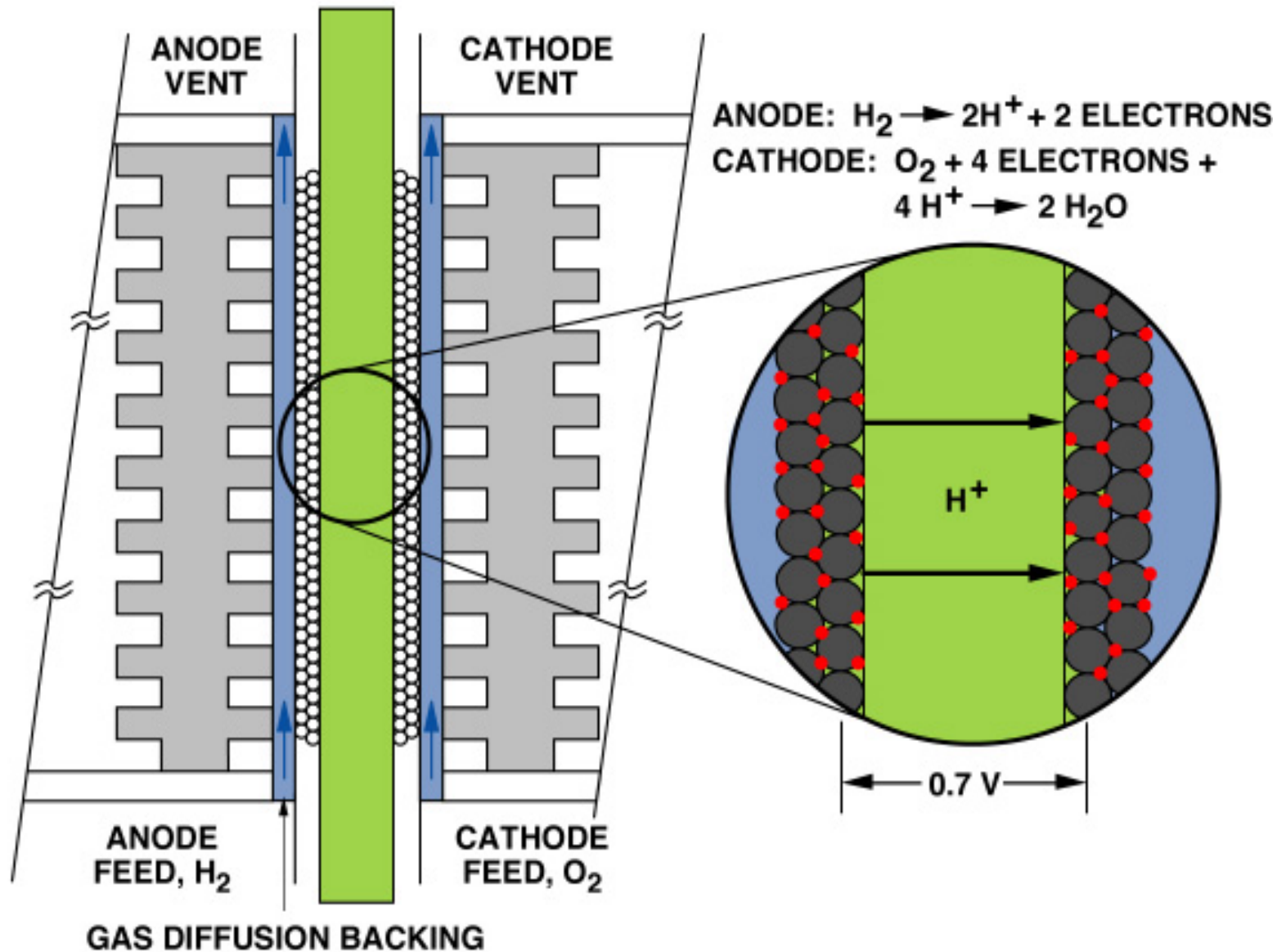


# **PEMFCs – CO Tolerance and Direct Methanol Operation**

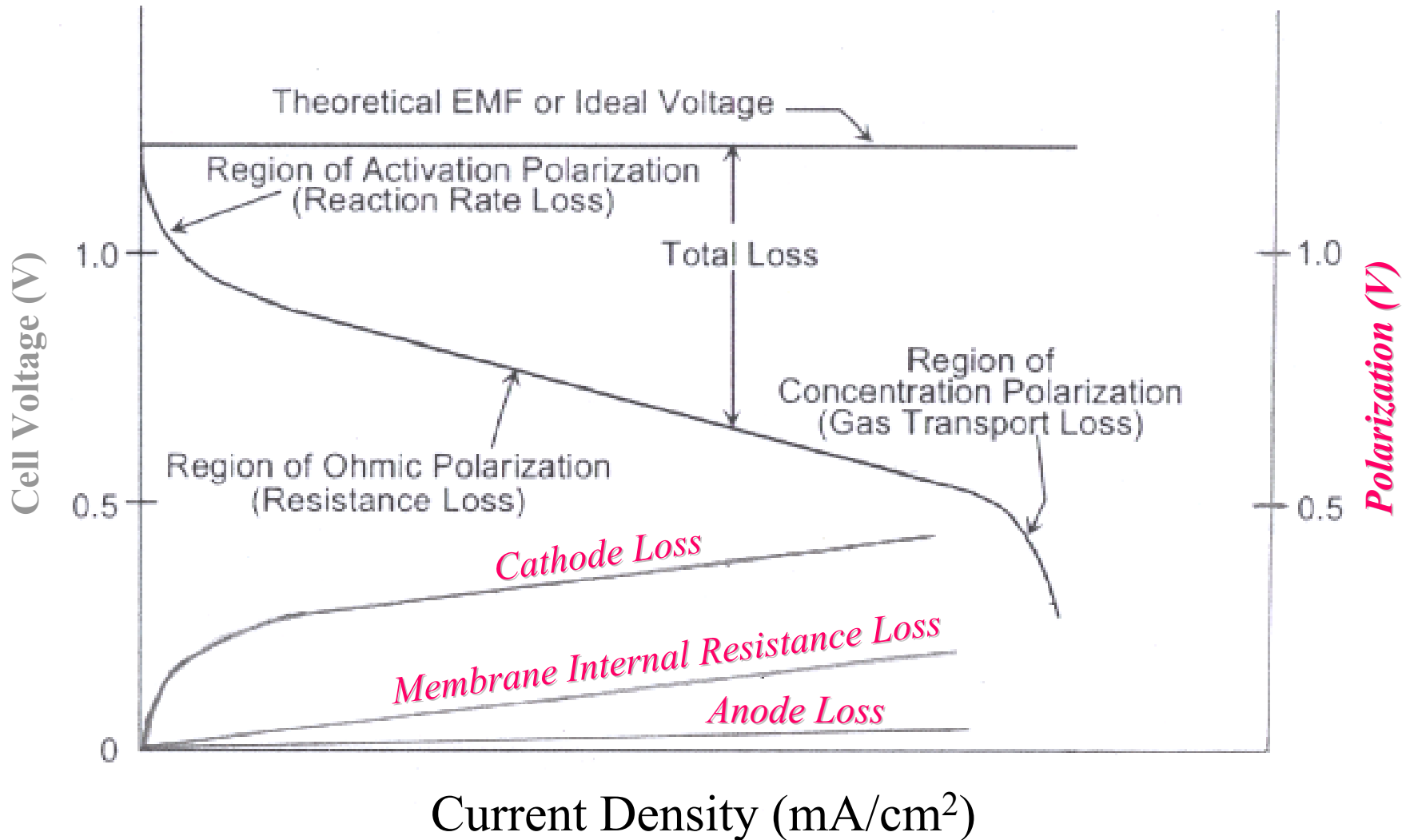
**J. M. Fenton**

**11/20/02**

# Cross Section of Proton Exchange Membrane Fuel Cell



# Performance Characteristics of a Fuel Cell



# Key Overpotential Sources

---

- Electrode losses
  - Kinetic losses
  - Transport losses
  - Resistive losses: ionic resistance
- Membrane internal resistance (IR) losses
  - Includes contact resistances
- Transport losses within the diffusion layers

**Objective:**  
**Minimize Losses; Ensure Longevity**

# Drawbacks of Direct Hydrogen Operation

- Hydrogen infrastructure – not yet available
- Systems issues (automobile):
  - fuel storage
  - weight and volume for reasonable range
  - ease of refueling?
  - safety?
- Direct hydrogen (pure hydrogen) does not seem feasible (and / or economically viable) in the near future

