novel Anode Catalyst**
- **Organic-Inorganic Membrane**

Fuel Cell Applications

- Heteropolyacid(HPA)-SiO_2 nanoparticles for high temperature operation of a direct methanol fuel cell
- Preparation and characterization of new carbon for fuel cell application
- Pulse Electrodeposition for Preparing PEM Fuel Cell Electrode
- Investigation of alloy catalyst for accelerating hydrogen release from NaBH4

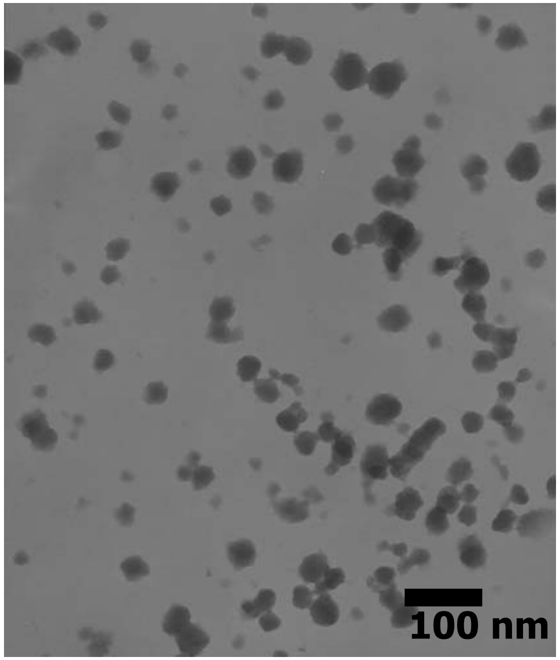
In this study

- Preparation nanohybride particle (HPA/SiO_2)
  By micro emulsion technique

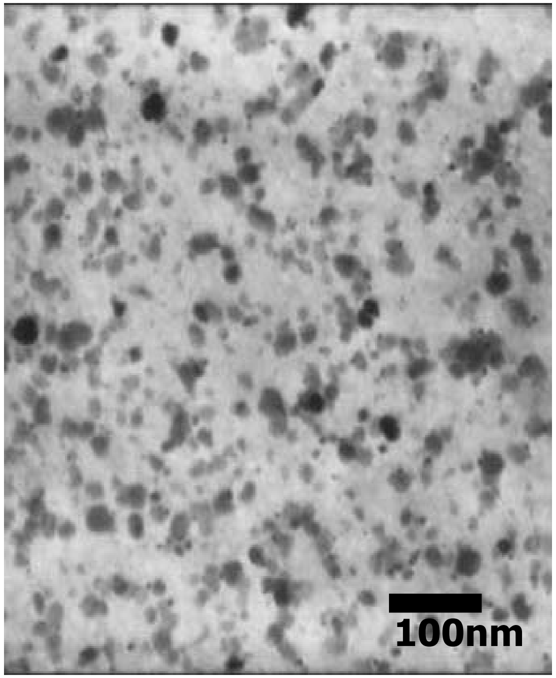


- Characterization :
  TEM, Solid state NMR, TMP adsorption, N_2 adsorption, FT-IR

Heteropolyacid-SiO_2 nanoparticles



TEM image of heteropolyacid-SiO_2 nanoparticle
(R=2, X=30%, 12hr)



TEM image of heteropolyacid-SiO_2 nanoparticle
(R=2, HPA 30%, 24hr)

R= [H_2O]/[AOT]
X=[Heteropolyacid]

^{31}P MAS NMR

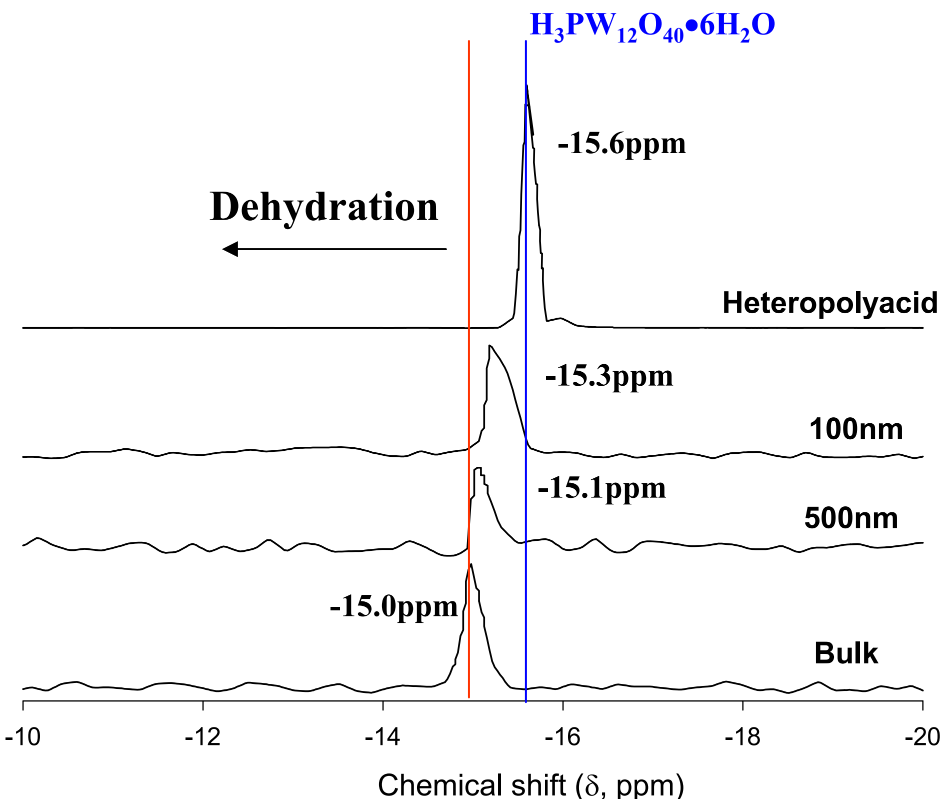
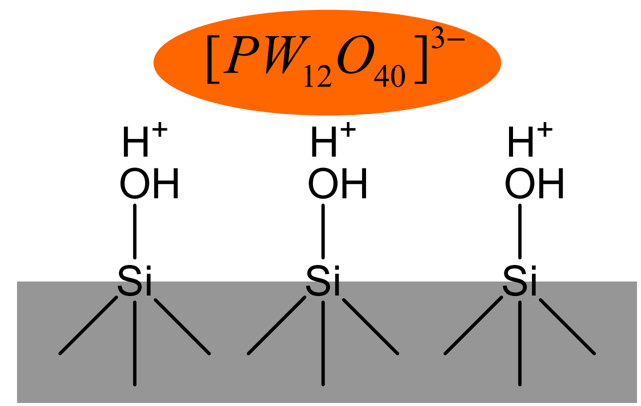


Fig. ^{31}P MAS NMR spectra of heteropolyacid and HPA/SiO_2

Dehydration of heteropolyacid

Heteropolyacid < nanoparticle < Bulk powder

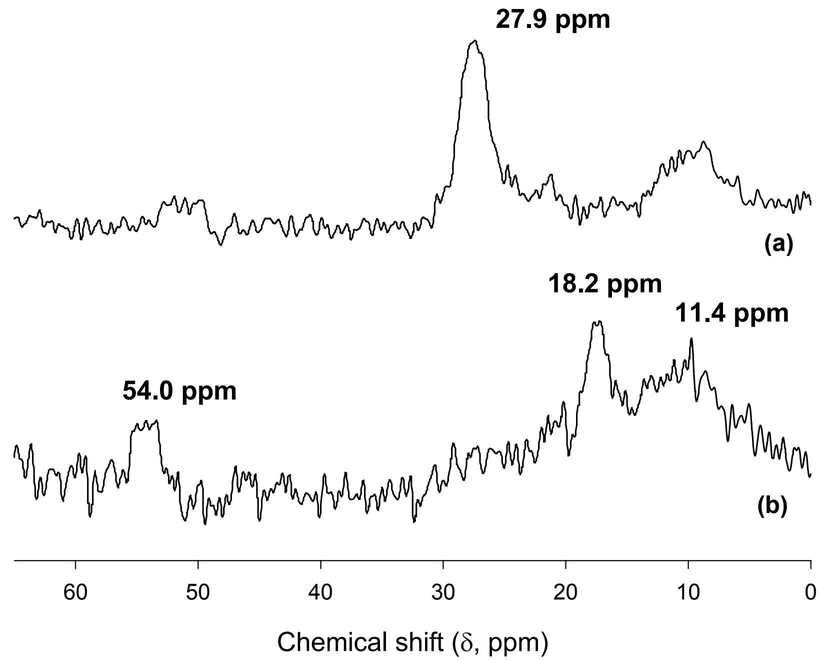
Trapping of acidic proton to OH group



Referenced from

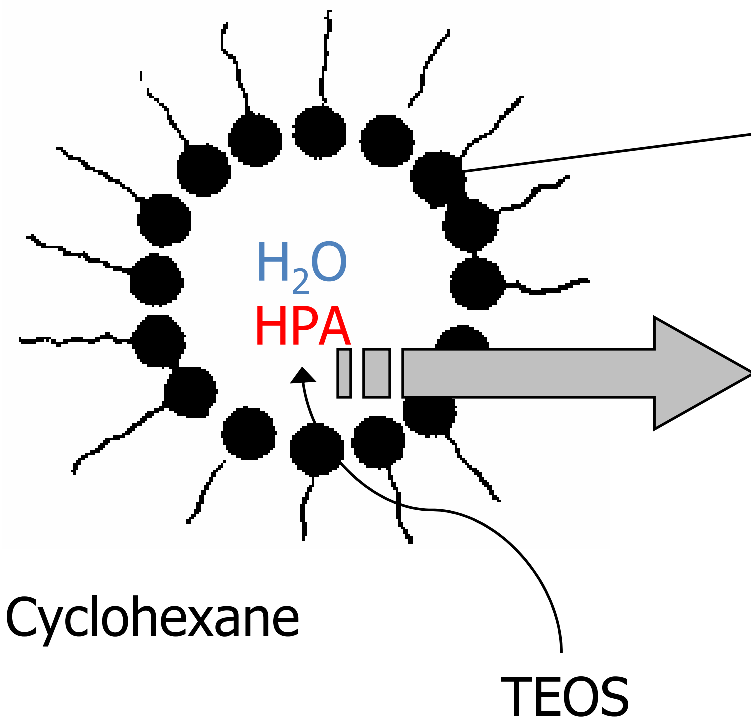
- M.Misono et al., J.Phys.Chem.B., 104 (2000) 8108
- F.Lefebvre et al., J.Chem.Soc.Chem.Commun, (1992) 756

^{13}C CP MAS NMR

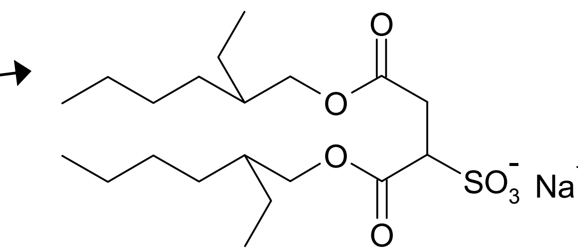


^{13}C CP MAS NMR spectra
(a) thiol- and (b) sulfonic-functionalized heteropolyacid-SiO_2 nanoparticle.

Preparation of inorganic particles in microemulsion



Aerosol-OT

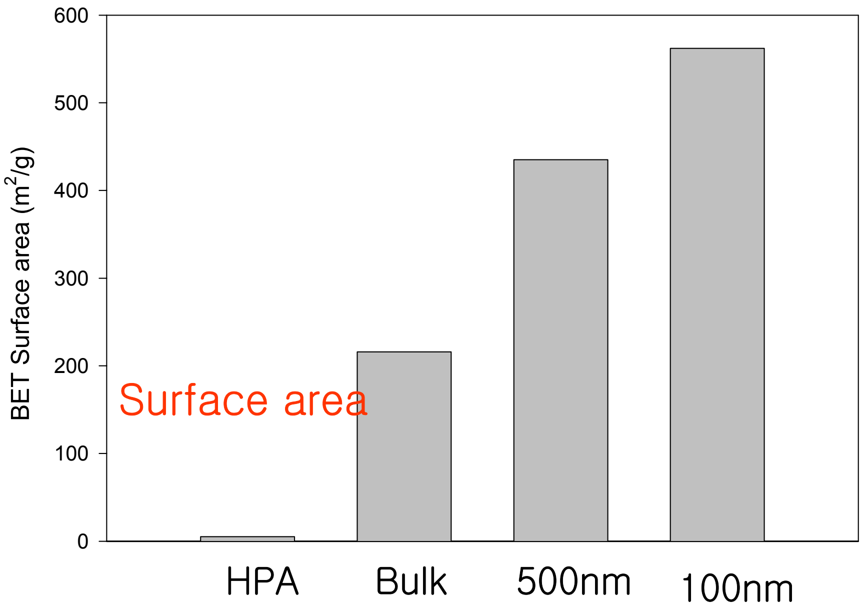


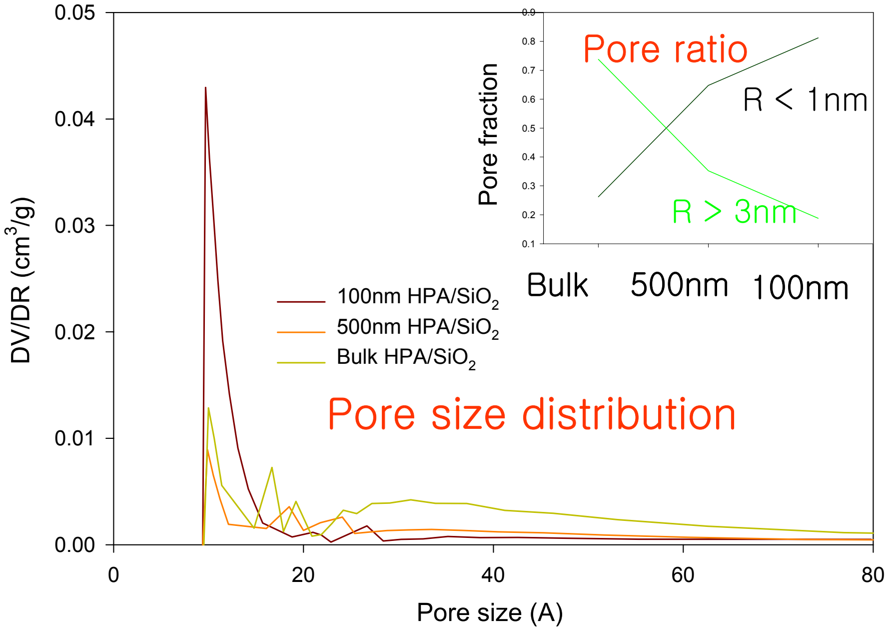
Sol-gel process

$Si(OR)_4 + 4H_2O \rightarrow Si(OH)_4 + 4ROH$

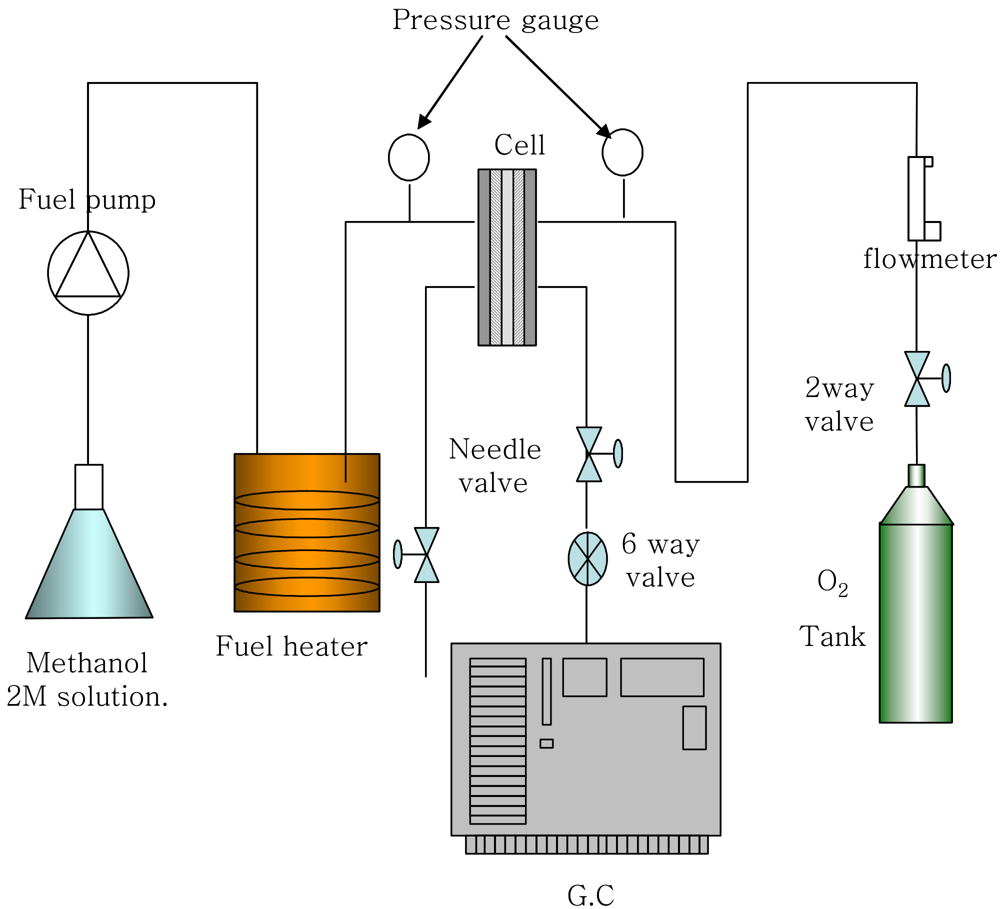
$Si\text{-}OH + HO\text{-}Si \rightarrow Si\text{-}O\text{-}Si + H_2O$

