Performance of the Gas-Phase Hybrid Sulfur Electrolyzer

Hybrid Sulfur Electrolyzer Workshop

April 20, 2008

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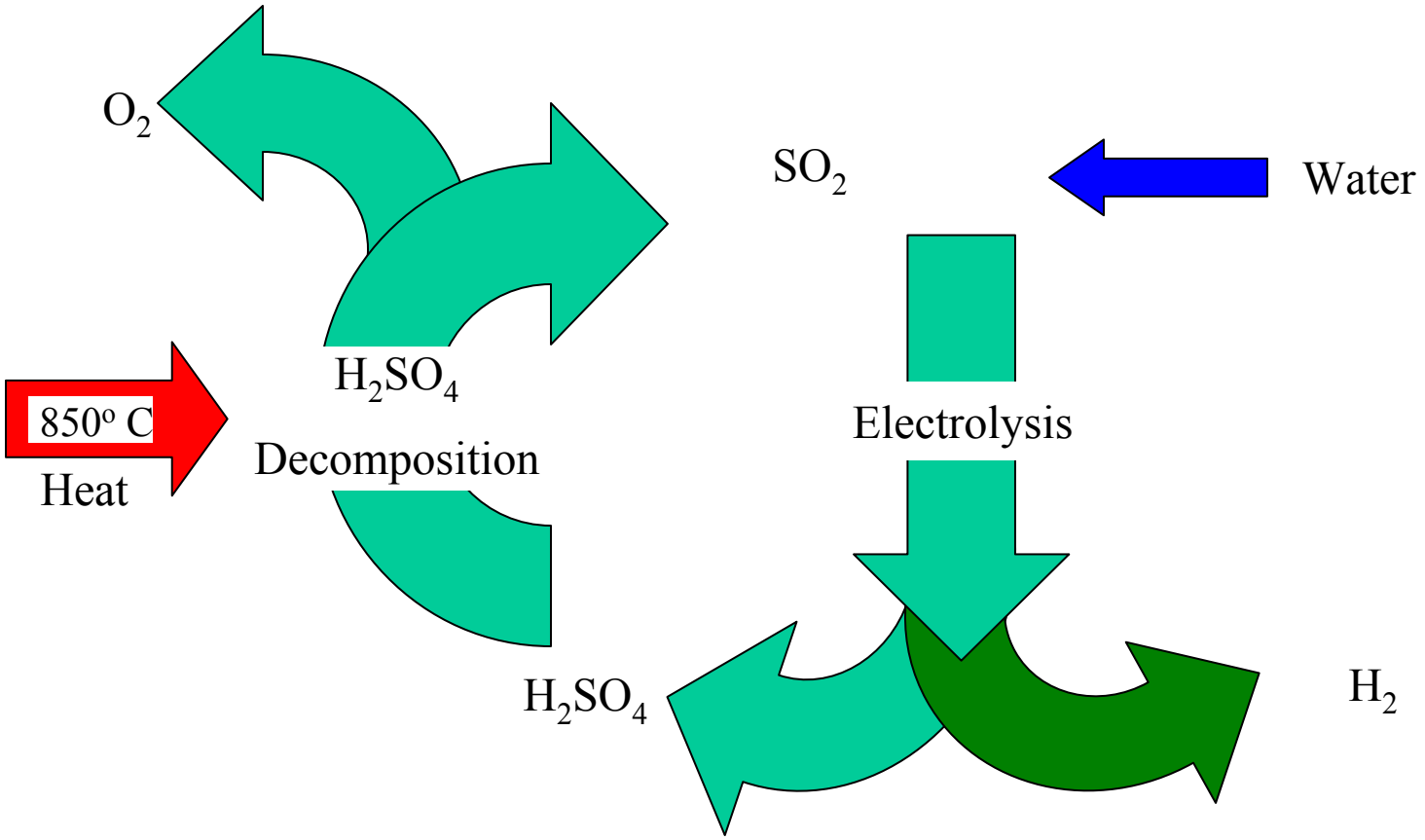
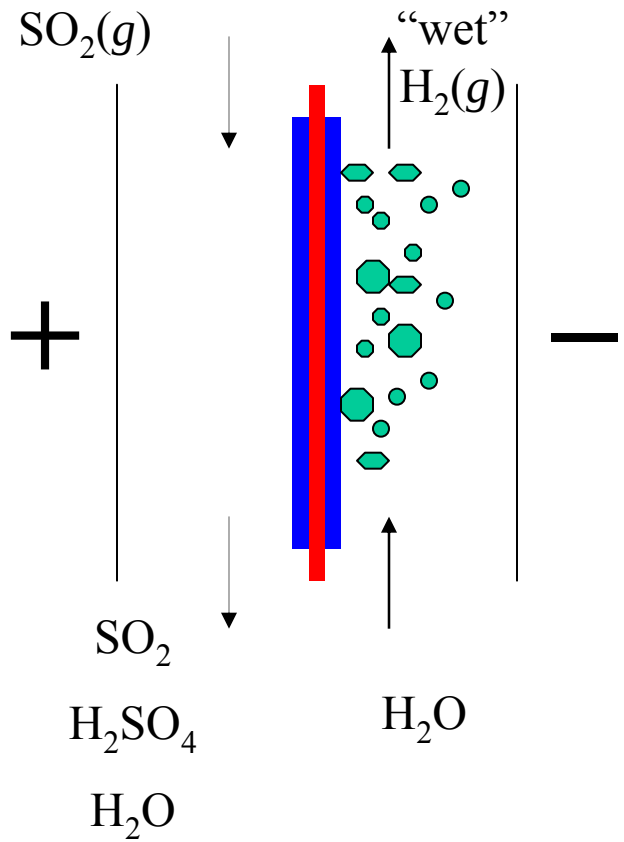
Hydrogen Production

- Water electrolysis
  - High-temperature
    - 40-50% efficient
    - Suitable for large-scale production
    - Significant materials concerns
  - Low-temperature
    - <40% efficient
    - Suitable for small, distributed systems
- Thermochemical cycles
  - Combines high- and low-temperature steps
    - Low-temperature PEM electrolysis step
    - High-temperature decomposition and recycle
  - Lower voltage than water electrolysis
    - 40-50% efficient
  - Suitable for large-scale production
    - Ideally suited to nuclear and/or solar power stations

Hybrid Sulfur (HyS) Process (Westinghouse)



USC Hybrid Sulfur Electrolyzer



Anode:

$$SO_2(g) + 2H_2O \rightarrow H_2SO_4 + 2H^+(aq) + 2e^-$$

Cathode:

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

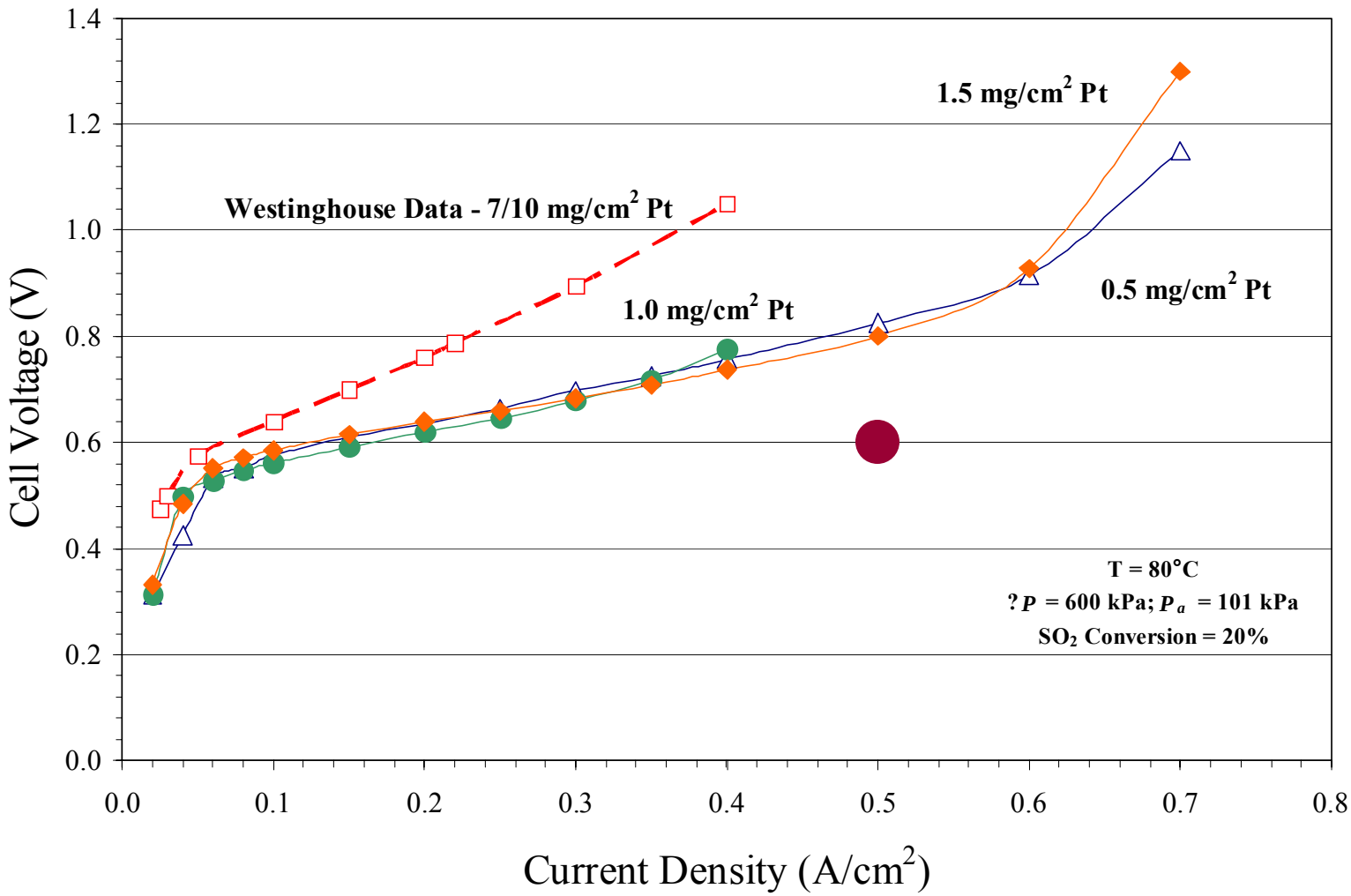
Overall:

$$SO_2(g) + 2H_2O \rightarrow H_2(g) + H_2SO_4$$

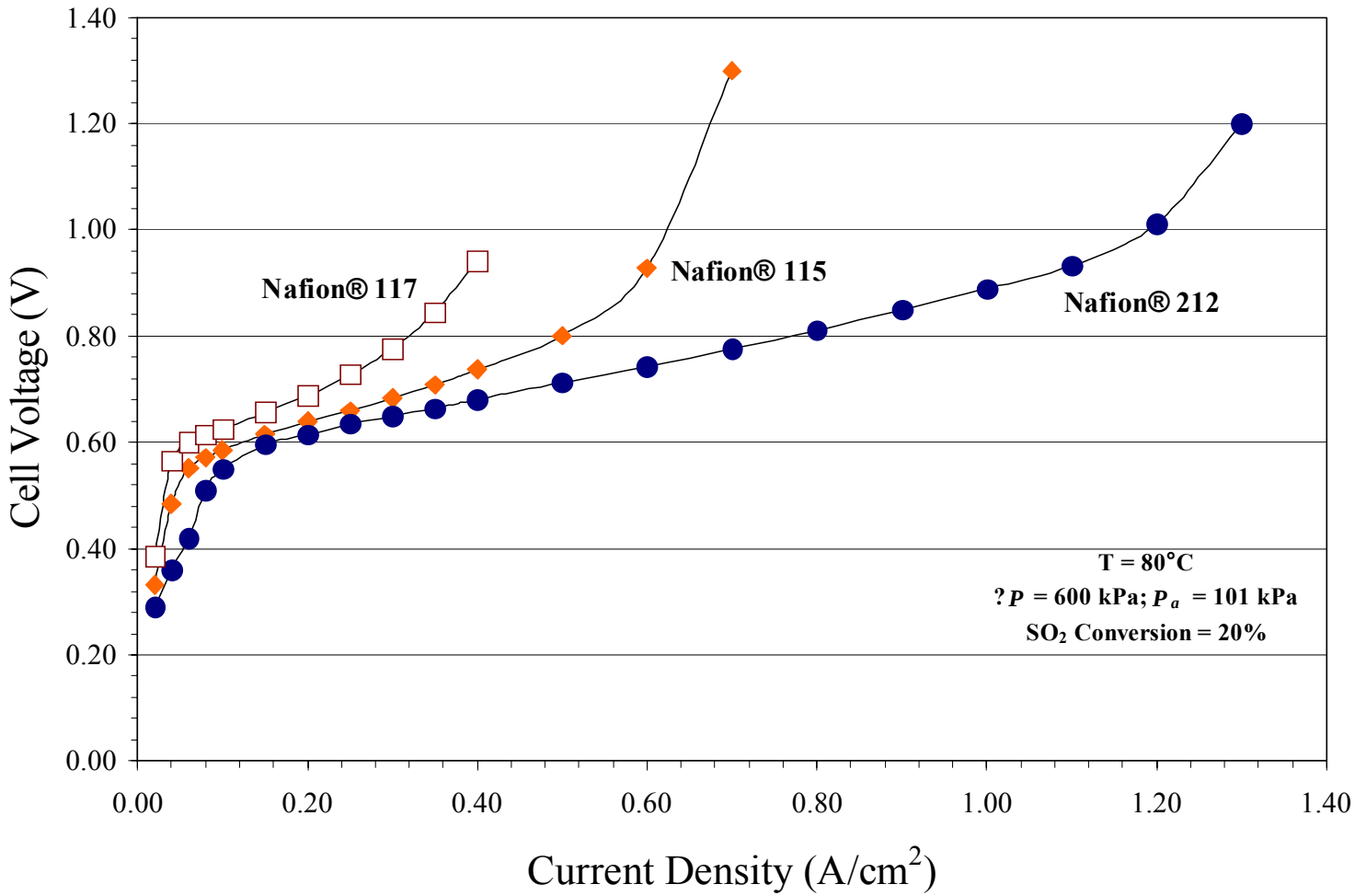
Poisoning Reaction:

