Membranes for Operation Above 100^{o}C

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*N.B. Strong Collaboration on several elements with Virginia Tech

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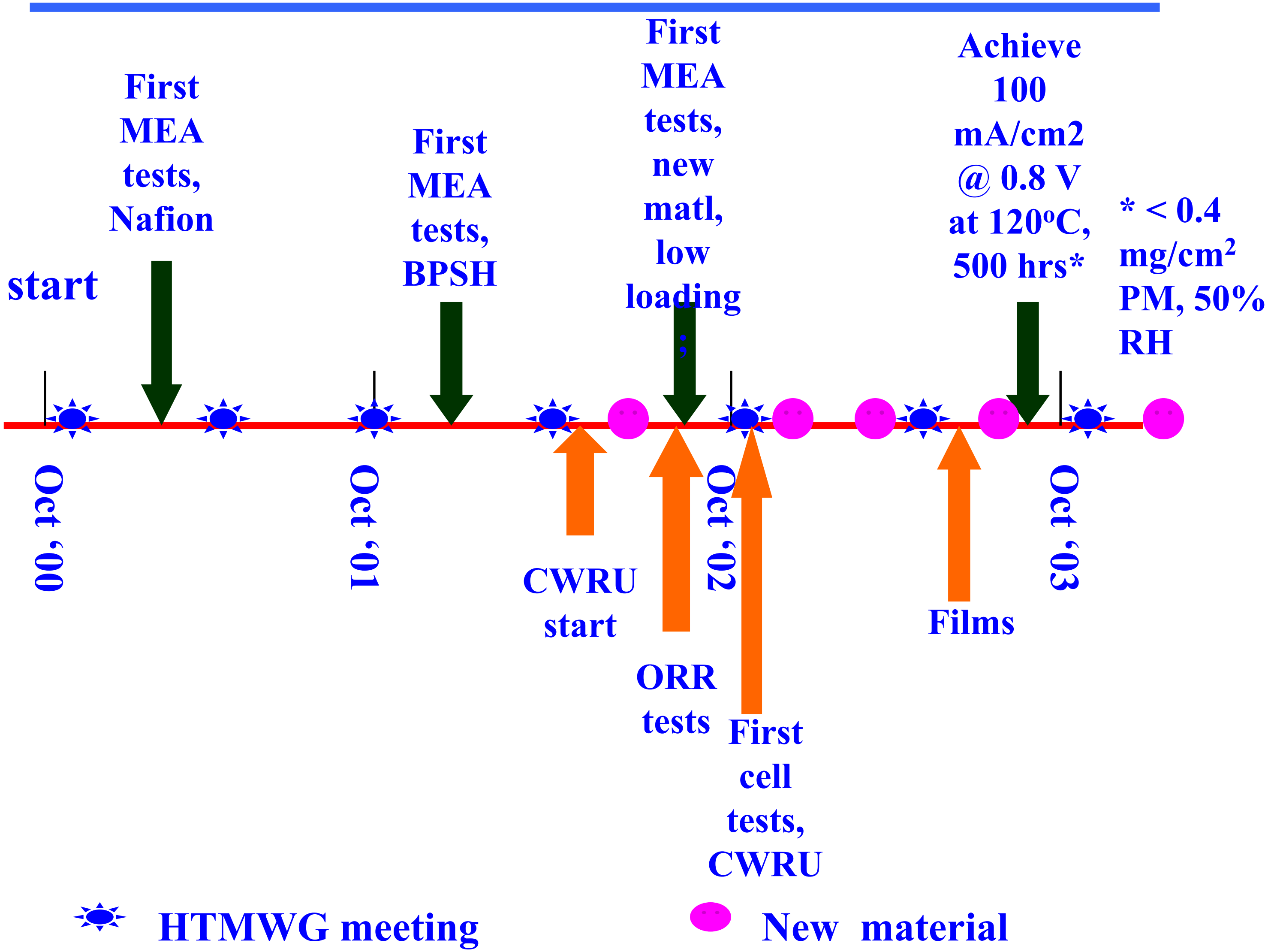
High Temperature Membranes
Outline and Approach

- Fundamentals
- New Electrolytes: Polymers and Additives
- MEAs
- High Temperature Membrane Working Group