Surface area vs. nano HPA/SiO_2



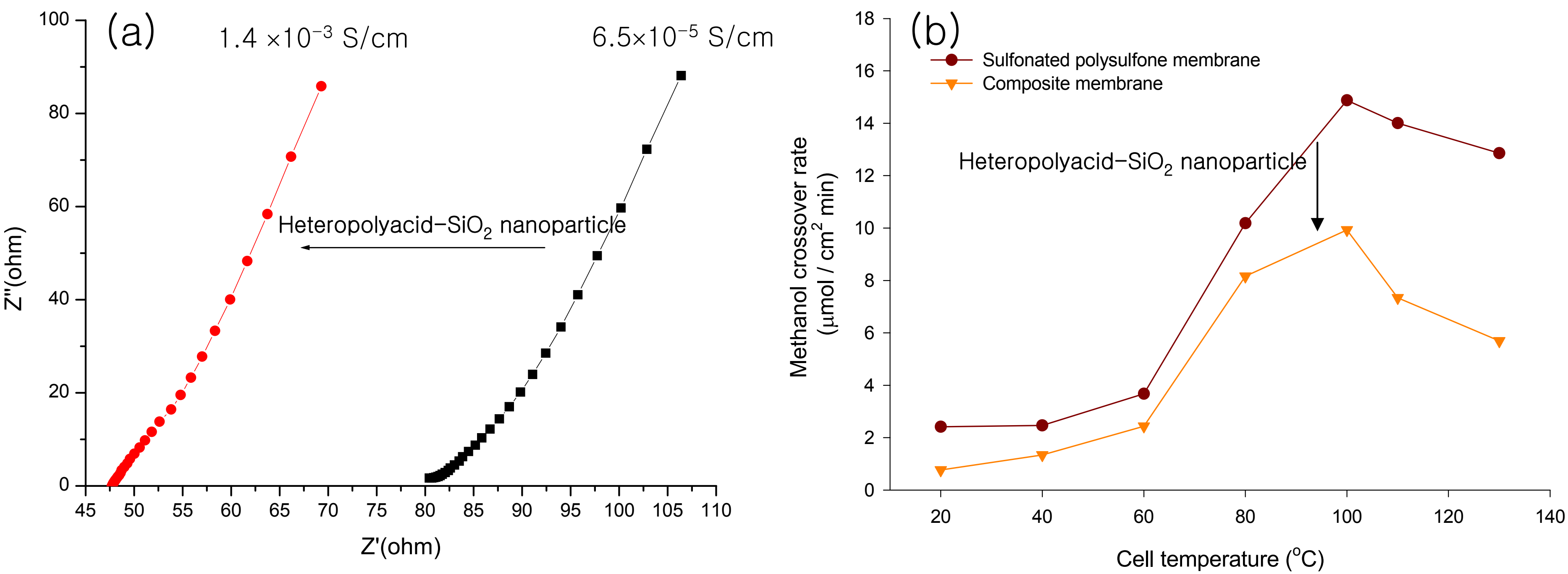


Application to DMFC



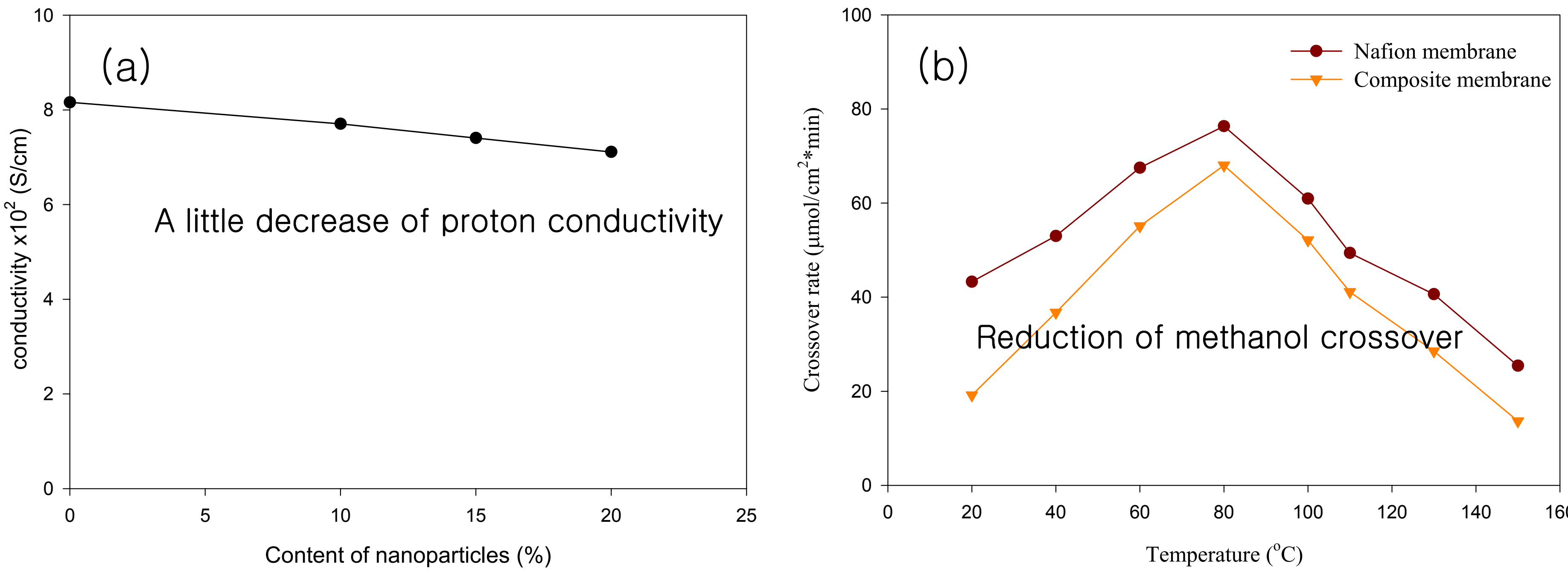
- Heteropolyacid
  → Proton conductivity
- Silica particle
  → Methanol blocker

Polysulfone/nanoparticle composite membrane



Complex impedance response(a) and methanol crossover rate(b) of the sulfonated polysulfone and sulfonated polysulfone / heteropolyacid – SiO_2 nanoparticle composite membrane.

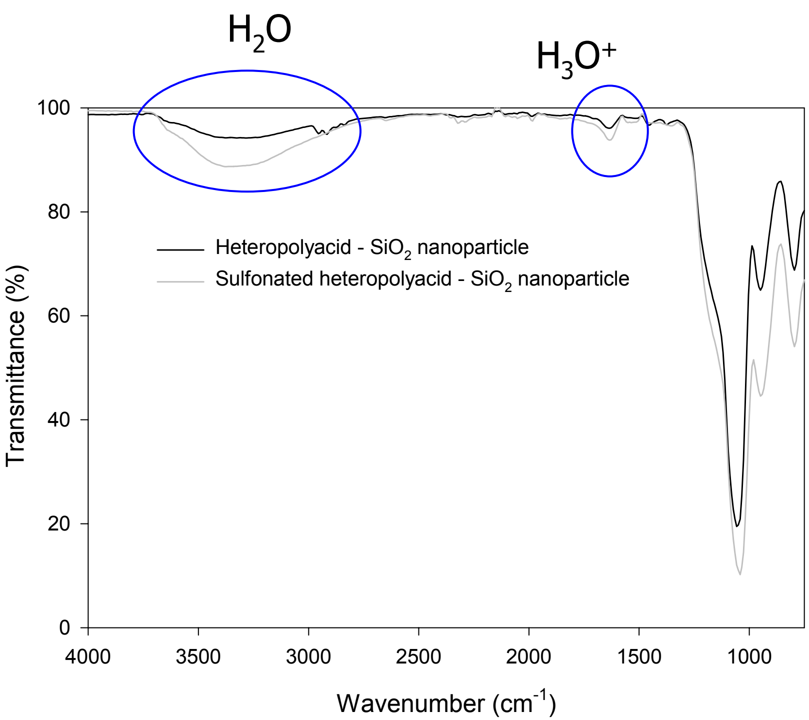
Nafion/nanoparticle composite membrane



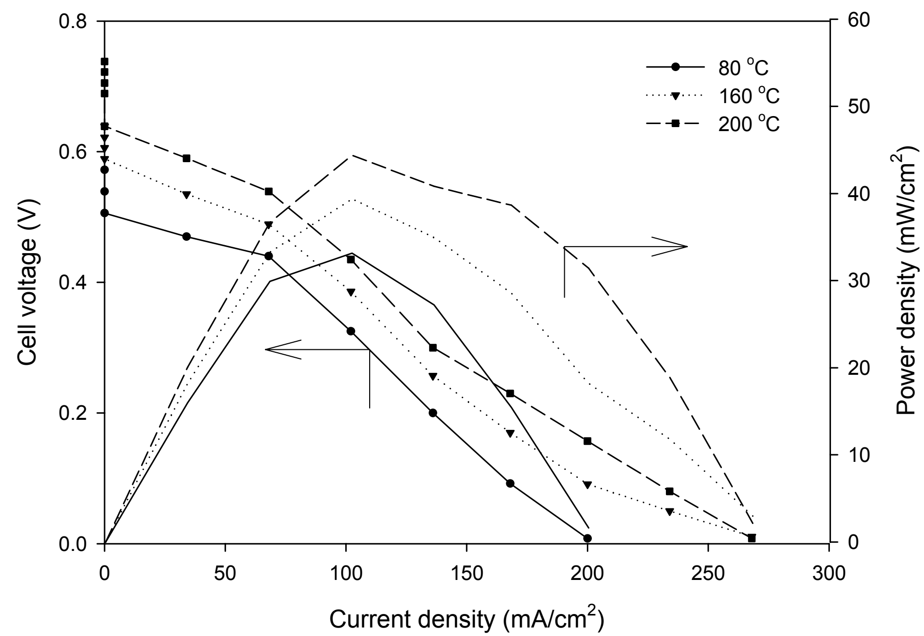
Proton conductivity(a) and methanol crossover rate(b) of the sulfonated polysulfone and sulfonated polysulfone / heteropolyacid – SiO_2 nanoparticle composite membrane.

Nafion-HPA/SiO_2 composite membrane

(Nafion / sulfonated heteropolyacid-SiO_2 nanoparticle composite membrane)



FT-IR spectra of sulfonated heteropolyacid-SiO_2 nanoparticle



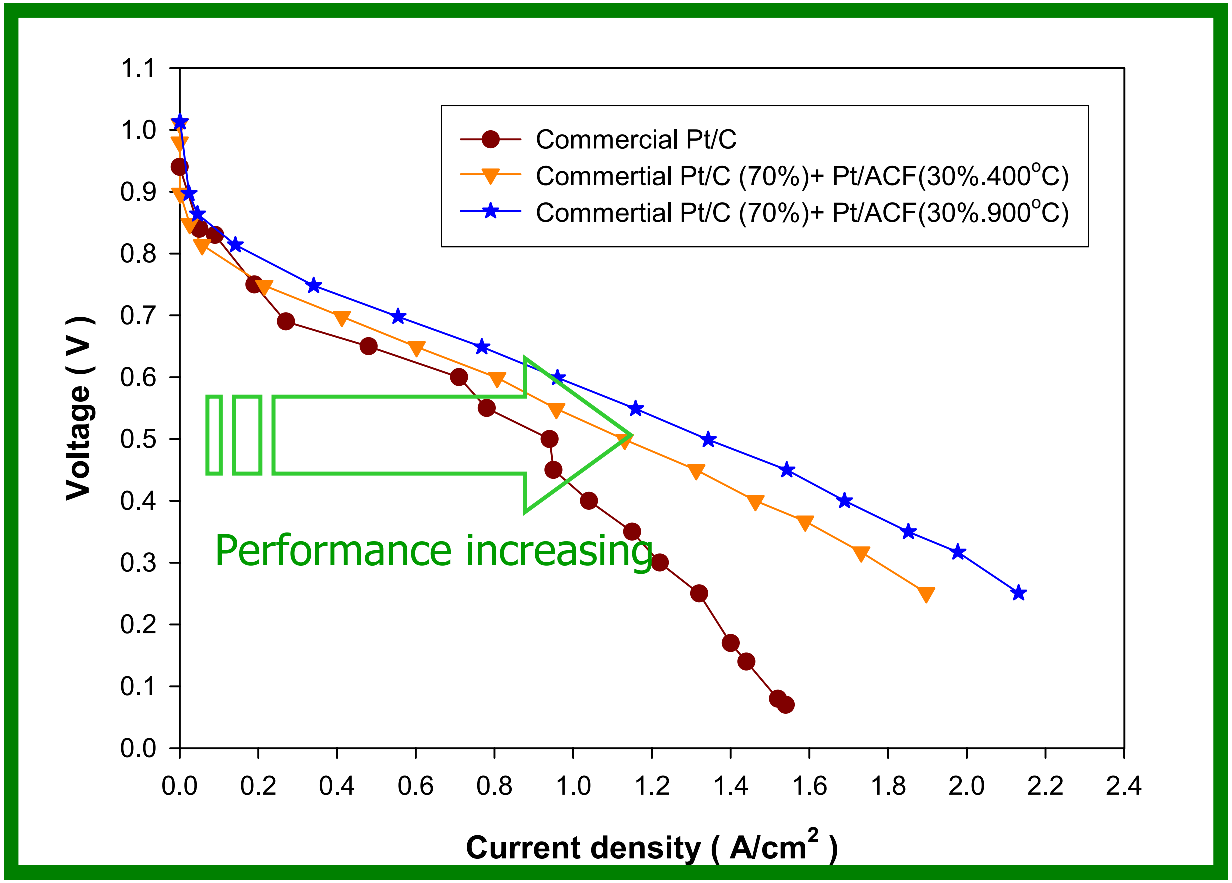
DMFC performance of composite membrane

Improvement of DMFC performance by increasing the cell temperature

Research of carbon material application

Caron structure	FC application	Performance	remark	Reference
Pt/CNT	PEMFC	0.7V, 0.7 mA/cm^2 (50^oC)	high electrocatalytic activity for oxygen reduction 3.6 ± 0.3nm	J.of power sources 139(2005) 73
Pt/mesoporous carbon (SBA-15)	DMFC	0.4V, 135 mA/cm^2 (65^oC)	Great potentiality for DMFC support **Johnson Mattheyat** 0.4V, 135 mA/cm^2 **(80^oC)**	J.Of power sources 130 (2005)
PtSn/ MWNT	DEFC	0.4V, 100 mA/cm^2	Improvement in liquid mass transfer for catalyst-3nm **PtSn/XC-72** **0.4V, 80 mA/cm^2**	Carbon 42 (2004)
Carbon fiber	Mg-H_2O_2 Semi-fuel cell	1.5V, 300mA/cm^2	Similar reference with Pt-Ir on carbon paper Mg: anode Microfiber carbon :cathode cathode side: 0.20M H_2O_2	J.Of power sources 96 (2001) 240
Carbon nanocoil	DMFC	0.4V , 170mA/cm^2 (60^oC)	Great potentiality for DMFC support material	Angew. Chem 2003,115, 4488
Carbon nanohorn	DMFC	0.4V , 130mA/cm^2		NEC

