Fuel Cells – 1

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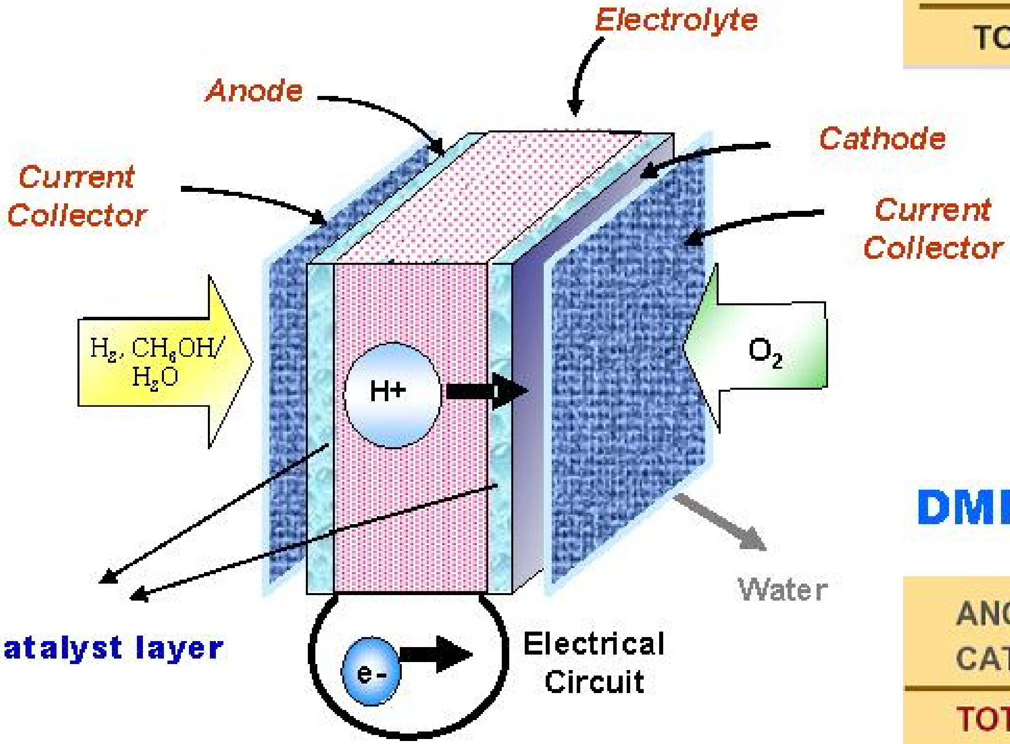
Fuel Cells

Electrochemical cell which can continuously convert the chemical energy of a fuel and an oxidant to electrical energy



PEMFC (Proton Exchange Membrane Fuel Cell)

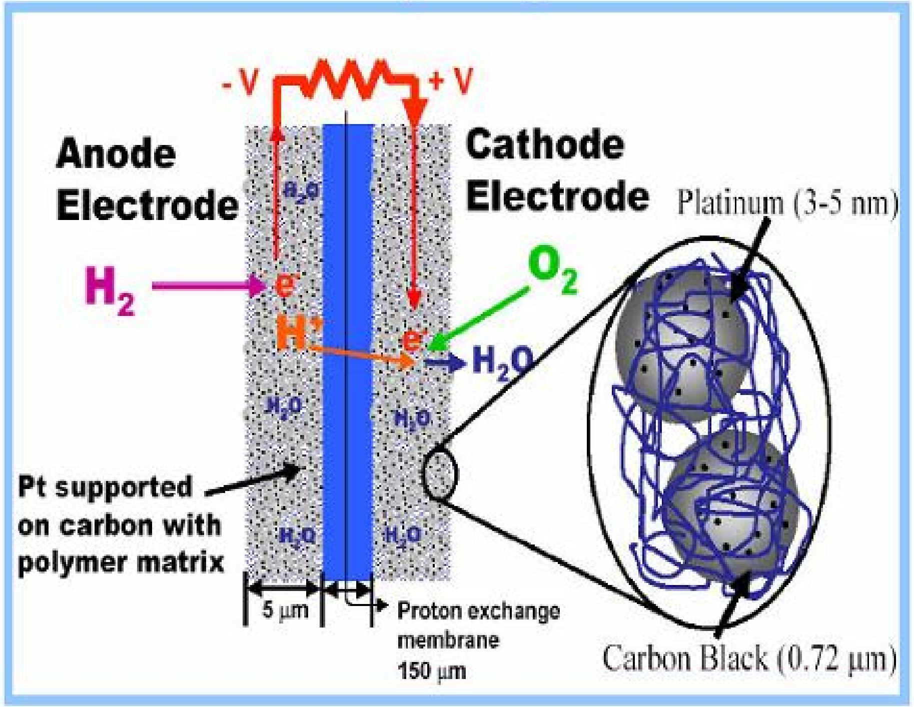
ANODE	: $H_2 = 2H^+ + 2e^-$		
CATHODE	: $1/2O_2 + 2H^+ + 2e^- = H_2O$		
TOTAL	: $H_2 + 1/2O_2 = H_2O$	$E^o = 1.23V$	

DMFC (Direct Methanol Fuel Cell)

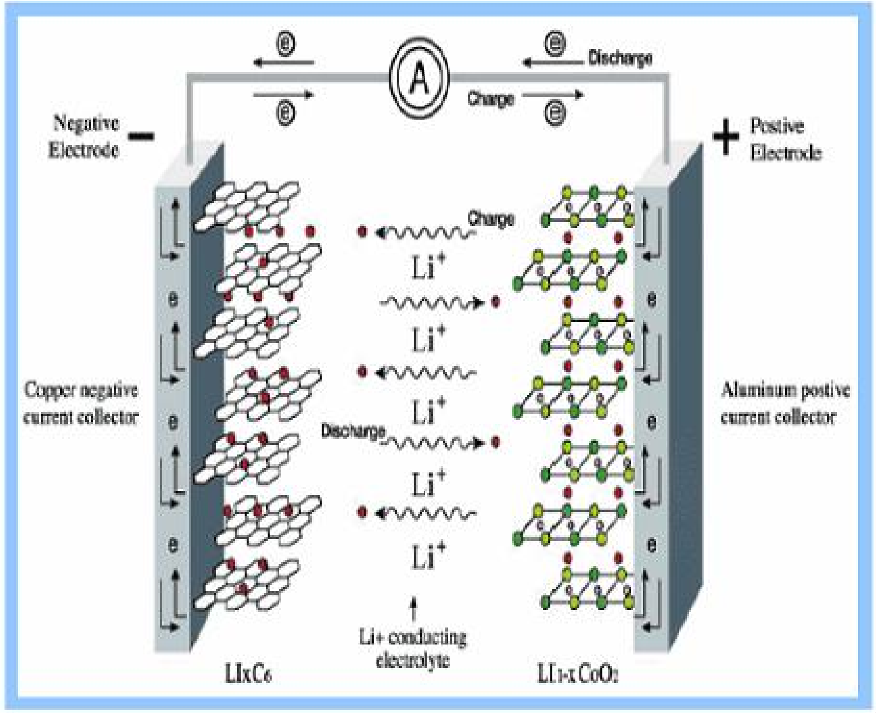
ANODE	: $CH_3OH + H_2O = CO_2 + 6H^+ + 6e^-$	
CATHODE	: $3/2O_2 + 6H^+ + 6e^- = 3H_2O$	
TOTAL	: $CH_3OH + 3/2O_2 = CO_2 + 2H_2O$	$E^o = 1.18V$

