

Through-thickness Membrane Conductivity Measurement for HTM Program: Issues and Approach

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Through-thickness membrane conductivity: **Motivation**

- Development of new ionomers and novel proton conductors is focused on improving membrane conductivity for challenging fuel cell operating needs
 - i.e., High conductivity at high T and low RH
 - Allows for system simplification to meet commercial applications
- There is a need for the ability to rapidly and accurately measure key membrane properties as a function of T and RH
- Through-thickness membrane resistance (or conductance) is a key property of interest for fuel cells
- Traditionally measured with catalyzed membrane (MEA) in 2-probe configuration (i.e., a single-cell fuel cell)
 - Must account for
 - R_{contact} (current collector/GDL, GDL/MEA)
 - $R_{\text{electronic}}$ (CC, GDL, leads)
 - $R_{\text{interface}}$ (electrolyte/catalyst)
 - Time consuming to make MEA, build FC and test

Through-thickness membrane conductivity: **Objective**

- Develop hardware and protocols to measure through-plane conductivity of PEMFC membranes
- Ideally, test device will
 - Use bare (uncatalyzed) membranes - 10 to 200 μm thick
 - Employ a 4-probe technique to eliminate confounding R_i
 - Operate over a wide range of atmospheric conditions
 - T, specific humidity / RH, pressure
 - Measurement would be fast \sim 15 min / test condition
 - Hardware and protocols would be robust
 - accurate, repeatable, reliable
 - user-friendly
- Versatile R&D tool to support development of HTMs
- HTM Program Year 1 Milestone: Prototype measurement system

Nomenclature

- Conductivity = σ (S/m)
- Conductance = κ (S)
- Resistivity = ρ (Ω -m)
- Resistance = R (Ω)

