Modeling of Electrochemical Cells: Proton Exchange Membrane Fuel Cells HYD7007 - 01

Dept. of Chemical & Biomolecular Engineering
Yonsei University
Spring, 2011

Prof. David Keffer
dkeffer@utk.edu

Course Information

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Class Meeting Location and Times

- GS Caltex building, 1st floor seminar room
- Wednesday 6:00 PM – 9:00 PM

Course Website

- http://utkstair.org/clausius/docs/fuelcells/index.html

Instructor Information

- Office YERC 174B
- Office telephone: 2123-5748
- email: dkeffer@utk.edu

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Objective

The objective of this portion of the course is to understand the molecular-level structure and transport processes of Proton Exchange Membranes (PEM) fuel cells.

Organization and Scheduling

The course is organized into four parts:

- Structure (May 11, 2011)
- Water & Charge Transport (May 18, 2011)
- Membrane Composition (May 25, 2011)
- Polymer Dynamics (June 8, 2011)

Course Grades

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Overall Course Grades

- The total course grade is an average of the three grades for each instructor.

Course Grade for this Portion

- Attendance: 20%
- Homework Assignments: 30%
- Final Exam: 50%

Homework Assignments

- assignment 1. Assigned: May 11, 2011. Due: May 18, 2011, beginning of class.
- assignment 2. Assigned: May 18, 2011. Due: May 25, 2011, beginning of class.
- assignment 3. Assigned: May 25, 2011. Due: June 8, 2011, beginning of class.

Final Examination

- Covers only this final third of the class
- date, time and location: To be determined.

Instructor: Prof. Keffer

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chemical engineer, molecular-level process and materials modeler

Modeling of Electrochemical Cells: Proton Exchange Membrane Fuel Cells HYD7007 – 01

Lecture 01. Overview of PEM Fuel Cell Structure

Dept. of Chemical & Biomolecular Engineering
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Lecture Outline

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- Motivation
- Macroscopic Structure of Fuel Cells
- Structure and Properties of Nafion
- Examination of Macroscopic Models

Sustainable Energy Cycles

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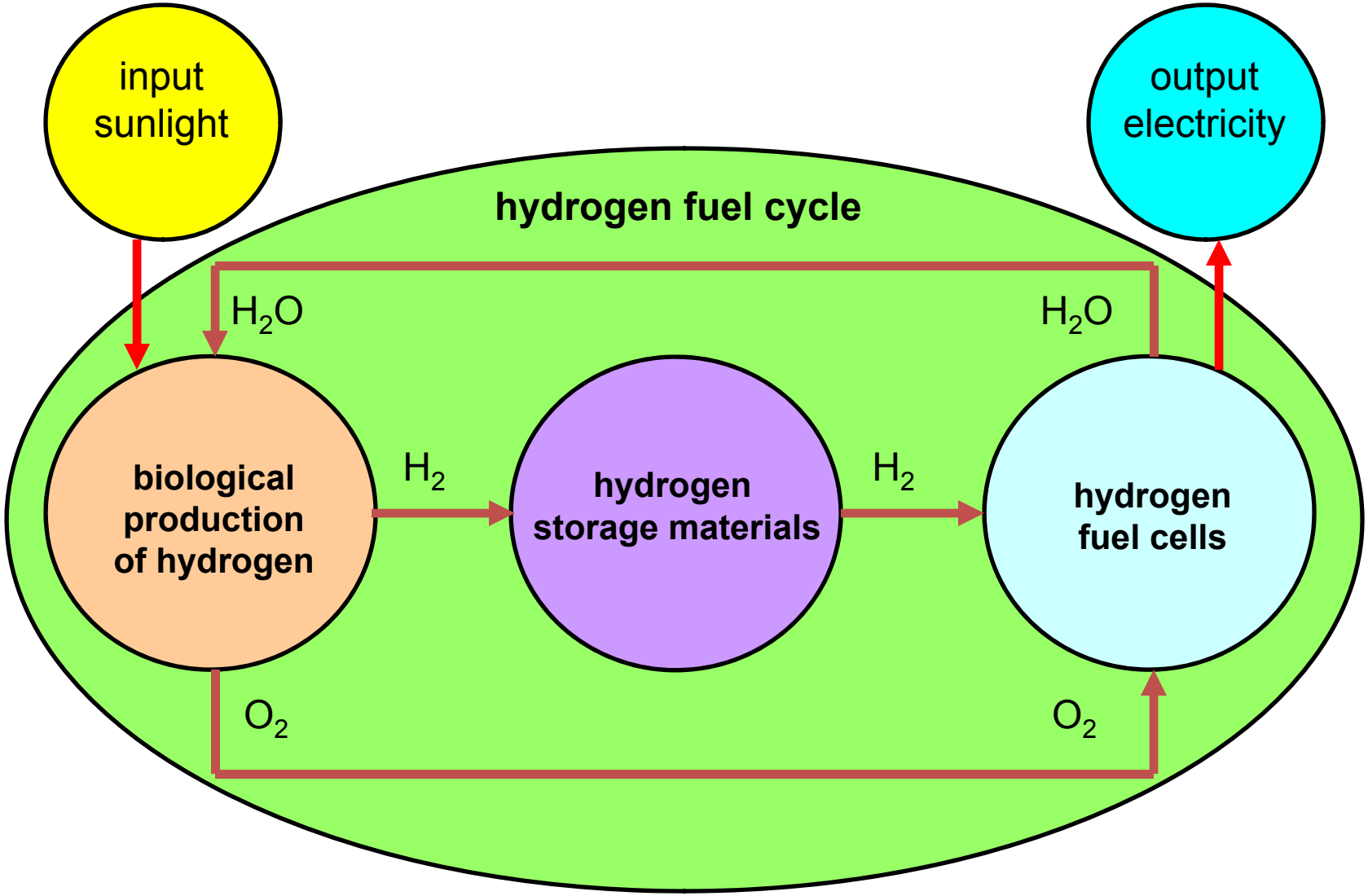

Sustainable Energy Cycles

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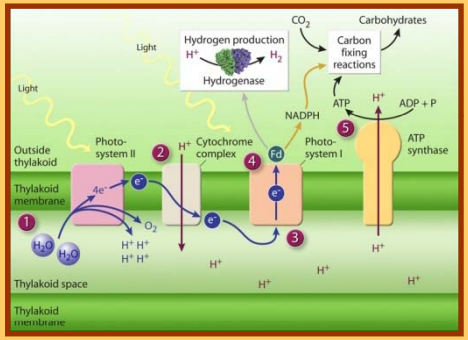
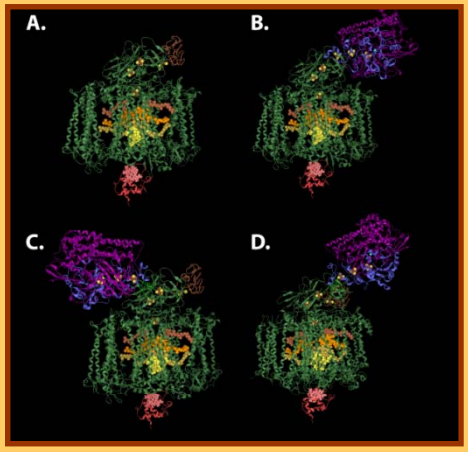
H_2 production

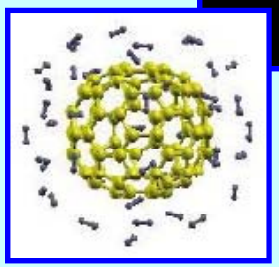
H_2O Photolysis in Algae and Cyanobacteria





H_2 storage

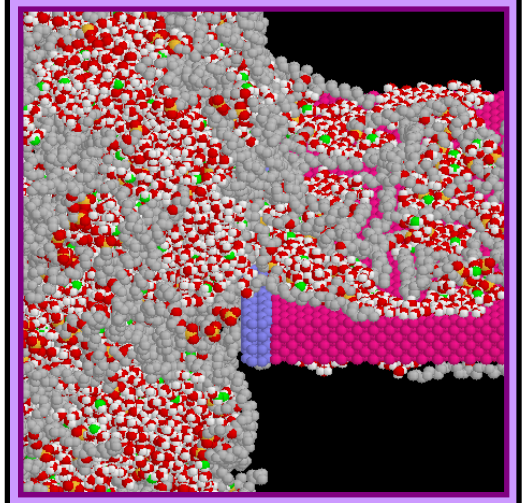
Materials discovery of novel nanoporous adsorbents with high capacity and fast charging



- metal-porphyrin frameworks
- decorated carbon fullerenes

H_2 conversion

Understanding structure-property relationships in proton exchange membrane fuel cells to aid design of next generation devices



Each task has significant challenges

Why Hydrogen Fuel Cells?