Fuel Cell vs. Battery

Membrane Electrode Assembly (MEA)



Li_xC_6/Electrolyte/CoO_2



- Chemical E → Electrical E
- Continuous generation of electricity.
- No need for electrical charging.

- Chemical E ↔ Electrical E
- Discontinuous generation of electricity.
- Need for electrical charging.

Classifications of fuel cells

● Direct Fuel Cell

- Operating T: Low(<100°C), intermediate(100-500), high(>500 °C)
- Type of fuels: natural gas, hydrogen, organics (hydrocarbons, alcohols), nitrogen compounds (ammonia, hydrazine)
- Nature of electrolytes: aqueous, molten salts, solid electrolyte (ceramic), polymer electrolyte

● Indirect Fuel Cell

- Organics to hydrogen (or other fuels) by reformer or catalyst
- Enzymatic decomposition of biomaterials to hydrogen

● Long-term direction

- New fuels & new fuel cell systems
- New organics, Biochemicals, etc.

Characteristics of fuel cells

i) High efficiency and reliability

- convert up to 90% of the energy in fuel into electric power & heat
  (high electrical conversion efficiency: 46% for PAFC, 60% for MCFC)
- fewer moving parts → higher reliability

ii) Environmental performance

- improving air quality: lower pollutant emission (SO_2, NO_x, CO_2, ash etc)
- reduce water consumption & waste water discharge
- quiet, no noise
- no used battery problem

iii) Unique operating characteristics

- economic benefits & technologies → research
- potential markets of fuel cell systems
- power plant, electrical vehicle, portable electronics

Basic Principles

Thermodynamics

$$\Delta G = \Delta H - T\Delta S, \qquad \Delta G^0 = -RT\ln K$$

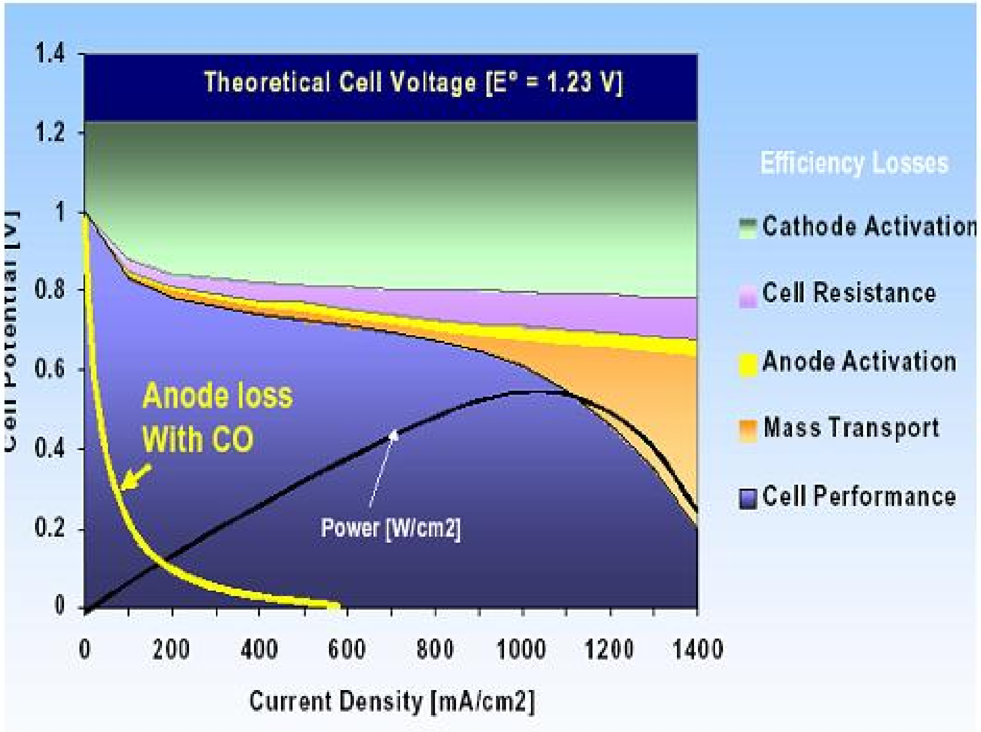
K ; equilibrium constant, $\Delta G < 0 \rightarrow$ a reaction can occur