$$S = \text{siemens} = 1 / \Omega = \text{mho}$$

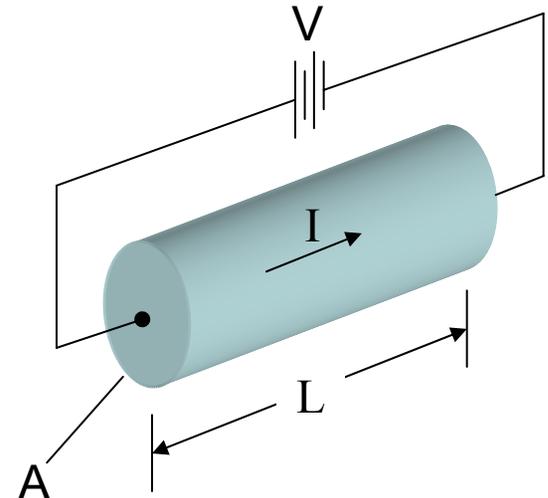
$$V = IR$$

$$R = \rho \frac{L}{A} = 1 / \kappa$$

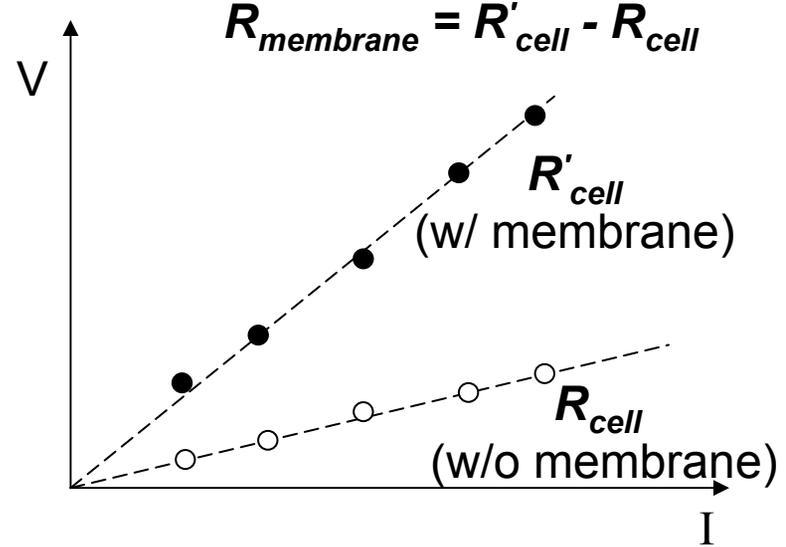
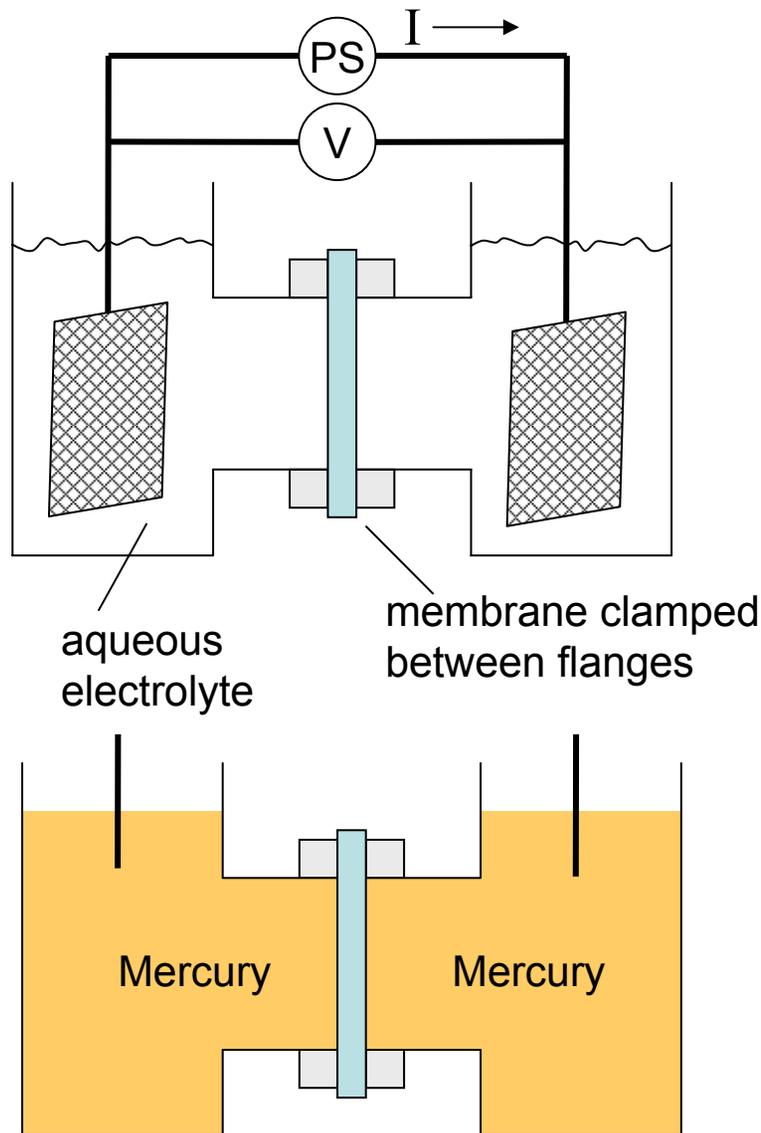
$$\sigma = 1 / \rho$$

- *Resistance* and *Conductance* are extrinsic properties dependent on specimen geometry
- **Resistivity** and **conductivity** are intrinsic material properties
 - e.g., density, elastic modulus, yield strength
 - independent of specimen geometry
 - orientation dependence for anisotropic materials
 - f (microstructure, T, humidity, ...)
- To obtain σ , we need to know V , I , L and A at the time of the measurement

$$\sigma = \frac{I L}{V A}$$

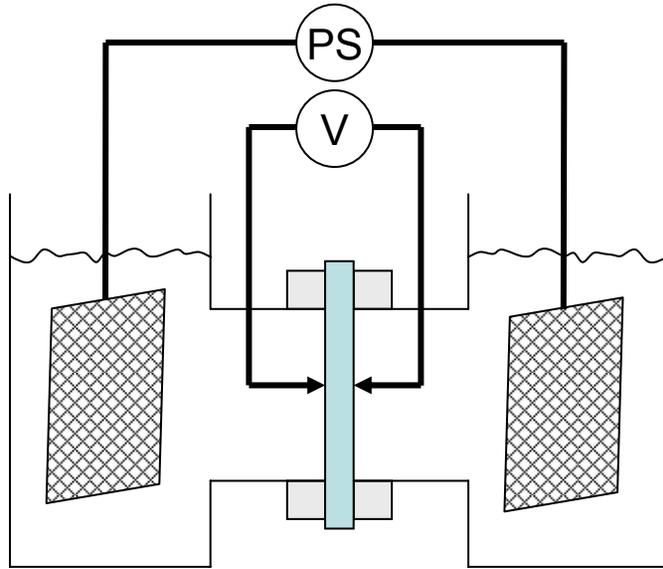


Ionic conductivity of membrane is always determined by measuring its resistance



- 2-probe measurement includes contributions from
 - leads, electrodes
 - contact
 - aqueous electrolyte
 - interfacial
 } = R_{cell}
- bringing electrodes in contact with membrane eliminates ionic resistance of electrolyte (but not others)
- concept behind Mercury cell