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Big (perhaps premature) emphasis on hydrogen under the Bush administration (2000-2008).

Originally Obama administration zeroed out the hydrogen budget. It was restored and some say that Secretary of DoE Steven Chu now admits the mistake. Program renamed as Fuel Cells.

There is no single silver bullet to the energy issue (except perhaps fusion). Many technologies must be explored.

Battery electric vehicle technology is closer to widespread implementation but pure BE vehicles have limited range. (30-40 miles)

Fuel cell vehicles would have much longer range (> 200 miles) but other issues (takes a while to “warm up”).

A fuel cell/battery electric hybrid may be eventual solution.

Interdisciplinary Research

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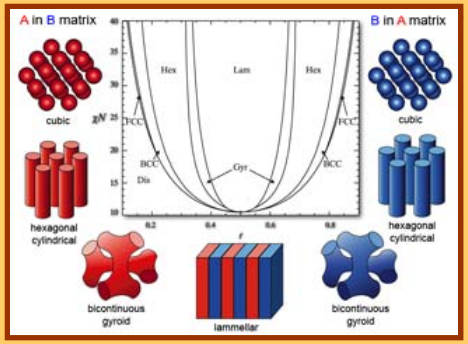
Understanding Structure/Property Relationships in Fuel Cells

synthesis

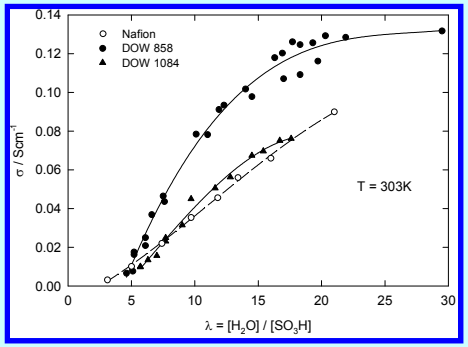
- novel fluorinated, sulfonated block co-polymers



- precise control over architectural elements
- two scales of morphology

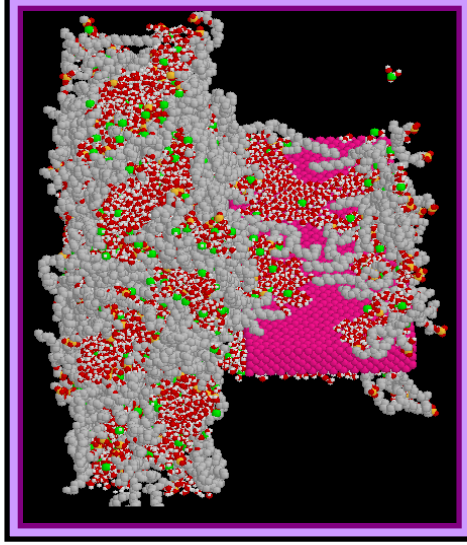
characterization

- neutron tomography
- SEM/TEM
- small angle x-ray scattering
- dielectric spectroscopy
- proton conductivity



modeling

- quantum mechanical calculations
- classical molecular dynamics simulation
- mesoscale modeling
- mean field modeling



Theory guides functionalization of next iteration of materials.

Fuel Cell-powered vehicles

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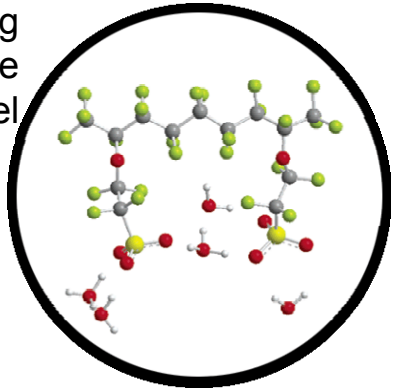
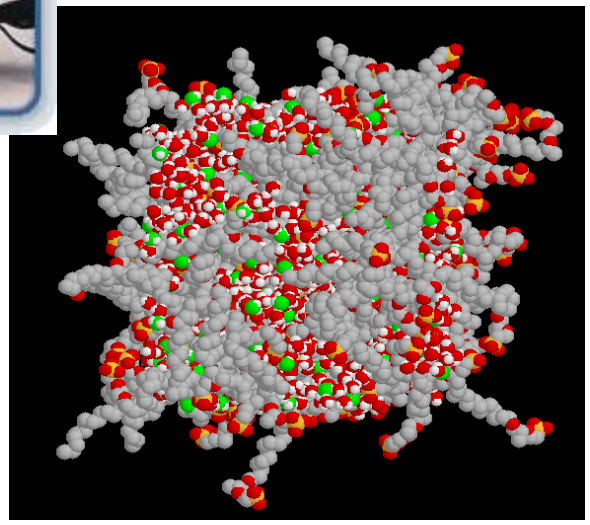
understanding starts at the quantum level



H_2-powered autos become a reality

leads to high-fidelity coarse-grained models



impacts fuel cell performance

improved nanoscale design of membrane/electrode assembly

how fuel cells work: conceptual level

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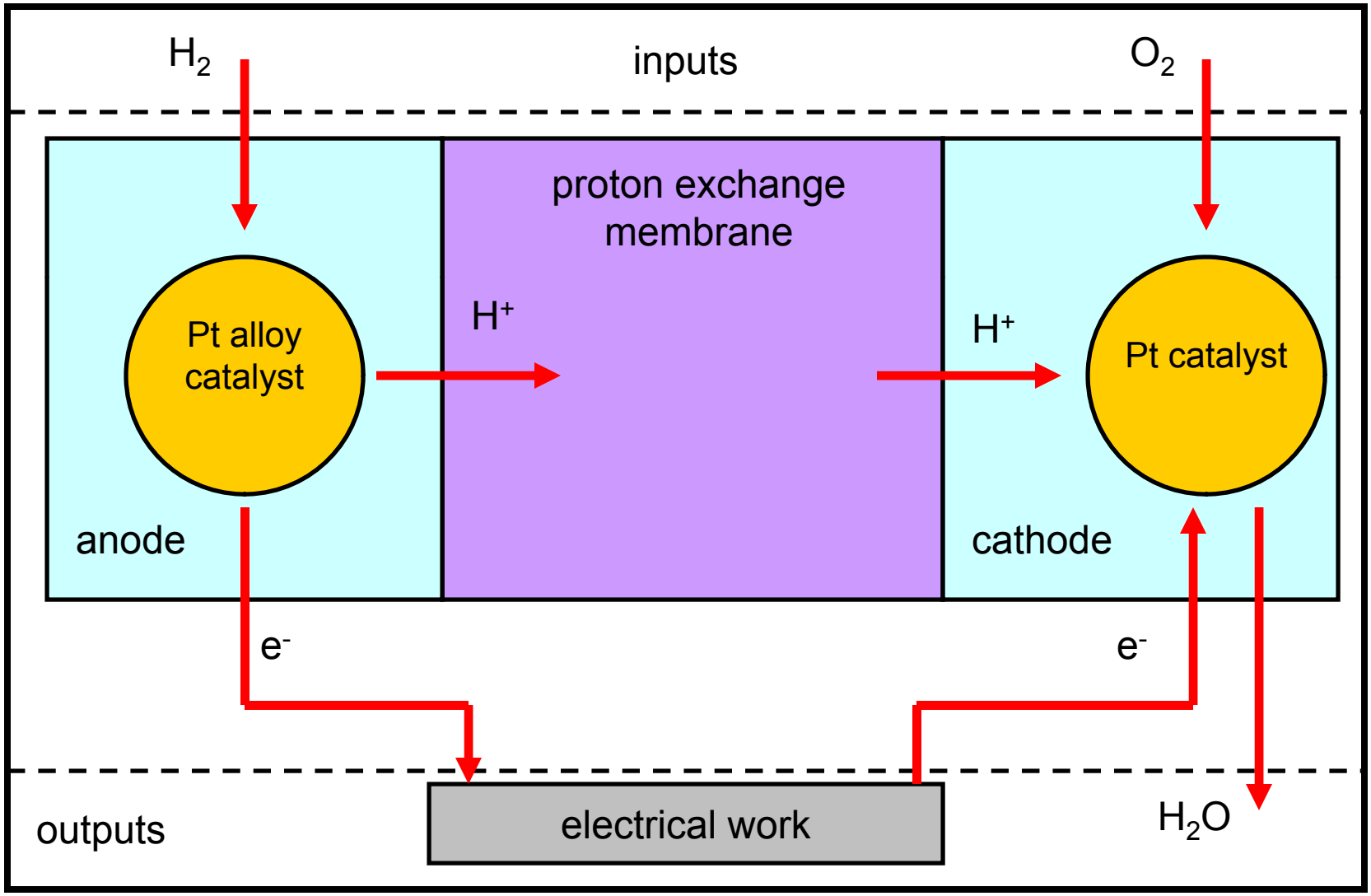