Timeline


start
First MEA tests, Nafion
First MEA tests, BPSH
First MEA tests, new matl, low loading
;
Achieve 100 mA/cm2 @ 0.8 V at 120°C, 500 hrs*
* < 0.4 mg/cm² PM, 50% RH
Oct '00
Oct '01
Oct '02
Oct '03
CWRU start
ORR tests
First cell tests, CWRU
Films
HTMWG meeting
New material

Membrane Fundamentals: Rationale and Approach

- There is a strong need to understand proton transport and coupled solvent transport in polymer electrolyte membranes
  - Energetics of proton transfer from acid moieties
  - Transport along pores
  - Acid-base interactions and how they facilitate proton transport

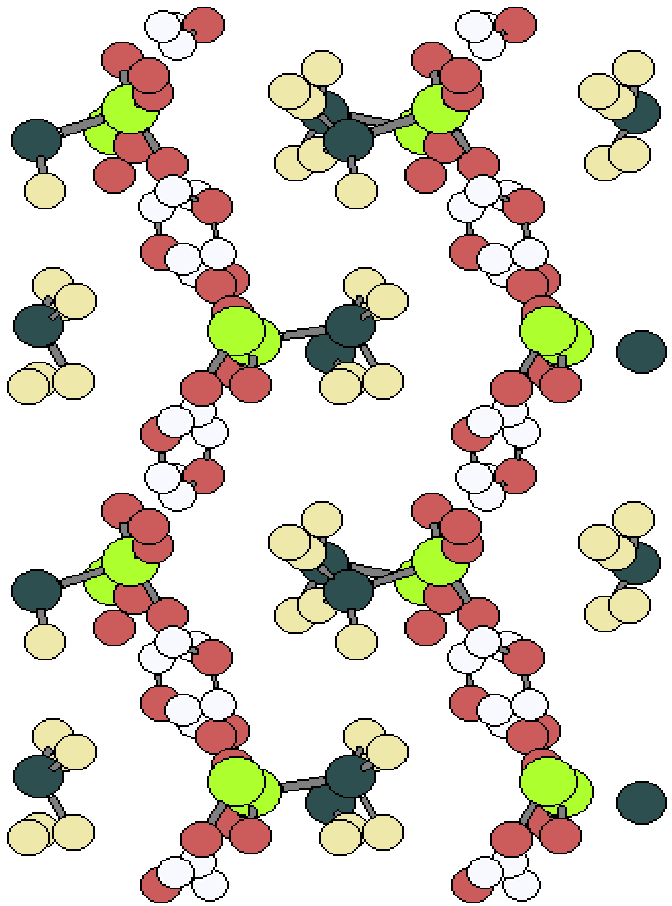
- Our Approach:
  - Develop computational tools to promote this understanding
  - Use computational methods for ‘screening’ of new structures
  - Develop new experimental approaches to obtain information on solvent structure, dynamics as well as on interactions within membrane