$$\Delta G = -nFE$$

Kinetics

- Overvoltage or Polarization: ohmic, activation, concentration

< Polarization curves of H_2-O_2 cell >



▶ Activation
- slow electrode RXN

▶ Ohmic
- resistance of electrolyte

▶ Concentration
- difference btn. surface & bulk

Electrode Mechanism

- H_2-O_2 fuel cell

- In acid electrolyte

anode: $H_2 \rightarrow 2H^+ + 2e^-$ $E_0 = 0.000$ V

cathode: $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$ $E_0 = 1.229$ V

Total: $H_2 + 1/2O_2 \rightarrow H_2O$ $E_0 = 1.229$ V

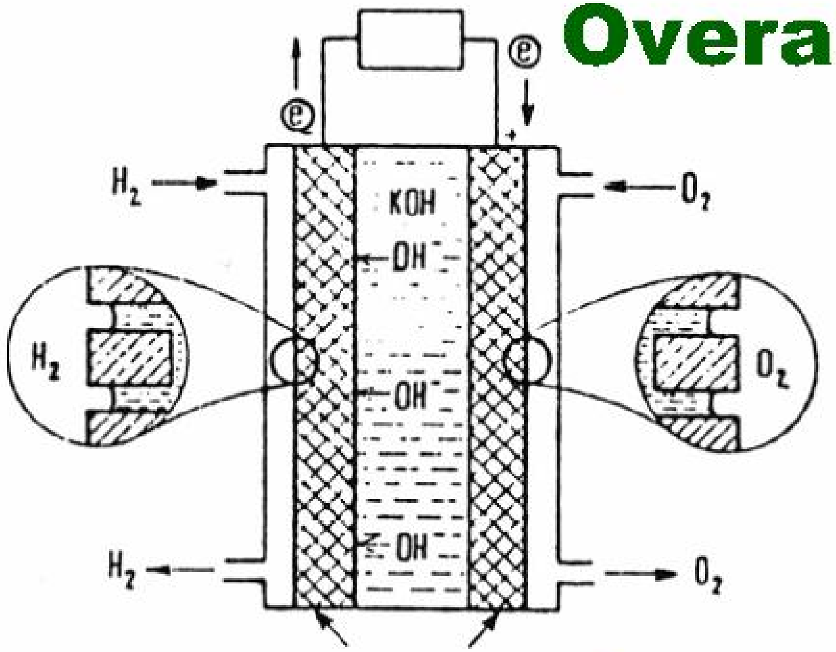
- In alkaline electrolyte

anode: $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$ $E_0 = -0.828$ V

cathode: $1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$ $E_0 = 0.401$ V

Total: $H_2 + 1/2O_2 \rightarrow H_2O$ $E_0 = 1.229$ V

Overall mechanism



$H_2 \rightarrow 2H^- + 2e^-$ $\quad$ $½O_2 + H_2O + 2e^- \rightarrow 2OH^-$

$2H^+ + 2OH^- \rightarrow 2H_2O$

1) Hydrogen enters the pores of anode and reaches the reaction zone, where gas, electrolyte and conducting material meet.

2) Hydrogen diffuses to the active site of catalyst and ionized.

3) H^+ react with OH^- of the electrolyte to form water.

4) Two electrons are available to the electrical circuit.
Cathode provides OH^- by $1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$

Anode Process

- Potential of hydrogen anode is constant: easier interpretation

in acid solution; $1/2H_{2,ads} + H_2O \rightarrow H_3O^+ + e^-$

in alkaline electrolyte; $1/2H_2 + OH^- \rightarrow H_2O + e^-$

● Mechanisms

1) Adsorption of H_2 on the electrode surface

$$H_2 \rightarrow H_{2,solv} \rightarrow H_{2,ads}$$

2) Hydration & Ionization of $H_{2,ads}$

a) Dissociation of H_2 with subsequent ionization/hydration

$H_{2,ads} \rightarrow 2H^+_{ads}$ (Tafel reaction)

$H^+_{ads} + OH^- \rightarrow H_2O + e^-$ (alkaline)

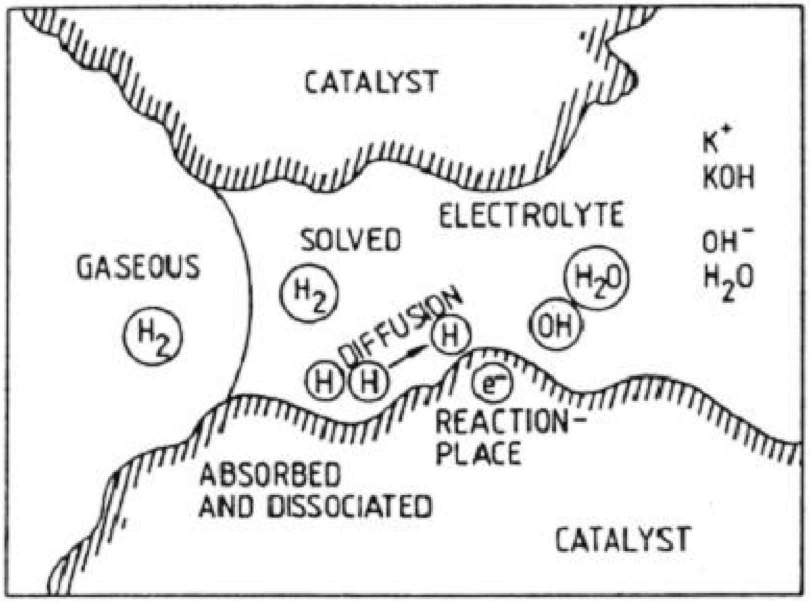
$H^+_{ads} + H_2O \rightarrow H_3O^+ + e^-$ (acid)

b) Hydration & Ionization in one step (Heyrovsky-Volmer mechanism)

$$H_{2,ads} + OH^- \rightarrow H_{ads} \cdot H_2O + e^- \rightarrow H^+_{ads} + H_2O + e^- \quad \text{(alkaline)}$$

$$H_{2,ads} + H_2O \rightarrow H_{ads} \cdot H_3O^+ + e^- \rightarrow H^+_{ads} + H_3O^+ + e^- \quad \text{(acid)}$$

3) Desorption of products (H_3O^+, H_2O) and transport into electrolyte



Reaction process on three phase border of H_2-electrode

- Hg, Ag:
  no H_2 chemisorption & no oxidation

- Pt, Ir, Rh, Pd, Au:
  chemisorption & oxidation

Cathodic Process

- Number of possible mechanisms of cathodic reaction
e.g., forming intermediate hydrogen peroxide

● Actual potential (1.05-1.15 V) < Theoretical (1.23 V)
→ due to the ***formation of hydrogen peroxide***

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \qquad E_0 = -0.07\ V$$

$$2HO_2^- \rightarrow H_2O_2 + O_2$$

● Nernst equation: concentration dependence of O_2/H_2O_2

$$E = E_0 - RT/nF \log Q$$

$$E = E_0 - 0.029 \log [(a_{OH-} a_{HO2-})/(p_{O2} a_{H2O})]$$

- $10^{-5} \sim 10^{-8}$ mol/l of H_2O_2 ⇒ 150 ~ 240 mV potential drop
- Active catalyst (Pt, Pd) reduces the concentration to 10^{-11} mol/l