$$SO_2 + 4e^- \rightarrow S + O_2$$

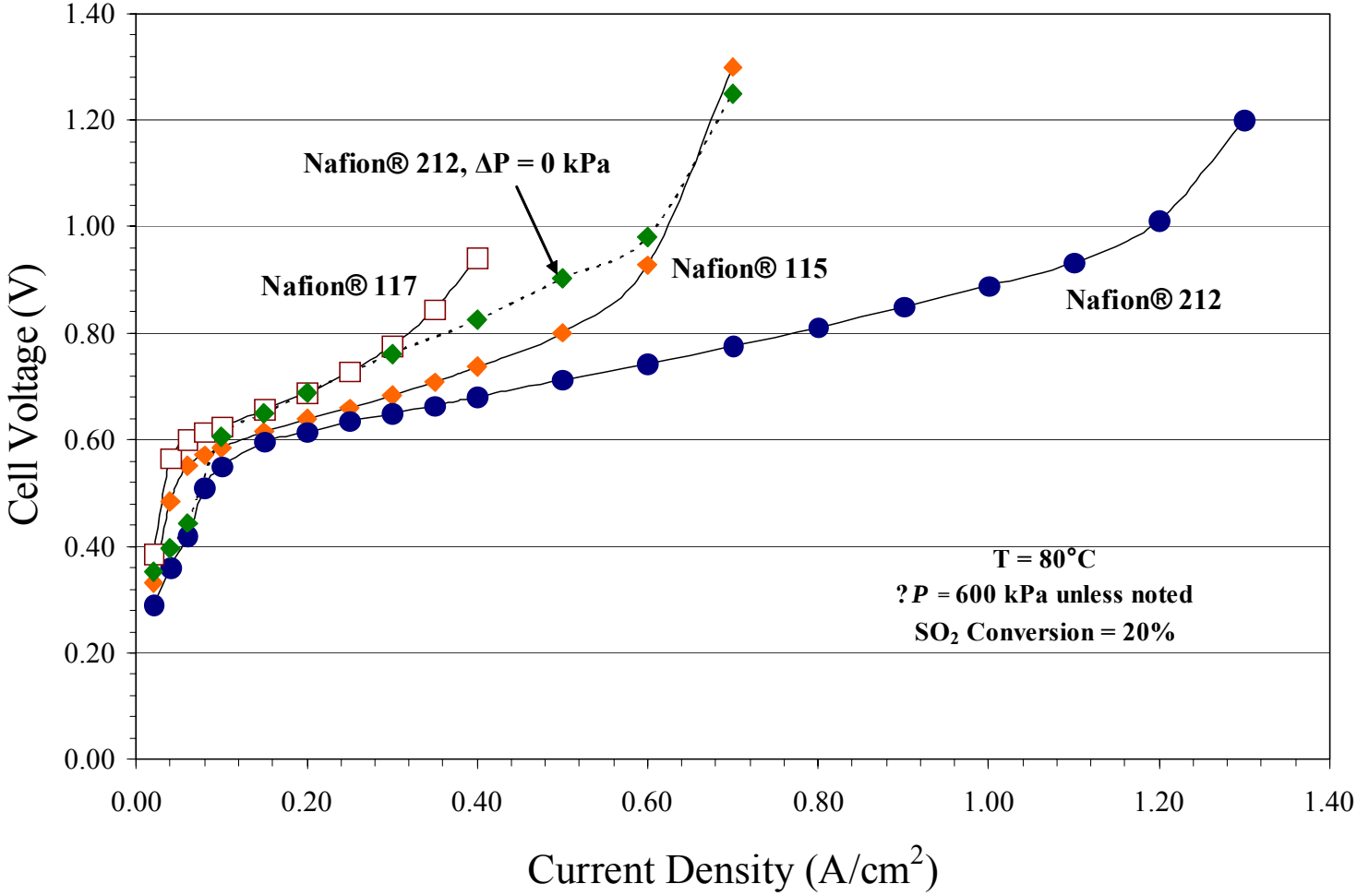
Effect of Catalyst Loading



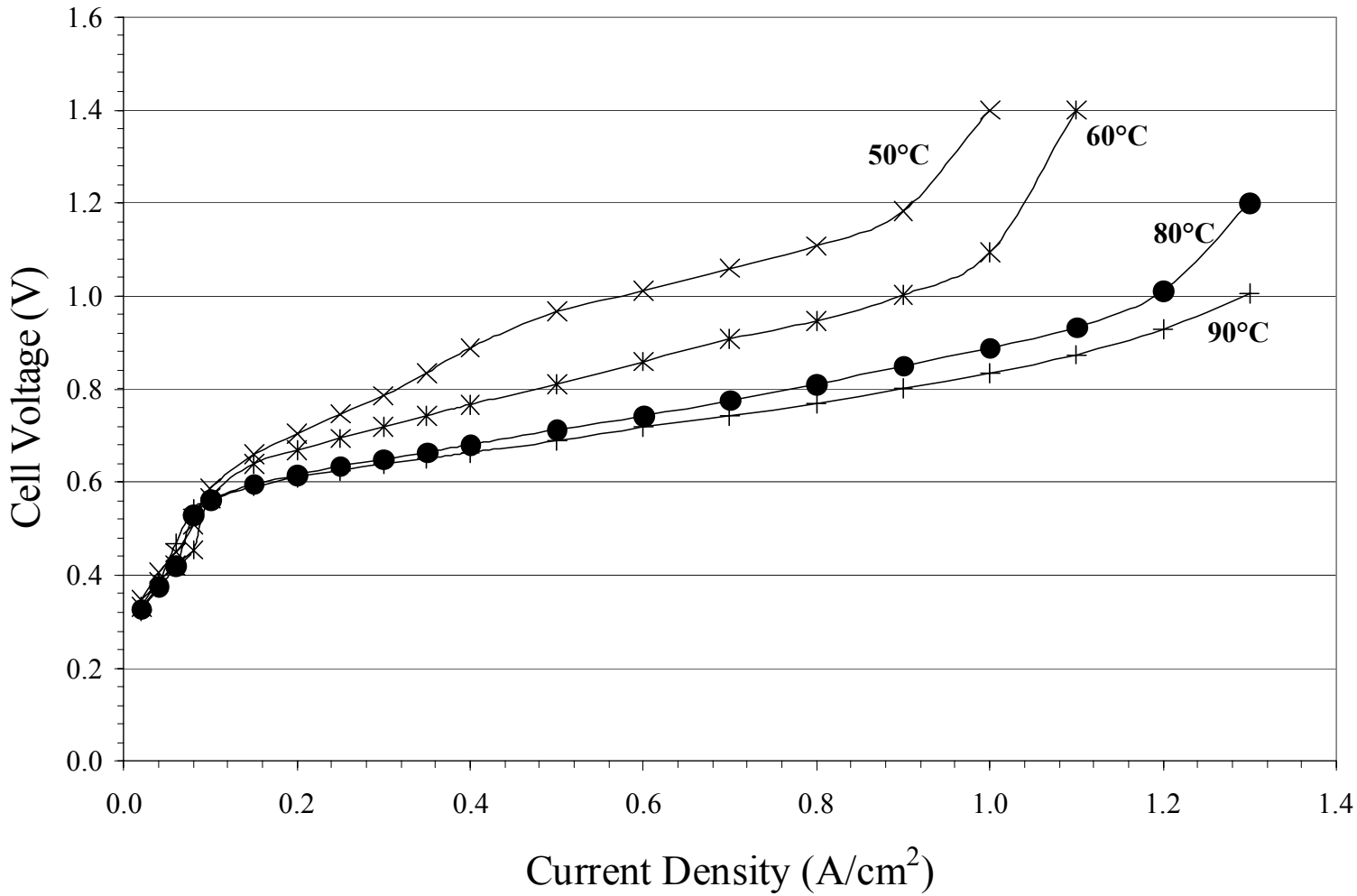
Effect of Membrane Thickness



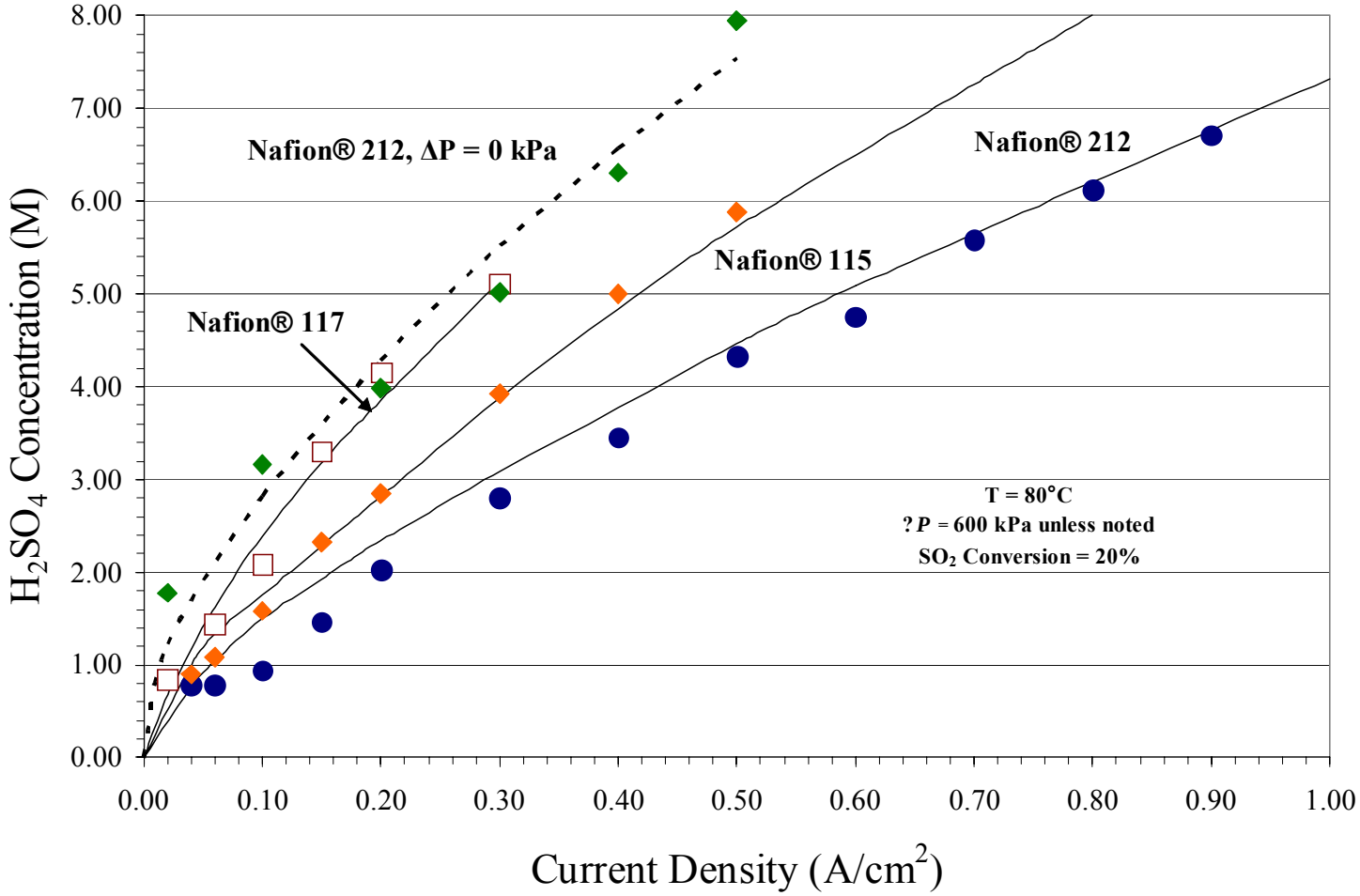
Effect of Membrane Pressure Differential



