Lead Research and Development Activity for DOE's High Temperature, Low Relative Humidity Membrane Program

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University of Central Florida-FSEC

May 19, 2009

Project ID # fc_01_fenton

FSEC Project Tasks and Team

- Project Management
  - Dr. Darlene Slattery and Leonard Bonville
- Development of poly[perfluorosulfonic acid] -phosphotungstic acid composite membranes (FSEC-1, FSEC-2 and FSEC-3)
  - Dr. Nahid Mohajeri and Benny Pearman
- Development of sulfonated poly(ether ether ketone) - phosphotungstic acid composite membranes (SPEEK, FSEC-SLR)
  - Dr. Nahid Mohajeri and Stephen Rhoden
- Fabrication of catalyst coated membranes
  - Dr. Paul Brooker
- Performance testing
  - Dr. Paul Brooker
- Durability testing
  - Dr. Marianne Rodgers
- Conductivity testing
  - Tim Bekkedahl, and Dr. Marianne Rodgers (in-plane) and Dr. Kevin Cooper (through-plane)
- Technical Advisor/Data Analysis
  - Dr. H. Russell Kunz
- Material Science (SEM, TEM, EDAX, FTIR, TGA)
  - Dr. Nahid Mohajeri, Dr. Marianne Rodgers and Graduate Students

Overview

Timeline

- April 1, 2006
- March 31, 2011
- 60% Complete

Barriers

- Barriers addressed
  - D. High Conductivity at Low RH & High T
  - C. High MEA Performance at Low RH & High T
  - A. Membrane and MEA durability
- Targets
  - Conductivity = 0.07 S/cm @ 80% relative humidity (RH) at room temp using alternate material – 3Q Yr 2 milestone
  - Conductivity >0.1 S/cm @ 50% RH at 120 ^{o}C – 3Q Yr 3 Go/No Go

Budget

- Total project funding
  - DOE share - $2,500K
  - Contractor share - $625K
- Funding for FY08 - $585K
- Funding for FY09 - $115K

Partners

- BekkTech LLC – In–plane conductivity protocols
- Scribner Associates – Through-plane conductivity protocols
- High Temperature Membrane Working Group

High Temperature Membrane Working Group

Funded Projects

- Arizona State University
- Case Western Reserve U (Litt)
- Case Western Reserve U (Pintauro-Vanderbilt)
- Clemson University
- Colorado School of Mines
- FuelCell Energy
- Giner Electrochemical Systems
- Pennsylvania State University
- U of Central Florida, FL Solar
- University of Tennessee
- Virginia Tech
- *Arkema*
- *3M*
- *Lawrence Berkeley National Laboratory*

Affiliation of Invited Speakers

- Giner Electrochemical Systems,LLC
- CARISMA
- Johnson Matthey Fuel Cells
- Ford Motor Company
- General Motors
- Chrysler LLC
- Virginia Tech
- United Technologies
- Nissan Research Center
- Argonne National Lab
- NREL
- BekkTech, LLC
- Scribner Associates, Inc.

Objectives

- Develop new polymeric electrolyte/phosphotungstic acid membranes to meet all DOE targets
- Develop standardized characterization methodologies
  - Conductivity f(RH, T, Prep. Procedure) [Through- & In-Plane]
  - Characterize mechanical, mass transport and surface properties of membranes
  - Evaluate fuel cell performance and predict durability of membranes and MEAs fabricated from other eleven HT Low RH Membrane Programs
- Provide HTMWG members with standardized methodologies
- Organize HTMWG biannual meetings

Milestones

Month/Year	Milestone or Go/No-Go Decision
Jun-08	Milestone: Establish MEA test protocol
Sept-08	Milestone: Complete manufacturing of first MEA from working group members
Dec-08	Go/No-Go Decision: Demonstrate conductivity of 0.1 S/cm, 50% RH, 120 °C
Jun-09	Complete in-plane conductivity characterization of best performing membranes
Sept-09	Complete round of evaluation of MEAs consisting of the best performing membranes

Approach

Improve Conductivity:

Task 1. FSEC develops non-Nafion® based Poly[perfluorosulfonic acid] -phosphotungstic acid composite membrane and membrane electrode assembly (MEA) fabrication (PFSA-PTA)

Task 2. FSEC develops sulfonated poly(ether ketone ketone) or sulfonated poly(ether ether ketone) - Phosphotungstic Acid Composite Membrane and MEA Fabrication (SPEEK-PTA)

