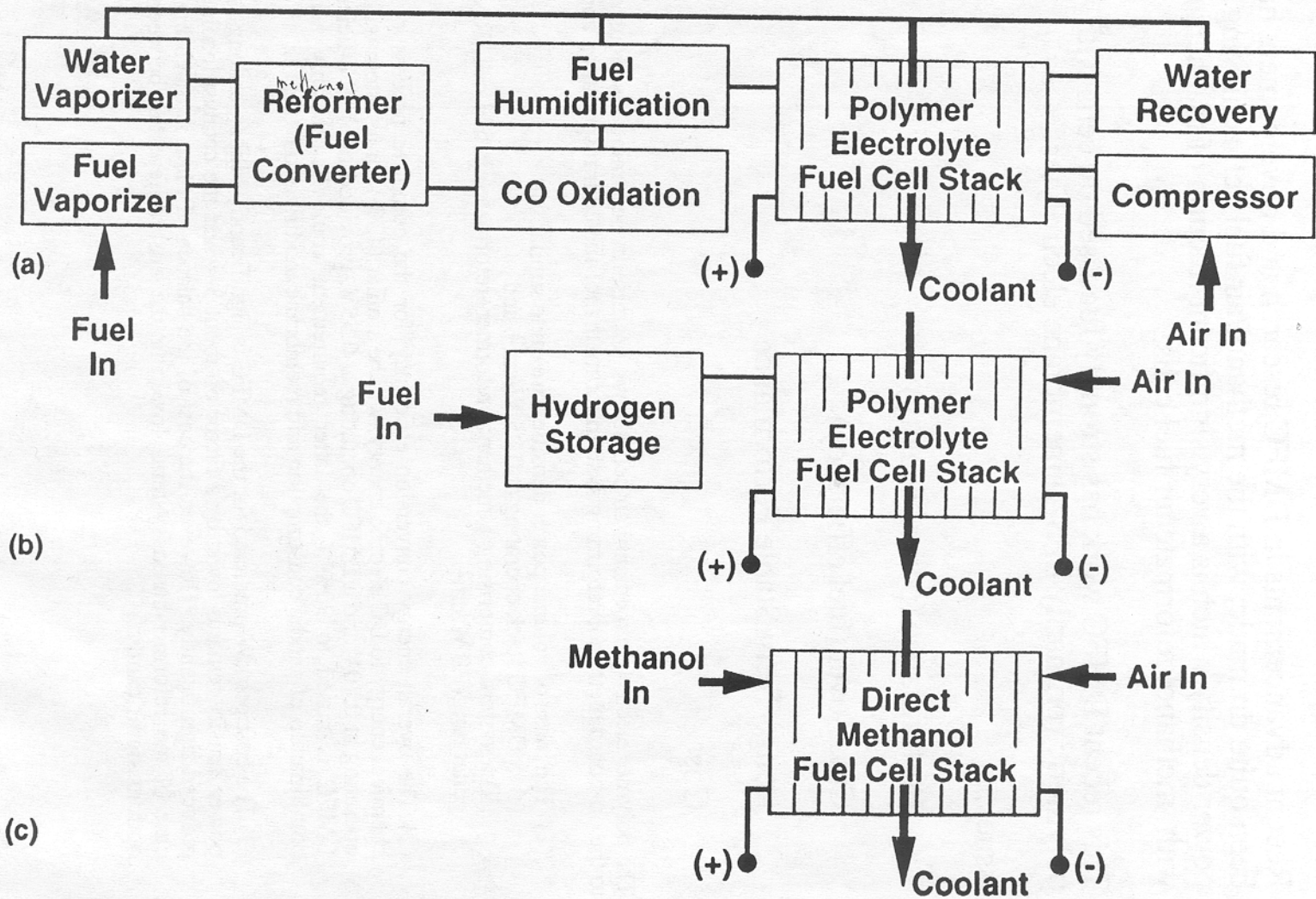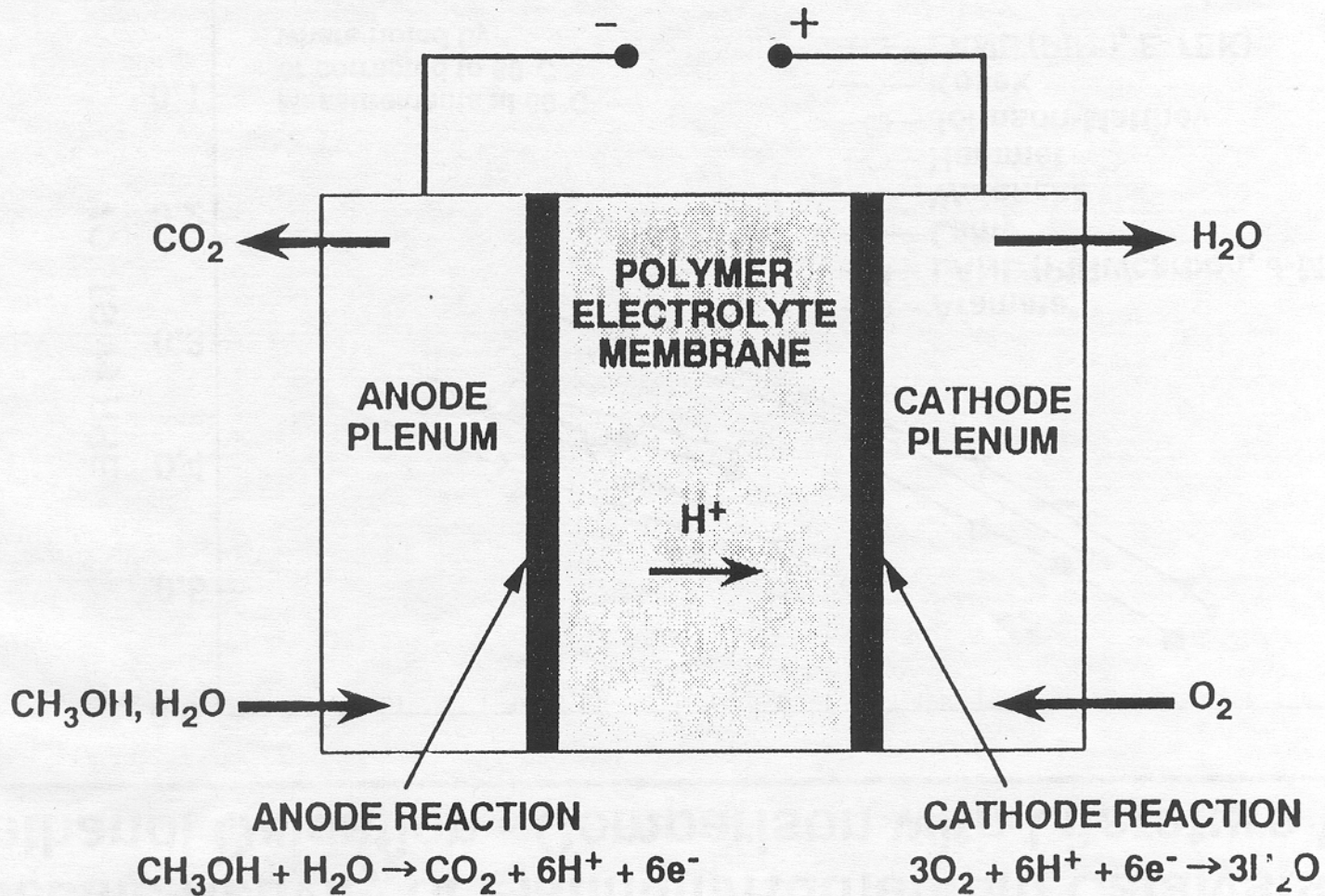# Direct Methanol Fuel Cells

Rationale for Direct Methanol Operation

- Greatly simplified system design

- Readily available fuel infrastructure

- High fuel energy density – lowered system weight and volume

- Ideal for mobile applications such as laptops, cellular phones

- Also of great interest to the military – to power individual soldiers' electronics

Fuel Cell Propulsion Systems: Increasing Simplicity

(a) Water Vaporizer, Fuel Vaporizer → Reformer (Fuel Converter) → Fuel Humidification, CO Oxidation → Polymer Electrolyte Fuel Cell Stack → Water Recovery, Compressor; Fuel In; (+) (−) Coolant; Air In

(b) Fuel In → Hydrogen Storage → Polymer Electrolyte Fuel Cell Stack ← Air In; (+) (−) Coolant

