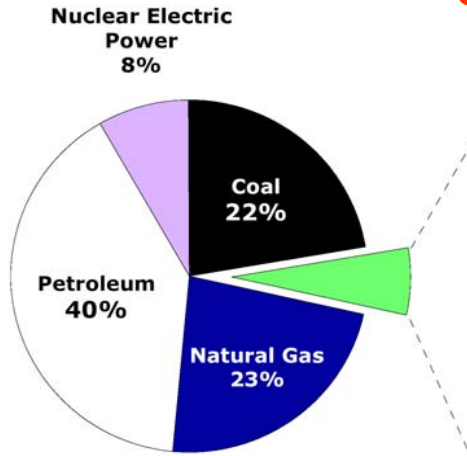


# Science and Technology of Fuel Cells

**Yang Shao-Horn**  
**Electrochemical Energy Laboratory**  
**Department of Mechanical Engineering**  
**MIT**

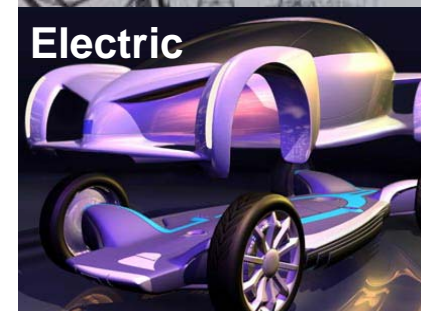
# Science and Technology For A Clean Energy Future

**Current Energy Supply (carbon)**

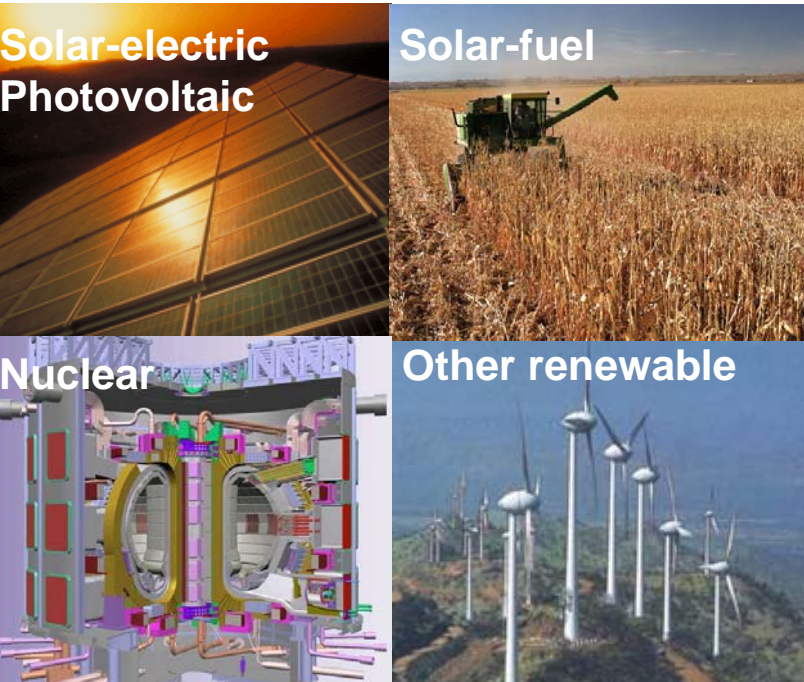


**CO<sub>2</sub> emission**  
Renewable Energy 6% →  
**unsustainable**

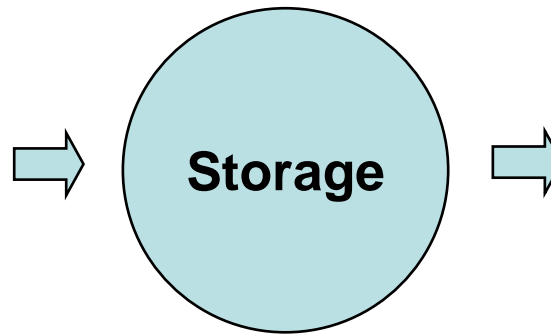
**Energy Demands**



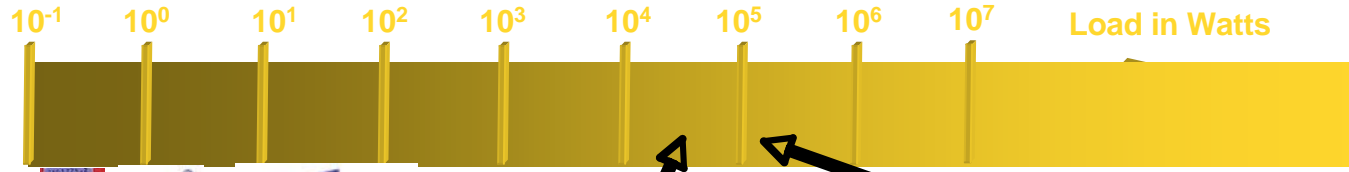
**Future Energy Supply (no net carbon)**



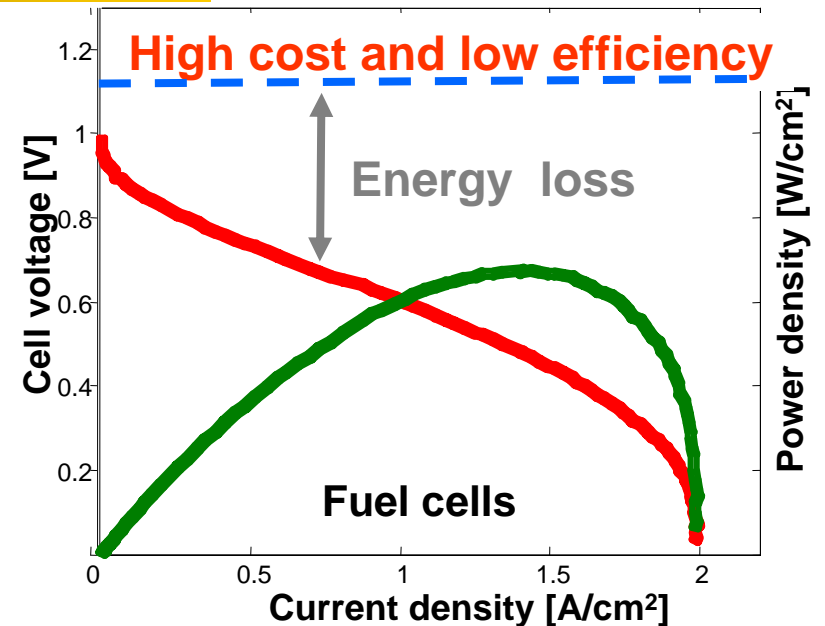
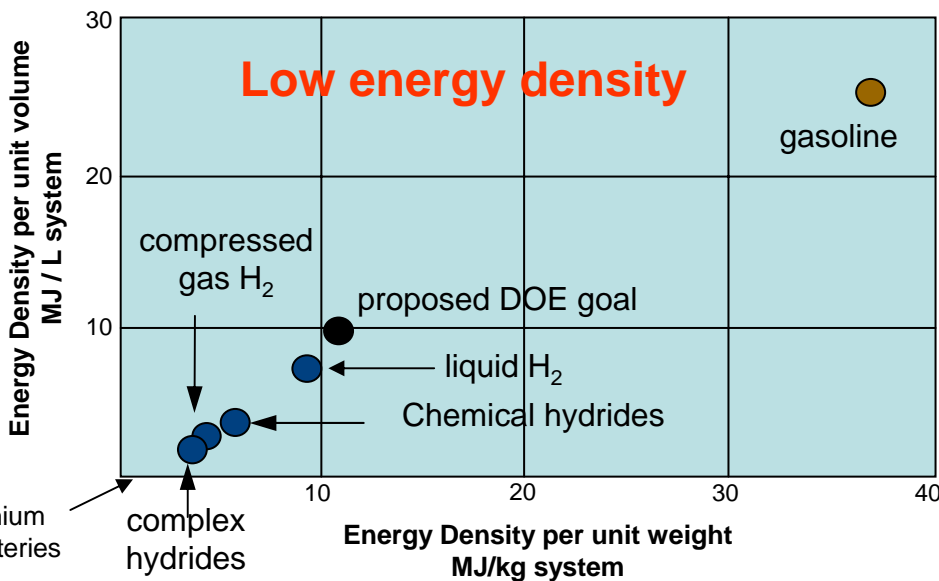
**Hybrid, efficient, clean, sustainable**



# Challenges in Energy Storage Technologies



**Energy Storage:**  
**Batteries**  
**Hydrogen + Fuel Cells**



# Ragone plot of power density versus energy density

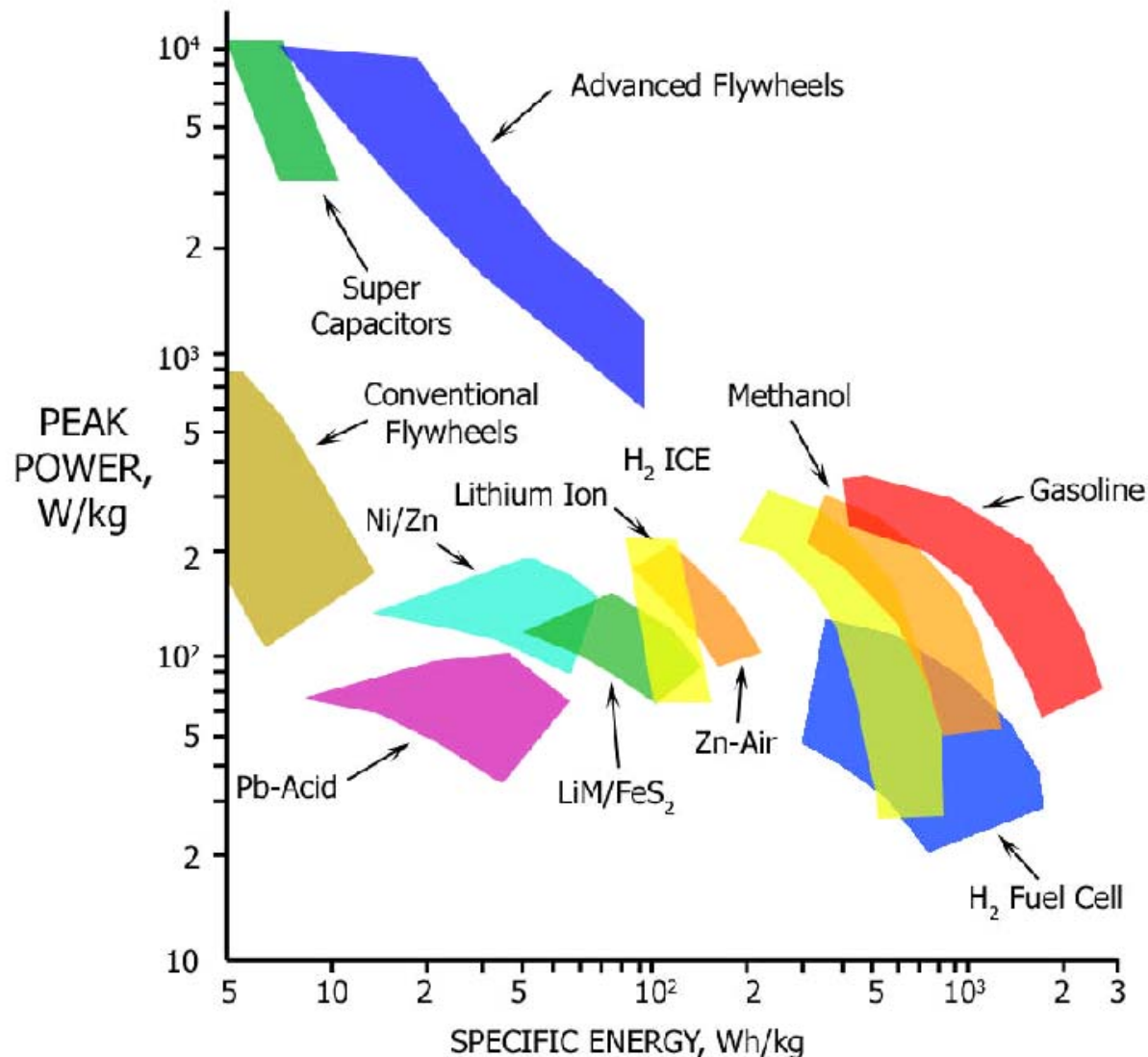
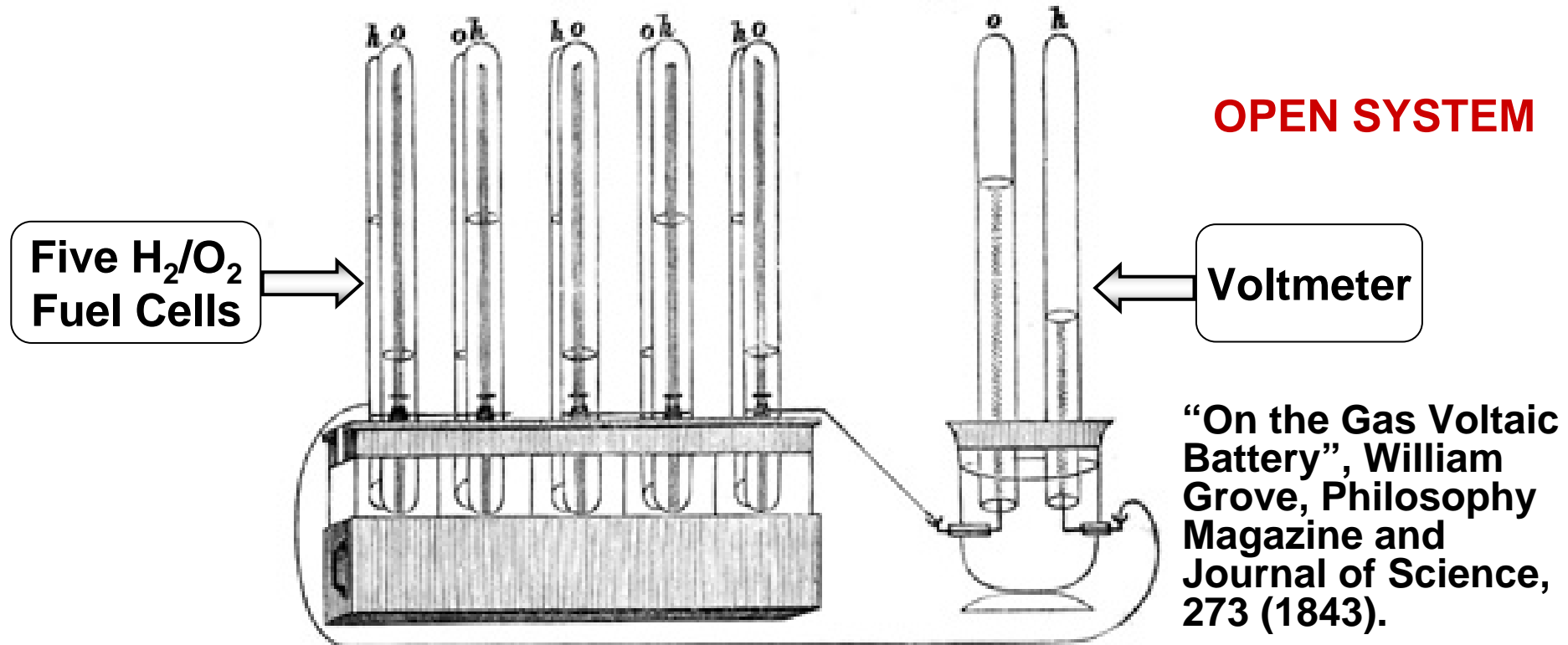


Figure 2 Lecture notes 10.391, 22.811 and ESD-166 from Professor Jeff Tester on sustainable energies – energy storage. Note that the specific power for lithium ion batteries is not updated as it should have values greater than 1kW/kg.

# What Are Fuel Cells – Energy Conversion?

- Fuel cells are steady-flow devices that accept fuel and oxidant and produce the reaction products and direct current electric power.



