Development of High Performance MEAs and Challenges for the Commercialization

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(LG 화학)

Development of High Performance MEAs and Challenges for the Commercialization

제 21회 한국막학회 춘계 심포지움

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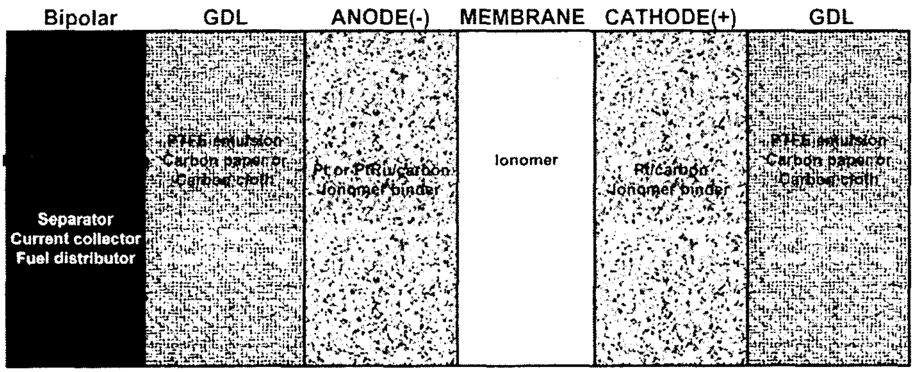
Outline

- Membrane Electrode Assembly
- Catalysts
- Membranes
- Modeling & Simulation
- MEA production

Design Factors for the MEA



Bipolar	GDL	ANODE(-)	MEMBRANE
•Corrosion resistance •Methanol resistance	•Porosity of carbon paper •PTFE content •Hydrophobitization of carbon on GDL	•Types of catalysts •Concentration of ionomer •Methods of coating •Hot pressing conditions	•Thickness •Composite?-post treatments •Types of membrane (hydrocarbon, fluoropolymer)

Catalysts (I)

DMFC - Catalysts

◆ DMFC catalysts and needful amount

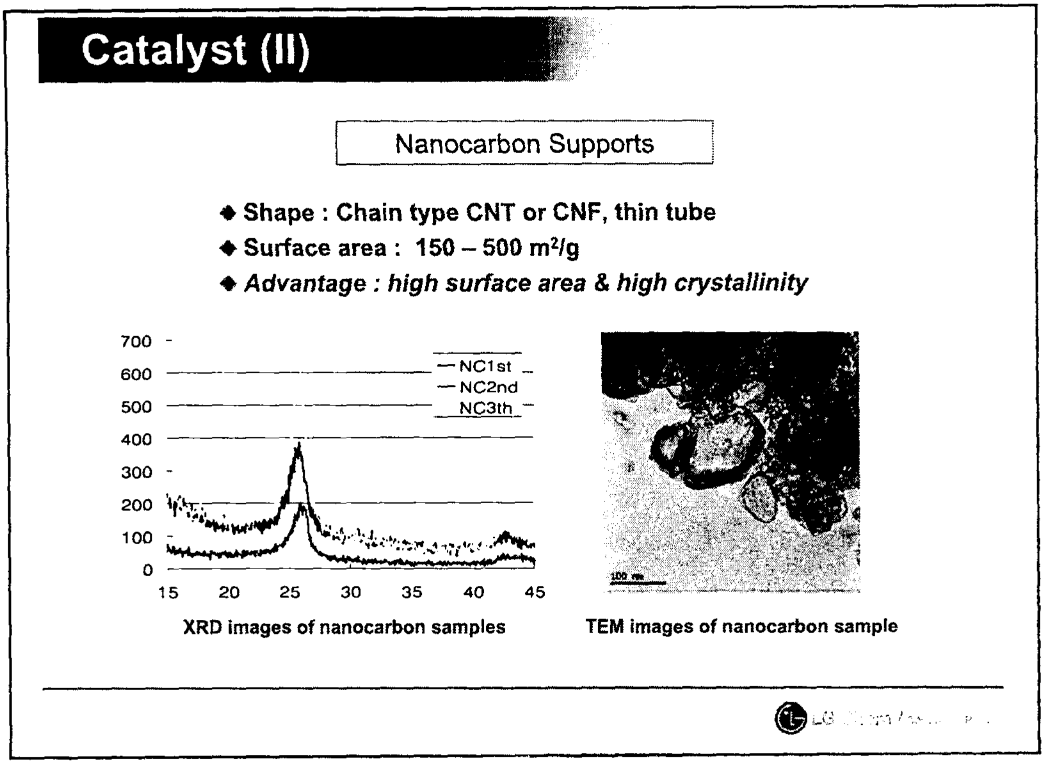
anode	cathode	Pt (mg/cm^2)
PtRu/C or PtRu black	Pt/C or Pt black	1 ~ 4