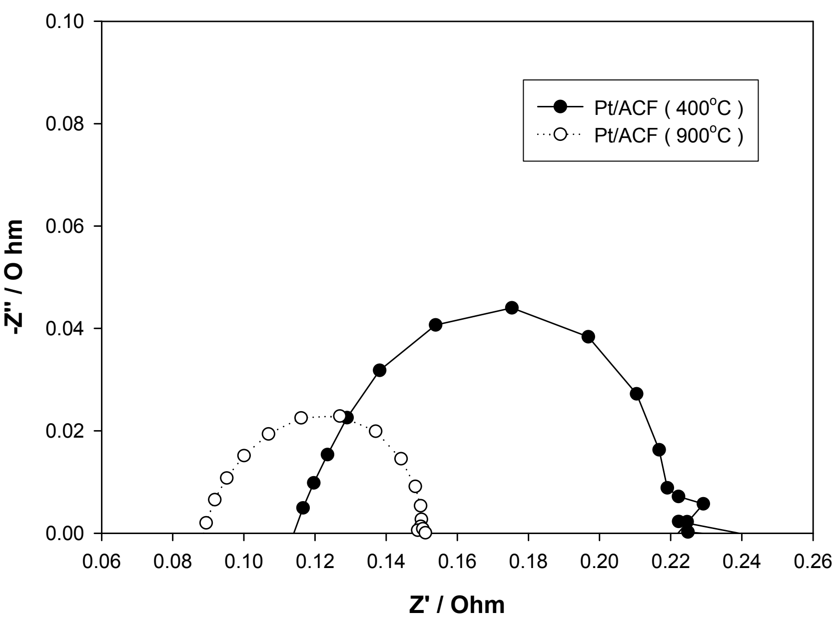
I-V curve for electrodes with commercial Pt/C and Pt/C+ Pt/ACF (900℃)



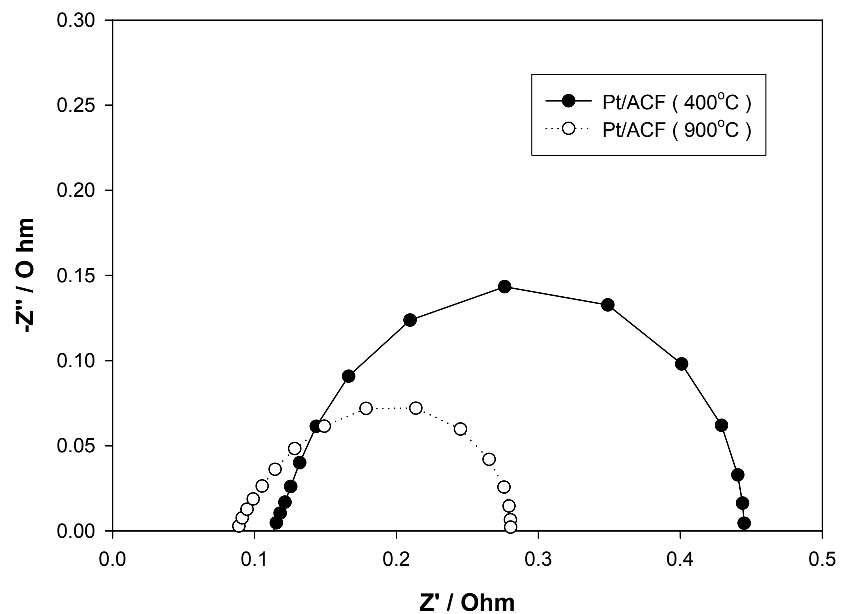
	Commercial Pt/C	Pt/C+Pt/ACF (400℃)	Pt/C+Pt/ACF (900℃)
Current density (mA/cm^2)	710	807	960

Cell Temp. : 80℃, Humidify condition : RH% 100 anode and cathode, Flow rate: Stoichiometry 1.5(Anode):2.0(Cathode)

Impedance for the electrodes manufactured with Pt/C, Pt/ACF(900℃) catalysts



Impedance spectra at 0.7V

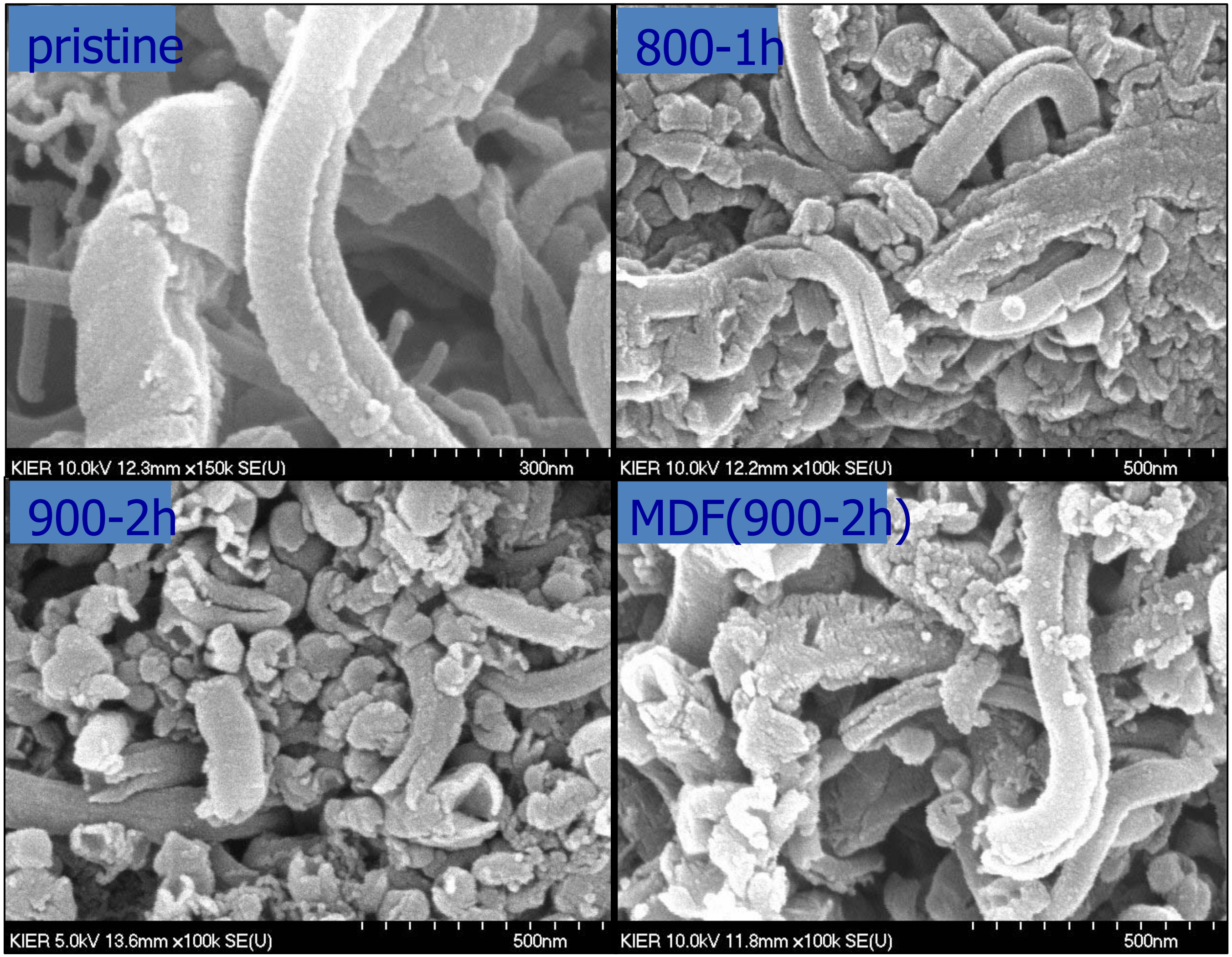


Impedance spectra at 0.8V

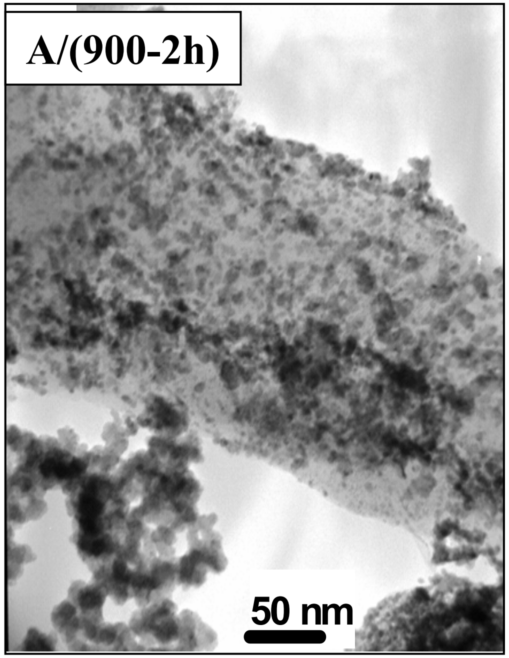
Specific surface area and average pore diameter of the CNF treated by KOH

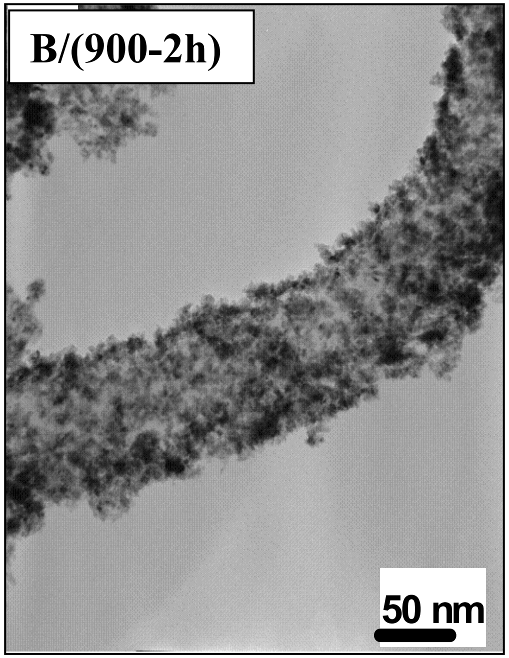
CNF	Activation condition	Surf. area (m^2 /g)	Avg. Pore diameter (Å)
	No activation	107.60	62.21
	750−1h	444.18	46.07
	800−1h	509.95	48.80
	900−1h	645.53	48.0
	900−2h	460.10	44.33
	Modified method	375.52	54.41
	900−3h	341.87	62.37
	950−1h	303.54	58.01

