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연료전지용 나노전극 소재

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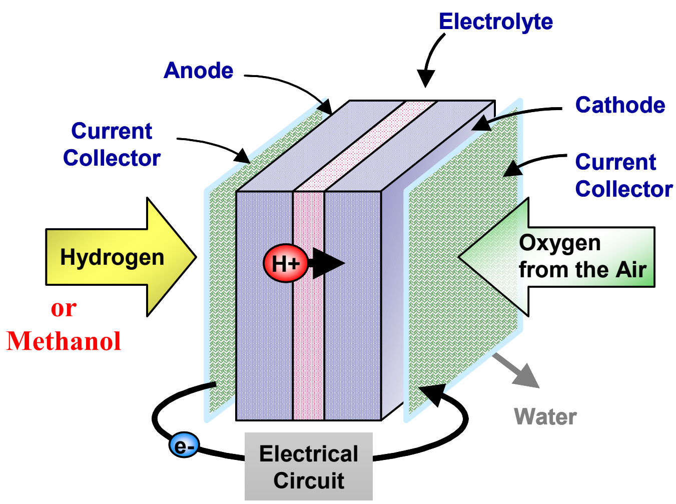
Fuel Cells


Electrolyte
Anode
Cathode
Current Collector
Current Collector
Hydrogen
or
Methanol
H+
Oxygen from the Air
Water
e-
Electrical Circuit

Issues in Fuel Cell Electrode

- ✓Nanostructure
- ✓Control of chemical and electronic structure
- ✓Nanoparticles *vs.* thin film materials
- ✓ Role of substrate
- ✓ Membrane-electrode interface & assembly

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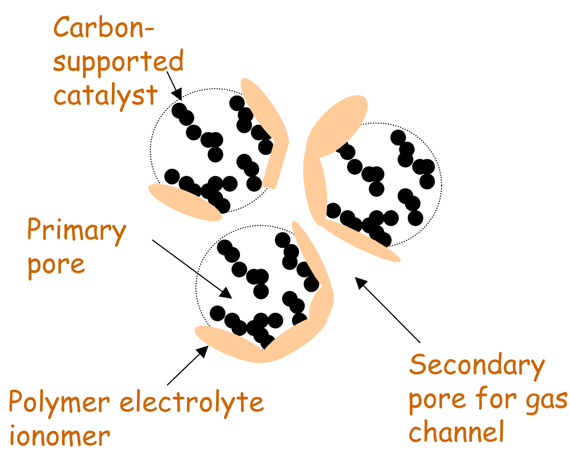
Fuel Cell Electrode



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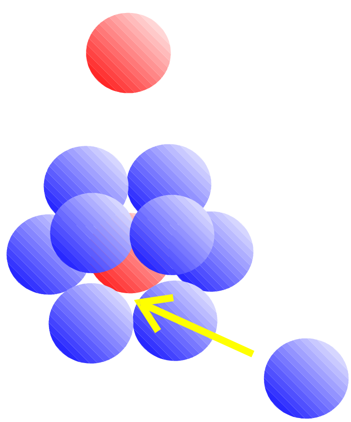
From Atom to Nanoparticle to Bulk Material

FCC cubo-octahedra: (111) triangle +(100) squares



Layer	N_S/N_B	d(nm)
1	100	
2	92	
3	76	1.17
4	63	1.62
5	49	2.07
6	45	2.53
7	39	2.98

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Preferablity of Nanoparticles

The size of Nanoparticle [nm]	# of Pt atoms per particle	Specific surface area [m^2/g]	Metal loading[mg/cm^2]
3.4	1362	82	1.55
3.0	936	93	1.26
2.5	542	112	1.05
2.2	369	127	1
2.0	227	140	0.9
1.7	164	170	0.75
1.5	117	186	0.68

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Comparison of Various Nanoparticle Syntheses