Overview of Structure

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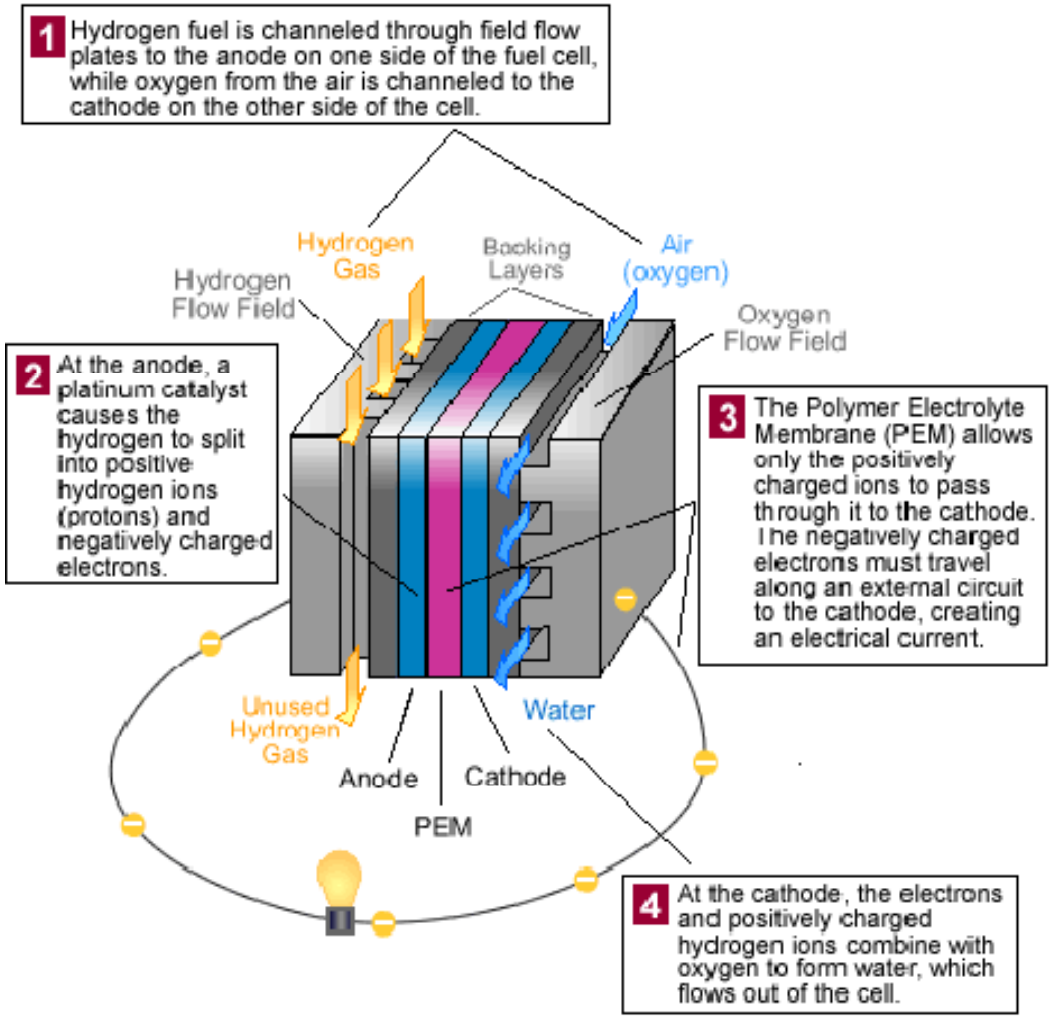

http://www.fueleconomy.gov/feg/fcv_pem.shtml

Overview of Structure

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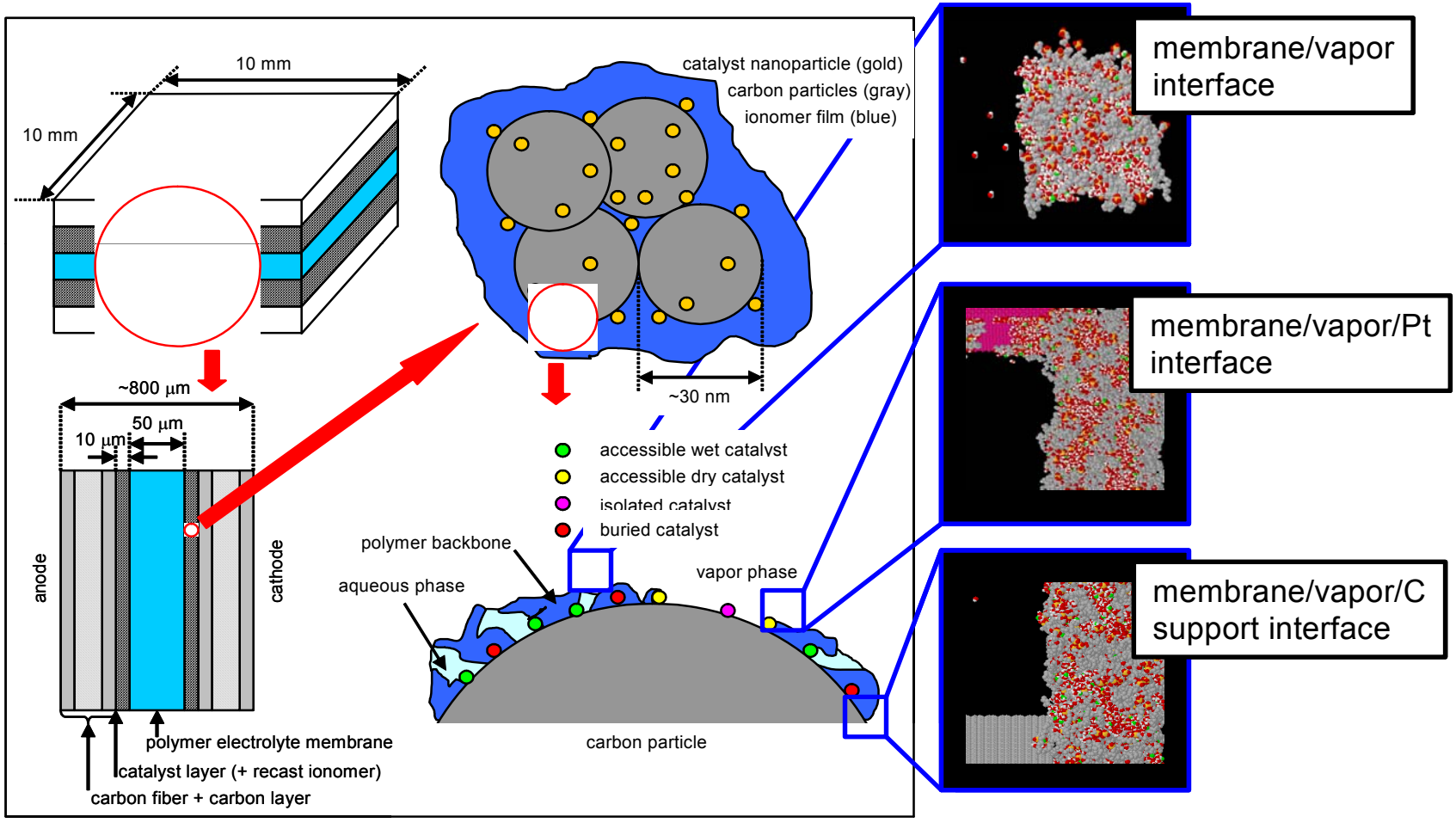
A membrane electrode assembly from the macroscale to the molecular scale