(c) Methanol In → Direct Methanol Fuel Cell Stack ← Air In; (+) (−) Coolant

Direct Methanol Fuel Cell

CO$_2$ ←

H$_2$O →

POLYMER ELECTROLYTE MEMBRANE

ANODE PLENUM

CATHODE PLENUM

H$^+$ →

CH$_3$OH, H$_2$O →

← O$_2$

ANODE REACTION

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

CATHODE REACTION

$3O_2 + 6H^+ + 6e^- \rightarrow 3I'_2O$

Comparison of Performance between H_2 PEMFC and DMFC with Nafion 117 at 60°C and 1atm
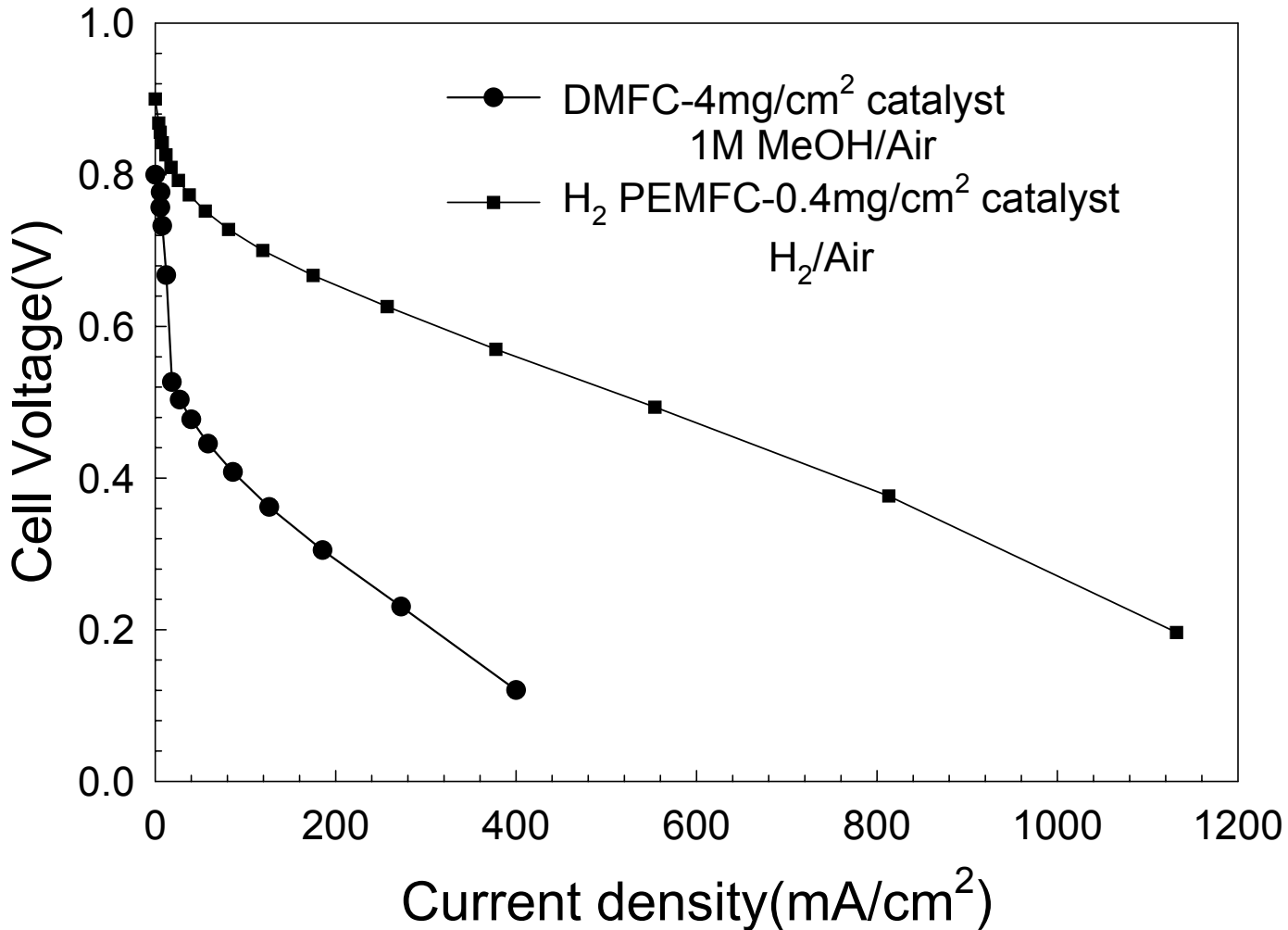
Principle Challenges in DMFC Operation

- Sluggish methanol oxidation (anode) kinetics:
  - 6 electron transfer as opposed to 2 electron transfer for H_2 oxidation
  - formation of CO as an intermediate in the multi-step methanol electrooxidation mechanism – poisoning of catalyst

- Large methanol crossover through the membrane:
  - linked to the electro osmotic drag
  - has detrimental effect on fuel efficiency
  - may poison the cathode
  - creates mass transport problems at cathode layer by wetting hydrophobic gas channels, leading to increased flooding.

- CO_2 removal at anode

Breakup of DMFC Losses

$$E_{cell} = E_{cathode} - E_{anode} = 1.23 - 0.046 = 1.2 \text{ V}$$

(Thermodynamic)
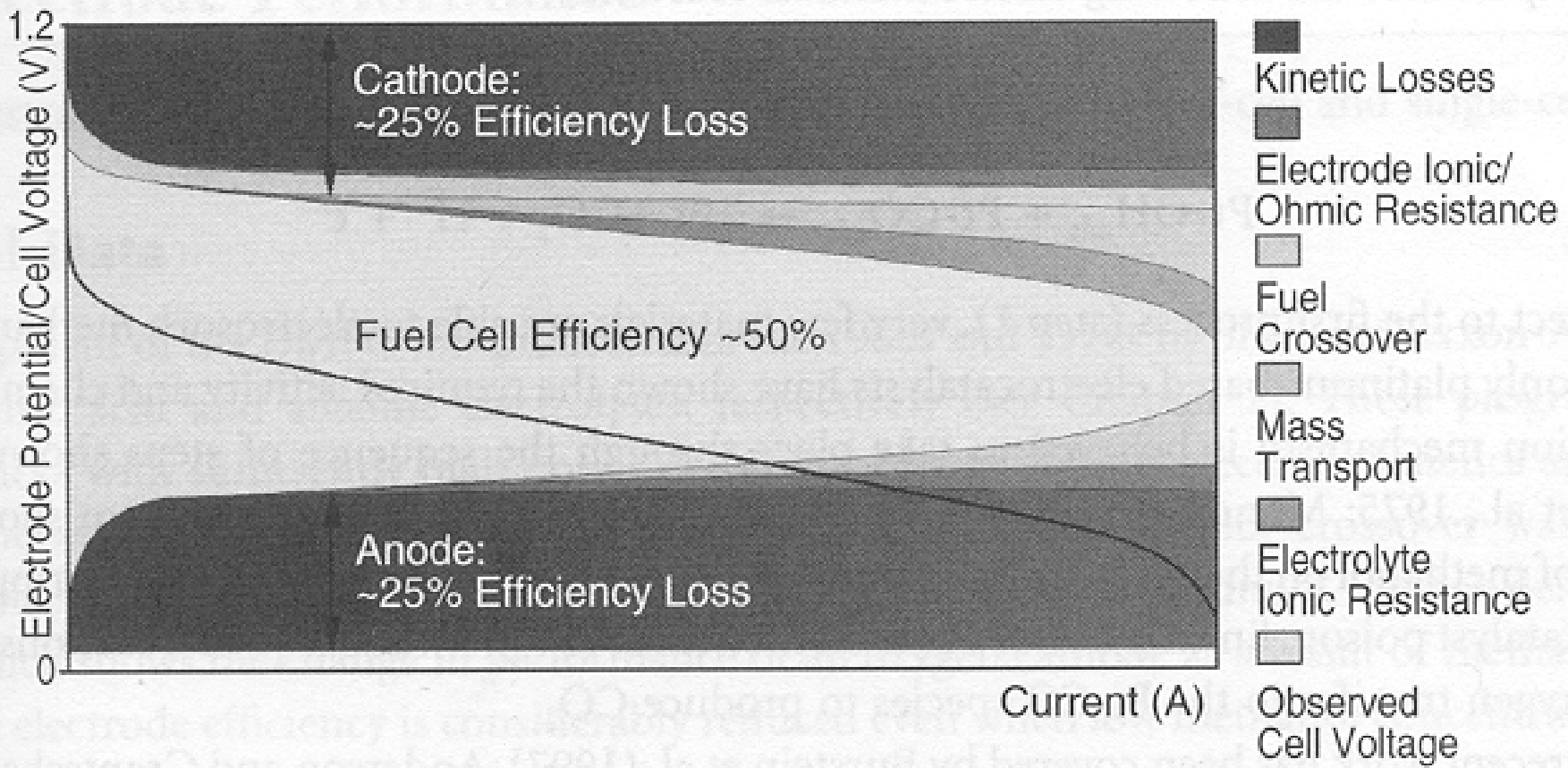
Anode Kinetics

- Thermodynamically, methanol oxidation and hydrogen oxidation occur at nearly the same potential (0.046 V and 0 V respectively)

- However, hydrogen oxidation is a 2 electron process, while methanol oxidation is a 6 electron process.

- It is very unlikely that all 6 electrons are transferred at the same time

- Therefore, transfer occurs step by step, leading to the formation of intermediates
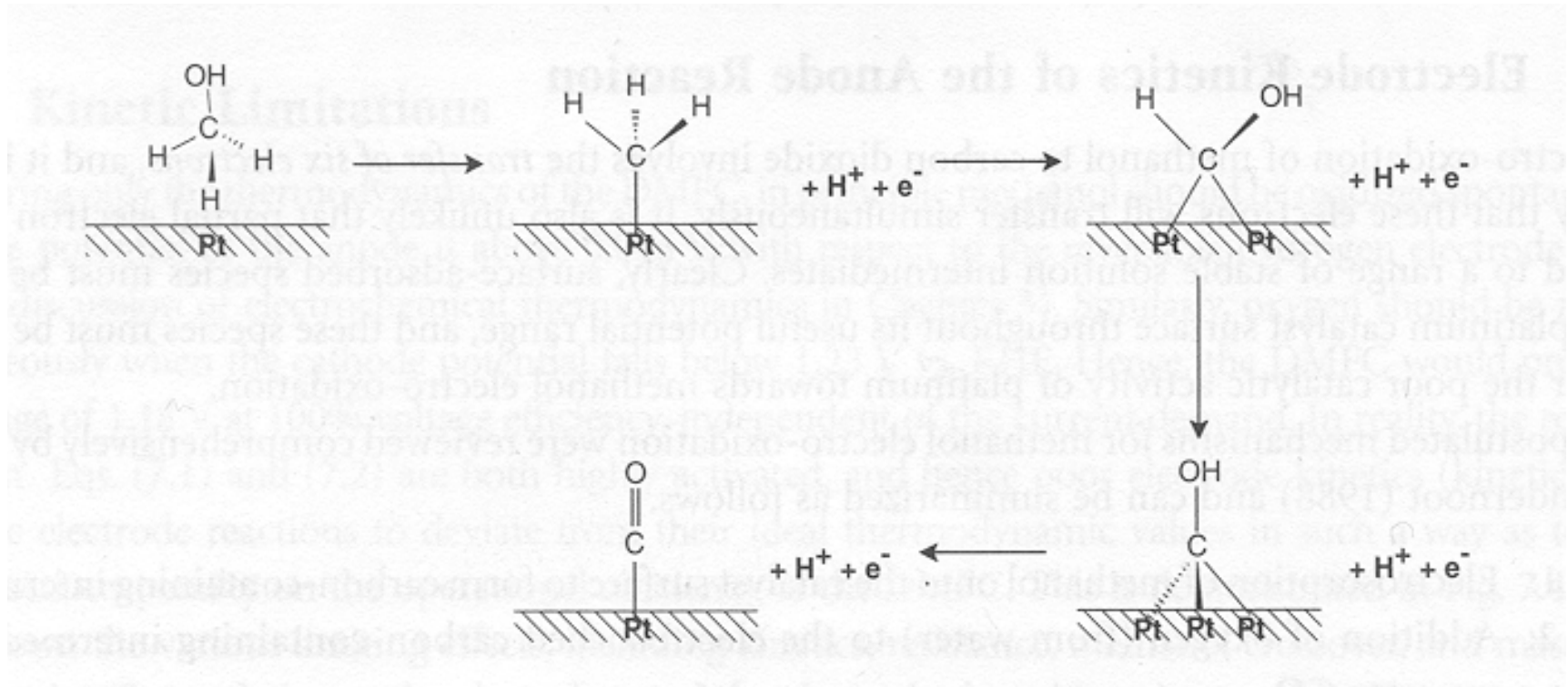
Proposed Methanol Oxidation Mechanisms

$Pt + MeOH = Pt\text{-}MeOH = Pt\text{-}CO_{ads}$ (methanol adsorption through a series of steps, see figure)

$Pt + H_2O = Pt\text{-}OH_{ads} + H^+ + e^-$ (generation of hydroxyl groups on catalyst)

$Pt\text{-}CO_{ads} + Pt\text{-}OH_{ads} = 2Pt + CO_2 + H^+ + e^-$ (Oxidation of CO to CO_2 - similar to CO oxidation in direct hydrogen systems)

Postulated Methanol Adsorption Mechanism

**Note:** Final stage is **CO adsorbed on Pt sites**

- Below 450 mV, Pt surface – entirely poisoned by CO

- No further methanol adsorption

- Further adsorption – requires CO electrooxidation – induces overpotential of 450 mV or greater for Pt catalysts

- Thus, E_{cell} = 1.23 - ~0.45 = ~ 0.8 V max. even at low currents!