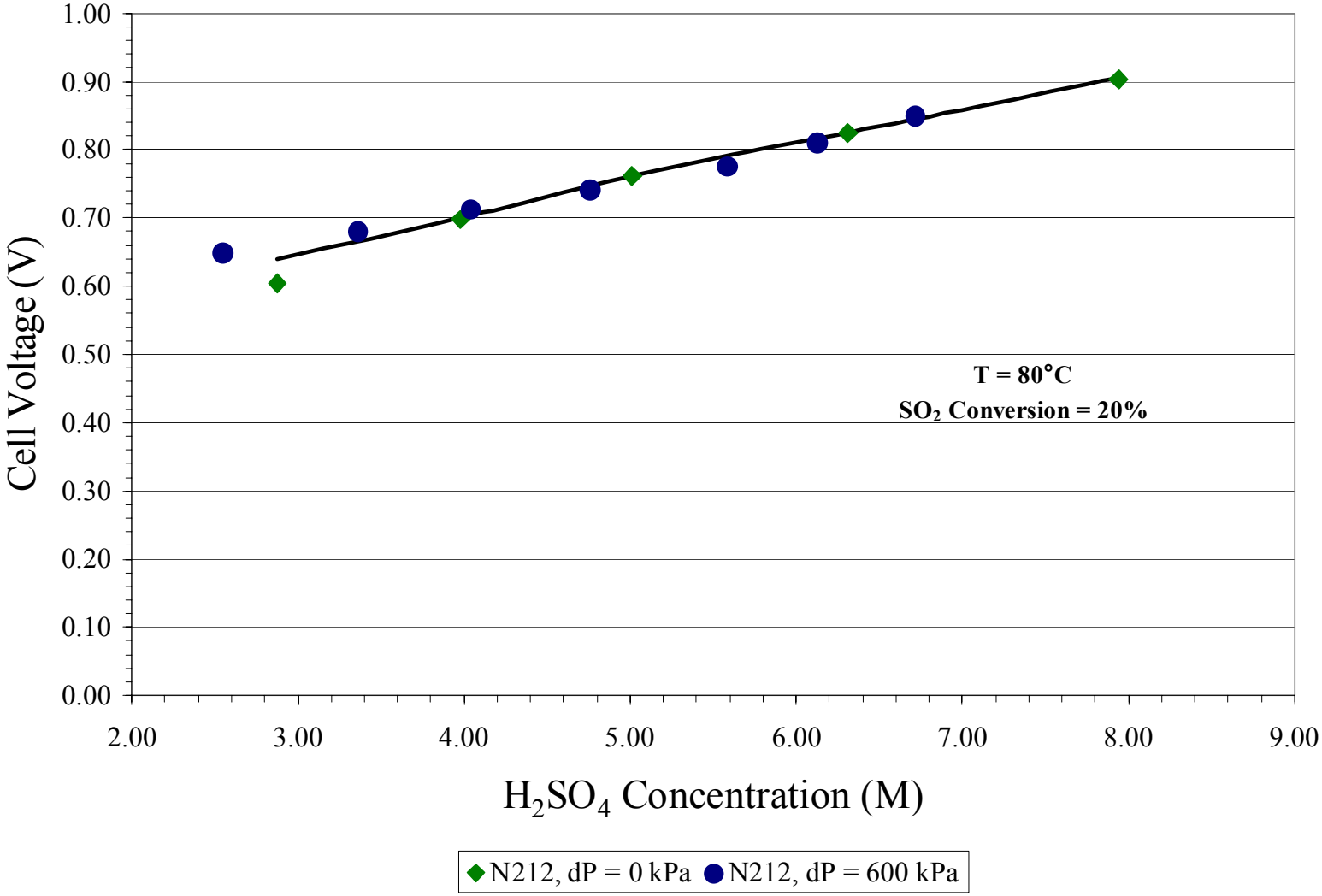
Effect of Temperature



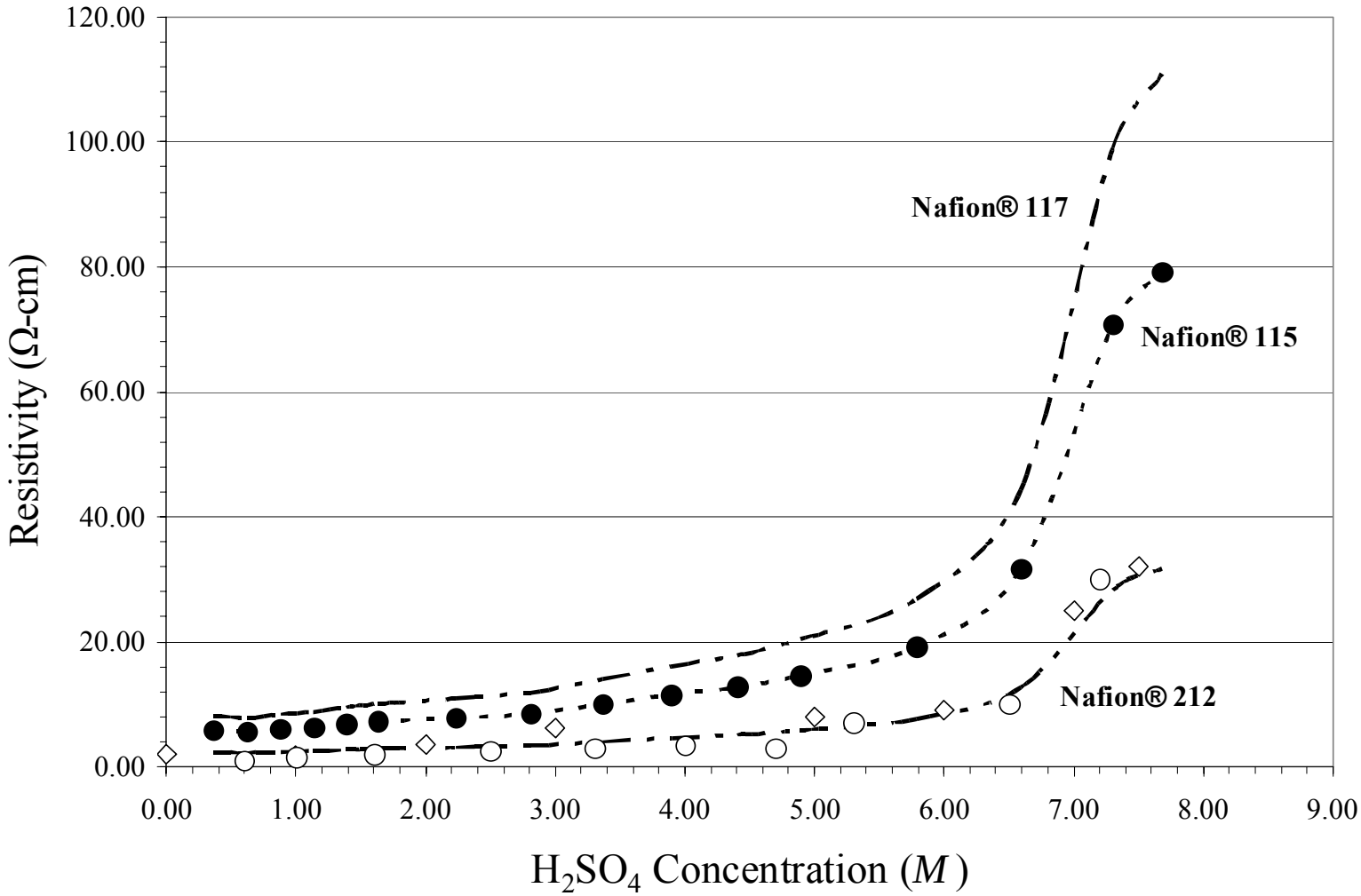
H_2SO_4 Concentration



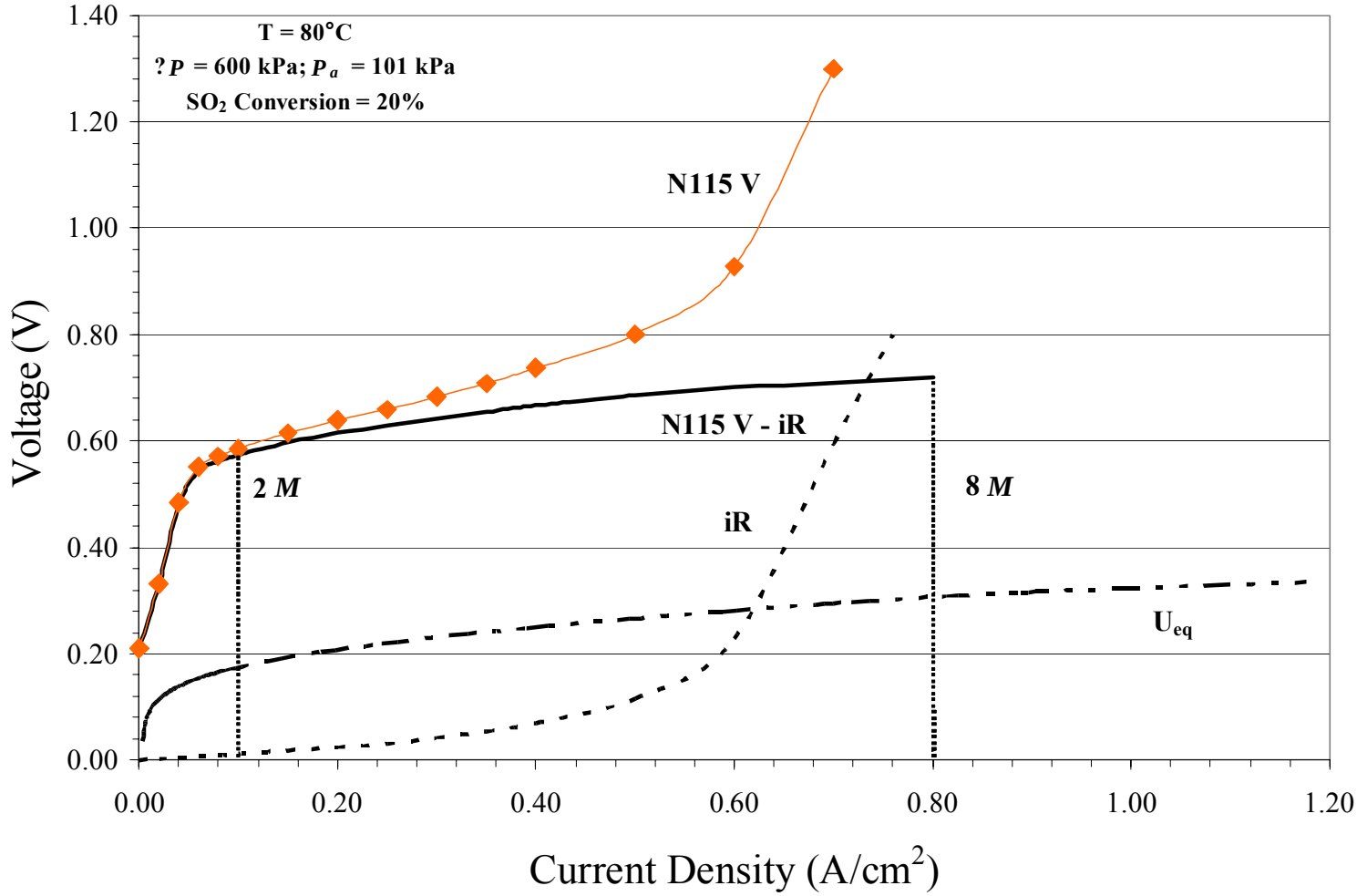
Concentration vs. Cell Voltage



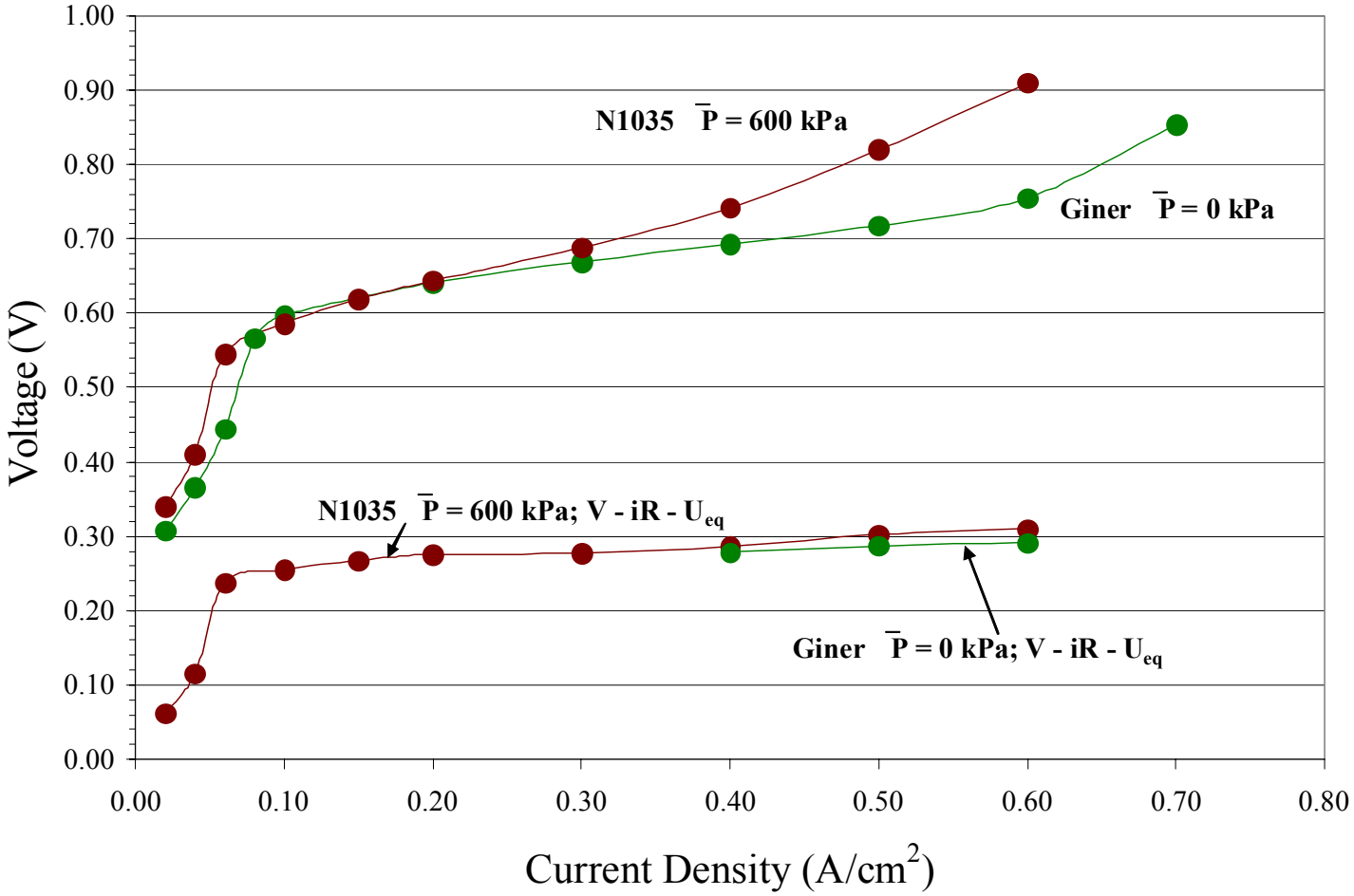
Membrane Resistance



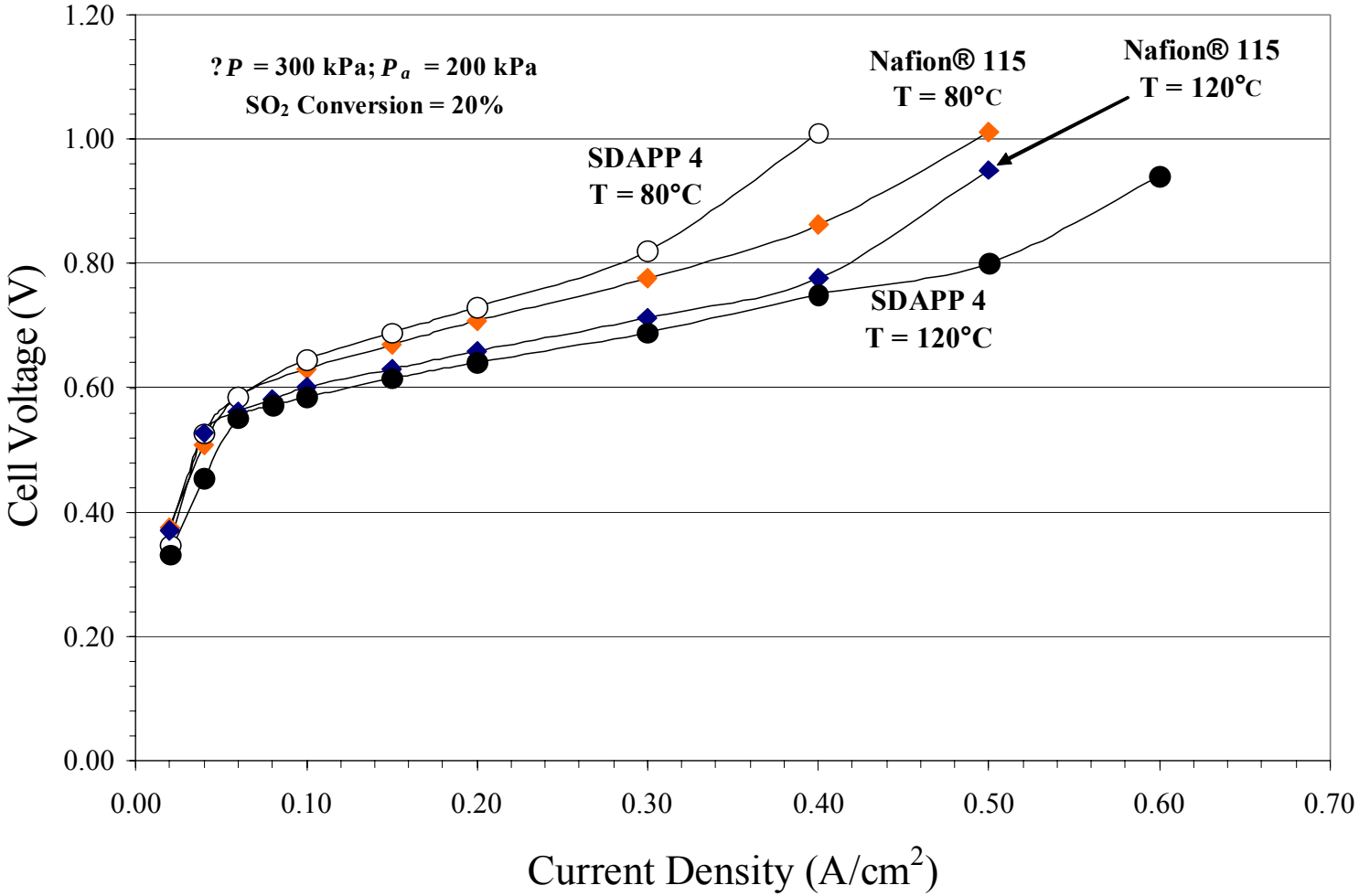
Cell Voltage



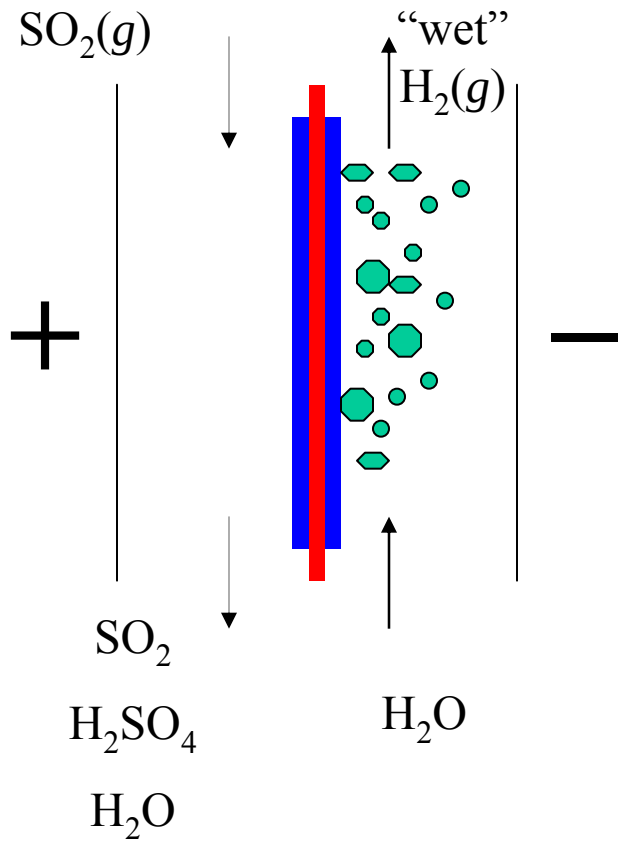
Giner Membranes



SDAPP Membranes



USC Hybrid Sulfur Electrolyzer



Anode:

$$SO_2(g) + 2H_2O \rightarrow H_2SO_4 + 2H^+(aq) + 2e^-$$

Cathode:

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Overall:

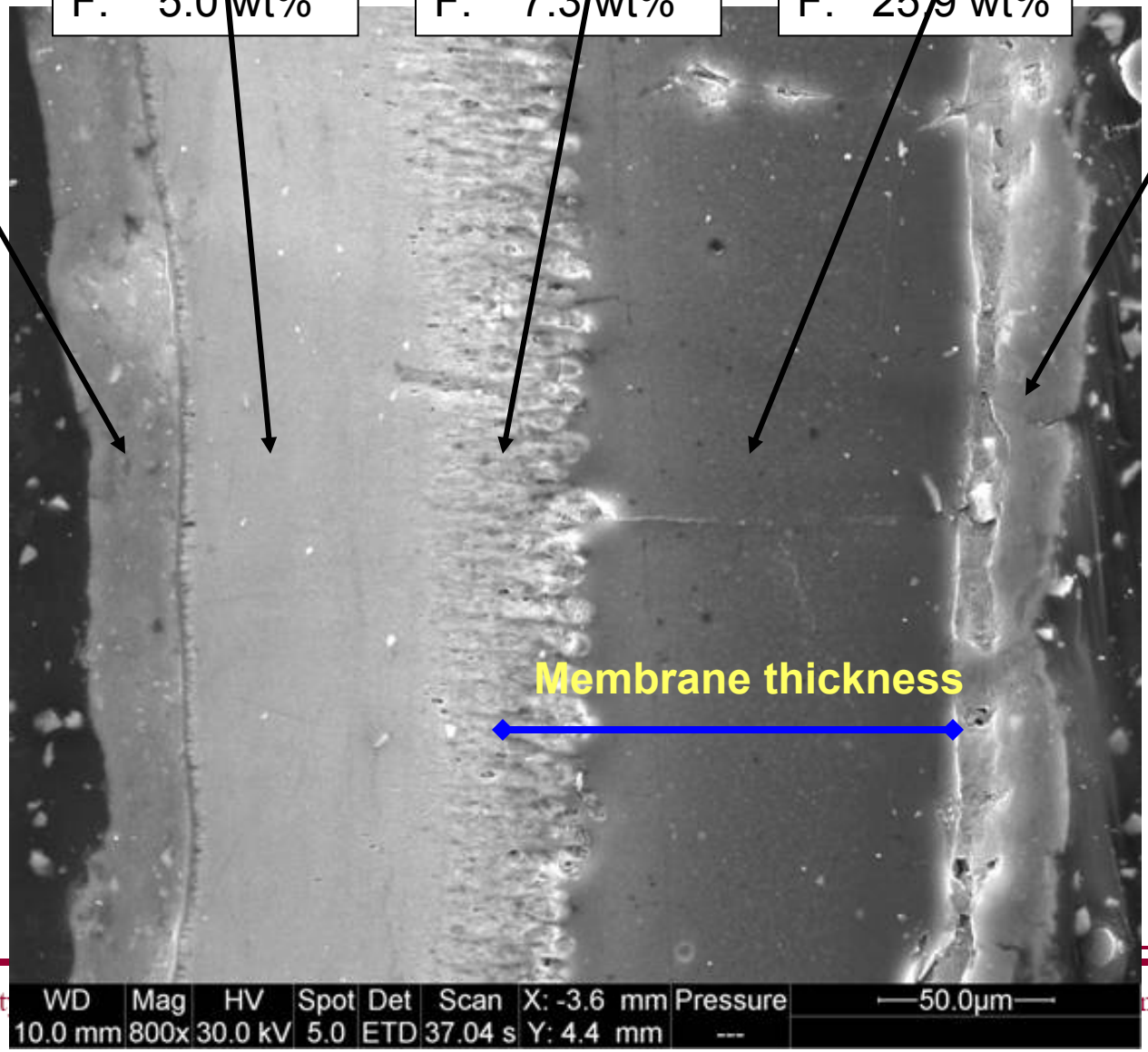
$$SO_2(g) + 2H_2O \rightarrow H_2(g) + H_2SO_4$$

Poisoning Reaction:

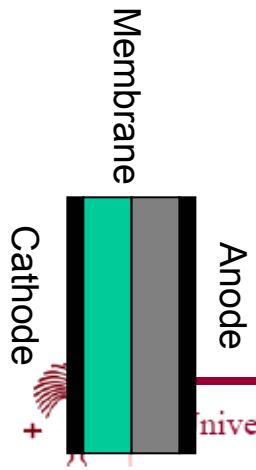
$$SO_2 + 4e^- \rightarrow S + O_2$$

Cathode	S layer	Interface	Membrane	Anode
Pt: 20.9 wt%	Pt: 0.50 wt%	Pt: 0.32 wt%	Pt: 2.2 wt%	Pt: 14.3 wt%
C: 69.5 wt%	C: 35.7 wt%	C: 42.6 wt%	C: 57.5 wt%	C: 80.8 wt%
S: 5.2 wt%	S: 58.7 wt%	S: 49.7 wt%	S: 14.4 wt%	S: 4.9 wt%
F: 4.4 wt%	F: 5.0 wt%	F: 7.3 wt%	F: 25.9 wt%	

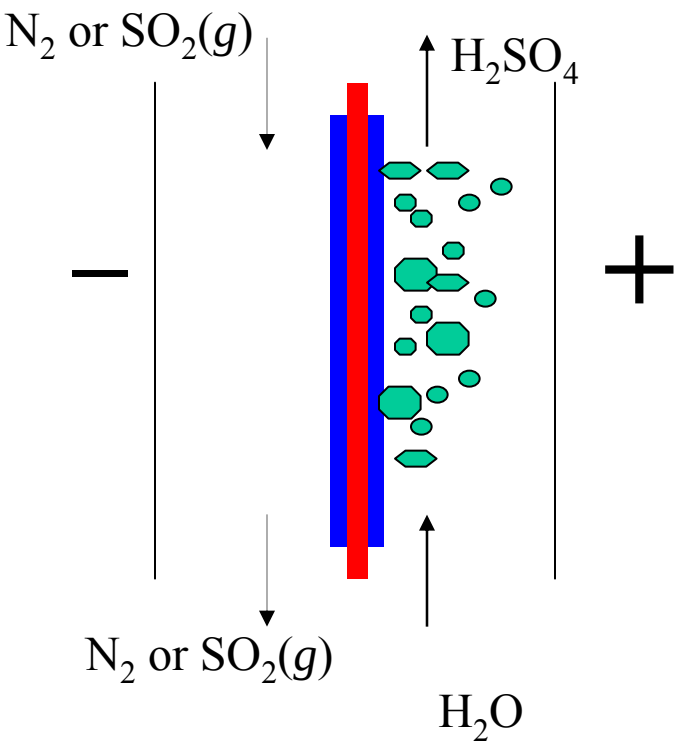
Cathode



Anode



Electrochemical Monitoring Technique



SO_2 Flux Across the Membrane:

$$N_{SO_2} = \frac{C_{SO_2} M_M}{\lambda \rho_M} N_w - D_{SO_2} \frac{dC_{SO_2}}{dx}$$

Solution when $N_w = 0$:[1]

$$i_{SO_2}(t) = \frac{2FD_{SO_2} C^*_{SO_2}}{\delta_M} \left(\frac{2}{\sqrt{\pi\tau}} \sum_{j=0}^{\infty} \exp\left[-\frac{(2j+1)^2}{4\tau} \right] \right)$$