Fuel cell issues

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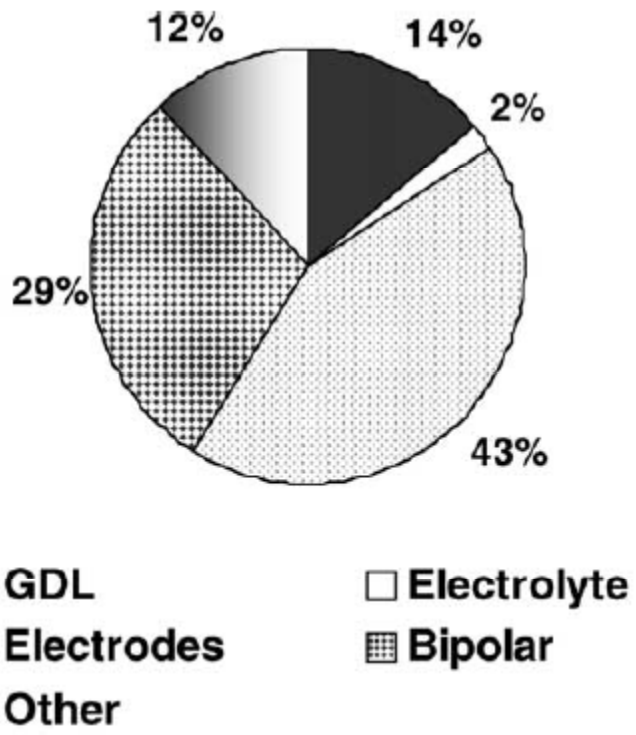
Pt is expensive.
- Gemini space program 28 mg/cm^2
- today <0.2 mg/cm^2
- today $200/kW

Goal $35/kW (electrode is 14% of cost) (from Partnership for a New Generation of Vehicles)

Pt can be poisoned by CO
- need very pure H_2 fuel

Part of the solution:
- Run at higher temperature
- Pt (and other metal catalysts) are more active and less susceptible to poisoning

BUT other parts of the fuel cell don't work at high temperatures.



Bar-On *et al.* J. Power Sources, 2002.

Industry Standard Membrane

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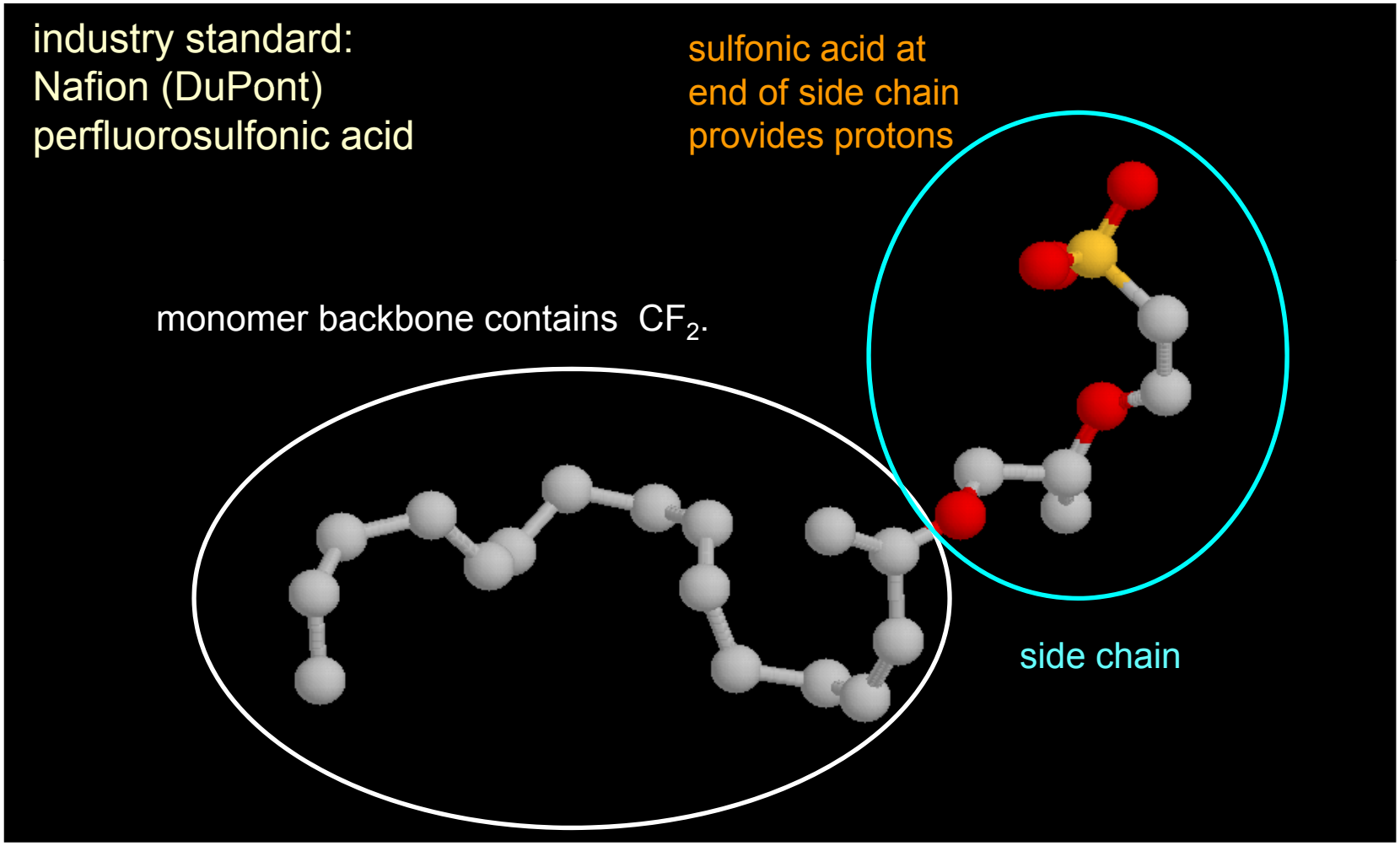
proton exchange membranes are polymer electrolytes



CF_2 = gray, O = red, S = orange, cation not shown.