Gas Diffusion Electrode

● **Porous gas diffusion electrode**

- provide a **large reaction zone area** with a minimum of mass transport hindrance for the **access of reactants and removal of products**

  e.g., smooth Pt: μA, porous electrode: A

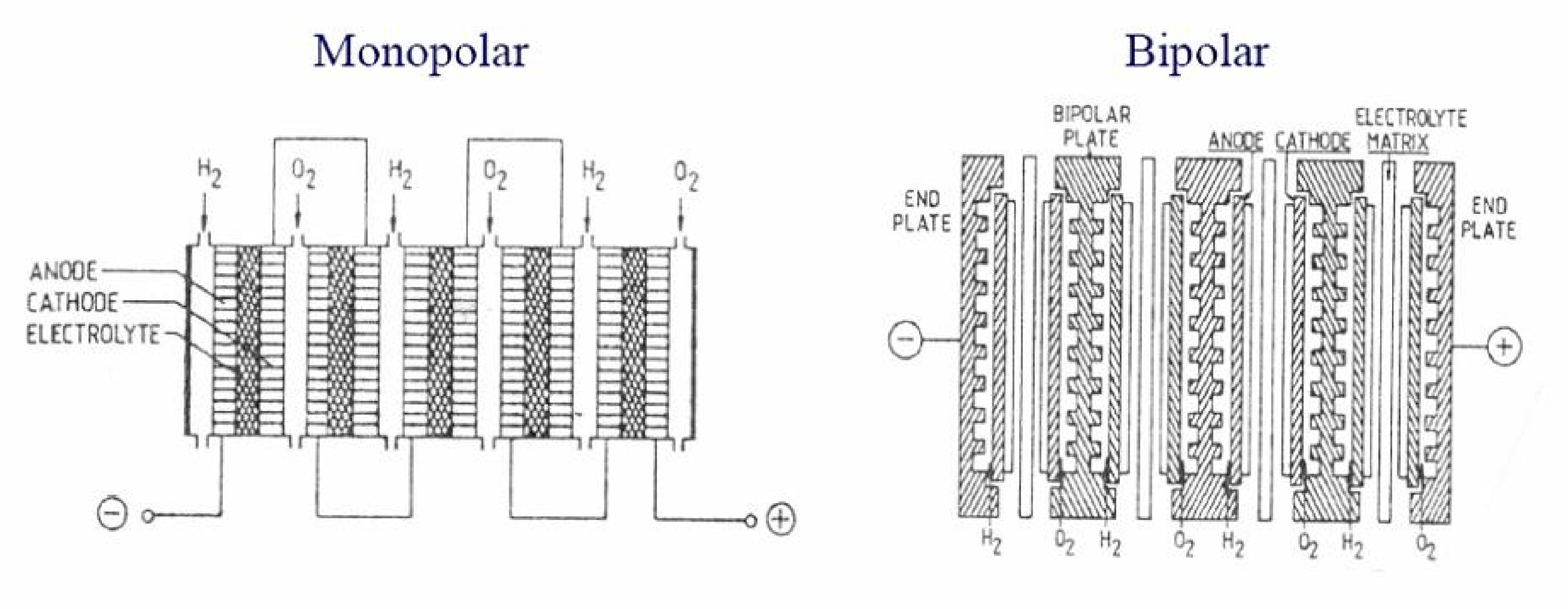
- **Three phase zone**: reactant, electrolyte and catalyst meet, large area can be achieved by metal powder (100 m^2/g) or carbon (1000 m^2/g)

- Hydrophobic gas diffusion electrodes: fine carbon powder bonded with polymer, e.g., polytetrafluoroethylene (PTFE)

- hydrophobic gas diffusion layer + electrolyte wettable thin layer

  → keeping the pores free and facilitating gas access to the reaction sites

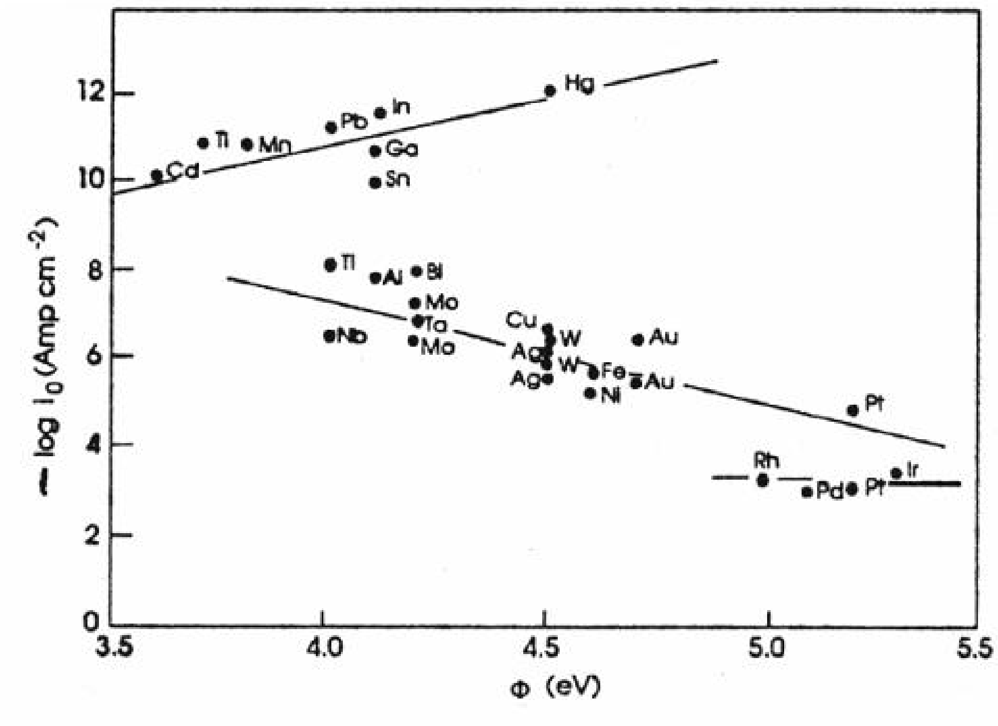
Two basic cell construction



- **Monopolar: edge collection of current, high conductivity, size up to 400 cm², no serious problem with one cell failure**
- **Bipolar: current collector, large size, low conductivity materials**

Electrocatalysts

- **Acceleration of electrode reaction by a substance which is not consumed in the overall reaction**
- **$H_2 \rightarrow 2H^+ + 2e^-$**