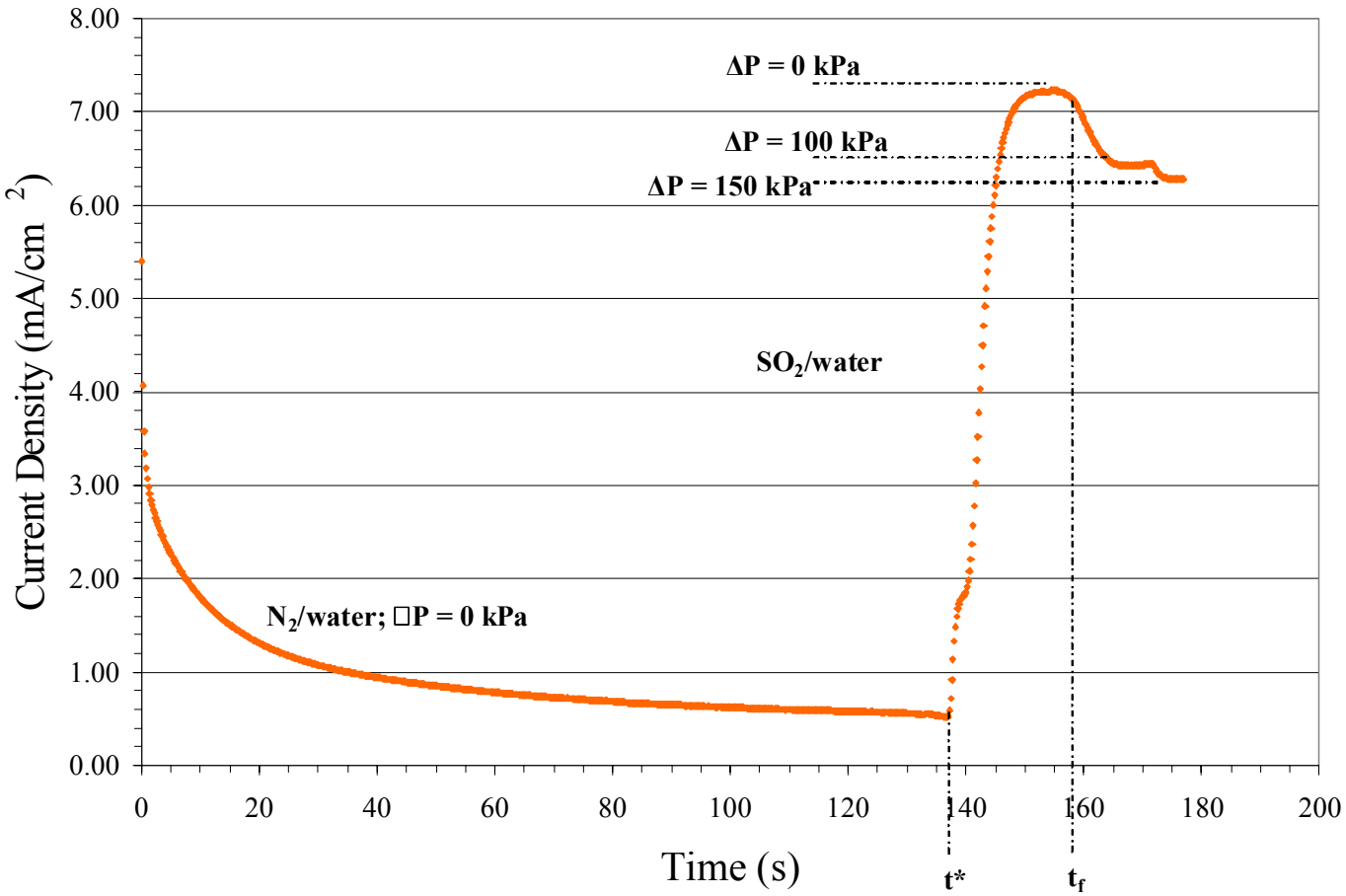
$$\tau = \frac{tD_{SO_2}}{\delta_M^2}$$

$$C_{SO_2} = C^*_{SO_2} \; @ \; x = 0$$

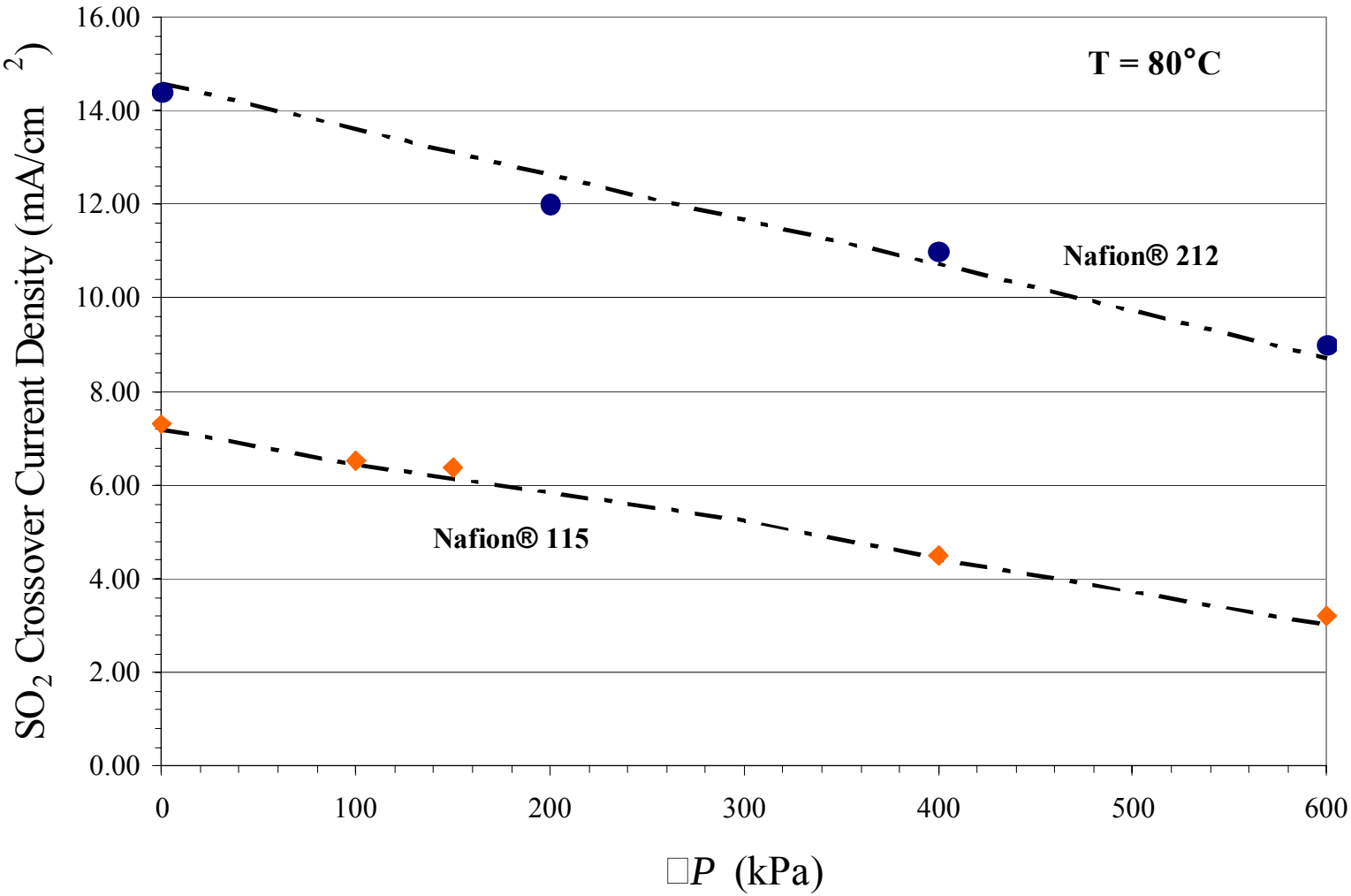
$$C_{SO_2} = 0 \; @ \; x = \delta_M$$

1. A.T. Haug and R.E. White, *J. Electrochem. Soc.*, **147**, 980 (2000)

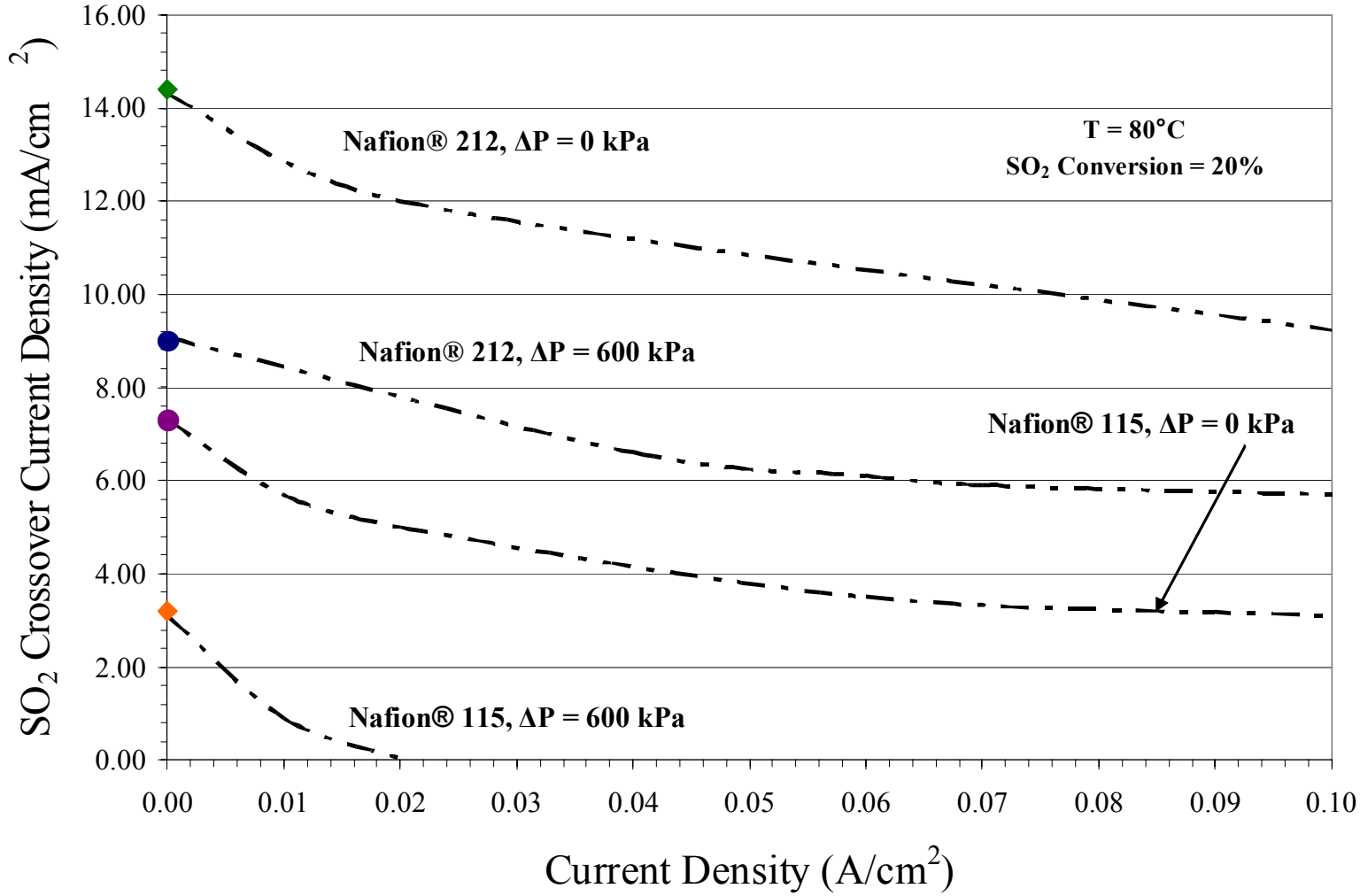
Electrochemical Monitoring Technique



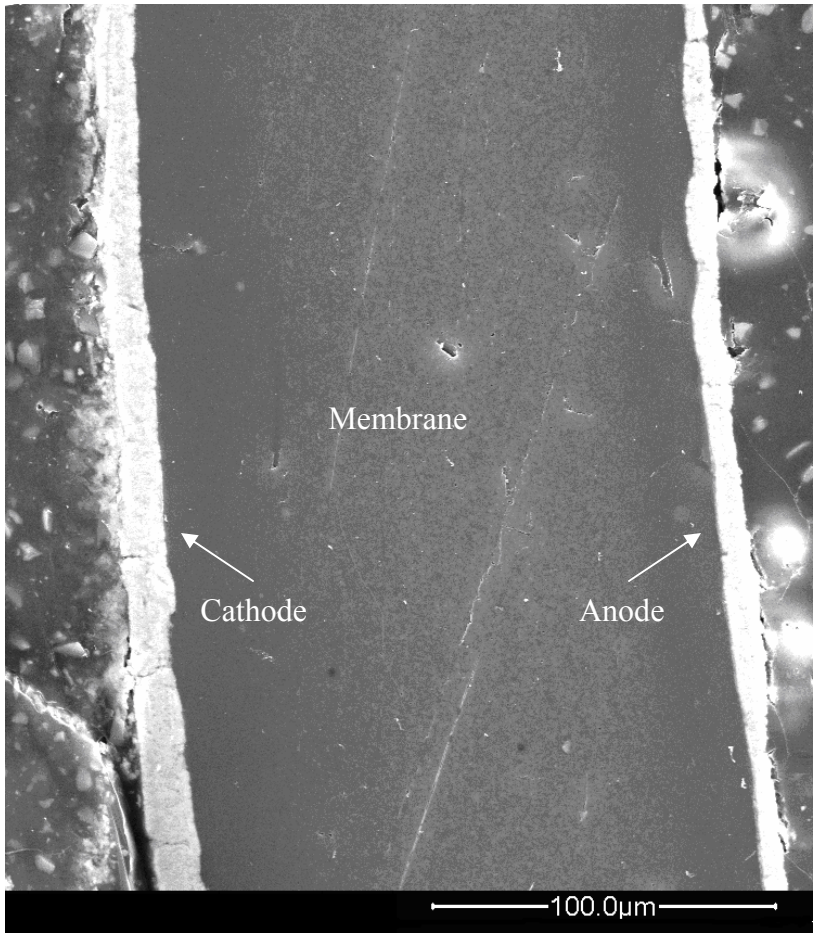
Effect of ΔP on SO_2 Crossover



SO_2 Crossover



Evidence of Sulfur Build-up



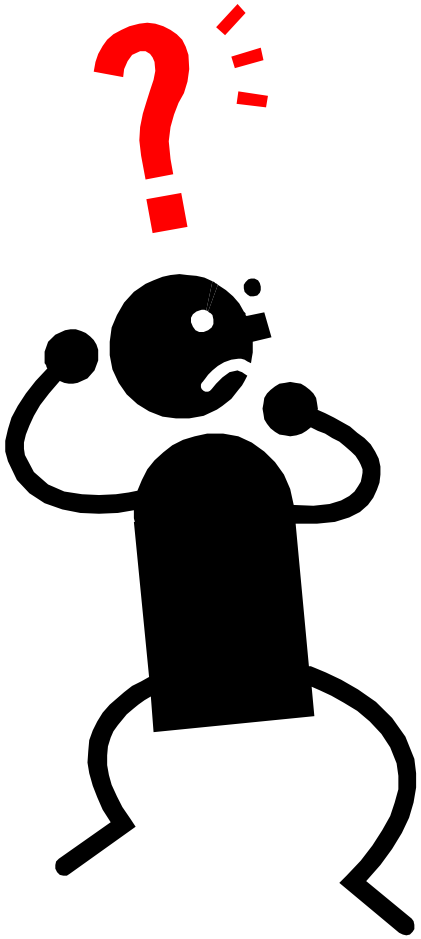
Sulfur Build-up

	Case 1	Case 2	Case 3	Case 4
Current Density (A/cm^2)	0.25	0.10	0.10	0.02
Time (hrs.)	15	16	8/4	100
ΔP	600	0	600/0	200
SO_2 Crossover (mol)	0	9.55×10^{-3}	2.41×10^{-3}	5.60×10^{-2}
Sulfur Deposited in Cathode (mol)	0	3.13×10^{-5}	8.92×10^{-6}	1.96×10^{-4}
% Sulfur Reduced	0	0.33	0.37	0.35

Case 4:

N115
i = 0.02 A/cm²
ΔP = 200 kPa
Time = 100 hours

Questions



Modeling Water Transport in the Gas-Phase Hybrid Sulfur Electrolyzer

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April 21, 2008

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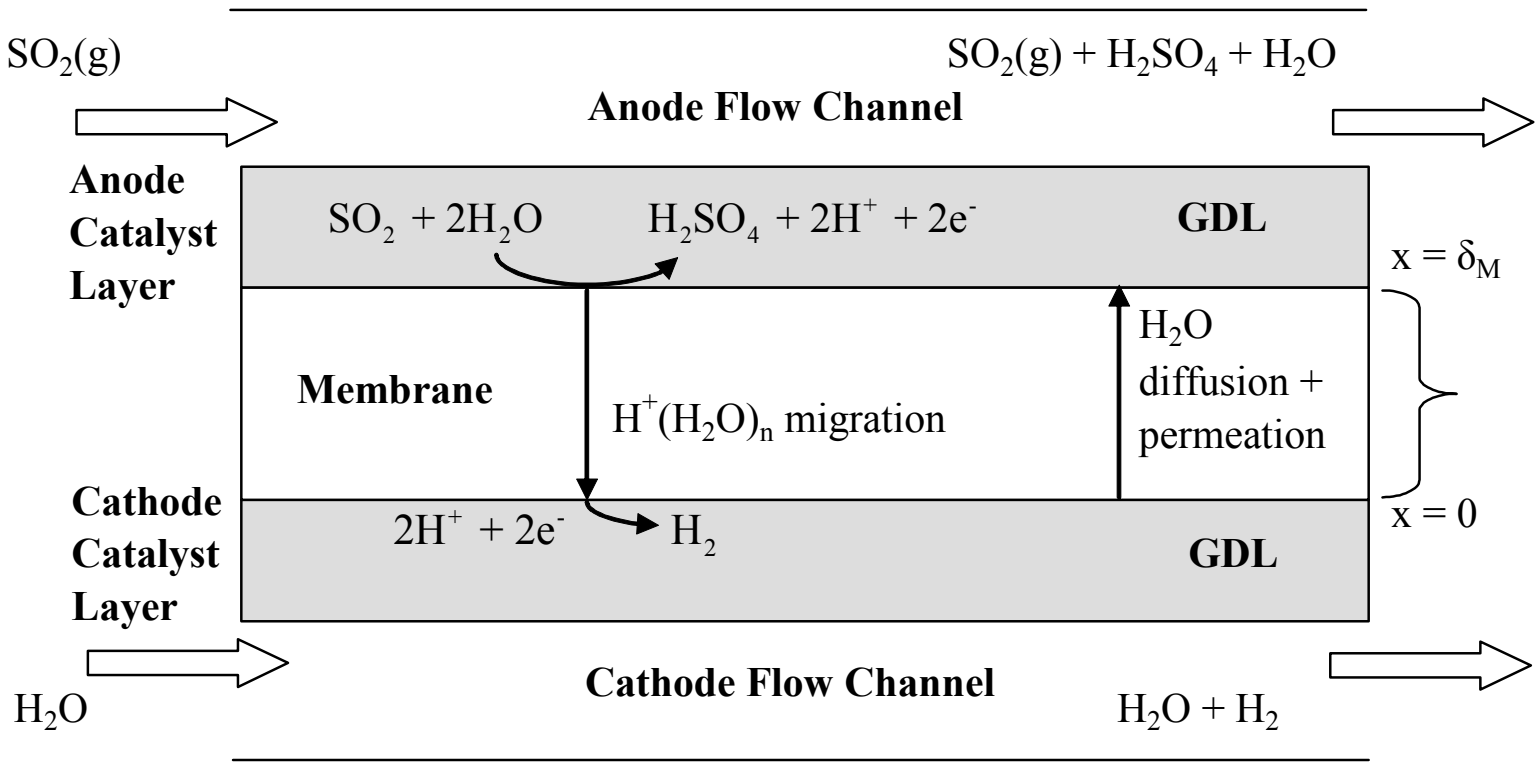
Water Transport



Water Flux Model

Water Flux Across Membrane: $$N_w = \frac{\rho_M}{M_M \delta_M} \int_{\lambda_a}^{\lambda_c} D_w \, d\lambda - \frac{\xi \lambda_a i_{H_2SO_4}}{\lambda_c F} + \frac{P_M}{\delta_M}(P_c - P_a)$$

Water Mole Fraction at Anode: $$a_w = \frac{N_w - \frac{i_{H_2SO_4}}{F}}{\left(N_w - \frac{i_{H_2SO_4}}{F}\right) + \frac{i_{H_2SO_4}}{2F}}$$

Water Content at Anode: $$\lambda_a = f(a_w)$$

Diffusion Coefficient:[1,2] $$D_w = A_1 \lambda_a (1 + e^{-0.28\lambda}) \exp\left[\frac{-2436}{T}\right]$$

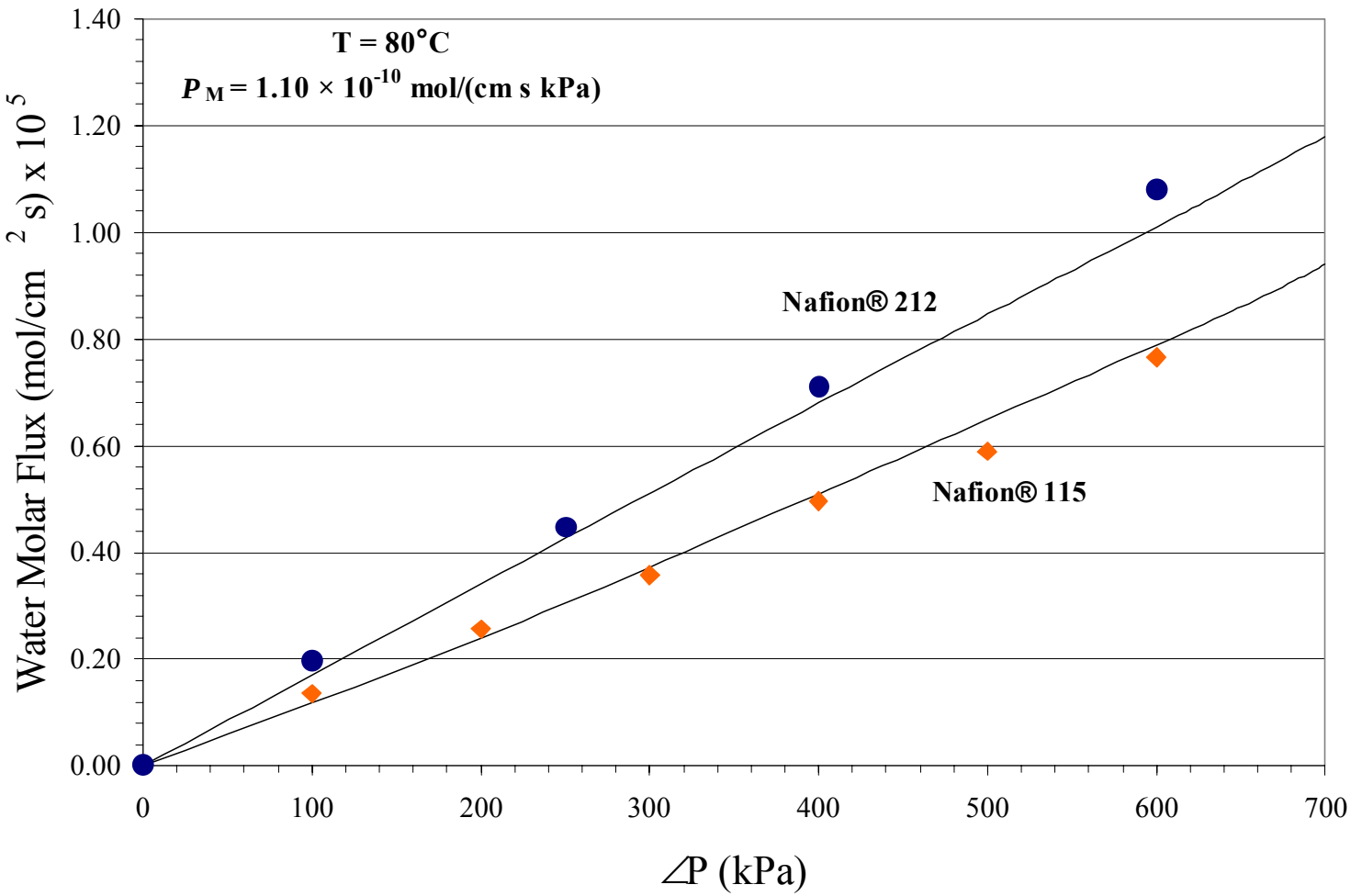
(for $0 < \lambda_a \leq 3$)

$$D_w = A_2 \lambda_a (1 + 161 e^{-\lambda_a}) \exp\left[\frac{-2436}{T}\right]$$