Industry Standard Membrane

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Chem. Rev. **2004**, *104*, 4535–4585

State of Understanding of Nafion

Kenneth A. Mauritz* and Robert B. Moore*

Department of Polymer Science, The University of Southern Mississippi, 118 College Drive #10076, Hattiesburg, Mississippi 39406-0001

NAFION

$$-(CF_2-CF_2)_n-CF-CF_2-$$
$$O-(CF_2-CF-O)_m-CF_2-CF_2-SO_3H$$
$$CF_3$$

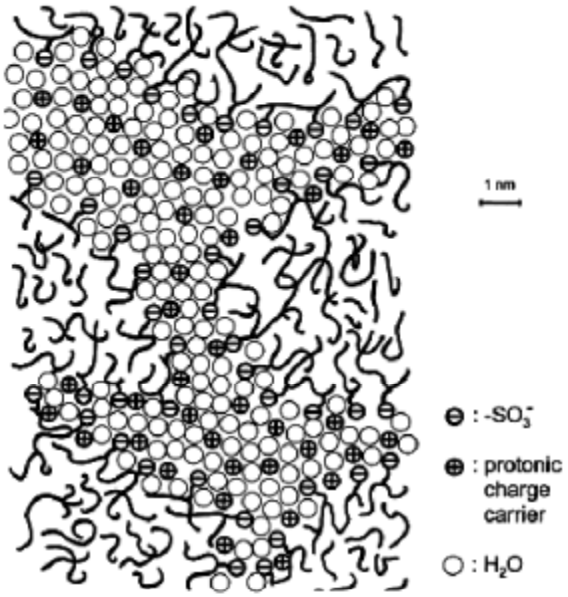

Figure 11. Stylized view of Kreuer of the nanoscopic hydrated structures of Nafion and sulfonated polyetherketone. (Reprinted with permission from ref 91. Copyright 2003 Elsevier.)

Membrane must be Hydrated

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Chem. Rev. 2004, *104*, 4637–4678

Transport in Proton Conductors for Fuel-Cell Applications: Simulations, Elementary Reactions, and Phenomenology

Klaus-Dieter Kreuer,*,‡ Stephen J. Paddison,§ Eckhard Spohr,# and Michael Schuster‡

Max-Planck-Institut für Festkörperforschung, Heisenbergstr.1, D-70569 Stuttgart, Germany, Department of Chemistry, University of Alabama in Huntsville, Huntsville, Alabama 35899, and Forschungszentrum Jülich, D-52425 Jülich, Germany

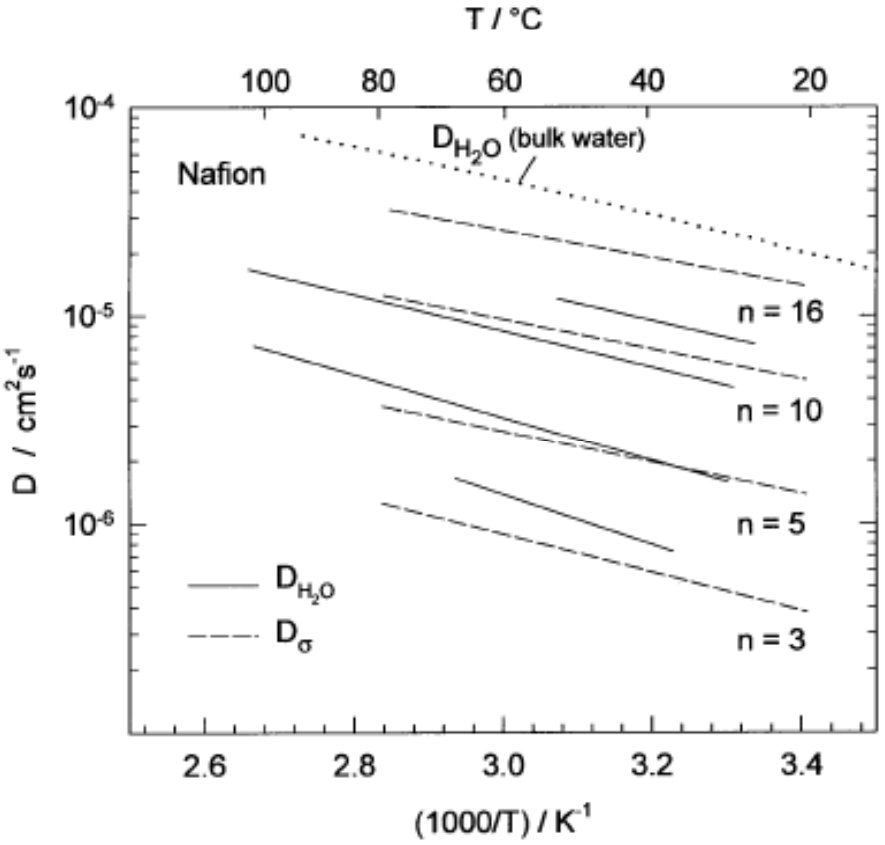

Figure 9. Proton conductivity diffusion coefficient (mobility) and water self-diffusion coefficient of Nafion 117 (EW = 1100 g/equiv), as a function of temperature and the degree of hydration ($n = [H_2O]/[-SO_3H]$).[197]

Kreuer et al., *Chem. Rev.* 2004.

Diffusion data

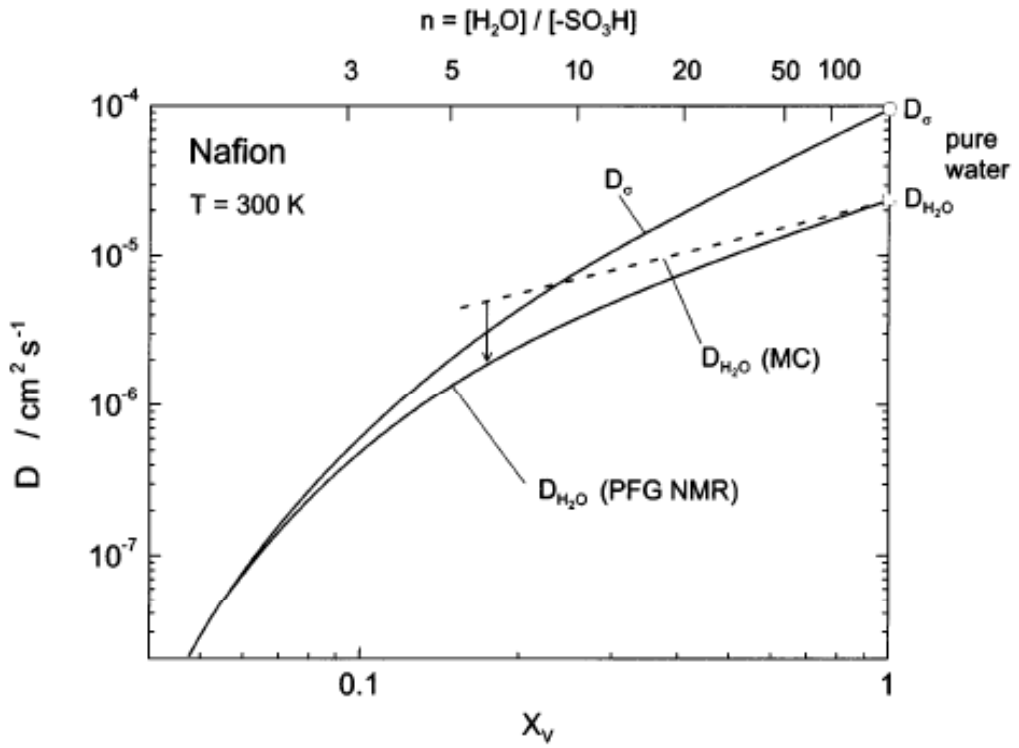

Figure 12. Water self-diffusion coefficient of Nafion 117 (EW = 1100 g/equiv), as a function of the water volume fraction X_V and the water diffusion coefficient obtained from a Monte Carlo (MC) simulation (see text). The proton conductivity diffusion coefficient (mobility) is given for comparison. The corresponding data points are displayed in Figure 14.