Ionic conductivity of membrane is always determined by measuring its resistance



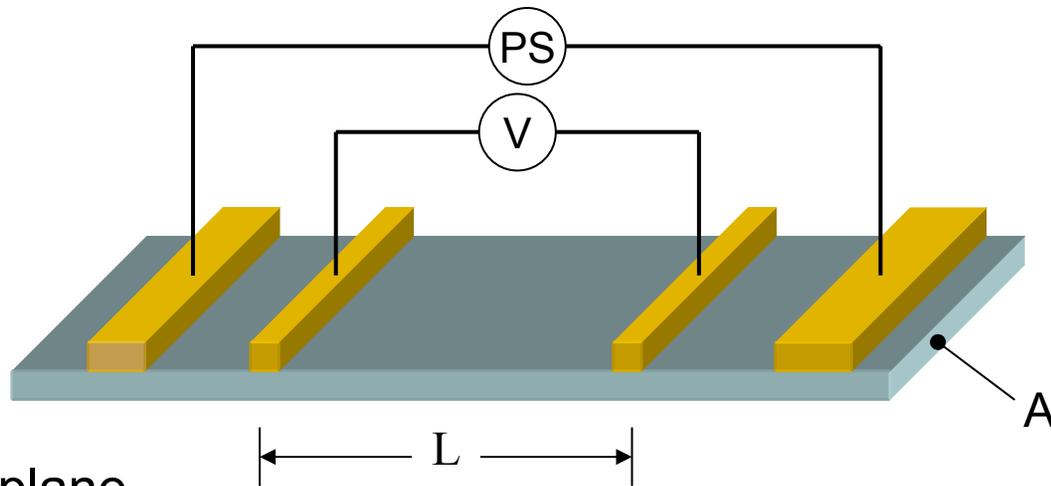
4-probe

- sense electrodes in Luggin probes monitor potential drop across membrane
- minimizes R_{cell}
- better

But aqueous electrolyte and mercury are not relevant test environments for PEM FC because these are not the conditions under which the membrane operates

Measurements must be made in humid gas at relevant temperatures and pressures

Electrodes must be in contact with membrane when measuring conductivity in gaseous environment



$$V_{IR} = \frac{I L}{\sigma A}$$

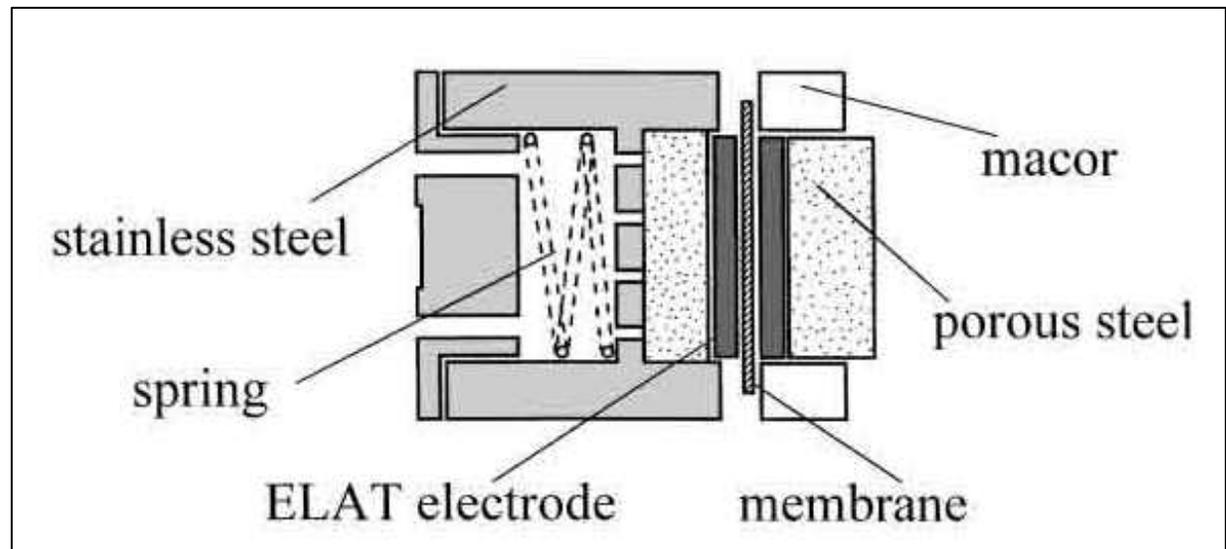
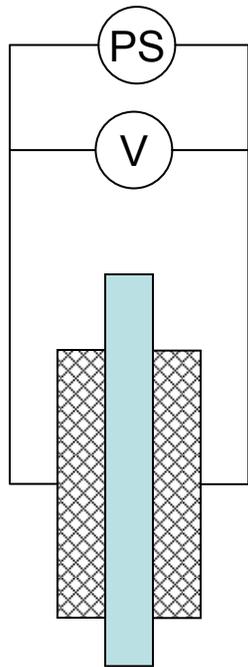
In-plane

