RECENT RESEARCH OF THE PBI/PA SYSTEM AS A PROTON CONDUCTOR IN ELECTROCHEMICAL SYSTEMS

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Presentation Outline

- Background on high temperature PEMs
- The PBI/PA system
- Vehicle conduction mechanism and acid migration in PA and PBI/PA system
- Nafion/PA system- how is it different?
- Things to think about?
- Acknowledgements

Why High Temperature PEMs

Greater tolerance to impurities
Smaller heat exchanger requirements
Simplified systems design

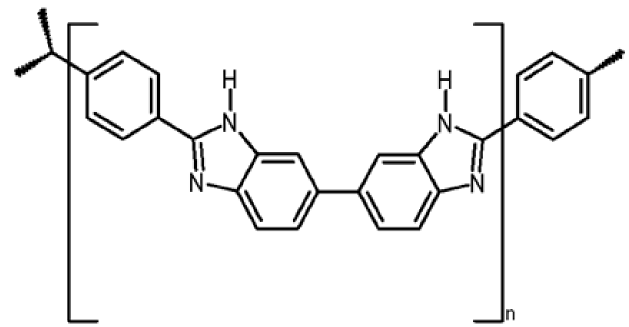
Potential Applications

- Fuel cells
  - Produces energy
- Water Electrolytic cells
  - Produces hydrogen
- Hydrogen Purifiers
  - Purify reformed Hydrogen
- Sensors and Chemical synthesis

High Temp PEMs based on acid doped basic polymers

PBI/PA Membranes

- PBI – Polybenzimidazole
  - Polymer with high thermal stability
  - Can be imbibed with phosphoric acid
  - Becomes proton conductive

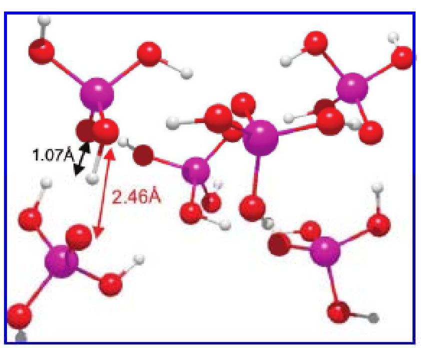


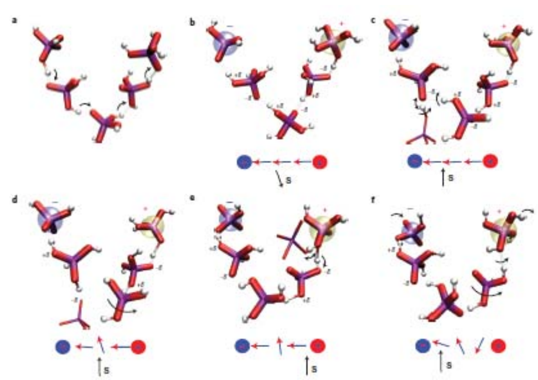
Polybenzimidazole repeat unit

Phosphoric Acid Conduction

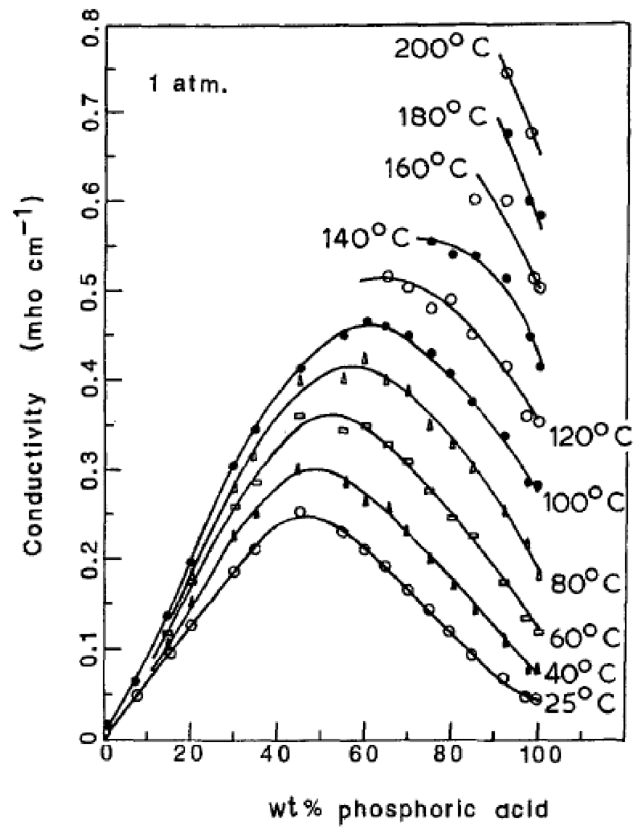
Recent theoretical studies
- The Grotthuss chain
- Hydrogen bonding network
- Minimum energy configurations
- Disorder degree and solvent interactions

Recent contributions on theoretical understanding of PA Grotthuss conduction
- Vilciauska, Paddison, Kreuer, J. Phys Chem., 113, 9193 (2009)
- Vilciauskas, Tuckerman, Bester, Paddison, Kreuer, Nature Chemistry, 4, 461 (2012)





- Very high conductivity
- Largely Grotthuss mechanism 98%

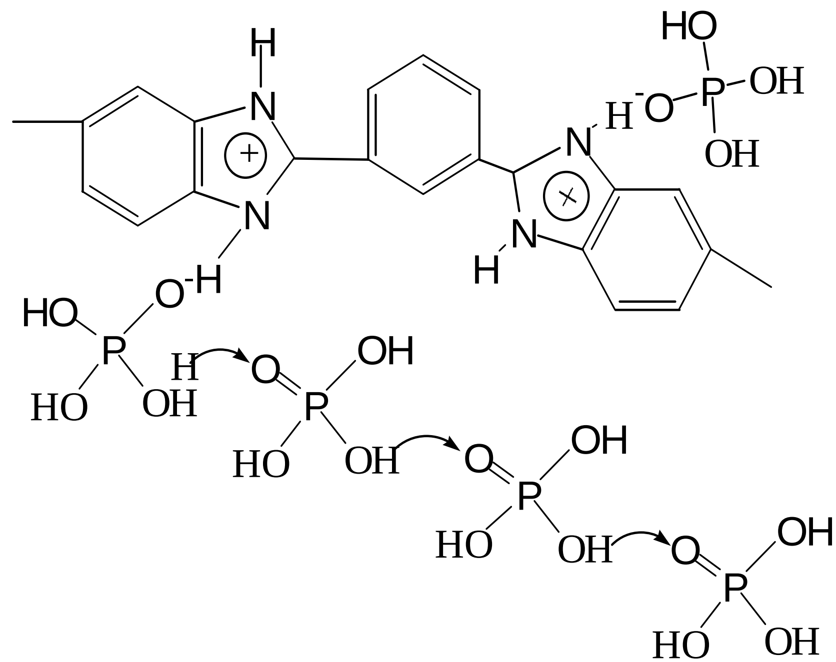


Chin, Chang, J . Appld Electrochem, 19, 95 (1989)