Method	Reductant	Solvent	Average Size [nm]	Onset Potential [V vs. NHE]
E-TEK	Unknown	Unknown	2.2	0.40
Impregnation Method	$NaBH_4$	H_2O	3~5	0.40
Colloidal Method 1	$NOct_4[BEt_3H]$	THF	2.3	0.39
Colloidal Method 2	$NaHSO_3$, H_2O_2	H_2O	2.2~2.5	0.38
K-JIST Method	$LiBH_4$	THF +	1.7	0.37

↑ Methanol oxidation (DMFC)

J. Electrochem. Soc. 149 (2002) A1299
J. Ind. Eng. Chem. 9 (2003) 63

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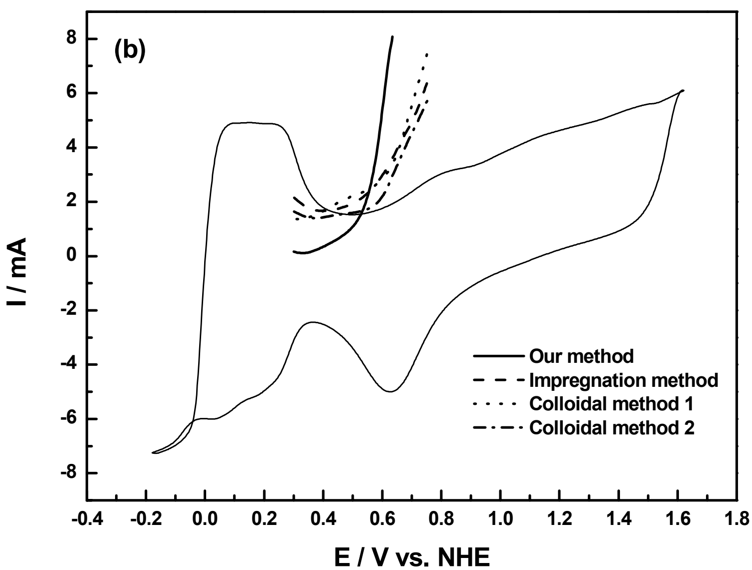
Methanol Electrooxidation



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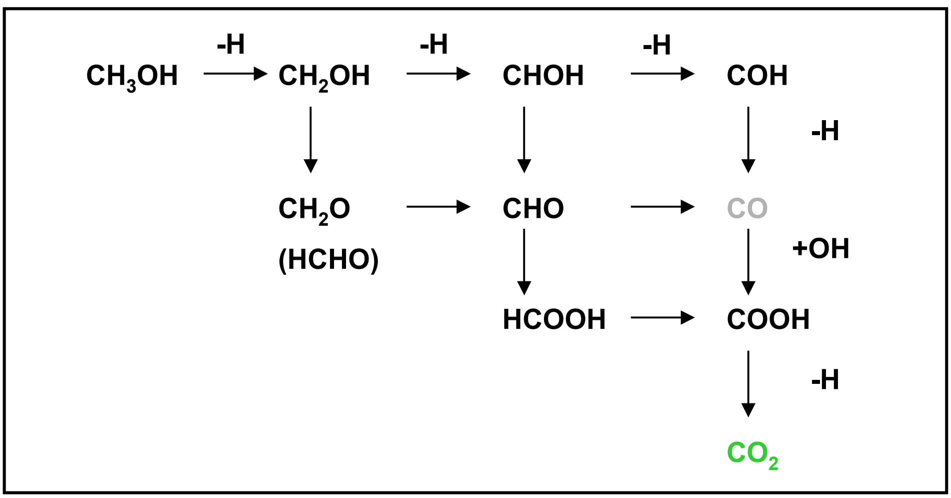
Mechanism of methanol electro-oxidation