1) Reduction of catalyst loading must be *achieved* before *commercialization.*

Breakdown of DMFC costs Catalyst (>50%) (10-20%) (30-40%)

2) Carbon supported catalyst is under consideration for cost reduction and stability.

Highly dispersed electrocatalyst with high loading on a carbon support is the research challenge.



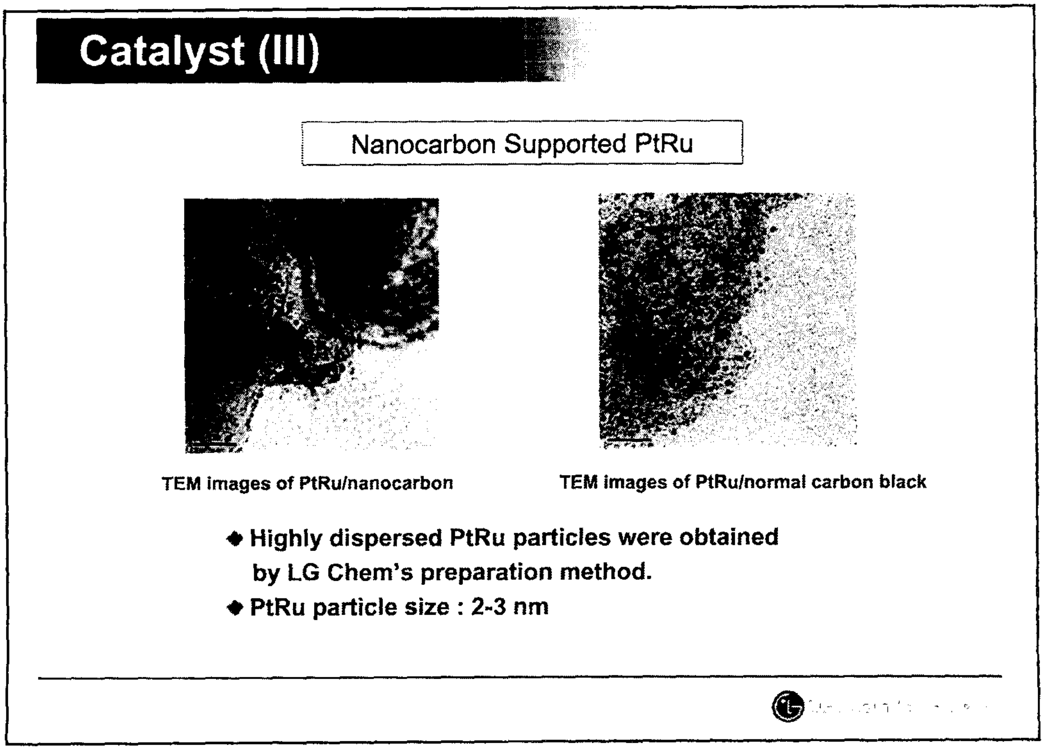
Catalyst (II)

Nanocarbon Supports

- Shape : Chain type CNT or CNF, thin tube
- Surface area : 150 – 500 m²/g
- *Advantage : high surface area & high crystallinity*

XRD images of nanocarbon samples

TEM images of nanocarbon sample



Catalyst (III)