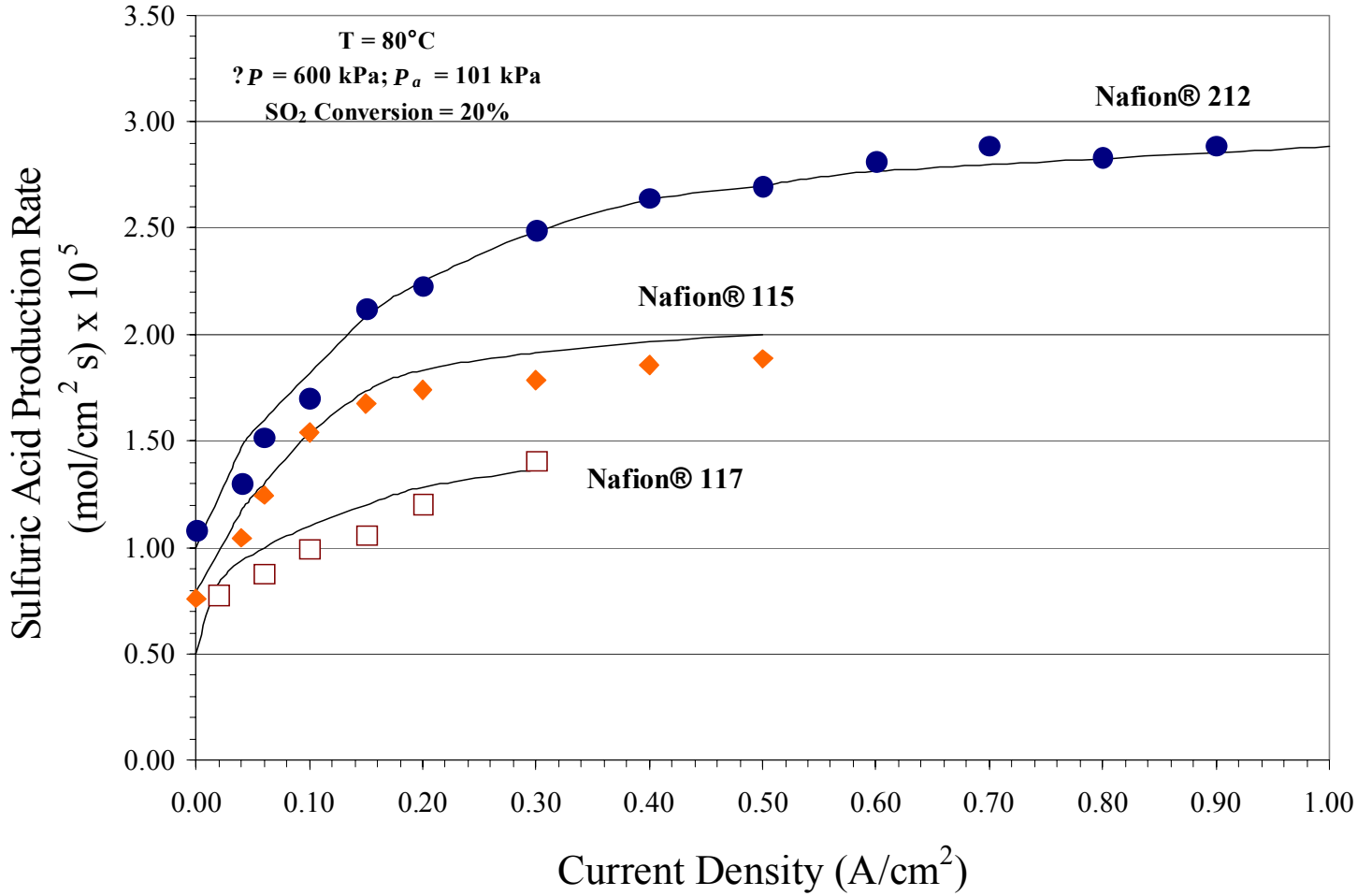
(for $3 < \lambda_a \leq 17$)

1. S. Motupally, A.J. Becker and J.W. Weidner, *J. Electrochem. Soc.*, **147**, 1371 (2000).
2. T.A. Zawodzinski, M. Neeman, L.O. Sillerud and S. Gottesfeld, *J. Phys. Chem.*, **95**, 6040 (1991).

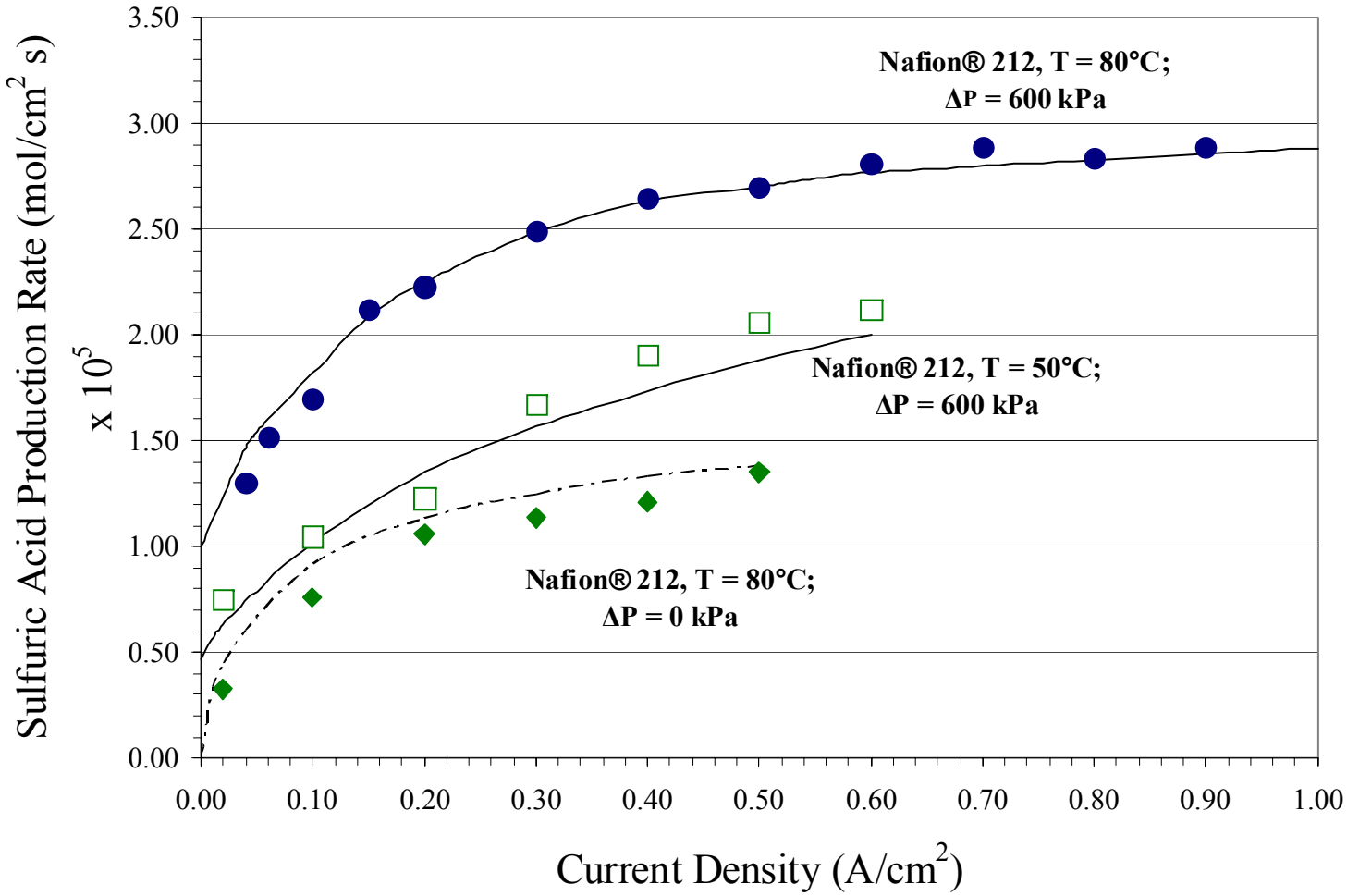
Water Flux vs. ΔP



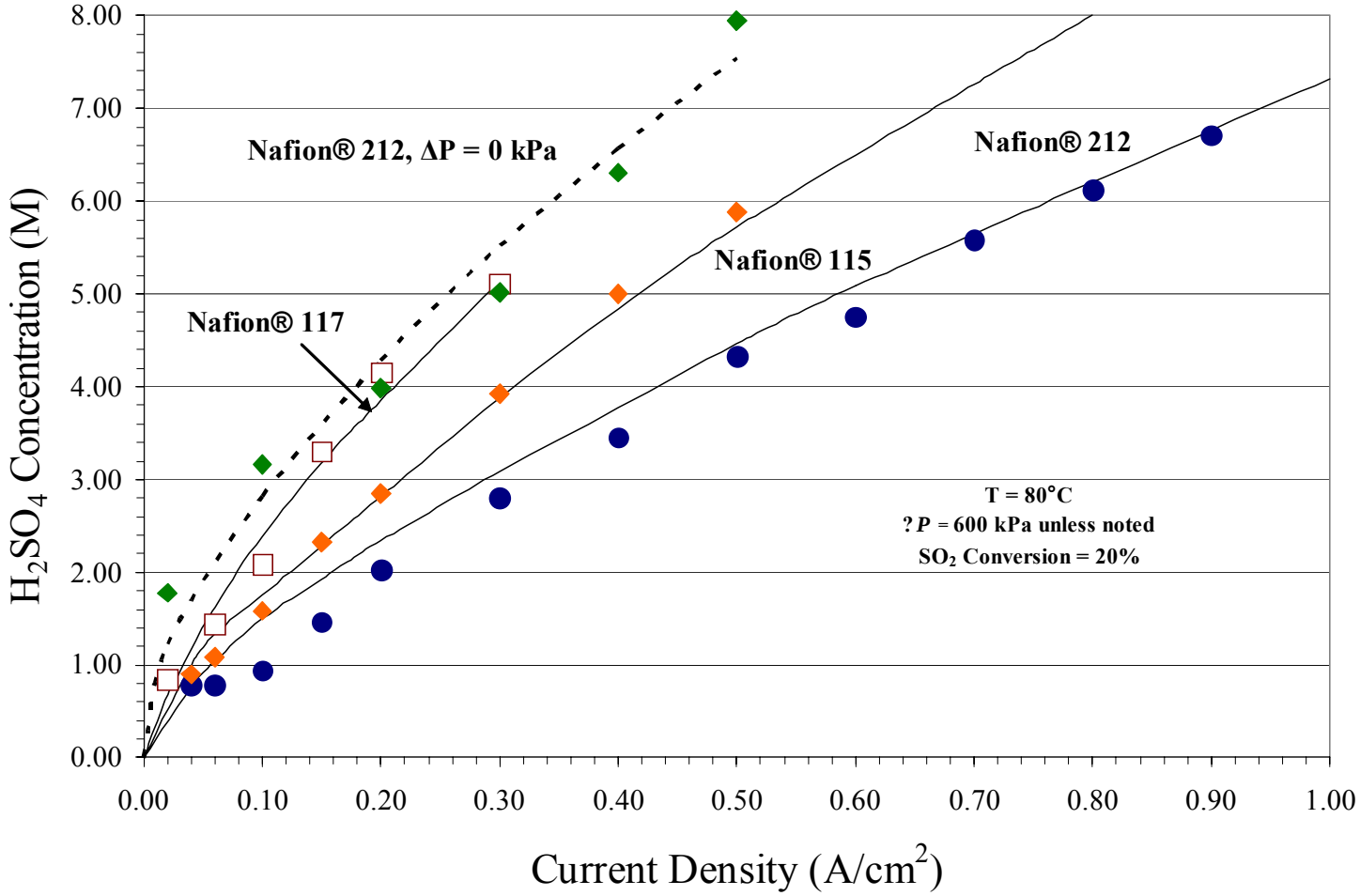
Sulfuric Acid Production



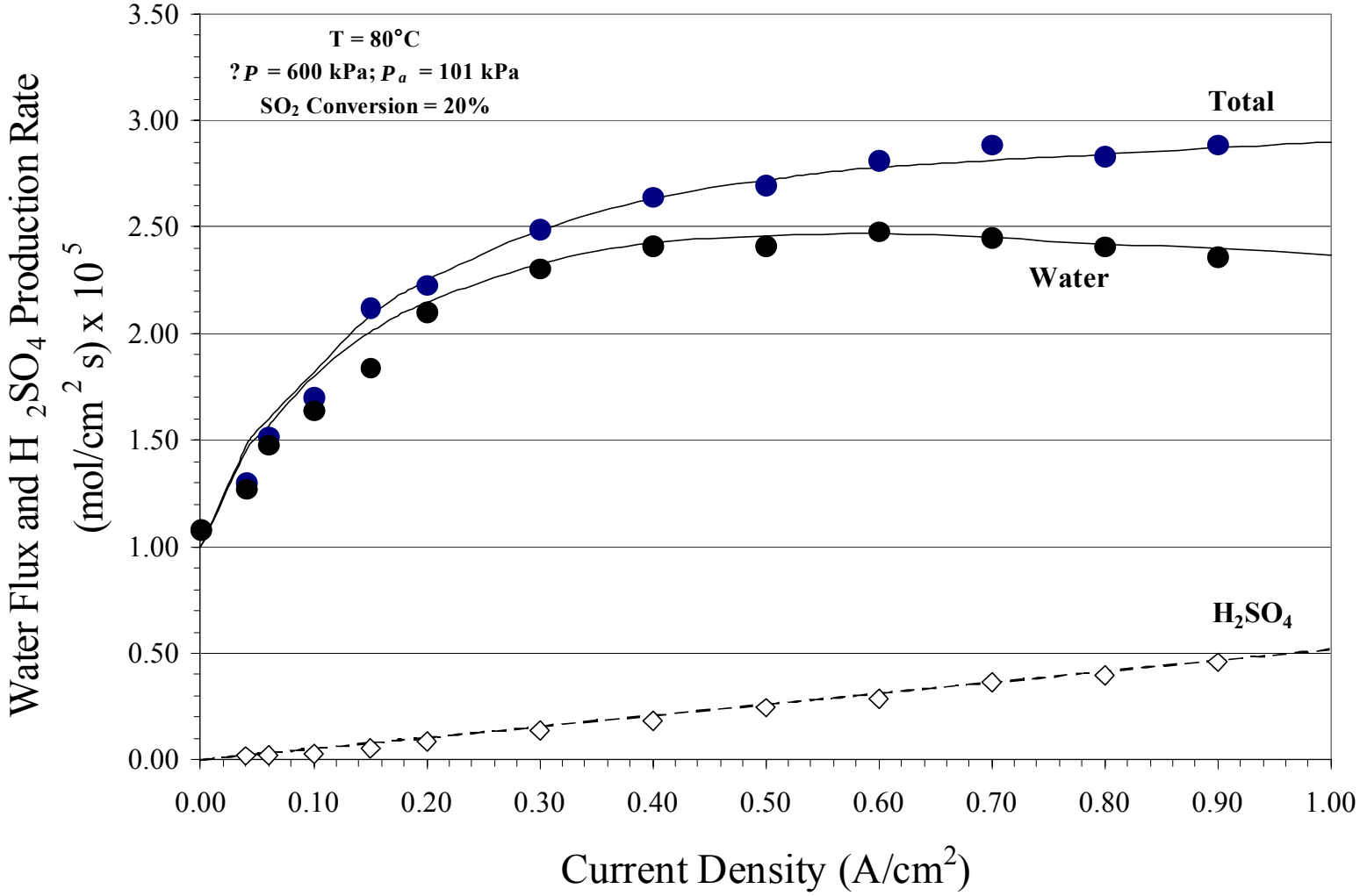
Effect of ΔP and T on Sulfuric Acid Production