Mechanisms of PBI/PA Conductivity

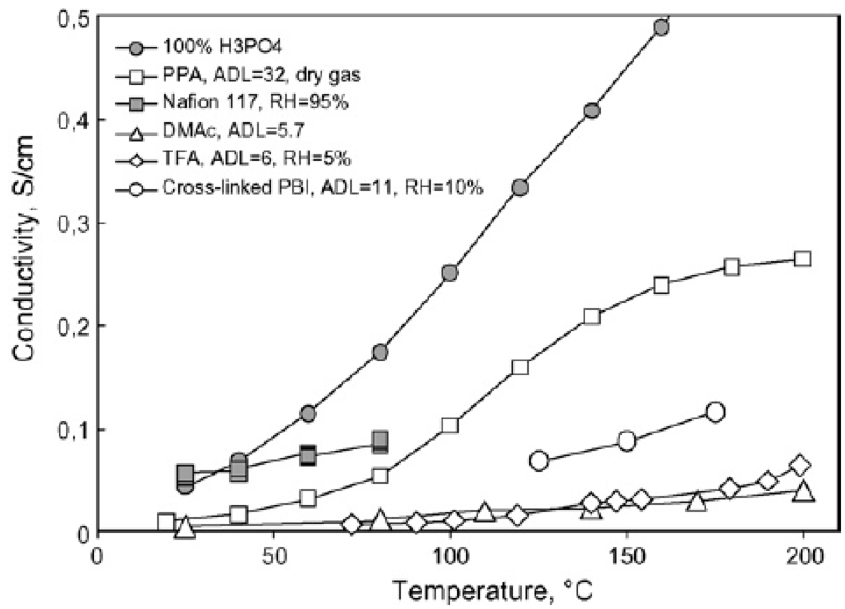
H_3PO_4 Protonates PBI

- **IR measurements indicate max protonation at n=2**
- Very low conductivity with n<2 indicating little N-H to N-H proton hopping
- **$H_2PO_4^-$ predominates over concentration range (n=6)**
- Solid state ^{13}C NMR shows interaction between acid and polymer
- Low activation volume measured
- **t_{H+} measured ~.98 for n=6**
- Activation energy consistent with Grotthuss mechanism



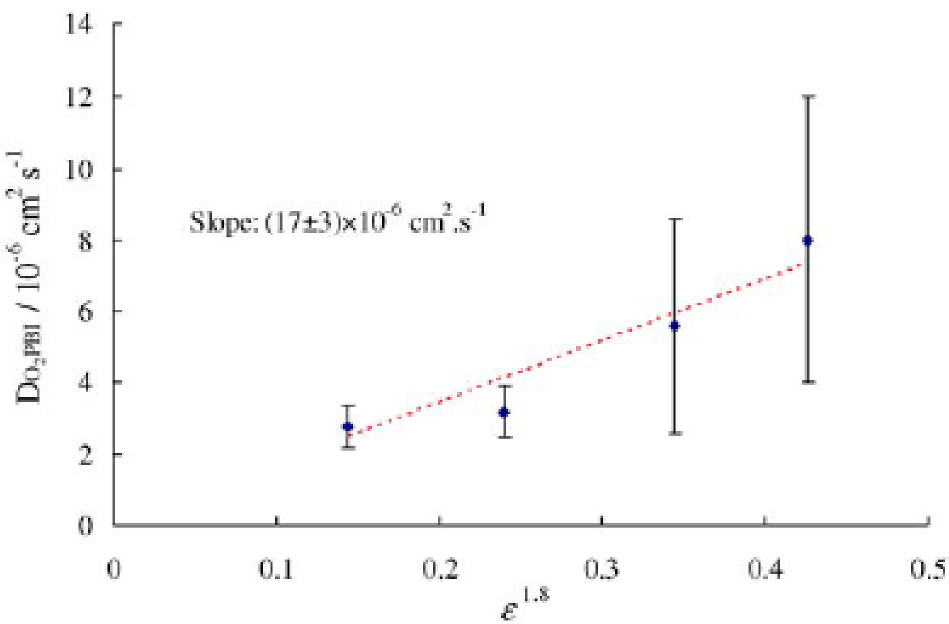
Conductivity and Transport Properties of PBI/PA System

Conductivity of Various PBI/PA Membranes and Nafion 117



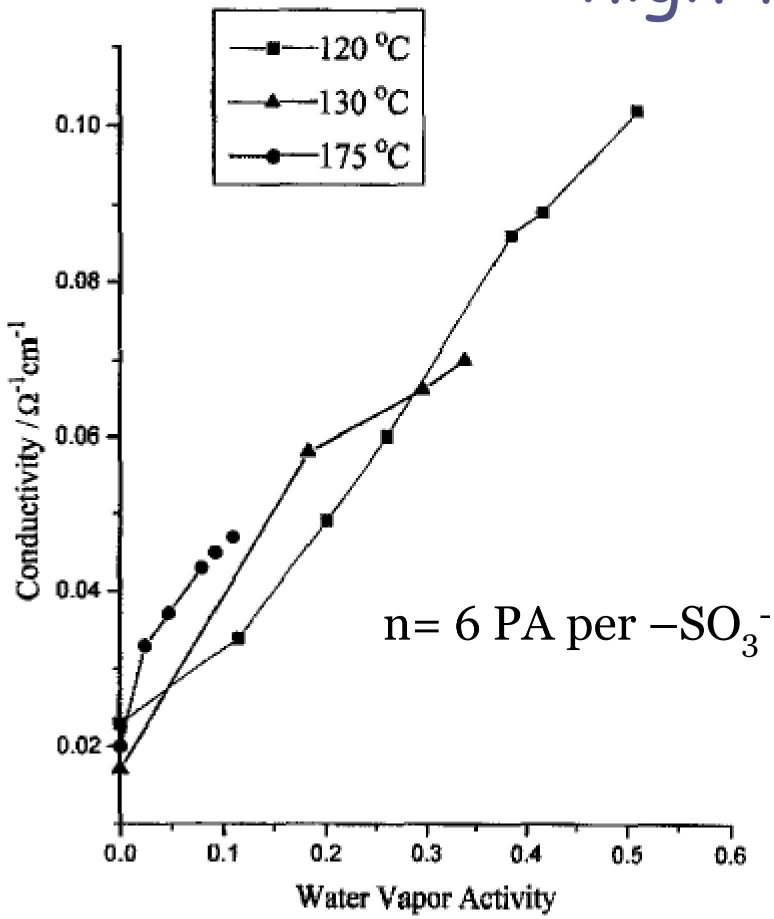
Q. Li, et al, Progress in Polymer Science, 2009; 34:449-477

Gas diffusion is through the amorphous PA phase



Z. Liu, Electrochimical Acta, 2006;51:3914-3923

Nafion doped with PA also conducts protons at high temperature



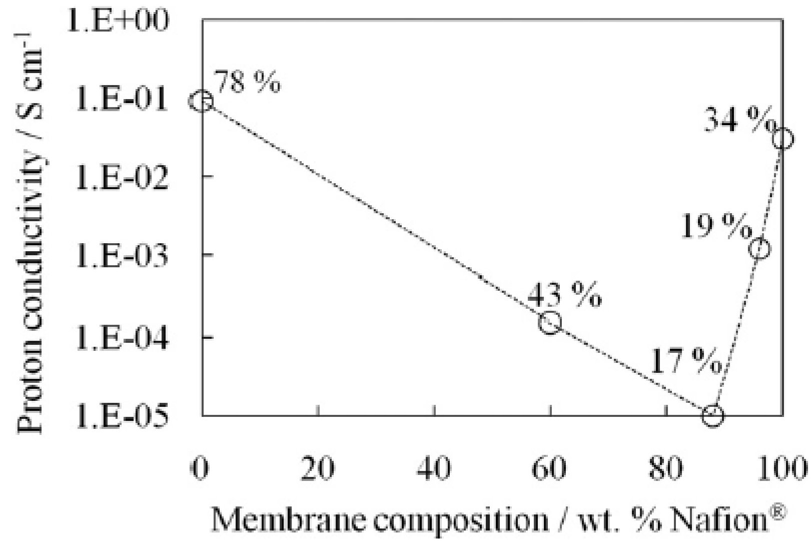


Fig. 7 – Proton conductivity of PA doped membranes at 130°C and relative humidity of 16–18%. The PA contents of the membranes are indicated in the figure.