Nanocarbon Supported PtRu

TEM images of PtRu/nanocarbon

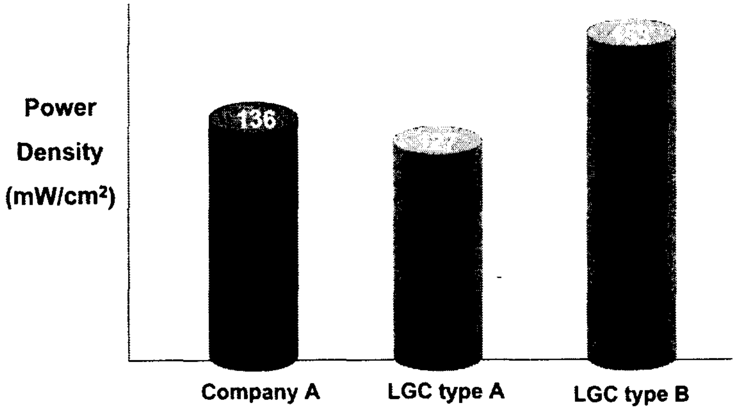
TEM images of PtRu/normal carbon black

- Highly dispersed PtRu particles were obtained by LG Chem's preparation method.
- PtRu particle size : 2-3 nm

Catalyst (IV)

Performance - DMFC

- Catalyst: PtRu/C 1mg/cm², Pt/C 2mg/cm²



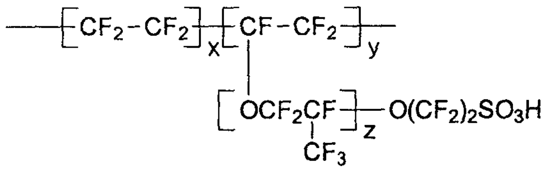
Membranes (I)

Required Membrane Properties

- **Ionic conductivity in the range of > 0.1 S/cm (80°C)**
- **Thermal and hydrolytic stability**
- **Oxidative and reductive chemical and electrochemical stability**
- **Mechanical stability and high flexibility**
- **Reasonable range of water uptake**
- **Low electro-osmotic water transport, $H_2O/H^+ = 1$**
- **Low methanol crossover, in case of DMFC**

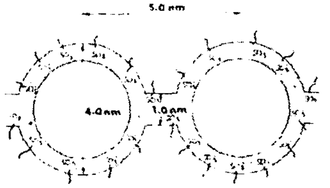
Membranes (II)

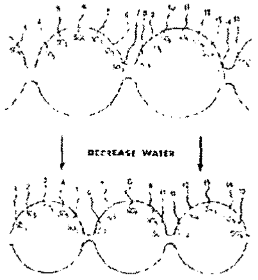
Currently the *only* Generally Accessible Membrane !



$$-\left[CF_2-CF_2\right]_x\left[\underset{\left[OCF_2\underset{CF_3}{CF}\right]_z O(CF_2)_2SO_3H}{CF}-CF_2\right]_y-$$

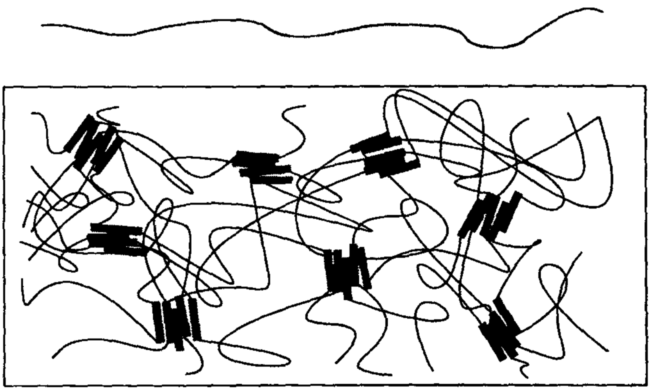
General structure of the Nafion® membrane :
x = 6-10, y = z = 1., Du Pont in 1966