The highest activity in Pt, Pd, Ni

● Requirements for high catalytic activity

- large, accessible surface (porosity)
- fine distribution
- adsorbability on the surface
- desorption property of product
- weakened bond in the adsorbed partner

● Low T H_2-O_2 fuel cell

- hydrogen electrode (Pt, Pd)
- oxygen electrode (Pt, Pd, special carbons, porphyrines, Ni etc)

● Nobel metal catalysts

- poisoned by impurities (CO, S, etc) → non-noble metal catalysts

Fuel Cell efficiency

- **Carnot efficiency** : theoretical efficiency of heat engine

$$\eta = (T_1 - T_2)/T_1$$

the efficiency can be unity 1) if T_2 is at absolute zero or 2) if T_1 becomes a very high value

- maximum Carnot efficiency: 40 - 50 %
- actual efficiencies ~ ½ of maximum efficiency

- **Thermodynamic efficiency**

$$\eta_{th} = \Delta G/\Delta H = 1 - T\Delta S/\Delta H$$

- typically ~ 90% ($H_2 + 1/2O_2 \rightarrow H_2O$, 83%)
- over 100% if the entropy of products > reactants
  ($C + 1/2O_2 \rightarrow CO$, 124%)

- **Electrochemical efficiency**: $\eta_{el} = - nFE_K / \Delta G = E_K/E_0$

Fuel cell systems

● **Classifications; T, P, fuels, electrolytes**

Fuel Cell System	Temperature (C)	Efficiency (cell)	Electrolyte	Anode	Cathode	Charge carrier	Fuel
Alkaline Fuel Cell (AFC)	60-90	50-60 %	35-50% KOH	Pt base	Pt base	H^+	수소
Phosphoric Acid Fuel Cell (PAFC)	160-220	55 %	Phosphoric acid	Pt base	Pt base	H^+	수소
Molten Carbonate Fuel Cell MCFC)	620-660	60-65 %	Molten Salts	Ni	NiO	CO_3^{2-}	수소
Solid Oxide Fuel Cell (SOFC)	700-1000	55-65 %	Ceramic	ZrO_2	Perovskite	O^{2-}	수소
Polymer Electrolyte Fuel Cell (PEMFC)	50-80	50-60 %	Polymer Membrane	Pt base	Pt base	H^+	수소
Direct Methanol Fuel Cell (DMFC)	2 -80	50-60 %	Ion Exchane Membrane	Pt base	Pt base	H^+	메탄올

Typical Electrochemical Reactions in Fuel Cells

Fuel Cell	Anode Reaction	Cathode Reaction
Alkaline Fuel Cells	$H_2 + 2(OH)^- \rightarrow 2H_2O + 2e^-$	$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$
Polymer Electrolyte Fuel Cells	$H_2 \rightarrow 2H^+ + 2e^-$	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Phosphoric Acid Fuel Cells	$H_2 \rightarrow 2H^+ + 2e^-$	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Molten Carbonate Fuel Cells	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$	$\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$
Solid Oxide Fuel Cells	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$	$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$

Break ???

Polymer electrolyte membrane FC (PEMFC)
Proton exchange membrane FC

● Advantages

- no corrosive liquid in the cell
- simple to fabricate the cell
- low operating temperature
- able to withstand large pressure differences
- minimal material corrosion problems
- long lifetime

● Disadvantages

- expensive fluorinated polymer electrolyte & high cell costs
- water-management in the membrane
- noble metal catalysts needed
- poor CO tolerance
- difficulty in thermally integrating with a reformer

Membranes

- the electrolyte to provide ionic communication btn. electrodes
- a separator for two reactant gases

Water management

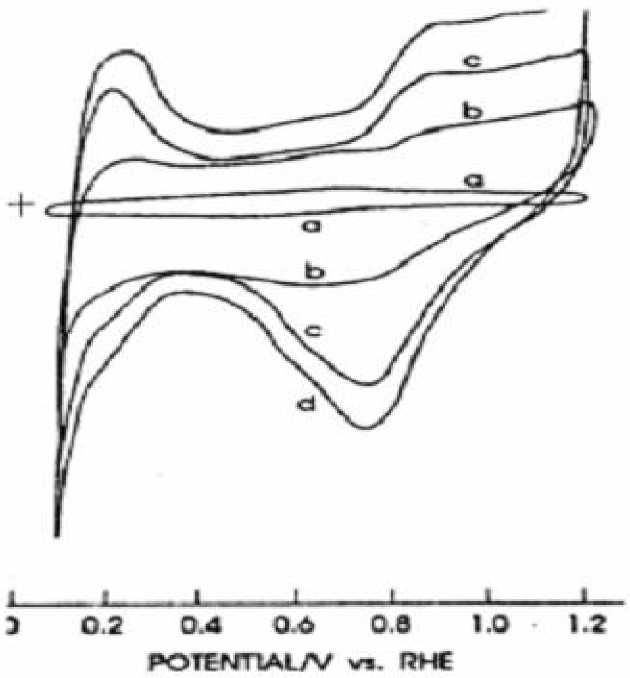
- Dehydration of membrane reduces conductivity
- Excess of water can lead to flooding of the electrodes

→ poor cell performance

→ to drain or supply water by capillary action, humidifying the reactants, flow design, temperature rising (increase water vapor).