Computational Studies: Targets

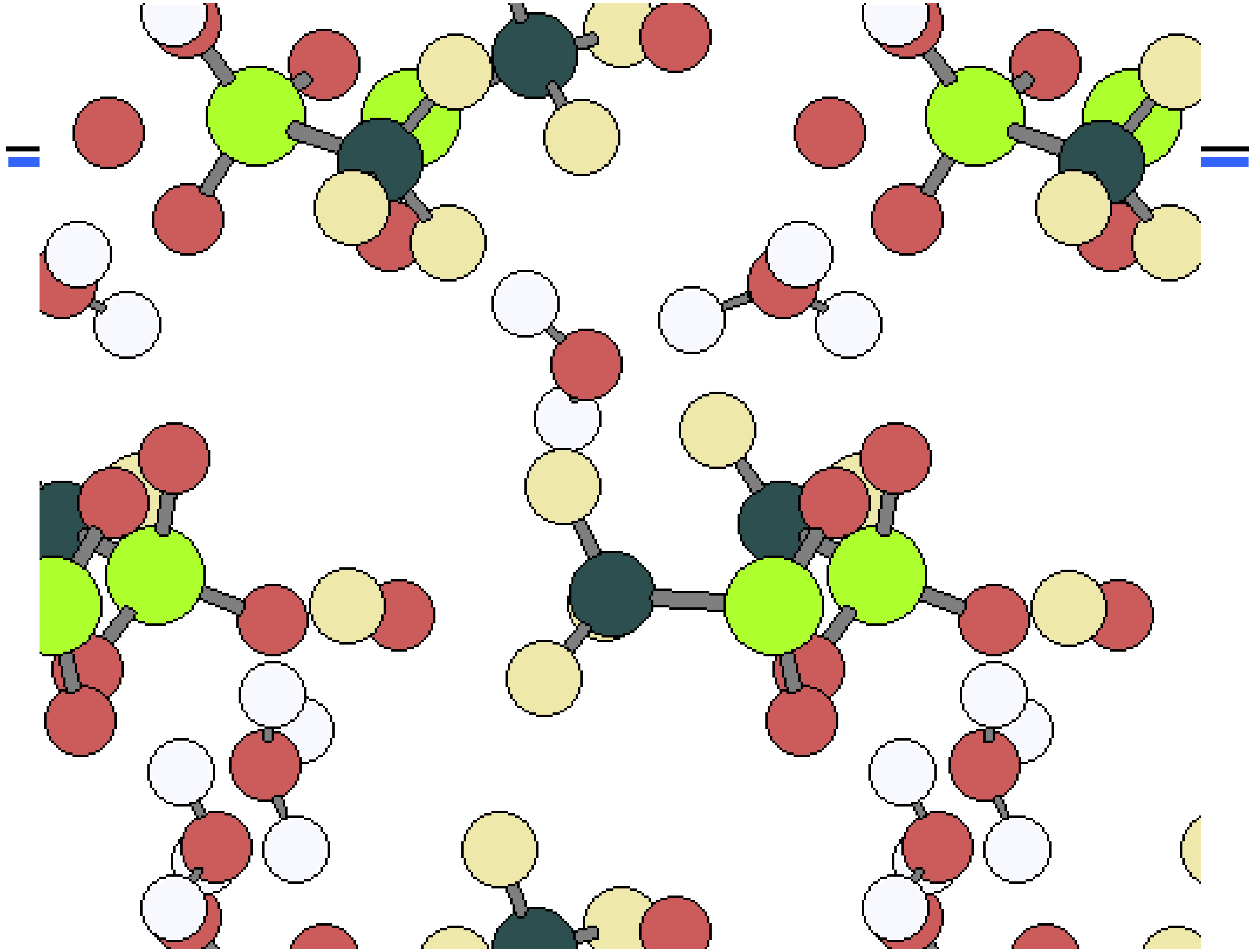
- Target 1: Understand proton transfer in aqueous-swollen polymer systems
  - Study energetics and dynamics of process
  - Compare strengths of various target acid
  - Morphology effects
- Target 2: Tailor bases to mimic water
  - Substituted imidazoles
  - Other proton carriers
- Target 3: Understand proton transport in phosphoric acid/basic polymer systems
- Target 4: Augment experiments on new polymers, additives of various types

Searching for Key Intermediates in H^+ Transport: *Ab Initio* MD Studies

Triflic Acid Monohydrate Crystal



After a microcanonical MD run of 20 000 time steps



A Zundel ion is formed during the thermalization !

Also: direct sidechain to sidechain transfer can be seen

New Materials Under Development

- Three classes of materials are presently in preparation and testing:

  1. Polymers and inorganic materials with controlled pore size to be modified with acid groups lining pores

  2. Polymeric systems with intrinsically stronger acid groups

  3. Polymer systems swollen or imbibed with tailored proton acceptors

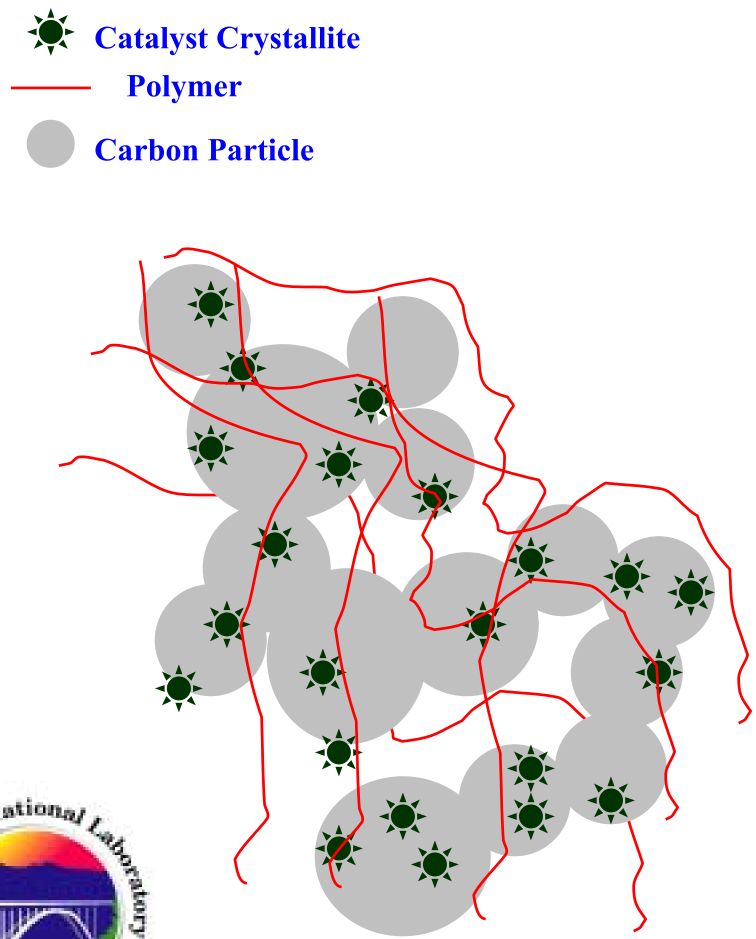
- These are useful both intrinsically and as test or model systems