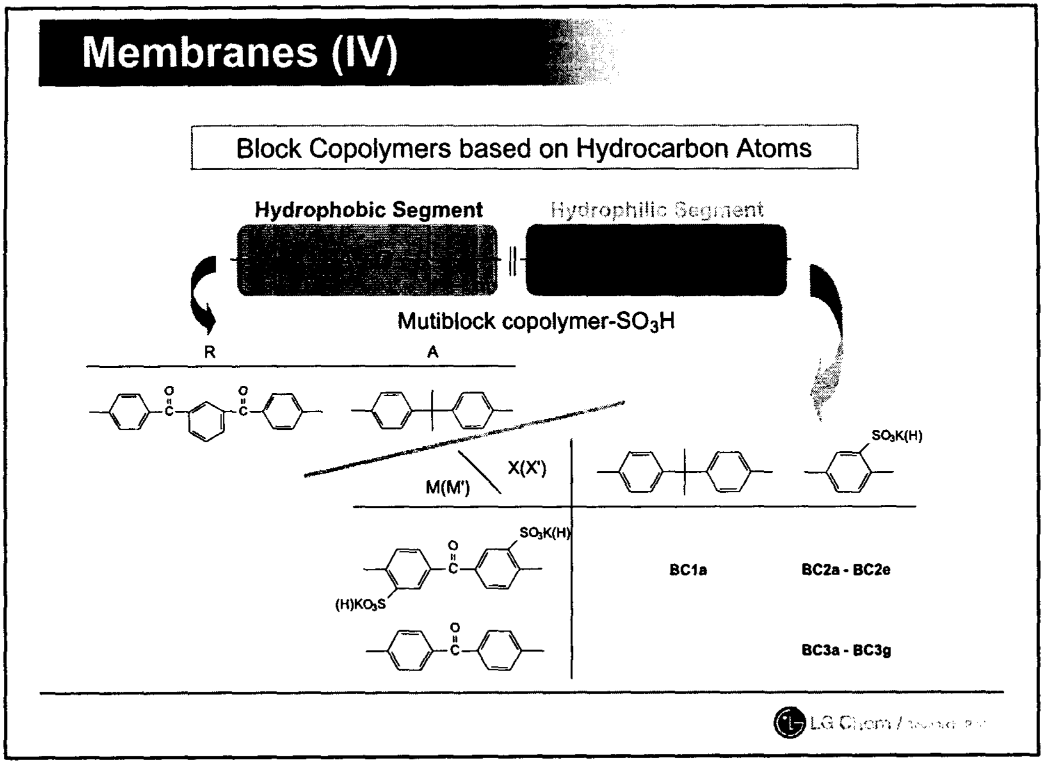


Membranes (III)

Strategy of the LG Chem, Ltd.



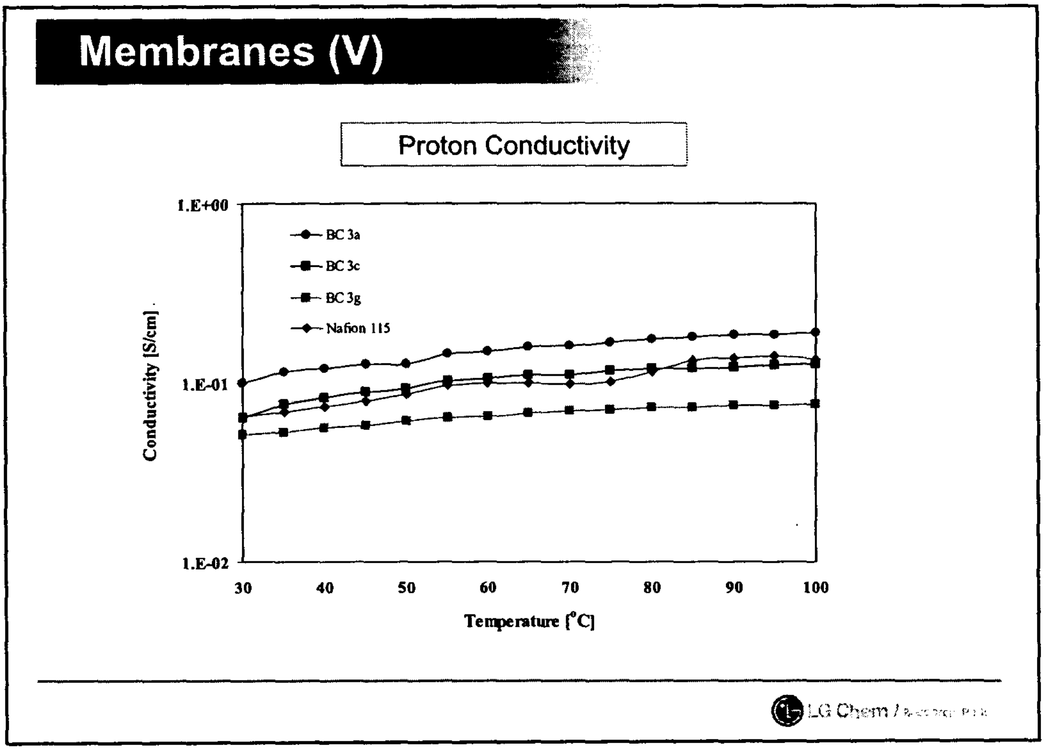
Schematic drawing of block copolymers and phase separation.
Red: hydrophilic blocks; Blue: hydrophobic blocks.