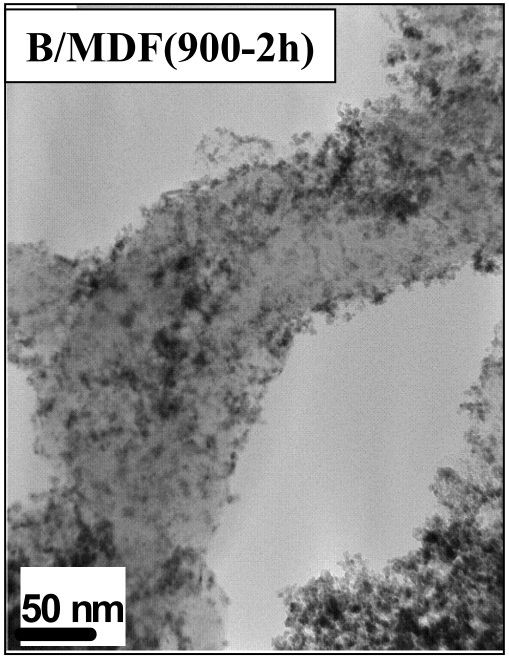
SEM - CNFs named 5H



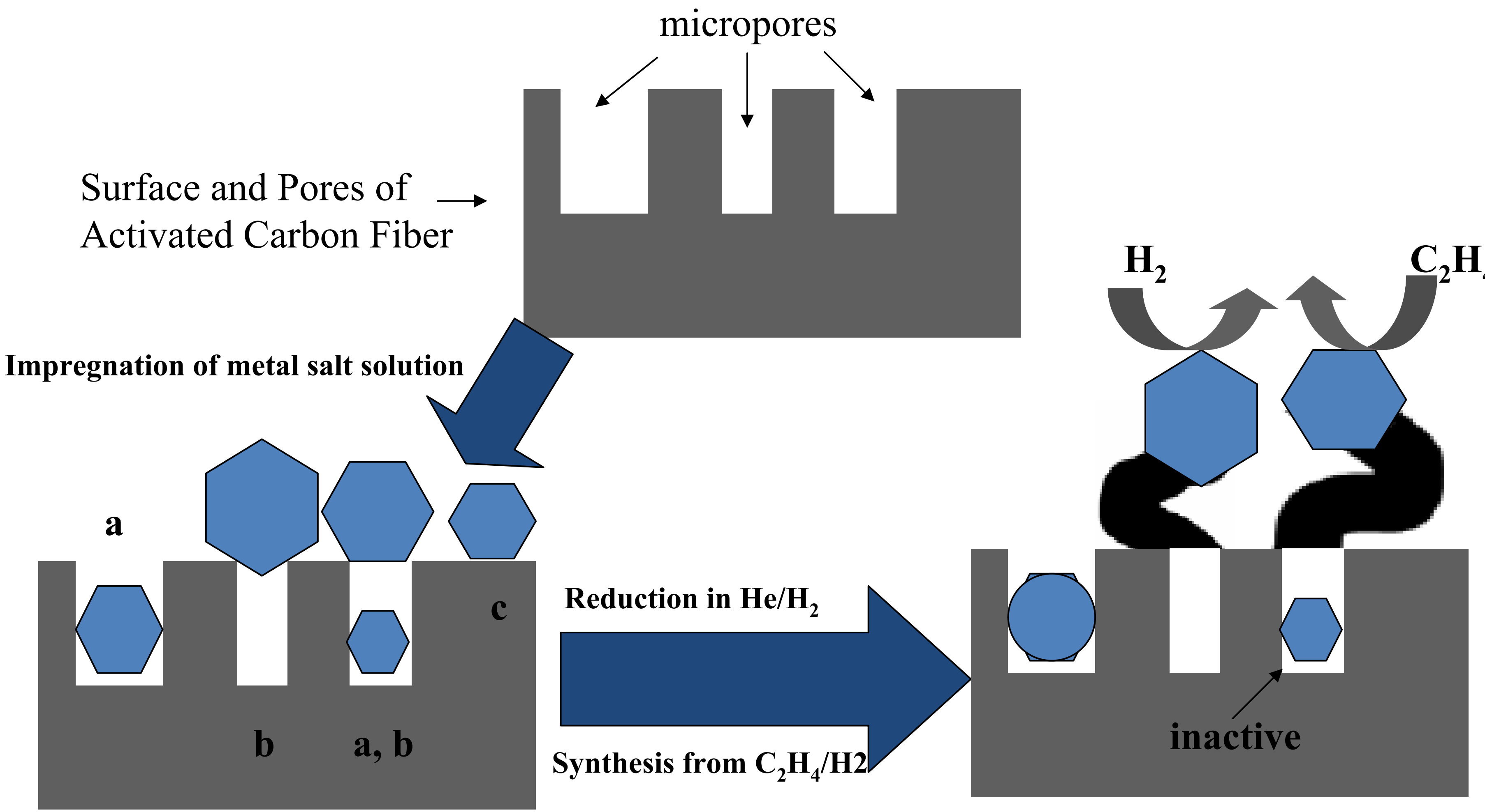
TEM - 60wt% Pt-Ru/CNF







Growth of nanofiber on ACF



Preparation of various carbon substrates

- CNF/ACF

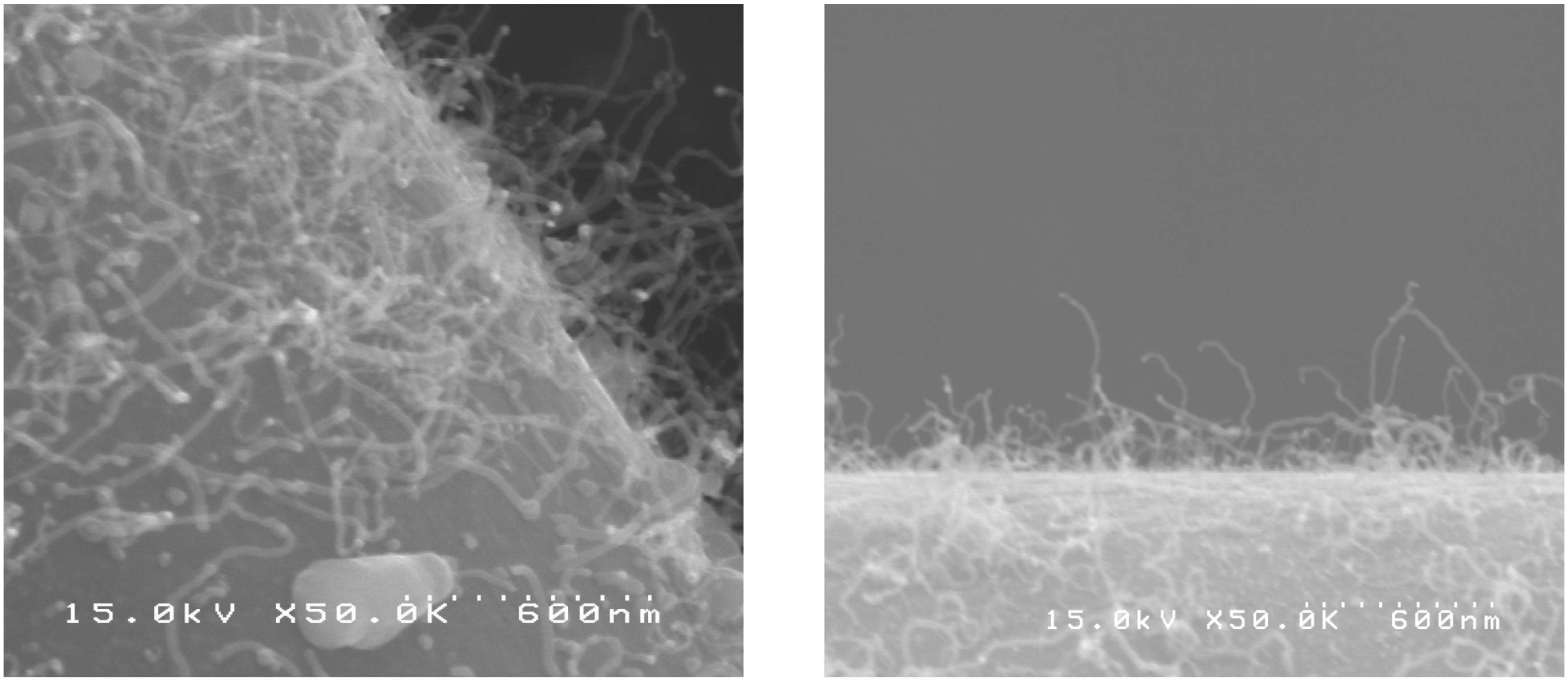


Fig. SEM images of carbon nano fibers grown on ACF

Preparation of platinum on ACF-CNFs

TEM Image of Pt/ACF-CNFs

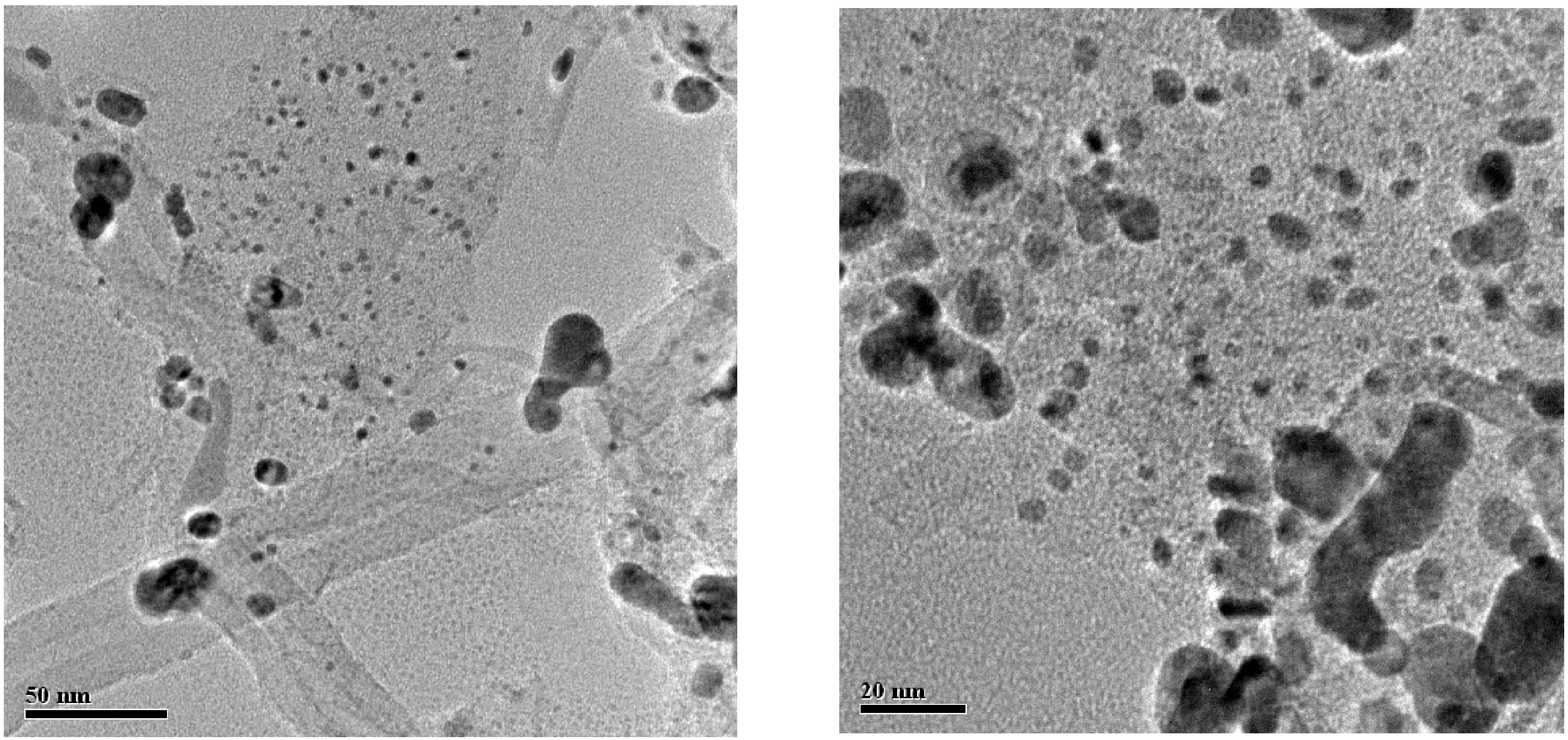


Fig. TEM images of Platinum oncarbon nanofibers grown on ACF

Preparation of platinum on ACF-CNFs

XRD patterns of Pt/ACF-CNFs

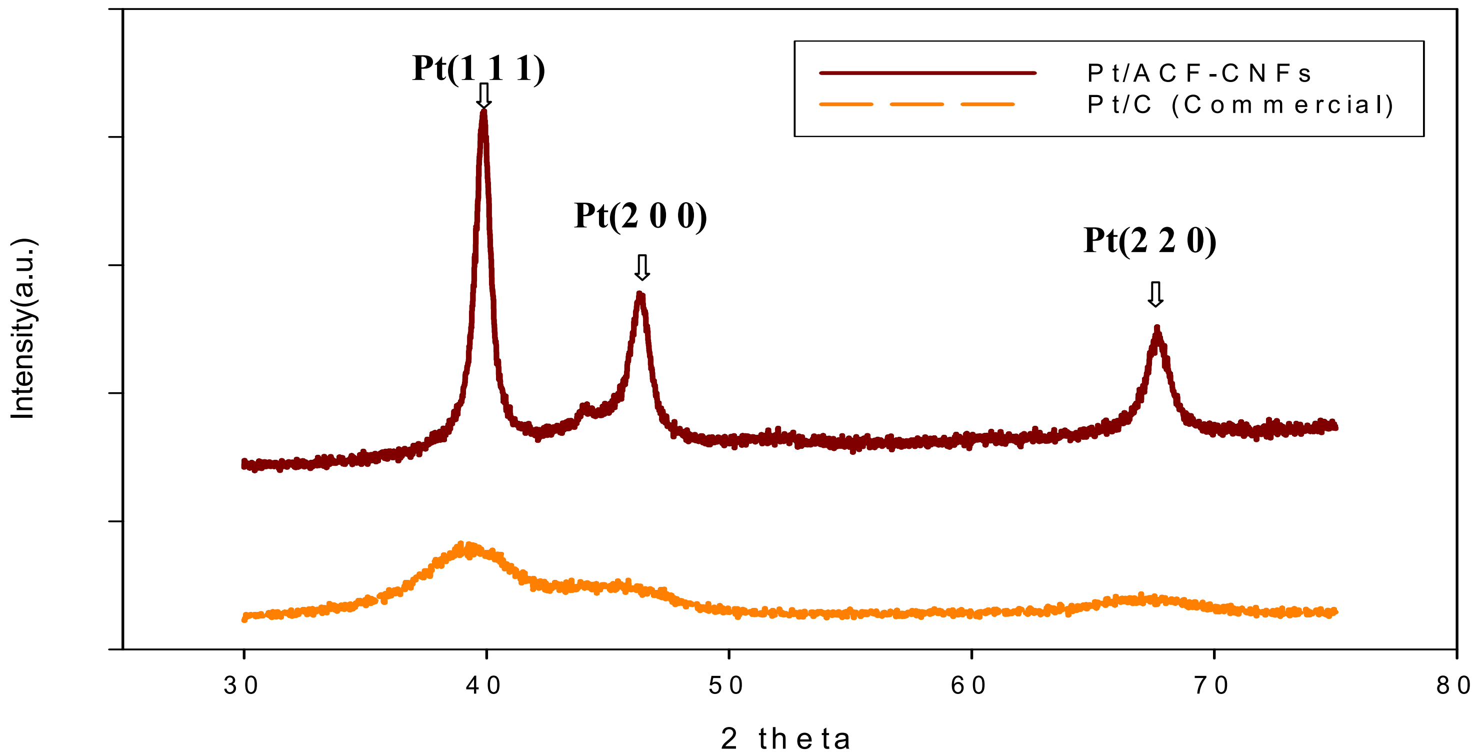


Fig. XRD pattern of Pt/ACF-CNFs

Single cell performance

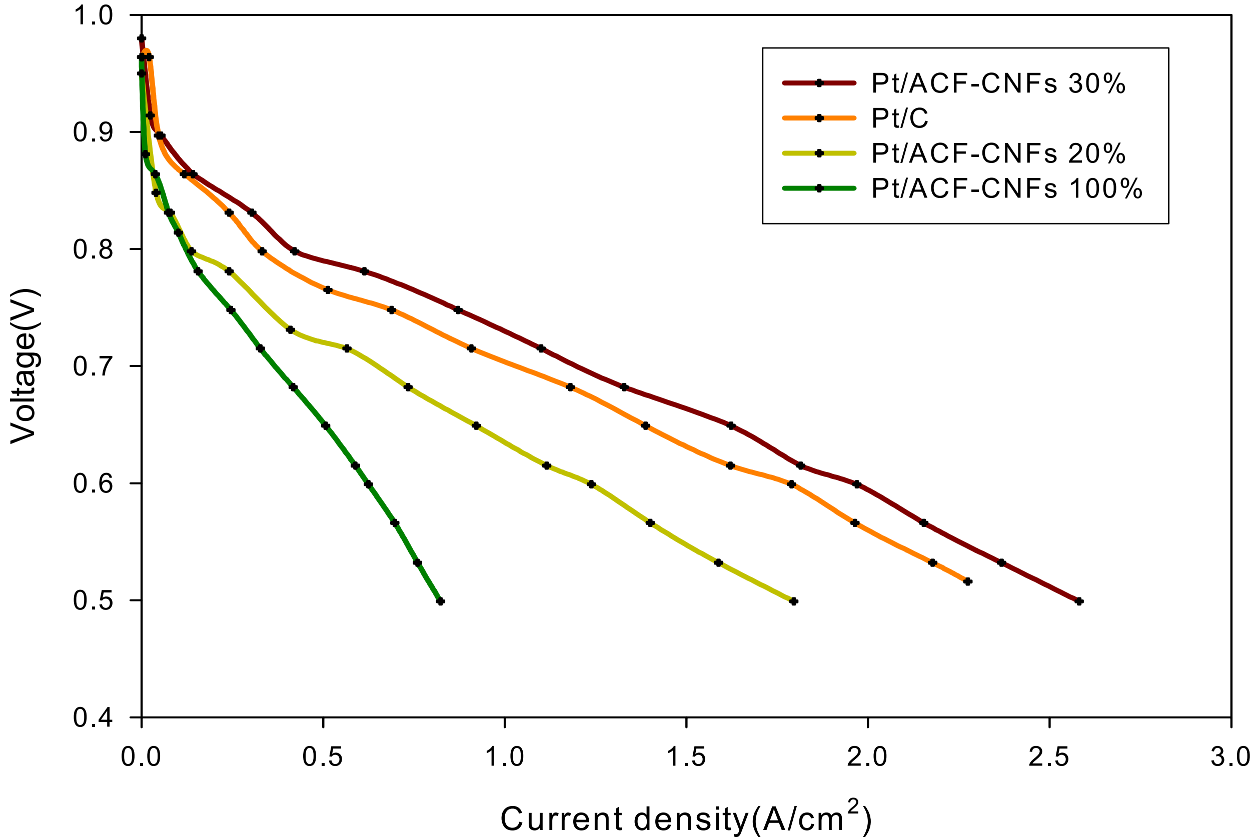


Fig. The performance of Pt/ACF-CNFs used in anode catalyst

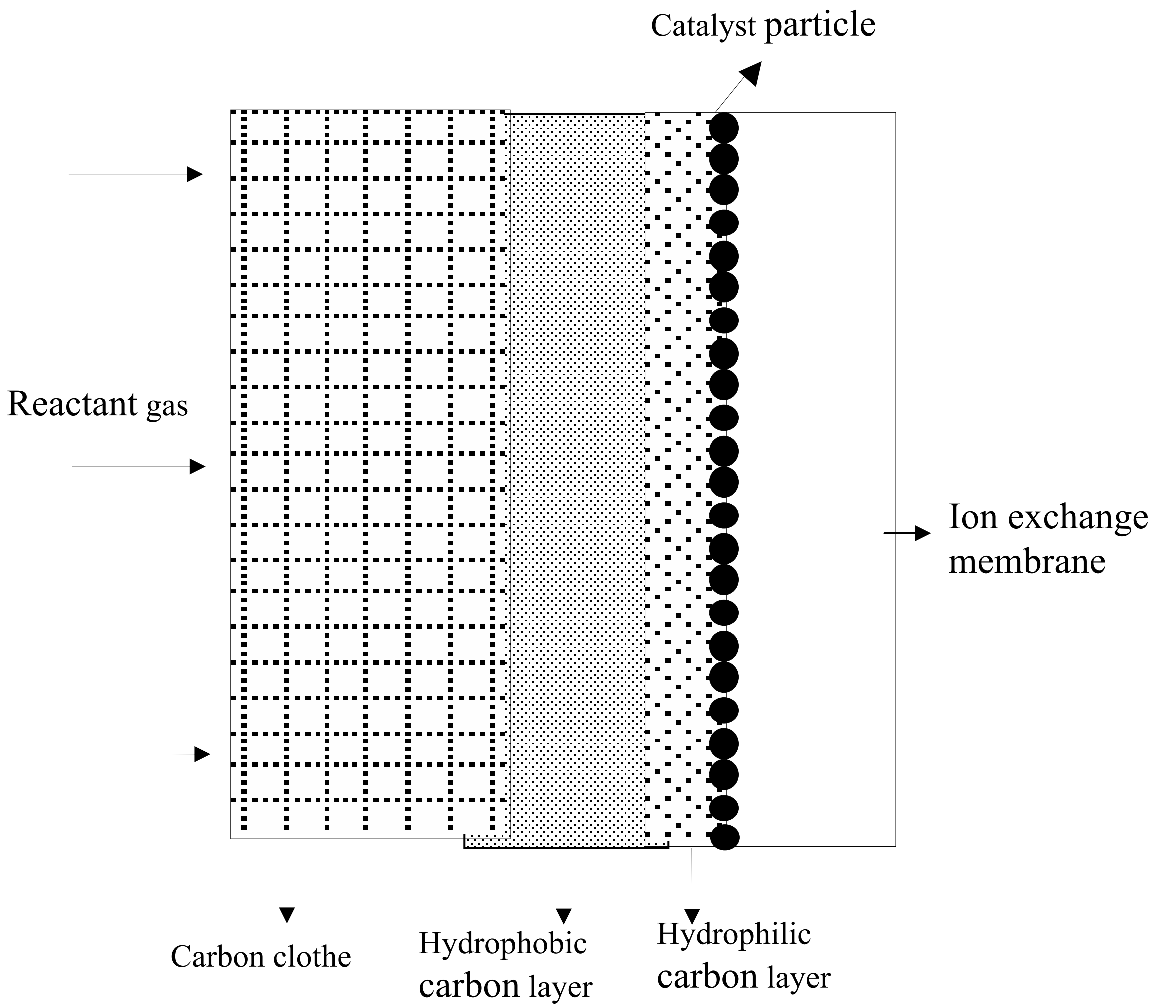