- At least two more types of materials are ‘on the drawing board’

MEAs: Size Related Hierarchy of Electrode Issues

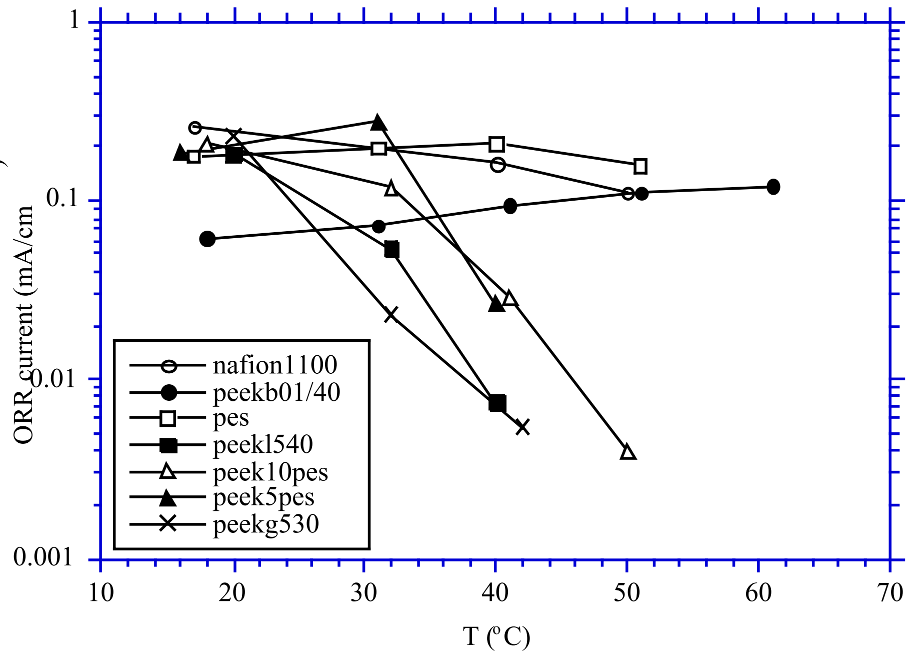
- Macro scale (CCM level): adhesion phenomena, polymer segregation in catalyst layer, mechanical properties of electrode and membrane
- Meso scale (agglomerate level): mass transport of gases, continuous proton and electron conducting pathways
- Nano scale (local level): proton accessibility to site, electrocatalysis, polymer adsorption, polymer mobility
- **Observed difficulties in preparing CCMs with good performance stem from each of these**

Microstructural Influences are Especially Important for High Temperature Electrodes



- Wide range of environments -> different degrees of proton access to surface
- Constrained dynamics., local interaction
- Polymer adsorption? Conformation?