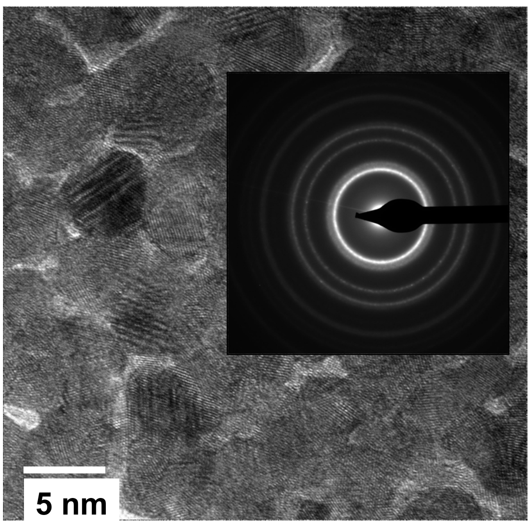
$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$

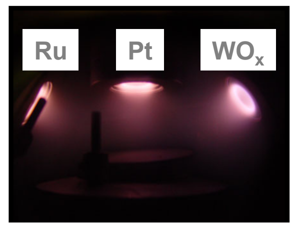


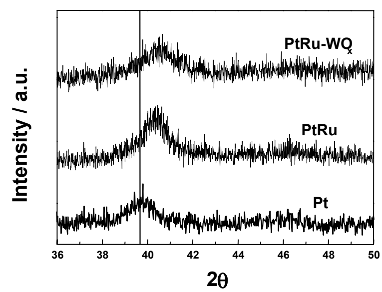
Ref. V. S. Bagotzky, Y. B. Vassiliev, O. A. Khazora, J. Electroanal. Chem., 81 (1977) 229

S. Park, Y. Xie, M. J. Weaver, *Langmuir*, 18 (2002) 5798

PtRu-WO_3 Nanocomposite Nanocomposite



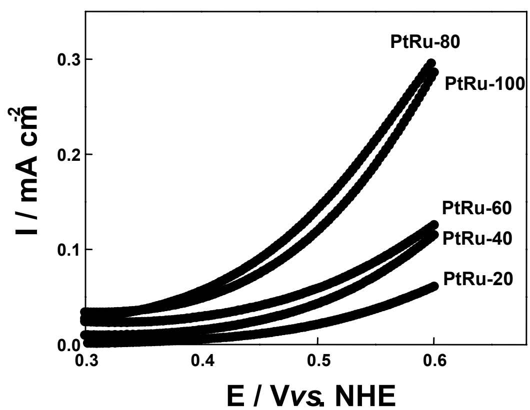




✓ **PtRu nanophase of 5 nm in size in amorphous tungsten oxide**

Appl. Phys. Lett., 82 **(2003) 1090.**

Pt/Ru alloy thin-film electrodes



✓ Pt/Ru(60:40) > (40:60) > (75:25) > (80:20) > (95:5) ~ pure Pt

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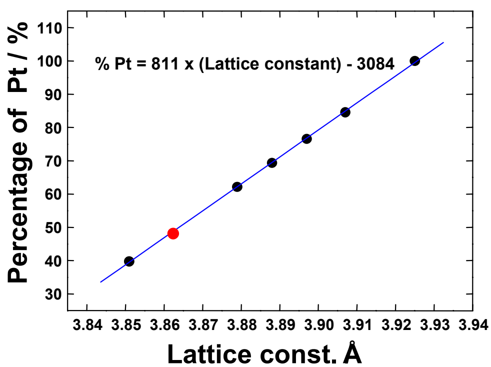
Pt/Ru Alloy Thin-Film Electrodes

XRD analysis : Alloy formation with various composition



Pt/Ru	a (Å)	% Pt
Pt	3.925	100
PtRu-20	3.907	84.56
PtRu-40	3.897	76.56
PtRu-60	3.888	69.36
PtRu-80	3.879	62.16
PtRu-100	3.851	39.76
PtRu (50:50) nanoparticle	3.862	48.08

Solid line: H. A. Gasteiger *group,* Surf. Sci. 293 (1993) 67.