Effect of anode overpotential – contributes to poor methanol performance seen in performance curve

Breakup of DMFC Losses

$$E_{cell} = E_{cathode} - E_{anode} = 1.23 - 0.45 = 0.8 \text{ V}$$

(small currents)
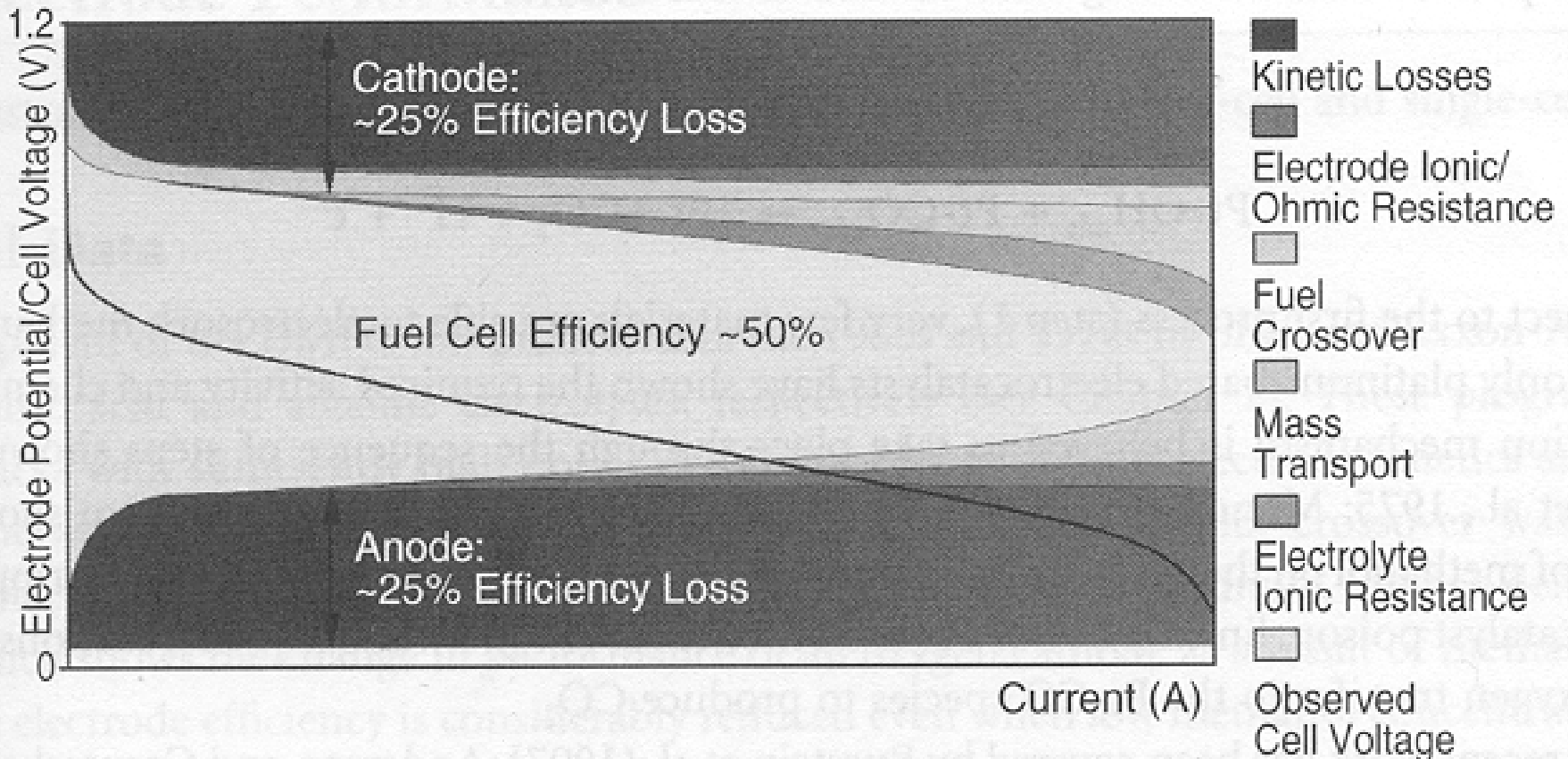
Direct Methanol vs. Direct Hydrogen

Direct Methanol

- Pt-CO formation due to adsorption of methanol and subsequent intermediate formation

- Pt-CO inhibits further methanol adsorption

- Large currents – requires CO electrooxidation to free catalyst sites for further methanol adsorption-– thereby inducing large overpotentials
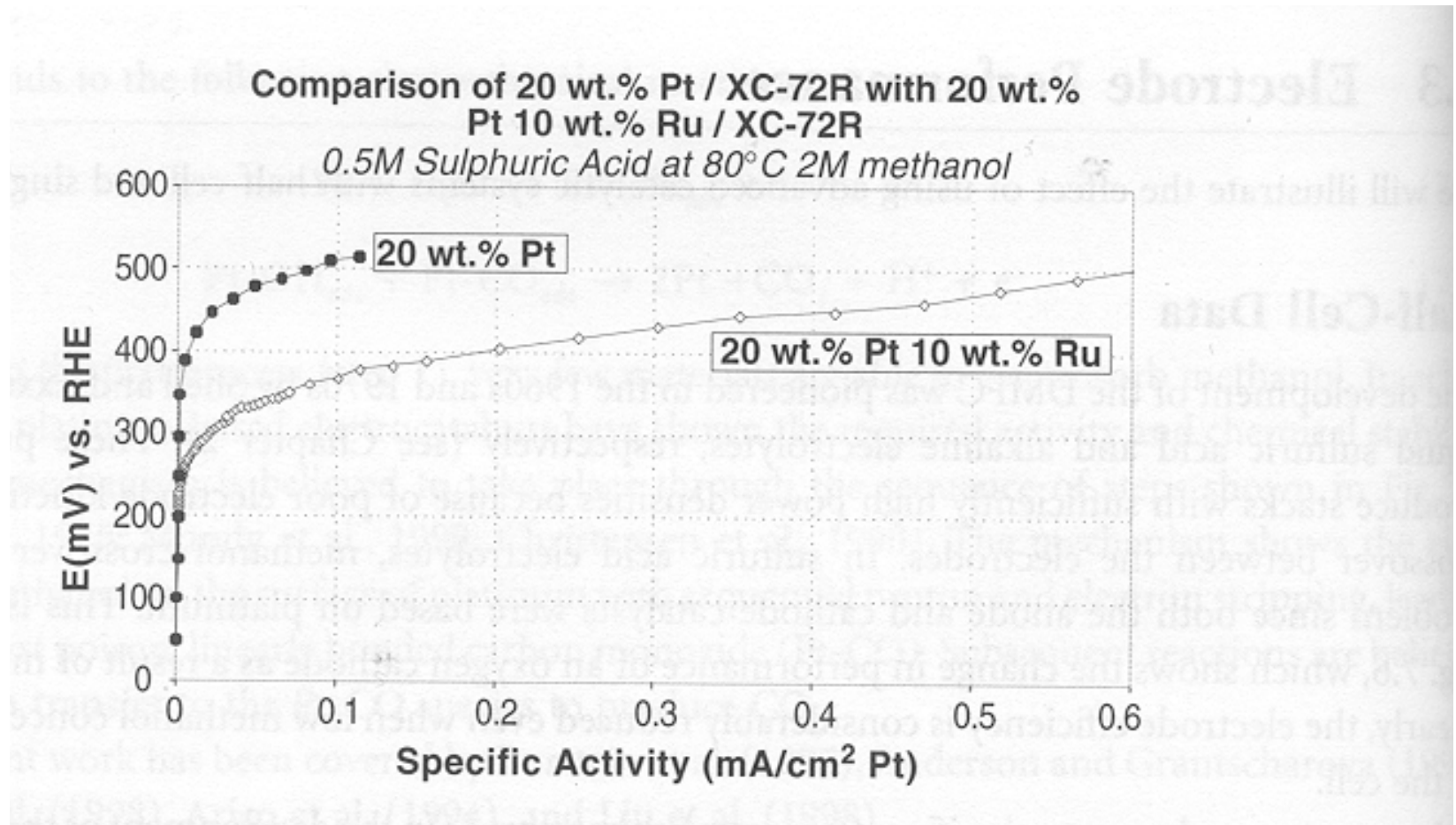
Direct Hydrogen

- Pt-CO formation is due to the adsorption of CO from the feed stream

- Pt-CO inhibits further hydrogen adsorption

- Large currents – requires CO electrooxidation to free catalyst sites for further hydrogen adsorption– thereby inducing large overpotentials

End Result – identical – POOR ANODE KINETICS

Improving Methanol Oxidation Kinetics

- Similar approaches to those taken for H_2/ CO operation:

    - Better electrocatalysts for enhanced efficacy of CO electrooxidation – surface hydroxyls generated at lower potential (see figure)

    - High temperature operation (> 100 ^{o}C) for improved anode kinetics – Note, this approach also pays significant dividends by reducing methanol crossover (cathode kinetics???)