Note: E. Yeager showed sulfonic acid protonates phosphoric acid

Savinell, Yeager, et al, J. Electrochem Soc, 141, L46(1994)
Aili, Hansen, Pan, Li, Christensen, Jensen, Bjerrum, Intr. J. Hydrogen Energy, 36 6985 (2011)

BUT……..

PAFCs work

PBI/PA FCs work

Nafion/PA FCs do not work???

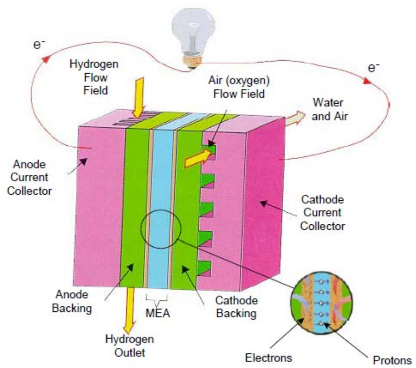


Figure 5-1 Principles of Operation of Phosphoric Acid Fuel Cell (Courtesy of UTC Fuel Cells)

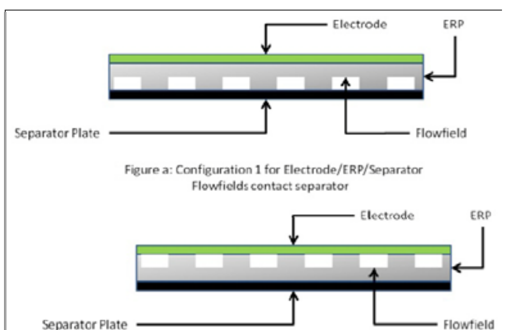
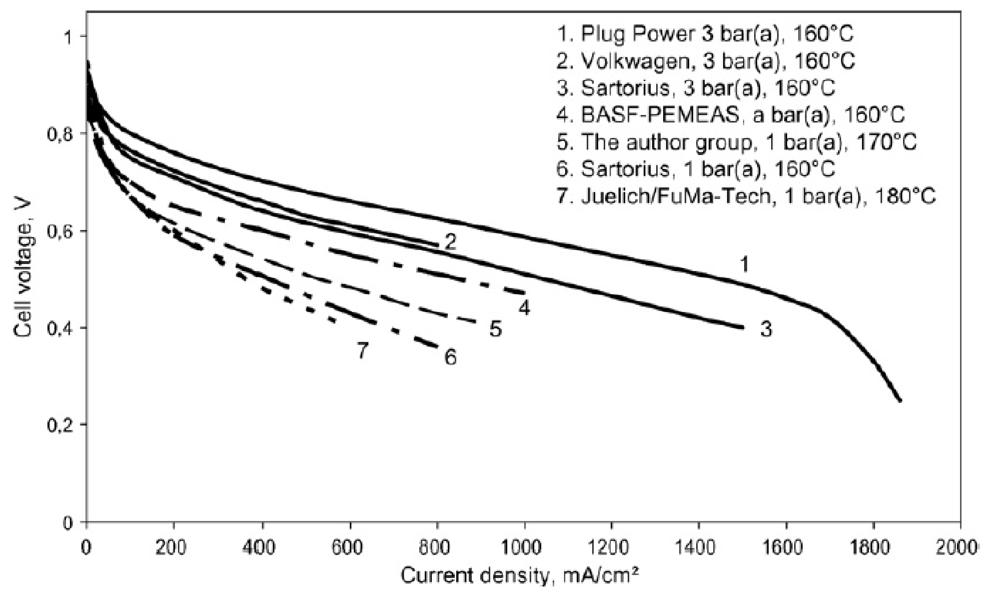


Figure a: Configuration 1 for Electrode/ERP/Separator Flowfields contact separator

Figure b: Configuration 2 for Electrode/ERP/Separator Flowfields contact electrode



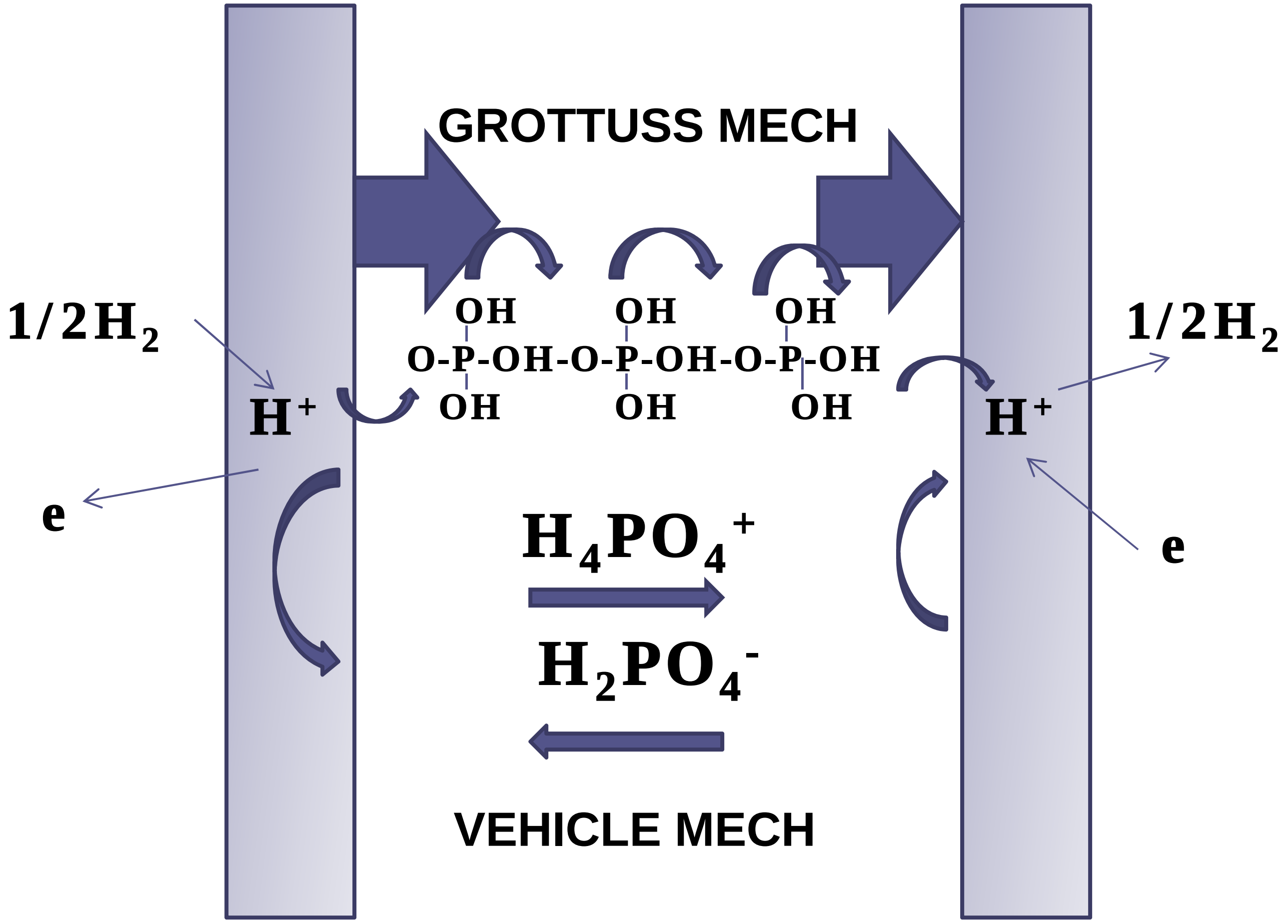
Objectives of Recent CWRU Research on PBI/PA