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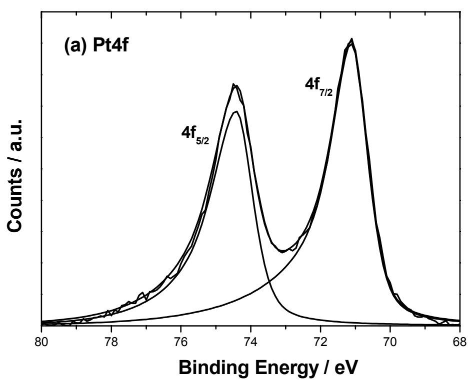
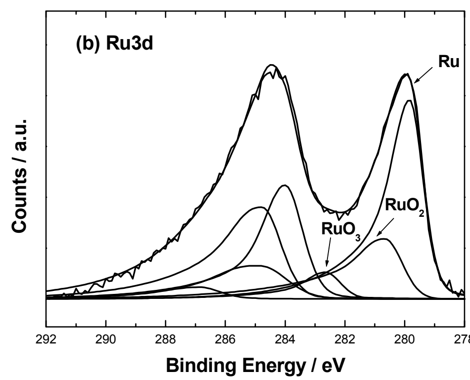
Surface analysis of PtRu nanoparticle by XPS





-- Pt contains metallic state only while Ru consists of various oxidative
- (RuO_2 and RuO_3) as well as metallic states

J. Phys. Chem. B 106 (2002) 1869, 104 (2000) 3518

Comparison of Chemical States: Ru

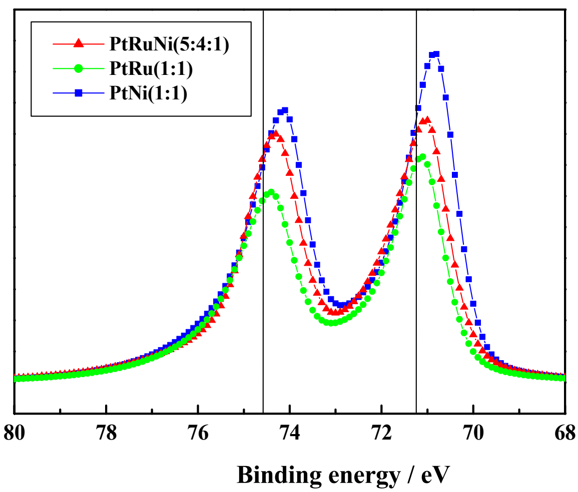
PtRu(1:1)

	XPS area ratio (%)		
	Disk-type	~5 nm	~1.7 nm
Metallic Ru	80.0	62.6	40.5
RuO_2	14.0	28.5	23.1
RuO_3	6.0	8.9	36.4

XPS: 2-3 nm depth

J. Electrochem. Soc. 150 (2002) A1299

Electronic Effect of Nanoparticles



▶Pt 4f peak shift to lower BE

PtNi ~ 0.4 eV

PtRuNi ~ 0.2 eV

PtRu ~ 0.09 eV

▪- Modified Pt : *Au-like?*

- CO binding energy *

Ir	>	Pt	>	Au
2.22		1.76		0.37 eV

Why?

- Electron transfer of 2nd metals to Pt
- Electronegativity

Ni(1.92) < Ru(2.2) < Pt(2.28)

J. Phys. Chem. B (2002)

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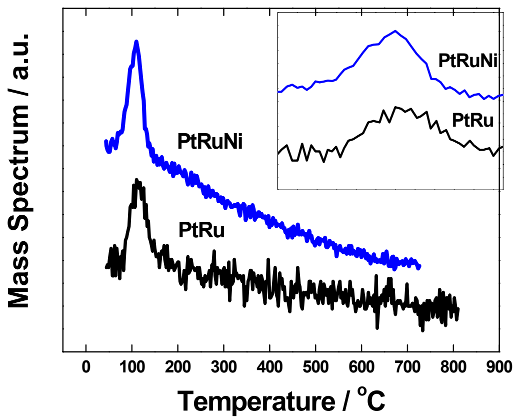
Pt-based Alloy Nanoparticles