- most readily adopted method because dimensions are reasonable to work with
 - small A + large $L \rightarrow$ large V_{IR} for small $I \rightarrow$ good
 - relatively easy measurement
- 4-probe technique easy to implement
- in-plane σ not through-thickness σ
 - anisotropic materials
 - suitable for rapid evaluation of new materials, trending
- surface vs. bulk conductivity

Measurement challenge: Through-thickness membrane resistance in gaseous environments

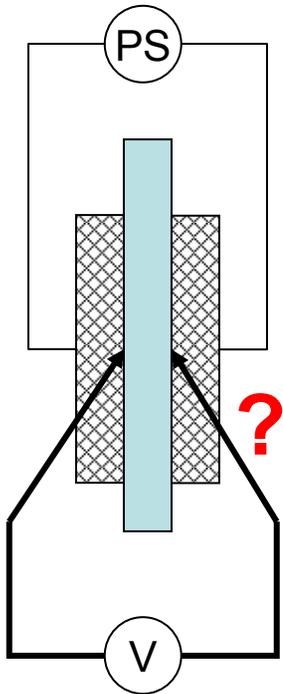
2-probe method

- suffers from very high contact resistance which confounds measurement of very small membrane resistance
- Alberti *et. al.* used up to 5-layer stacks of membrane in order to determine conductivity of low-resistance membranes



G. Alberti, et. al., *J. Membrane Science* **185** 73 (2001)

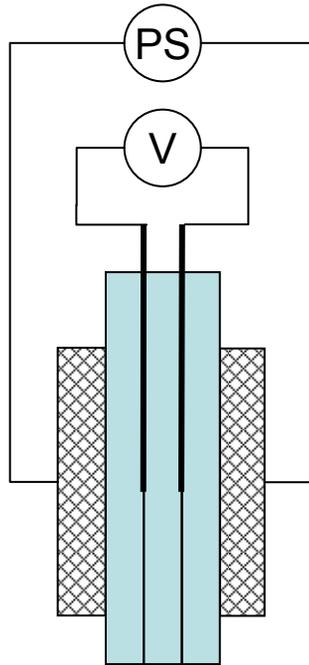
Measurement challenge: Through-thickness membrane resistance in gaseous environments



Making a 4-probe measurement in thin electrolyte presents a challenge

How to place the V-sense electrodes “in” the electrolyte without disturbing the current distribution?

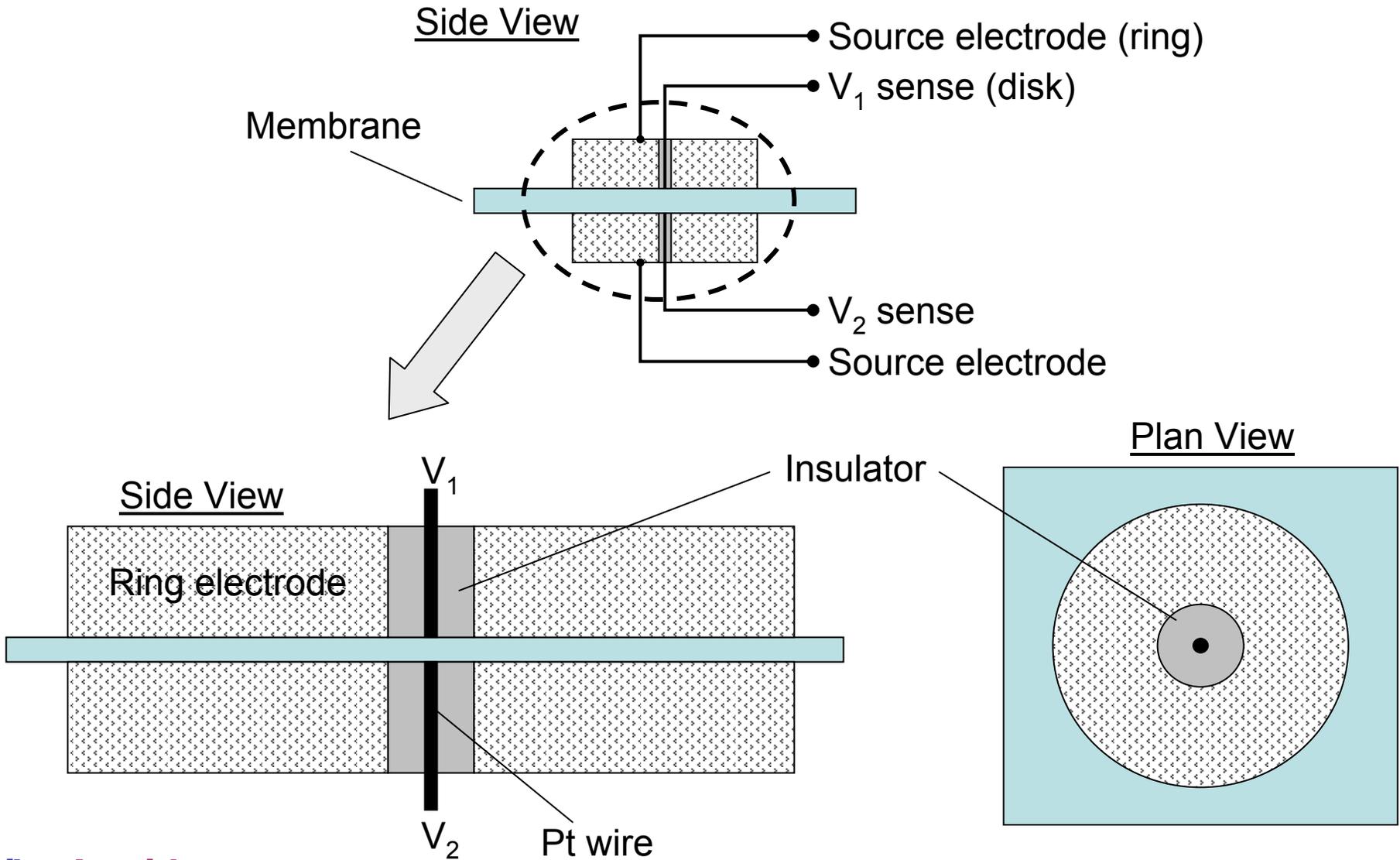
Measurement challenge: Through-thickness membrane resistance in gaseous environments