# Other Options??

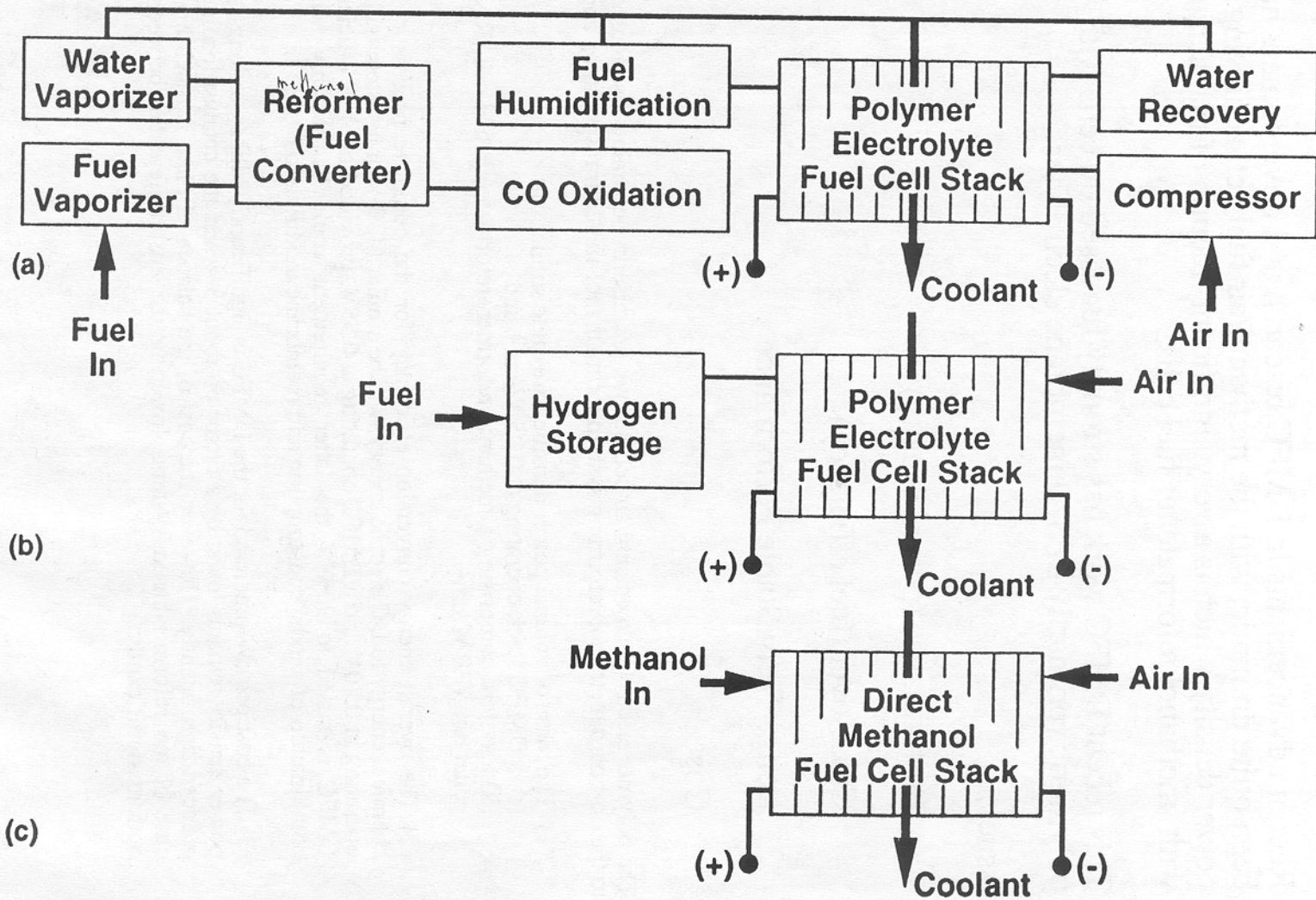
## Indirect Hydrogen

- Reform readily available liquid fuel (or natural gas for stationary applications)
- Use H<sub>2</sub> thus synthesized in the fuel cell
- In-situ, continuous generation
- Mature technology (reforming)

## Direct Methanol

- Feed methanol (and water) directly into fuel cell anode
- Oxidize methanol (instead of hydrogen) at the anode
- Methanol may be fed as a liquid or as a vapour
- Greatly simplifies system and infrastructure issues

# Fuel Cell Propulsion Systems: Increasing Simplicity



# Indirect Hydrogen – Effect of CO

- Reformate stream – contains CO and CO<sub>2</sub>
- CO can be minimized by shift conversion (0.4 – 2 % CO), and further reduced by partial oxidation (< 100 ppm CO)
- However, even 10 ppm of CO – detrimental to electrocatalyst – adsorbs on active sites - increases anode overpotential
- Clearly, need better fuel processing (and) CO tolerant electrocatalysts (and) a technique to minimize CO adsorption



# Effect of CO in Reformate on Performance

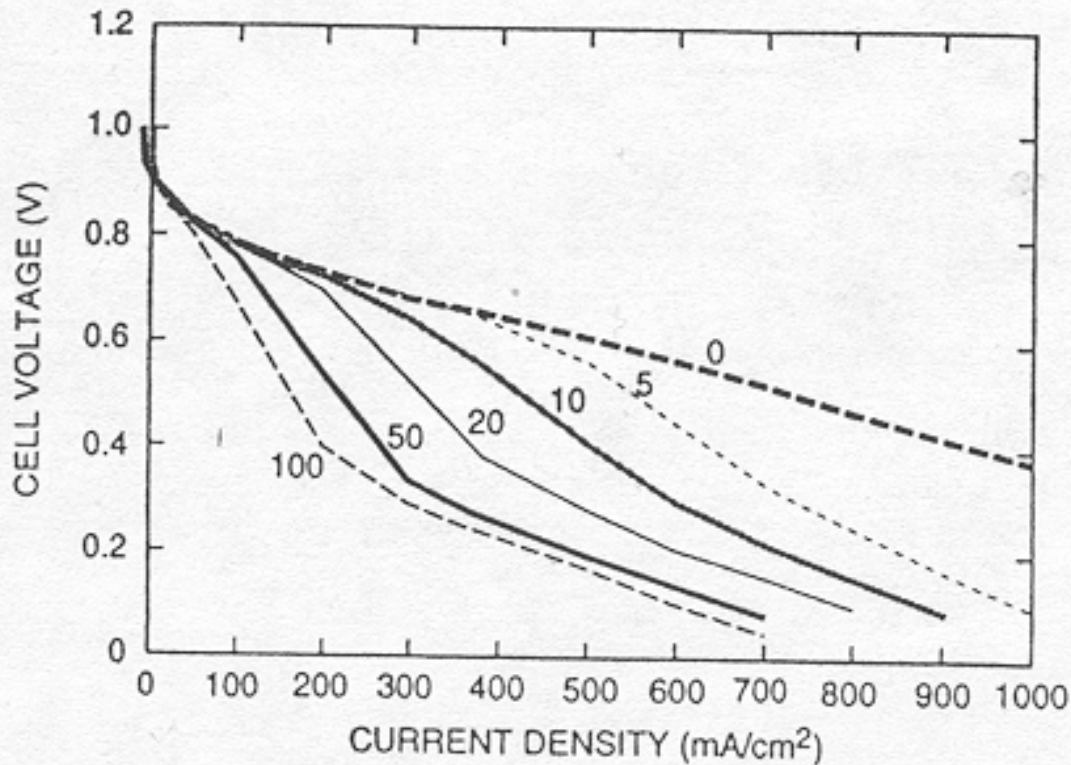
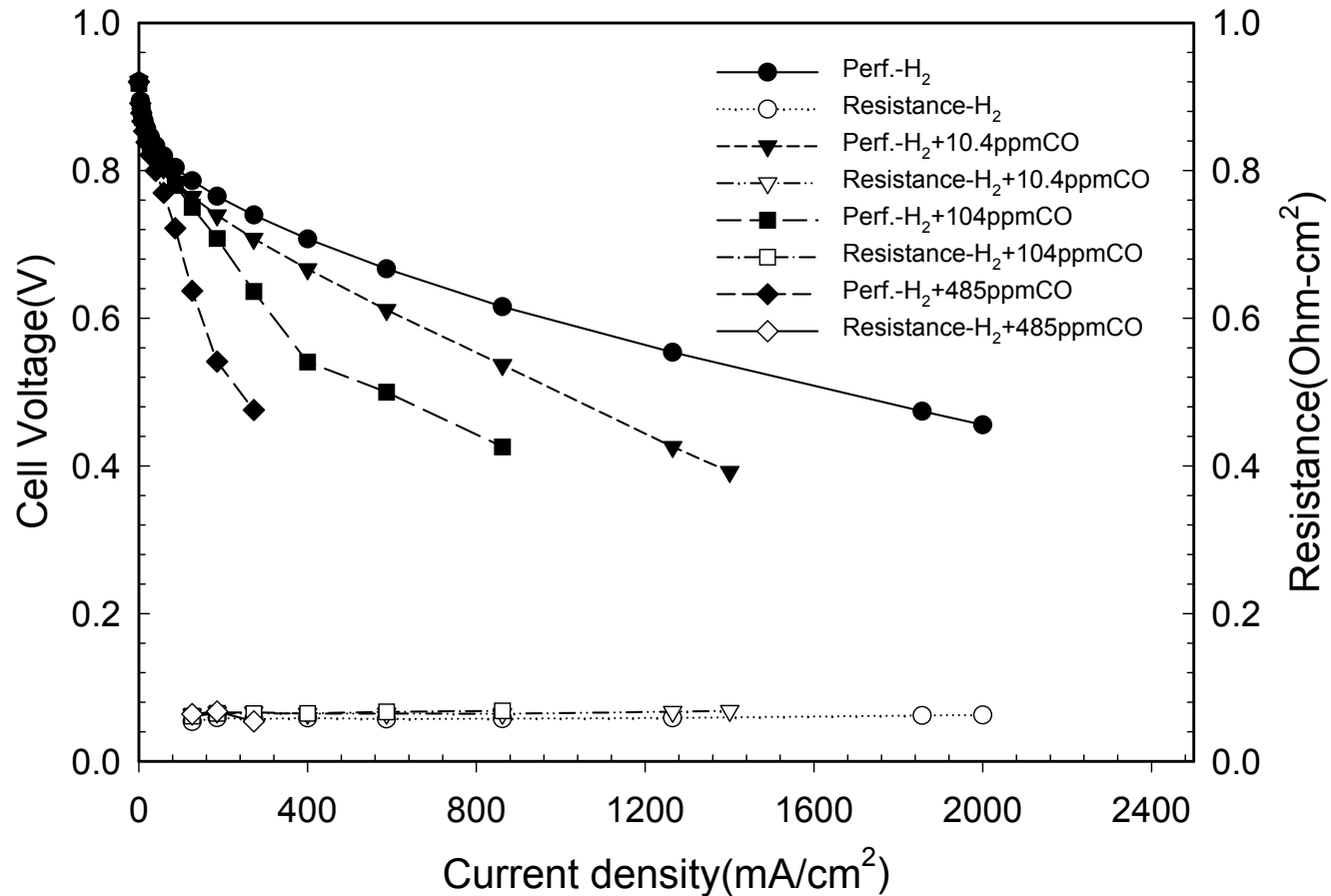


Fig. 13. Effects of CO level (ppm) in the hydrogen feed stream on the performance of a PEFC at 80 °C. Both electrodes were based on an ionomer-impregnated Pt/C catalyst and thin sputtered platinum film, of total loading 0.45 mg Pt/cm<sup>2</sup> [17].