Temperature-programmed desorption (TPD) of CO)



- ✓ **Binding energy of the adsorbed CO by TPD spectrum ~ XPS Pt*4f* peak shift**
  : Pt/Ru/Ni(383 K) < Pt/Ru(388 K) < Pt (400K).
- ✓ **The shift of d electron density from Ni to Pt would reduce the Pt-CO bond energy.**

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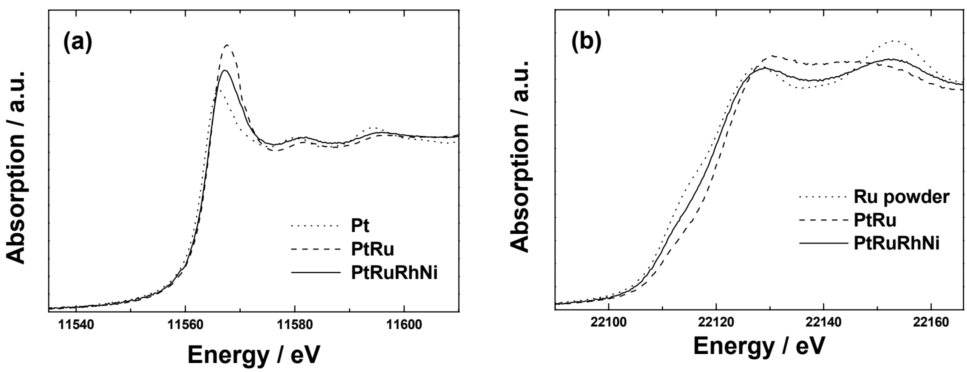
XANES Spectra

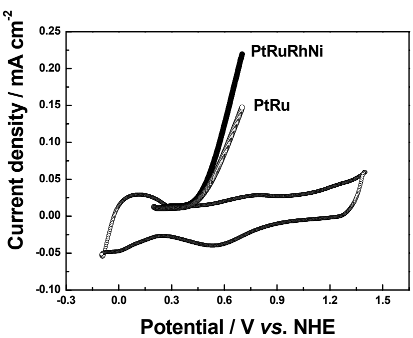


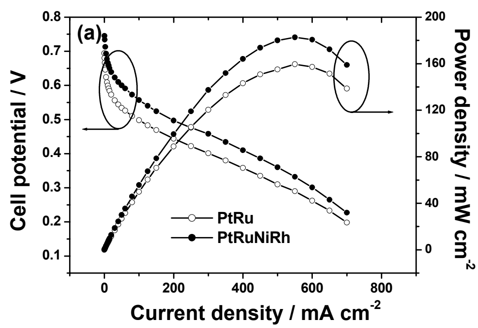
Pt LIII edge

Ru K edge

XRD & TEM for alloy nanoparticles

PtRu(1:1)