- Understand the degree of acid migration in PA doped membranes and effect on operation
- Investigate PBI/PA membranes for a hydrogen pump cell application- limited discussion related to acid transport here
- Improve mechanical strength of high acid content PBI/PA membrane through a simple composite structure- will not be discussed here

Questions about the proton conduction mechanism in the PBI/PA system

- What is the extent of acid migration due to a vehicle mechanism and where does the acid go?
- What is the role of the PBI on PA dissociation, and Nafion on PA dissociation?
- Why does PBI/PA seem to work but Nafion/PA does not in an operating fuel cell?

Proton Conductivity of Phosphoric Acid
Grotthuss and Vehicle Mechanism



Phosphoric Acid Equilibrium/Conductivity

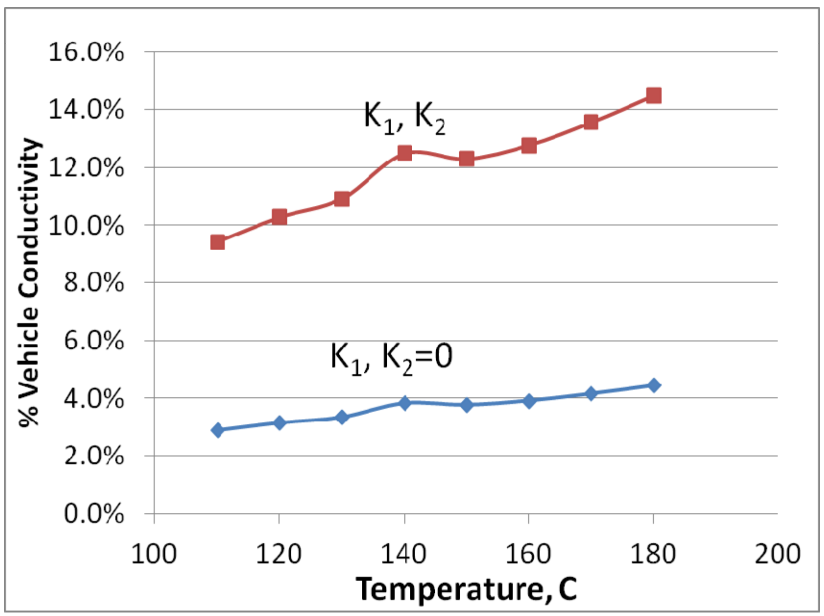
$$2H_3PO_4 \rightleftharpoons H_4PO_4^+ + H_2PO_4^-$$
$$3H_3PO_4 \rightleftharpoons H_3O^+ + H_4PO_4^+ + H_2P_2O_7^{-2}$$