Cell Temp. : 80℃, Humidify condition : RH% 100 anode and cathode, Stoichiometry anode: cathode = 1.5: 2.0
Membrane : nafion 112:, anode : 20%Pt/C, cathode : 20%Pt/C and 20%Pt/ACF-CNFs+20%Pt/C, Back pressure : 1bar

Pulse Electrodeposition for Preparing PEM Fuel Cell Electrode

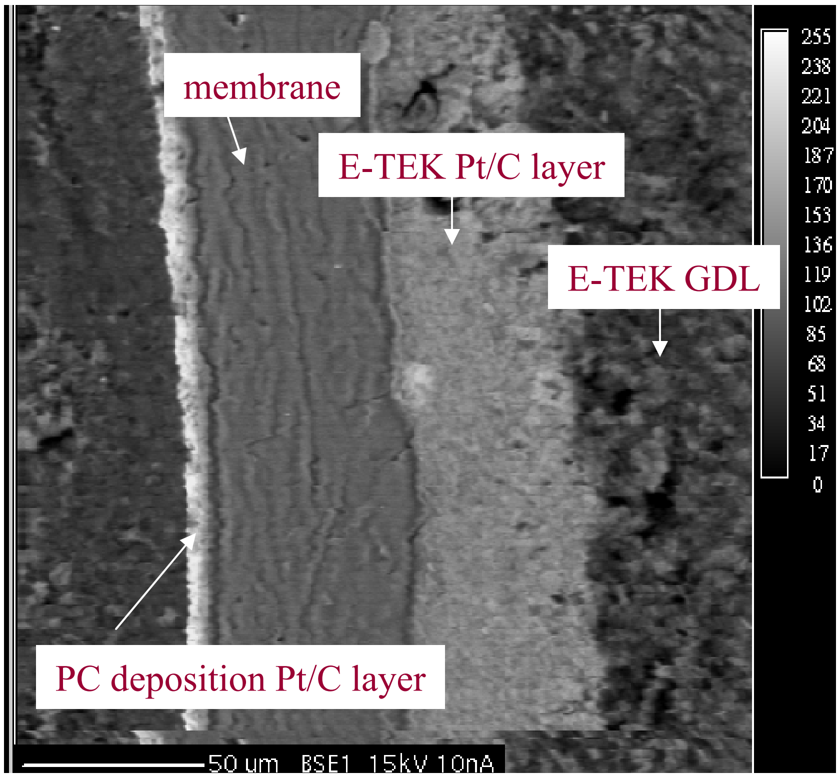
- Objectives
  - Reducing cost of electrode by decreasing Pt loading
  - Decreasing particle size
  - localizing Pt on the surface of electrode in contact with membrane and increasing efficiency of Pt

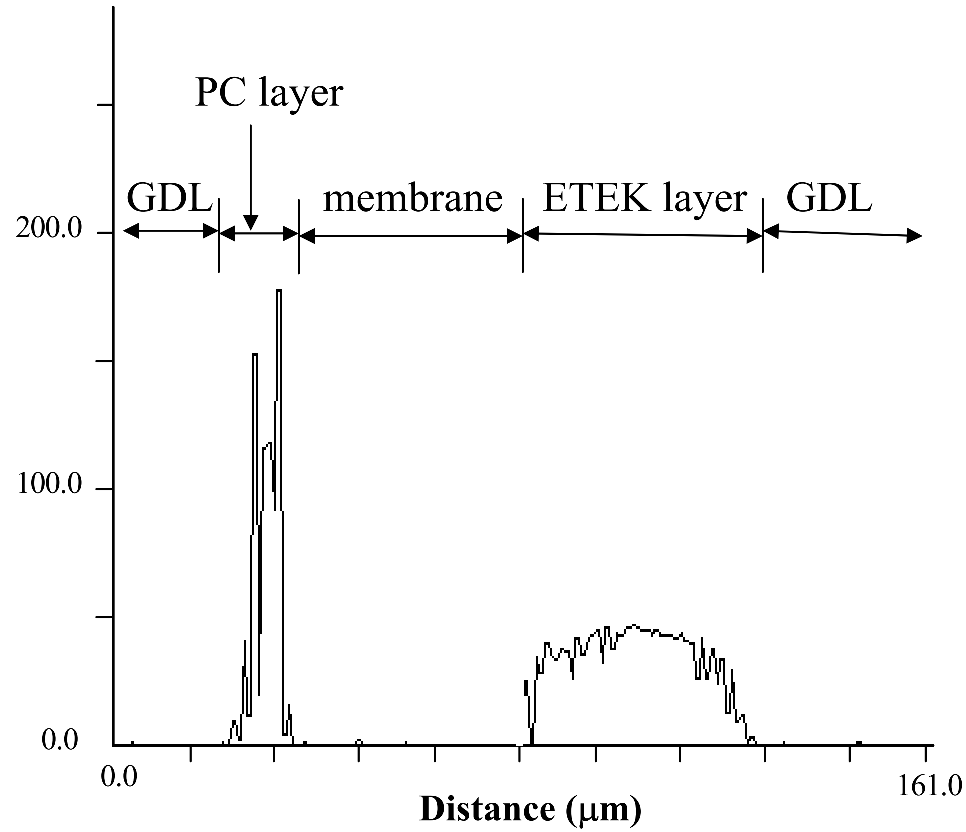
- Advantages of pulse electrodeposition
  - Low cost
  - Easy of control
  - Versatility

Schematic Diagram of The Electrode Prepared by Pulse Electrodeposition

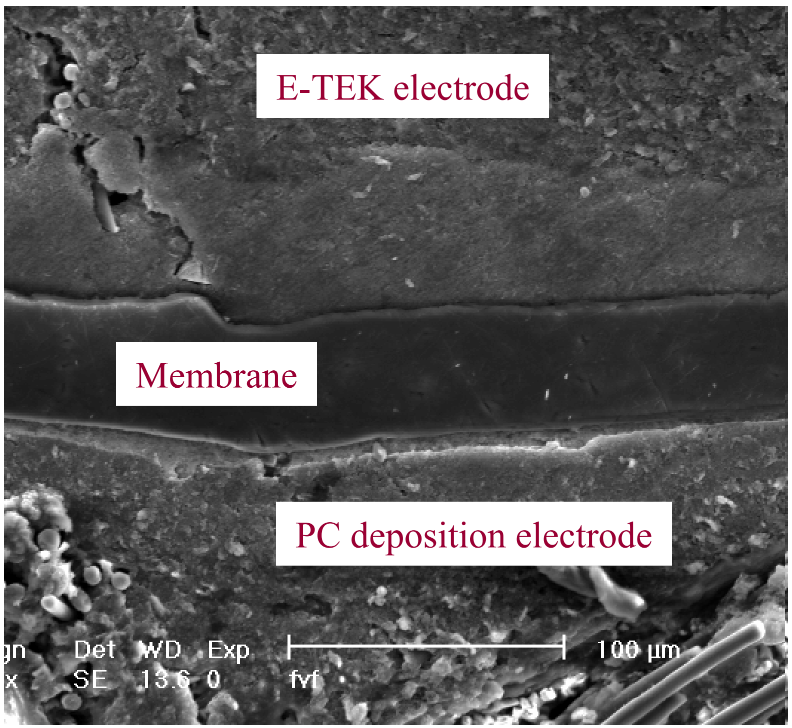


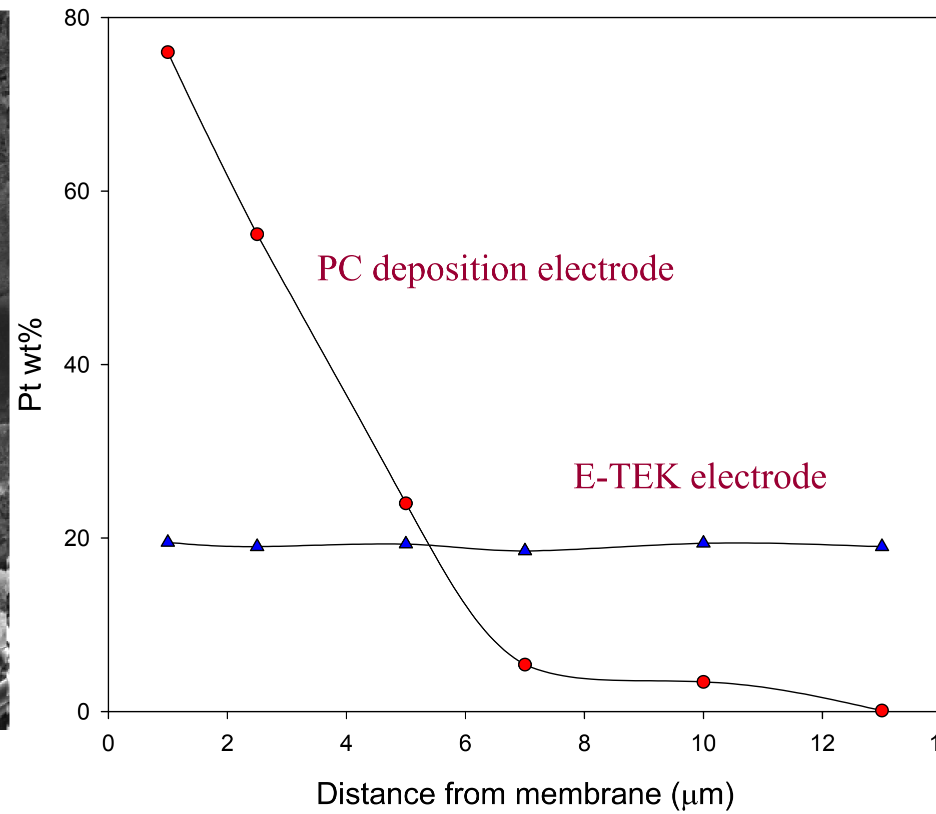
Back-Scattered Electron Image and Pt Line Scan of The Cross Section of MEA using EPMA