Pressurized Operation??

# Effect of CO in Reformate on Performance



Cell Performance with Various CO Concentrations at 80°C and 1atm  
Anode:H<sub>2</sub>+CO at 90°C, 40%Pt-Ru/C; Cathode: O<sub>2</sub>

# Why the Performance Loss?

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

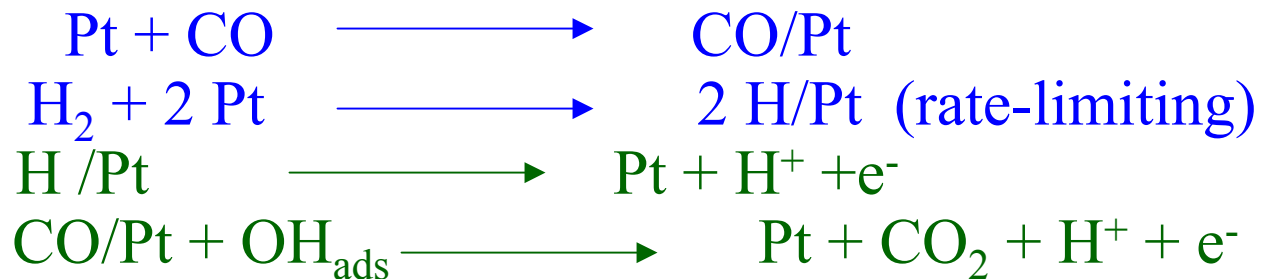
Thermodynamically:

$$E_{\text{cathode}} = 1.23 \text{ V } (\text{O}_2 + 4 \text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O})$$

$$E_{\text{anode}} = 0 \text{ V } (\text{H}_2 = 2\text{H}^+ + 2\text{e}^-)$$

Therefore  $E_{\text{cell}}(\text{max}) = 1.23 \text{ V}$

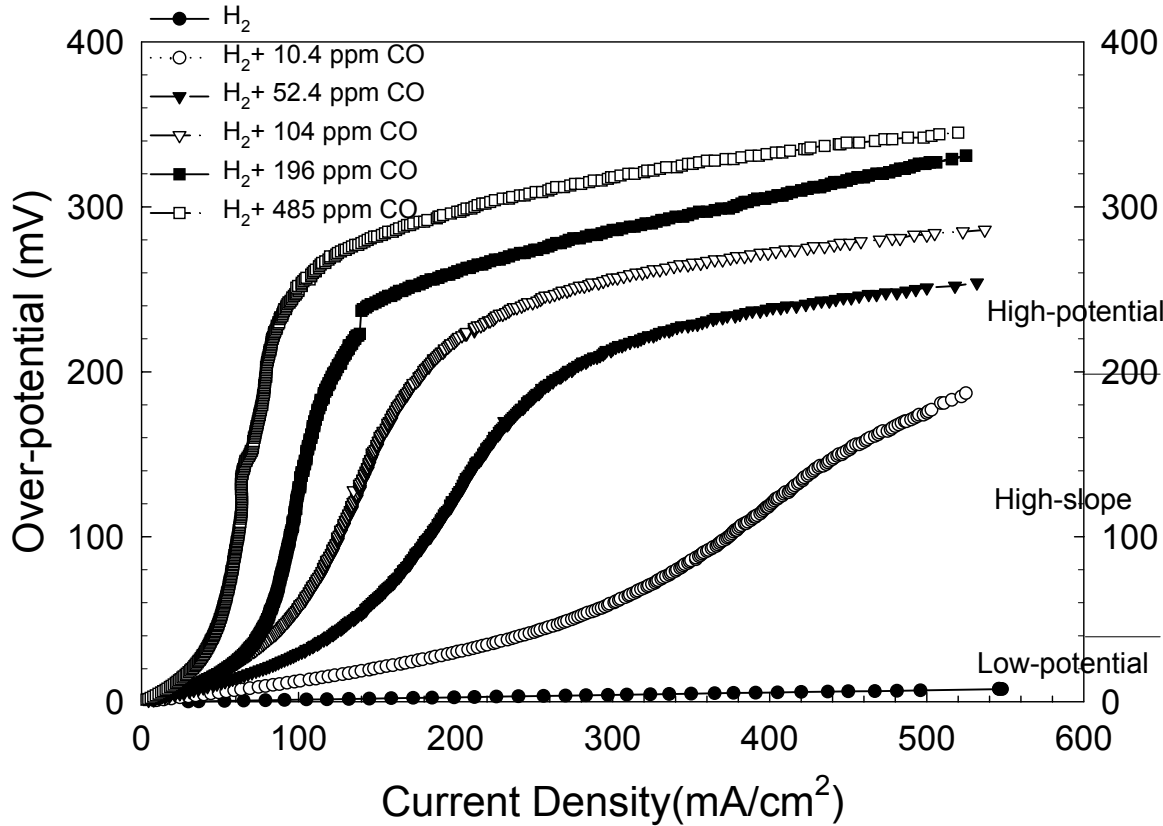
In the presence of CO, two electrochemical reactions occur:



- Anode overpotential – determined by the relative contribution of CO oxidation
- Low currents – hydrogen requirements met by adsorbed H<sub>2</sub>
- High currents (or large CO concentrations) – adsorbed H<sub>2</sub> insufficient for faradaic requirements
- Therefore, CO removal (via electrooxidation) has to occur – higher anode overpotential, **higher E<sub>anode</sub>** – **lower E<sub>cell</sub>**

**Key Strategy: minimize CO adsorption on catalyst**

# Anode Overpotentials of 40% wt Pt-Ru/C (Pt/Ru = 1/1) with H<sub>2</sub> containing CO (10.4 to 485 ppm) at 80 °C (100% R.H.).



Recall: Performance characteristics chart – contribution of anode overpotential (slide 3)

**Note:** increasing overpotential with: increasing CO concentration and increasing currents

# How to Deal with CO?

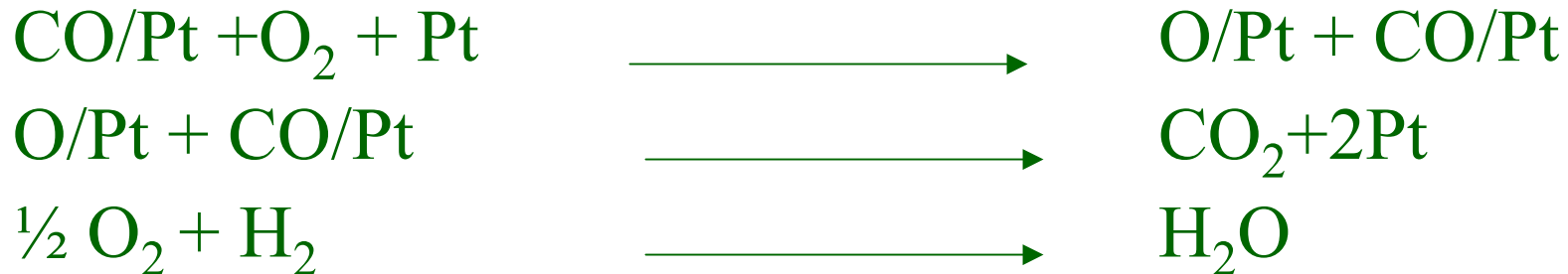
- Air – Bleed (or oxygen bleed)
- Better (more CO tolerant) anode electrocatalysts
- Elevated temperature operation

**Each of above briefly discussed in forthcoming slides**

**Note – improvements in reforming, shift conversion and partial oxidation steps are also of great use – however, these approaches are not discussed in this lecture**

# Air / Oxygen Bleed

- CO surface coverage – biggest problem
- Bleeding oxygen (as oxygen or as air) into the fuel stream helps:
  - CO poisoning Pt sites are oxidized in the presence of free platinum to give CO<sub>2</sub>



- The strong preferential adsorption of CO on Pt actually helps this mechanism!

# Demonstration of Air Bleed Efficacy

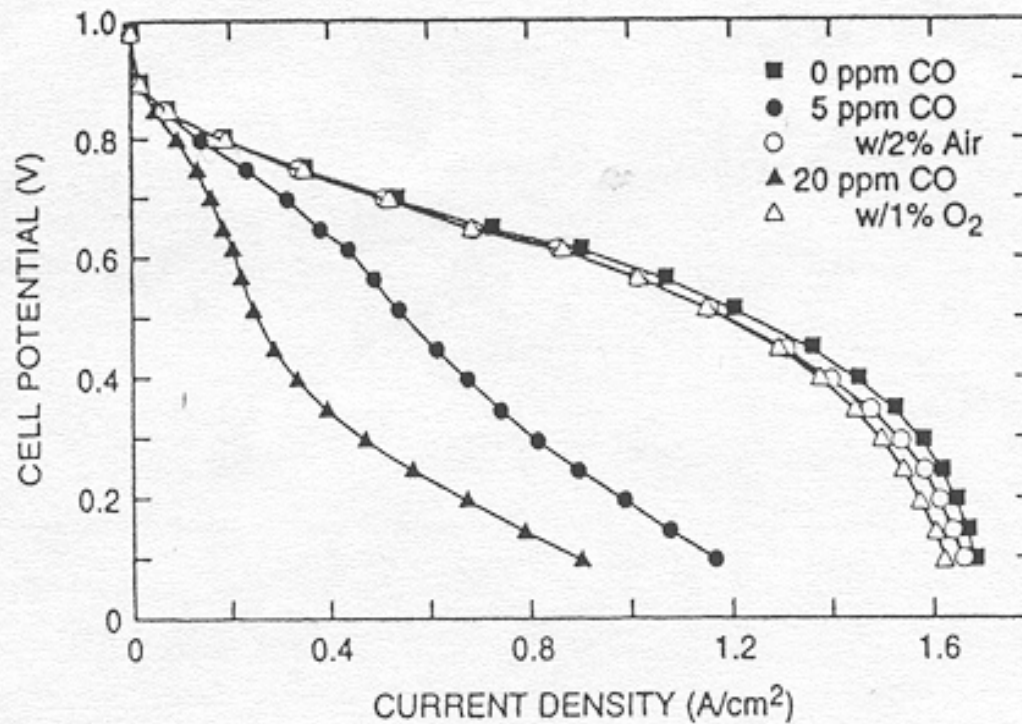


Fig. 14. Cleansing by oxygen bleeding of a platinum anode catalyst in the presence of 5–20 ppm CO in the hydrogen fuel, demonstrated for a platinum anode catalyst of ultra-low loading (0.14 mg Pt/cm<sup>2</sup>), consisting of a Pt/C//ionomer thin film composite bonded to the membrane [21]. (Reprinted by permission of the American Chemical Society).