$$K_1 = [H_4PO_4^+][H_2PO_4^-] = 0.14$$

$$K_2=[H_2P_2O_7^{-2}]^2[H_4PO_4^+]=.042$$

Spec's M/l	H2P2O7=	H4PO4+	H2PO4-
K_1, K_2=0	0	.37	.37
K_1, K_2	**.28**	.82	.26

$$\sigma_{measured} = F^2 \sum z_j^2 u_j c_j + \sigma_{Grotthuss}$$

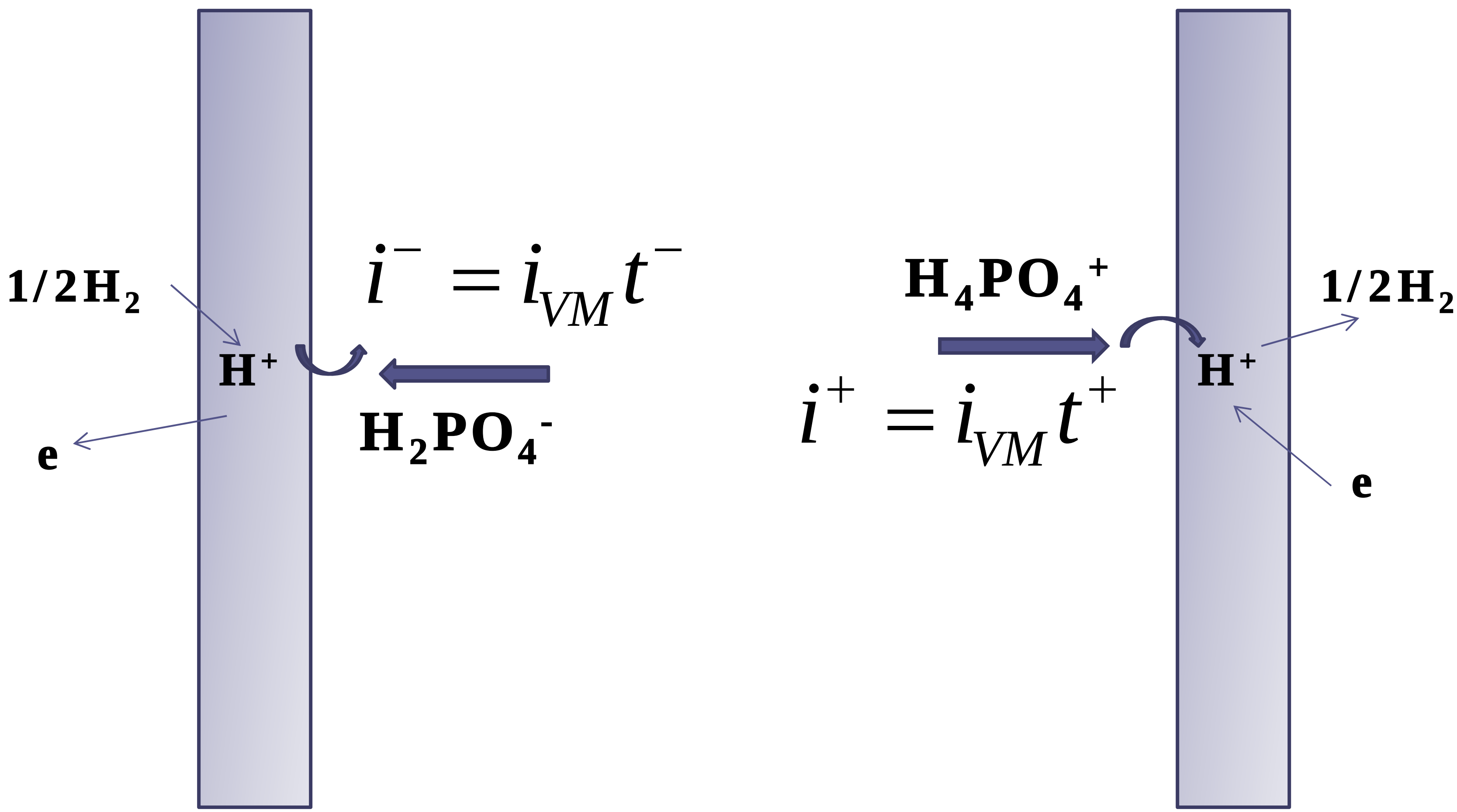


$$\frac{D\mu}{T} = Const$$

R. Munson, J.PhysChem, 68, 3374-3377 (1964)

Vehicle Current Density with Uniform Species Concentration

$$i_{VM} = i_{TOT} - i_{GROT} = \%_{vm}\, i_{TOT} = i^{+} + i^{-}$$

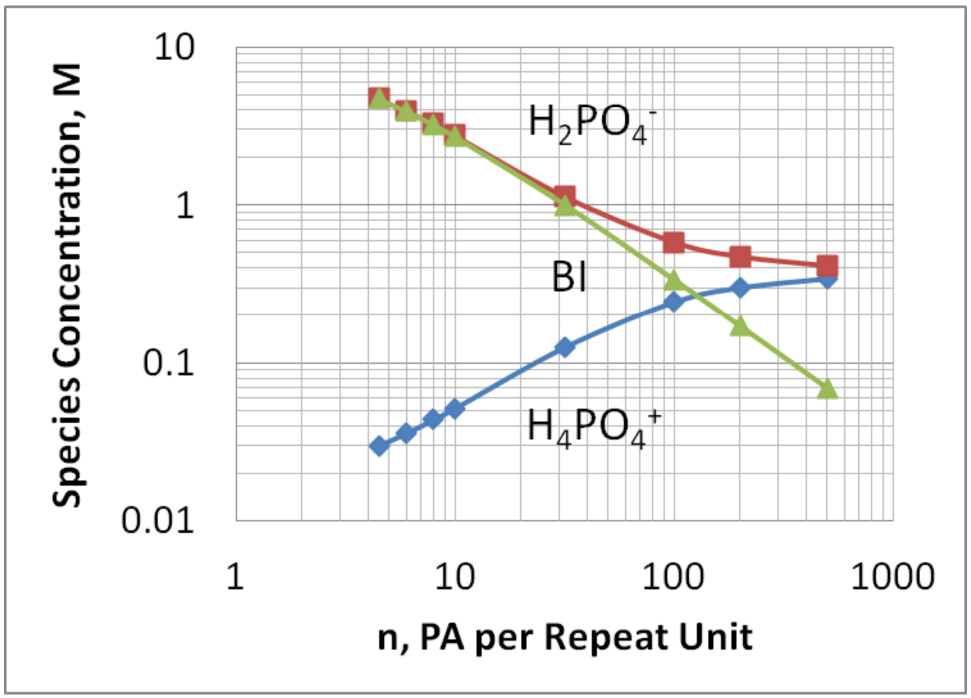


Effect of PBI on Phos Acid Speciation

$$BI + H_3PO_4 = BI^+[H_2PO_4^-]$$

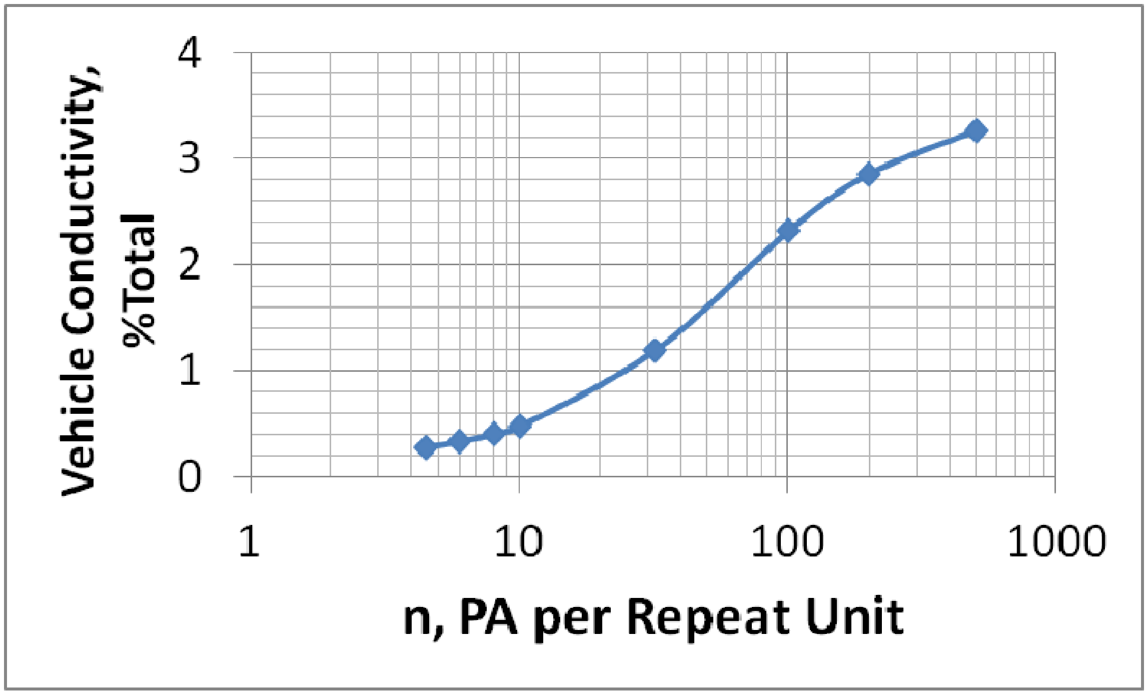
$$[BI][H_4PO_4^+] + [H_4PO_4^+]^2 - K_1 = \sqrt{K_2}[H_4PO_4^+]$$