Kreuer et al., *Chem. Rev.* 2004.

Conductivity data

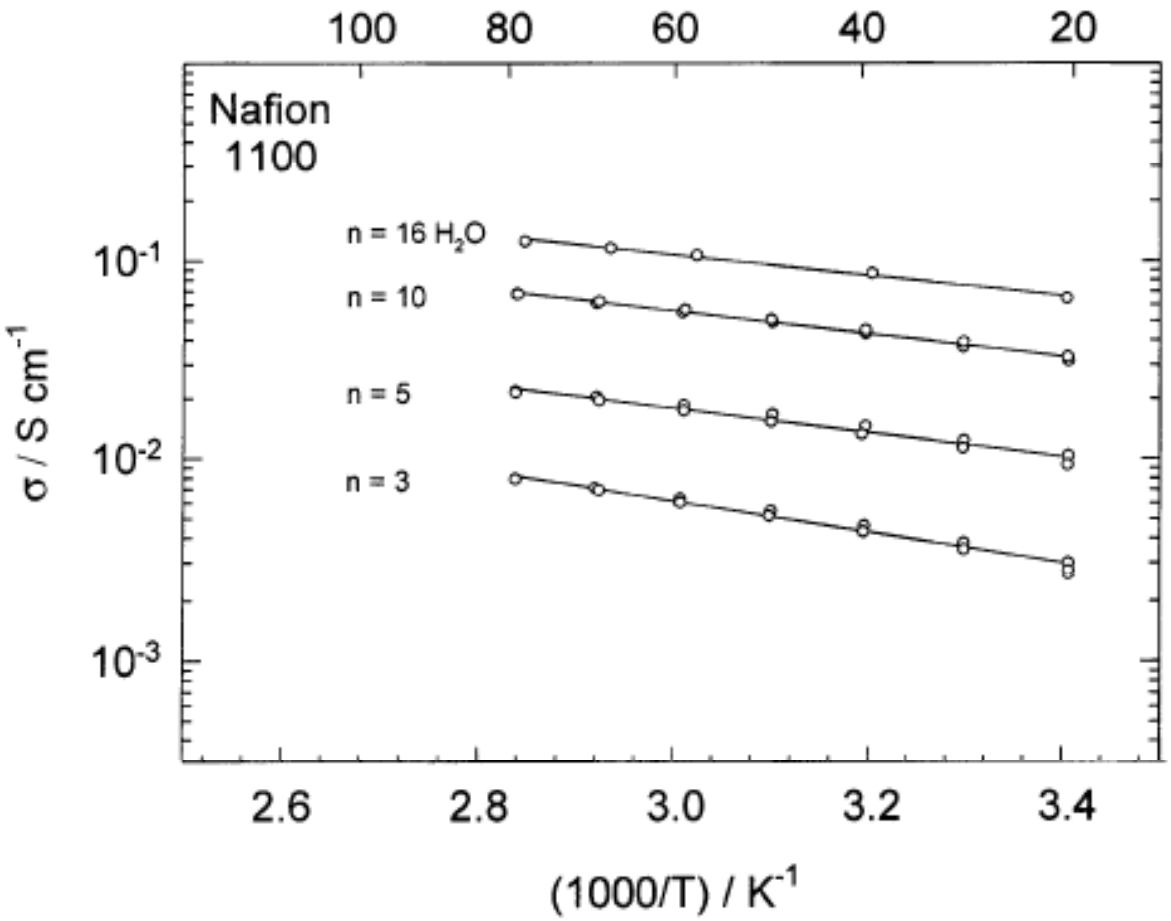

Figure 18. Proton conductivity of (a) Nafion 117 (EW = 1100 g/equiv) and (b) a sulfonated poly(arylene ether ketone), as a function of temperature and degree of hydration ($n = [H_2O]/[-SO_3H]$).[197]

Kreuer et al., *Chem. Rev.* 2004.

High Temperature Fuel Cells

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Running a fuel cell at higher temperatures has advantages but poses technological challenges.

Advantages:

- requires less catalyst
  catalyst more inherently more active at higher temperature because
- lessens the requirement on fuel purity because
  catalyst is less susceptible to CO poisoning
  - at lower temperature, CO adsorbs irreversibly, occupies sites on the Pt catalyst, preventing those sites from participating in useful electrochemical reactions
  - at higher temperature, the CO adsorption isotherm is shifted to the gas phase, freeing up more of the catalyst surface to participate in useful electrochemical reactions

Technological Challenges:

- requires advanced membrane technology that maintains a high conductivity at higher temperatures, by either
  - retaining more moisture at higher temperature, or
  - having a higher conductivity at reduced moisture contents
  - moving to a water-free membrane

Macroscopic Modeling

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Chem. Rev. 2004, *104*, 4727–4766

Fundamental Models for Fuel Cell Engineering

Chao-Yang Wang*

Departments of Mechanical Engineering and Materials Science and Engineering, Electrochemical Engine Center (ECEC), The Pennsylvania State University, University Park, Pennsylvania 16802

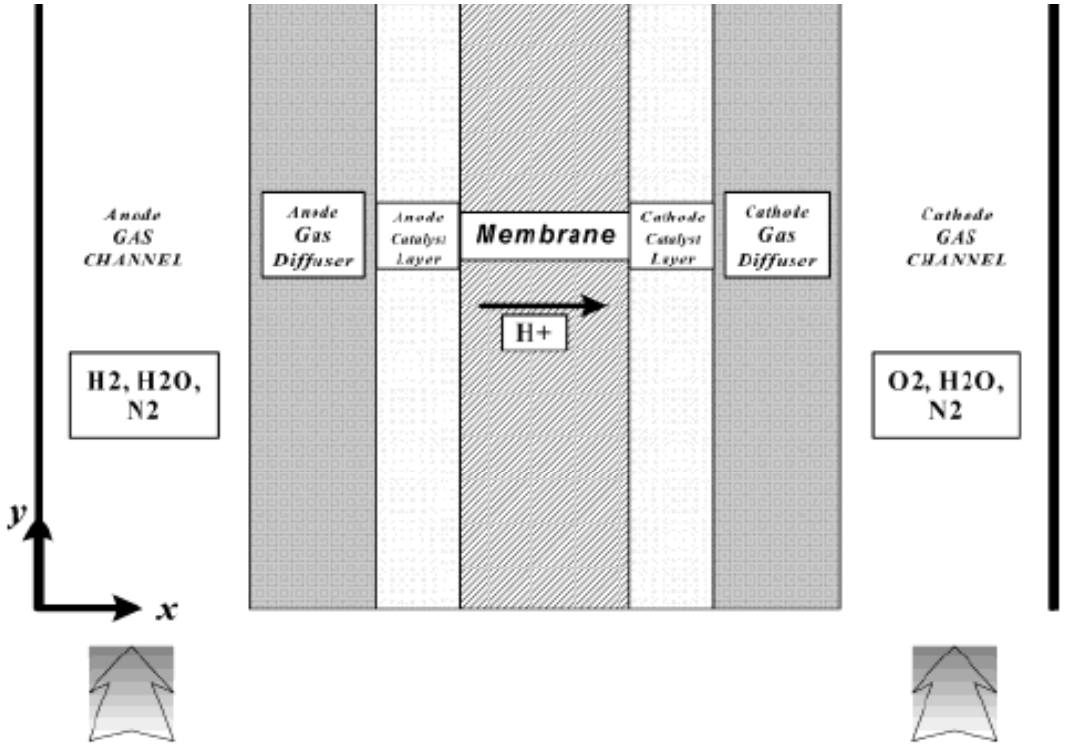

Figure 6. Schematic diagram of a polymer electrolyte fuel cell.

Wang, *Chem. Rev.* 2004.