Membranes (IV)

Block Copolymers based on Hydrocarbon Atoms

LG Chem /



Membranes (V)

Proton Conductivity

LG Chem /

Membranes (VI)

Characterization

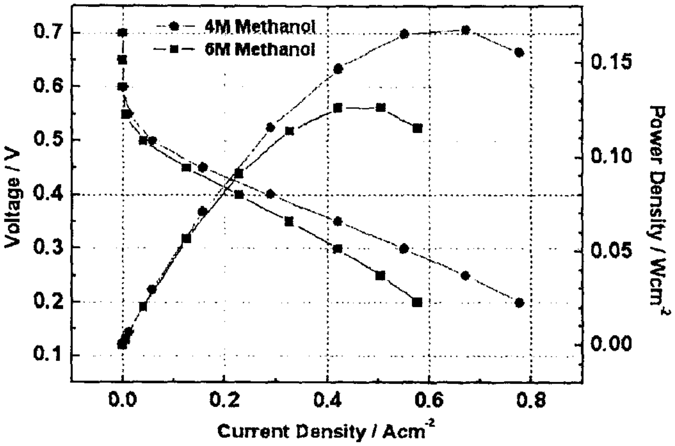
	Membrane	R.T.	40 °C	60 °C	80 °C	100 °C
Water Uptake (%)	BC3a	38	42	55	84	100
	BC3c	20	24	40	50	65
	BC3g	18	20	28	35	46
	Nafion 115	22	25	28	32	38

	Membrane	R.T.	40 °C	60 °C
Methanol Uptake (%)	BC3a	50	80	110
	BC3c	30	45	60
	BC3g	22	35	50
	Nafion 115	52	85	130

	Membrane	R.T.	40 °C	60 °C	80 °C
Methanol Crossover [illegible]	BC3a	1.51	1.98	3.15	4.43
	BC3c	0.89	1.40	2.41	2.92
	BC3g	0.64	0.95	1.68	2.24
	Nafion 115	2.40	3.43	5.50	7.16

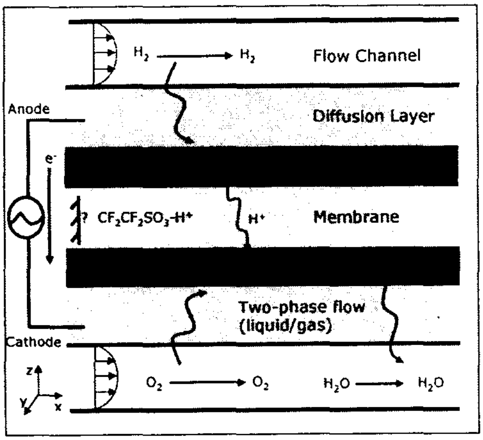
Membranes (VII)

Performance - DMFC



Fuel Cell Simulation (I)

Integrated Multi-Scale Simulation for PEMFC



Model Development

- Model accessibility: inherent material properties
- System extendibility: water treatment, stack

Benefits of CFD

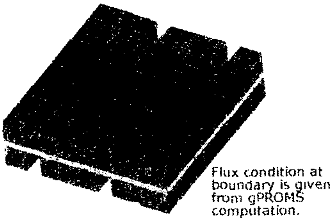
- Observation of distributive phenomena
- *Gaining insight and understanding*
- Leads to novel ideas & concepts
- [illegible]
- [illegible]
- [illegible]
- [illegible]

Fuel Cell Simulation (II)

FLUENT/gPROMS Hybrid Scheme

Fluent 6.1.18 (3D)

FC | DL | CL | MB | CL | **DL | FC**



Flux condition at boundary is given from gPROMS computation.