Ignoring pyrophosphoric acid, i.e. K_2=0



Note: $H_2PO_4^-$ predominant species

Fraction of total conductivity due to the vehicle mechanism

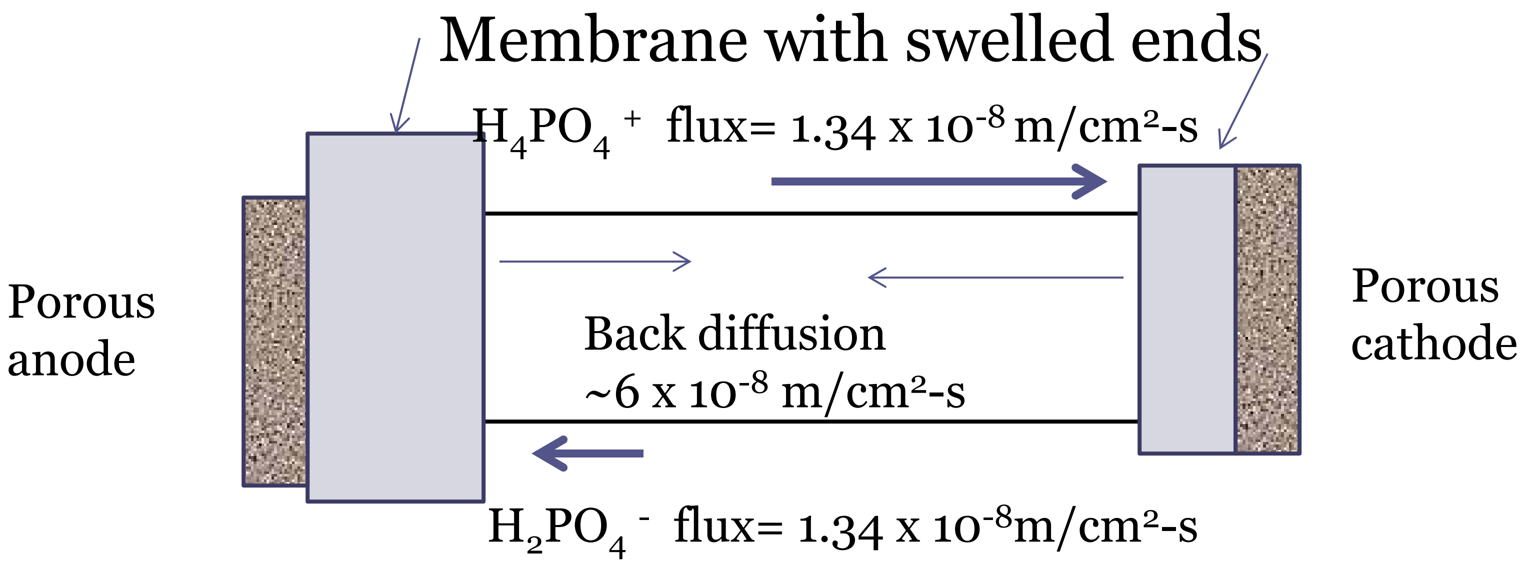


PA: pK=2.12
BI: pK~4.8
Assumes all protonated BI forms low dissociating BI-H_2PO_4 salt

t^+=.49 t^- =.51

Assumes a diffusion coefficient of ionic species in PA of 8.5 x 10^{-6} cm^2/s

Where does the migrating acid go??
Example: Total current density=200 mA/cm^2

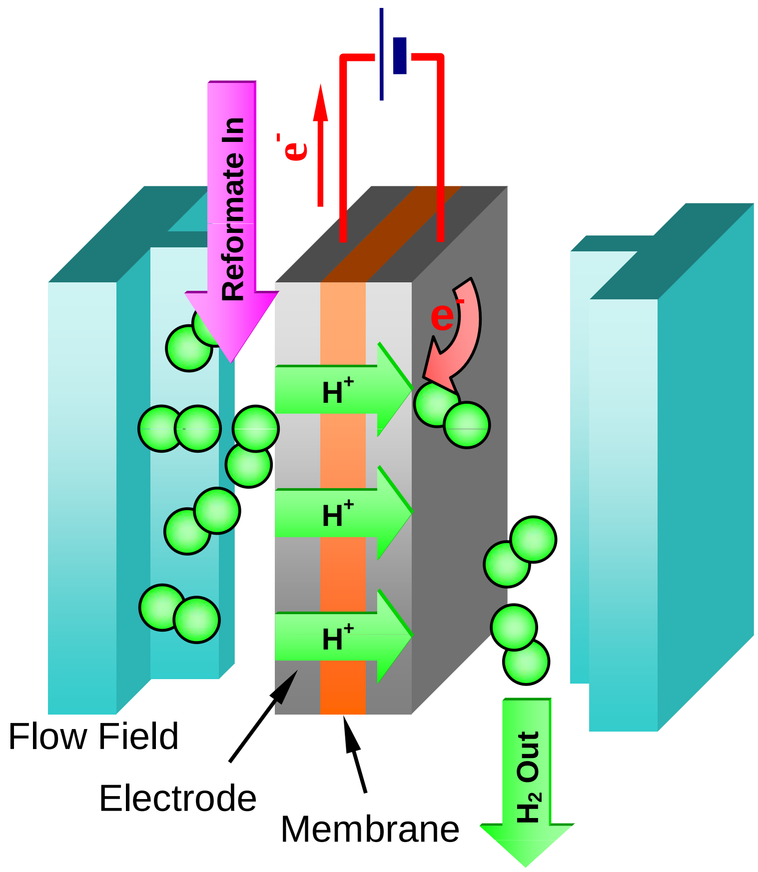


Back diffusion driven by polymer swelling and/or internal stress

Electrochemical fluxes in excess of back diffusion will leak into porous electrodes- surface tension driving forces of unsaturated larger pores drive acid back into sub-microporous membrane

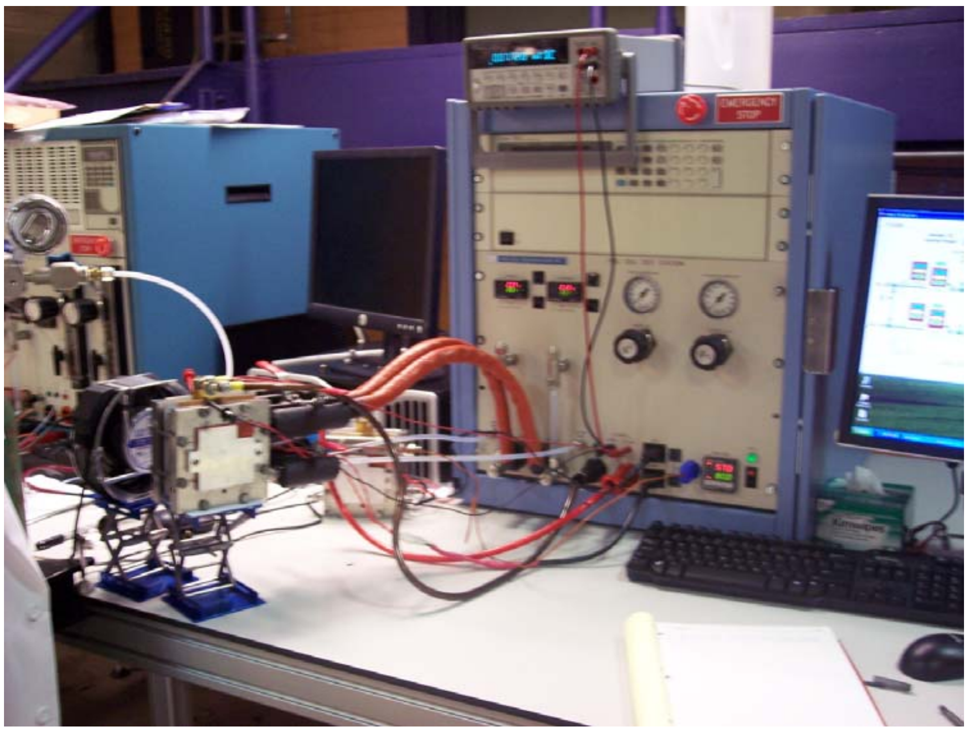
Acid Migration in a Hydrogen Pump Cell

- Hydrogen is oxidized at the anode and reduced at the cathode – H_2 pressurization and purification
- Simplest system to experimentally investigate the proton transport-symmetrical and no complications with ORR and water generation