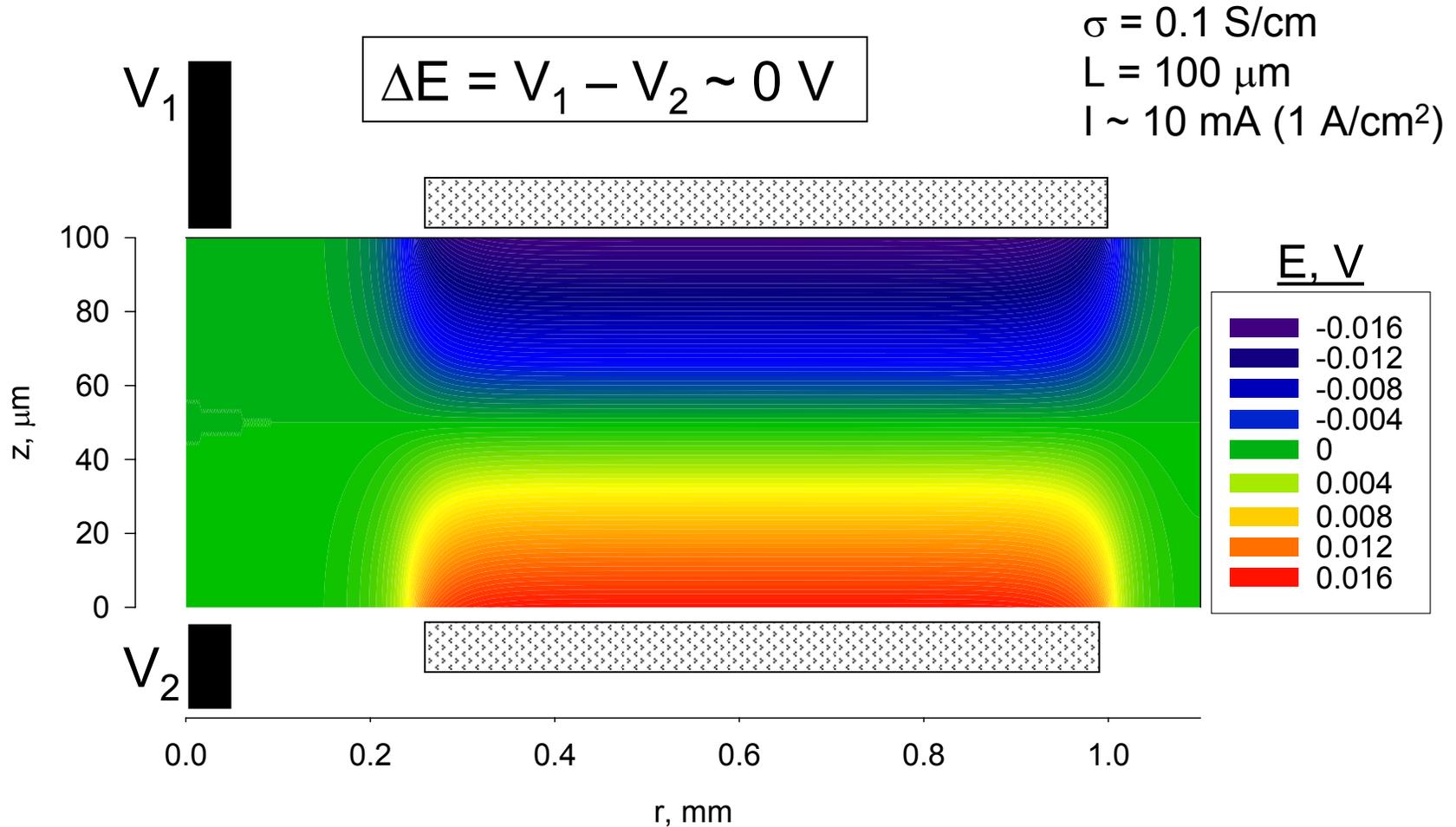
- sandwich and hot-press V-sense electrodes between layers of membrane
- not feasible for this project