# Fuel Cell Types

- **Proton exchange membrane (PEM) fuel cells, 80°C**
  - Automotive applications (50kW)
- **Direct methanol fuel cells (<100°C)**
- **Alkaline fuel cells, 50 - 200°C**
  - Space applications (1kW+)
- **Phosphoric acid fuel cells, ~220°C**
  - Commercially available for premium power applications (50kW+)
- **Molten carbonate fuel cells, ~650°C**
  - Industrial and commercial cogeneration systems (100kW+)
- **Solid oxide fuel cells (SOFCs), 600 - 1000°C**
  - Auxiliary power units (25kW) and stationary power applications (100kW+)



# Current Applications of Fuel Cells

**GM Autonomy**



**Ballard Buses in Chicago**



**Stationary Power Units**



# Direct Methanol Fuel Cells for Portable Devices



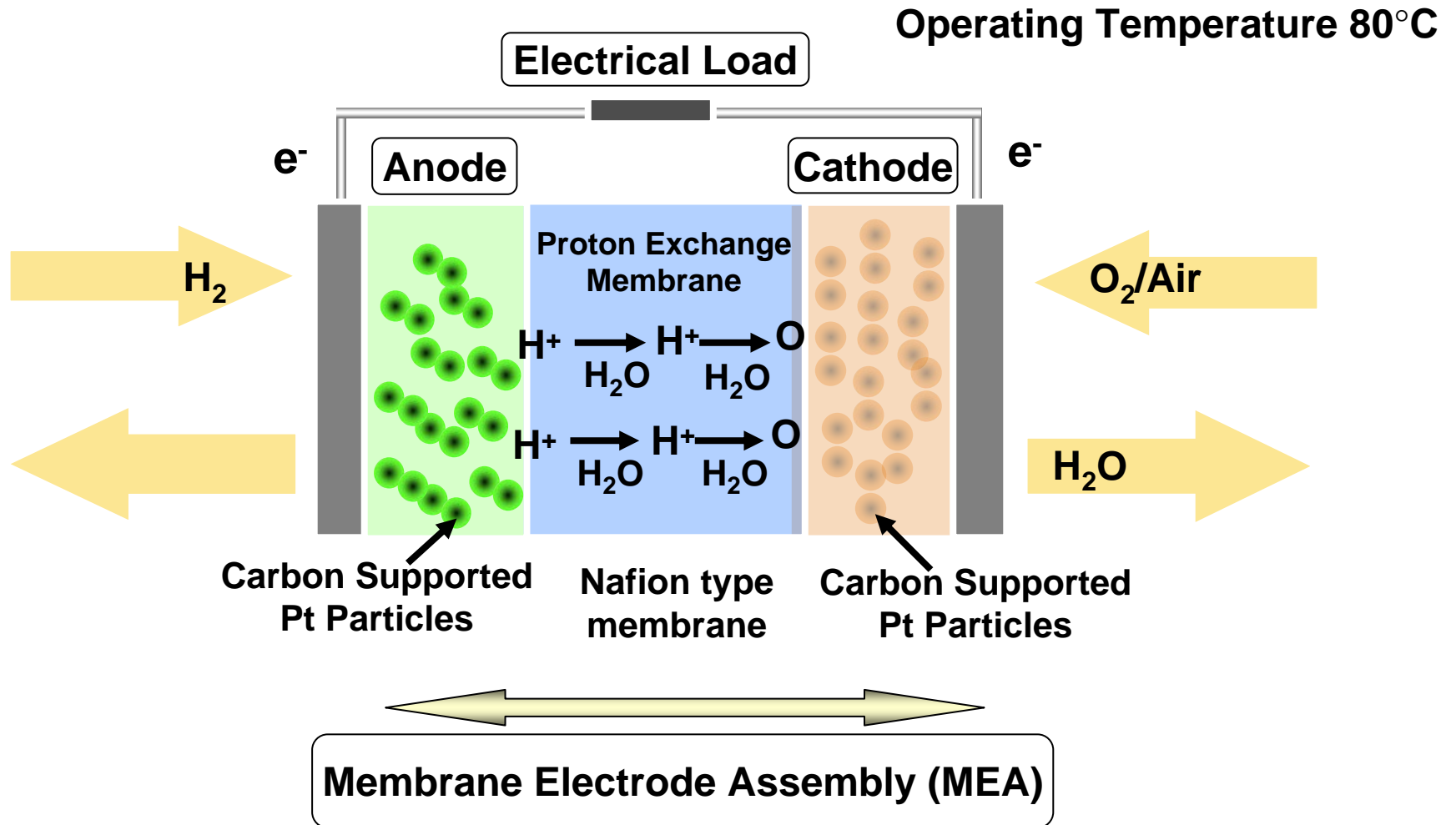
Toshiba- DMFC, 100 mW, 2cc Fuel Tank, 99.5% methanol



NEC- avg  
14W output,  
300 cc fuel,  
10%  
methanol,  
last ~5 hrs

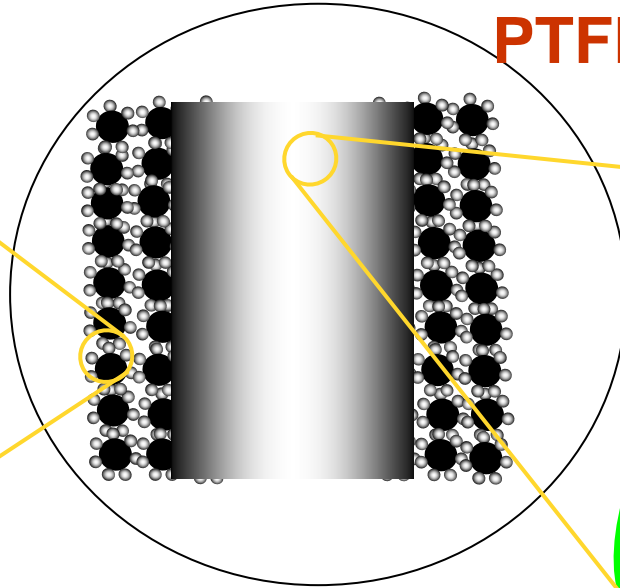
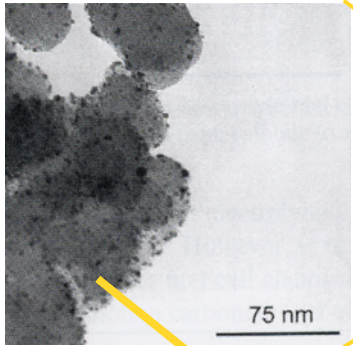


# Proton Exchange Membrane Fuel Cells

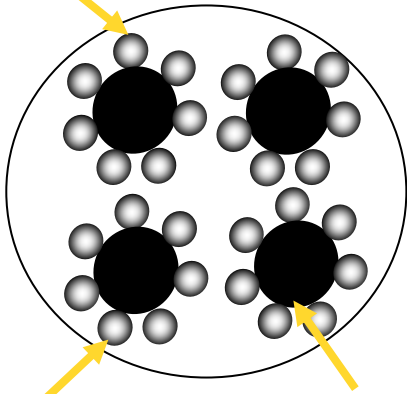
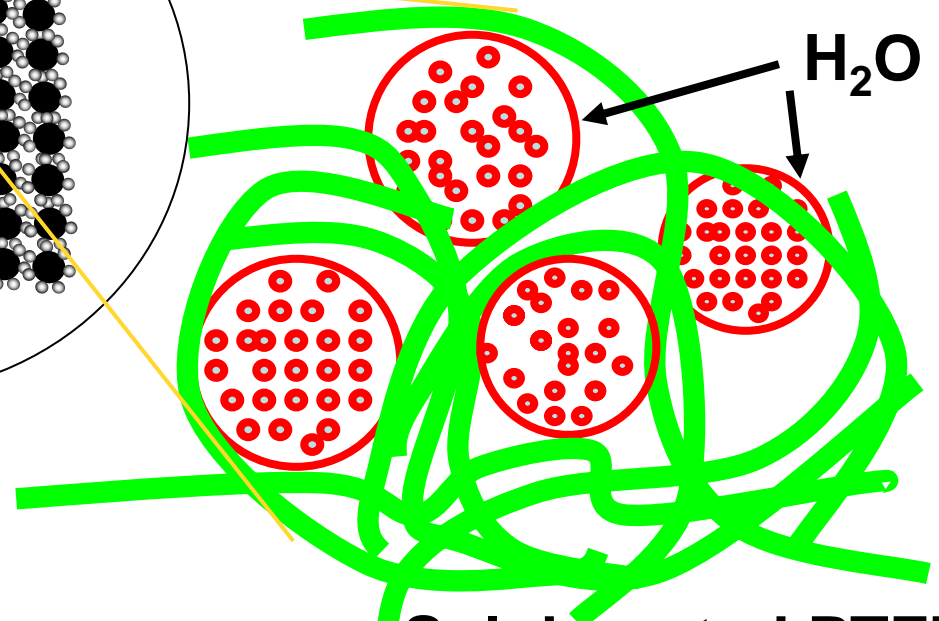


# Membrane Electrode Assembly (MEA)

Porous electrode structure



PTFE - polytetrafluoroethylene  
Nafion-type membrane



Sulphonated PTFE  
CLUSTERS 3 - 5 nm

Pt nanoparticles Carbon particles

# Proton Exchange Membrane (PEM) Fuel Cells

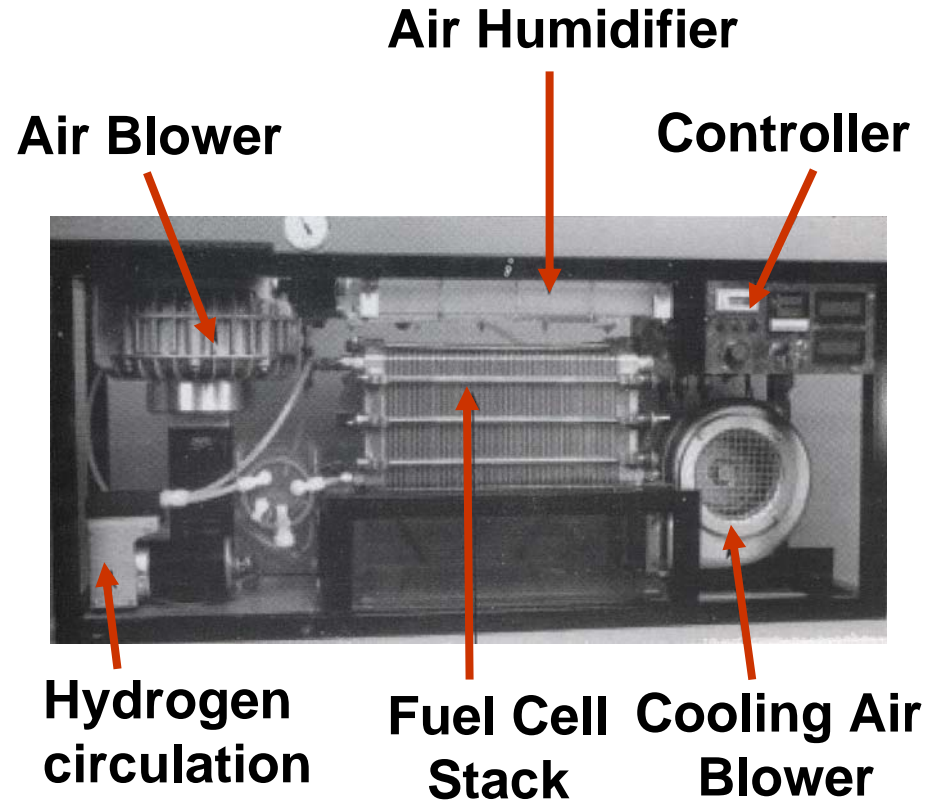
Fuel Cell Stack



Connecting Cells in Series

'Fuel Cell Technology Handbook', Edited by Gregor Hoogers, CRC press (2003).

'Fuel Cell System Explained', James Larminie and Andrew Dicks, John Wiley & Sons (2000).

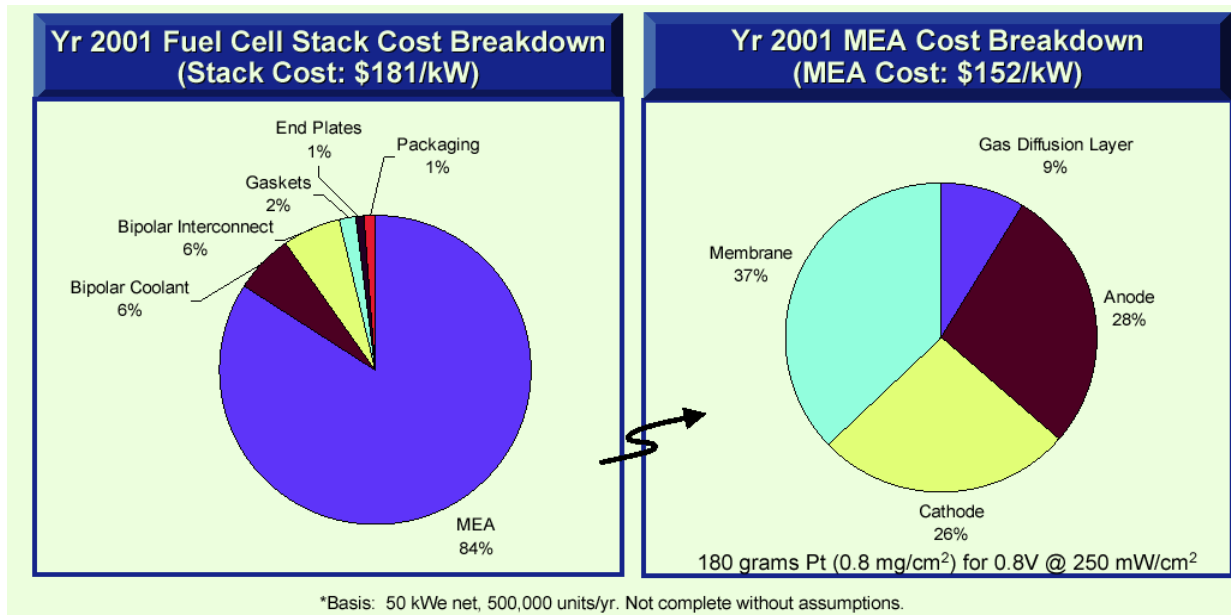


2kW unit Paul Scherrer Institute

# Challenges in Fuel Cell Developments

- **High Cost**
  - Current - \$275/kW and target - \$30- \$50/kW for transportation
- **Poor Durability**
  - Current - 1500 hours and target - 5000 hours for transportation
  - Current – 10,000 hours and target - 40,000 hours for stationary

The membrane electrode assembly (MEA) in PEM fuel cells consists of two catalyst layers and an ion-conducting media, which is the most expensive component.

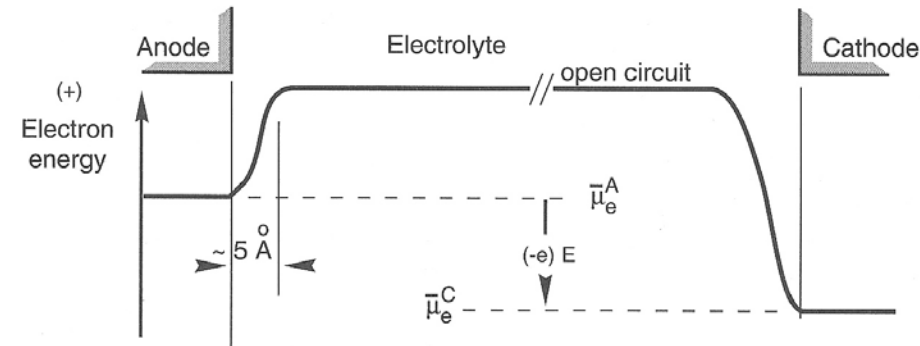
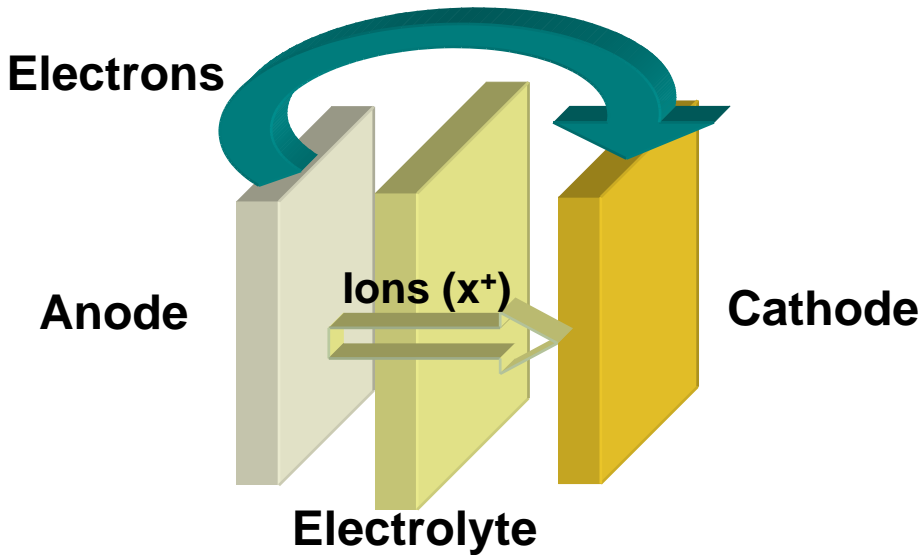


**Catalyst layers have high Pt loading:  
0.2mg/cm<sup>2</sup>**

**\$2000-\$4000  
per fuel cell vehicle**

# Thermodynamics of Electrochemical Systems

- Electrochemical energy (maximum work) is obtained by moving electrons through a difference in electric potential.