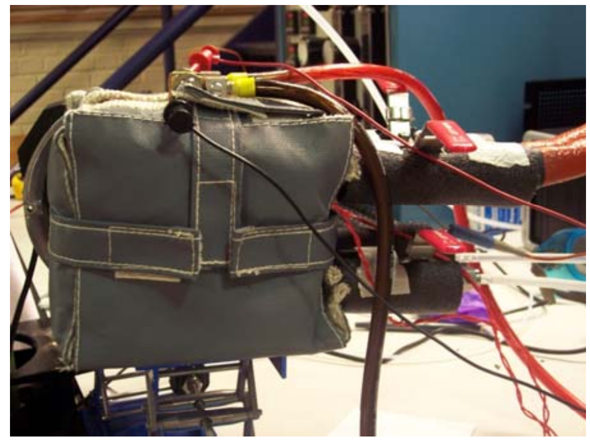


H_2 Pump Cell - experimental

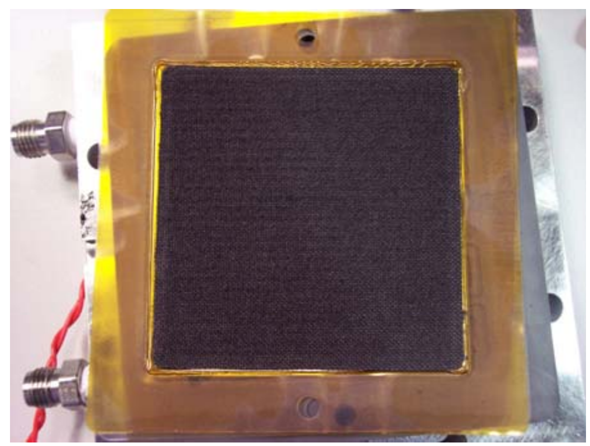
$H_2 \rightarrow 2H^+ + 2e$ anode
$2H^+ + 2e \rightarrow H_2$ cathode



Fuel Cell Technologies Test Stand and cell assembly



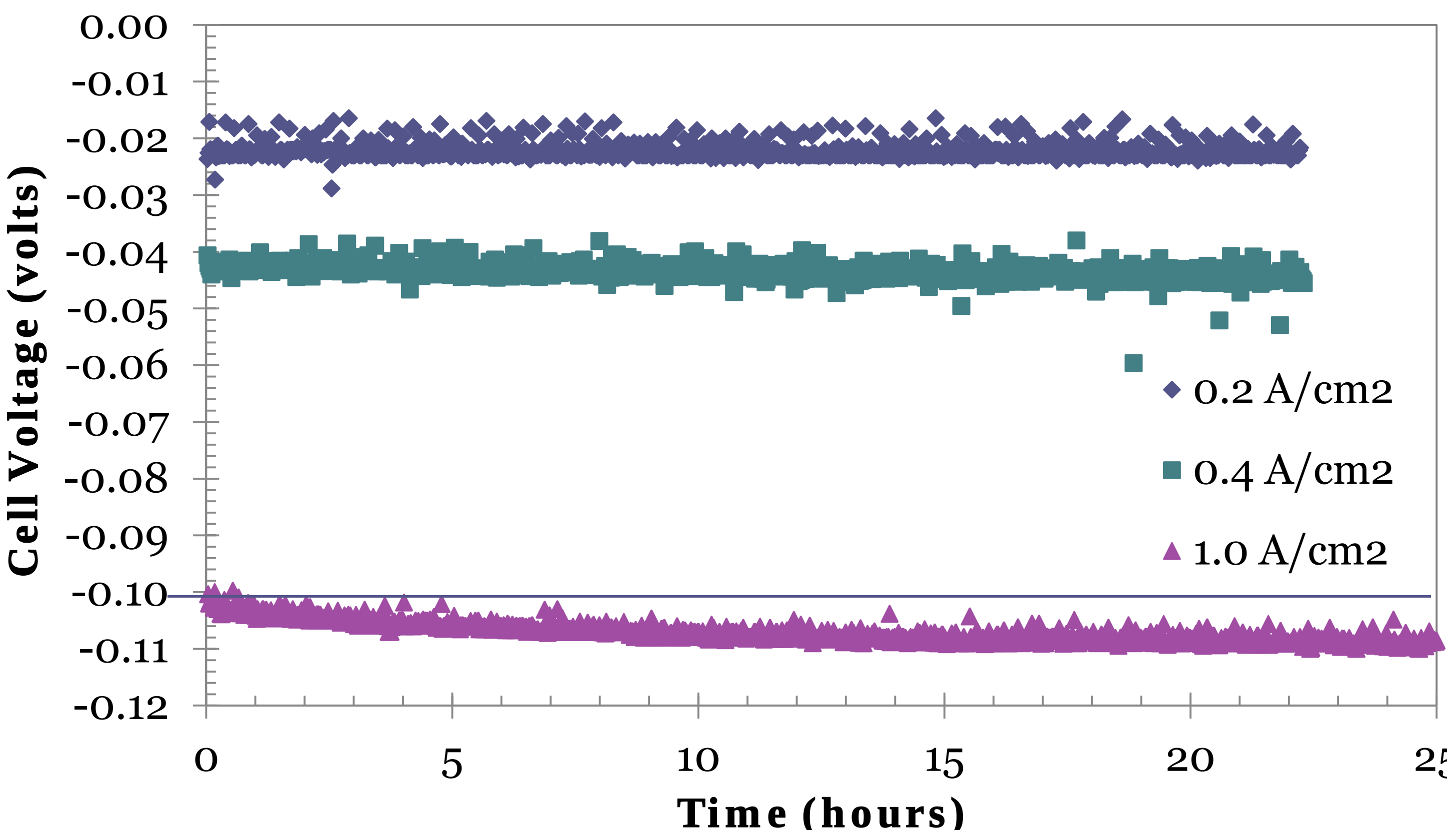
Cell assembly with insulating jacket



BASF Celtec-P-1000 MEA (PBI/PA)

Hydrogen Pump Cell Testing
- Constant current density

COULD THE DECAY AT 1 A/cm² BE DUE TO ACID MIGRATION??