Pt Microelectrode Studies of ORR with Various Polymers

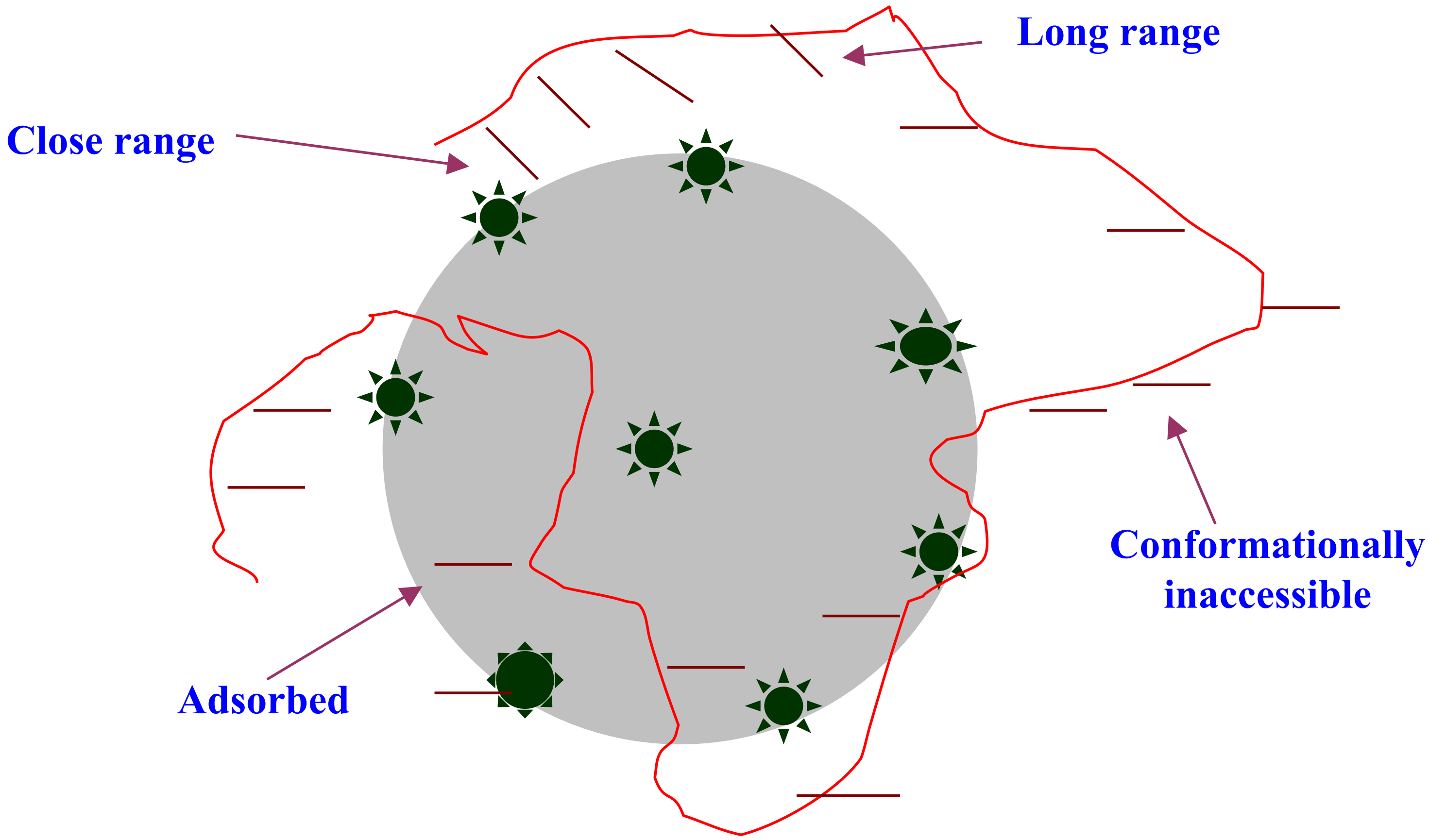


Conclusion: dramatic negative impact of using weaker acid electrolyte under conditions of low water content in film

>>>consistent with results observed in fuel cell electrodes

ORR current density at 0.85 V as a function of temperature for a series of water-vapor equilibrated polymer samples.