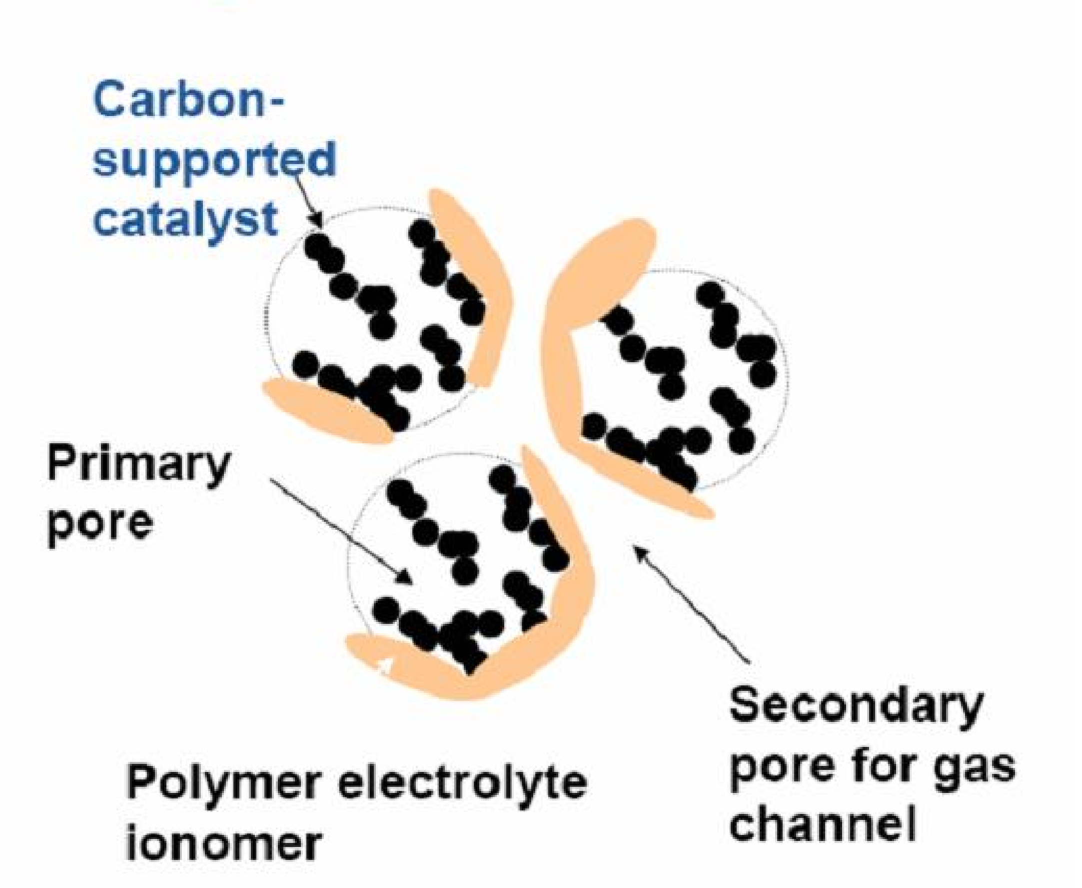
● Electrodes: gas diffusion electrodes

- porous carbon cloth with catalyst (Pt or supported Pt)
- how to reduce Pt loading
  : smaller nanoparticles, changes in electrode structure,
  Pt on surface only, supported Pt
- Cyclic voltammetry: 10-20% Pt was active for hydrogen/oxygen adsorption/desorption



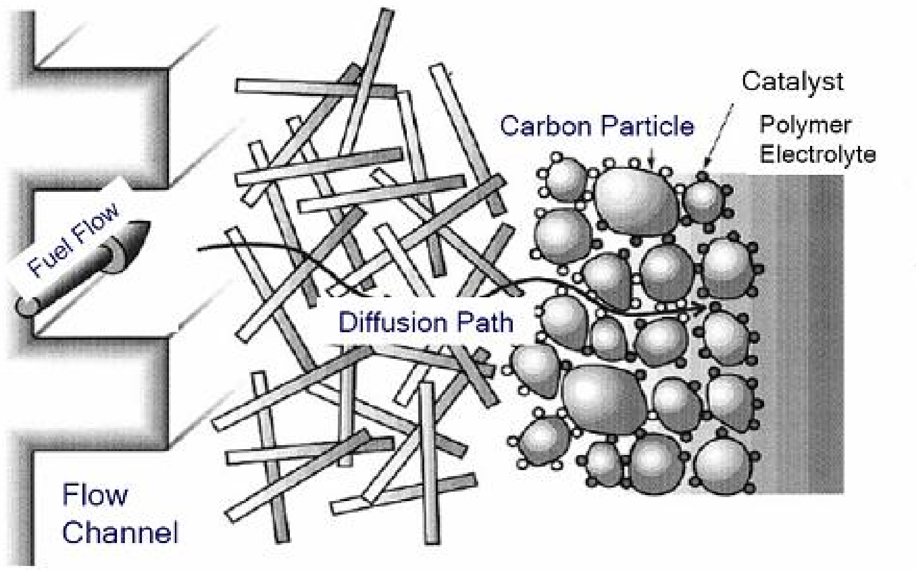
Cyclic Voltammograms
(a) uncatalyzed
(b) 10wt% Pt/C
(c) 20wt% Pt/C

Catalysts and Substrates



- **Ionomer**

ion containing polymer, polyelectrolyte copolymer – nonionic and ionic repeat unit



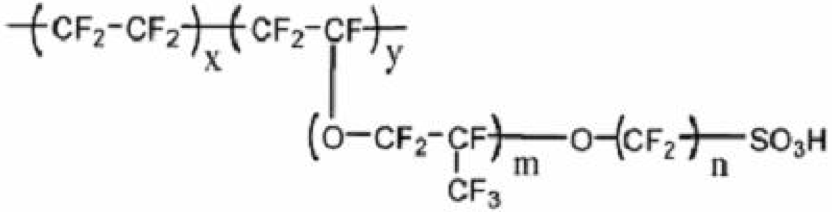
MEA (membrane–electrode assembly) 구조

Gas diffusion layer : current collecting, water removing, physical support, fuel diffusion

Catalyst layer: electrode (anode, cathode)

Membrane: electrolyte

Polymer Membrane: NAFION



Nafion®117	m≧1, n=2, x=5-13.5, y=1000
Flemion®	m=0, 1; n=1-5
Aciplex®	m=0, 3; n=2-5, x=1.5-14
Dow membrane	m=0, n=2, x=3.6-10

- **Thickness : 50~175μm, equivalent weight : 1,100 mEq/g**
- **High oxygen solubility, high proton conductivity, low density, high chemical and thermal stability, high water solubility**
- **H_2SO_4 solution as pretreatment**

● Problem

- **Low water content => low proton conductivity**
  High content => flooding in electrode => inefficient reaction
- **Methanol crossover in DMFC**
- **High cost**

Production Company for Membrane

- **US : Du Pont (Nafion), Dow Chemical (XUS), W.L. Gore & Associate (Gore-Select)**
- **Canada : Ballard Advanced Materials (BAM3G)**
- **Japan : Asahi Chemical (Aciplex), Asahi Glass (Flemion), Chlorine Engineer (Product 'c'),**
- **German : Hoechst**

Membranes	Equivalent weight (g/mol SO_3^-)	Thickness, dry(μm)	Water content(%)	Conductivity (S/cm)
XUS	800	125	54	0.114
Aciplex-S	1000	120	43	0.108
Nafion 115	1100	130	34	0.059
Gore-Select	1100	20	32	0.053
Flemion	900	50, 80		