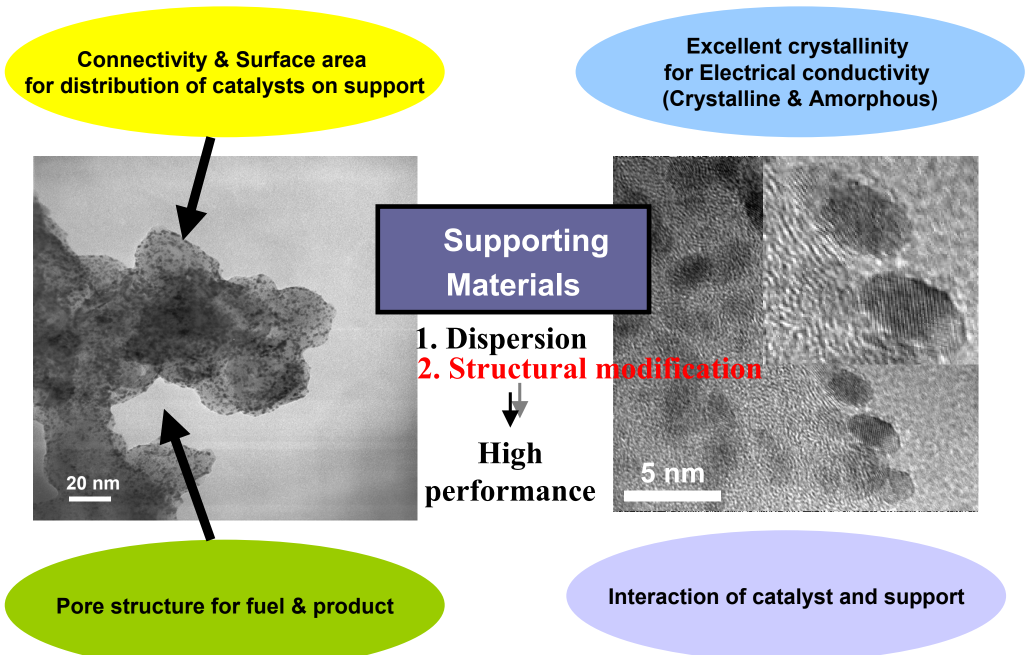




Pure Pt: 39.8º
PtRu: 40.5º

(111) plane
Pure Pt: 0.228 nm
PtRu: 0.224 nm

Carbon-supported Catalysts



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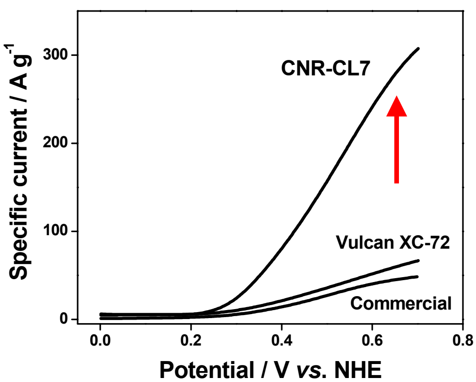
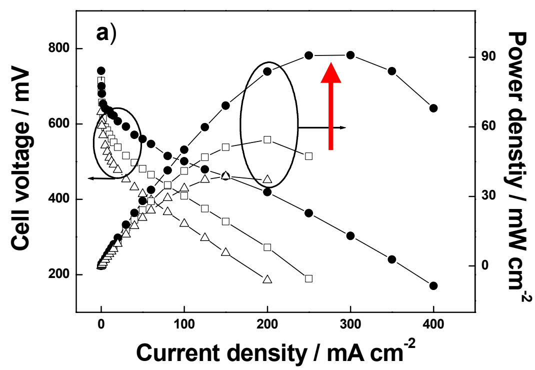
Carbon Nanocoil as a Support (collaboration with Prof. Hyeon in SNU)





- ✓ Methanol oxidation: 6 times higher than Vulcan XC-72 or commercialized electrode materials
- ✓ Twice higher DMFC performance at room temperature

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Modified Membrane for High Concentration Fuels

Electrochem. Comm. 5 (2003) 571.

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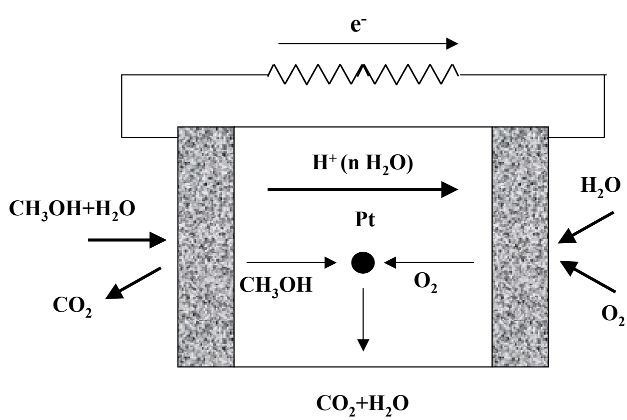
Modification of Nafion*: Nanocomposite*