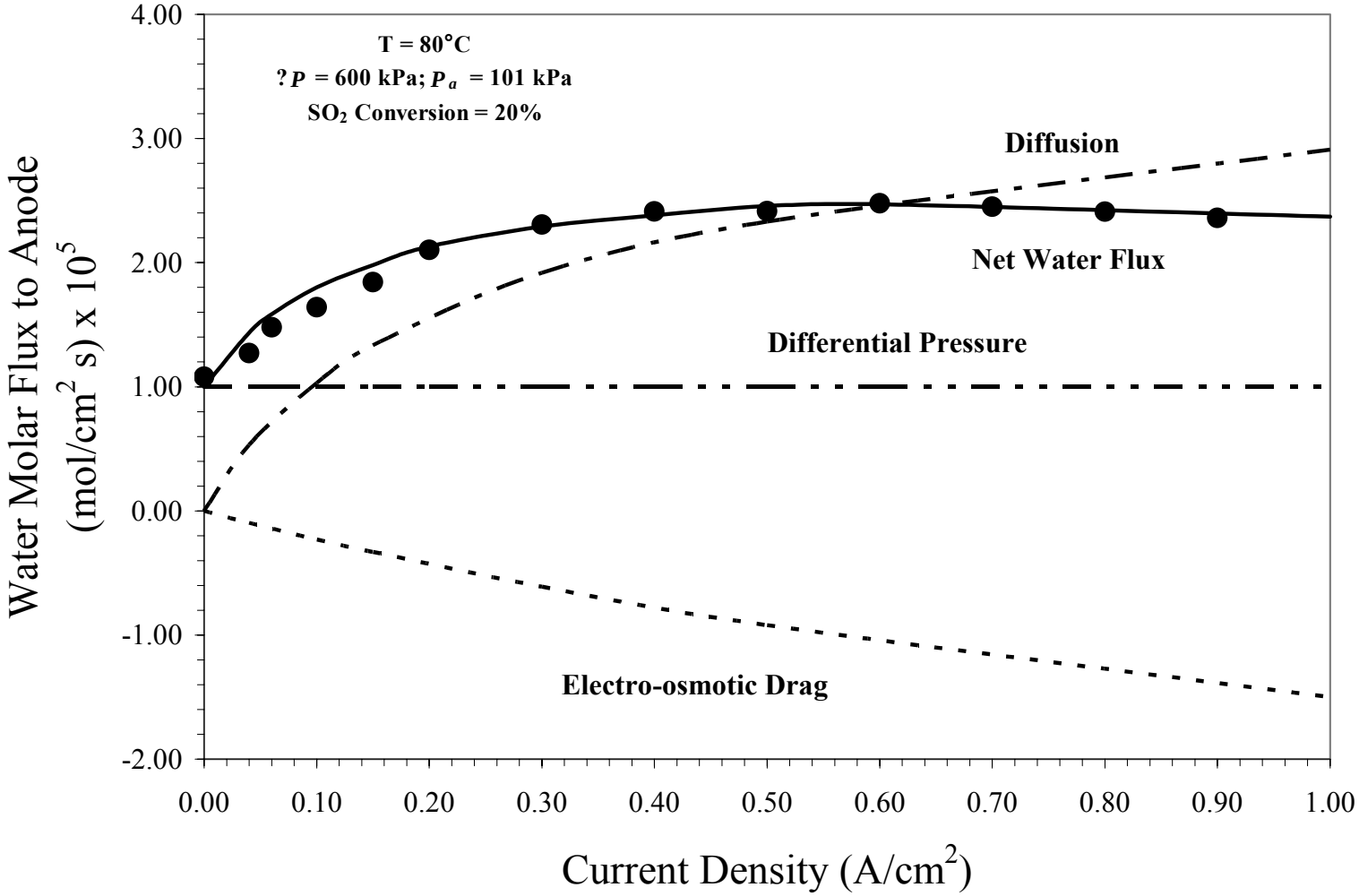
H_2SO_4 Concentration



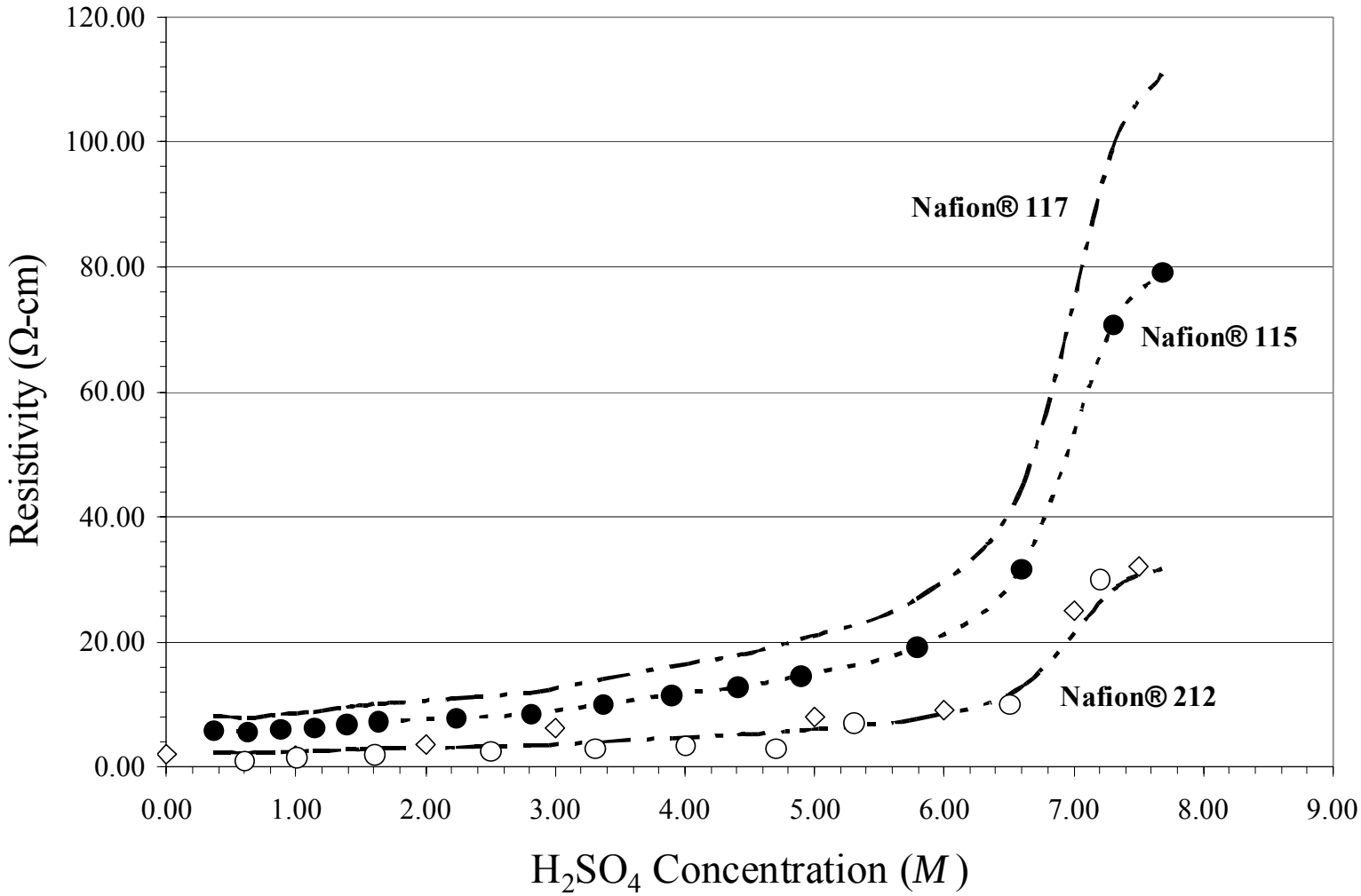
Contributions to Flux



Total Water Flux



Membrane Resistance

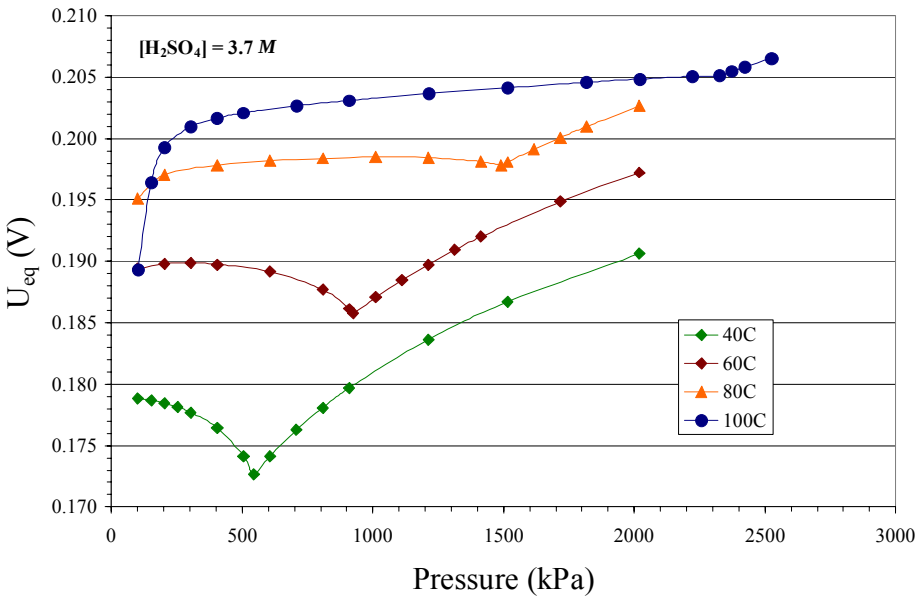


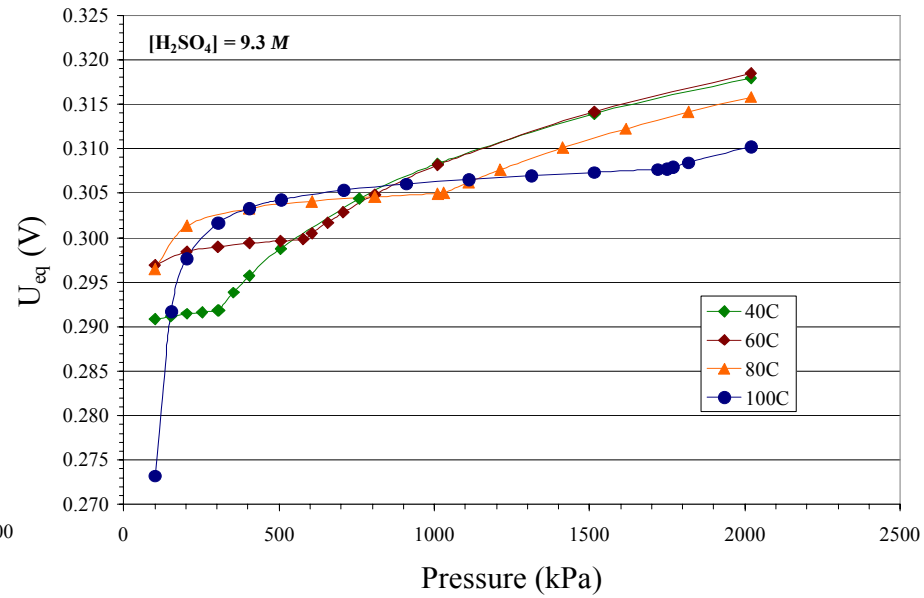
Reversible Voltage

Nernst Equation: $$E_T = E_T^o - \frac{RT}{nF} \cdot \ln Q_T$$

Activity from Aspen: $$Q_T = \frac{(a_{SO_2}) \cdot (a_{H_2O})^2}{(a_{SO_4^=}) \cdot (a_{H_2}) \cdot 10^{-2\,pH}}$$

Temp. dependence: $$E_T^o = E^o + (T - 298.15) \cdot \left(\frac{dE^o}{dT} \right)$$





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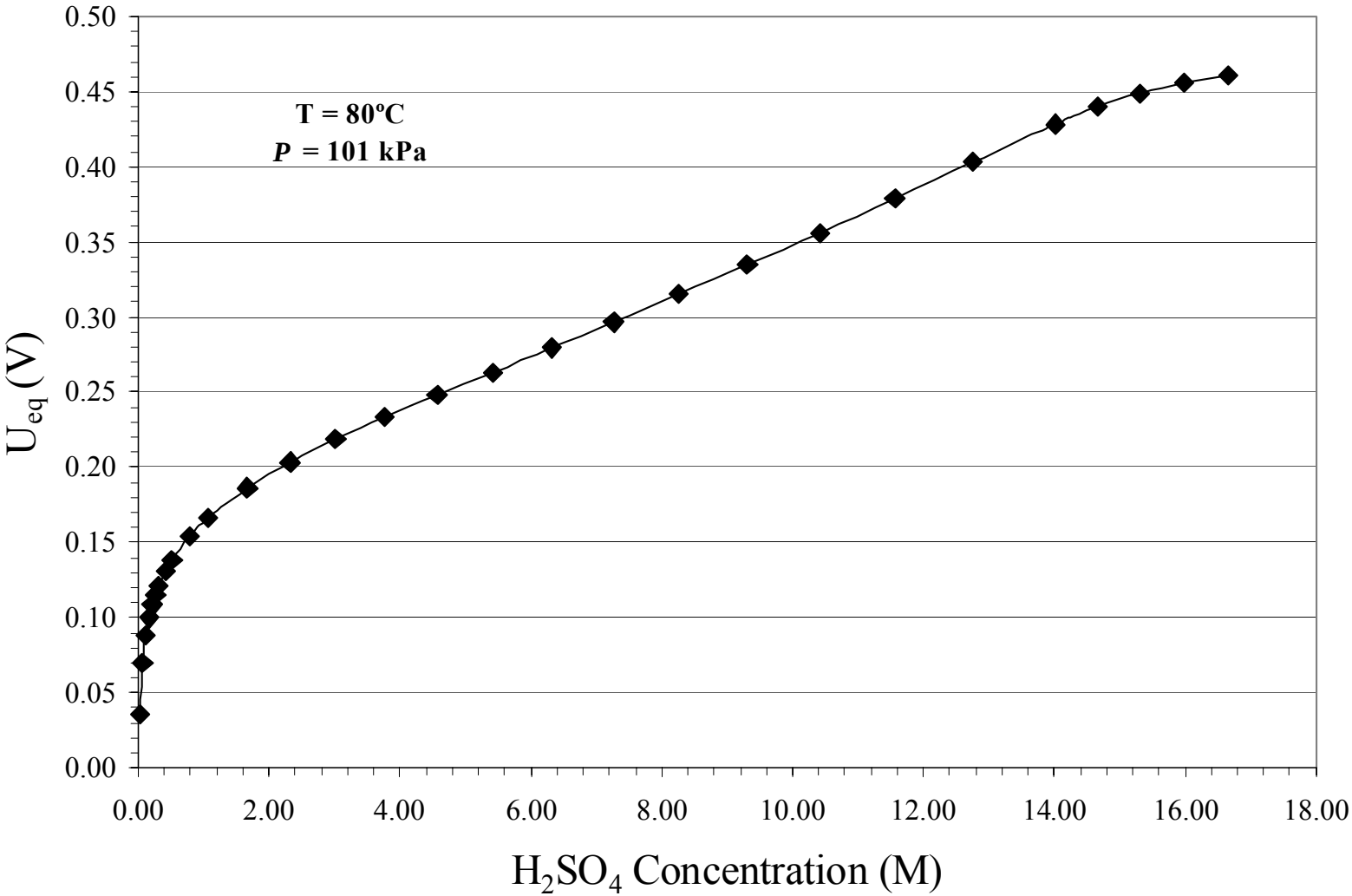
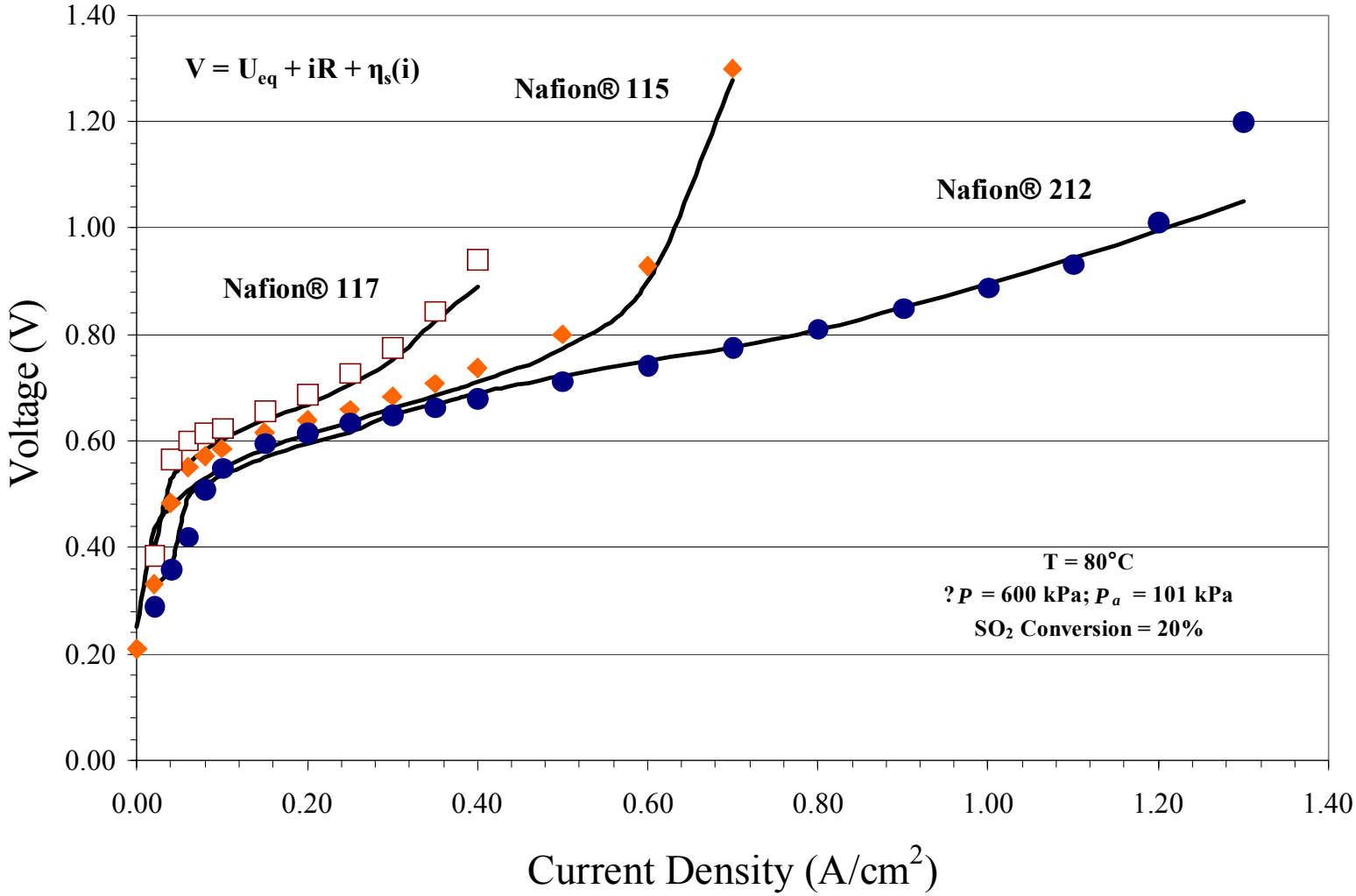
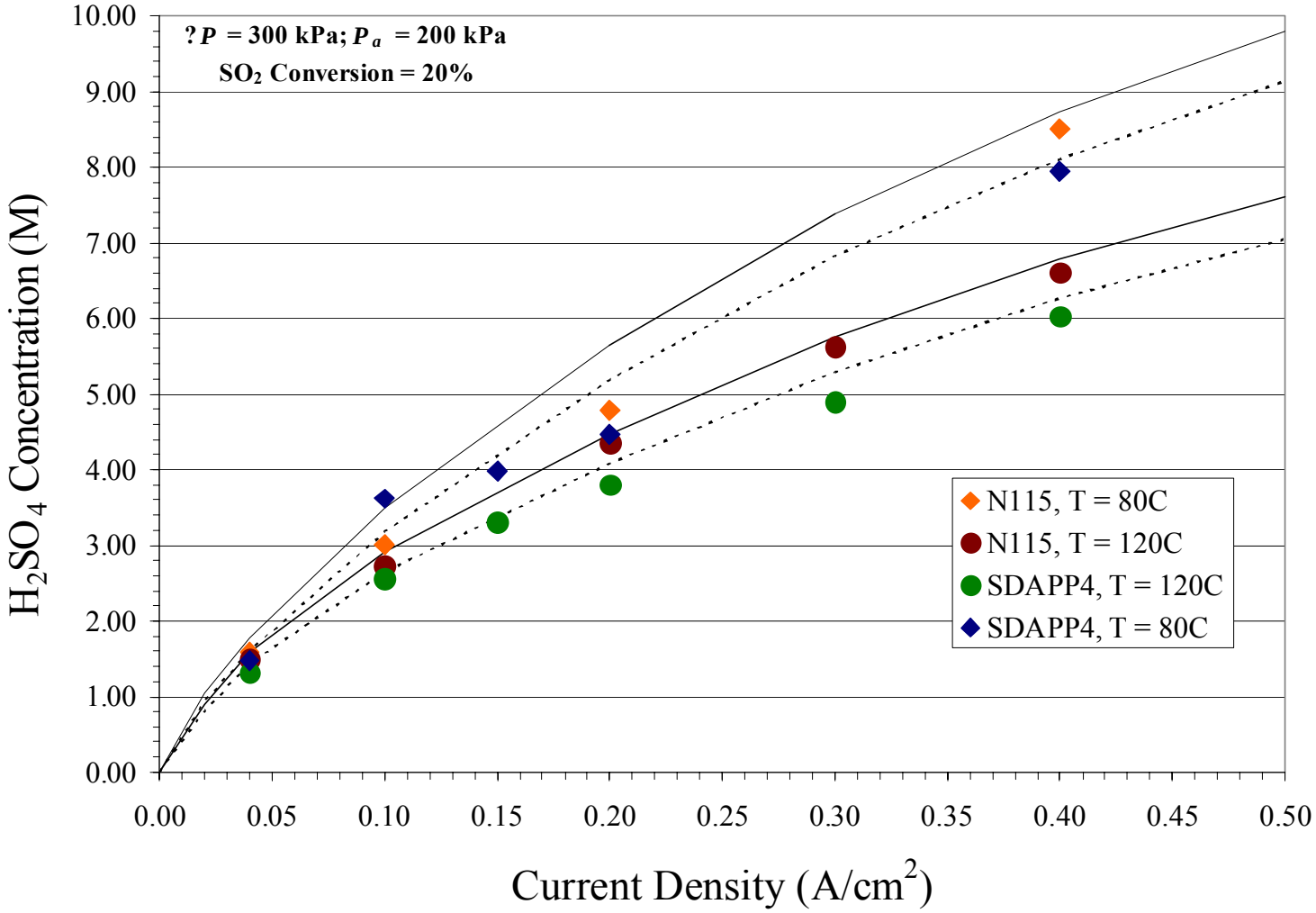