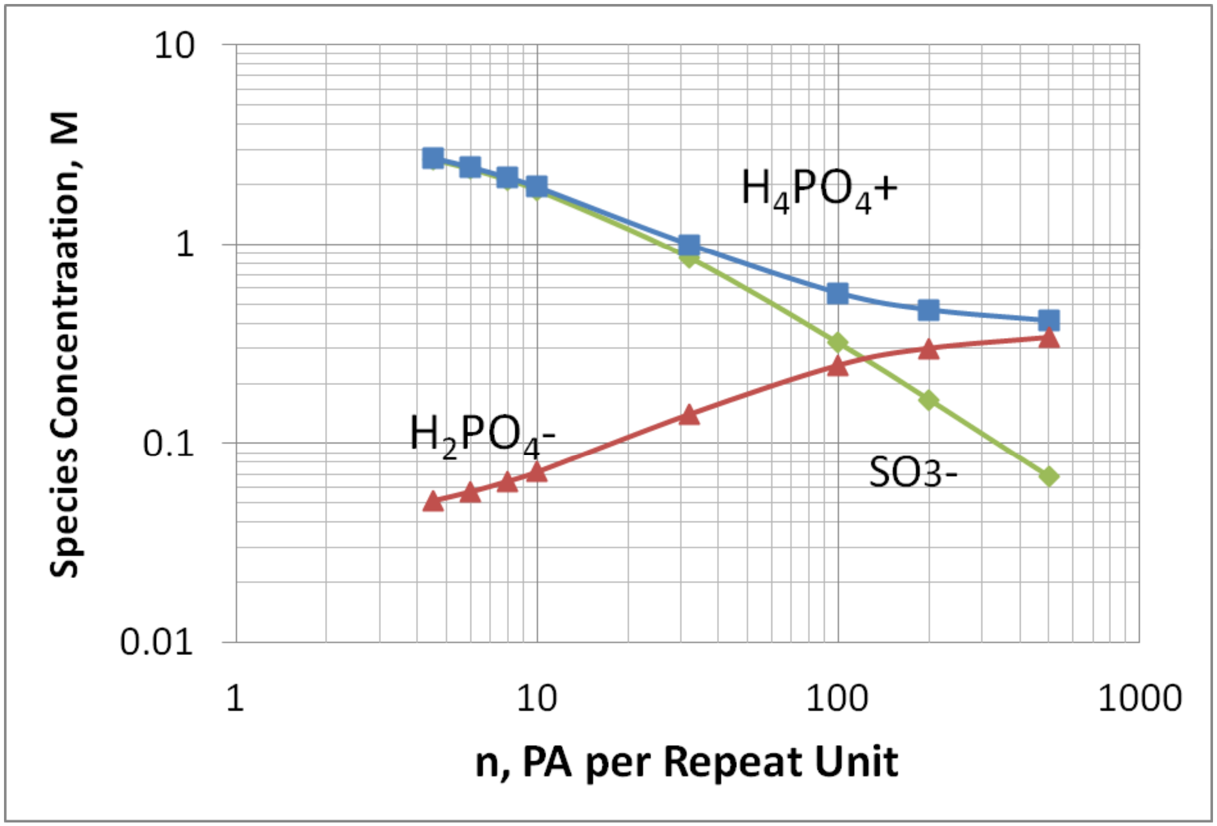


- 150°C
- Both sides
  - 100% H2
- 5% RH both

$$\Delta V_{tot} = E^{\circ} - \frac{RT}{nF}\ln\frac{\rho_{H_2}^{cath}}{\rho_{H_2}^{anode}} - \frac{RT}{nF\,i_0^{pure\ H_2}}\frac{\rho_{total}^{anode}}{\rho_{H_2}^{anode}}\,i - \frac{RT}{nF\,i_0^{pure\ H_2}}\frac{\rho_{total}^{cath}}{\rho_{H_2}^{cath}}\,i + \frac{RT}{nF}\ln\left[1 - \frac{i}{i_L^{cell}}\right] - i\sum \tilde{R}_{cell} - i\tilde{R}_{ionic}$$

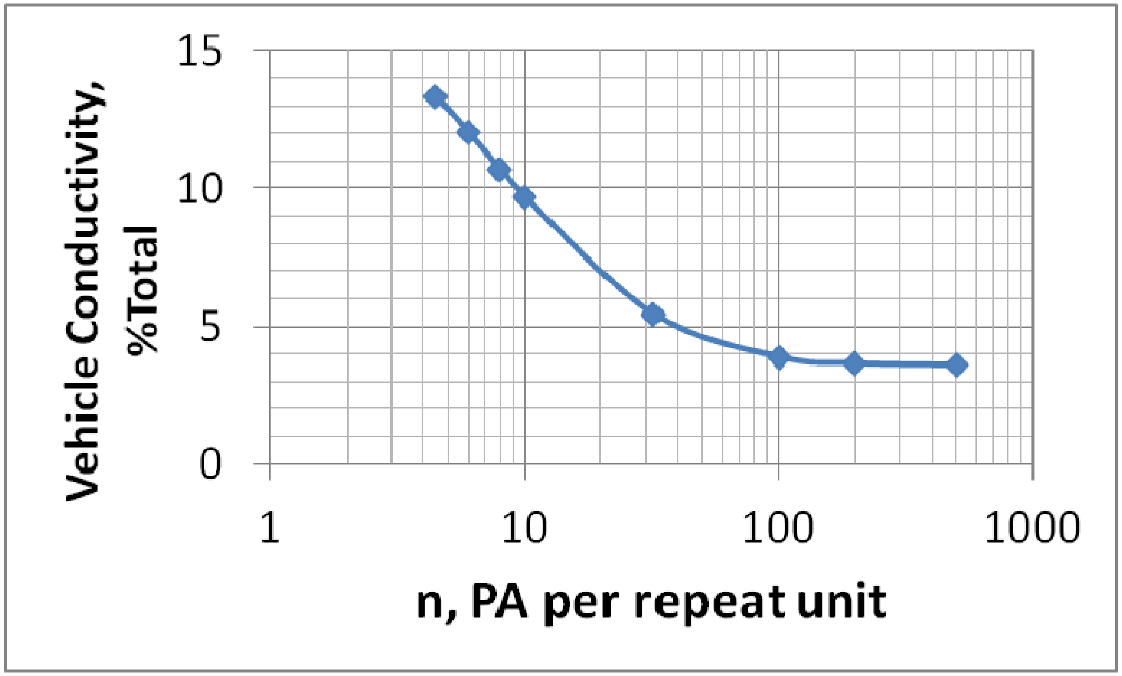
What about Nafion?........ Effect of Nafion on Phos Acid Speciation

$$-SO_3H + H_3PO_4 = -SO_3^- + [H_4PO_4^+]$$



Note: $H_4PO_4^+$ predominant species
Sulfonic acid of Nafion is a very strong acid

Fraction of total conductivity due to the vehicle mechanism



PA: pK=2.12
Nafion: pK<0
Assume protonated PA are ionized

t^{+}=.98-.55
t^{-} =.02-.45

At n=6, %VM is about 12% --acid migration an issue??
Will excess $H_4PO_4^+$ enhance Grotthuss conduction??
Low PA/Nafion ratios drive transport number to high t^+

Some things to think about……..

- •Polymer and acid pKa have a role in the vehicle conductivity mechanism in an acid doped membrane system
- •Effective diffusion coefficient related to polymer structure and morphology-affects %vehicle transport?
- •Acid permeation into electrodes might be controlled by electrode structure, interfacial surface properties, and porosity as well as polymer swelling capability and acid back diffusion rates

So…..understanding factors affecting acid movement and distribution will help improve durability and performance of theses types of systems –opportunities to innovative on polymer chemistry and morphology, and electrode structures

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CASE SCHOOL OF ENGINEERING

YCES

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