S. Ma, A. Kuse, Z. Siroma and K. Yasuda, "Measuring Conductivity of Proton Conductive Membranes in the Direction of Thickness," Espec Technology Report No. 20 (ESPEC) 12-20 (Year?).

4-probe configuration #1: Concentric disk-ring



Electrode configuration #1: Modeling Results

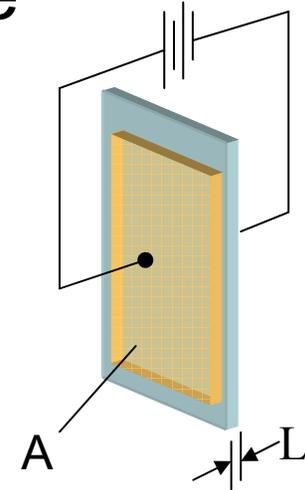


Conclusion: concentric disk-ring concept not feasible - electrode geometry required are not possible with traditional or micro-machining, or lithography

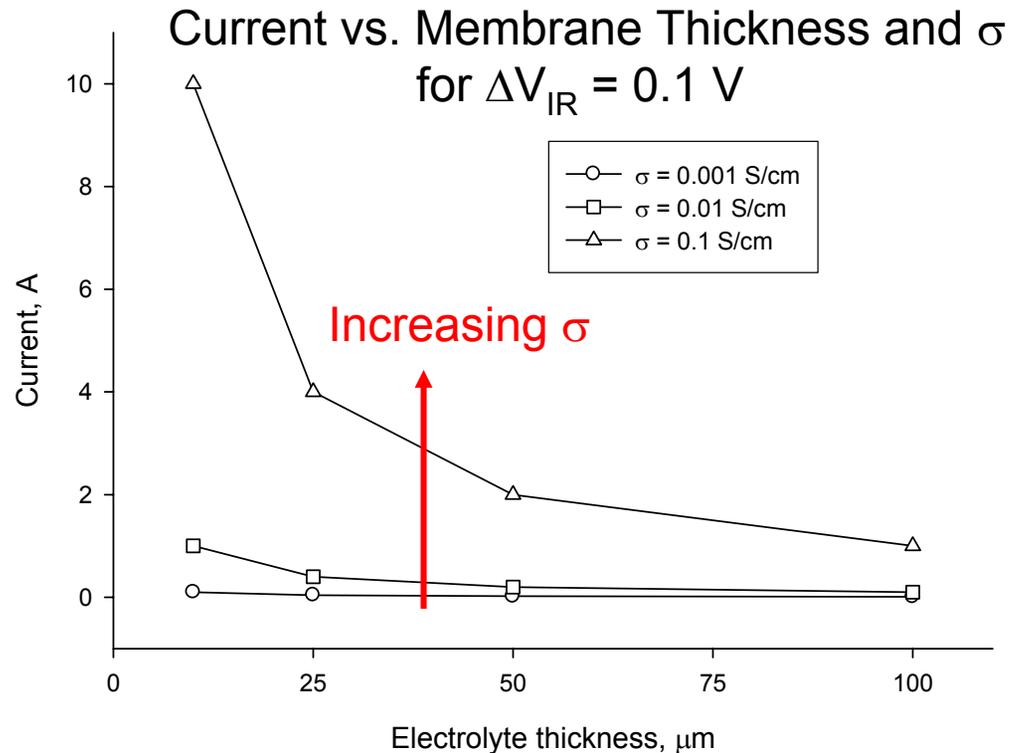
For fuel cell, we want small ohmic voltage loss through the membrane