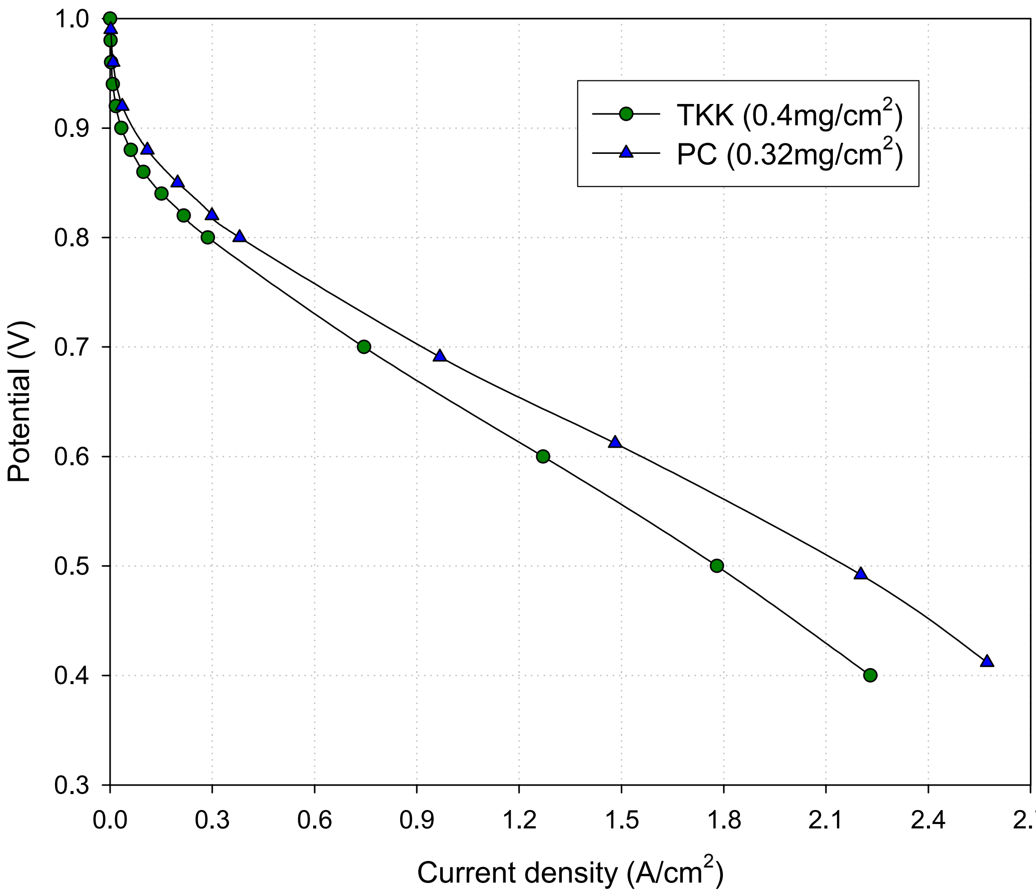


ESEM Image and Pt Concentration Profile of the Cross Section of MEA Using EDX Spot Analysis



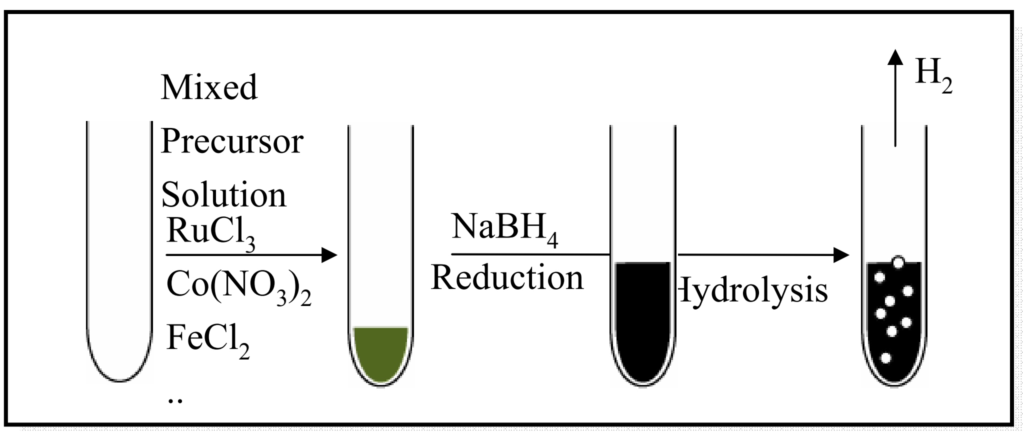


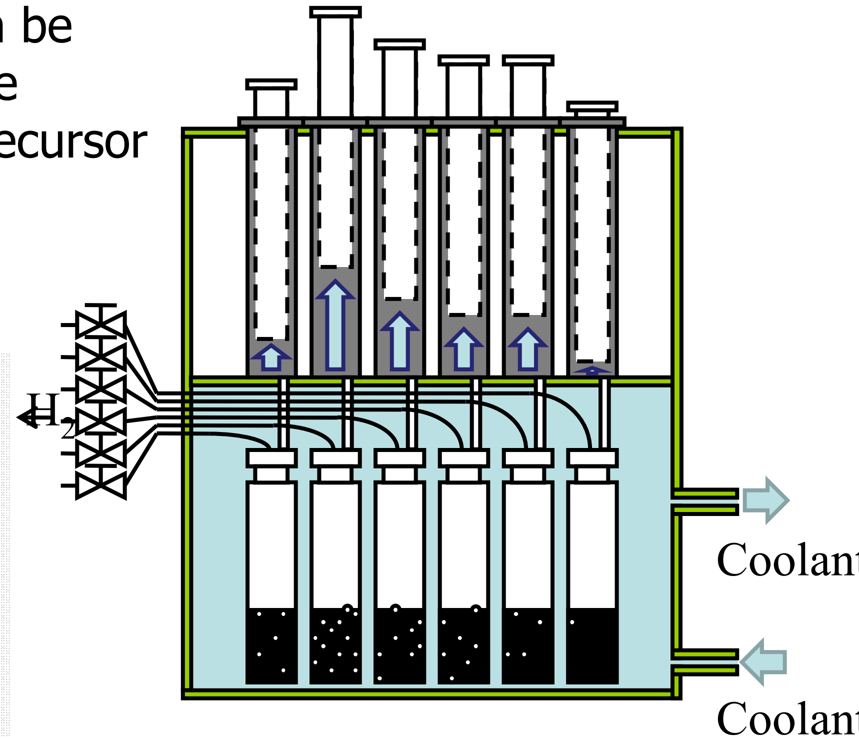
Comparison of MEA performance between pulse electrodeposited electrode and TKK



High Throughput Screening (HTS) test

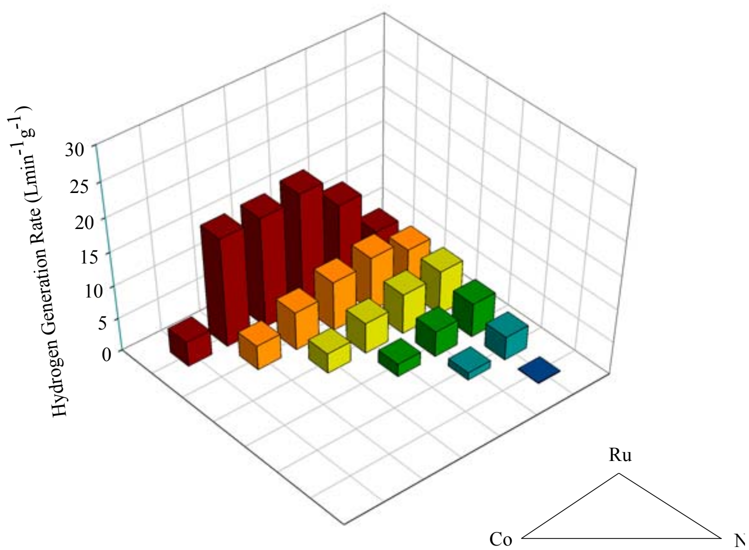
- Hydrogen release rate of metal catalysts can be measured without catalyst synthesis procedure
- To apply metal alloy catalyst, amounts of precursor solutions can be mixed to accurate ratios.

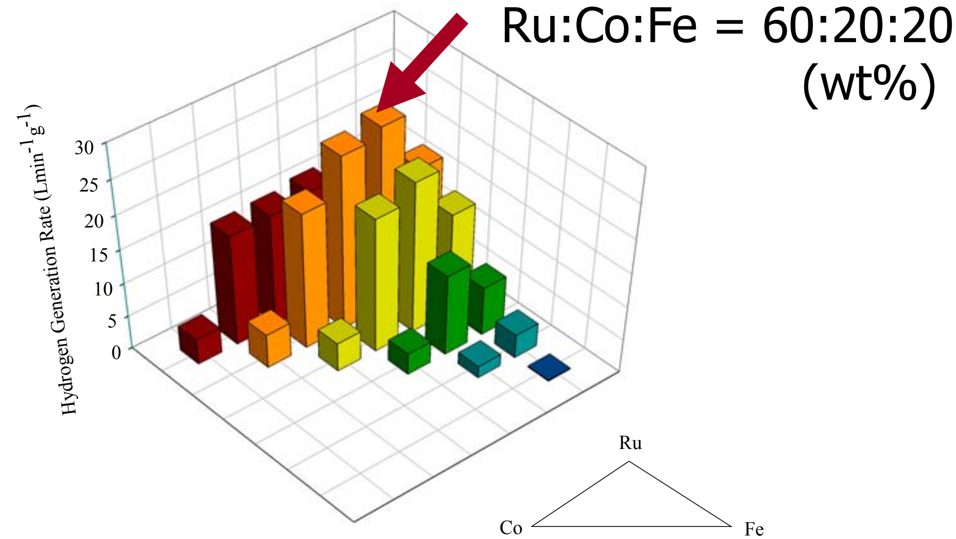




Schematic diagram of simplified HTS test microreactors

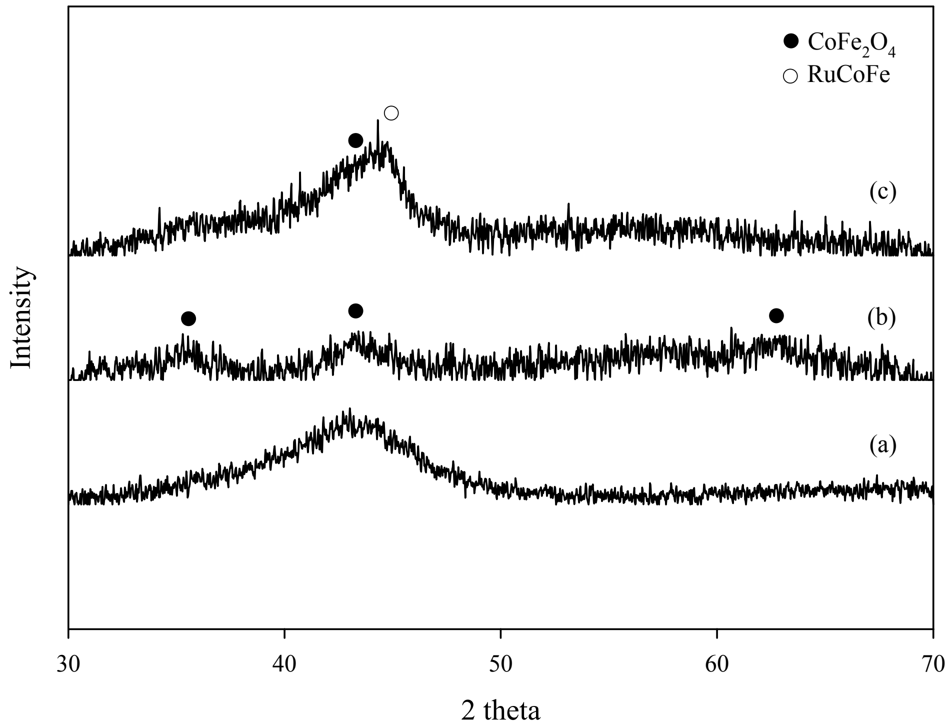
Hydrogen release test (Ternary alloy)





Hydrogen release rate of (a) Ru-Co-Ni, (b) Ru-Co-Fe from 10 wt% $NaBH_4$ solution with 4 wt% NaOH (Temperature fixed to 25°C)

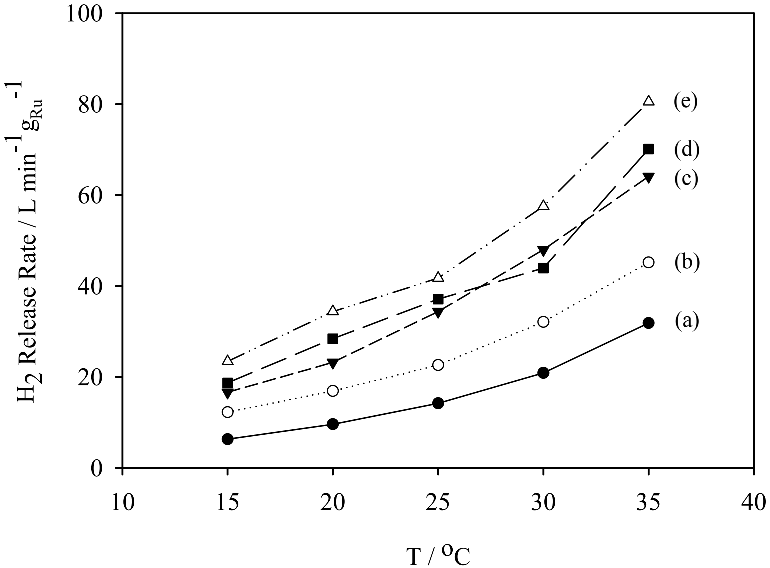
XRD Patterns

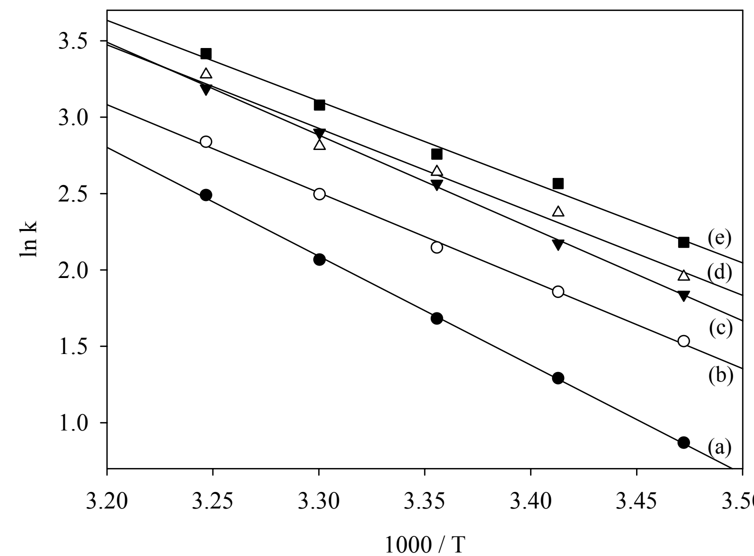


- Co and Fe were not reduced completely when $NaBH_4$ only was used for reduction.
- After the additional reduction by using hydrogen, CoFe alloy were shown

XRD Patterns of (a) Ru/ACF; (b) $NaBH_4$-reduced $Ru_{0.6}Co_{0.2}Fe_{0.2}$/ACF; (c) $NaBH_4$ and H_2-reduced $Ru_{0.6}Co_{0.2}Fe_{0.2}$/ACF catalyst

RuCoFe/ACF nanocatalyst





	catalyst	Reduction Agent	hydrogen release rate at 25 °C ($Lmin^{-1}g_{Ru}^{-1}$)	Activation Energy ($kJmol^{-1}$)
(a)	10 wt% Ru/ACF	H_2	14.21	59.23
(b)	16 wt% $Ru_{0.6}Co_{0.2}Fe_{0.2}$/ACF	H_2	22.63	47.91
(c)	16 wt% $Ru_{0.6}Co_{0.2}Fe_{0.2}$/ACF	$NaBH_4$	34.37	50.54
(d)	13 wt% $Ru_{0.75}Co_{0.25}$/ACF	$NaBH_4$ + H_2	37.12	45.44
(e)	16 wt% $Ru_{0.6}Co_{0.2}Fe_{0.2}$/ACF	$NaBH_4$ + H_2	41.73	44.01

Conclusions

Nano materials may lead to drastic improvement in fuel cell application

1)Nanohybride electrolyte (HPA-SiO_2+Nafion®) was effective for the high temperature operating of DMFC