Direct Energy Conversion fundamentals of electric power production, Reiner Decher, Oxford University Press (1997)

$$\Delta G = Q - W + P\Delta V - T\Delta S$$

$$\Delta G = -W$$

**Electrochemical cell voltage**

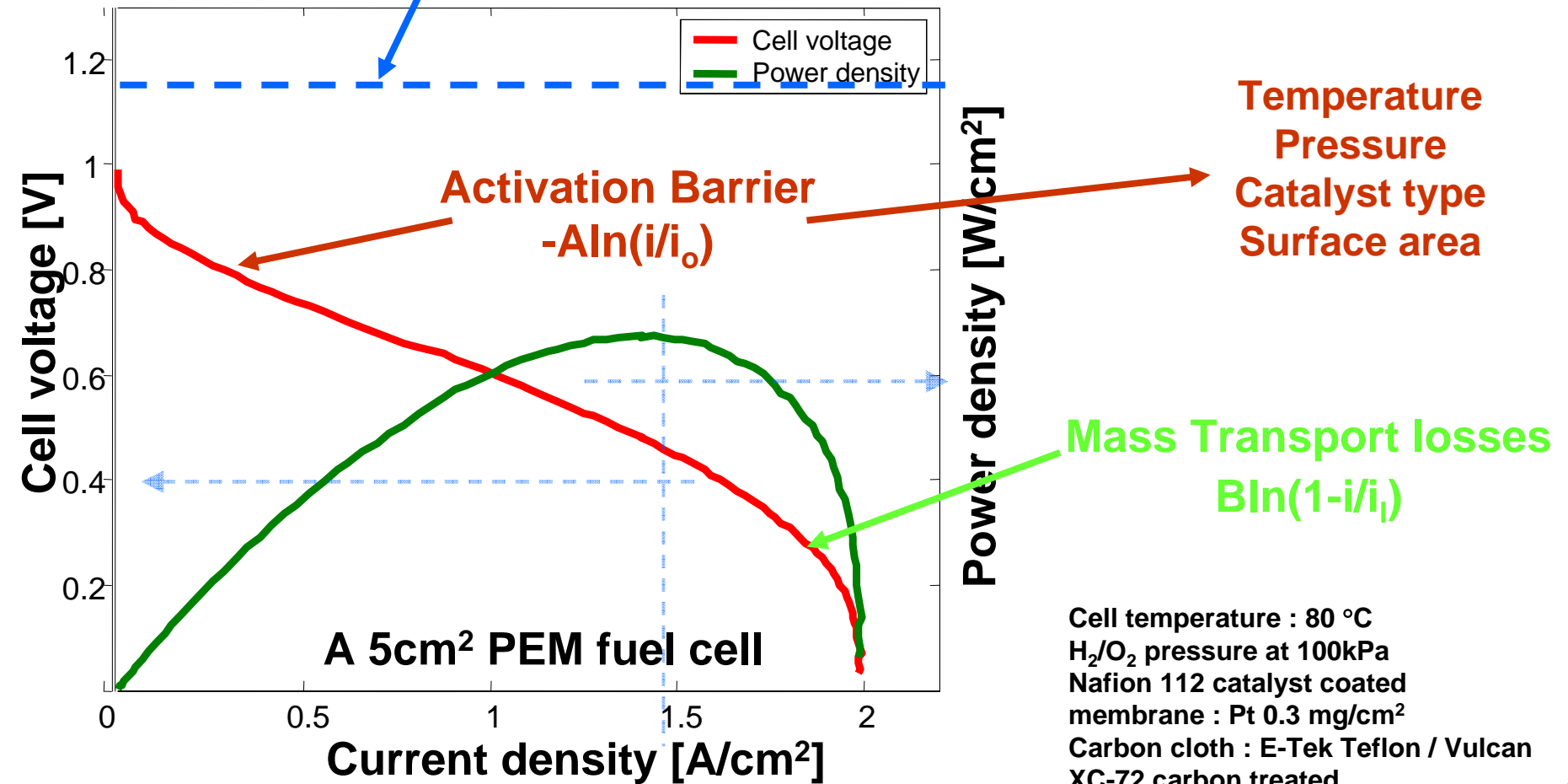
$$E = -\Delta G/nF$$

$$E_{\text{theoretical}} = E^{\circ} + \frac{RT}{nF} \ln \left( \frac{a_{\text{reactants}}}{a_{\text{products}}} \right)$$



# PEM Fuel Cell Performance

$$E = E^{\circ} - i \cdot R - A \ln(i/i_0) + B \ln(1 - i/i_l)$$



# Electrochemical Energy Conversion Efficiencies

- Maximum thermal efficiency - Thermodynamics

$$\eta_{ideal} = \frac{-W}{\Delta H} = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H}$$

H<sub>2</sub>/O<sub>2</sub> fuel cells (25°C  
and 1atm) 83%

- Second Law efficiency (Voltage efficiency)

$$\eta = \frac{E_{measured}}{E^{\circ}}$$

**Electrode Kinetics**

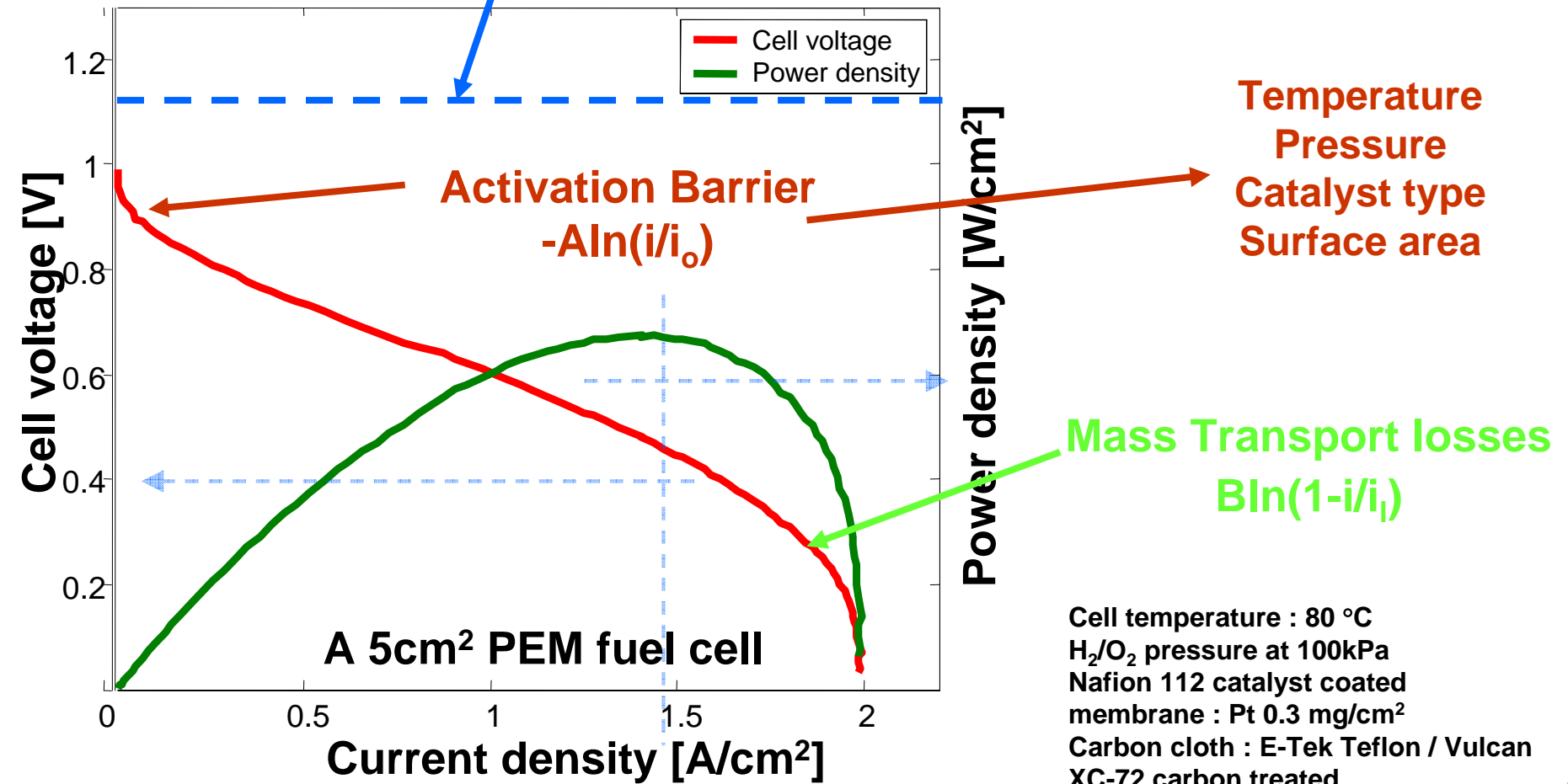


# Overpotentials - Fuel Cell Voltage Losses

- **Activation losses – the most significant**
  - Slow reaction rates on the electrode surface
- **Ohmic losses**
  - Resistance to electron flow
  - Resistance to Ion flow
- **Mass transport losses**
  - Reduction in the reactant concentration
  - Accumulation of products

# Voltage Loss Contributions in Fuel Cells

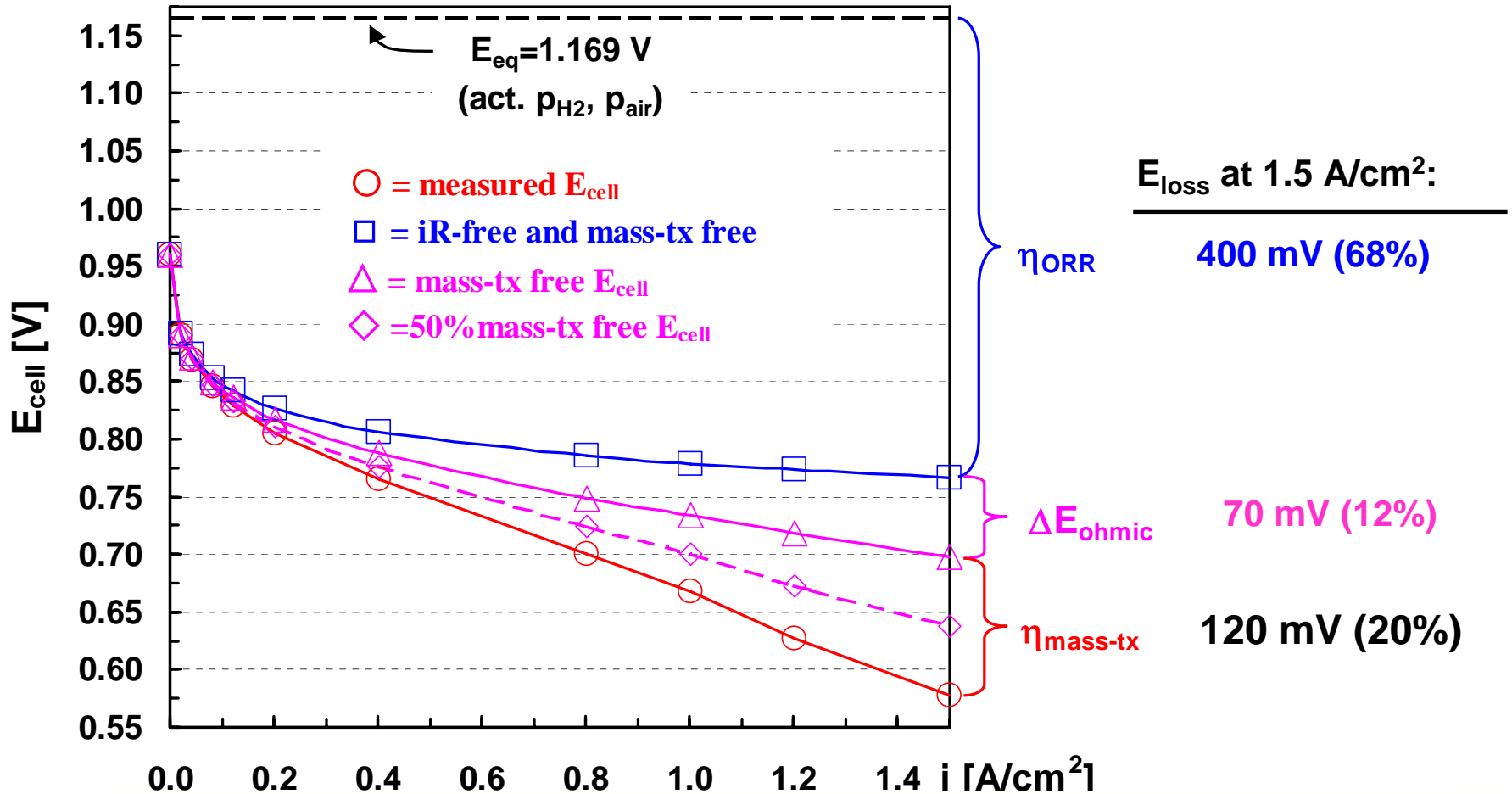
$$E = E^{\circ} - i \cdot R - A \ln(i/i_0) + B \ln(1 - i/i_l)$$





# Voltage Loss Contributions in PEM Fuel Cells - H<sub>2</sub>/Air

(H<sub>2</sub>/air (s=2/2) at 150kPa, 80C, and 100%RH - 0.4mg<sub>Pt-cathode</sub>/cm<sup>2</sup>)



↪ major losses due to poor cathode kinetics (ORR)

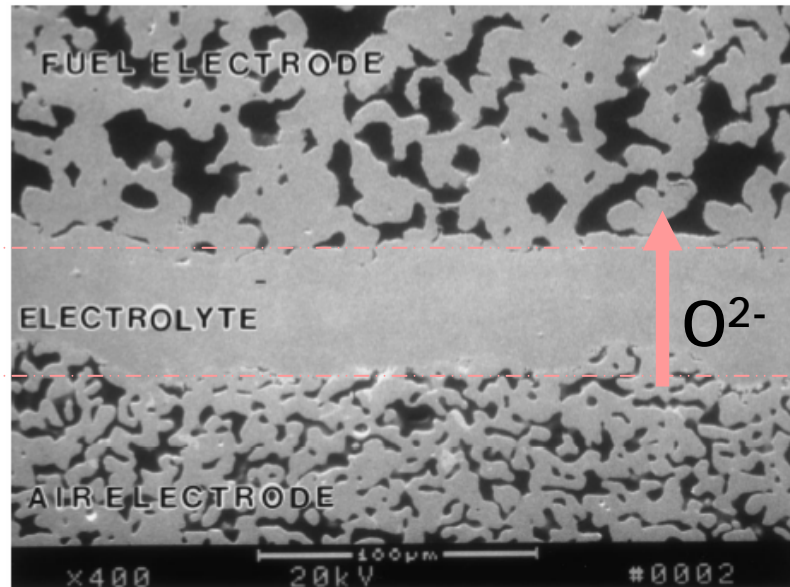
↪ minor losses by ohmic resistance (50%  $R_{\text{H}^+, \text{membrane}}$ , 50%  $R_{\text{contact}}$ )

↪ significant voltage/power-density via FF/DM optimization (mass-tx)

# Solid Oxide Fuel Cells

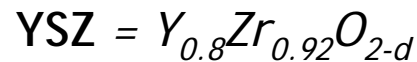
- All-ceramic fuel cells with high operating temperatures (600-1000°C)

Anode (Ni/YSZ)



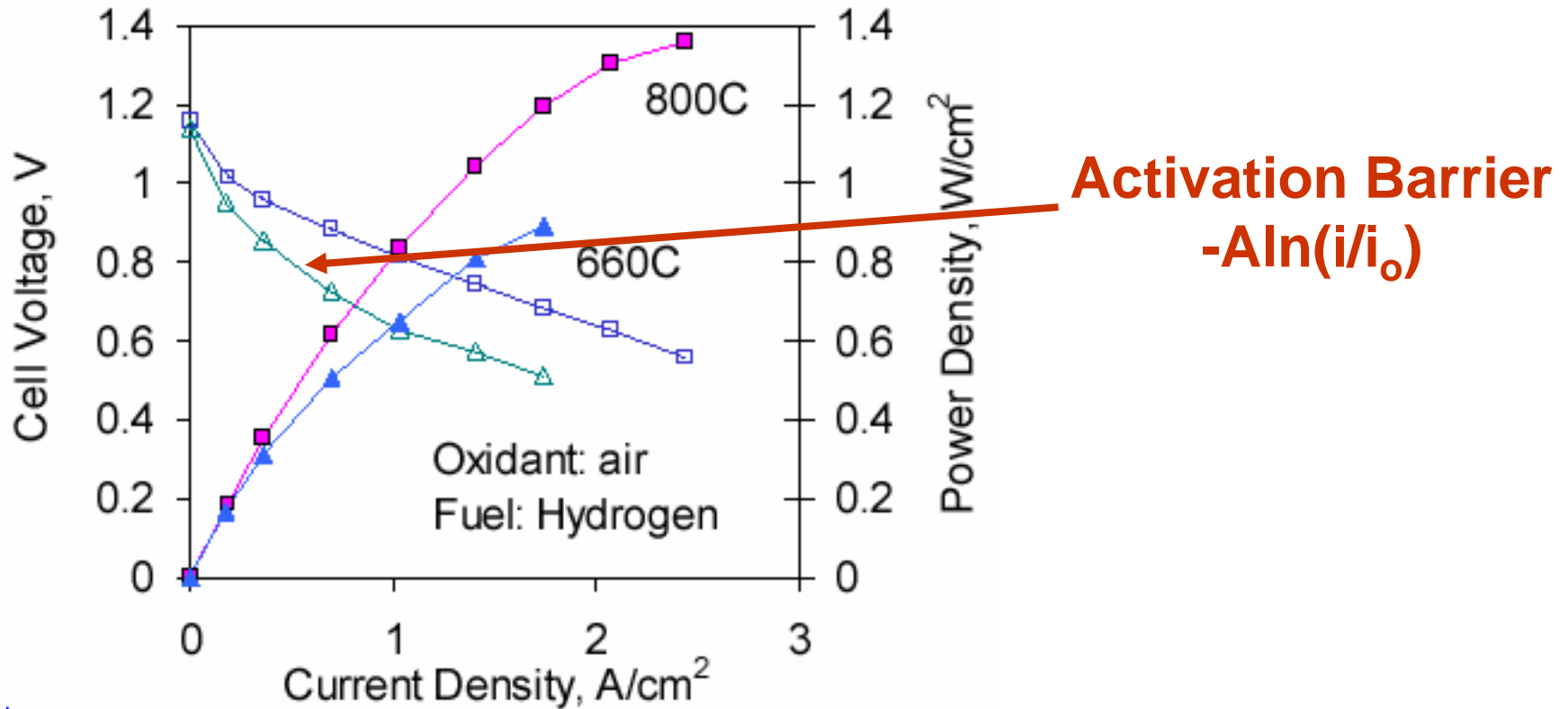
$$E^\circ = \sim 1.0\text{V}$$

at 800°C



Singhal, S. C., Solid State Ionics 135(1-4): 305-313 (2000)