- i.e., small R
 - small L (thin)
 - big A
 - big σ

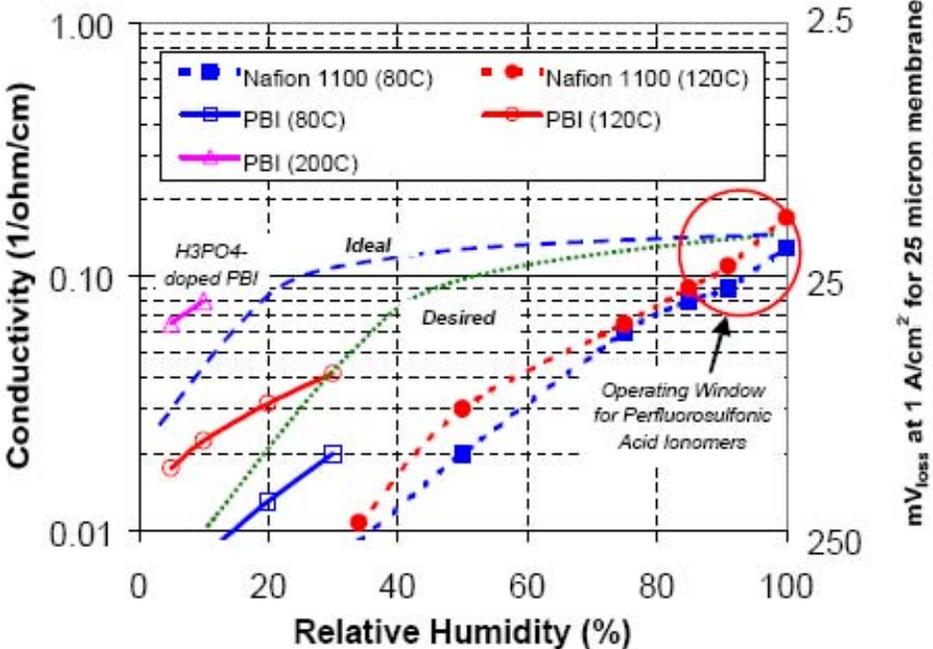
$$V = IR = \frac{I \circledast L}{\circledast \sigma A}$$



- What is “good” for fuel cell can make it difficult for property measurement
 - Large I required for reasonable ΔV_{IR}



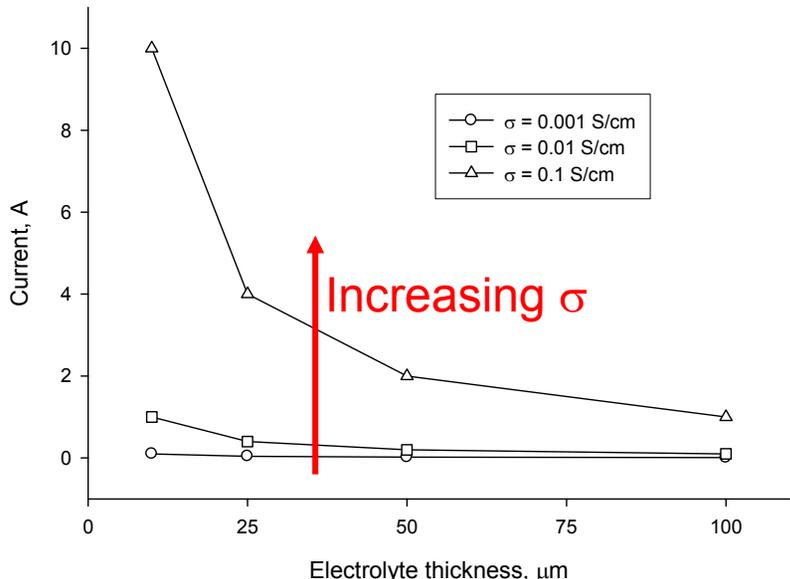
Measurement challenge: Wide range of conductivity and membrane thickness