2)New nano carbons are promising to enhance the catalytic activity in fuel cell

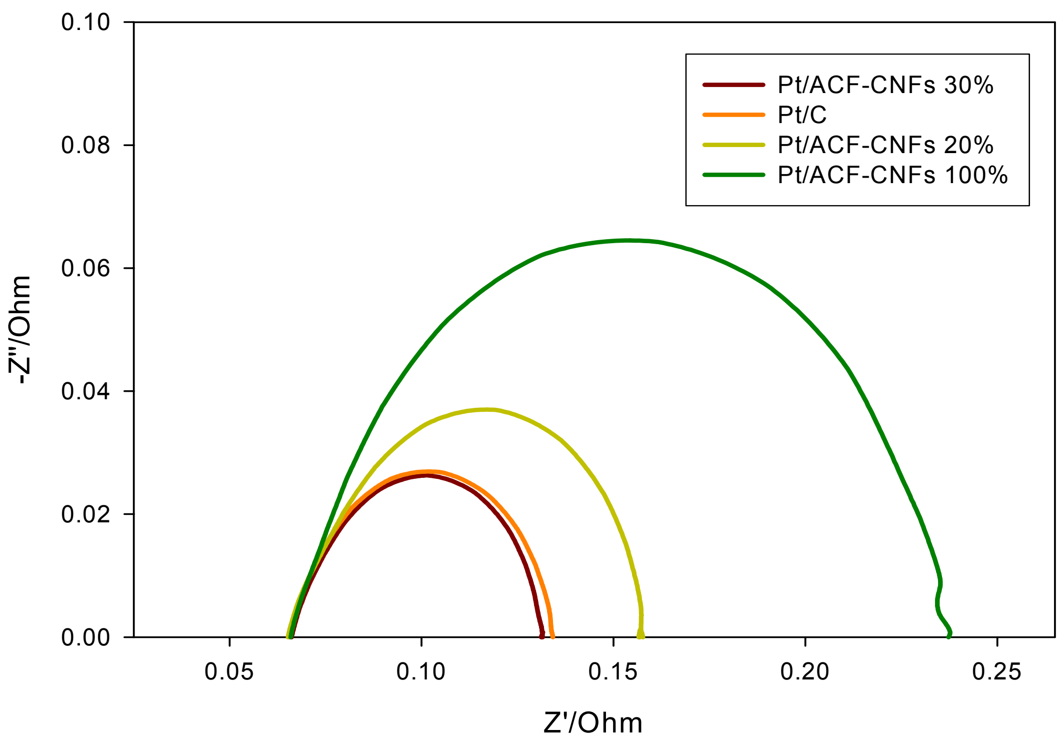
3) Nano alloy will be effective to release control of the H_2 from chemical hydride ($NaBH_4$, NH_3BH_3)

4) Electrodeposition is effective to reduce the amount of Pt loading

Acknowledgement

Backup slides

Impedance spectra



Membrane resistance	0.063Ω
Interfacial resistance (Mixture ratio 20%Pt/C:20%Pt/ACF-CNFs)	
Only 20% Pt/C	0.069Ω
Only 20% Pt/ACF-CNFs	0.175Ω
2:8	0.096Ω
3:7	0.065Ω

Fig. Impedance spectra of single cell

Cyclic voltammogram

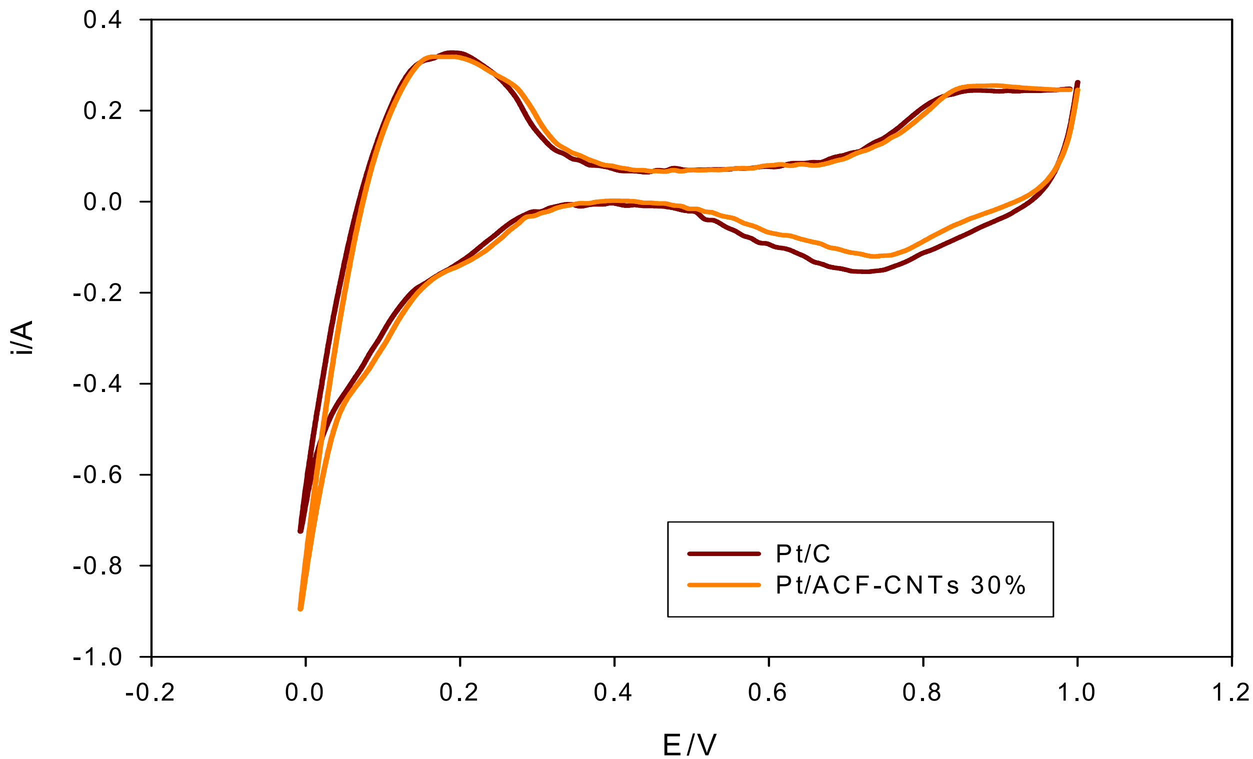


Fig. Cyclic voltammograms of Pt/ACF-CNFs used oxygen

Technical Barriers of Electrodes for PEM Fuel Cells

➢ Electrode performance

- 400 mA/cm^2 at 0.8V with H_2/Air and 1atm
- Novel method of pulse electrodeposition
- Pt-X alloy

➢ Material Cost

- 0.2 g (Pt loading)/peak kW
- Non-precious catalyst (Pt-free)

➢ Durability

- 40,000 hours operation with <10% performance degradation in stationary applications.

Why Pulse Electrodeposition (Dependence of Nucleation Rate on Overpotential)

Rate of 2D-nucleation *

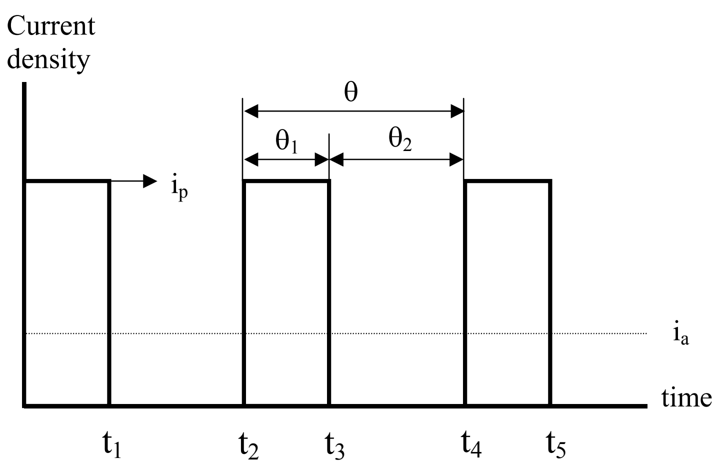
$$J = K_1 \exp\left[\frac{-bs\varepsilon^2}{zekT\eta}\right]$$

Tafel expression for overpotential

$$\eta = \alpha + \beta \log i$$

Pulse electrodeposition

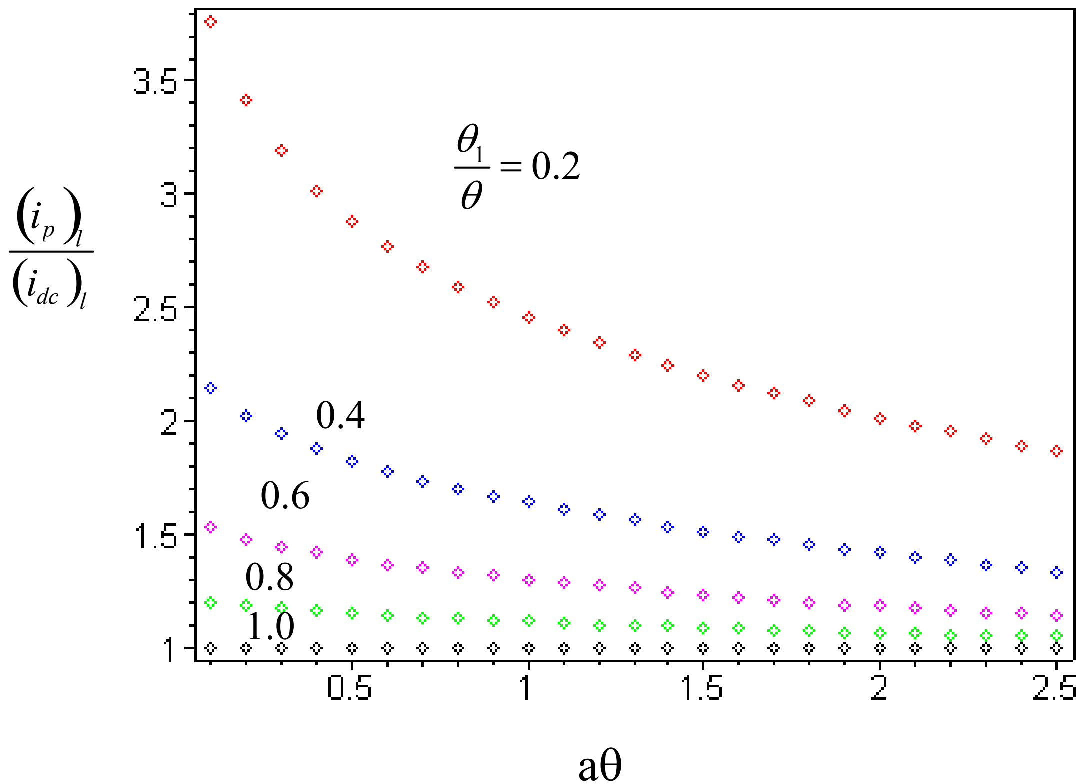
- Off time
- Concentration of electrolyte is recovered
- Electrodeposition at high current density



- K_1 – rate constant
- S – surface area occupied by one atom on the surface of the nucleus
- *e* – the charge of the electron
- *z* – the electronic charge of the ion
- k – the Boltzmann constant
- *T* – the temperature
- $b=P^2/4S$, where P is the perimeter and S is the surface area
- i – current applied
- α, β – Tafel constants
- η – Overpotential
- θ_1: on time
- θ_2: off time
- Ip: peak current density
- Ia: average current density
- Duty cycle: θ_1/θ

Comparison of the Limiting Current Density between Pulse and Direct Electrodeposition

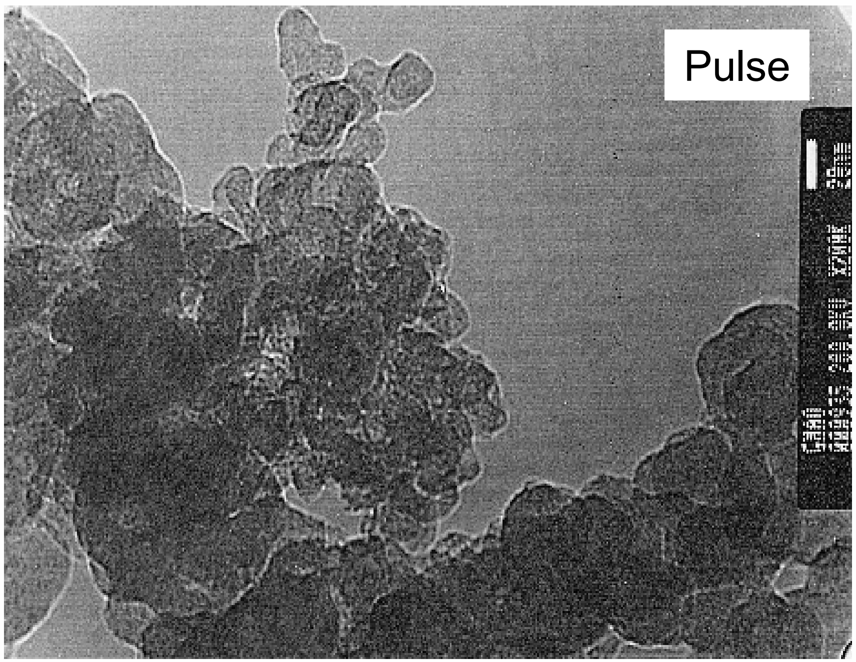
diffusion model by H. Y. Cheh,

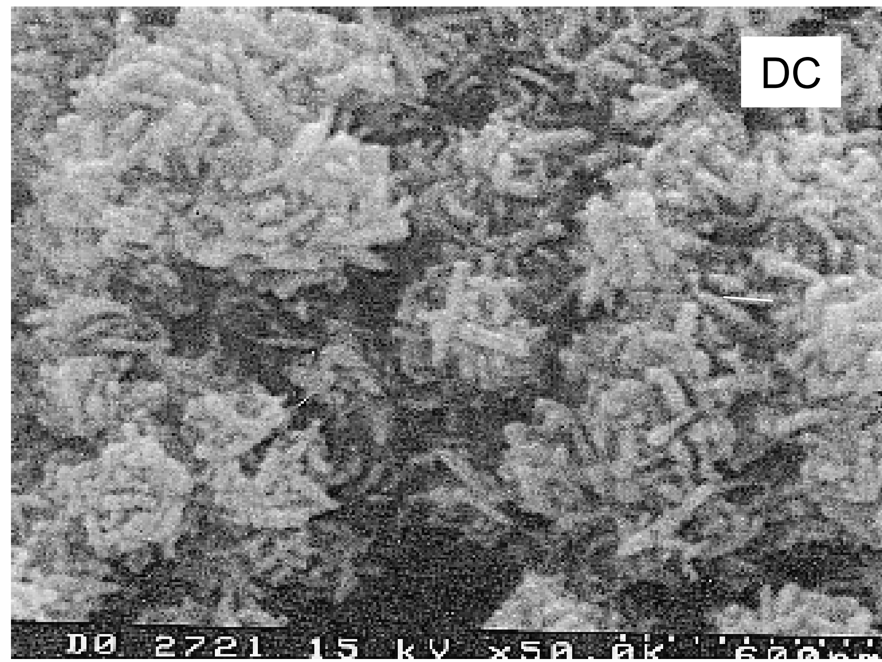


$$\frac{(i_p)_l}{(i_{dc})_l} = \frac{1}{1 - \frac{8}{\pi^2} \sum_{j=1}^{\infty} \frac{1}{(2j-1)^2} \cdot \frac{\left(\exp\left[(2j-1)^2 a\theta_2\right] - 1\right)}{\left(\exp\left[(2j-1)^2 a\theta\right] - 1\right)}}$$