Enhanced Activity of Alloy Catalysts

Comparison of 20 wt.% Pt / XC-72R with 20 wt.%
Pt 10 wt.% Ru / XC-72R
0.5M Sulphuric Acid at 80°C 2M methanol

Clearly, for a given Specific Activity (current density at a high voltage / unit active catalyst area), Alloy catalysts have lower overpotentials for methanol oxidation
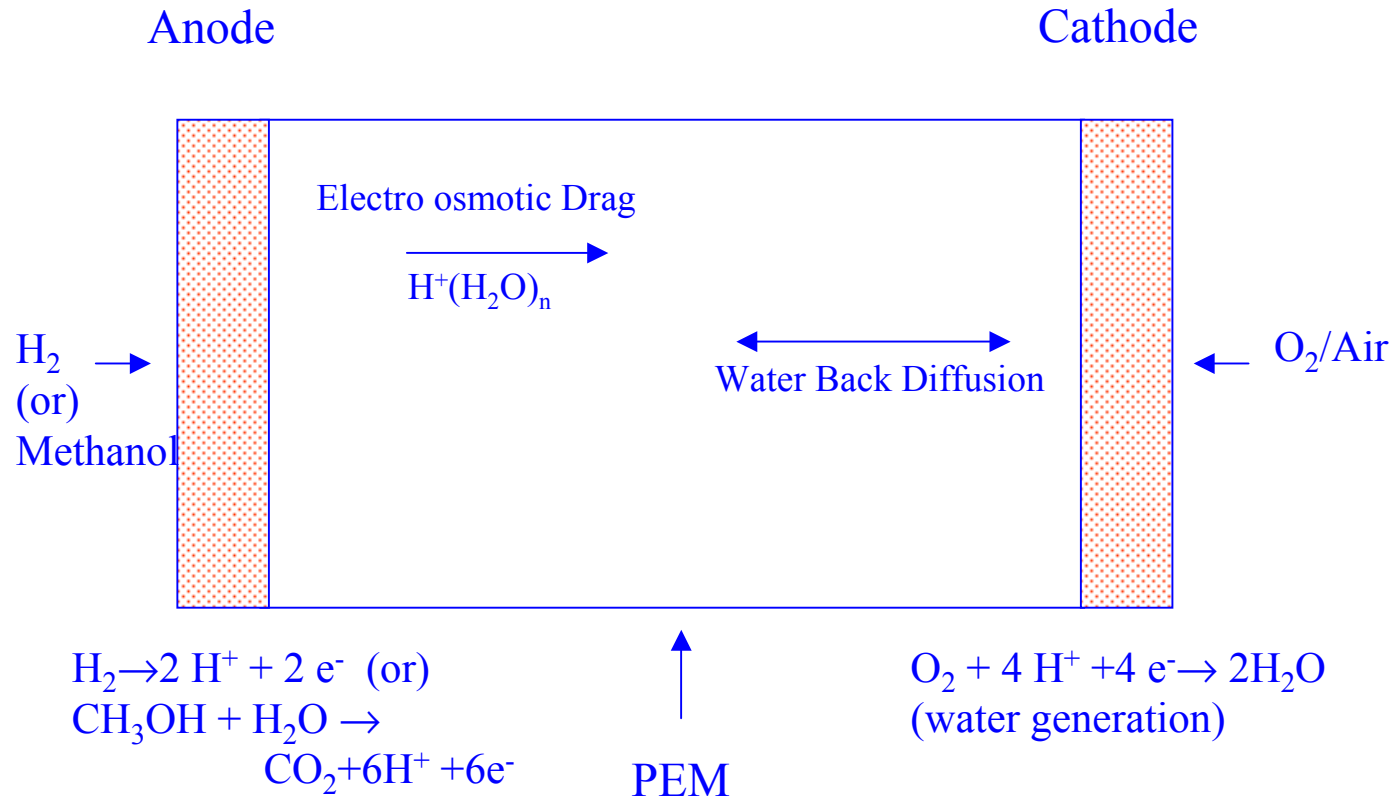
Anode kinetics alone does not account for the significant performance loss seen in DMFC systems

The effect of methanol crossover is equally important and affects parameters such as fuel efficiency, cathode kinetics, and mass transport in the cathode layer. Methanol crossover, and techniques to limit it are discussed in the following slides

Another important aspect of DMFCs (not discussed in this lecture) is the efficiency of CO_2 removal at the anode.

Methanol Crossover

- Ionomeric membranes have a complex water distribution during operation:

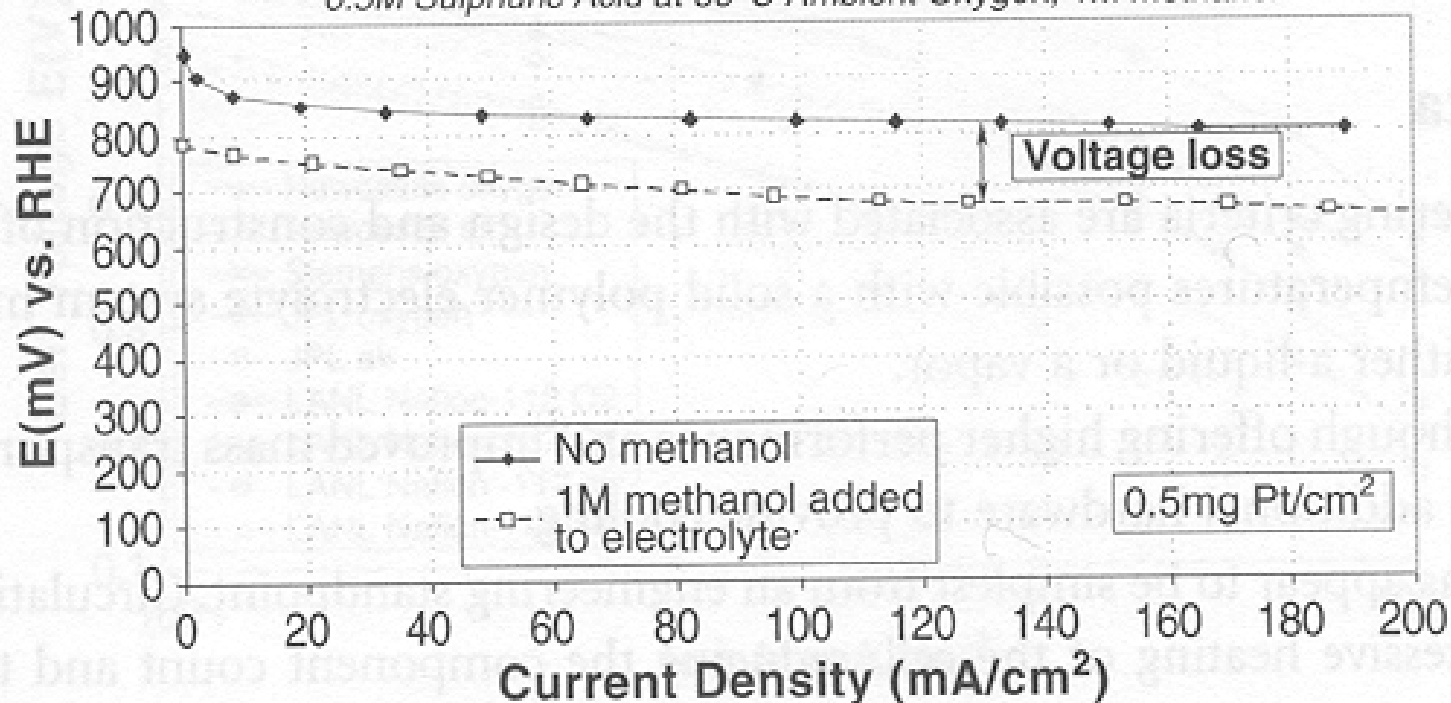Anode   Cathode

Electro osmotic Drag

$H^+(H_2O)_n$ →

H_2 (or) Methanol →

Water Back Diffusion ←→

O_2/Air ←

$H_2 \rightarrow 2\ H^+ + 2\ e^-$ (or)
$CH_3OH + H_2O \rightarrow$
$\quad\quad CO_2 + 6H^+ + 6e^-$

PEM

$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2H_2O$
(water generation)

Why (& How) does Methanol Crossover?

- As water moves from anode to cathode (osmotic drag), methanol migrates along with the water

- On the cathode side, it is adsorbed onto the cathode electrocatalyst, thereby reducing efficiency

- The flux of methanol across the membrane depends upon:

    - methanol concentration in fuel stream

    - current density

    - membrane selectivity (ratio of protonic conductivity to methanol permeability; property of membrane)

    - membrane thickness

Detrimental Effects of Methanol Crossover

- Reduced fuel efficiency

- Cathode mixed potential (due to competing methanol oxidation and oxygen reduction) – lowering of open circuit voltage

- Cathode poisoning – CO adsorption on cathode catalyst, lowered cathode activity (see figure)

- Mass-Transport limitations at cathode (especially for air based applications) – methanol wets the hydrophobic gas channels, and permits flooding – thereby increasing diffusional resistance

Effect of Methanol on Oxygen Reduction (Cathode) Kinetics

Effect of Methanol on the Oxygen Reduction Performance of 20% Pt / XC-72R
0.5M Sulphuric Acid at 80° C Ambient Oxygen, 1M methanol

Voltage loss

0.5mg Pt/cm^2

Legend:
- No methanol
- 1M methanol added to electrolyte

Y-axis: E(mV) vs. RHE (0 to 1000)
X-axis: Current Density (mA/cm^2) (0 to 200)

Effect of Methanol Concentration and Membrane Thickness on Crossover
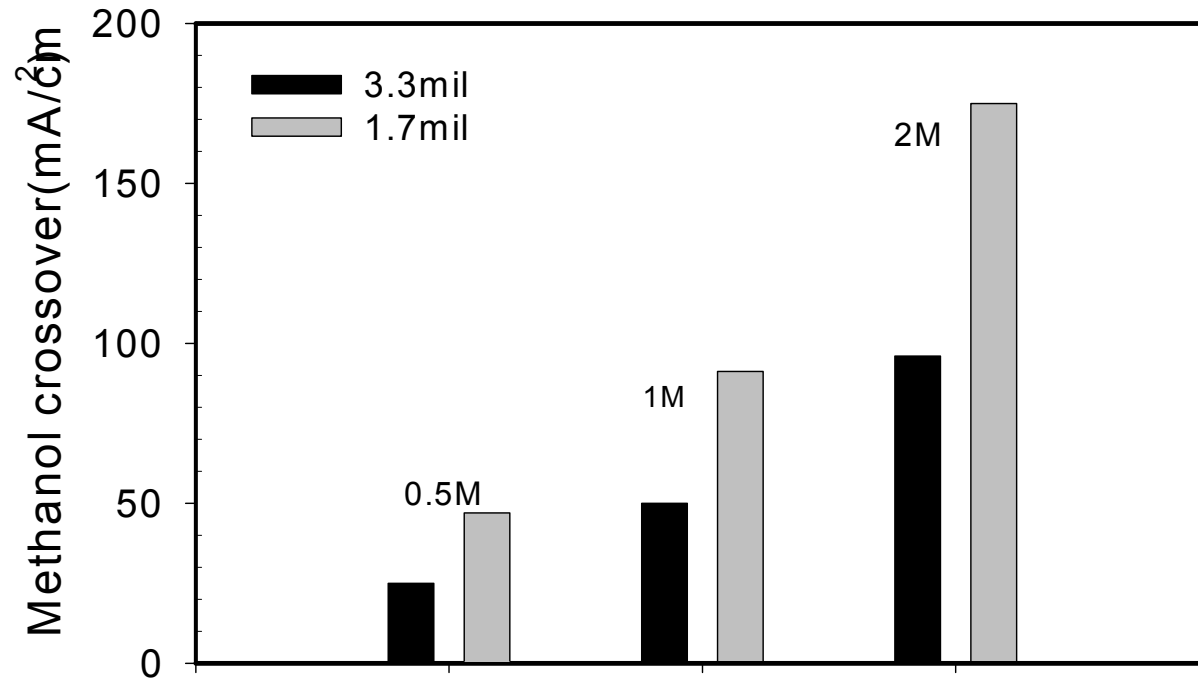
Evidently, crossover increases as methanol concentration increases and as membrane thickness decreases

Why the Concentration and Thickness Effect?