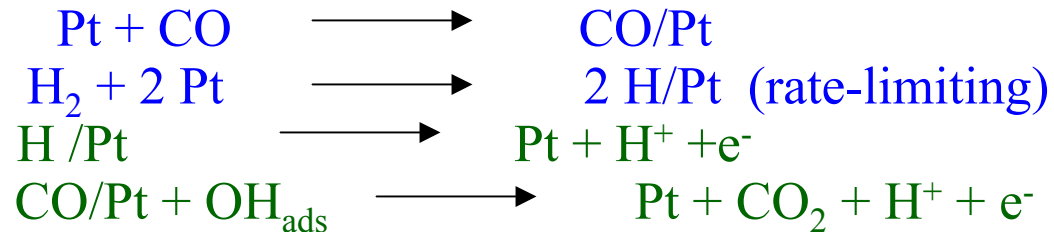


# Demerits of Air Bleed Technique

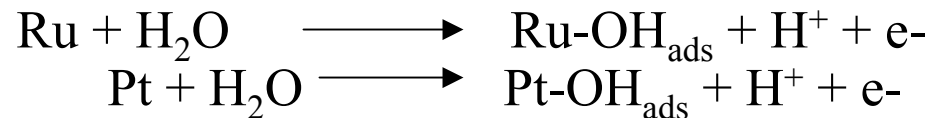
- Explosive limit of  $O_2$  in  $H_2$  is 5%. This limits amount of CO tolerated to  $\sim 100$ ppm
- Some loss in fuel efficiency due to chemical oxidation of hydrogen
- This loss increases as amount of oxygen introduced increases (2 fold increase) – thus the larger the amount of CO in stream, the larger the loss of fuel efficiency

# CO Tolerant Electrocatalysts

**Recall:** mechanism of CO and H<sub>2</sub> oxidation in a mixed stream:



Now, for CO electrooxidation, the catalyst site must be hydrated (have an attached hydroxyl group on its surface)



The potential at which this group is generated varies from catalyst to catalyst:

- 0.5 V for Pt
- **~ 0.2 V for Ru!**

- Thus, catalysts with Ru will have a lower anodic overpotential at high currents (or high CO concentrations) than catalysts containing Pt
- Ru – not a very good catalyst for H<sub>2</sub> oxidation
- Pt-Ru alloys – have been successfully used

**However – limitations such as increasing anode overpotential with increasing CO concentration and increasing currents are not eliminated by this approach**

- The extent of CO tolerance depends greatly on the catalyst structure and formulation
- Even for the best catalysts, the improved CO tolerance all but vanishes for high currents
- However, a combination of precisely formulated catalyst (typically 1:1:: Pt:Ru) and air / oxygen bleed has been found to be effective at high currents as well

# Elevated Temperature Operation

- CO adsorption on Pt is an exothermic process
- By the Le-Chatelier – Braun principle, increasing the system temperature favours the endothermic CO desorption reaction
- Effect of increasing system temperature is to lower the fraction of catalyst covered with CO, thereby lowering anode overpotential
- The effect has been clearly demonstrated

$\text{CO} + \text{Pt} = \text{CO-Pt}$  (associative adsorption)

$\text{H}_2 + 2 \text{ Pt} = 2 \text{ H-Pt}$  (dissociative adsorption)

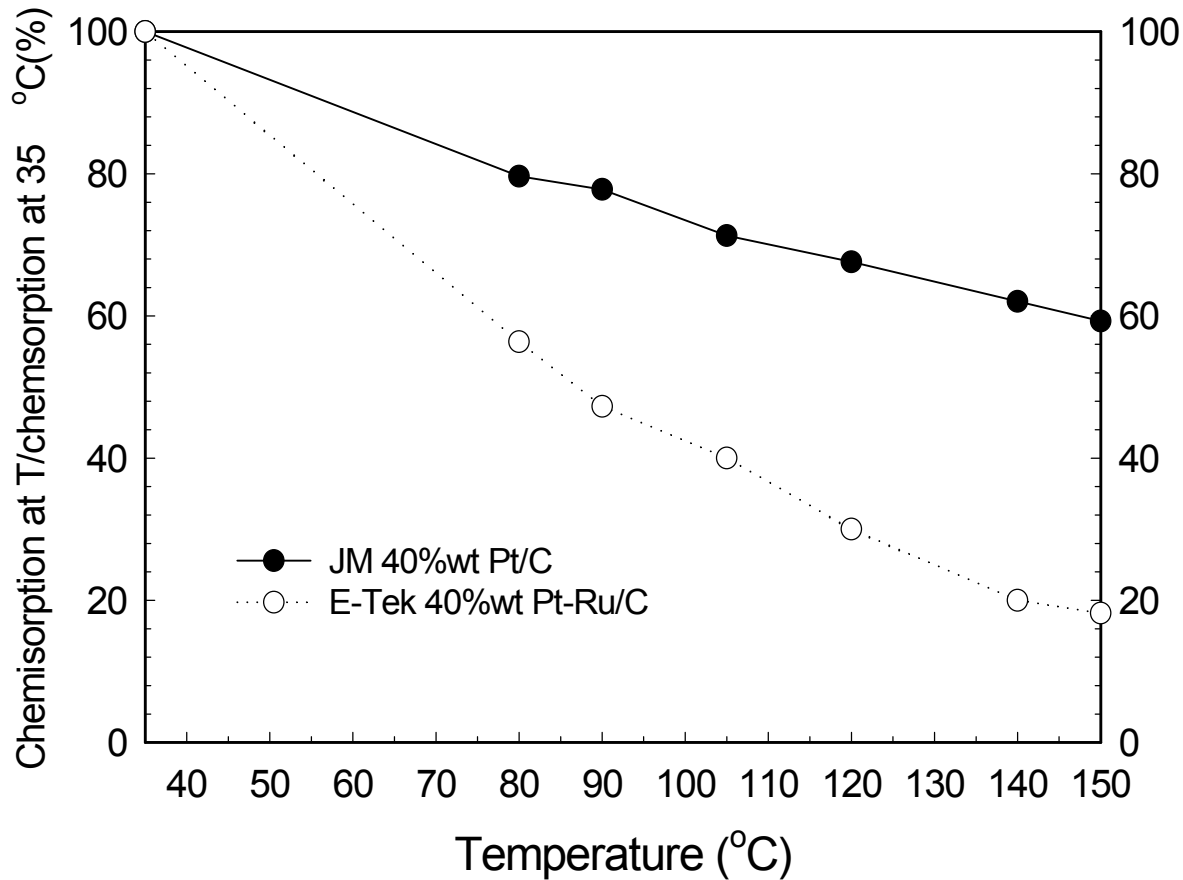
Fractional coverage (f) of CO and H given by:

$$f_{\text{CO}} = K_{\text{CO}} P_{\text{CO}} / [1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{H}}^{0.5} P_{\text{H}}^{0.5}]$$

$$f_{\text{H}} = K_{\text{H}}^{0.5} P_{\text{H}}^{0.5} / [1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{H}}^{0.5} P_{\text{H}}^{0.5}]$$