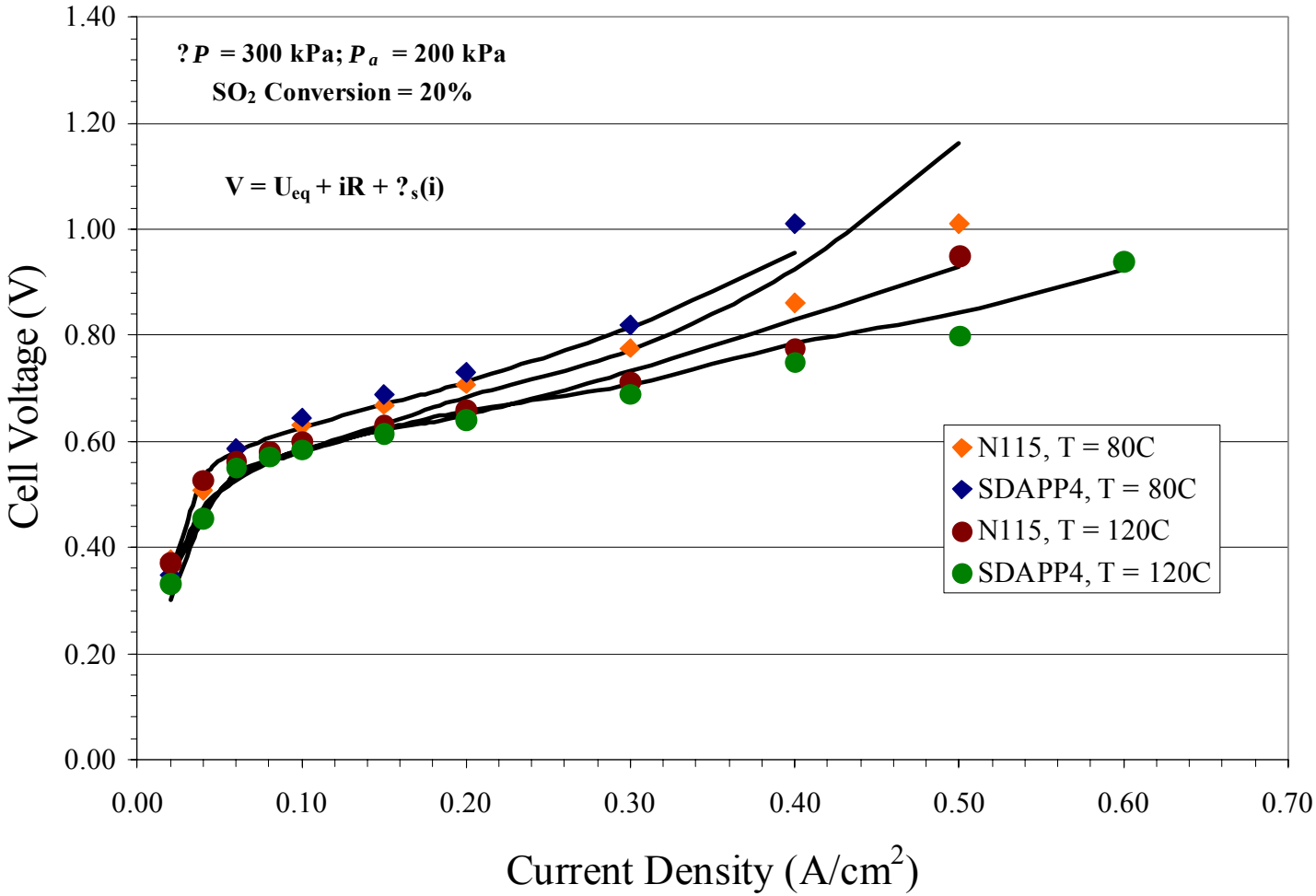
Cell Voltage



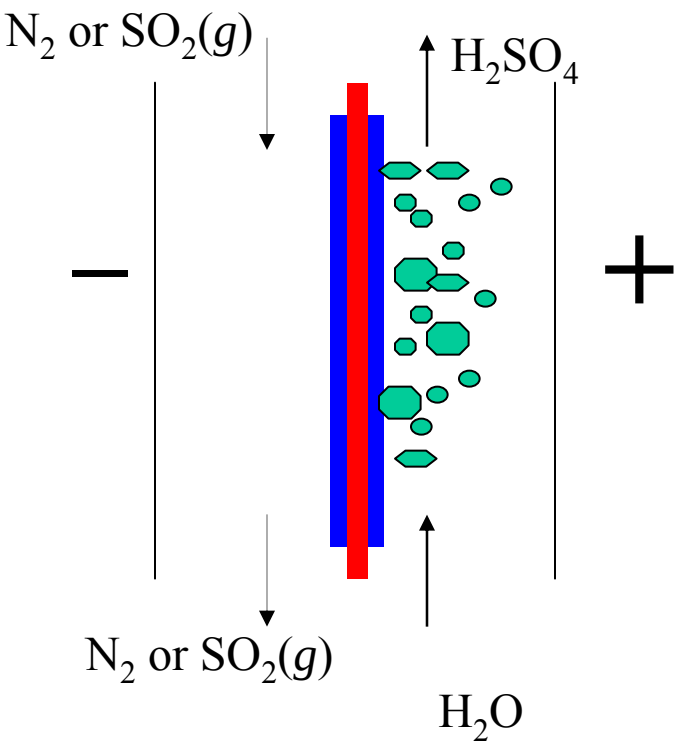
Sulfuric Acid Concentration



SDAPP4 and N115 Polarization



Electrochemical Monitoring Technique



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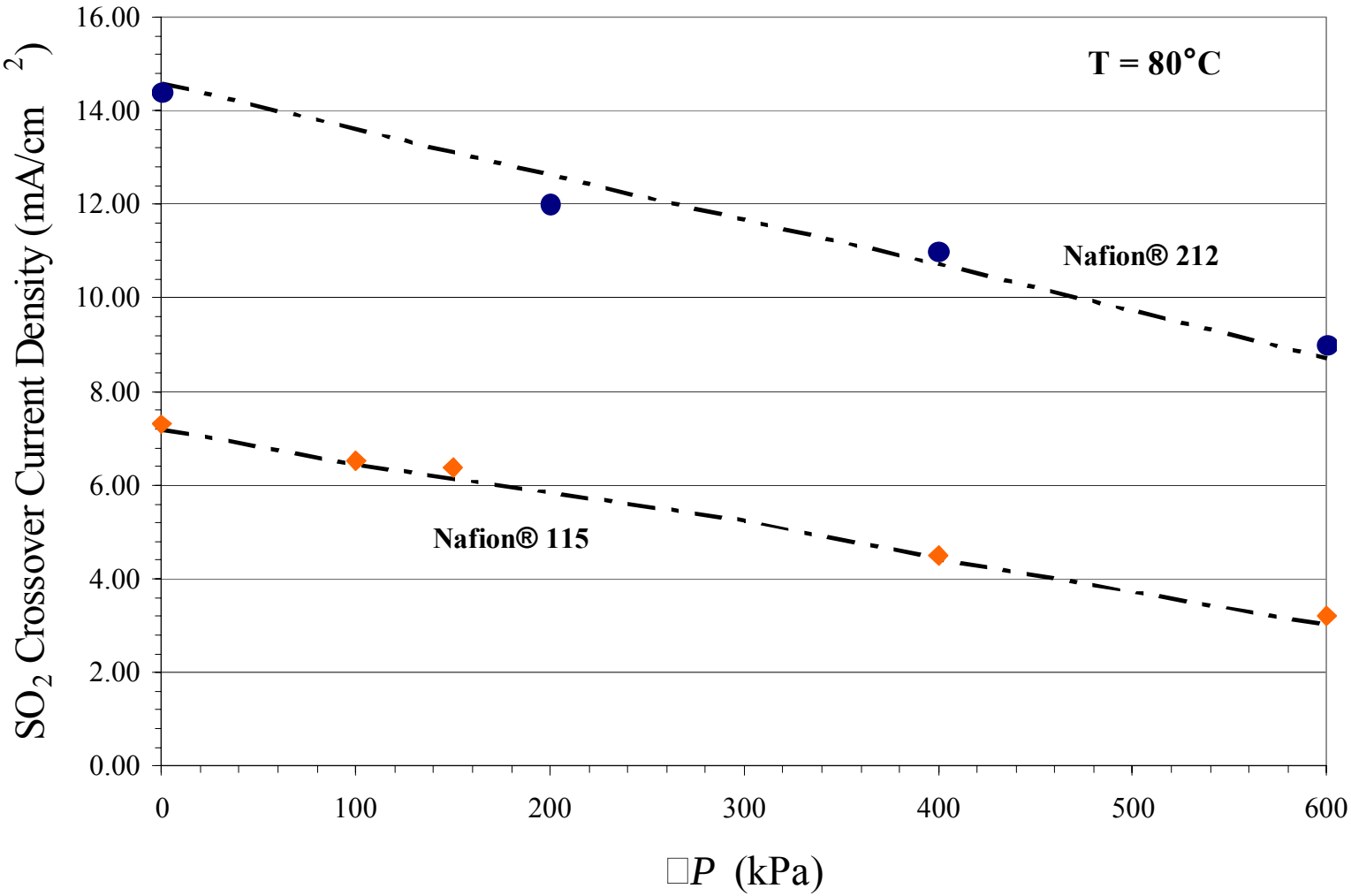
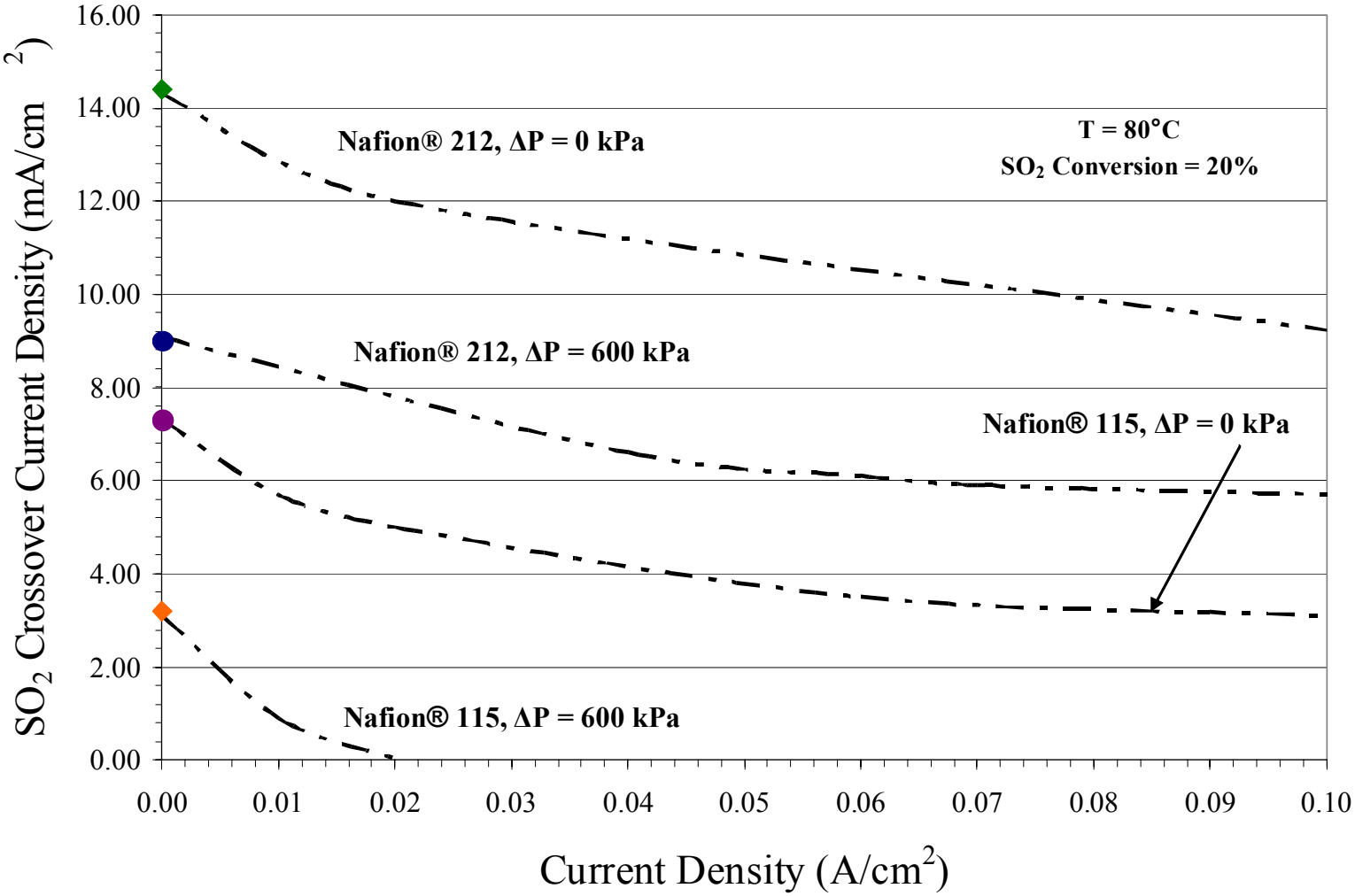
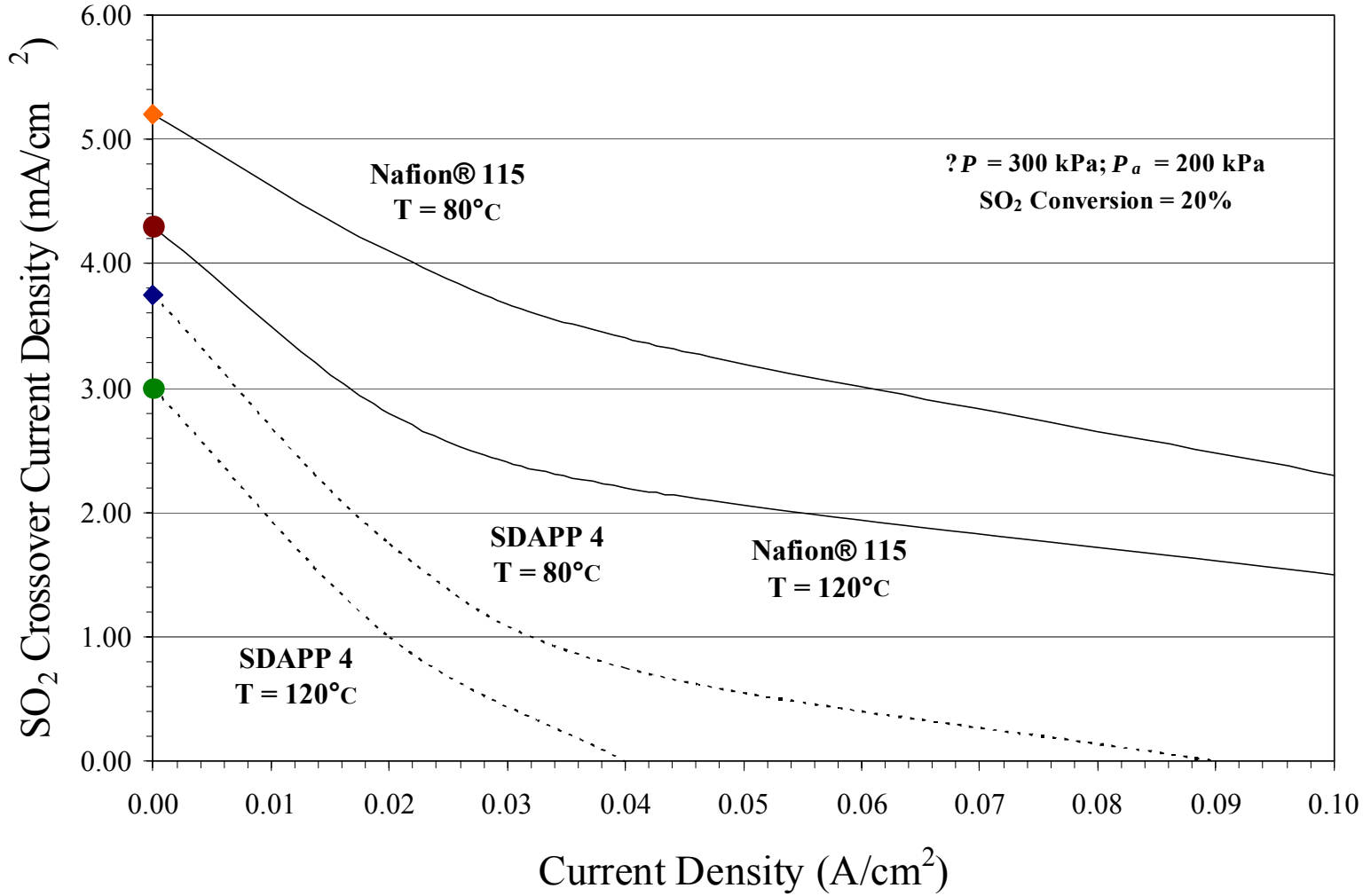
Effect of ΔP on SO_2 Crossover



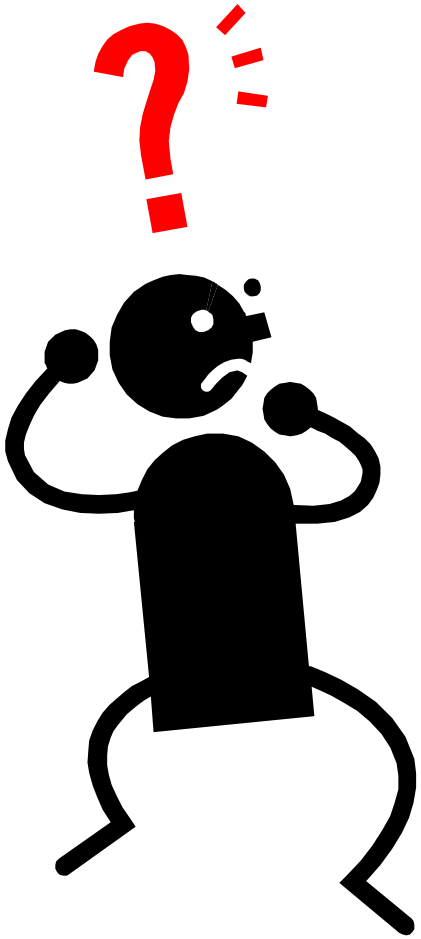
SO_2 Crossover



SO_2 Crossover, ΔP = 300 kPa



Questions



Hy-S Conclusions

- Gas-phase electrolyzer improvement over liquid-phase process
- Water management crucial to operation
  - Affects sulfuric acid concentration
    - Determines U_{eq}
    - Influences membrane resistance
  - Affects SO_2 flux to cathode
    - Limits reduction to S at cathode
    - Reduces impurities in hydrogen stream
- Voltage predictions
  - Predict voltage vs. T, membrane thickness, ΔP
  - Voltage tied to water management

Future Work

- Kinetic studies
  - RDE analysis
- SO_2 at cathode
  - Quantify amount of SO_2 in H_2 stream
- Pressurize gas side of electrolyzer
  - May Lead to higher SO_2 flux to cathode
  - Operation at T>100°C
  - Continued evaluation of novel membranes at high pressure

Acknowledgements

- Dr. Weidner
- Committee Members
- Dr. Weidner's research group
- Folks at SRNL (Bill Summers, David Hobbs, Max Gorensek and Hector Colon)
- Mike Hickner (SNL and Penn State)
- Godfrey Sikha
- Deborah Soto

NASA Glenn Research Center

www.wikipedia.com

NASA Glenn Electrochemistry Branch

- Batteries
  - Ni-H_2 life cycle testing (Space Station)
  - Li-based, PEM battery for reusable launch vehicle (RLV)
- **Fuel Cells**
  - **Regenerative fuel cell**
  - **ERAST Helios prototype**
  - **Power plant for RLV**

http://www.grc.nasa.gov/WWW/Electrochemistry/doc/activities.html

Objective

- Develop regenerative fuel cell for aeronautical and space applications
  - Limited H_2 and O_2 fuel required
  - System is smaller, less costly to launch
- Water management is an issue
  - Draw water away from cathode to prevent flooding
  - Also aids in water capture for electrolysis