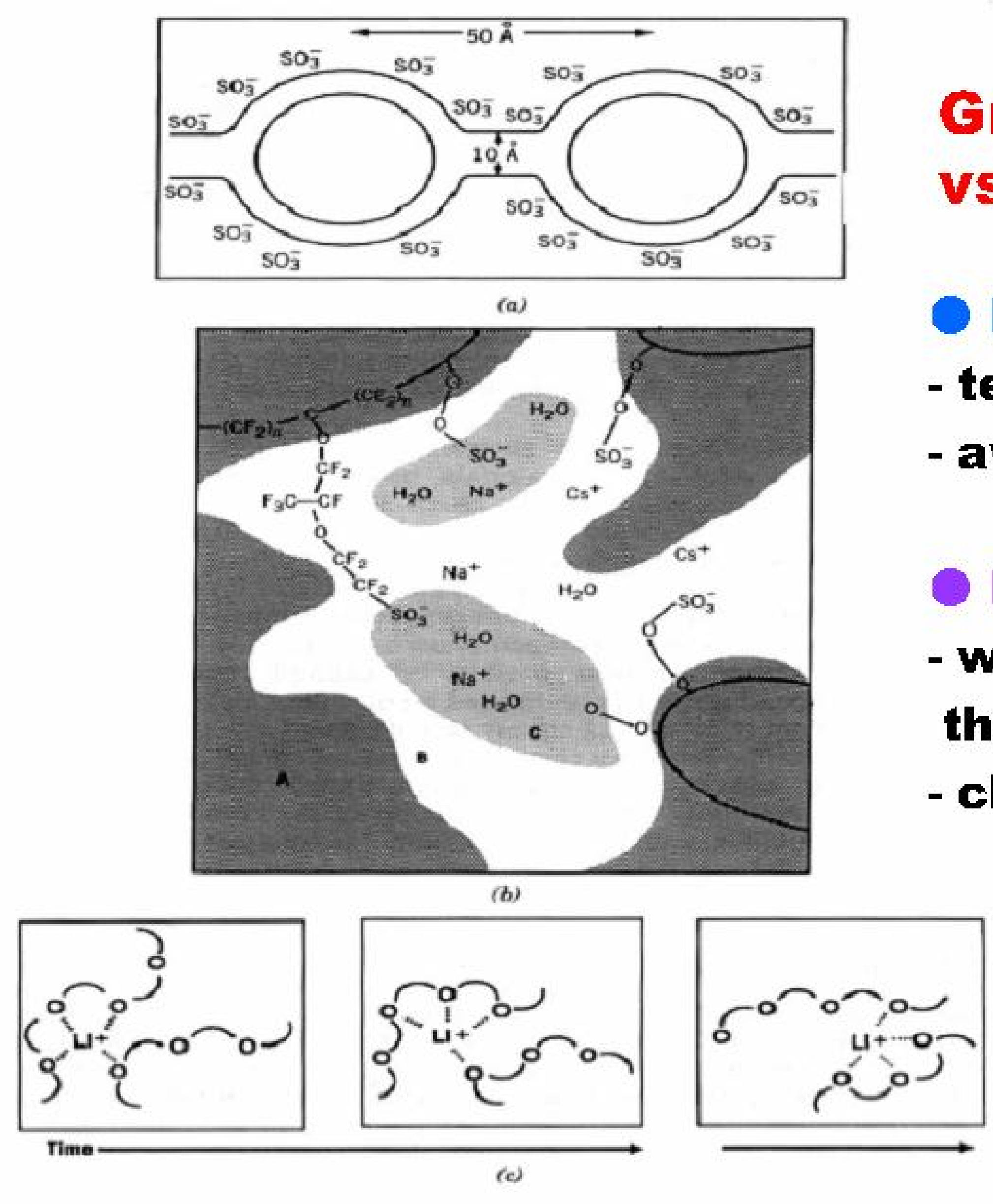
● Aciplex, Dow membrane

- Short side chain
- High ratio of SO3H/CF2
- High specific conductivity

● Gore-Select

- Fine mesh PTFE support impregnated with Nafion
- high mechanical stability ~ 10μm

Conducting Mechanisms



Grotthus mechanism vs vehicle mechanism

● **Polar ionic groups**

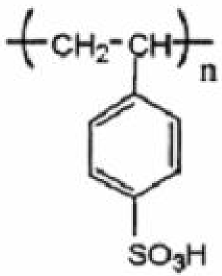
- tend to cluster together,
- away from nonpolar backbones

● **Reversible crosslinker**

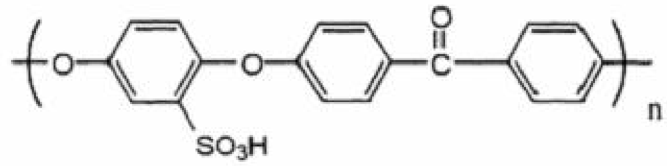
- when heated, ionic groups loose their attraction
- chains move around freely

Sulfonated Aromatic Polymers

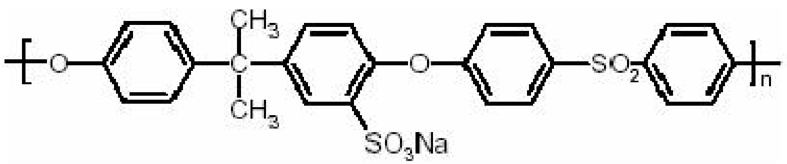
Poly(styrene) (PS)



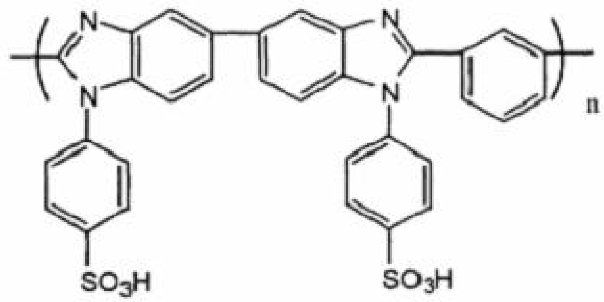
Poly(ether ether ketone) (PEEK)



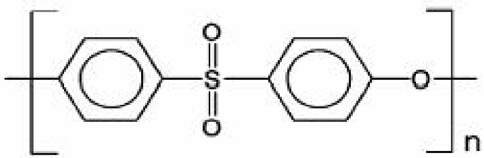
Polysulfone (PSf)