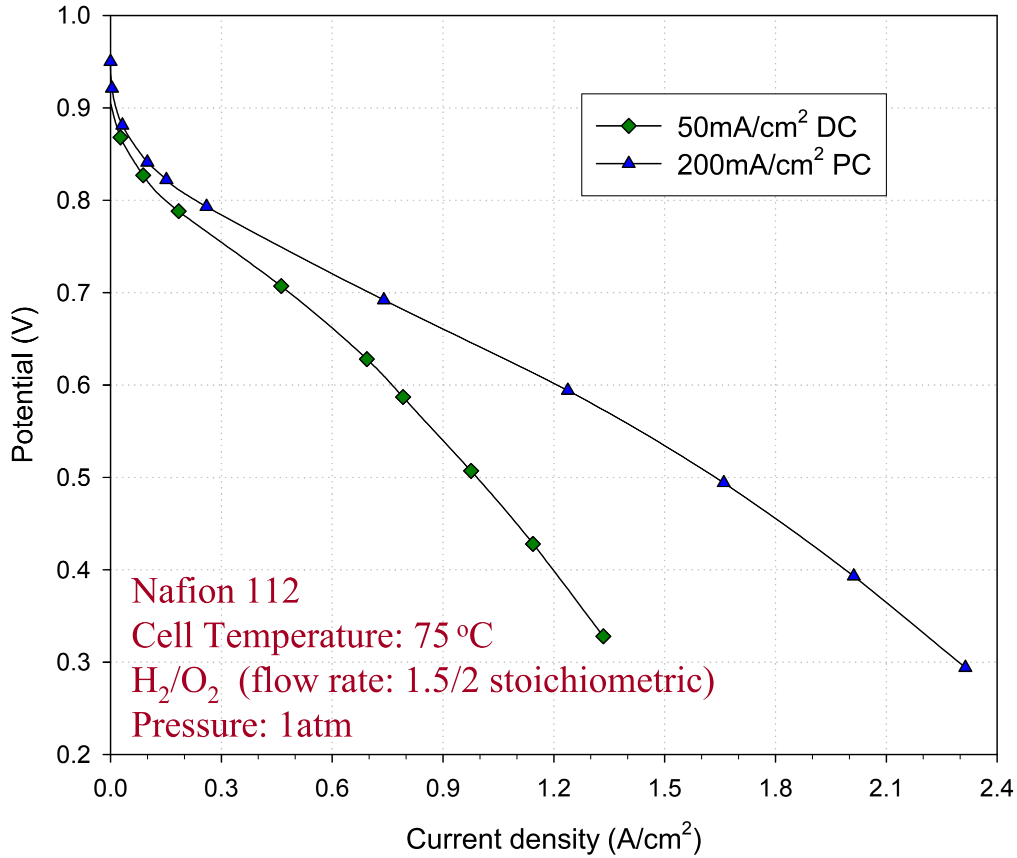
$$\mathrm{a} = \pi^2 D / 4\delta^2 \ (\mathrm{sec}^{-1})$$

TEM and SEM image of Pt electrodeposited electrodes



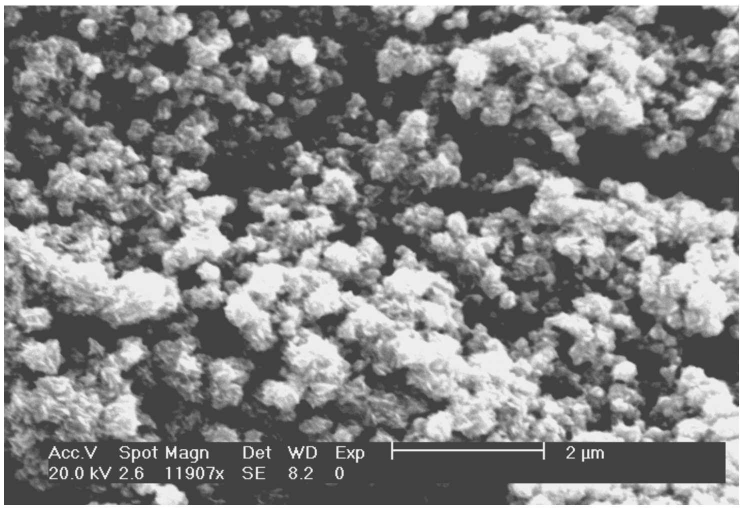


Polarization Curves of MEAs Prepared by Direct Current and Pulse Electrodeposition

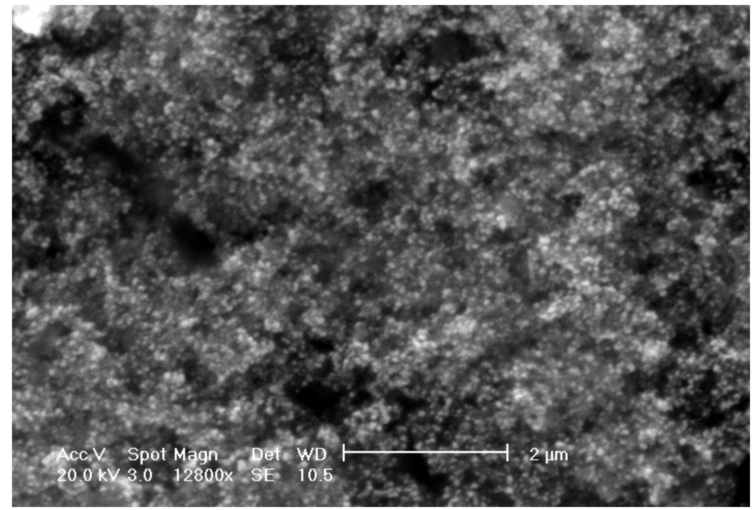


The conditions of pulse electrodeposition: 200mA/cm^2 of peak current density, 5.2ms on time and 70ms off time. Total charge is fixed at 6C/cm^2 on both cases.

SEM Images of Pt Electrodeposited Electrodes by D.C or P.C mode. (Total charge is fixed at $6C/cm^2$ on both cases)

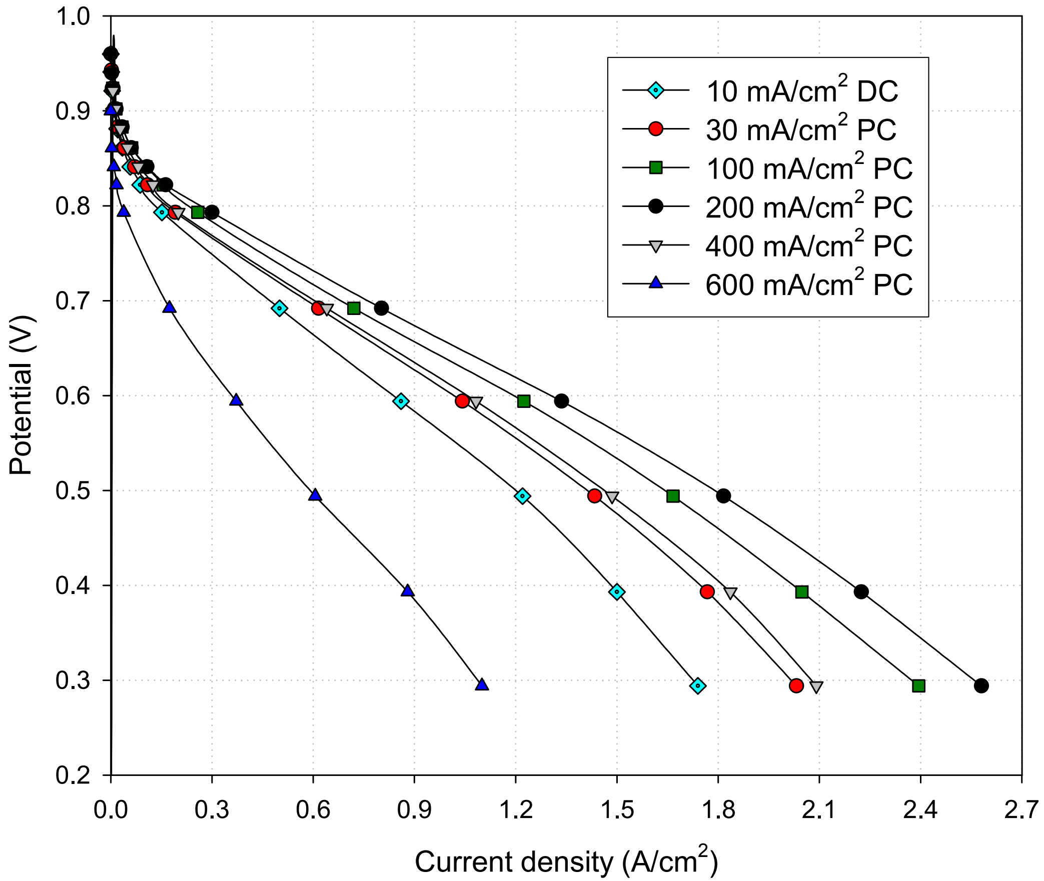


$50mA/cm^2$ of D.C. electrodeposition

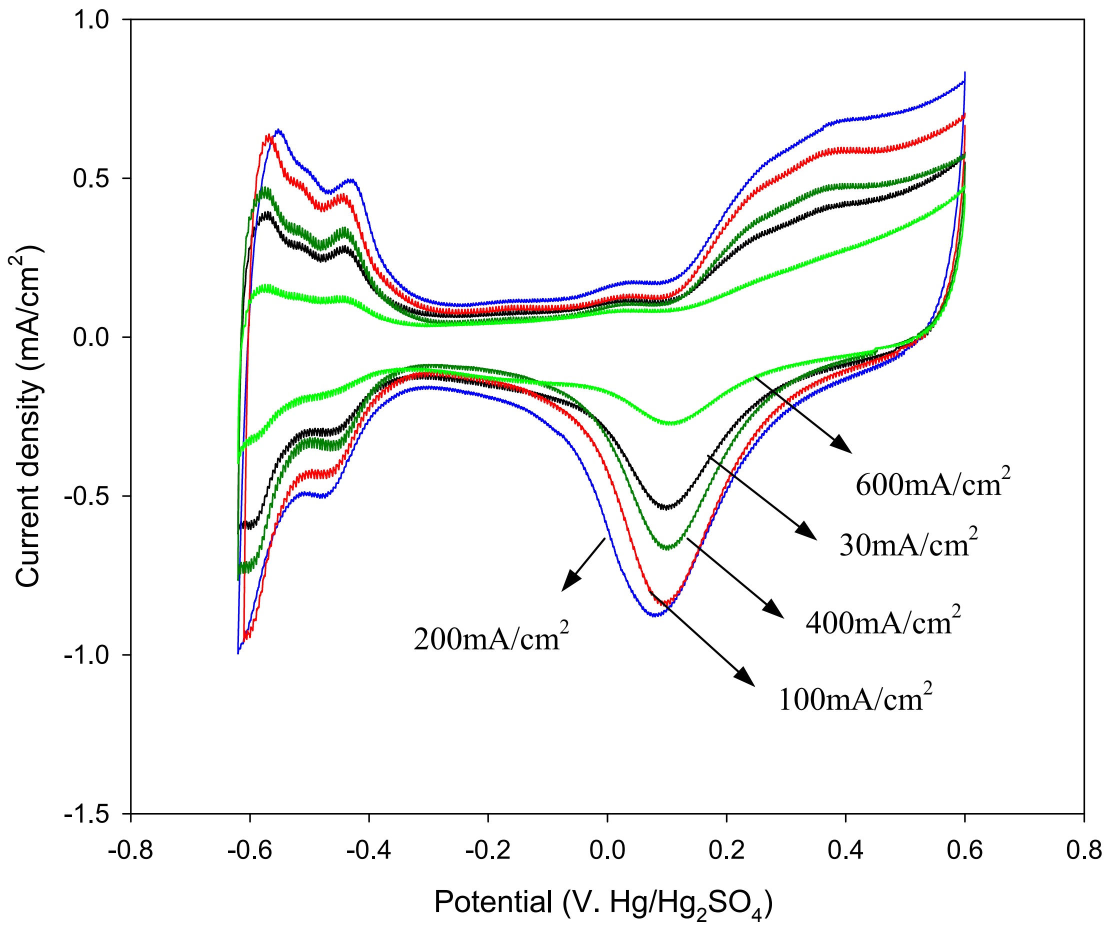


$200mA/cm^2$ of peak current density, 5.2ms on time and 70ms off time

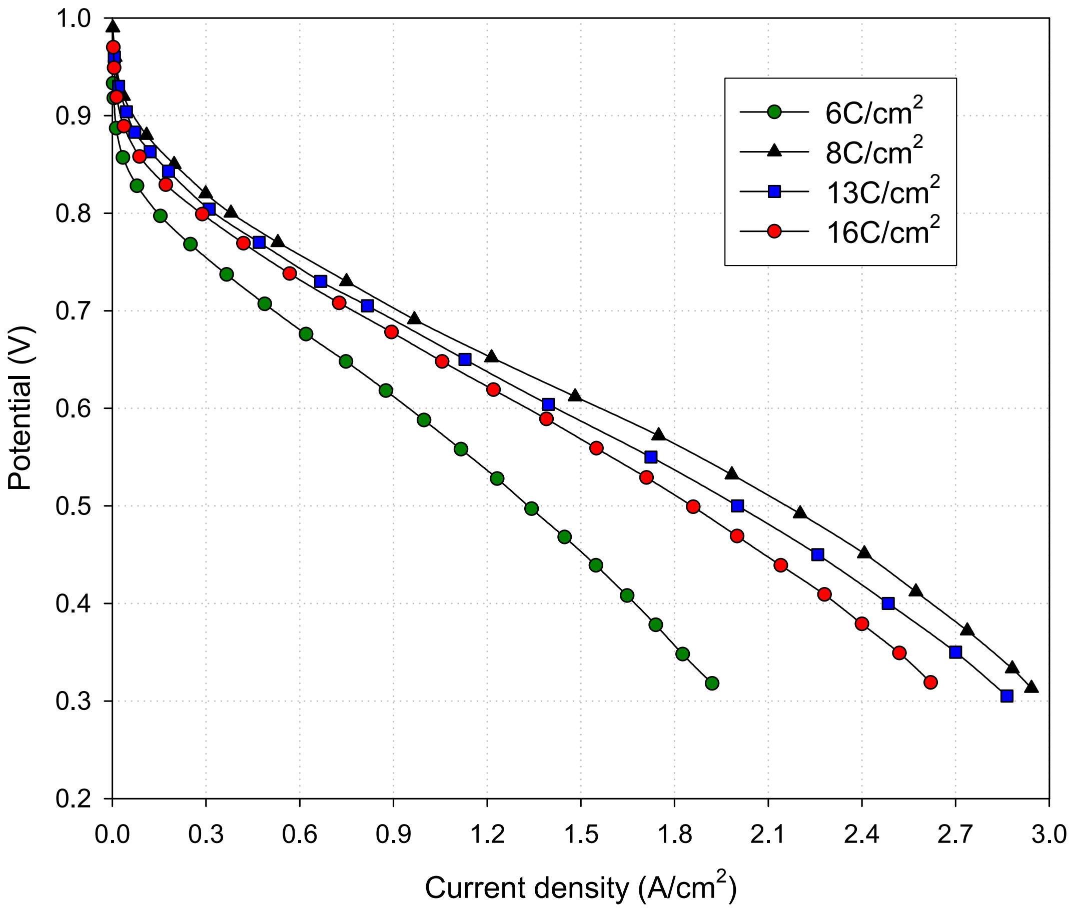
Effect of the peak current density of pulse electrodeposition on the performance of the PEM fuel cell



Cyclic Voltammograms of the Electrodes Prepared at Different Peak Current Densities in Pulse Electrodeposition



Effect of Charge Density on the Performance of PEM Fuel Cell



Comparison of Pt line scan image in the cross section of the MEA (A) 8C/cm^2 and (B) 20C/cm^2