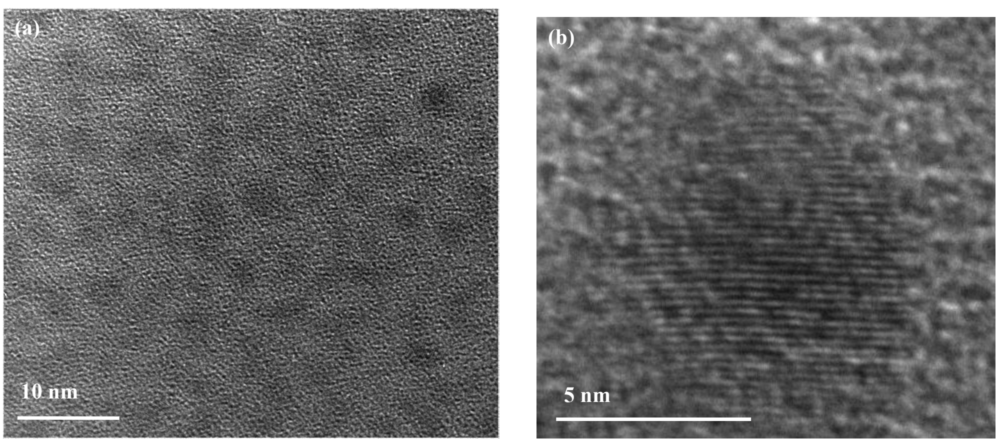
Dispersion of platinum nanoparticles in Nafion

→ **oxidizing methanol at the Pt**

→ **Reduce of amount of methanol reaching the cathode**



Pd Nanoparticle in Nafion



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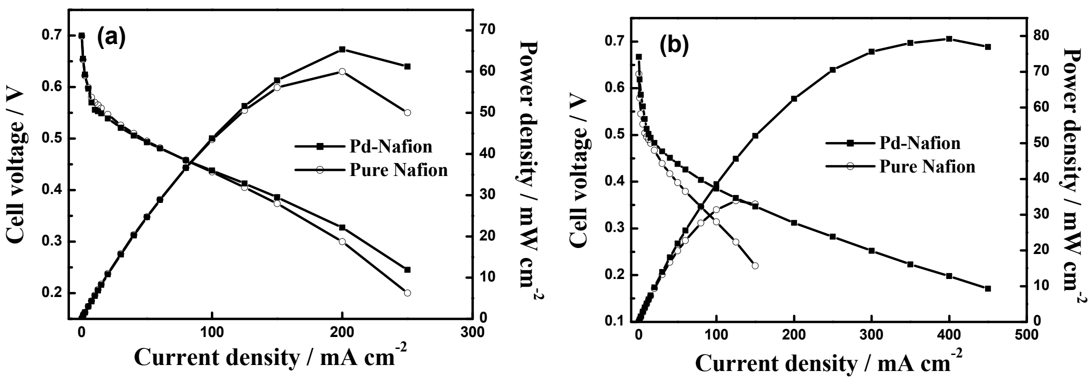
***MeOH crossover issue*: Pd Nanoparticle in Nafion**



Polarization curves Pd-Nafion and pure Nafion at 30 °C using (a) 2 M and (b) 10 M methanol as a fuel.

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High Efficient Fuel Cell Electrode Design

- ✓ **Nanoparticle Size & Distribution**
- ✓ **Role of Chemical & Electronic Structure**
- ✓ **Substrate Materials & Their Roles**
- ✓ **Thin Film Technologies for Fuel Cells**
- ✓ **Electrode-membrane Interface**
- ✓ **Methanol Crossover Tolerance**

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