Methanol flux ~ concentration gradient

High concentration, low thickness – maximum concentration gradient (dC/dx)

C_{left}

C_{right}

x
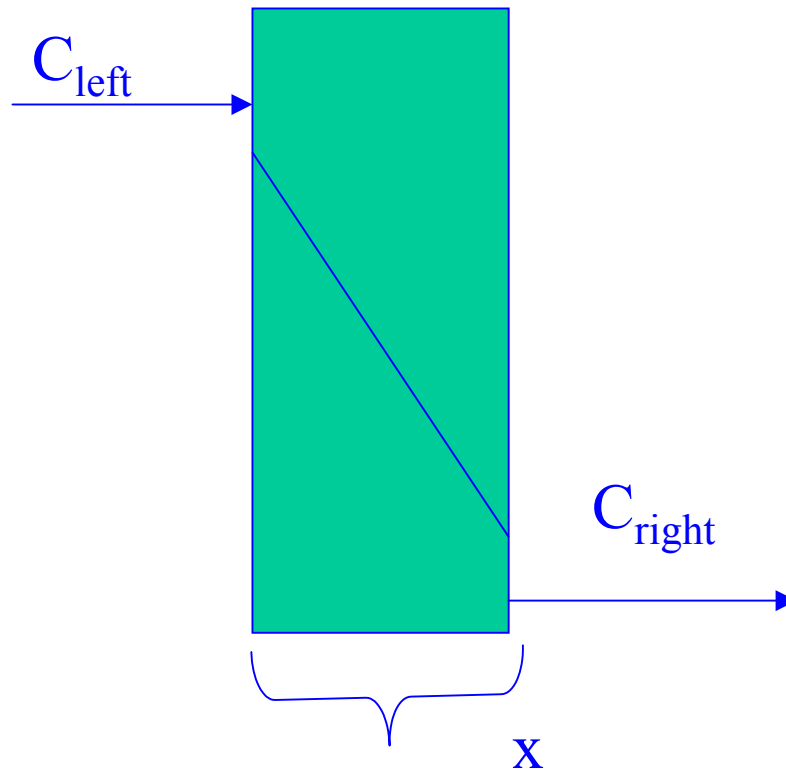
Note…

- Cannot use very low concentrations of methanol – this is because the energy density of the fuel goes down with dilution, and very low methanol concentrations will increase system weight and volume

- Can however use neat methanol as fuel, and dilute using water tapped from the cell (cathode) prior to injection into anode – approach adopted by LANL

Effect of Current Density and Concentration on Methanol Crossover
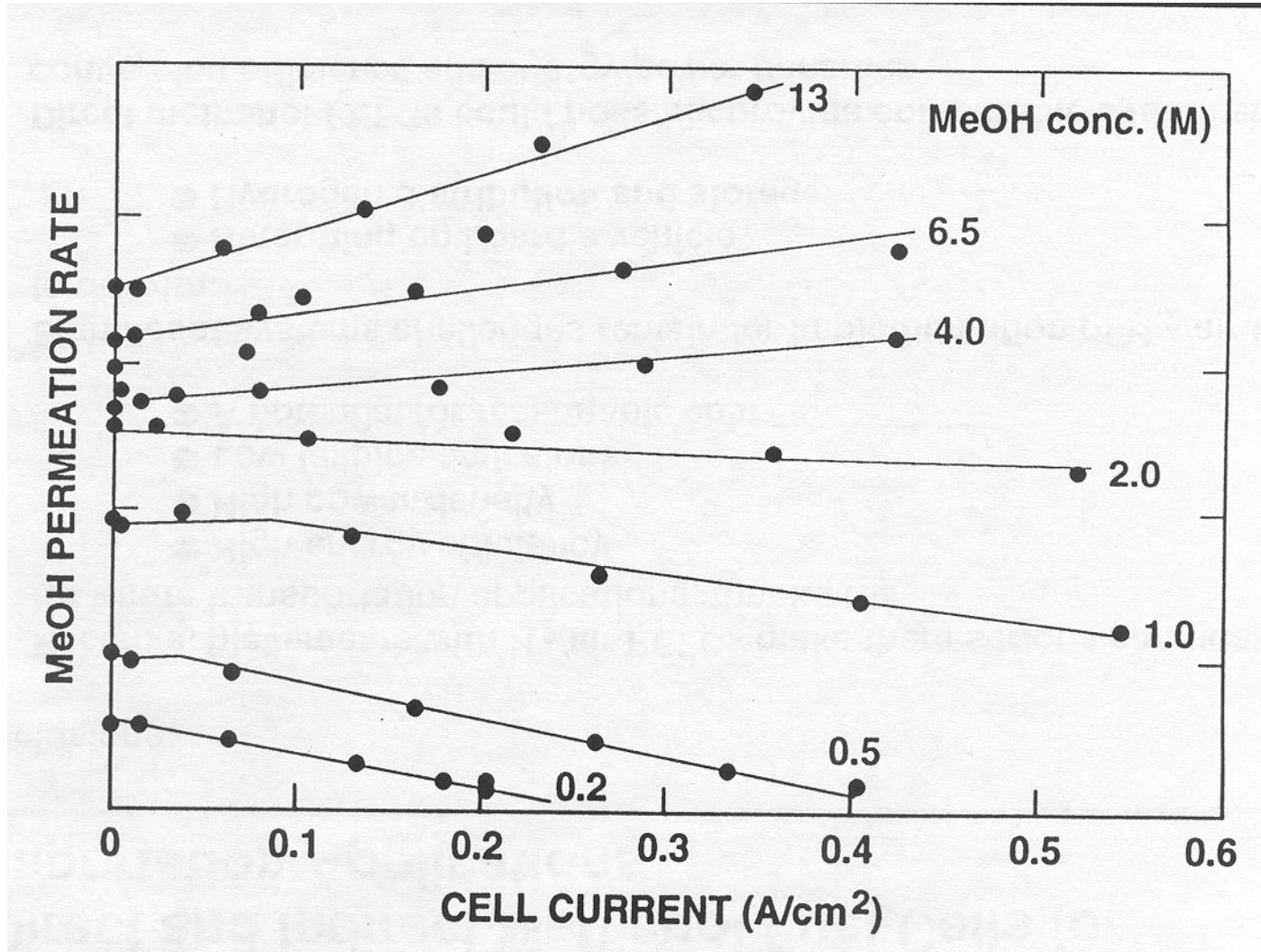
- Current – plays two competing roles:

  - increased faradaic electrooxidation of methanol at anode (lowers concentration at anode, reduces flux) – **positive effect**

  - increased protonic current – increased water transport to cathode by electro osmotic drag – larger methanol crossover – **negative effect**

Clearly, the former effect dominates at low methanol concentrations, and the latter at high methanol concentrations

Effect of Temperature on Methanol Crossover
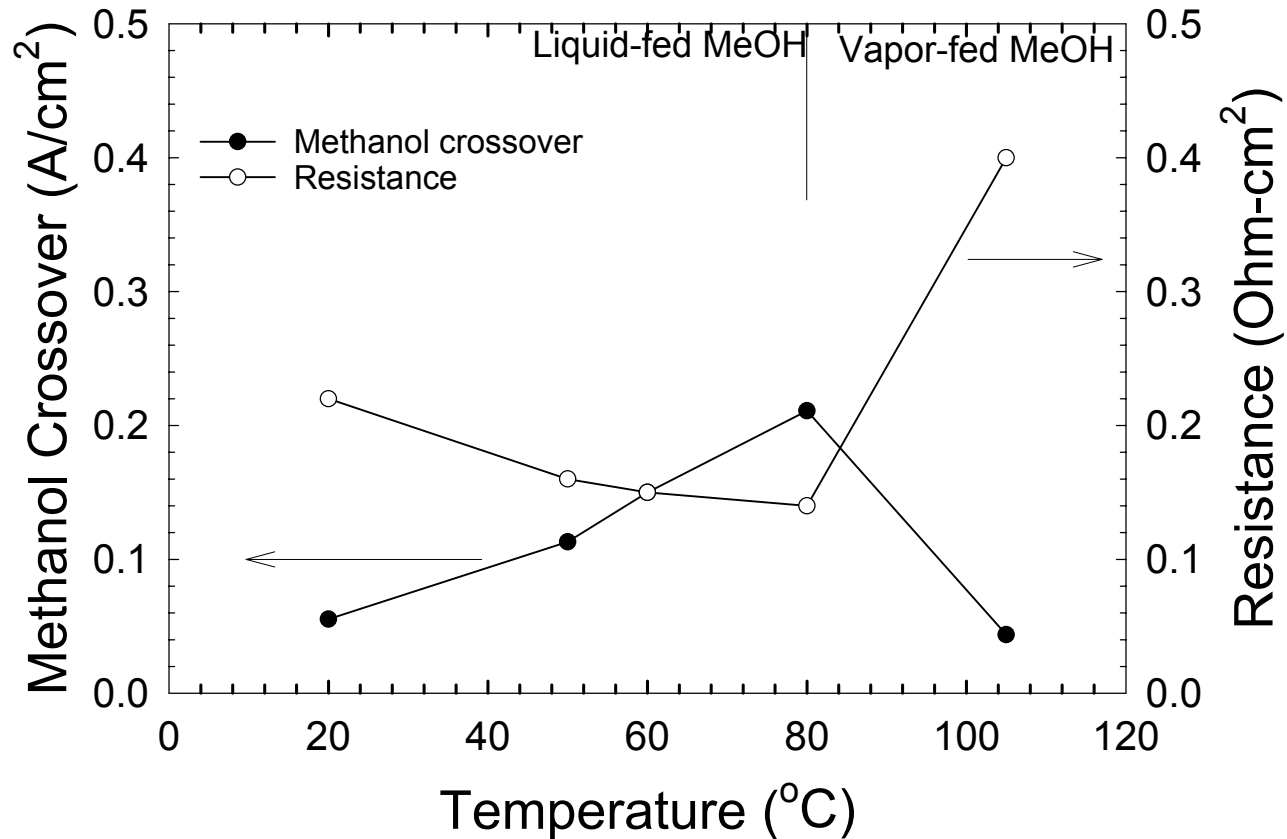
- Methanol crossover increases with temperature up to a temperature of ~ 100°C

- This is because the diffusion coefficient increases with temperature

- Above ~ 100°C, there is a precipitous drop in crossover

- This drop occurs due to reduced water transport through the membrane as liquid water does not exist at ambient pressure – recall water uptake chart

Note – membrane resistance also increases with increasing temperature (decreasing relative humidity)– therefore, a tradeoff exists!