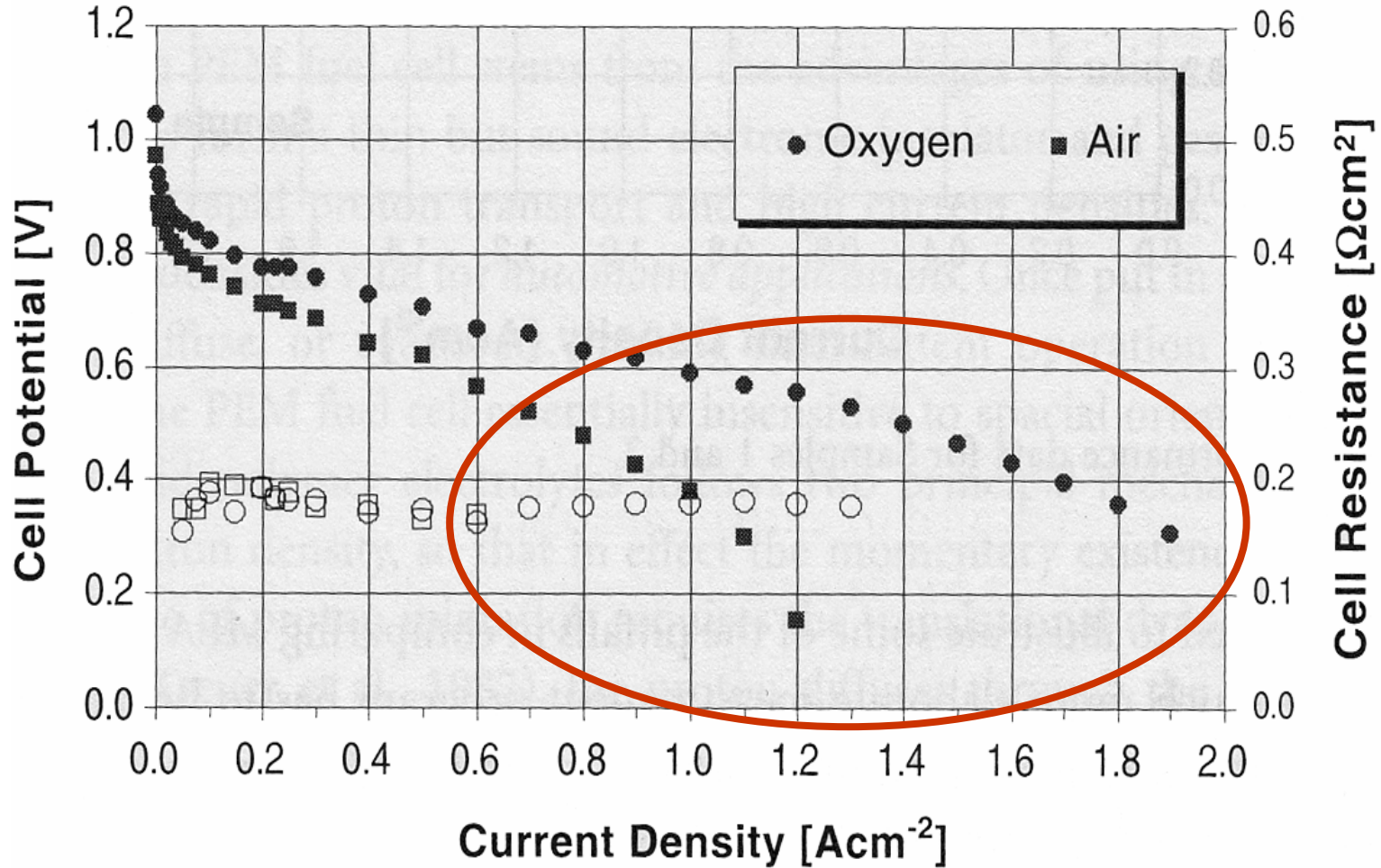
# SOFC - LSM - Oxygen Reduction Electrode



Large voltage losses in the LSM/YSZ cathode at temperatures lower than 800°C.

# H<sub>2</sub>-O<sub>2</sub> and H<sub>2</sub>-Air Fuel Cells

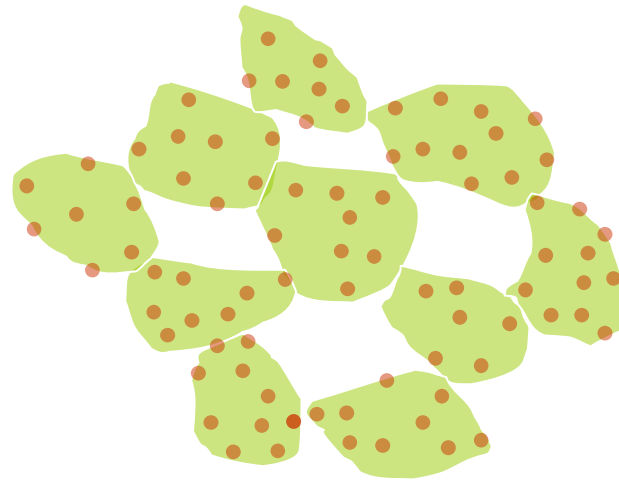
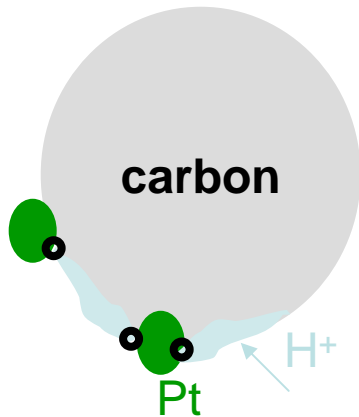
## Sample 1 - Air vs. Oxygen



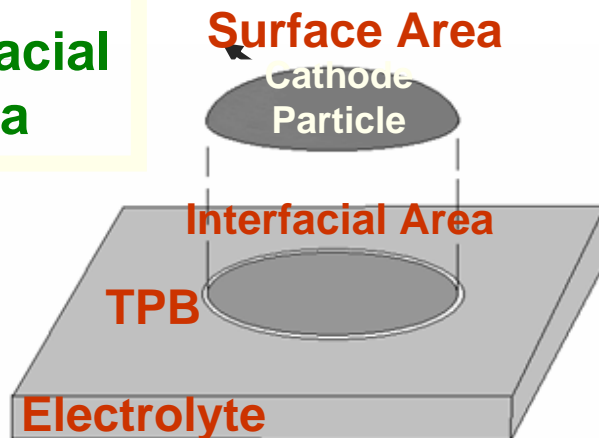
$$\eta(mt)_{H_2-O_2} < \eta(mt)_{H_2-O_{air}}$$

# Fuel Cell Electrode Architecture

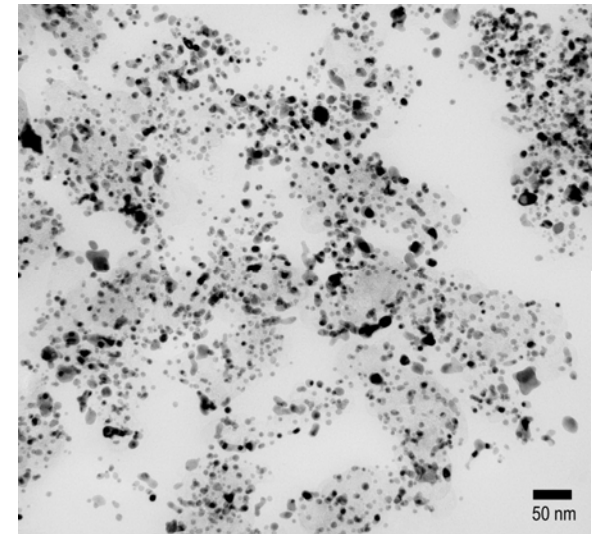
## Triple phase boundaries (TPB)



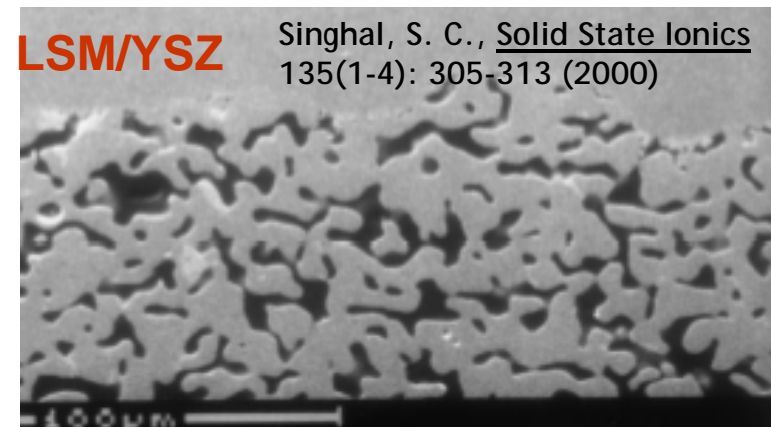
**Electrocatalysis**  
**Surface/Interfacial**  
**phenomena**



## PEMFCs



## SOFCs





# General Requirements for Fuel Cell Electrodes

- High TPB length per electrode surface and volume (**Activation**)
  - Electronic and Ionic conductivity (**Ohmic**)
- 3D nanopores for transport of gaseous molecules (**Transport**)
  - Chemical and mechanical stability

**Cost**

Electrode - 0.2 mg/cm<sup>2</sup> of Pt  
projected \$275/kW  
target \$30/kW

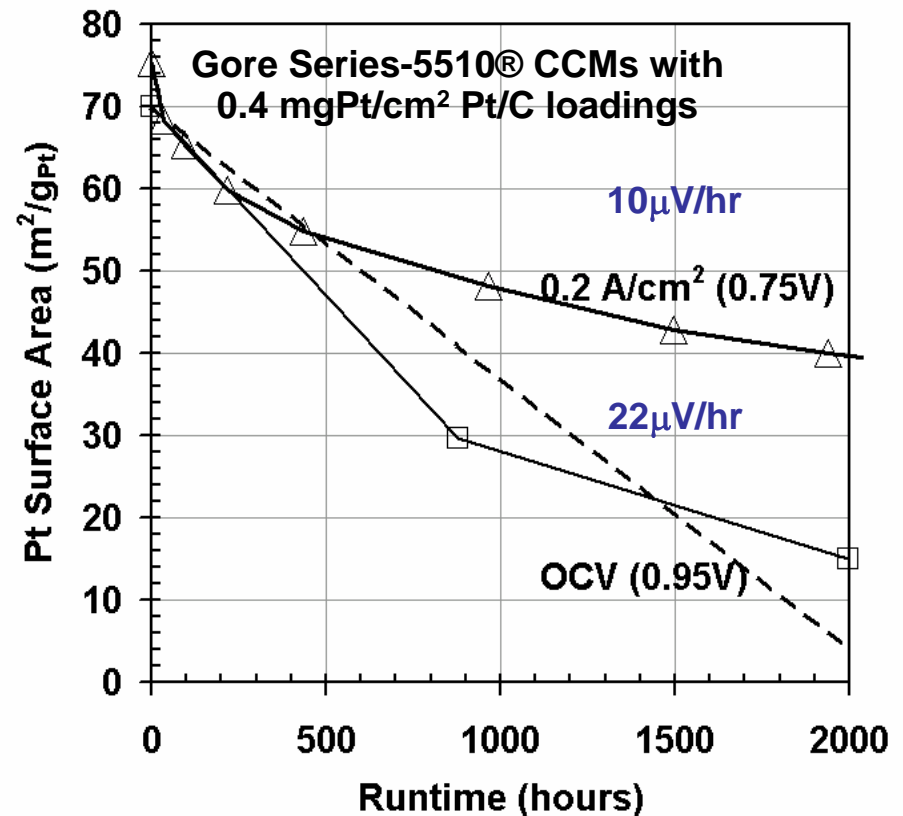
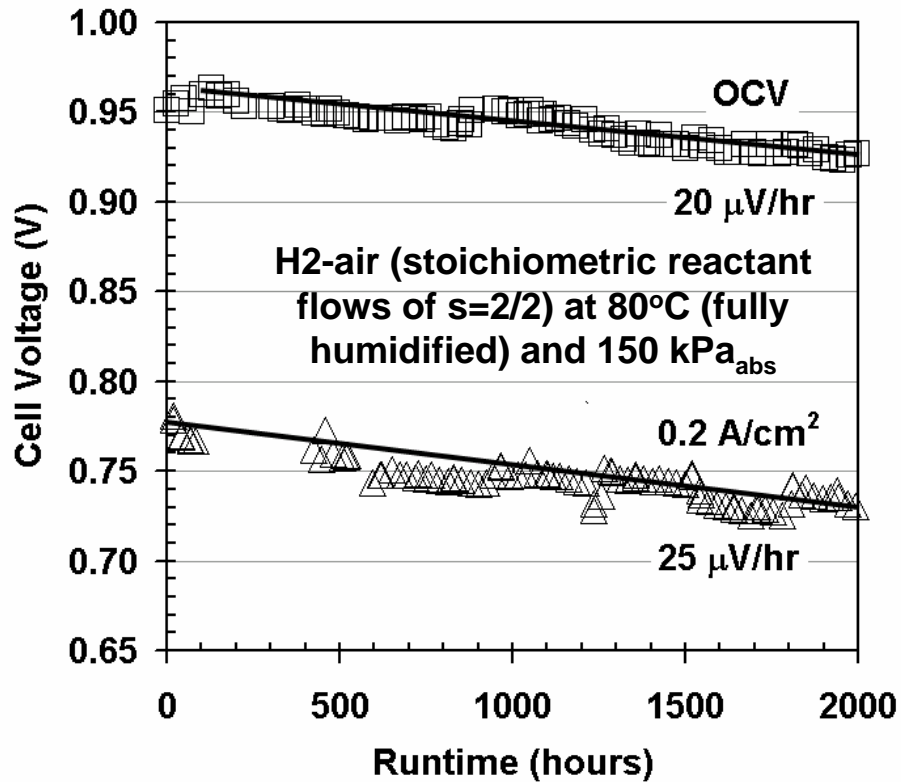
**Power**

**Durability**

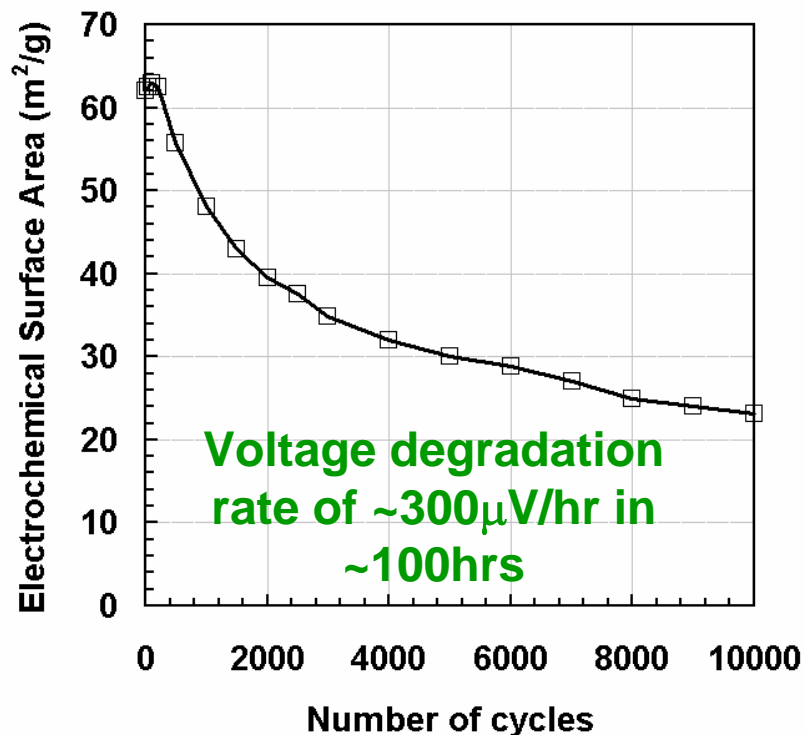
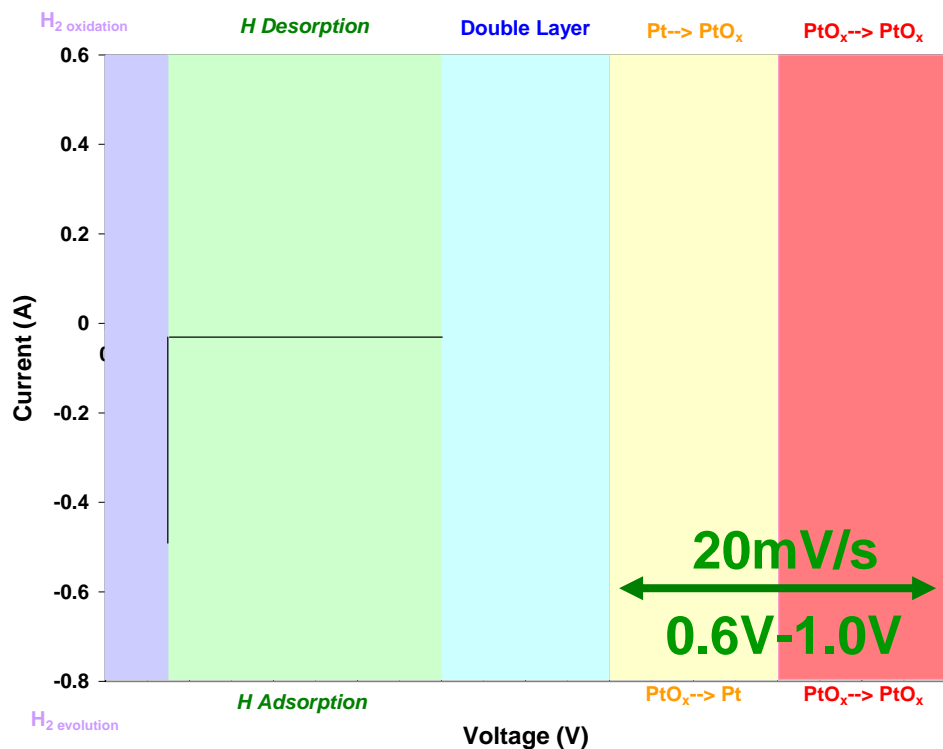
Current - 1500 hours  
target - 5000 hours for  
transportation