$\sigma = f(RH, T)$

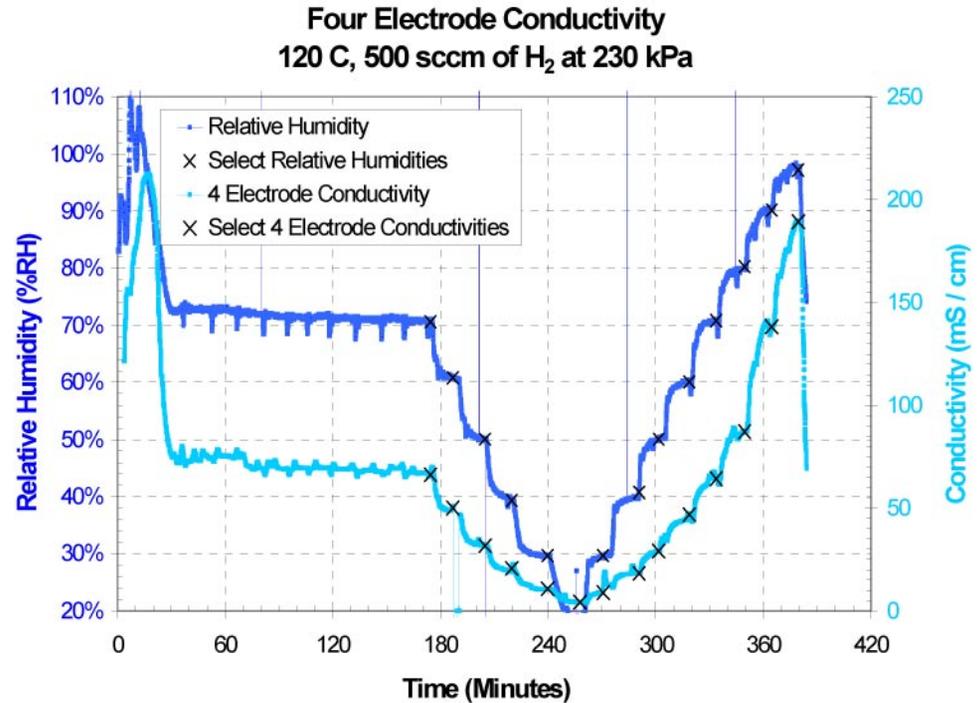
- To accommodate membranes of various thicknesses and broad range in σ , the measurement system must be able to accommodate large changes in V and/or I

Current vs. Membrane Thickness and σ for $\Delta V_{IR} = 0.1 V$

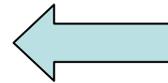


Measurement challenge: Rapid relative humidity cycling in both directions

RH \rightarrow \sim 20% to 100 %
 T \rightarrow ambient to $>$ 120 $^{\circ}$ C

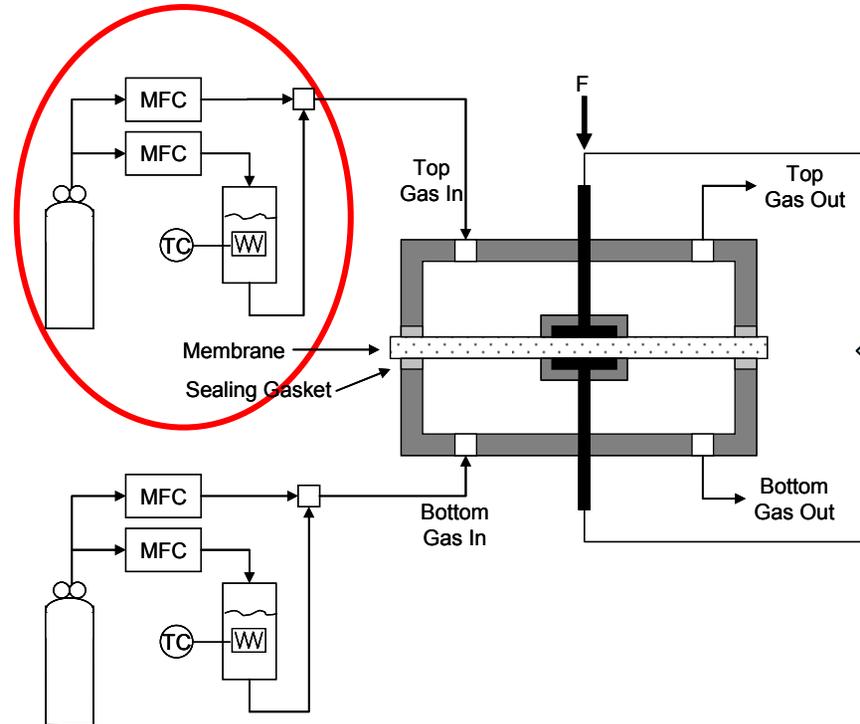


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Approach: Wet + dry gas mixing

- ✓ precise control of RH
- ✓ rapid \uparrow / \downarrow in RH
- ✓ Scribner has experience with this system
- ✗ more complex and \$ than single MFC



Path forward ...

- 4-terminal electrode concept developed
 - approach validated with 2-D model
 - electrodes designed, fabricated and under proof-of-concept testing
- Cell hardware with electrode / membrane clamping mechanism being fabricated
 - pressurized operation feasible for >100 °C, high RH test capability
- Gas humidification system being evaluated
 - accuracy
 - stability – within a day
 - repeatability – day to day