- Transport Equations
- Flow Channel & Gas Diffusion Layer

gO:CFD Reactive Membrane Interface

ass Fraction
emperature
ressure

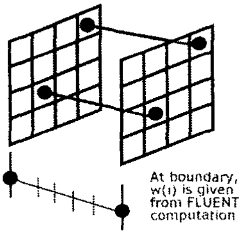
ass Flux
eat Flux
onitored

$$\int(\mathbf{n}\cdot \mathbf{J}_i)dS = \frac{1}{\Delta n}\int(\mathbf{n}\cdot \mathbf{J}_i)dV$$

$$(\Delta n \cdot dS = dV)$$

gPROMS 2.3.4 (1D)

FC | DL | **CL | MB | CL** | DL | FC



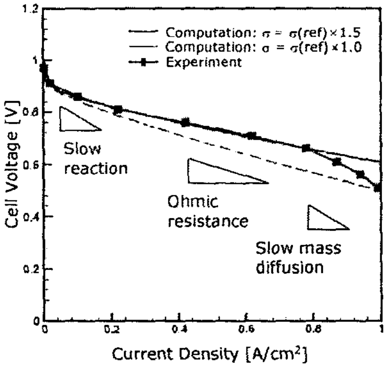
At boundary, w(i) is given from FLUENT computation

- Kinetic Equations
- Catalyst Layer & Membrane

(In House Modeling Required)

Fuel Cell Simulation (III)

Fuel Cell Module Verification



Electron Production Rate

$$j \equiv \frac{d[e^-]}{dt} = (aj_0^{ref}) \cdot \left(\frac{C_k}{C_k^{ref}}\right)^{\gamma} \cdot \left(\exp\left(\frac{\alpha_a F}{RT}\eta\right) - \exp\left(-\frac{\alpha_c F}{RT}\eta\right) \right)$$

$$(aj_0^{ref})_a = 5 \times 10^8 / J_c = 5$$

$$(aj_0^{ref})_c = 1 \times 10^2 / J_c = 1 \times 10^{-6}$$

$$C_i / C_{i,ref} = (x_i / x_{i,ref})(P/P_{ref})(T_{ref}/T),$$

$$(\tilde{C}_{H_2,ref} = 546.5[mol/m^3], \tilde{C}_{O_2,ref} = 3.39[mol/m^3])$$

Ionic Conductivity

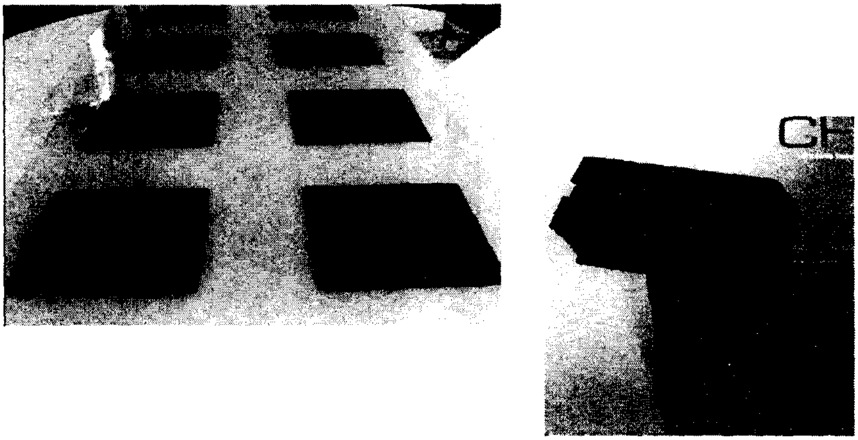
$$\sigma_e^{ref}(T) = (c_1^{con}) \times \exp\left(c_2^{con}\left(\frac{1}{1.01} - \frac{1}{T}\right)\right) \times (f_\lambda(\lambda))$$

$$(c_1^{con} = 10^2[S/m]/\sigma_c, c_2^{con} = 1268/300 = 4.22667)$$

※ S. Um, C.Y. Wang, K.S. Chen, Computational fluid dynamics modeling of proton exchange membrane fuel cells, J. Electrochem. Soc. 147 (2000) 4485

MEA Production

- ◆ **LG Chem established pilot scale MEA production facilities.**



Challenges for the Comm

- ➢Hydrogen storage
- ➢Methanol cartridge infra
- ➢Improving performance
- ➢Costs
- ➢**Durability**
- ➢High temperature operation