**Electrocatalysis**  
**Materials Degradation**  
**New Electrode Architecture**  
**Diagnostic Tools and Modeling**

# Steady-State PEM Fuel Cell Operation – Pt Surface Loss



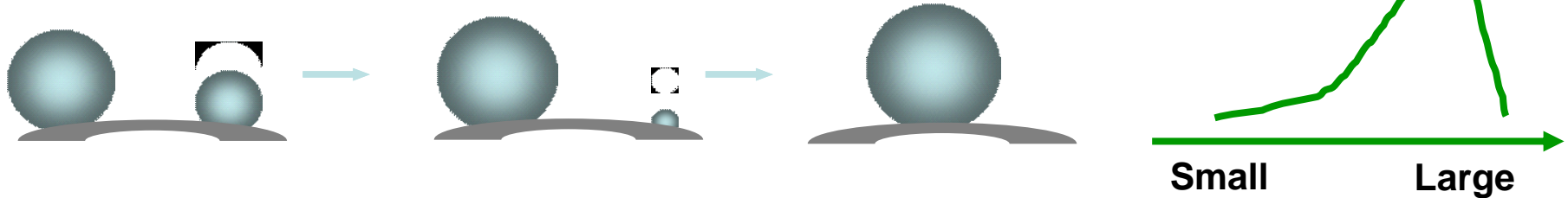
# Electrochemically Active Surface Area Loss in the Cathode Upon Potential Cycling



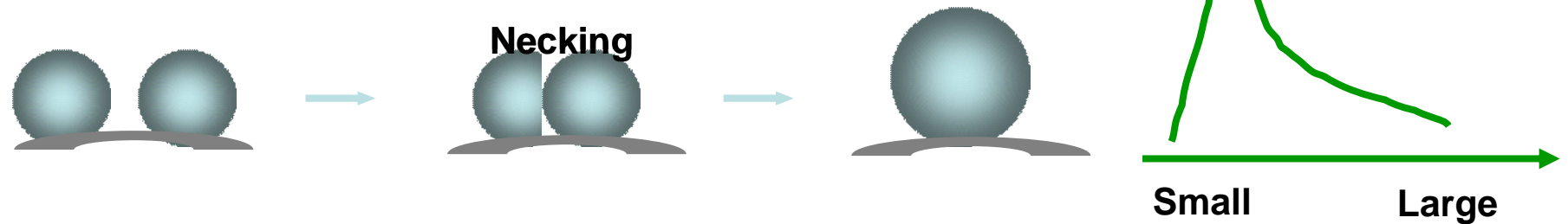
**50cm<sup>2</sup> fully humidified H<sub>2</sub>/N<sub>2</sub> fuel cell  
at 80°C and ambient pressure  
0.4mg/cm<sup>2</sup> and 46% Pt/Vulcan**

# Pt Crystal Size Distributions $\Leftrightarrow$ Pt coarsening mechanisms

## Ostwald Ripening



## Coalescence of Pt Crystals/Particles



Pt crystal size distributions obtained from X-ray powder diffraction data of cycled MEA cathode cannot be used to deduce Pt coarsening mechanism

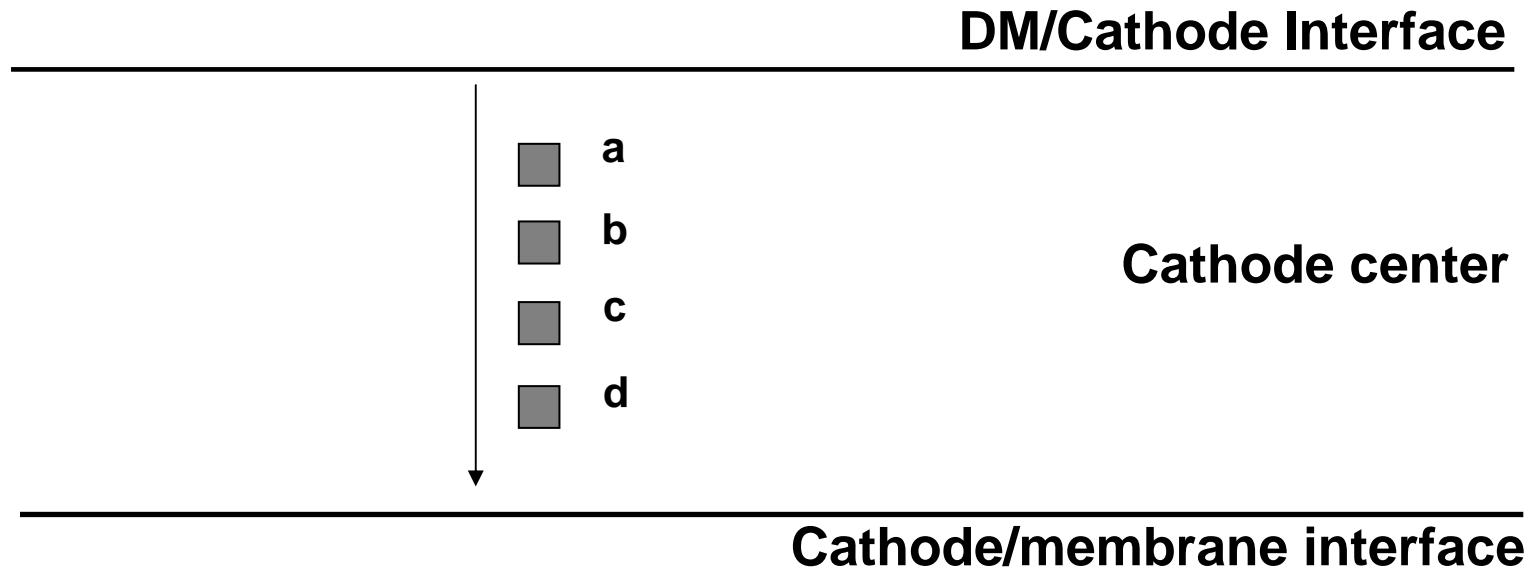
C. C. Granqvist & R. A. Buhrman, *Journal of Catalysis*, **42**, 477-479 (1976).

I. M. Lifshitz & V. V. Slyozov, *J. Phys. Chem. Solids*, **19**, 35 (1961).

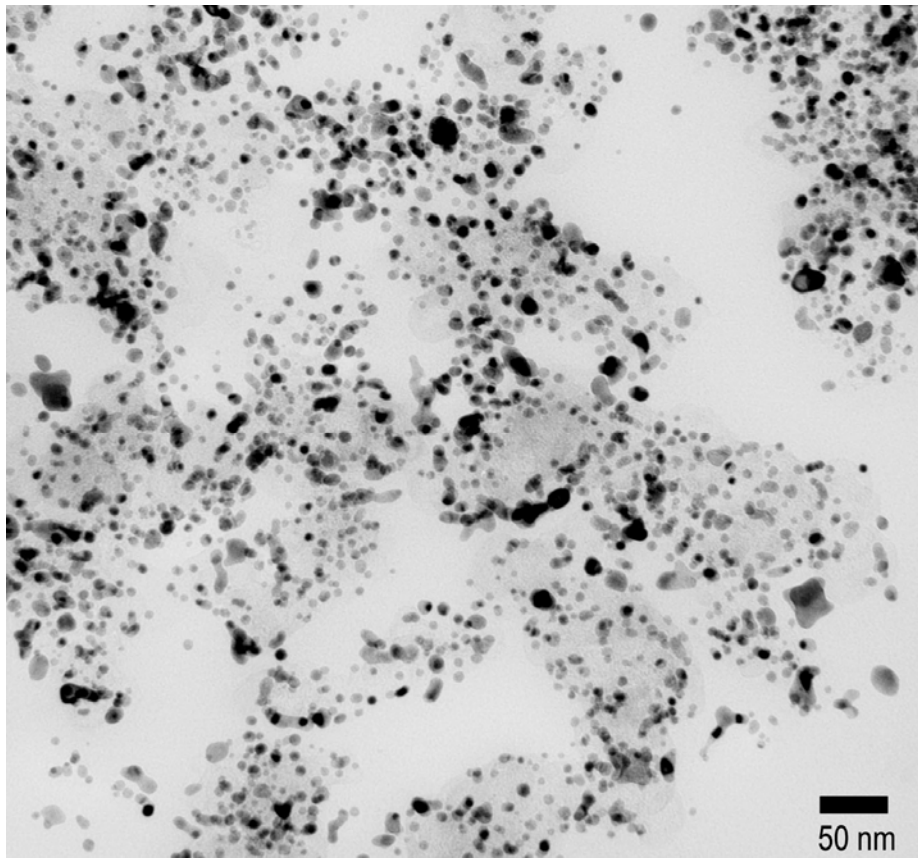
C. Wagner, *Z. Elektrochem.*, **65**, 581 (1961).