Macroscopic Modeling

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Table 1. Single-Phase PEFC Model: Governing Equations with Source Terms Identified in Various Regions[a]

		source terms		
	conservation equations	diffusion layers	catalyst layers	membrane
mass	$\partial(\epsilon\rho)/\partial t + \nabla(\rho\vec{u}) = S_m$		$S_m = \sum_k M_k S_k + M_{H_2O}\nabla(D_{w,m}\nabla C_{H_2O})$	
momentum	$1/\epsilon[\partial(\rho\vec{u})/\partial t + 1/\epsilon\nabla(\rho\vec{u}\vec{u})] = -\nabla p + \nabla\tau + S_u$	$S_u = (-\mu/K)\vec{u}$	$S_u = (-\mu/K)\vec{u}$	$\vec{u} = 0$
species	$\partial(\epsilon C_k)/\partial t + \nabla(\vec{u}C_k) = \nabla(D_k^{\text{eff}}\nabla C_k) + S_k$		$S_k = -\nabla[(n_d/F)i_e] - (s_k j/nF)$	$S_k = -\nabla[(n_d/F)i_e]$
charge	$\nabla(\kappa^{\text{eff}}\nabla\Phi_e) + S_\Phi = 0$ $\nabla(\sigma^{\text{eff}}\nabla\Phi_s) - S_\Phi = 0$		$S_\Phi = j$	
energy	$\partial[(\rho c_p)_m T]/\partial t + \nabla(\rho c_p \vec{u} T) = \nabla(k^{\text{eff}}\nabla T) + S_T$		$S_T = j[\eta + T(\mathrm{d}U_o/\mathrm{d}T)] + (i_e^2/\kappa^{\text{eff}})$	$S_T = i_e^2/\kappa^{\text{eff}}$

[a] Electrochemical reaction $\sum_k s_k M_k^z = ne^-$, where $M_k \equiv$ chemical formula of species k, $s_k \equiv$ stoichiometry coefficient, and $n \equiv$ number of electrons transferred. In PEM fuel cells there are (anode) $H_2 - 2H^+ = 2e^-$ and (cathode) $2H_2O - O_2 - 4H^+ = 4e^-$.

Macroscopic models use macroscopic mass, energy and momentum balances to predict fluxes.

Effective mass transfer coefficients and conductivities are required as inputs.

Wang, *Chem. Rev.* 2004.

Macroscopic Modeling

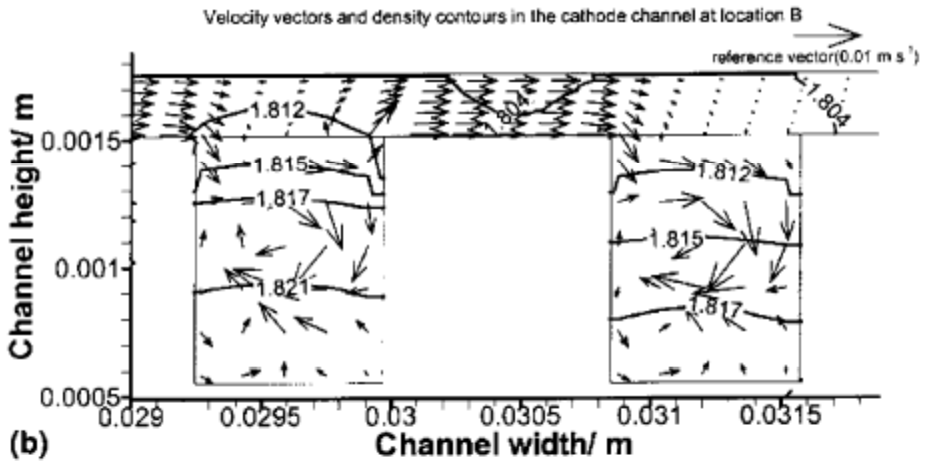

Figure 7. Velocity vectors and gas density contours under very low humidity operation: (a) in the middle and (b) at the exit of a 10 cm^2 PEFC.[58]

Example outputs from macroscopic models: flow field in the bipolar plate channels.

Wang, *Chem. Rev.* 2004.

Macroscopic Modeling

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Table 2. Comparisons of Representative CFD Models for Polymer Electrolyte Fuel Cells (PEFCs)

Model Features	CFDRC	Fluent	Penn State U.	STAR-CD Japan	STAR-CD N. America	U. Kansas	U. Miami	U. South Carolina	U. Victoria
Domain Meshed									
Catalyst layers	✓	✓	✓	✓	×	×	✓	×	×
Membrane	✓	✓	✓	✓	×	×	✓	×	✓
Gas diffusion layers	✓	✓	✓	✓	✓	✓	✓	✓	✓
Gas channels	✓	✓	✓	✓	✓	×	✓	✓	✓
Approach/Assumptions									
Species variable	mass fraction	mass fraction	molar conc./ mass fraction	molar conc. /mass fraction	mass fraction	mole fraction	mole/mass fraction	mass fraction	mass fraction
Density	variable	variable	variable/ constant	variable	variable	N/A	constant	variable	variable
Mass source/sink in continuity equation	×	✓	✓	✓	✓	×	×	✓	×
Physics Included									
CL ohmic loss	✓	✓	✓	✓	×	×	✓	×	×
CL transport loss	✓	✓	✓	✓	×	×	✓	×	×
Water transport thru membrane	×	×	✓	✓	✓ (w/ const. properties)	×	×	✓ (w/ const. properties)	×
Electron transport	✓	✓	✓	✓	×	×	×	×	×
Contact resistance	×	✓	✓	✓	×	×	×	×	×
Non-isothermal	×	×	✓	✓	✓	×	✓	✓	✓
Two-phase flow in GDL	M^2 Model	×	M^2 Model	M^2 Model	×	UFT Model	M^2 Model	×	UFT Model
GDL hydrophobic effects	×	×	✓	✓	×	×	×	×	×
Two-phase flow model in channels	mist flow	×	mist flow & annular film	mist flow	×	×	×	×	un-specified
References/Notes	63, 73	90	55, 59, 14, 64, 67, 81	based on PSU model	based on SC model	69-71	54, 72	57, 58, 60	62, 74

Wang, *Chem. Rev.* 2004.

Macroscopic Modeling

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Modeling of Catalyst Layers (Electrode/Electrolyte Interface)

In most of the macroscopic models reported in the literature the active catalyst layer was not the main point of interest but rather treated either as an infinitely thin interface or a macrohomogeneous porous layer. There were a few detailed models specifically developed for PEFC catalyst layers based on the theory of volume averaging. In this field distinction is further made between a homogeneous approach, a film model, and an agglomerate model. The homogeneous model assumes the catalyst layer to be a two-phase system consisting of ionic and electronic phases only, without gas voids. The gaseous reactant transports through the catalyst layer via the electrolyte phase as a dissolved species, and thus the diffusion rate is poor. In the film model gas pores are assumed to exist along with the electronic particles covered by a thin film of polymer electrolyte. On the other hand, the agglomerate model considers gas pores to surround agglomerates consisting of electrolyte films and electronic particles, i.e., a three-phase system. Depending on the pore geometry, agglomerates are planar, cylindrical, and spherical. Nonetheless, all three models belong to the macroscopic theory for multiphase systems in which there is neither resolution to capture pore-level phenomena nor ability to assess the morphological effects.

Wang, *Chem. Rev.* 2004.