Membrane Failure

- ➢Chemical degradation by H_2O_2 at ORR
  - $O_2+4H^++4e^-\rightarrow 2H_2O$ (1.229V)
  - $O_2+2H^++2e^-\rightarrow H_2O_2$ (0.695V)
  - $H_2O_2+2H^++2e^-\rightarrow 2H_2O$ (1.763V)
- ➢Permeation of oxygen to anode also allows H_2O_2 to form on anode

LIFETIME OF MEMBRANES

- All membranes have lifetime issues
- Generally PFSA is better than aromatics in FC environment
- Thermal stability
  - -C-S bond homolysis for sulfonated aromatics
- Oxidative stability
  - - Free radical generated

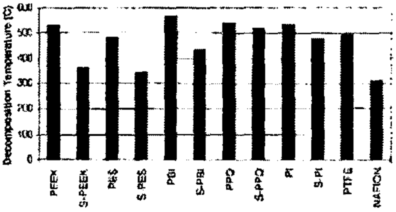


Fig. 3. Temperature of 5% weight loss in helium

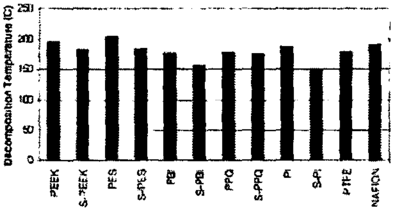
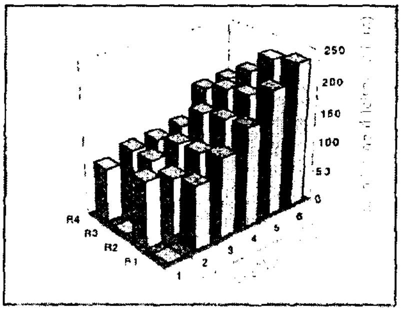


Fig. 4. Temperature of 5% weight loss in saturated vapor for 24 h.

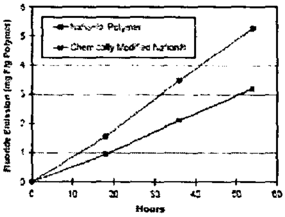
Polym. Deg. Stability, 67(2000), 335

LIFETIME OF MEMBRAN

- ABB Membrel PEM electrolyser operated by SWB GmbH
- 1.7 year operation at 400 A, 80 °C
  - -Pt catalyst on hydrogen side (cathode)
  - -Ru/Ir catalyst on oxygen side (anode)
- Nafion shows >50% thickness loss
- -SO_3H lost at same rate as thickness
- Fluoride detected in water effluent
- Erosion of membrane from hydrogen electrode side
- Most thinning near oxygen output end



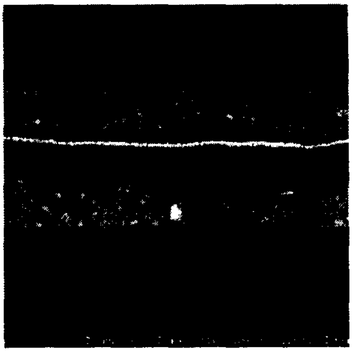
J. Appl. Elect., 28(1998), 1041



J. Power Sources., 131(2004), 41

Catalyst Migration

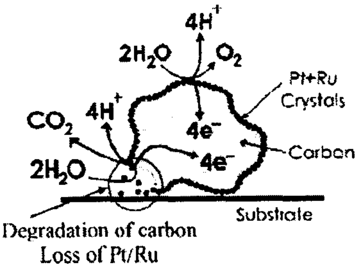
- Potential cycling allows Pt to dissolve and redistribute
- Pt stability is a challenge even for low temperature fuel cells



R. Darling and J. Meyers, Kinetic modeling Of Pt dissolution in PEMFCs", J. Eectrochem., 150, A1523 (2003)

Carbon Corrosion

- Degradation of carbon catalyst support during operation in the absence of fuel
- Partial hydrogen coverage on anode
  - *Fuel introduction on start up*
  - Blockage of fuel channel with water
- High potentials between solution and cathodes (1.8V)
  - *Corrosion of carbon supports*
  - Oxygen evolution



$C+2H_2O \rightarrow CO_2+4H^++4e^-$

J. Power Sources., 127(2004), 127