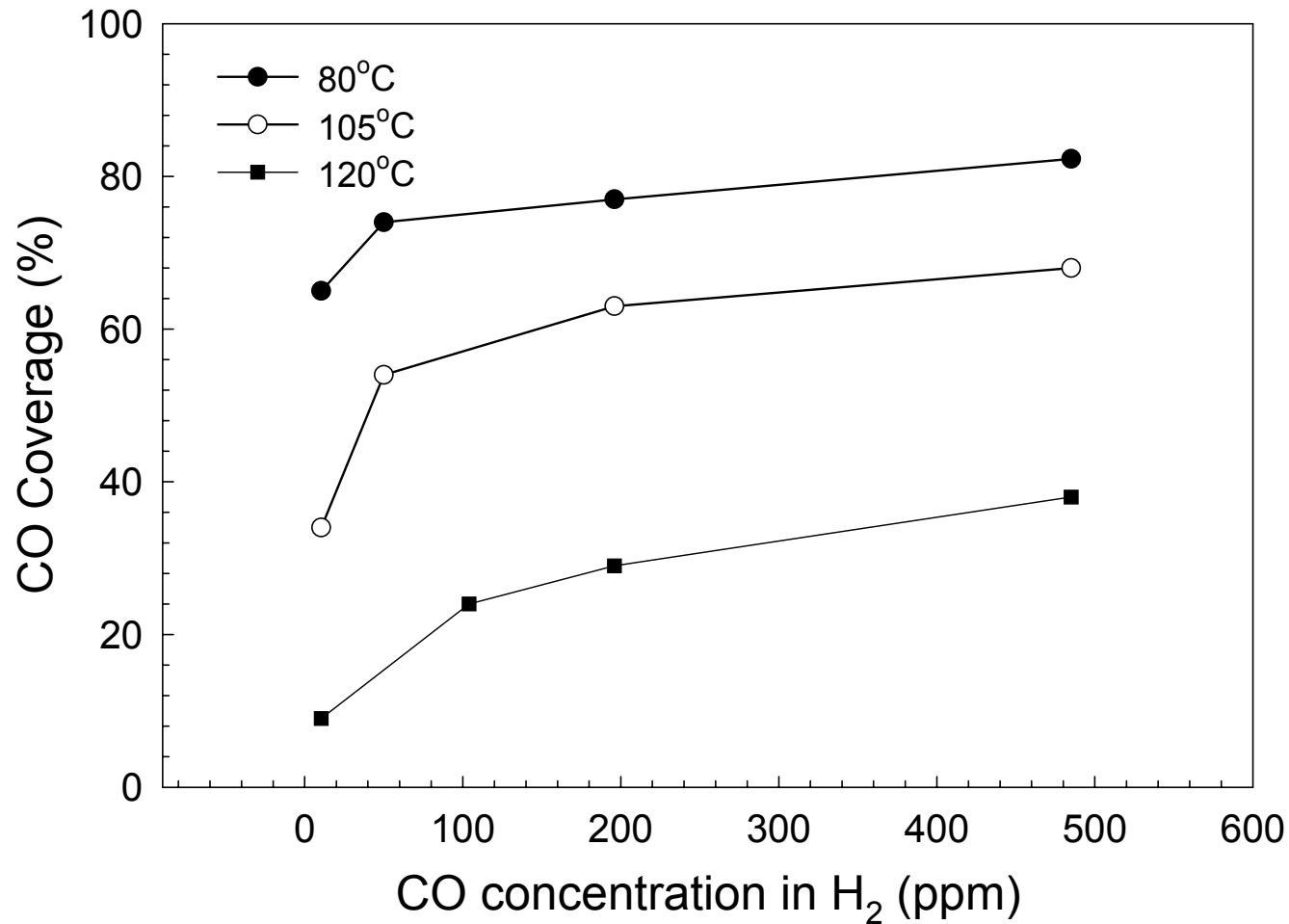
$K$  = equilibrium constants,  $P$  = partial pressures

**As  $T$  increases,  $f_{\text{H}}$  increases as H adsorption is less exothermic than CO adsorption, and because H adsorption requires 2 sites as opposed to one for CO adsorption**

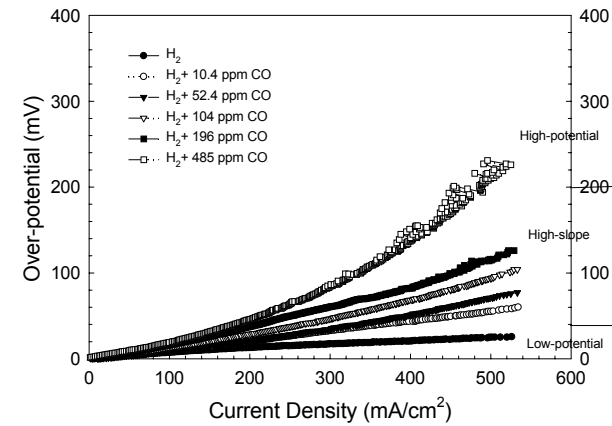
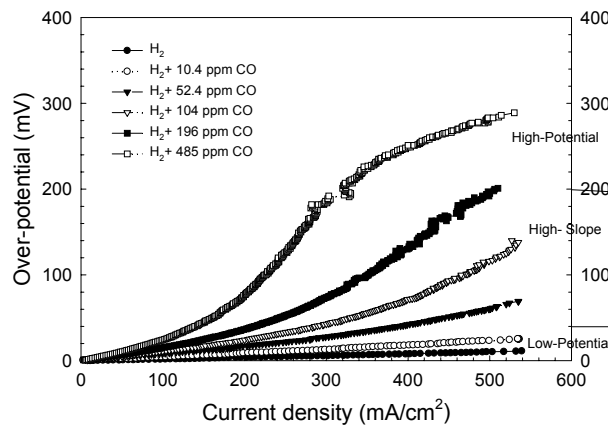
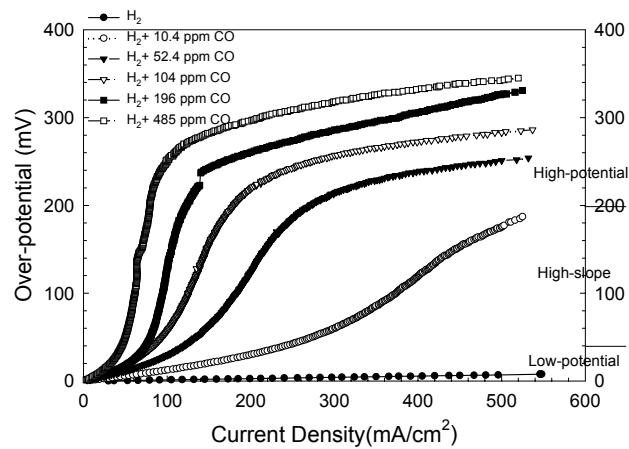


**Effect of temperature on CO chemisorption on potential Anode catalysts – note also the exceptional CO tolerance of Pt-Ru alloys when compared to Pt**

# CO Coverage on the Pt-Ru Catalyst Surface at Various Temperatures



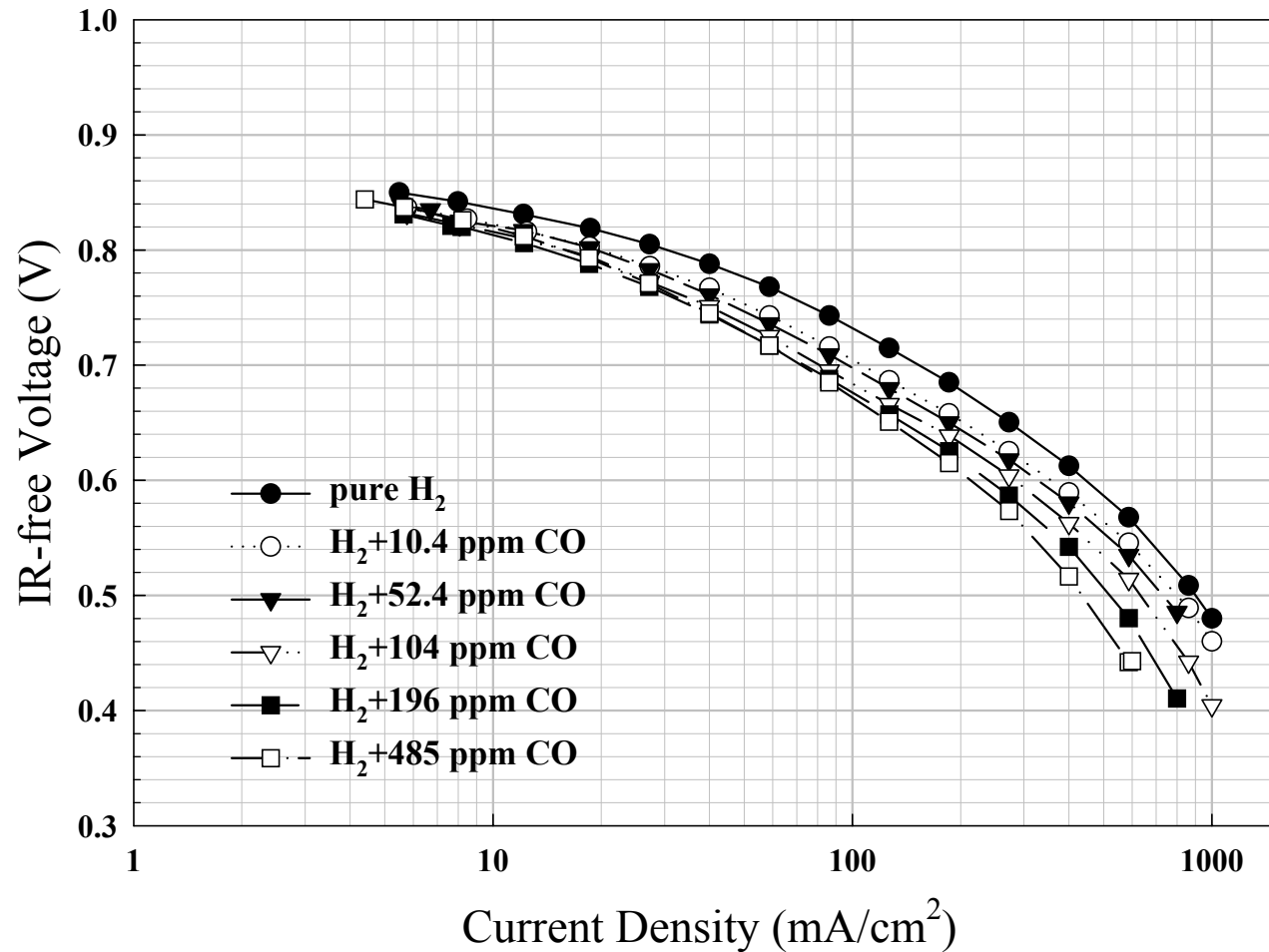




## Anode overpotentials vs. current density and CO concentration on Pt-Ru catalyst

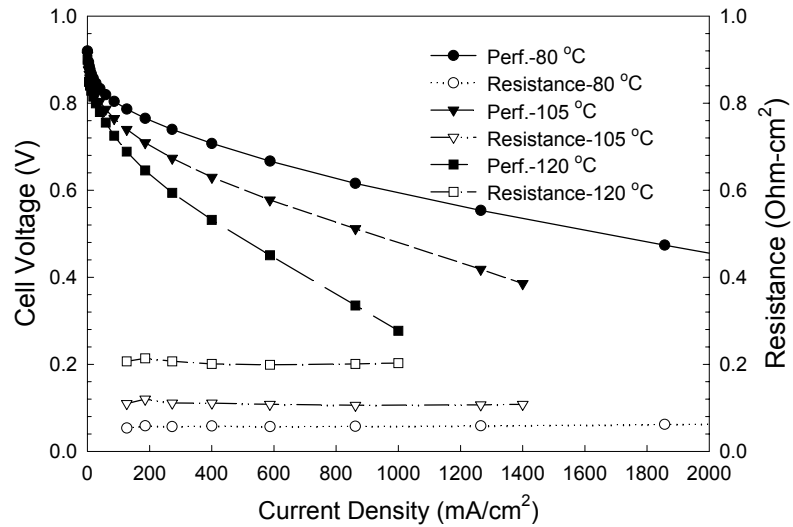
Similar scales, increasing temperature from left to right (80C, 105C and 120C)