P. W. Voorhees, *Journal of Statistical Physics*, **38**, 231-252 (1985)

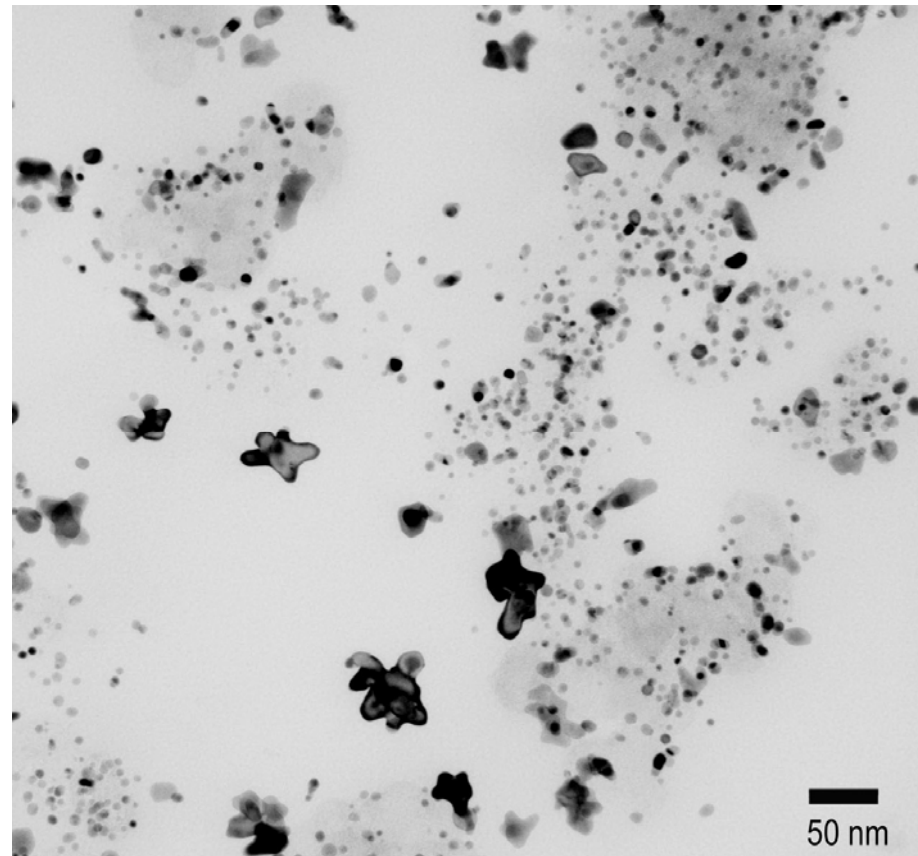
# Cross-Sectional TEM Analysis of MEAs



# TEM Images of Cycled MEA Cathode Cross-Sections: Locations a and b

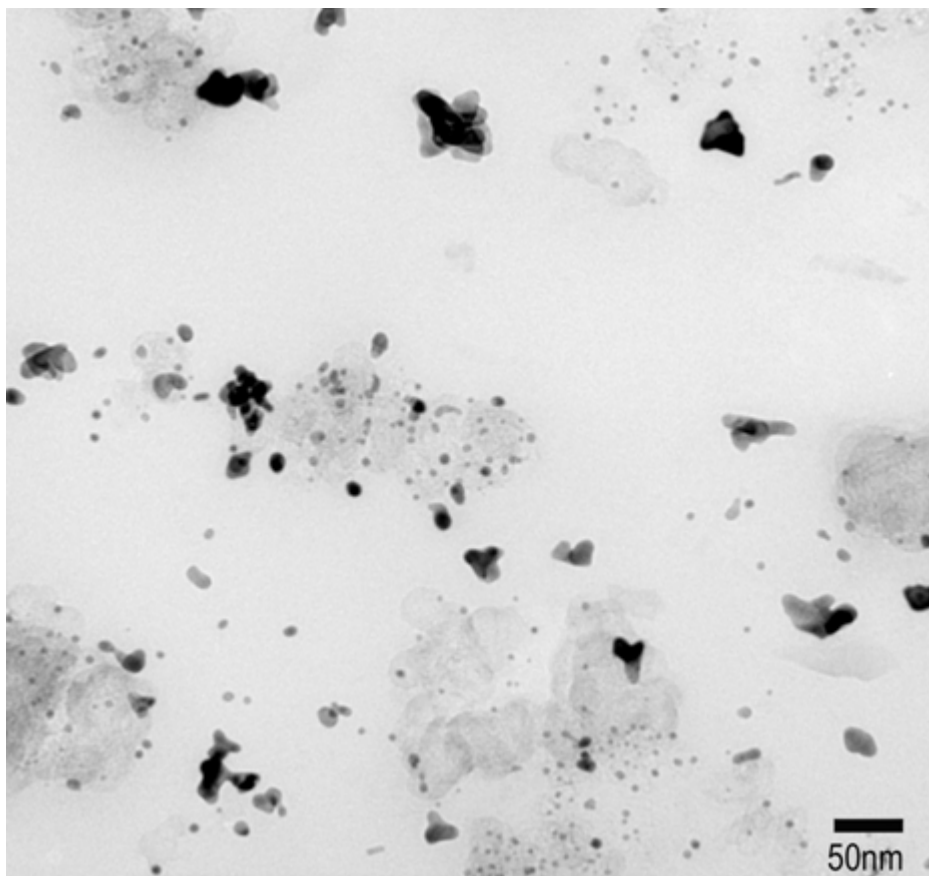


1micron from DM

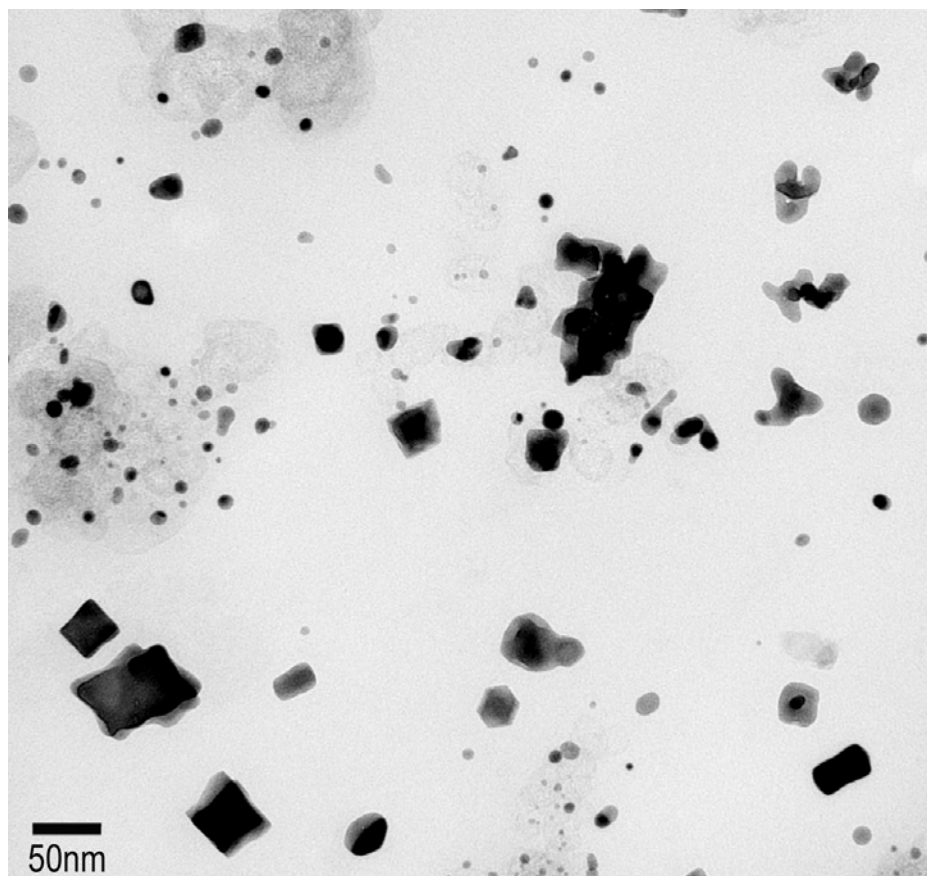


4micron from DM

# TEM Images of Cycled MEA Cathode Cross-Section: Locations c and d



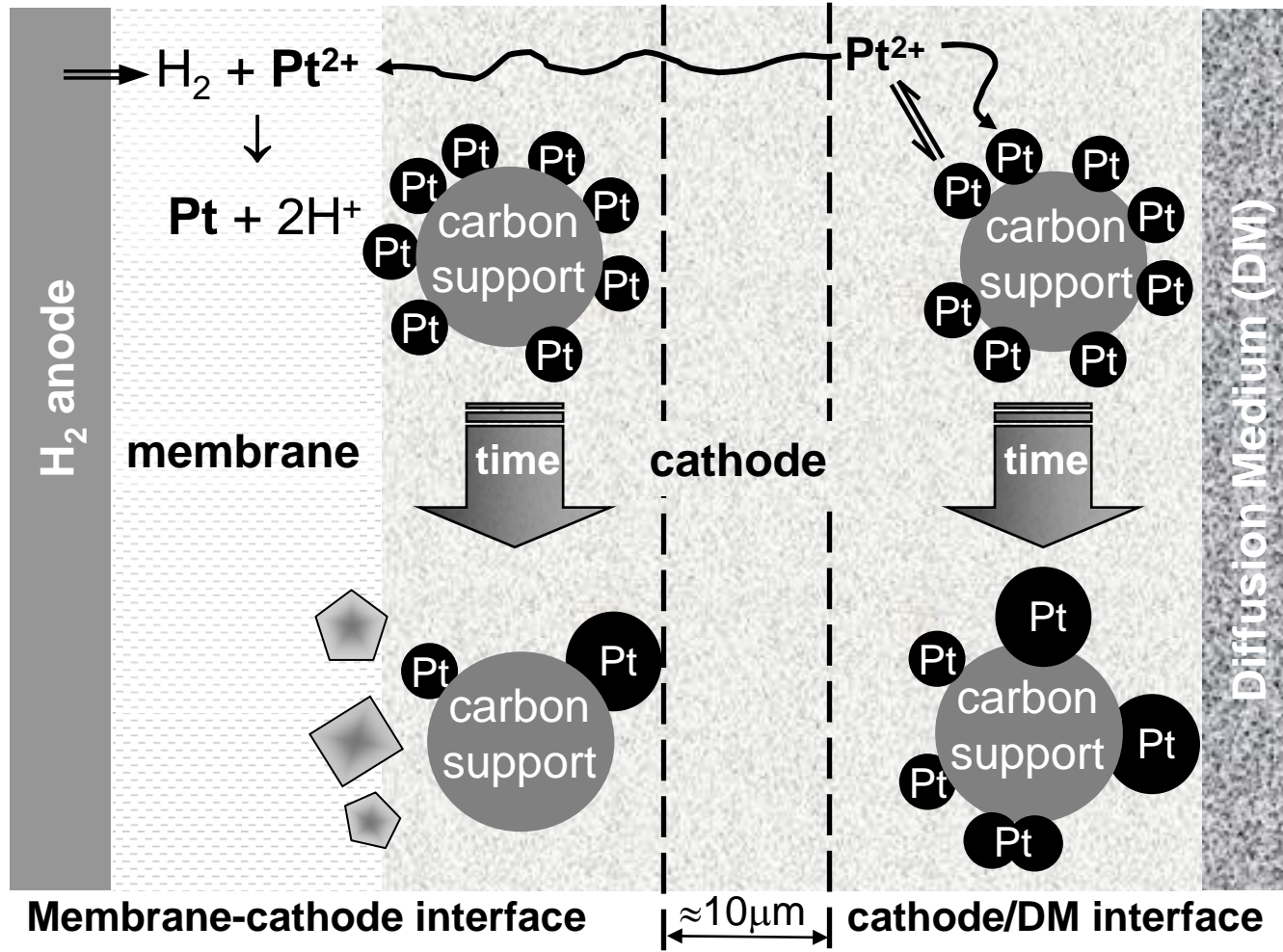
7micron from DM



10micron from DM



# Proposed Pt Catalyst Coarsening Mechanism



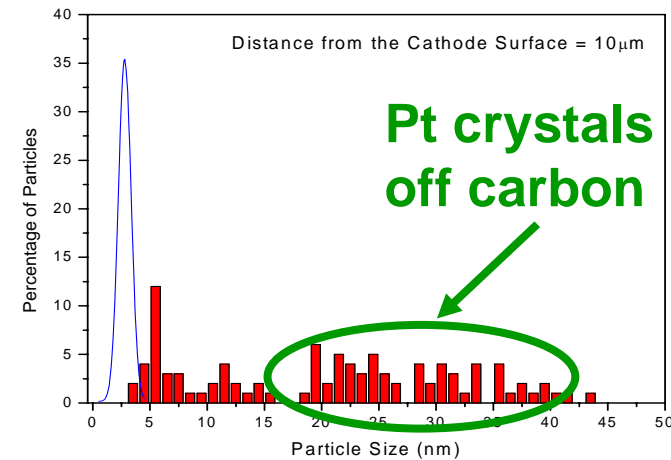
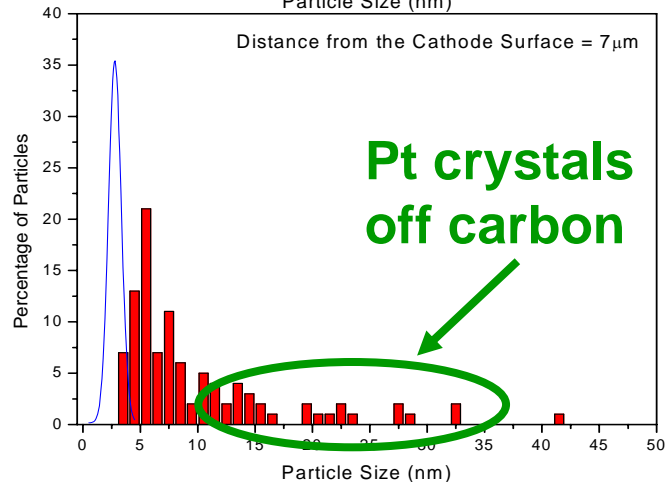
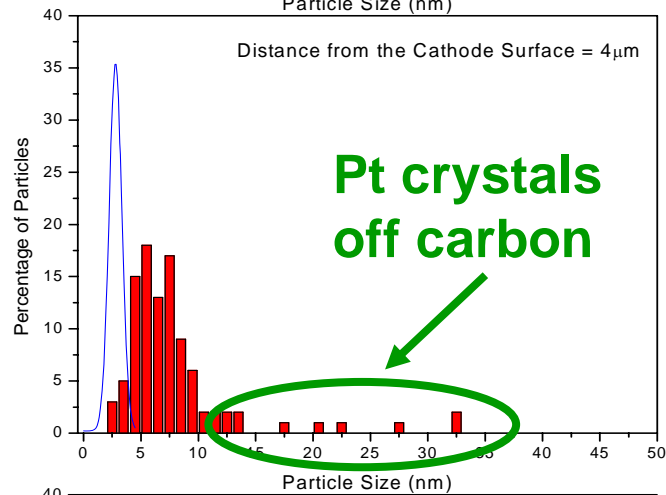
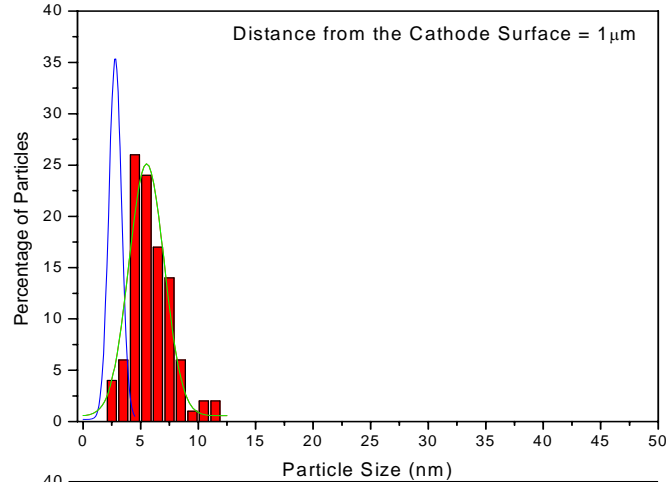
Nanometer-scale  $\rightarrow$  Ostwald ripening of Pt particles on carbon

Micrometer-scale  $\rightarrow$  Pt dissolution and precipitation of Pt crystals off carbon

# Crystal Size Histograms of the Cycled MEA Cathode Sample

## From DM/Cathode Surface to Cathode/Membrane Interface

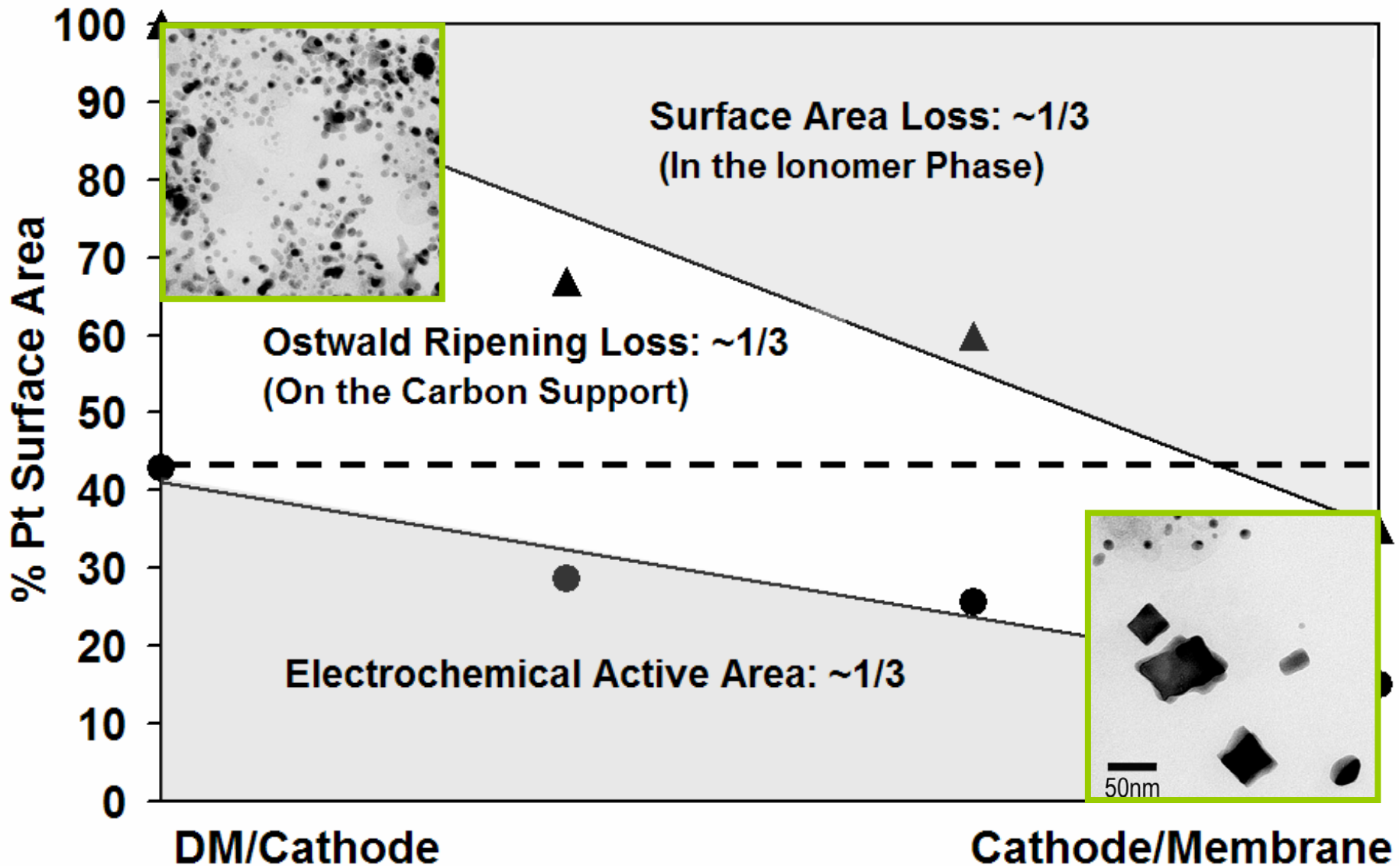
Pt crystal size distributions obtained from X-ray powder diffraction data of cycled MEA cathode cannot be used to deduce Pt coarsening mechanism



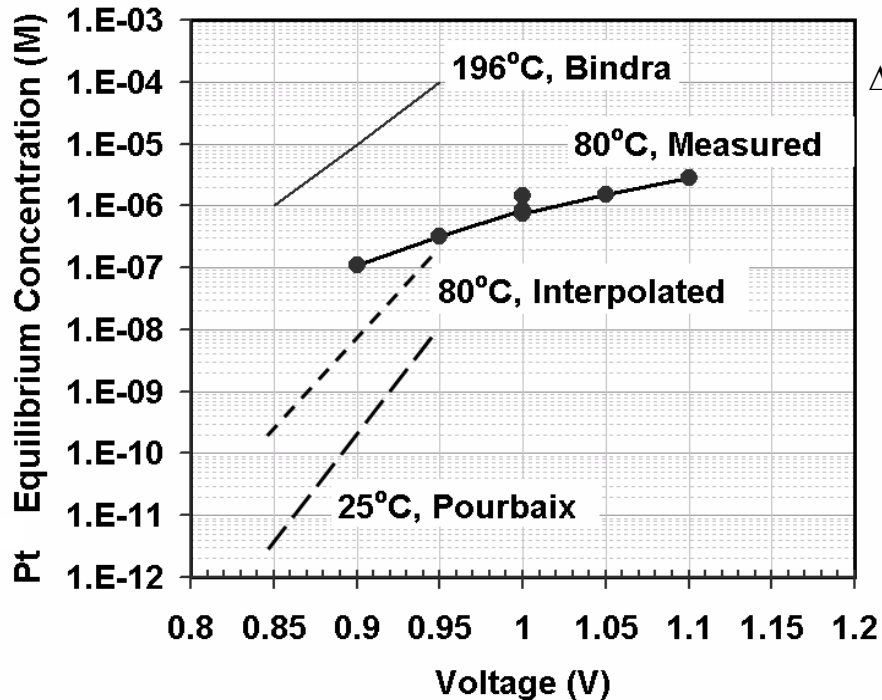
J. Aragane, T. Murahashi & T. Odaka, *Journal of the Electrochemical Society*, **135**, 844-850 (1988).

J. Aragane, H. Urushibata & T. Murahashi, *J. Appl. Electrochem.*, **26**, 147 (1996).

# PEM Fuel Cell Operation – Pt Surface Loss



# Open Questions



46wt% Pt/C (from Tanaka) coated carbon-fiber paper substrate at  $0.67\text{mg}_{\text{Pt}}/\text{cm}^2$  immersed into 120 ml 0.5M  $\text{H}_2\text{SO}_4$  in a three-compartment electrochemical cell maintained at 80 °C.

$$\Delta G_r^o(T) - \Delta G_r^o(T_o) = \Delta c_p^r \cdot (T - T_o) - \Delta S_r^o \cdot (T - T_o) - \Delta c_p^r \cdot T \cdot \ln(T / T_o)$$

$$\Delta G_r^o(T) - \Delta G_r^o(T_o) = \Delta c_p^r \cdot (T - T_o) - \Delta S_r^o \cdot (T - T_o) = C \cdot (T - T_o)$$



the reversible potential of the reaction at 80 °C



Nernstian soluble  $\text{Pt}^{2+}$  concentrations

**Soluble platinum species include oxidized species other than  $\text{Pt}^{2+}$**

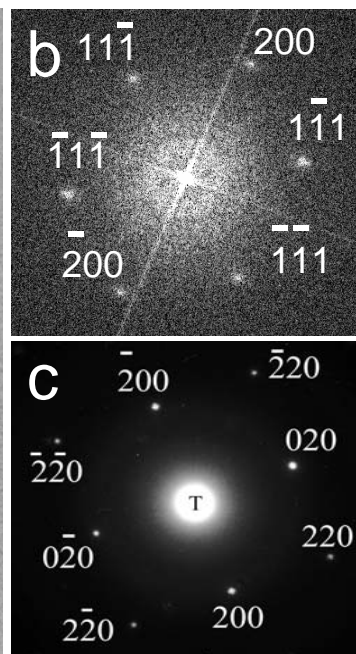
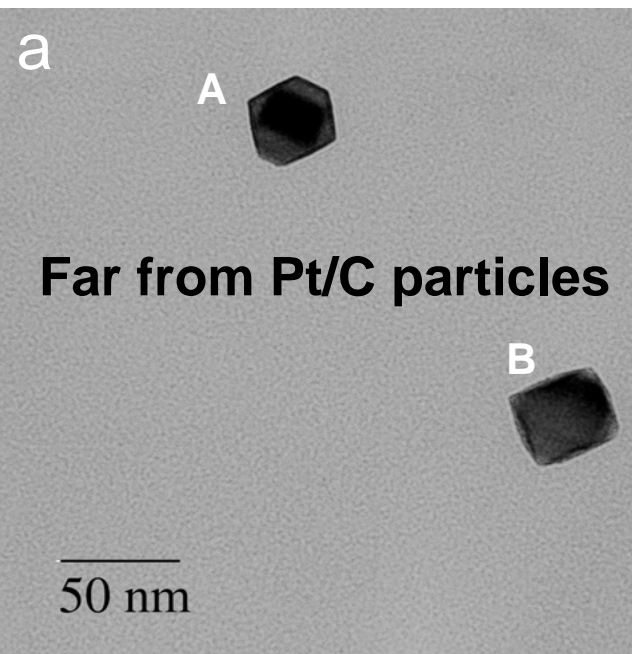
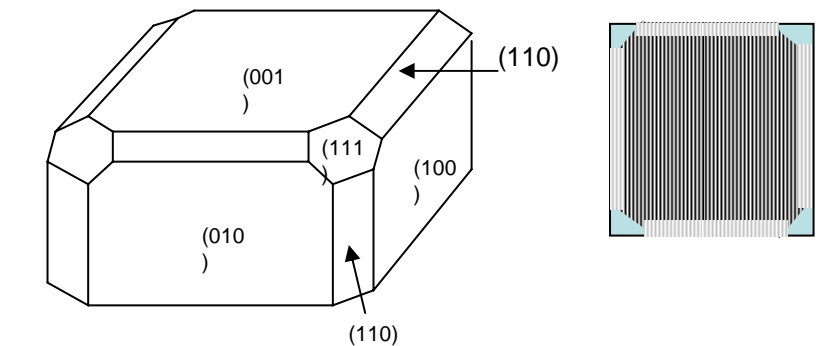
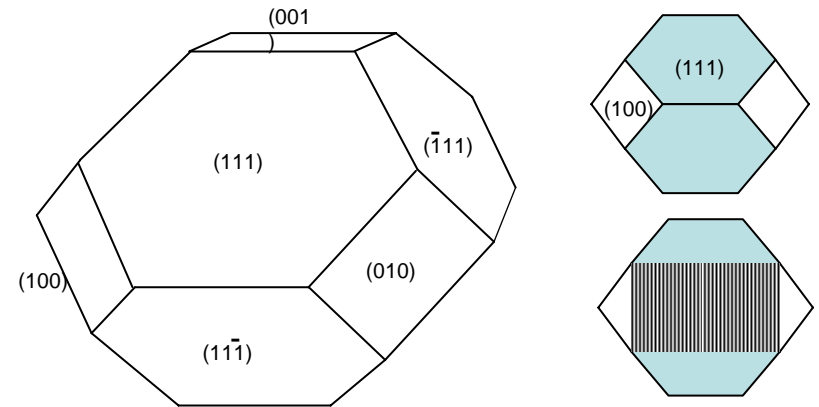
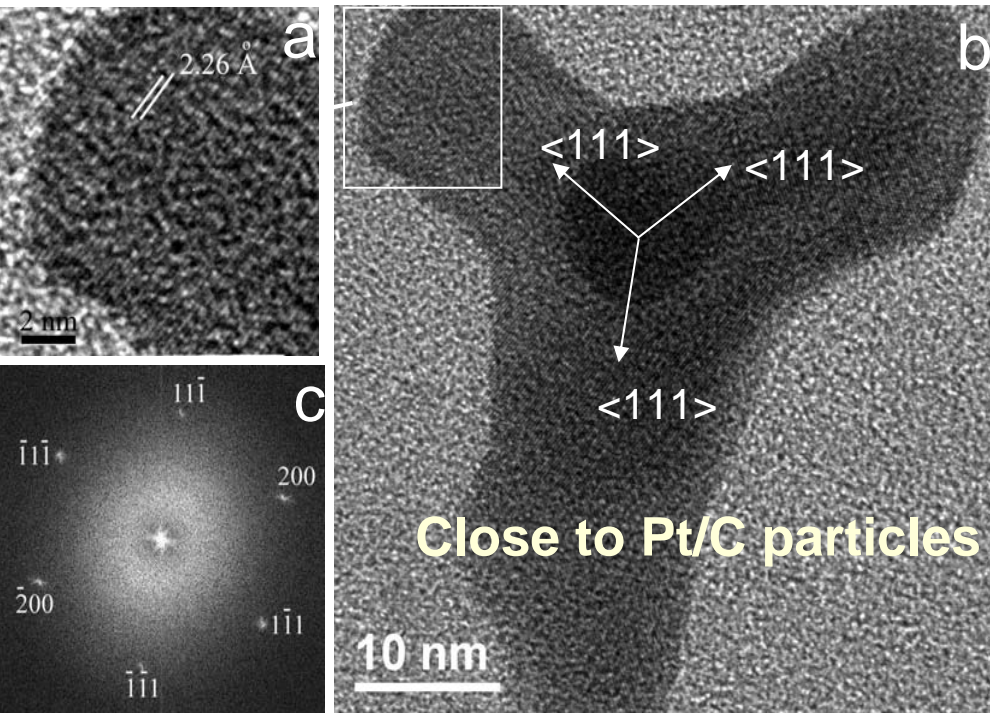
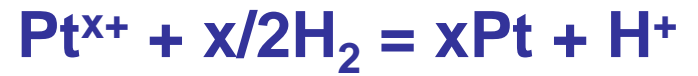
**What is the nature of soluble Pt species?**