Possible Solution

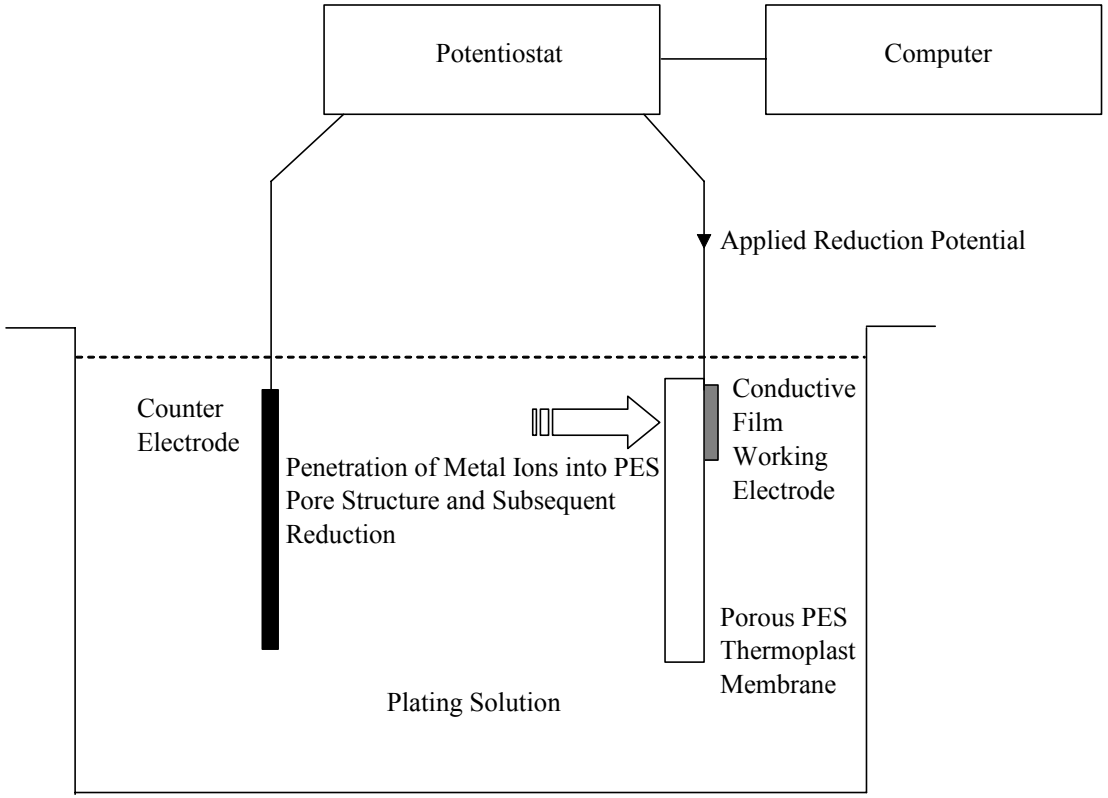
- Porous PES membrane (0.2 μm)
  - Allows water passage through pores
  - 50 psia O_2 bubble pressure resists O_2 passage
- Not conductive
  - 10^{16} Ω-cm resistivity
  - Must be conductive for integration into stack

http://www.mitsui-chem.co.jp/info/pes_e/pes_e_pdf/pes_t_brochuredoc.pdf

Proposed Approach

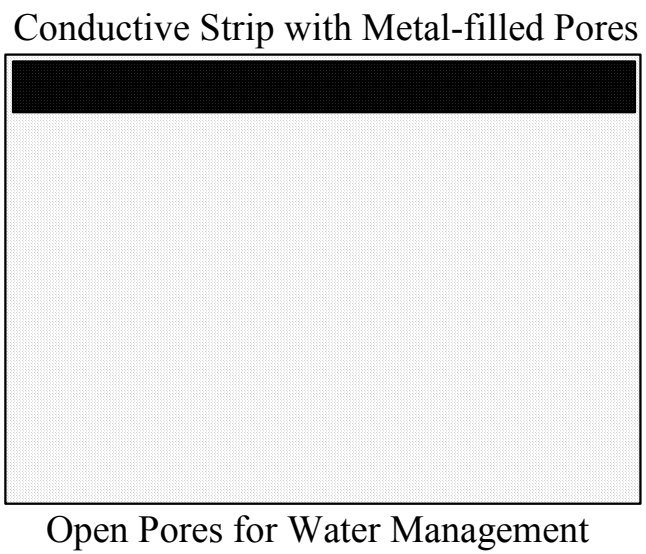
- Sputter (or spray) conductive strip to one side
- Mask off sprayed side, immerse in plating solution
- Plate metal into pores
- Sputter (or spray) another conductive strip to other side

Plating Setup

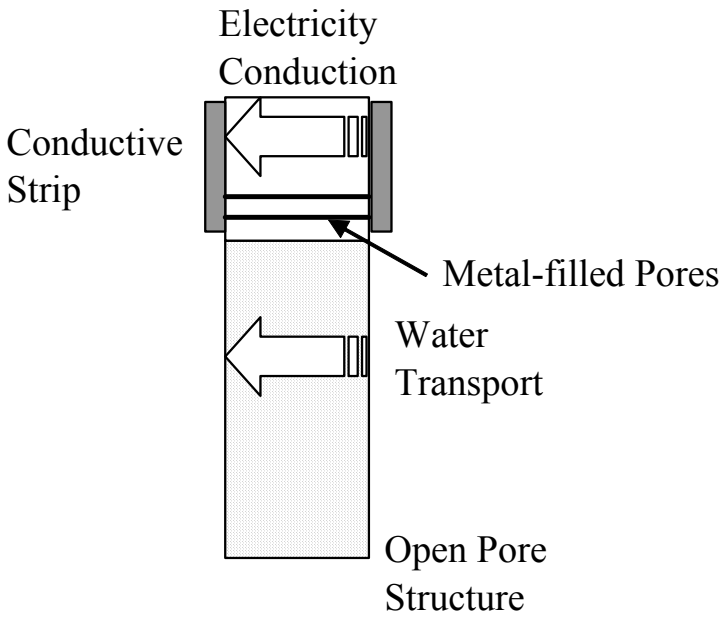


- Mask off WE
- Plate metal into pores
- Should provide pathway for electricity

NASA Coated Membrane



Metall-doped PES Membrane
Front View



Metall-doped PES Membrane
Side View

- Two conductive strips in electric contact through metal-filled pores
- Allows for electrical contact with each cell in stack
- Most pores still open for water management

Initial Work

- Paint Pt/C catalyst ink to one side
- Tape off back of membrane
- Use 0.1 M $Cu(NO_3)_2$ plating solution
- Plating method was unsuccessful
  - No increase in conductivity through membrane
  - Painting one side of membrane prevents plating solution from penetrating pores

New Plating Method

- Tape membrane to Pt foil
- Expose small area for plating
- Plate at 30 mA for 10 minutes
- Plating method is successful
  - ~500 Ω resistance through membrane
  - Need lower resistance, but project feasibility has been demonstrated

Improved Conductivity

- Plate at 5 mA for 72 hours
- Rough Cu surface is observed
- Plate for 40 hours, smoother surface
  - Unable to produce smooth surface
  - Not feasible for use in URFC
- Resistance across membrane is 0 Ω

Gold Nanoparticles

- Synthesize Au nanoparticles
  - $HAuCl_4$ reduced by sodium citrate
  - Particle size ~20 – 50 μm
- Filter through membrane w/vacuum
  - Use butanethiol as binder
  - Attempt to fill pores with Au
- Resistance across membrane is 2000 Ω
  - Not effective in filling pores
- Try reducing $HAuCl_4$ *inside* pores
  - Still unable to fill pores

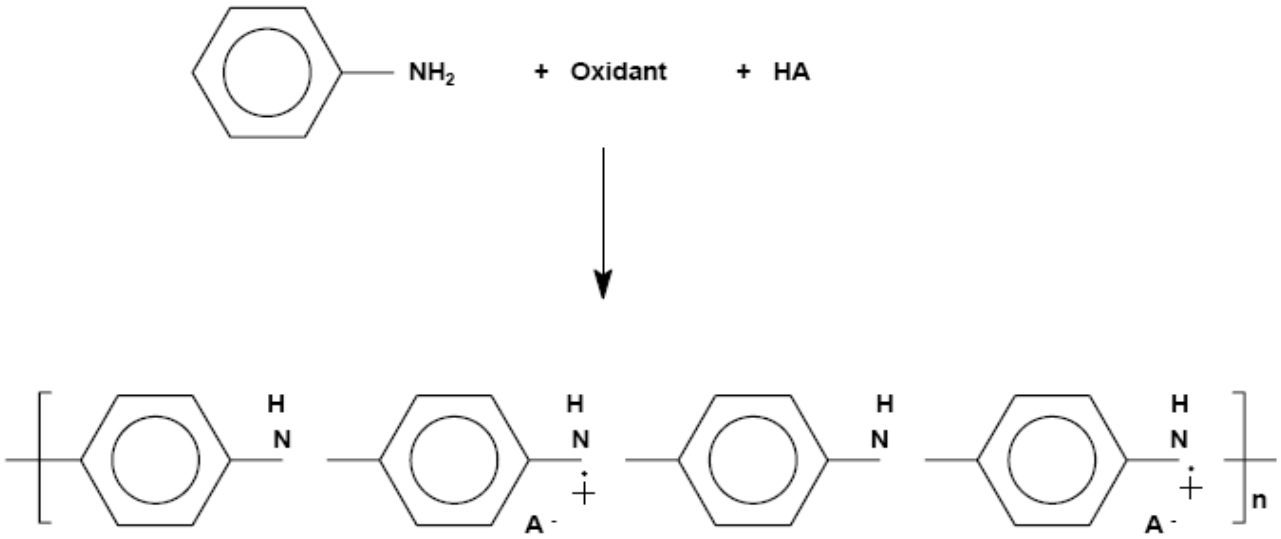
Conductive Polymers

- Polyaniline supplied by Crosslink USA
  - Proprietary solution
  - Developed for dip-coating
  - Temperature and chemical resistant
- Filter through membrane w/vacuum
  - Solution fills pores readily
  - Good surface layer developed
- Resistance across membrane is 100 Ω
  - Much lower resistance
  - Promising method for imparting conductivity to PES

Acknowledgements

- Mark Hoberecht and Ken Burke at NASA Glenn
- Mike Hickner at Sandia National Labs
- Prof. Weidner for advising this work
- Committee members for listening to me

EMPAC



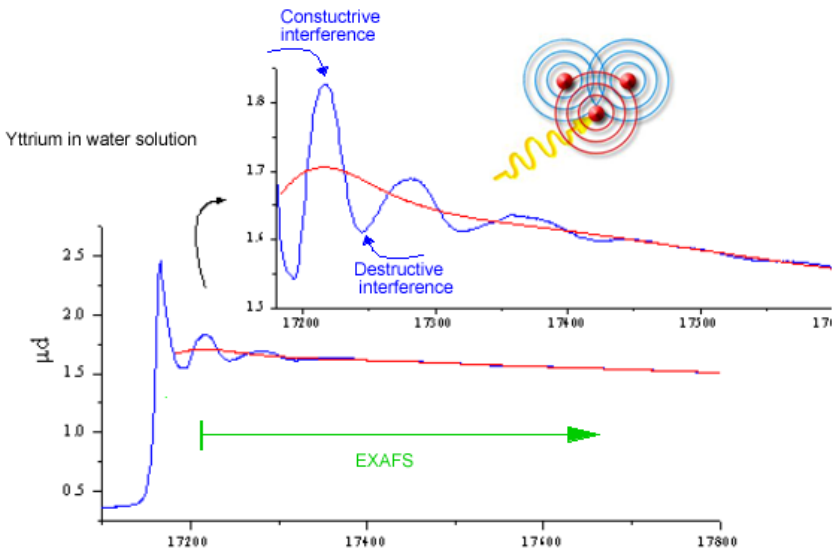
Soluble Emeraldine Salt

CROSSLINK™ ENERGY MATERIALS

Proprietary & Confidential

EXAFS

- Used to determine co-ordination number and atomic distances
- Target atom absorbs photon, emitting photoelectron
- Photoelectron (spherical wave) scattered by neighboring atoms
- Often the only possible characterization method for materials that do not have long-range order



- Iztok Arcon, *Extended X-Ray Absorption Fine Structure*, http://www.p-ng.si/~arcon/xas/exafs/exafs.htm [online] August 8, 2007

XRD

- Samples with long-range order
- Photon collides with electron and is deflected.
  - Thompson Scattering – only momentum transferred, wavelength stays the same
  - Compton Scattering – energy transferred, wavelength of photon changes
- Peaks correspond to structure
  - Sharp peak corresponds to crystalline structure
  - Peak height corresponds to atomic distance
  - $2d\sin\Theta = n\lambda$, Bragg's Eq.

- *Introduction to X-Ray Diffraction*, Materials Research Laboratory, UC Santa Barbara, http://www.mrl.ucsb.edu/mrl/centralfacilities/xray/xray-basics/index.html, [online], August 8, 2007.

Brewer Plot

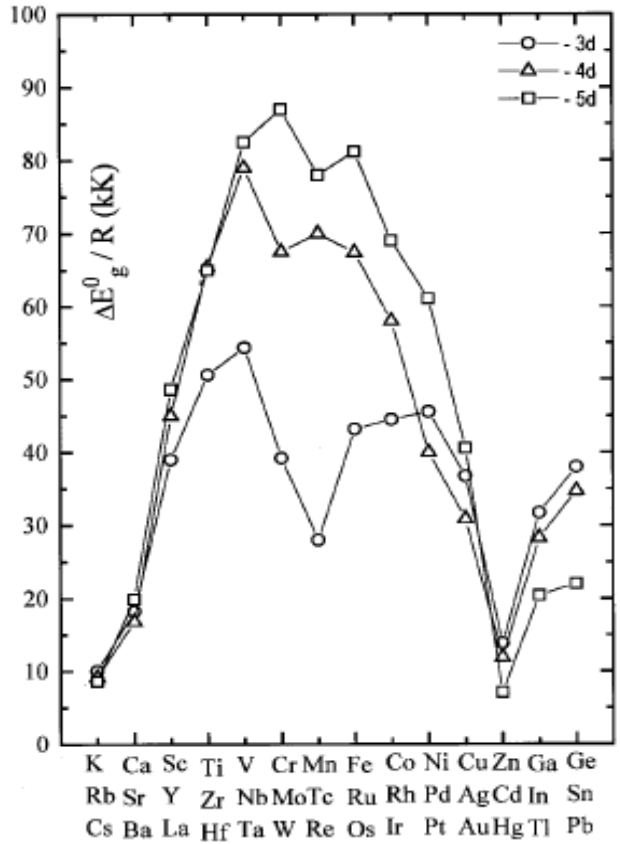


Fig. 1. The Brewer plot of energy of vaporization of liquid metals ($\Delta E^{\circ}_g/R$) to their ground state atom at melting point, along the Periodic Table (Jakšic after Brewer [22]).

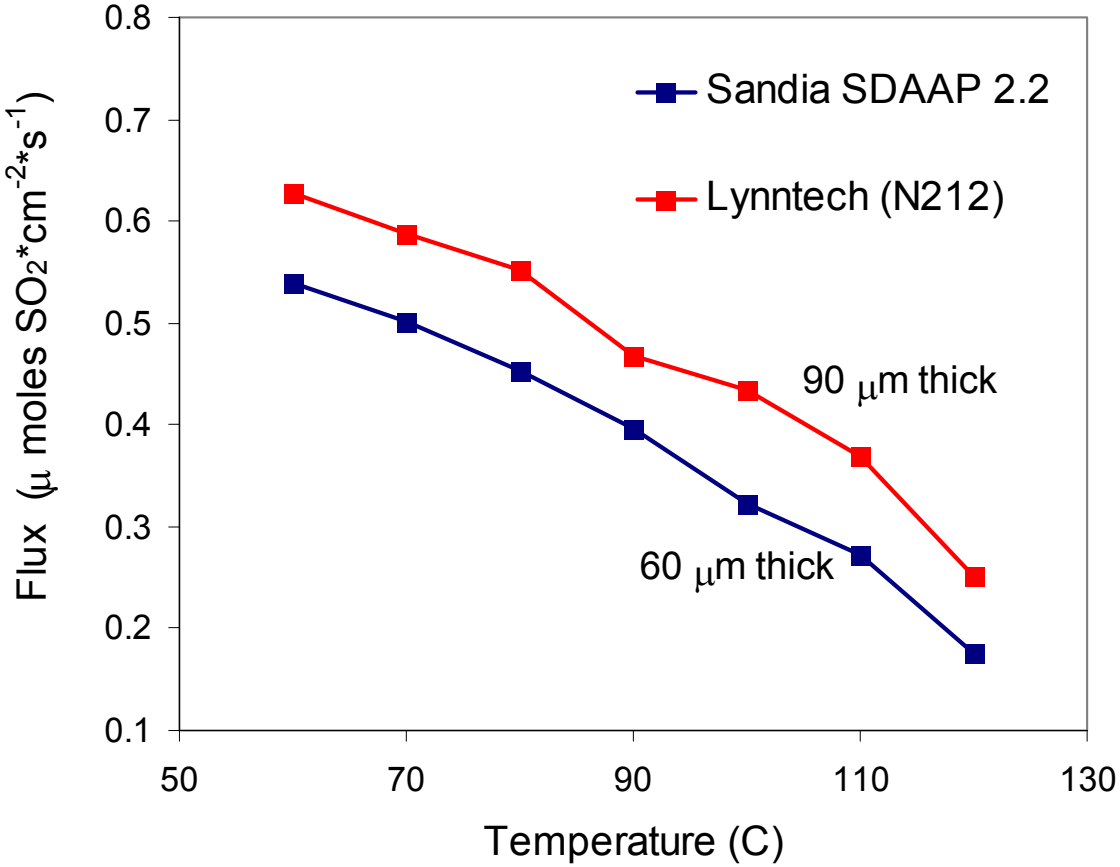
- Brewer Plot to identify metals suitable for HER
- Plots energy of vaporization of liquid metals to ground state atom at melting point
- Metals of top of plot are most suitable for HER

- M.M. Jaksic, *Electrochemica Acta*, **45**, 4085 (2000).

Catalyst Synthesis

- Start with precursors
  - Nickel (II) Acetylacetonate powder
  - Manganese (II) Acetylacetonate powder
  - WCl_6
  - $Al(C_5H_7O_2)$
- Sonicate carbon support in EG containing 0.2-0.4 *M* NaOH 45 minutes
- Add precursor powder to carbon/EG mixture, stir 2 hours
- Heat at 160°C 3 hours
- Cool 2 hours
- Add 1 *M* HNO_3 until solution pH is 1
- Stir 3 hours
- Filter catalyst and dry 3 hours
- Dry catalyst in vacuum at 105°C 6 hours
- Reduce under H_2 at 400°C 3 hours

Decreased SO_2 Crossover Using SNL Membranes – less process loss, higher efficiency



Steady-state SO_2 flux for Sandia membrane SDAAP 2.2 meq/g (4-141-D) and Nafion 212 (Lynntech MEA).

SO_2 crossover
- process loss
- parasitic H_2 consumption
- elemental sulfur buildup on the cathode, block reaction sites

SO_2 flux to cathode is lower for Sandia membranes even though SNL membranes are thinner.

Mike Hickner with permission

Model Assumptions

- 1. The Nafion membrane is the primary barrier to water transport before condensation, and the concentration of water is uniform across the gas diffusion layer and flow channel.
- 2. The water/SO2 vapor mixture obeys the ideal gas law.
- 3. A solution of H2SO4 forms at the electrolyzer inlet at the MEA/gas diffusion layer interface and the concentration is governed by a simple thermodynamic relationship.
- 4. Diffusion of H2SO4 across the membrane is negligible.
- 5. The membrane thickness is the same for the cases in which the membrane is dry and when it is wet.
- 6. The electrolyzer system is maintained at a uniform temperature throughout.
- 7. The water permeability across the Nafion membrane is negligible.
- 8. The same functional form of the diffusion coefficient can be used for this system as reported in the previous paper for the water/N2 system.

Model Utilization

- Water mole fraction changes with H_2SO_4 concentration
- H_2SO_4 concentration is the same at each point in the flow channel – 1D model
- Changing water mole fraction influences water diffusion due to the changing concentration gradient
- Water mole fraction determines λ, the water content at each point along the flow channel
- Changes integration limit for water flux equation
- Integrate using *quad* function in Matlab

HER Mechanisms

- HER in acid medium

$$M + H^+ + e^- \leftrightarrow M\text{-}H_{ads}$$

$$M\text{-}H_{ads} + H^+ + e^- \leftrightarrow H_2 \uparrow + M$$

$$2M\text{-}H_{ads} \leftrightarrow H_2 \uparrow + 2M$$