Performance curves follow

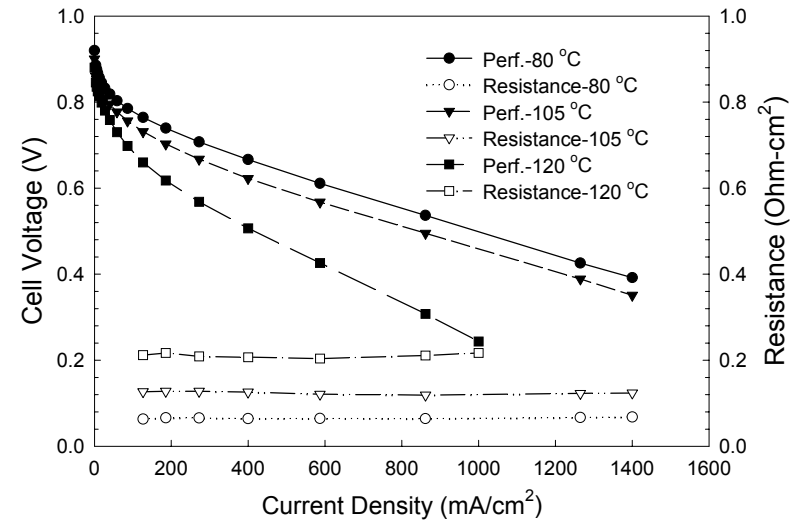


## IR-Free H<sub>2</sub>/O<sub>2</sub> Cell Performance with Different CO Concentrations at 120 °C on Pt-Ru

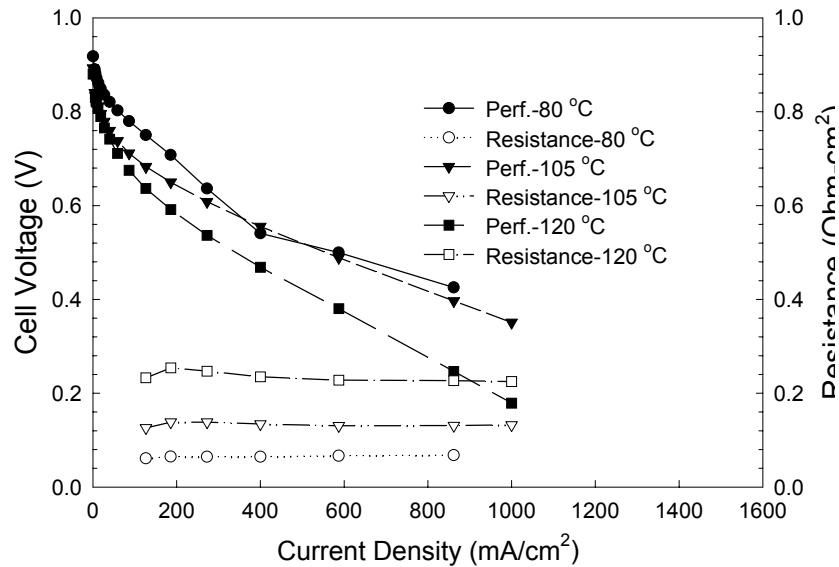
## Pure H2



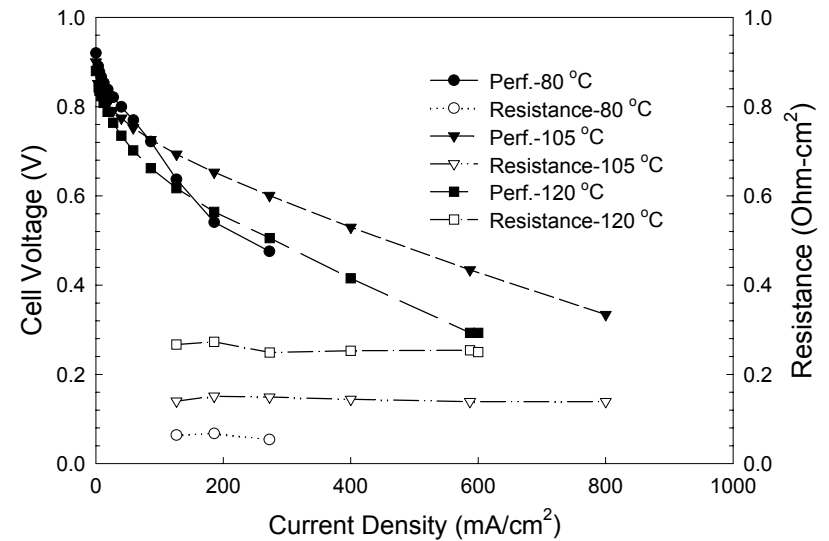
## H2+10.4ppm CO



## H2+104ppm CO



## H2+485ppm CO



1 atm, H<sub>2</sub>/O<sub>2</sub>,

NTZHP membrane

Si

# Can we extend this infinitely?

- **NO!!!**
- Materials issues rise to the fore – especially the ionomeric membrane in a PEMFC
- **Note:** previous figures indicated 105°C to be a better CO tolerant operating temperature than 120°C – contrary to expectation based on Le-Chatlier- Braun principle
- This apparent contradiction – effect of membrane resistance, cathode overpotential and system water content. These issues will be discussed in the following slides

**Note – membrane conductivity ( $\rho$ ) determines its resistance at any given condition for a given thickness ( $t$ ) and active area ( $A$ )( $R = \rho t/A$ )**

# Temperature and Relative Humidity

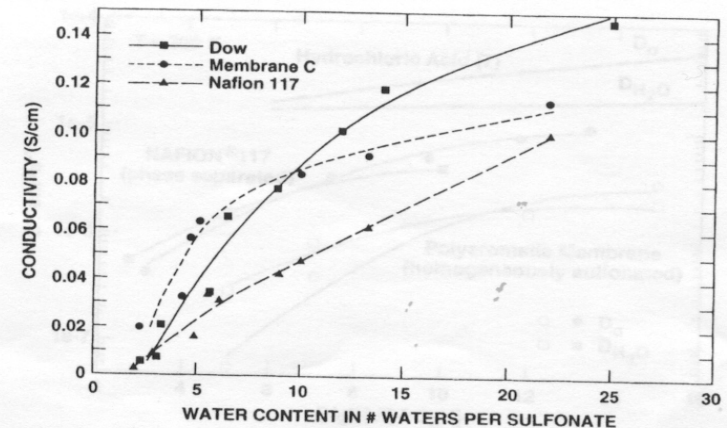
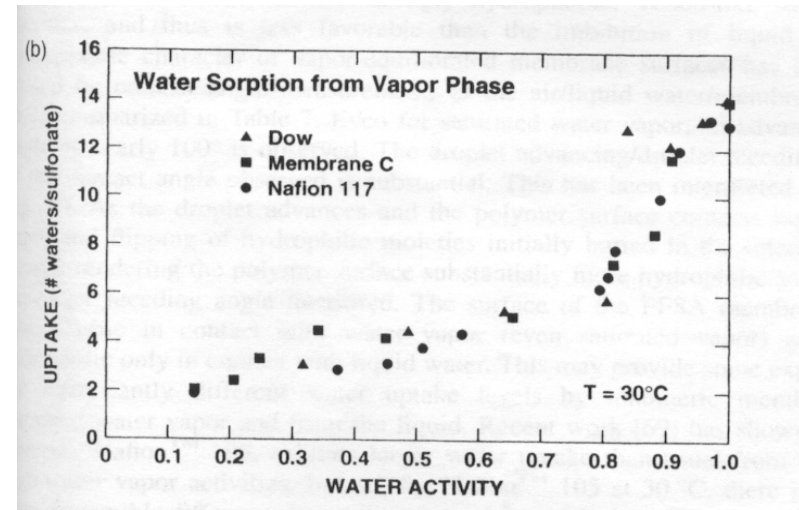
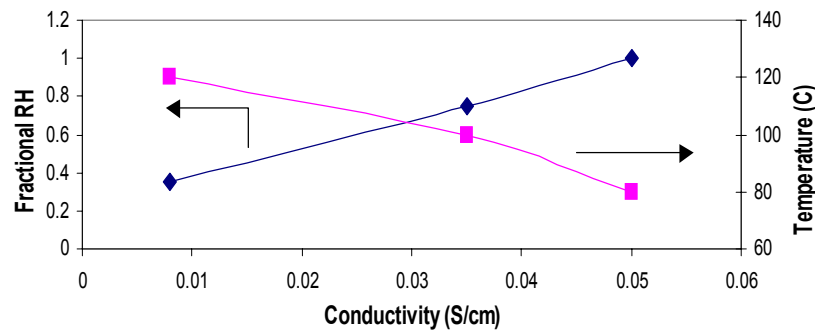
- Linked to one another
- Maintaining a saturated environment above 100°C – requires system pressurization
- Leads to parasitic power losses and complex systems
- Need exists to develop membranes for high temperature / low relative humidity operations

**Is proton conductivity influenced by temperature and water content??**

# Limitations of Current PEM Technology

- Conductivity – strong function of water content
- Drops in under saturated environments
- Increased membrane and electrode resistance at High T / Low RH