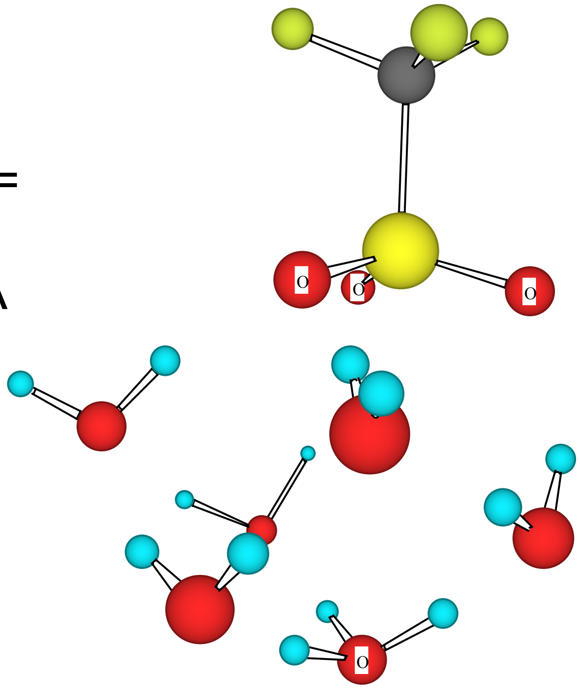
Interactions between Polymer-bound Acid Groups and Catalyst Particles