Angerstein-Kozłowska (1973) proposed:

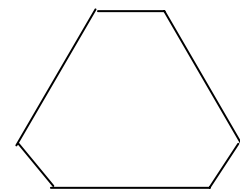
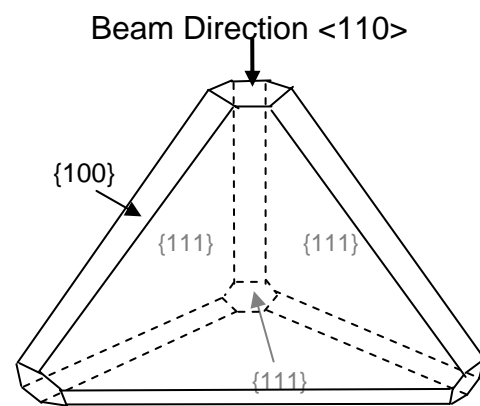
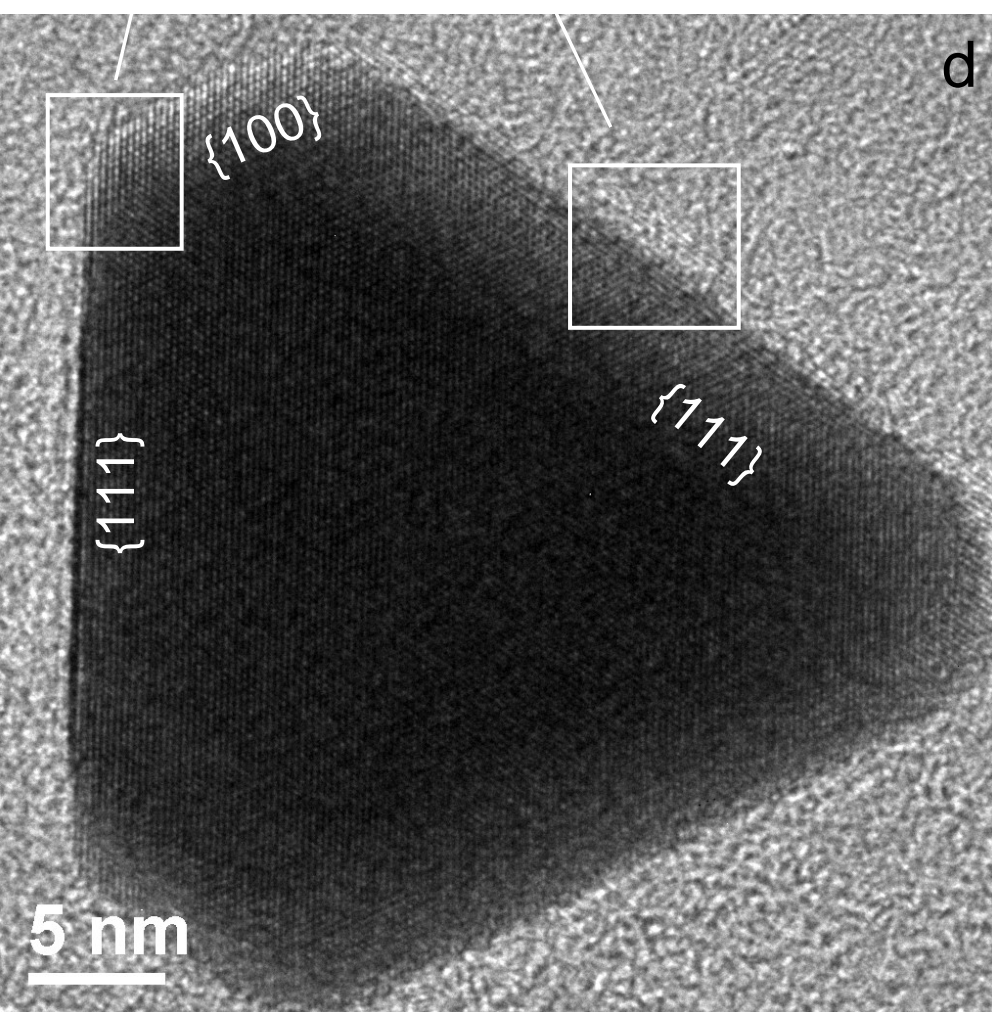
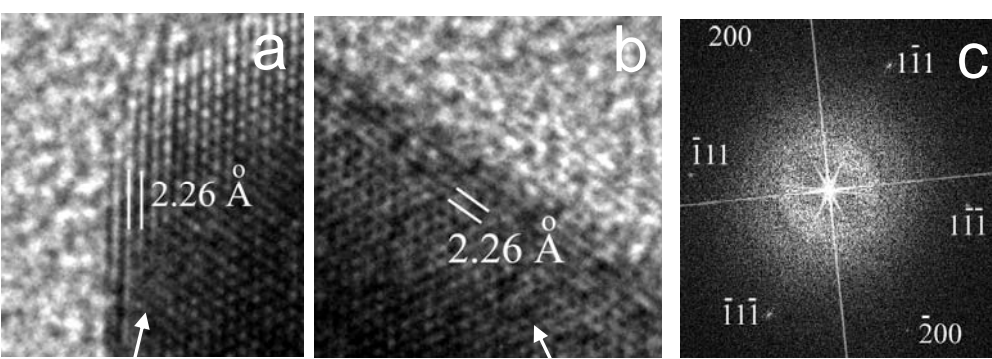
The formation of sublattices as a result of  $\text{OH}_{\text{ad}}$  ordering on the Pt surface.



# Pt crystals in the ionomer and membrane





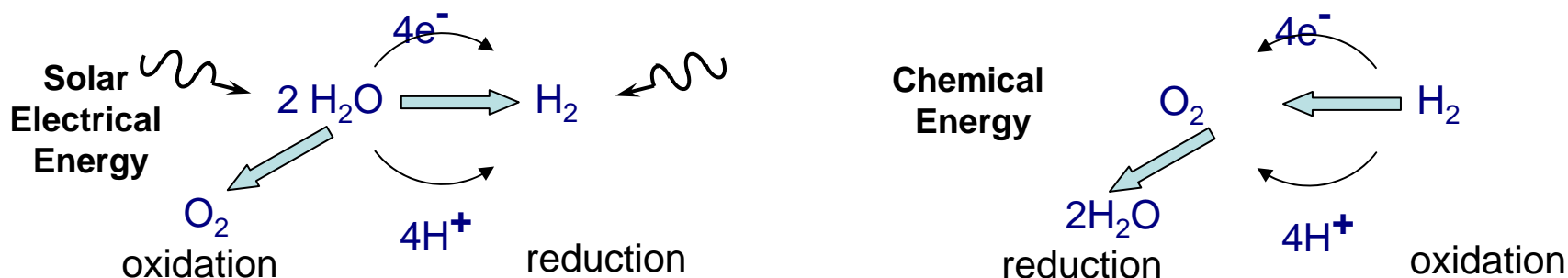


# Grand Challenges in Fuel Cells

Breaking down  $\text{H}_2\text{O} \Rightarrow$  producing  $\text{H}_2$  and  $\text{O}_2$

Breaking down  $\text{O}_2 \Rightarrow$  producing  $2\text{O}^{2-}$  and  $4\text{e}^-$

## A four-electron reaction



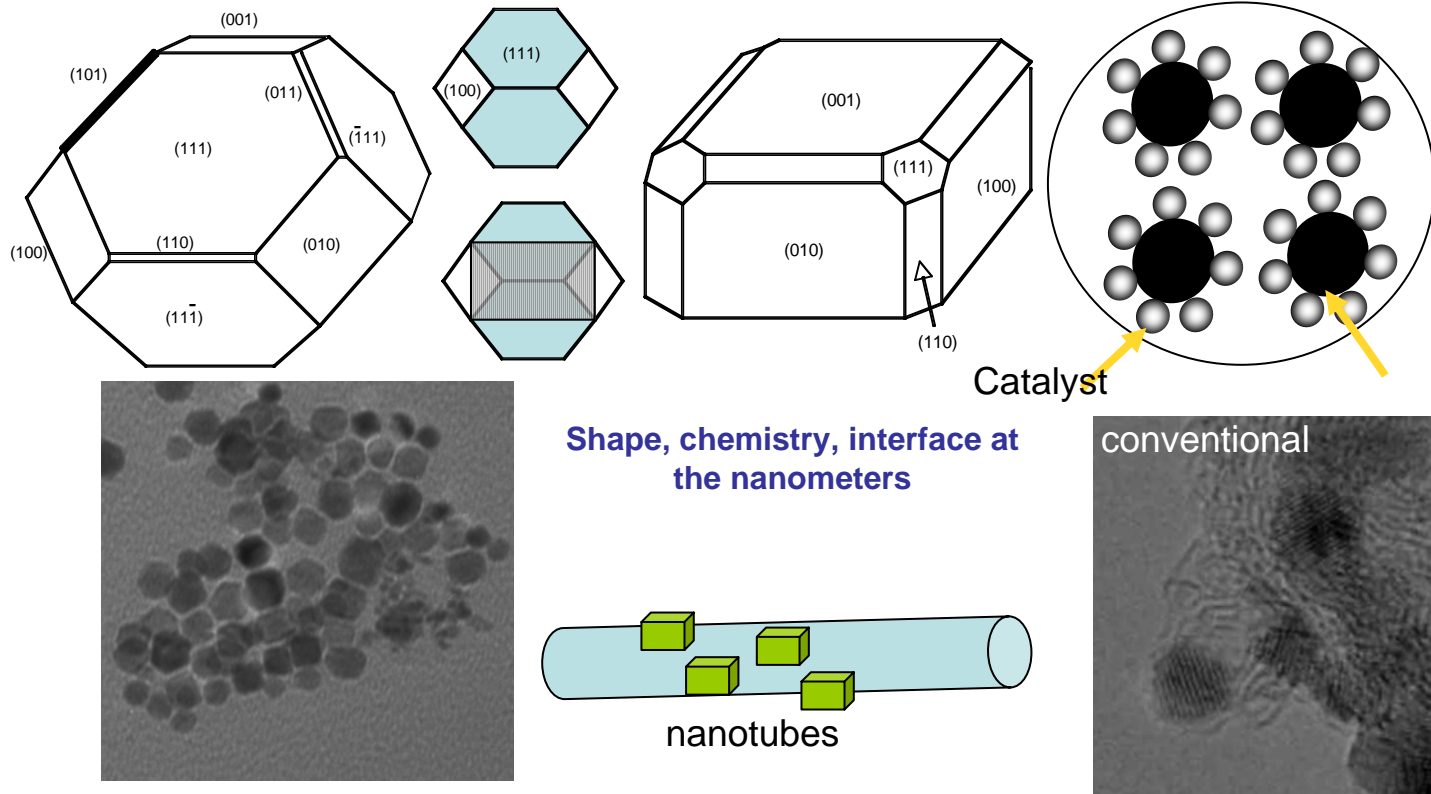
**Catalyst  $\Rightarrow$  High cost and low efficiency**

**Lack of understanding at the molecular level**



# Research Opportunities in Fuel Cells I

## Creating New Electrocatalyst Systems

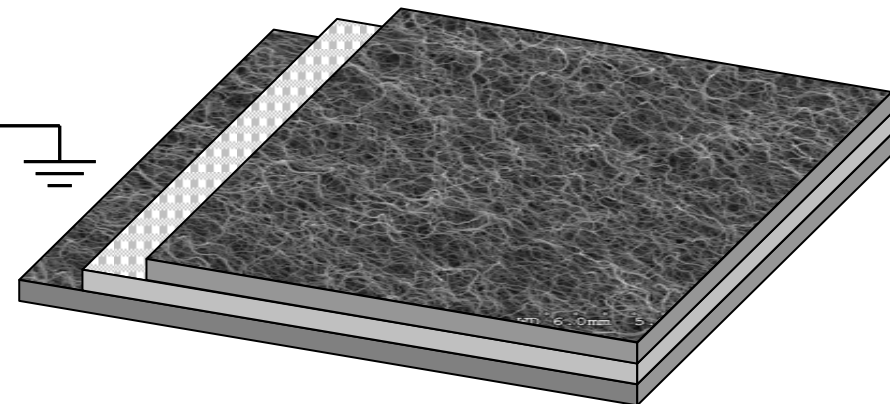
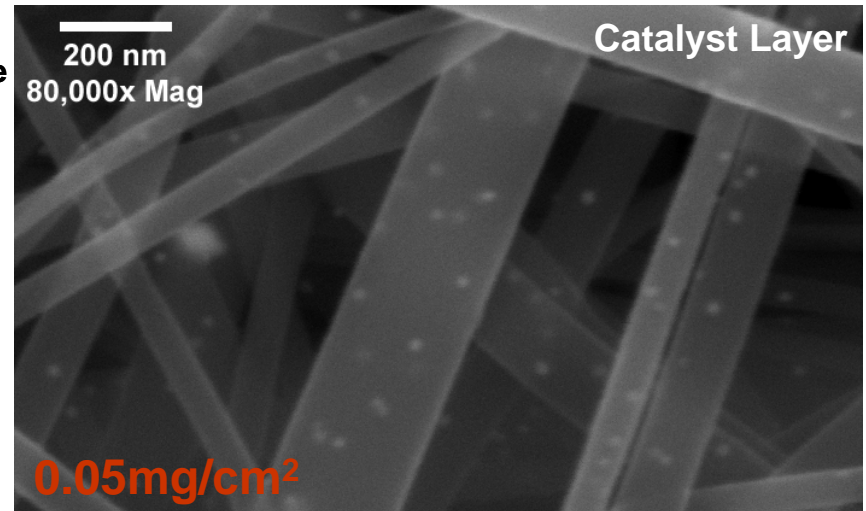
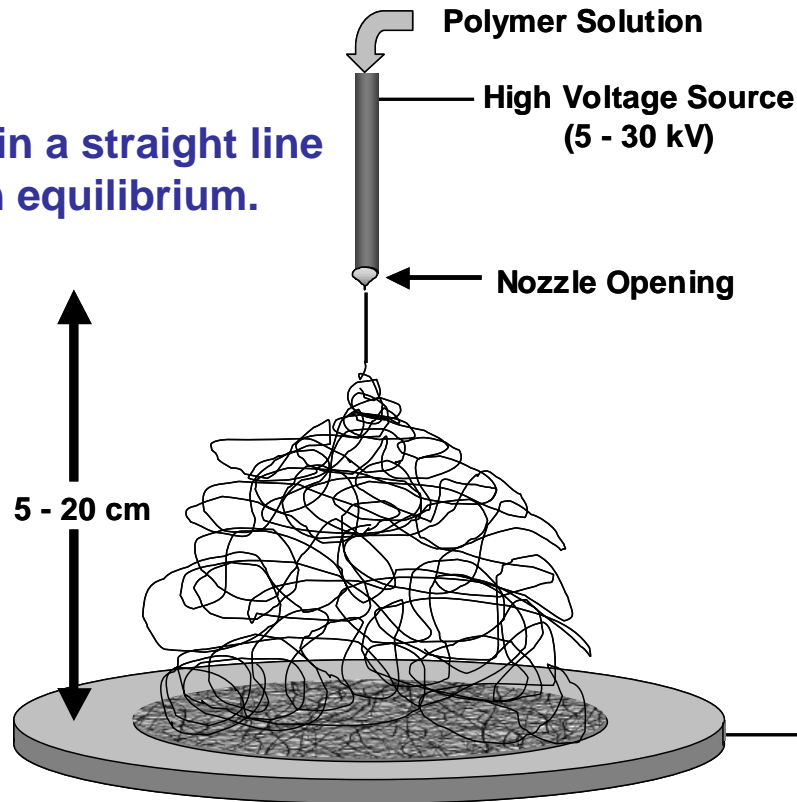


In collaboration with K. Hamad-Schifferli

# Electrospun Fuel Cell Electrodes

We have used electrospinning and prepared catalyst layers with carbon fibers in the range of 50 to 200 nm and with uniformly distributed catalysts (mean crystal size = 10nm).