Conductivity vs. T and RH - Nafion 112



# Conductivity Mechanisms

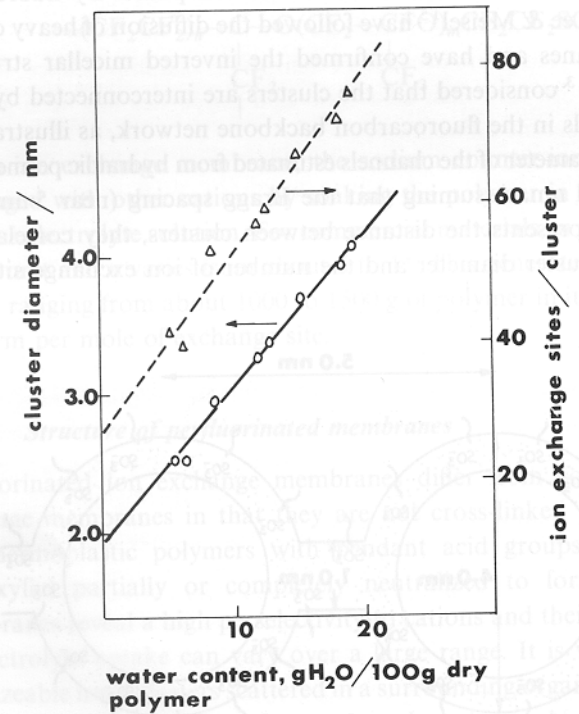
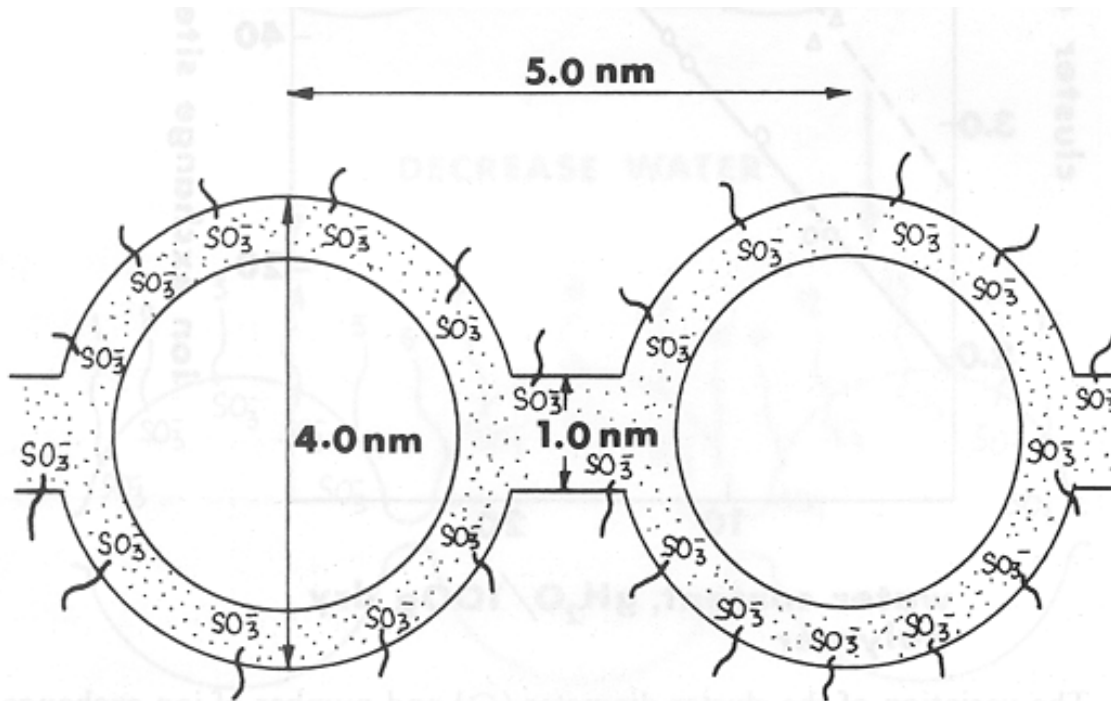
## “Vehicular” mechanism

- Proton attached to solvent (“vehicle”) molecule – e.g.  $\text{H}_3\text{O}^+$
- Moves at rate of vehicular diffusion
- Vehicle counter diffusion
- **Net proton transport – governed by vehicle diffusion rates**

## Grotthuss mechanism

- Also called “hopping” mechanism
- Stationary vehicles (only local motion)
- Proton “hops” from vehicle to vehicle
- **Always** within H bond environment
- Solvent reorientation – provides  $\text{H}^+$  pathway
- **Continuous motion**

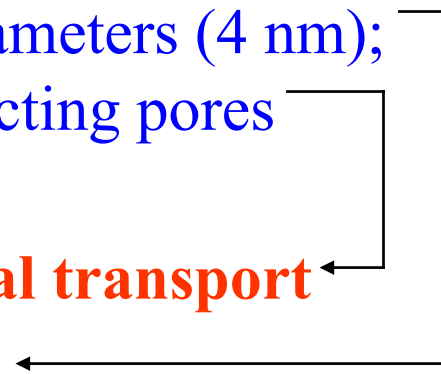
# Gierke Cluster Network Model for Nafion®





# Conductivity in Nafion®

## LT / 100% RH

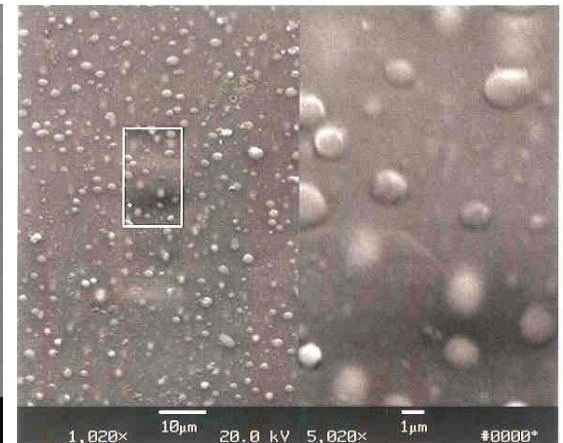
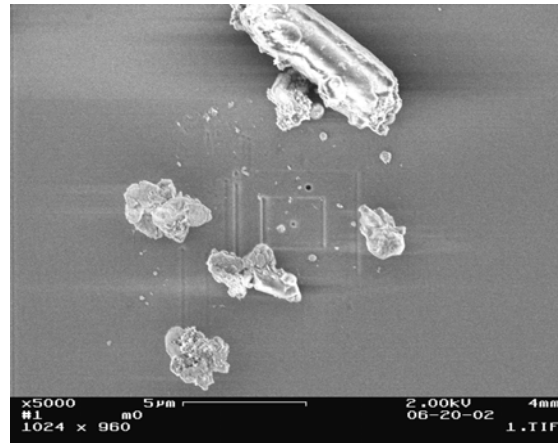
- High water uptake
  - **Combined vehicular / Grotthuss mechanisms**
  - Large water content – symmetric environment
  - Easy, quick reorientation
  - Large cluster diameters (4 nm); large interconnecting pores (~ 1nm)
  - **Good diffusional transport**
  - **Fast hopping**
  - **High conductivity!**
- 

## HT / LRH

- Low water uptake
- Cluster shrinks (~ 2.4 nm)
- **Hopping – difficult**
- **Proton transport – vehicular mechanism**
- Pore narrowing
- **Poor diffusional transport**
- **Low conductivity!**

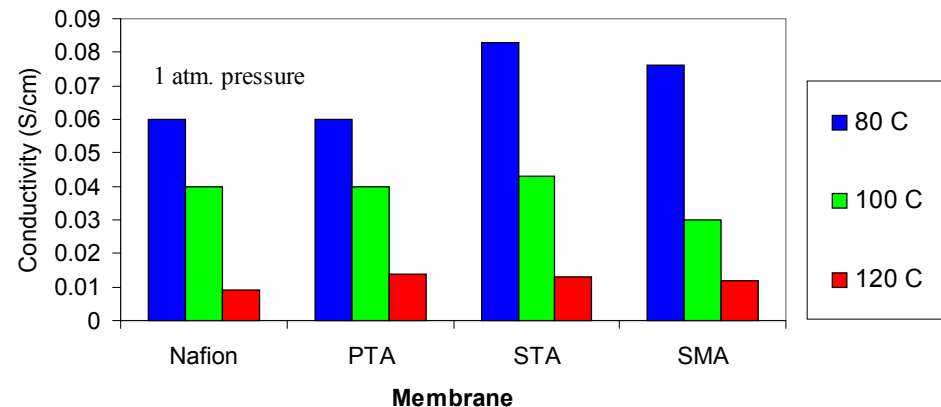
# Alternate Strategy

- Nafion<sup>®</sup> composite membranes
- Incorporation of inorganic additives to Nafion<sup>®</sup> matrix
- Additives used – Heteropolyacids (HPAs), layered phosphates, metal oxides, etc.