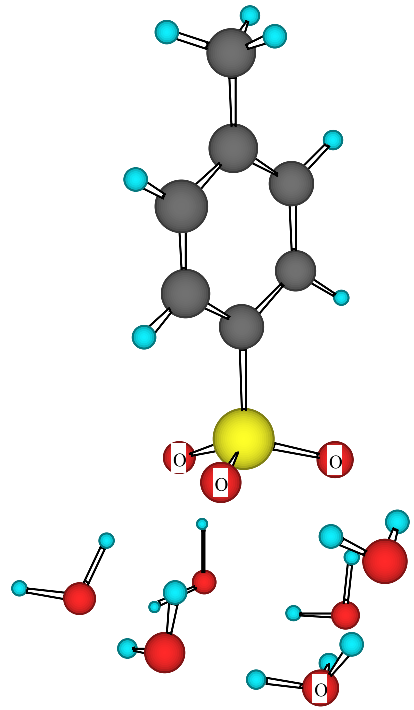


Solvation of Protons:
Direct DFT Computations on Water-Acid Complexes

r(**O–O**)=

4.235 Å



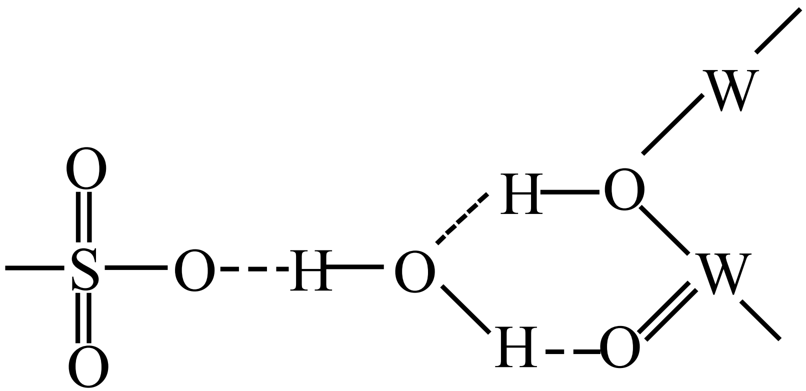


r(**O–O**)=

3.914 Å

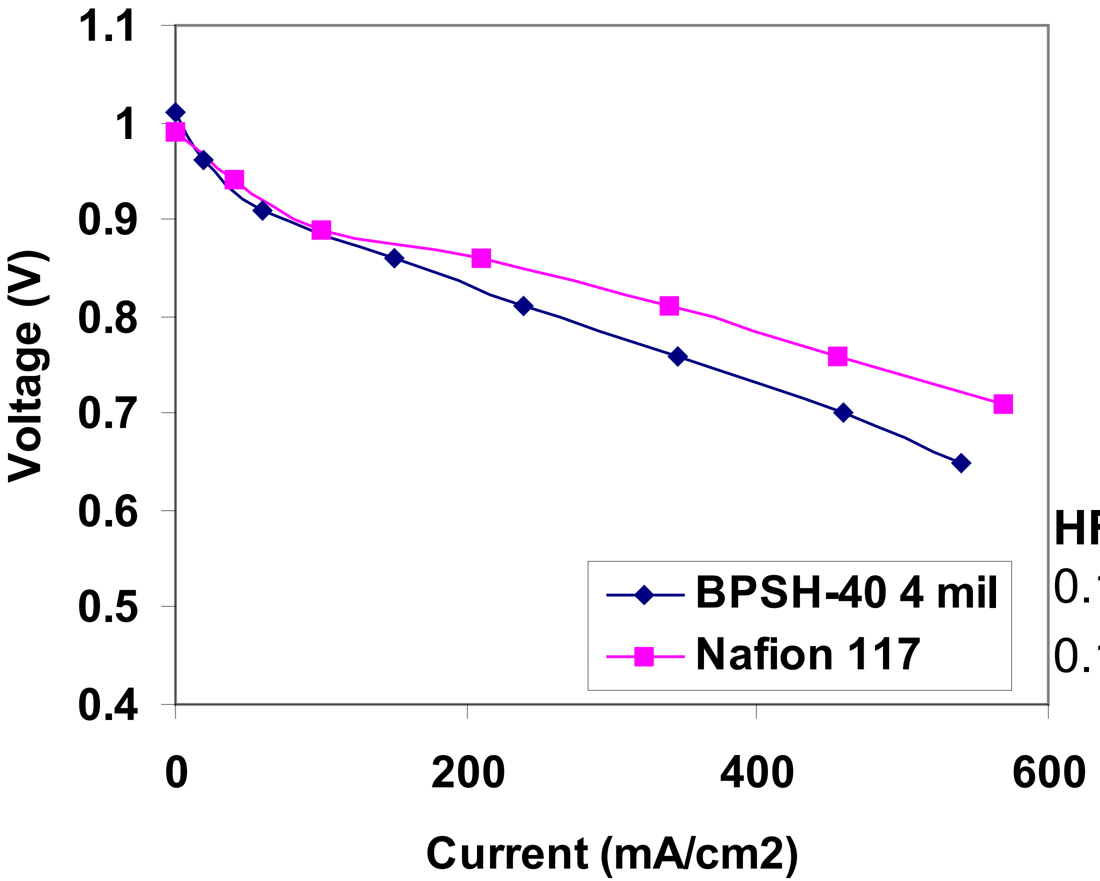
Differences in acid strength
--> Differences in separation distances
---> Large energetic differences for proton donation

Proton transfer at PTA/SO_3H interface: An example of intimate interaction needed to facilitate conduction



- Nanocomposite formed in BPSH/PTA membrane
- FT-IR results indicate H-bonding interaction
- Intimate interaction is required for good conductivity
- How to translate to electrodes?

MEA Results with VPI Polymer



Anode: 10 mg/cm^2 Pt/Ru black
Cathode: 6 mg/cm^2 Pt black

80°C cell temperature
30 psig An/Cath

HFR

0.11 $\Omega\cdot cm^2$

0.17 $\Omega\cdot cm^2$

note: BPSH-40 membrane with BPS anode and Nafion cathode

High Temperature Membrane Working Group

- Meeting bi-annually (typically associated with ECS meetings)
- Fall '01 Meeting
  - Presentations from PA/PBI researchers, UConn
  - Impromptu presentations from Gore, VPI
  - Industry input on targets
  - Discussed roadmap

- Spring '02 Meeting to be held in Philadelphia after ECS

- Representatives from a variety of industry, academic and national lab groups
- Universities involved in program
  - CWRU, Penn State, VPI, UConn, Northeastern, Wisconsin
  - New: JPL, Arizona State

Status and Near Future Milestones

- **Computational Studies: will be reported on in full in Fall ‘02**
- **Initial novel electrolytes to be tested in cell by September ‘02**
- **MEAs: Initial tests on enhancing electrode performance in progress**
- **Extensive synthesis work underway**

- **Team at CWRU**
  - Staff including polymer, molecule synthesis, polymer properties testing and fuel cell testing capability to be in place by July

- **Interactions with Outside World**
  - Beginning to make industrial contacts from CWRU for interaction
  - HTMWG established, meeting regularly with good participation from companies etc.

Future Work

- Computational Studies: more extensive work on novel systems
- Membrane Development: Developing methods for screening new concepts at higher rate; New electrolytes to be tested in fuel cells on 4 month cycle starting in fall
- MEAs/Electrodes: Expand initial tests on enhancing electrode performance; develop capability for probing ORR at temperature ex situ; develop understanding of interactions at buried interfaces within electrodes
- Develop reliable MEA fab approaches
- Developing means for scale-up of polymers, film-making and MEA production to modest scale-->Polymers are materials and must be developed to a certain level to be reliably tested
- Interactions with Outside World
  - Beginning to make industrial contacts from CWRU for interaction; emphasis on tech transfer, dissemination of ideas
  - HTMWG put on a more organized basis (streamlined funding mechanism, improved meeting scheduling); evolution toward a discussion group format, idea exchange