High Temperature Membranes

- Recall discussion on elevated temperature membranes
- These membranes can be used for high temperature DMFCs
- The liquid water (and hence methanol) transport rates through the membrane remain minimal
- However, the resistance at elevated temperatures is greatly reduced
- Comparative performance data – reveals that this technique permits superior performance. Reasons include:

  - lower crossover (above discussion)

  - lower resistance (above discussion)

  - improved anode kinetics (CO desorption favoured)

Low Temperature DMFC Approaches

- Certain applications (cellular phones) – require operation at room temperature (or low temperatures)

- The high temperature approach is clearly invalid under these conditions

- Lowering methanol concentration is achieved by tailoring the membrane microstructure

- Proven technique – using a polymer that does not permit methanol transport (e.g. PVDF)

Unfortunately…

- Such polymers do not conduct protons well either!

- Therefore, it is important to look at the membrane selectivity

- A tradeoff clearly exists between eliminating crossover and retaining protonic conductivity

- Illustrated in the following diagrams

**Methanol permeability decreases with PVDF content**
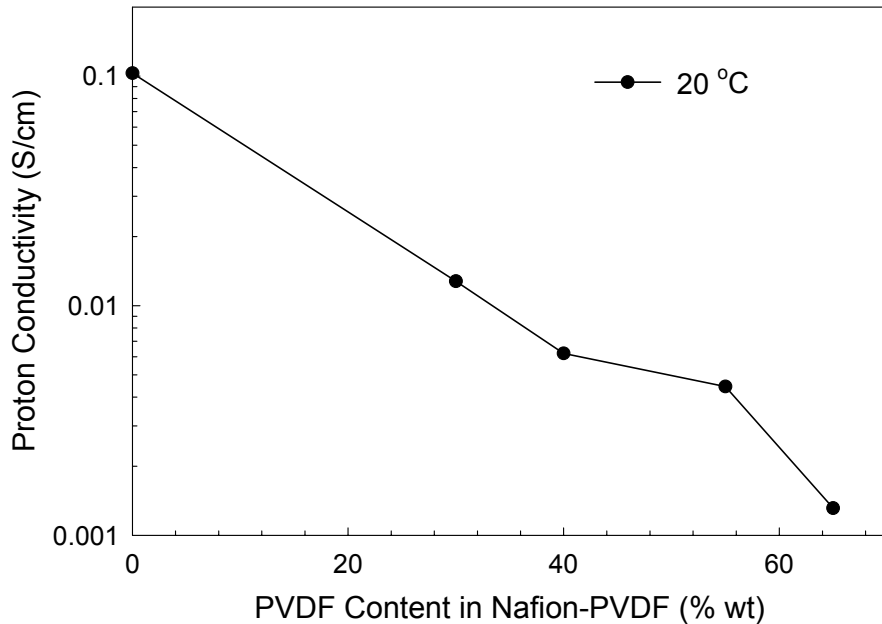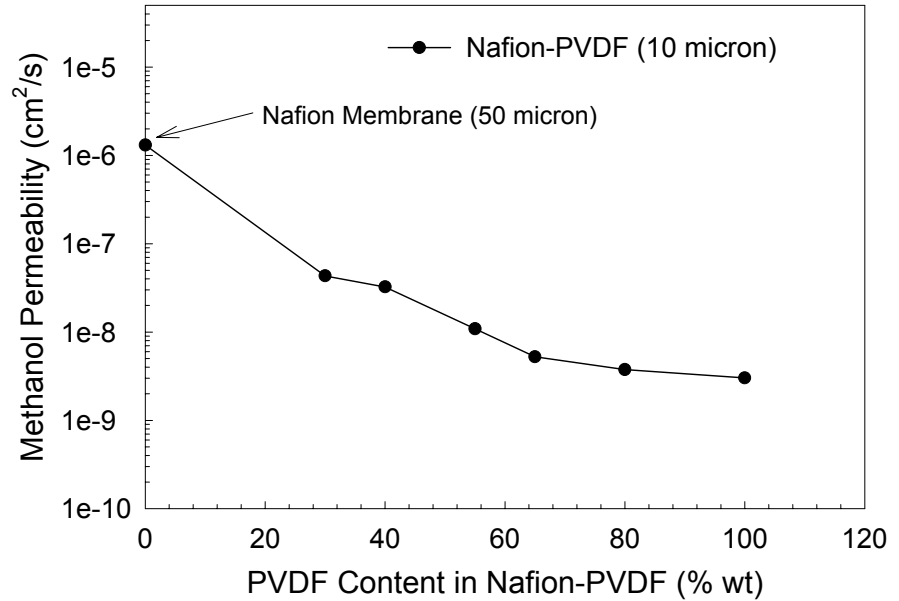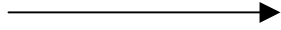
So does protonic conductivity

Optimal PVDF Content will determined experimentally, depends upon thickness

Si

Alternate Design

- Use a thin layer of methanol barriers such as Nafion – PVDF blends sandwiched between proton conducting Nafion® layers

- Recall – resistance ~ thickness/conductivity

- Therefore, very small thickness of barrier – acceptable increase in resistance

- The thin layer is reasonably effective in keeping methanol out

- Thickness of barrier layer – determined experimentally

# Methanol Concentration Profile Through Layered membrane

C_{left}

Nafion layer

C_{right} ($<<$ C_{left})