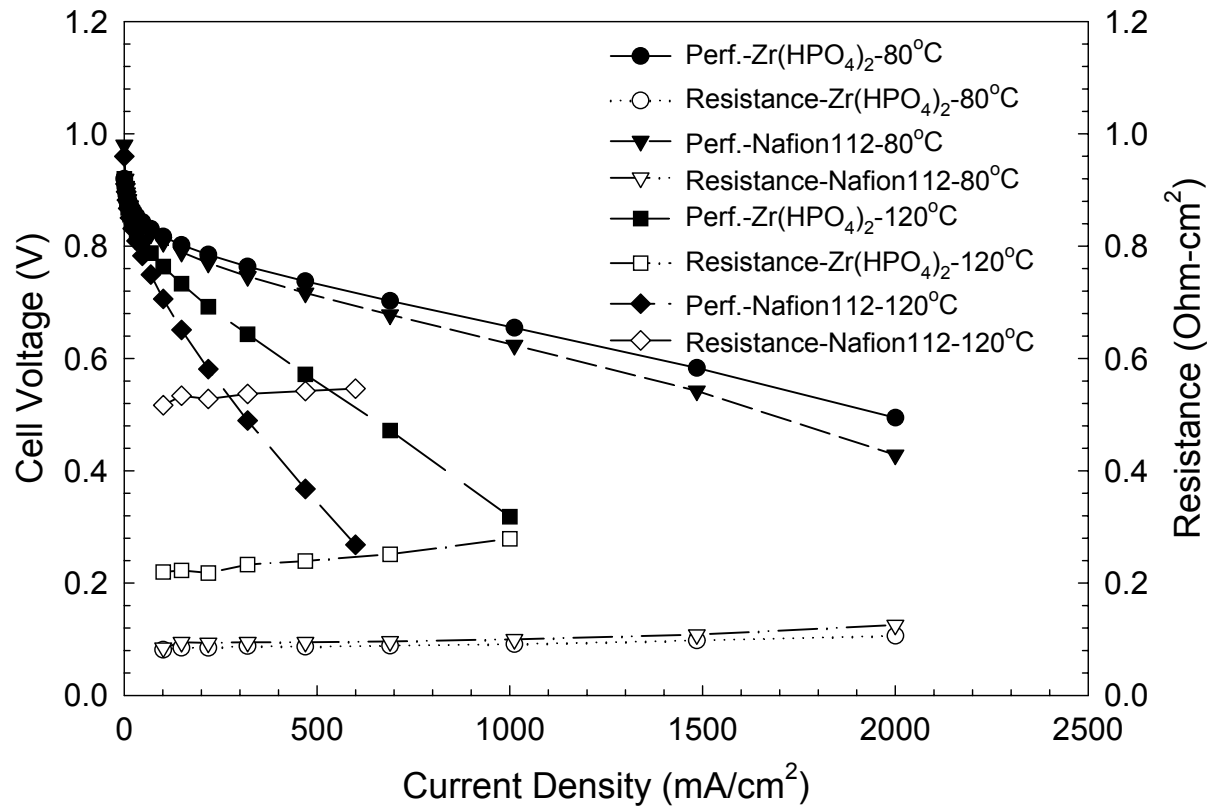


Nafion<sup>®</sup> 112

Nafion<sup>®</sup> / PTA



Nafion<sup>®</sup> vs. composite membranes



**H<sub>2</sub>/O<sub>2</sub>, 1 atm**

**Effectiveness of composite membranes at high temperatures and low relative humidities**

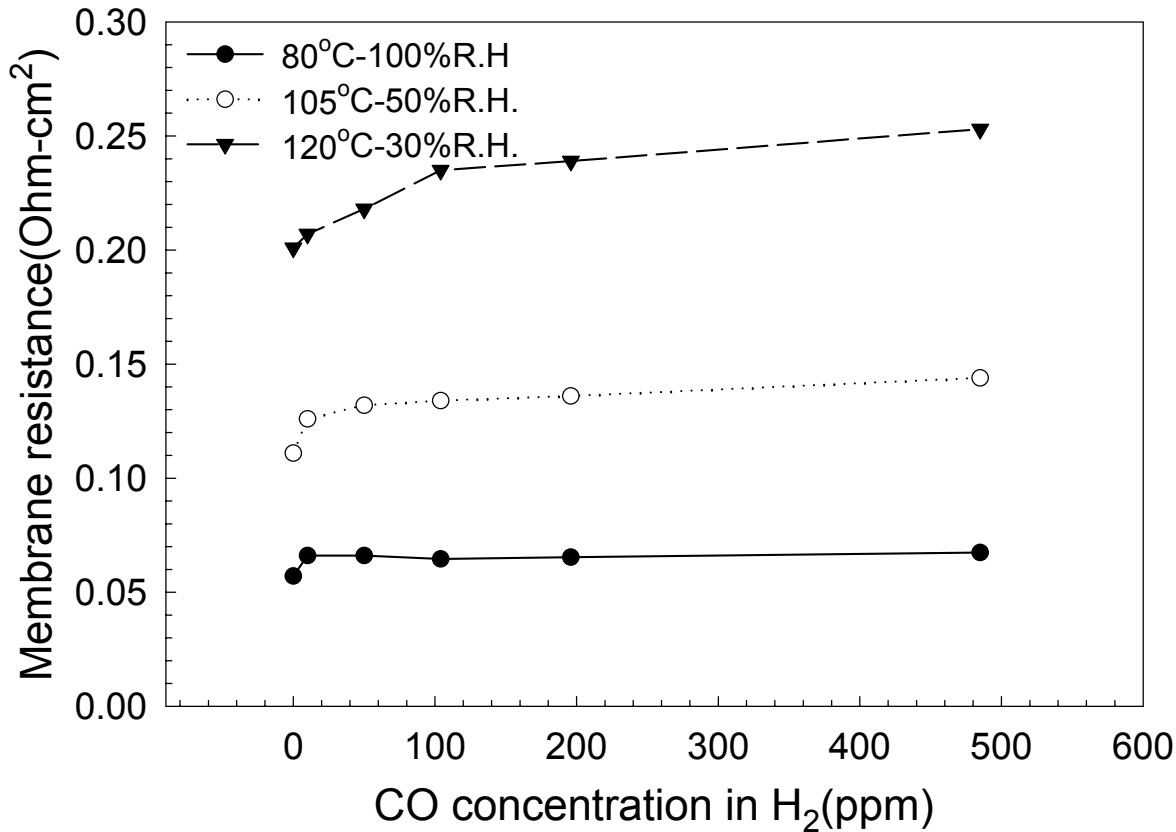
- The development of such composite membranes permits operation at higher temperatures – though resistive losses are still greater than at 80°C
- The temperatures currently attainable at ambient pressure (130°C) allow operation (in conjunction with CO tolerant catalysts) with up to 100ppm CO with minimal losses (when compared to operation with pure H<sub>2</sub> at 130°C)
- This approach can be combined with techniques such as air-bleed for greater efficacy
- Further improvement hinges on improved membranes and electrocatalysts

# Effect of Water Content on CO Tolerance

- **Recall:** CO oxidation **requires** the generation of hydroxyl (OH<sup>-</sup>) groups on the catalyst surface
- Such groups are generated by the oxidation of **water**
- Thus, better CO tolerance can be achieved under well hydrated conditions

**Trade off exists between Temperature (and lower surface coverage) and humidity (and more hydroxyl groups generated on catalyst)!!**

# Effect of CO on Membrane Resistance



## Resistance:

- Constant at 100% RH,
- Increases slightly with CO concentration at 50% RH
- Increases perceptibly at 30% RH

# Why Does Resistance Increase?

- The oxidation of CO to CO<sub>2</sub> will occur at a rate determined by the current output of the cell
- Thus, all available water is used up (to generate hydroxyl groups) at a particular CO concentration
- Any increase in CO concentration will result in water being sucked out from the membrane to support CO oxidation – thereby increasing membrane resistance
- The CO concentration at which this starts to occur is lower at lower relative humidities

# Effect of CO<sub>2</sub> on PEMFC Performance

- CO<sub>2</sub> – neither chemically nor electrochemically inert!
- Can be chemically reduced to give CO (reverse water gas shift: CO<sub>2</sub> + H<sub>2</sub> = CO + H<sub>2</sub>O)
- Can be electrochemically reduced to give CO
$$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- = \text{CO} + \text{H}_2\text{O}$$
- Approaches similar to those adopted for CO tolerance have been shown to improve CO<sub>2</sub> tolerance as well



# Effect of CO<sub>2</sub> – Treatment Using Air-Bleed

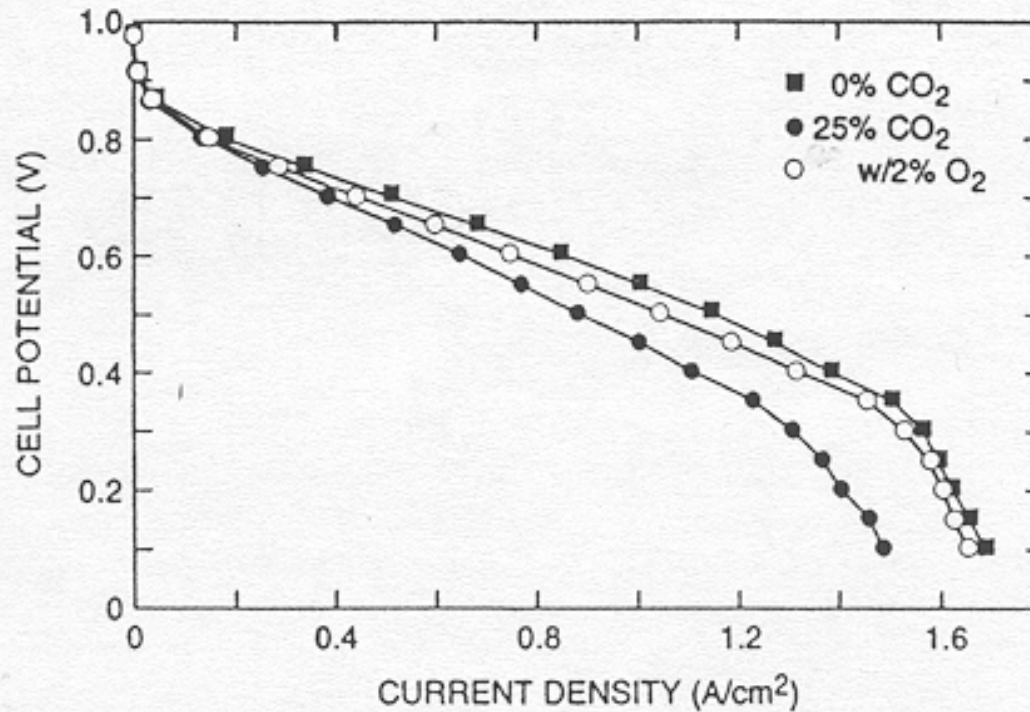


Fig. 16. Effects of CO<sub>2</sub> at the level expected in amethanol reformat, and of subsequent oxygen addition to the anode, in the case of a H<sub>2</sub>/air PEFC with a 0.12 mg Pt/cm<sup>2</sup> thin-film anode [21]. (Reprinted by permission of the American Chemical Society).