Modeling Reviews

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Chem. Rev. 2004, *104*, 4679–4726

Modeling Transport in Polymer-Electrolyte Fuel Cells

Adam Z. Weber* and John Newman

Department of Chemical Engineering, University of California, Berkeley, California 94720-1462

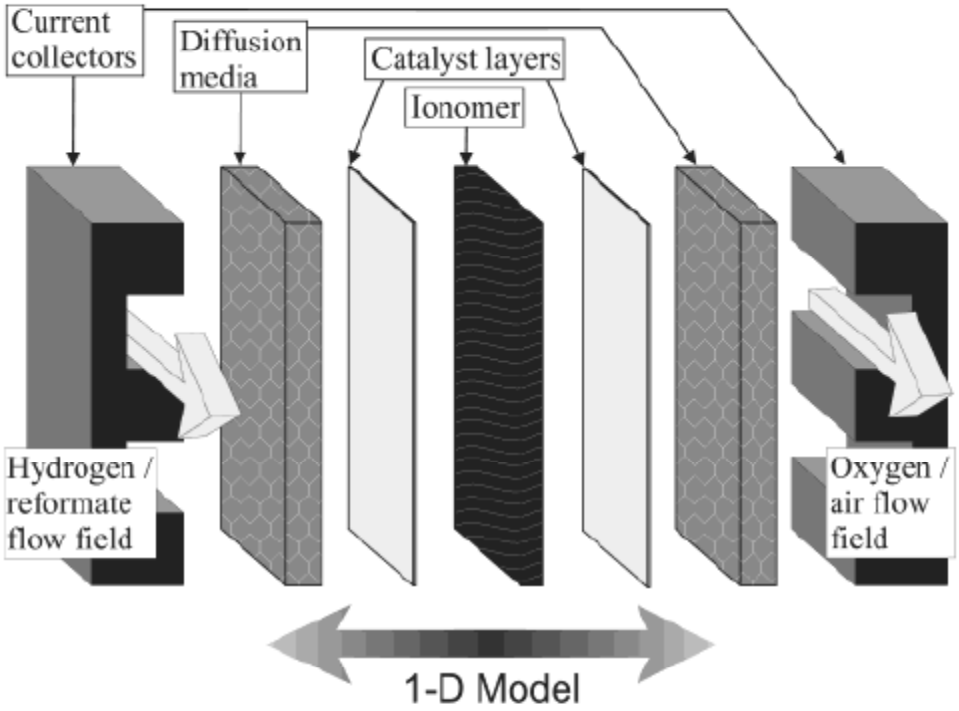

Figure 5. 3-D schematic showing the various layers of the fuel-cell sandwich.

Weber & Newman, *Chem. Rev.* 2004.

Modeling Reviews

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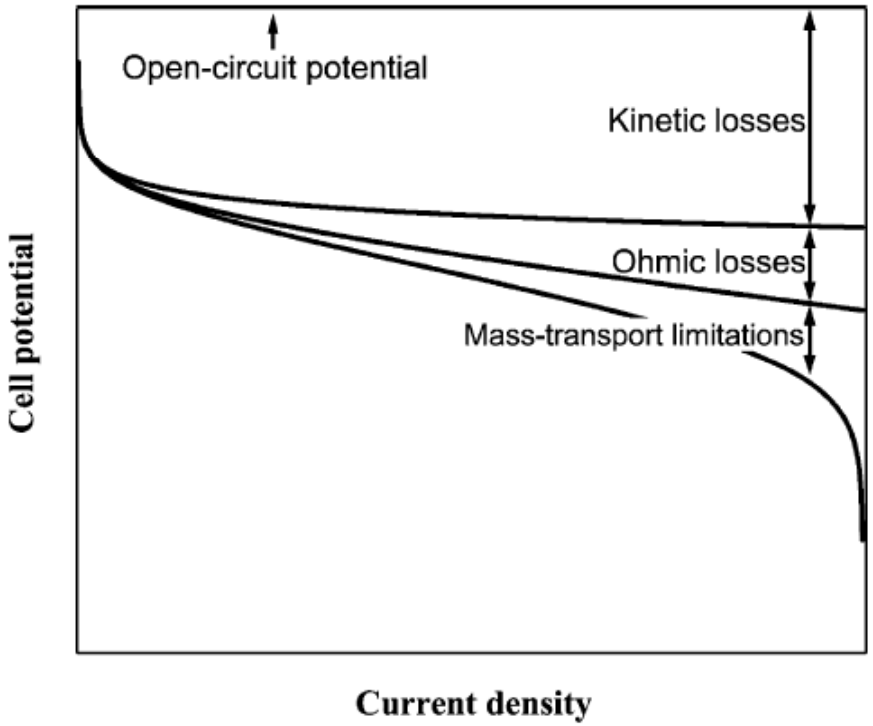

Figure 3. Example of a polarization curve showing the typical losses in a polymer-electrolyte fuel cell.

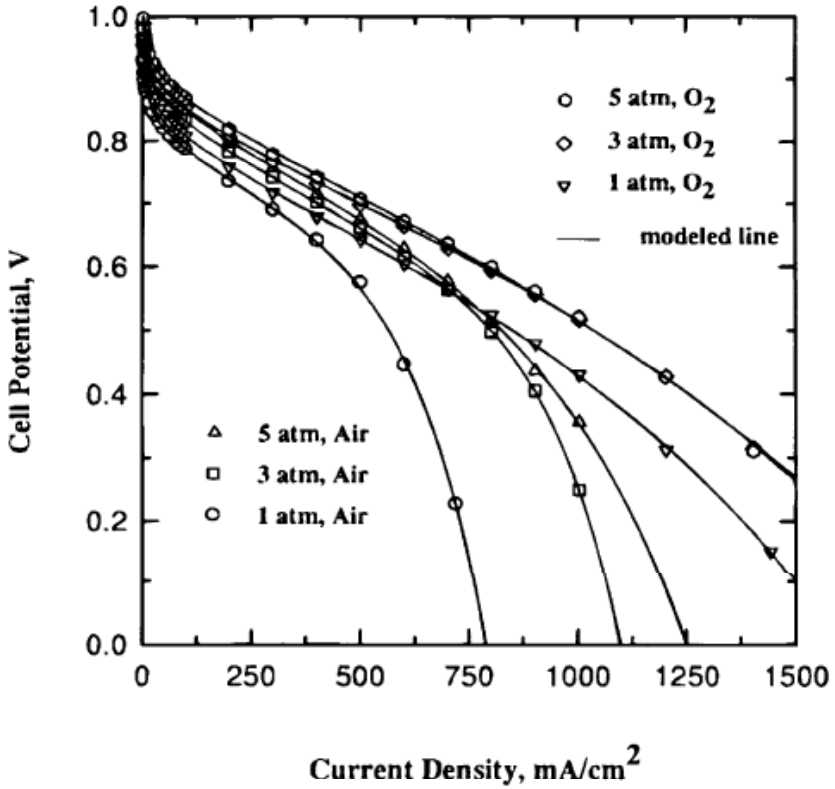

Figure 4. Model and experiment comparison of polarization curves for air or oxygen at different gas pressures and at 70 °C using eq 20. (Reproduced with permission from ref 12. Copyright 1995 The Electrochemical Society, Inc.)

Weber & Newman, *Chem. Rev.* 2004.

Modeling Reviews

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Modeling of Catalyst Layers (Electrode/Electrolyte Interface)

Overall, the interface models are basically 0-D. They assume that all of the relevant variables in the catalyst layers are uniform in their values across the layer. This has some justification in that the catalyst layers are very thin, and it is adequate if other effects that are modeled are more significant; however, the catalyst layers should be modeled in more detail to ensure that all the relevant interactions are accounted for and to permit optimization of such parameters as catalyst loading.

Weber & Newman, *Chem. Rev.* 2004.

Conclusions

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In the development of next generation fuel cells, there are several points that become apparent:

- Optimization of membranes with high performance at higher temperatures requires an understanding of the molecular-level mechanism for water and charge transport through the membrane.
- This understanding can guide synthetic chemists to develop new membrane materials with superior performance.
- Lecture 02 in this course provides a picture of the current understanding of molecular-level structure of proton exchange membranes.

- The interface between the electrode and electrolyte (the catalyst layer) is the area of greatest ignorance.
- Molecular level understanding of the structure of and transport through these interfaces would be very useful to design nanostructured interfaces with enhanced performance.
- Lecture 03 in this course provides a picture of the current understanding of molecular-level structure of the electrode/electrolyte interface in PEM fuel cells.