Charges in a straight line are not in equilibrium.



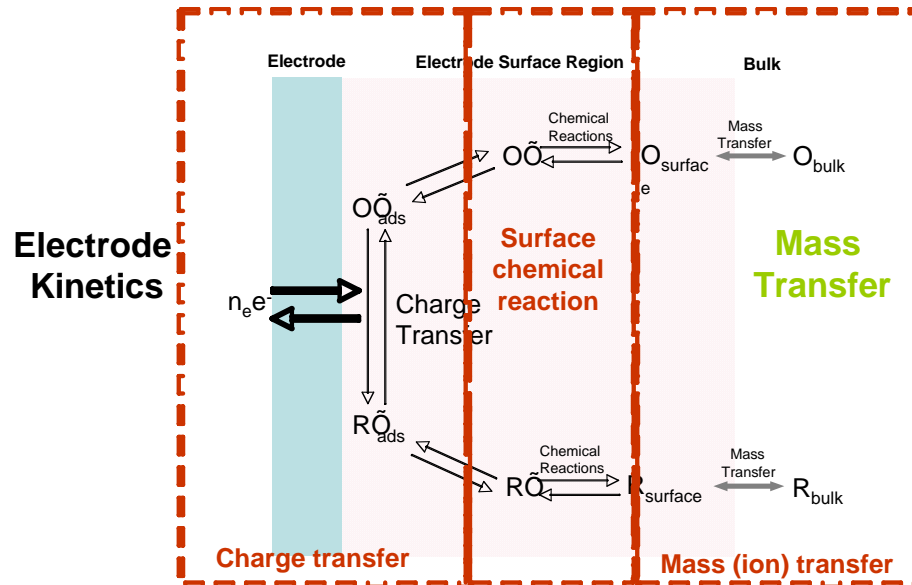
*Patent pending: Fiber Structures Including Catalysts and Methods Associated with the Same*, filed on July 23, 2004 by Wolf, Greenfield & Sacks, P.C, WGS file no. M0925.70145US00.

**Membrane Electrode Assembly**

# Research Opportunities in Fuel Cells III

## Understanding Electrocatalytic Processes at the Molecular Level

### Electrocatalysis of Oxygen Reduction Breaking down $O_2 \Rightarrow$ producing $2O^{2-}$ and $4e^-$

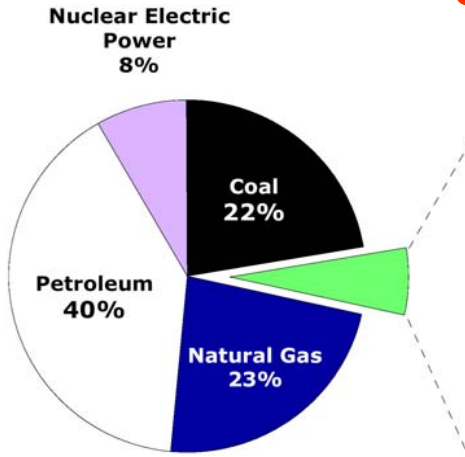


### Advanced tools

- Synchrotron X-ray scattering
- Electron Microscopy
- Scanning Tunneling Microscopy
- Theory and computation

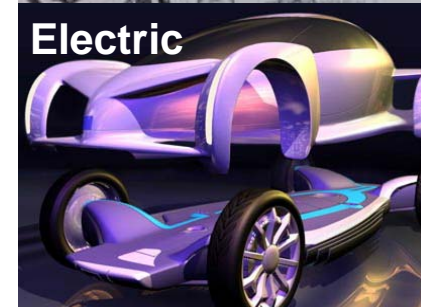
# Science and Technology For A Clean Energy Future

**Current Energy Supply (carbon)**

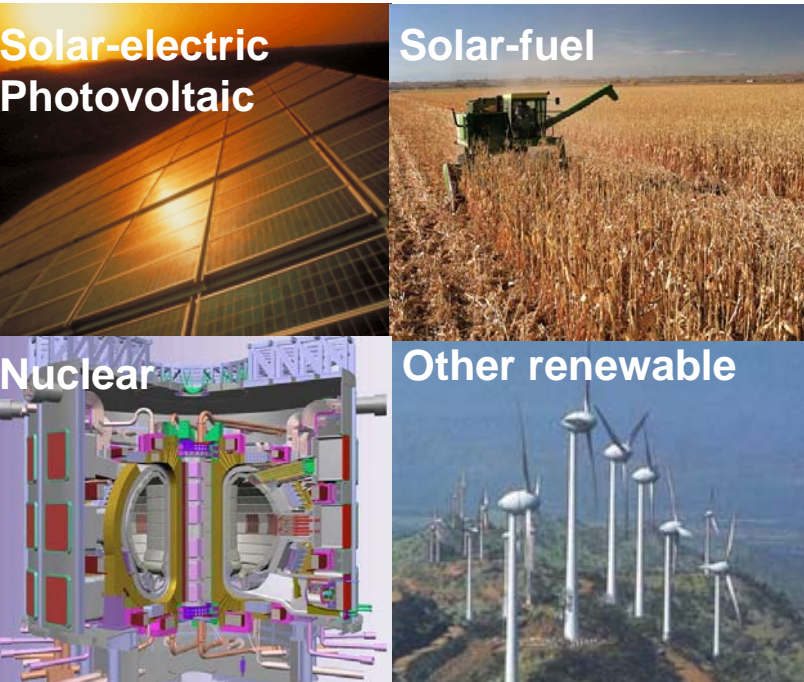


**CO<sub>2</sub> emission**  
Renewable Energy 6% →  
**unsustainable**

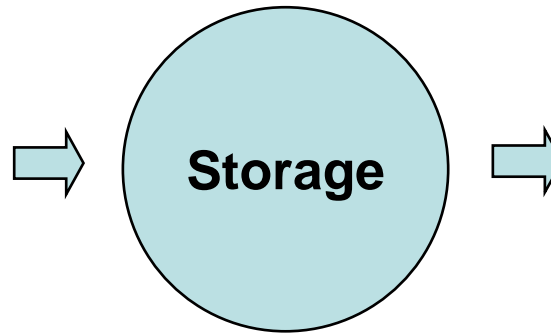
**Energy Demands**



**Future Energy Supply (no net carbon)**



**Hybrid, efficient, clean, sustainable**



# Acknowledgments

## Sponsors

- Automotive industry (Ford and GM)
- Portable electronics industry (Energizer)
- MIT (Mechanical Engineering and Deshpande Center)
- Office of Naval Research
- NSF MIT CMSE
- DOE Basic Energy Sciences

## Collaborators

- P. Ferreira, University of Texas in Austin
- H. Tuller, A. Mayes, G. Ceder, MIT
- E. Murray, FORD Research and Development Center
- H. Gasteiger, GM Fuel Cell Activities
- L. Croguennec, ICMCB-CNRS, France
- C Grey, SUNY Stony Brook
- D. Morgan, University of Wisconsin

# The MIT Energy Initiative

**In her inaugural address, President Susan Hockfield announced:**

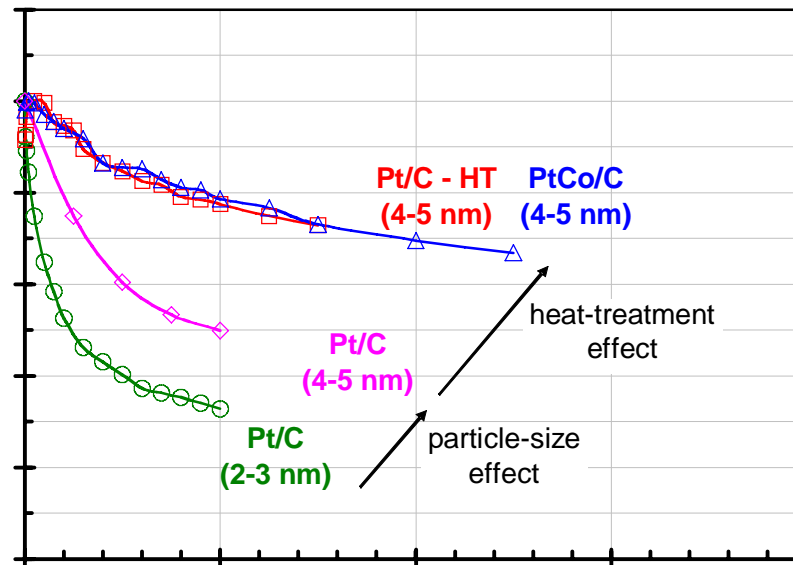
*"... a major new Institute-wide initiative on energy. This initiative will foster new research in science and technology aimed at increasing the energy supply and bringing scientists, engineers, and social scientists together to envision the best energy policies for the future. We will seed this initiative with resources for new interdisciplinary faculty positions. Together, I believe we will make an enormous difference." May 6, 2005*

**The report of the MIT Energy Research Council was released on May 3, 2006.**



# Strategies to reduce Pt loss in the MEA cathode

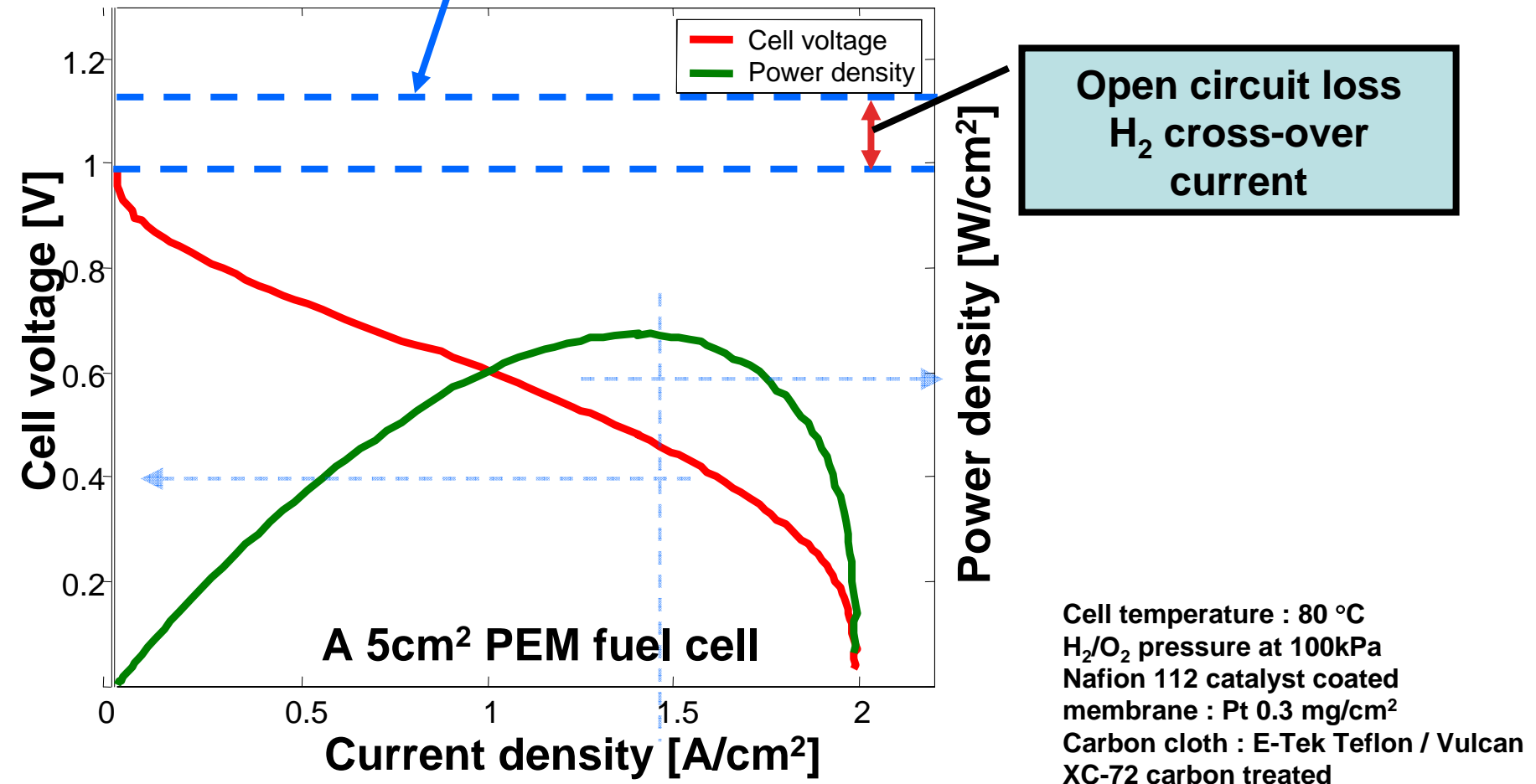
- Reduce the concentration of soluble Pt species in the cathode
  - Modifying PEM fuel cell operating conditions (temperature, voltage, relative humidity, etc.)
  - Increasing PH values of the ionomer phase
  - Application of PtM alloys and heat-treated Pt catalysts





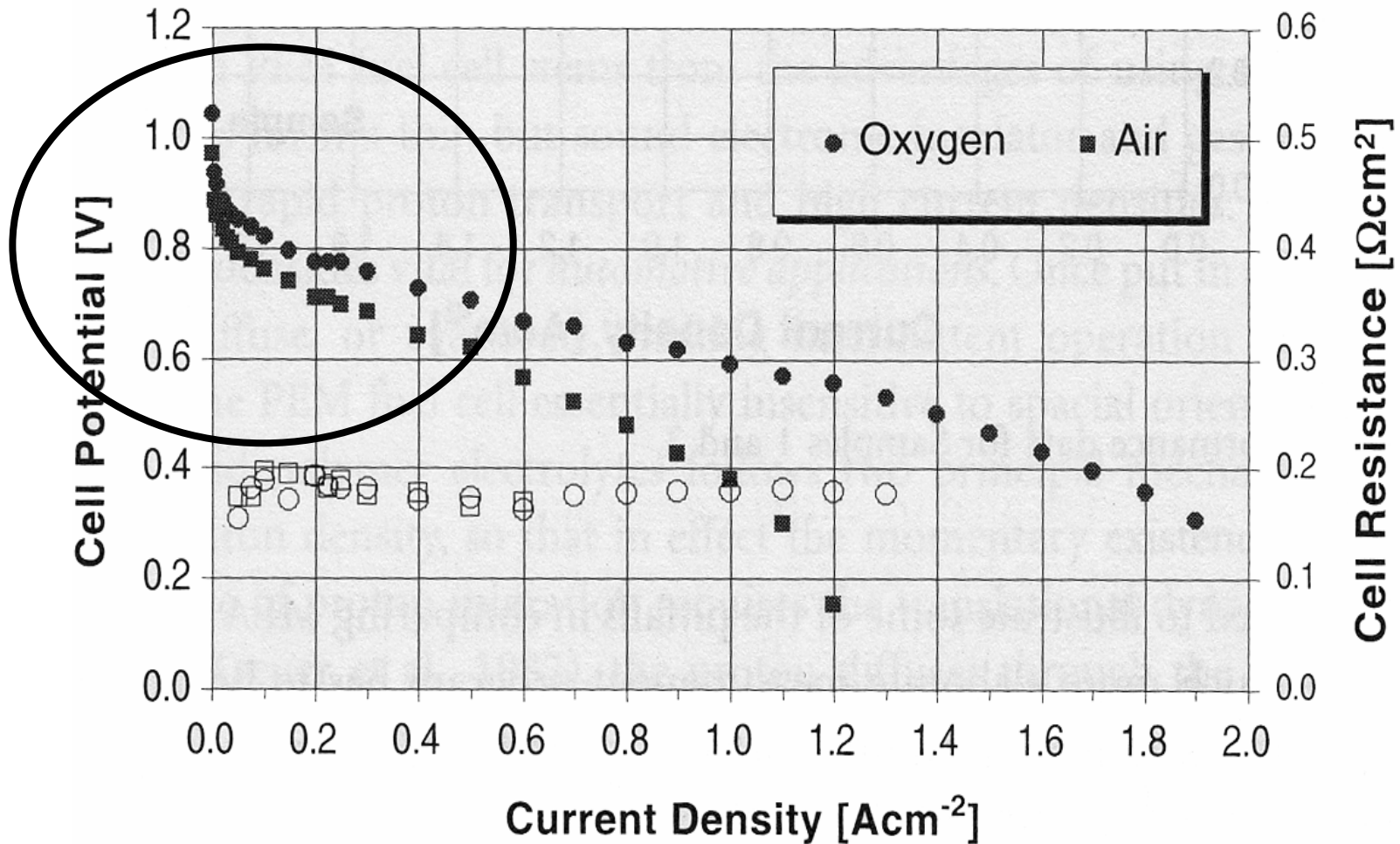
# Voltage Loss Contributions in Fuel Cells

$$E = E^{\circ} - i \cdot R - A \ln(i/i_0) + B \ln(1 - i/i_l)$$



# H<sub>2</sub>-O<sub>2</sub> and H<sub>2</sub>-Air Fuel Cells

## Sample 1 - Air vs. Oxygen



$$OCV_{H_2-O_2} > OCV_{H_2-air}$$