Barrier Layer –
Nafion$^®$ / PVDF
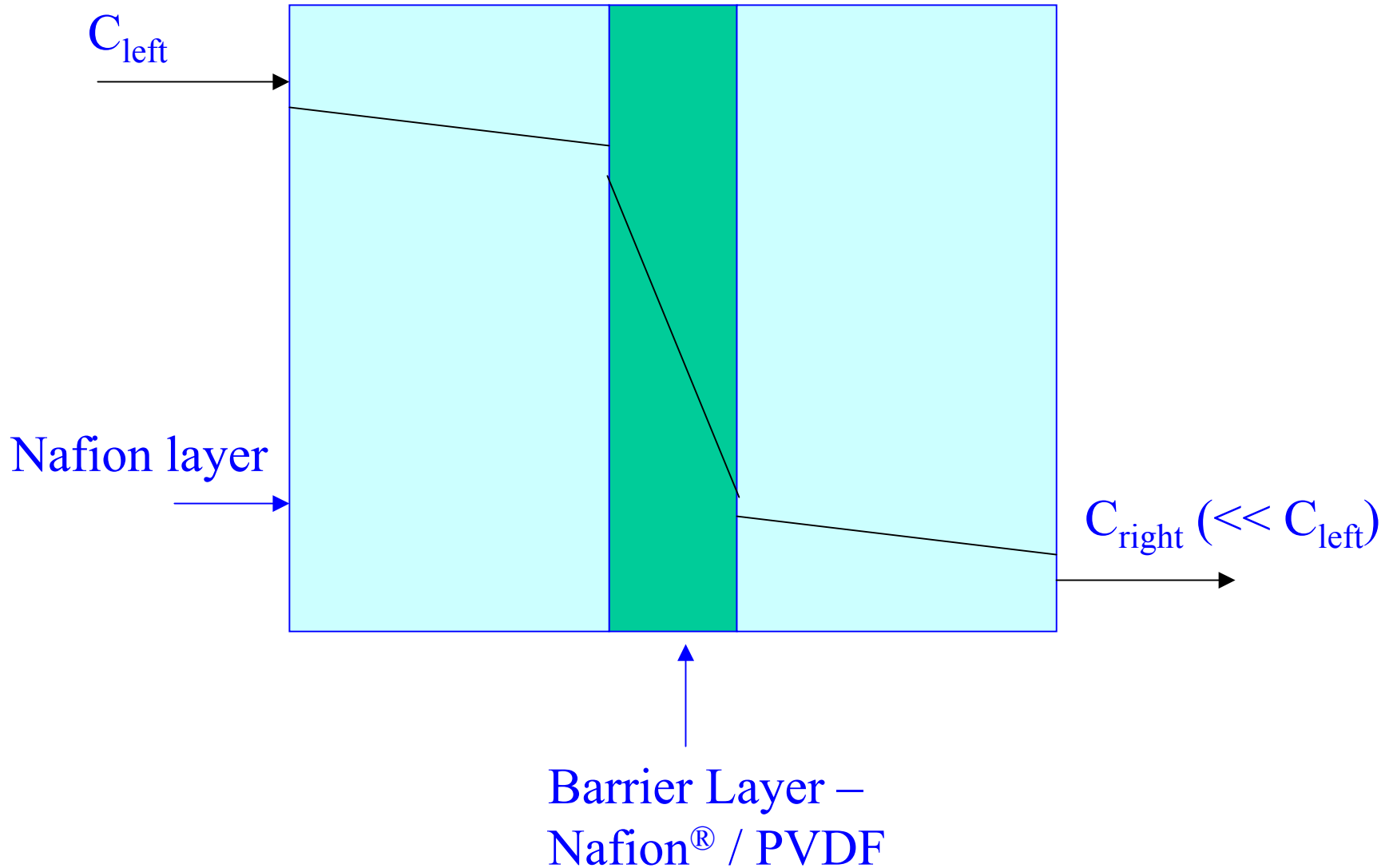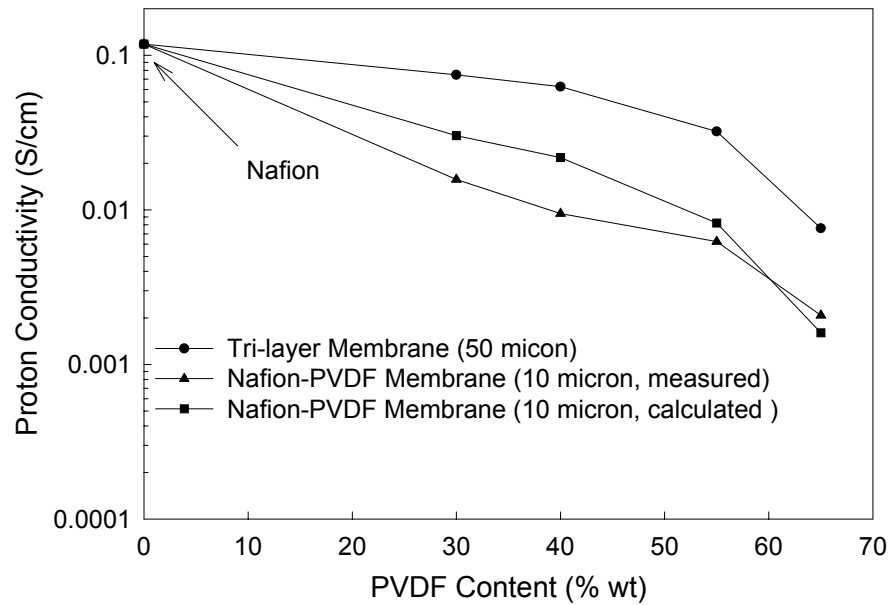
Proton Conductivity of 50 μm Tri-layer Membrane Containing a 10 μm Nafion®-PVDF Barrier Layer as a Function of PVDF in the Barrier Layer.
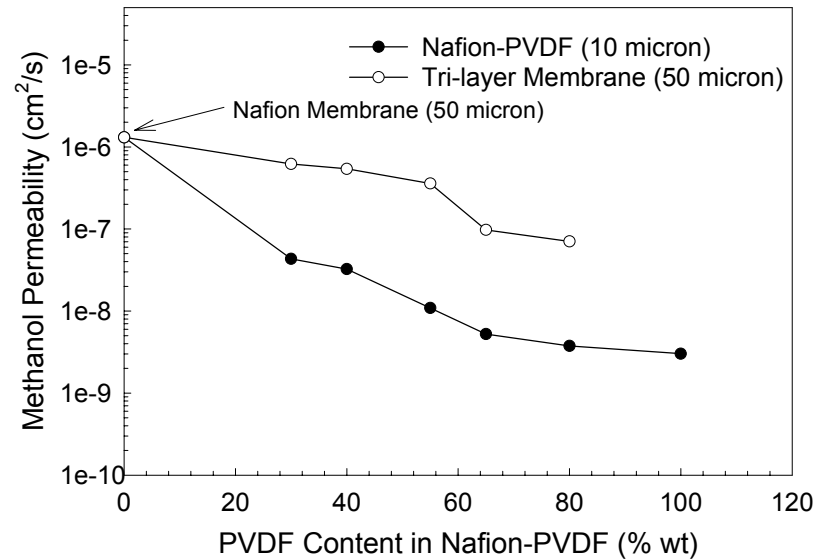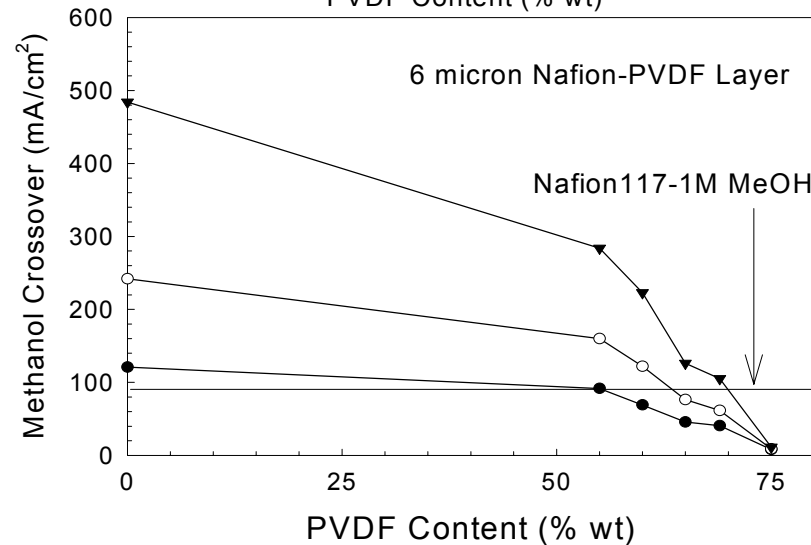
Methanol Permeability of 50 μm Tri-layer Membrane Containing 10 μm Nafion®-PVDF Barrier Layer as a Function of PVDF Content in Nafion®-PVDF.

# Effect of Barrier Layer Thickness on Methanol Crossover
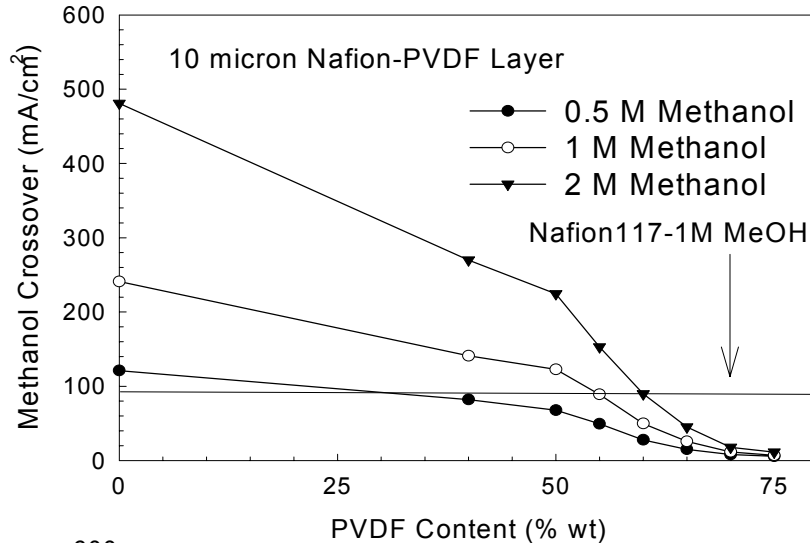
Note 1. – The comparison is made against a Nafion® membrane 175 μm thick, and for a 1M methanol concentration
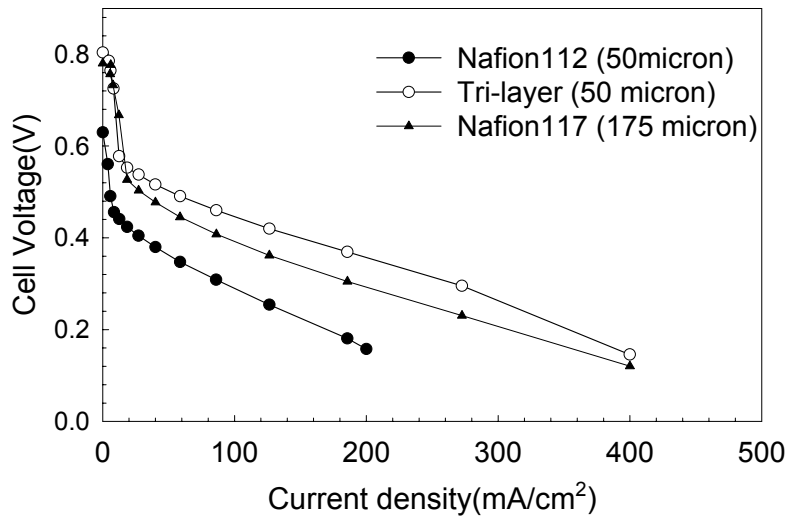
Note 2. – for a thinner barrier layer, a greater fraction of methanol barrier component (namely PVDF) is required to attain a comparable crossover

# Effect of Barrier Layer Thickness on Proton Conductivity
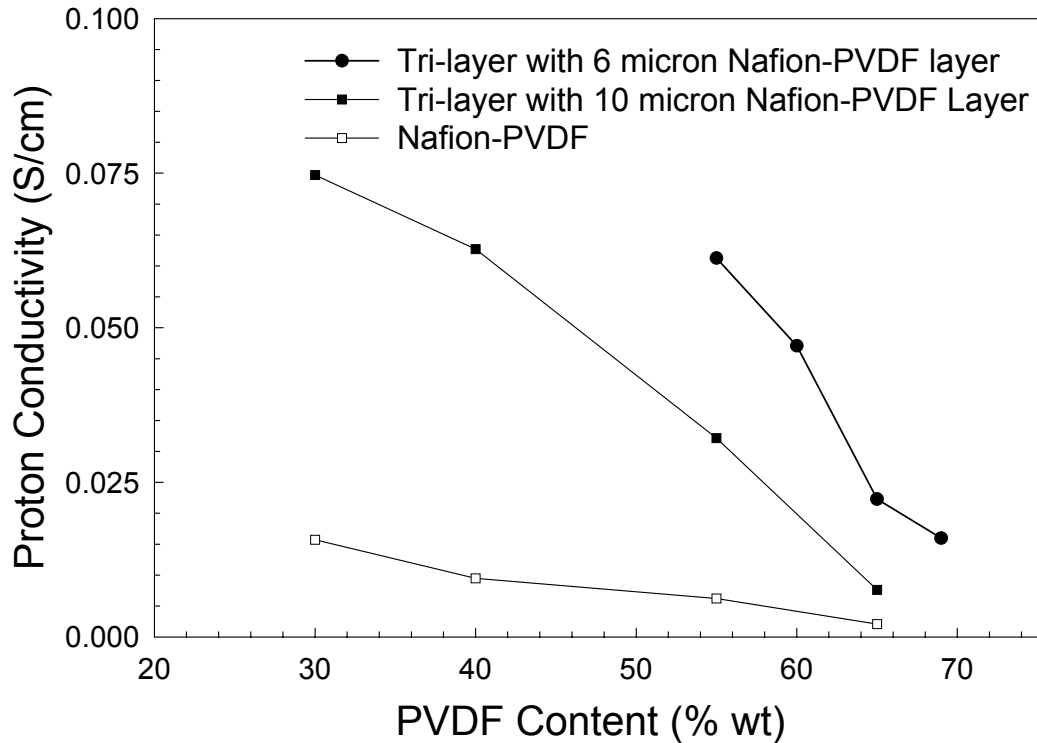
Note – thinner barrier layer – larger conductivity for a given PVDF content