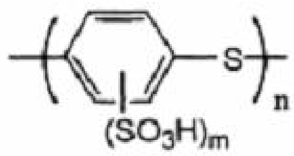
Poly(benz imidazole) (PBI)



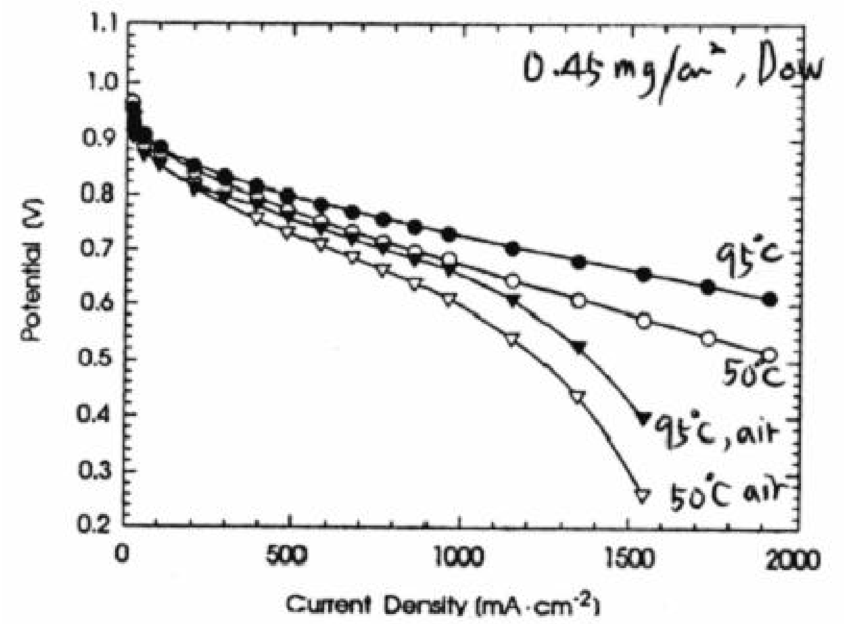
Poly(ether sulfone) (PES)

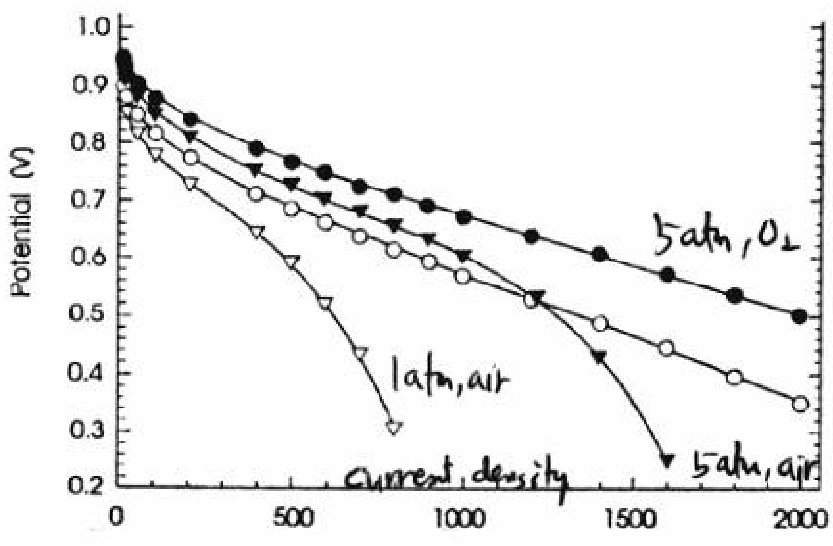


Poly(phenylene sulfide) (PPS)



Performance of PEMFC





● **Effect of temperature**

T↑ → resistance of electrolyte↓

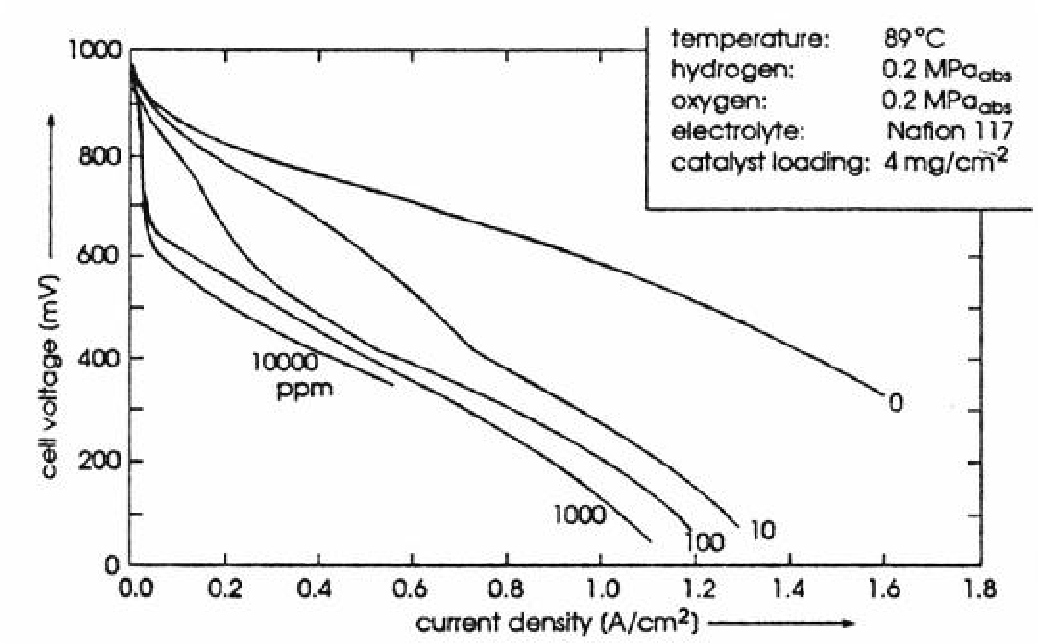
→ cell performance ↑

● **Effect of cathodic reactant composition & pressure**

P↑, O_2↑ → increase of MT

→ cell performance ↑

Performance of PEMFC



- **Effect of CO in the fuel gas**

  → **reduce CO content (selective oxidation of CO to CO_2 by passing with small oxygen or air through a small reactor containing Pt)**

  → **CO-tolerant Pt catalysts**