Performance with Layered Membranes

Cell Voltage(V) vs Current density(mA/cm^2)
- Nafion112 (50micron)
- Tri-layer (50 micron)
- Nafion117 (175 micron)

Power density (mW/cm^2) vs Current density (mA/cm^2)

Performance and Power Density with 50 μm Nafion®112 and 50 μm Tri-Layer Membrane and 175 μm Nafion®117 at 60 ºC with 1M Methanol/Air under 1atm Pressure.
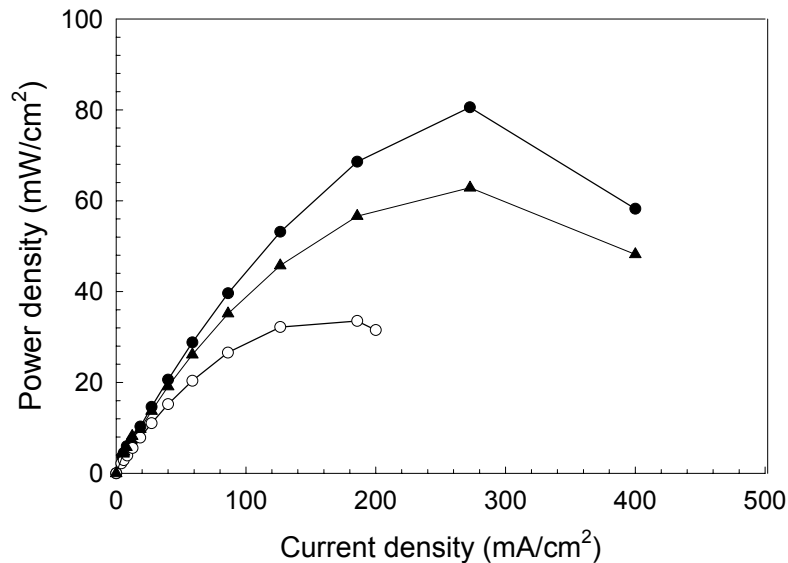
**The efficacy of the layered membrane approach is evident**

Other Techniques to Reduce Crossover

- Air/oxygen bleed – to oxidize the CO formed at the anode

- High oxidant flow rates:

    - enhances oxidant crossover – oxidizes CO

    - may reduce methanol crossover by inducing a suitable pressure profile

- Pressurized cathodes – pressure based disincentive for methanol crossover

DMFC Summary (Anode)

Hoogers
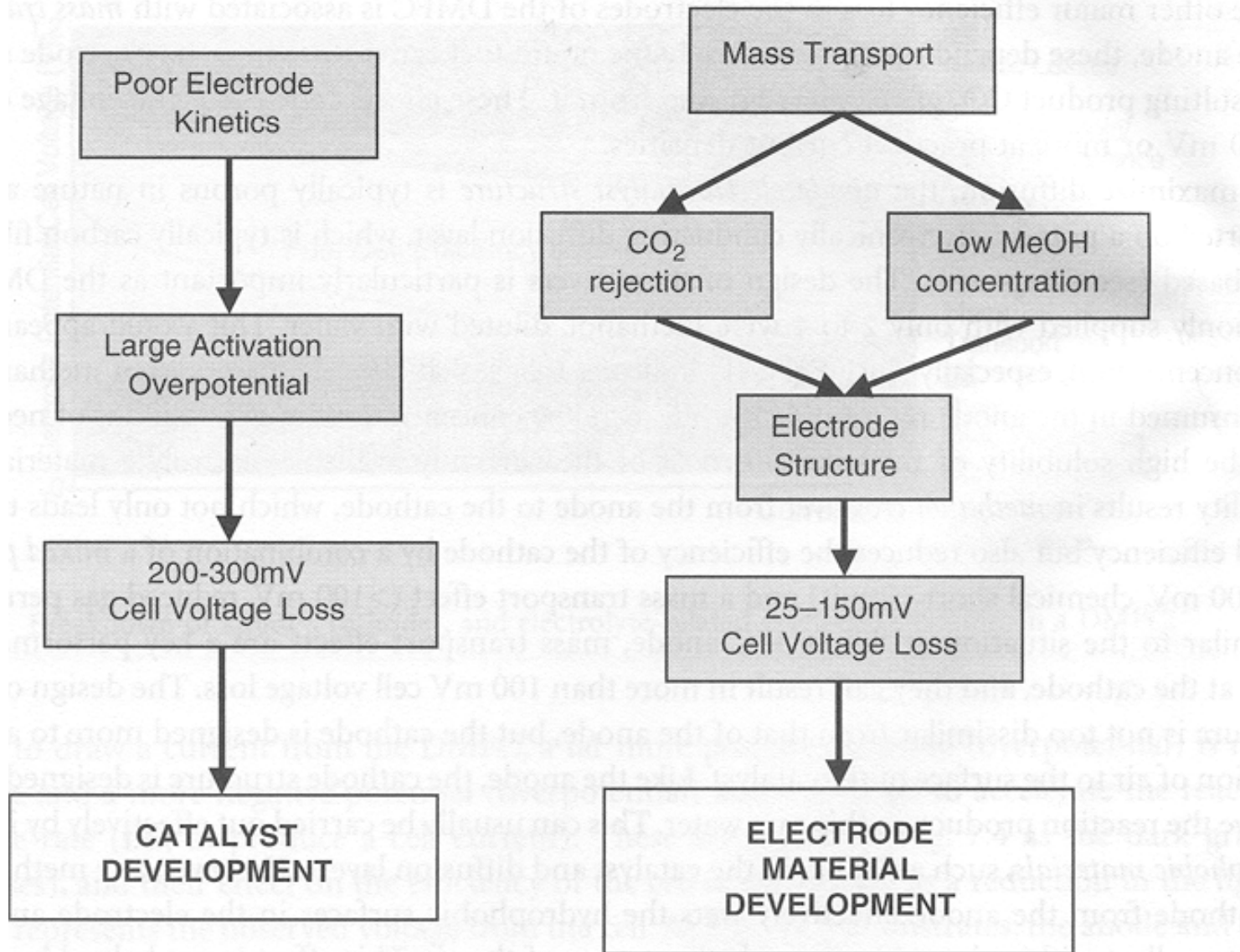
DMFC Summary (Cathode)
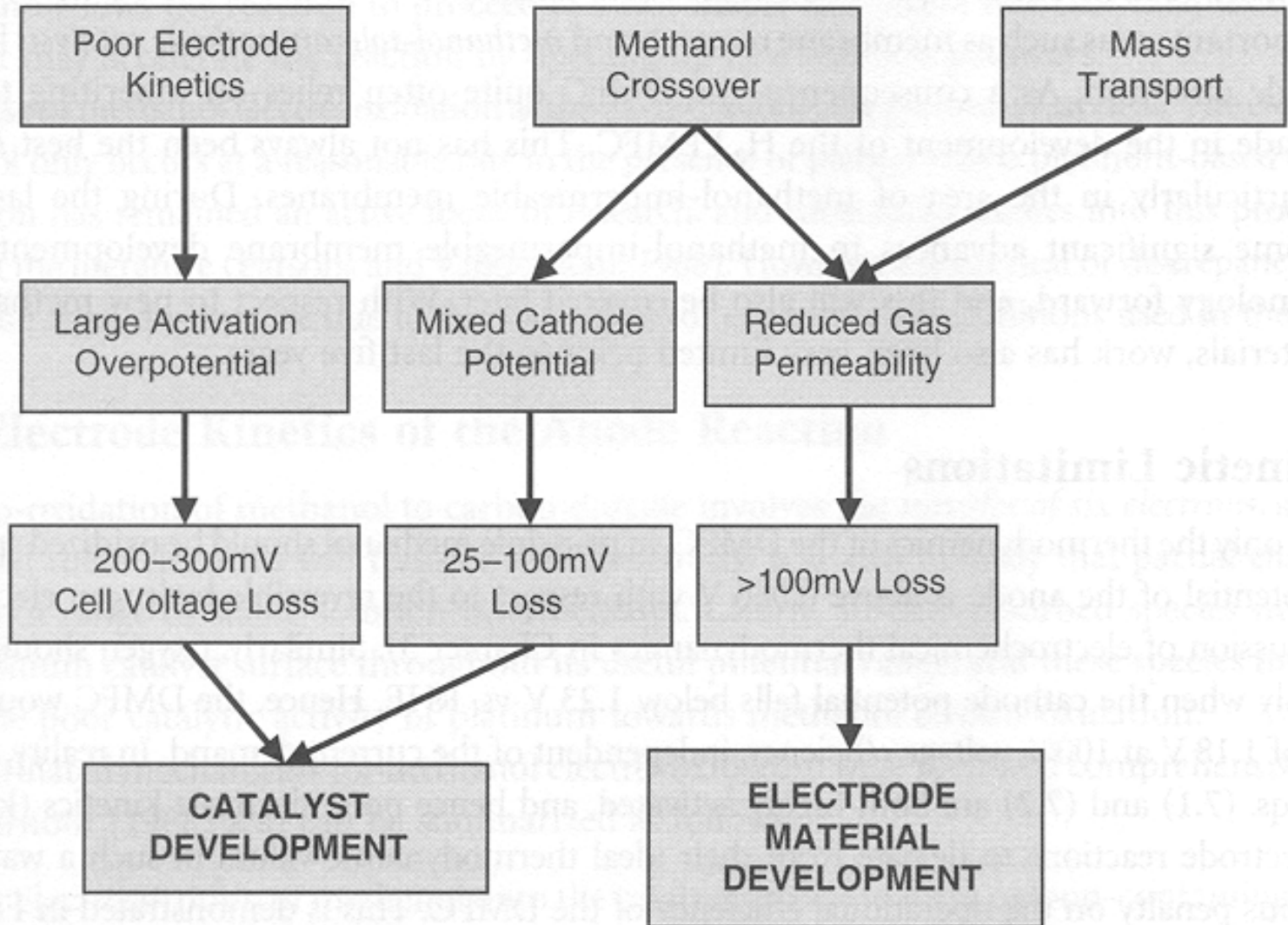
Recap of Challenges – Electrodes

- Operation of a fuel cell with Reformate (w / CO and CO_2) and on direct methanol have similar challenges on the electrode front:

  - better catalysts for efficient CO electro oxidation at low noble metal loadings

  - in-situ techniques for enhanced CO electrooxidation and reduced CO adsorption

  - better materials to facilitate high temperature operation (to permit lower CO adsorption)