Improve FC Performance:

Task 5. Characterize performance of MEAs for Topic 1 members

Task 6. Characterize membrane and MEA durability for Topic 1 members

Standardize Testing

Task 3. In-Plane conductivity measurements by partner

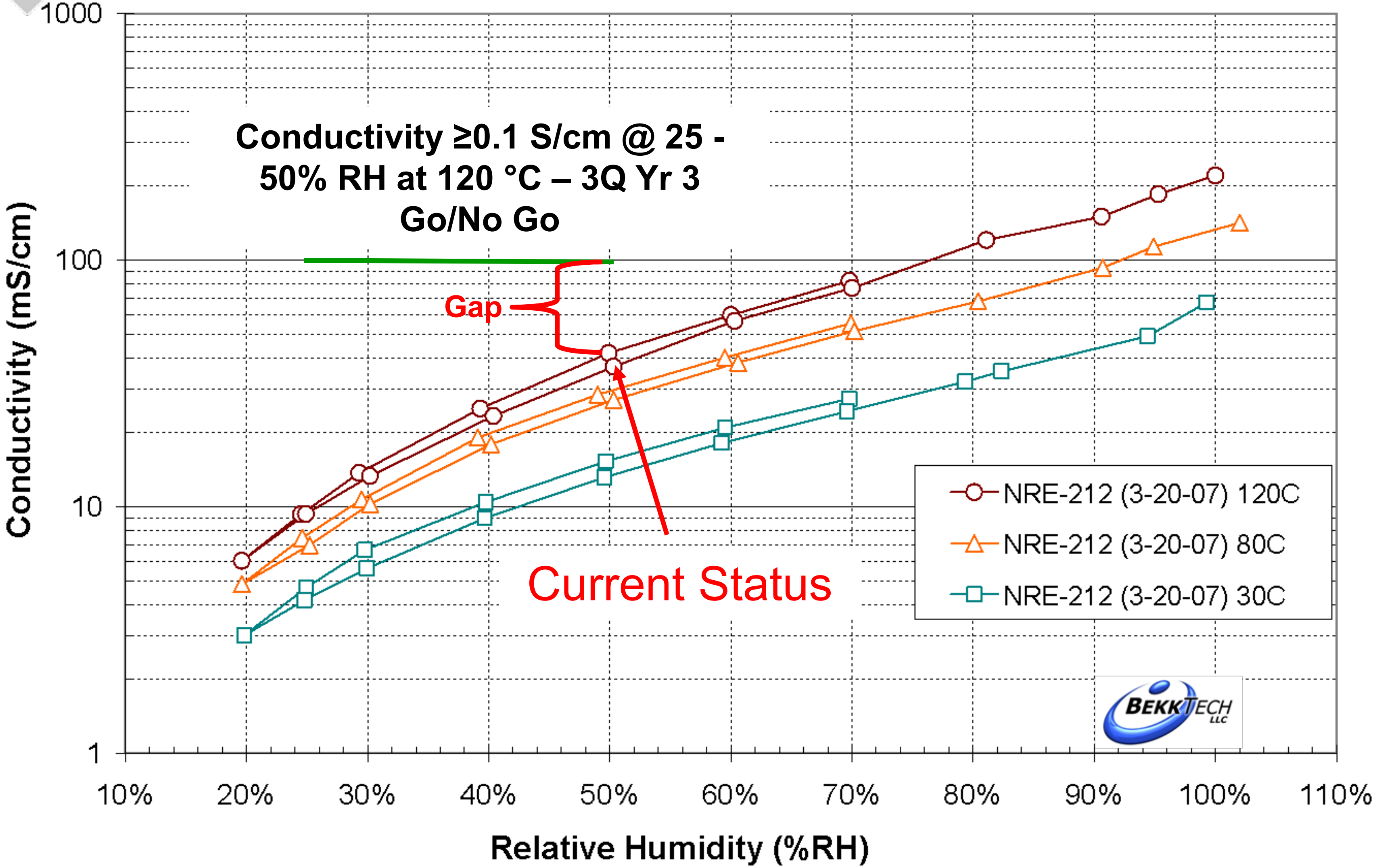
Task 4. Through-Plane conductivity measurements by partner

Task 7. Meetings and Activities of HTMWG

Technical Accomplishments/ Progress/Results

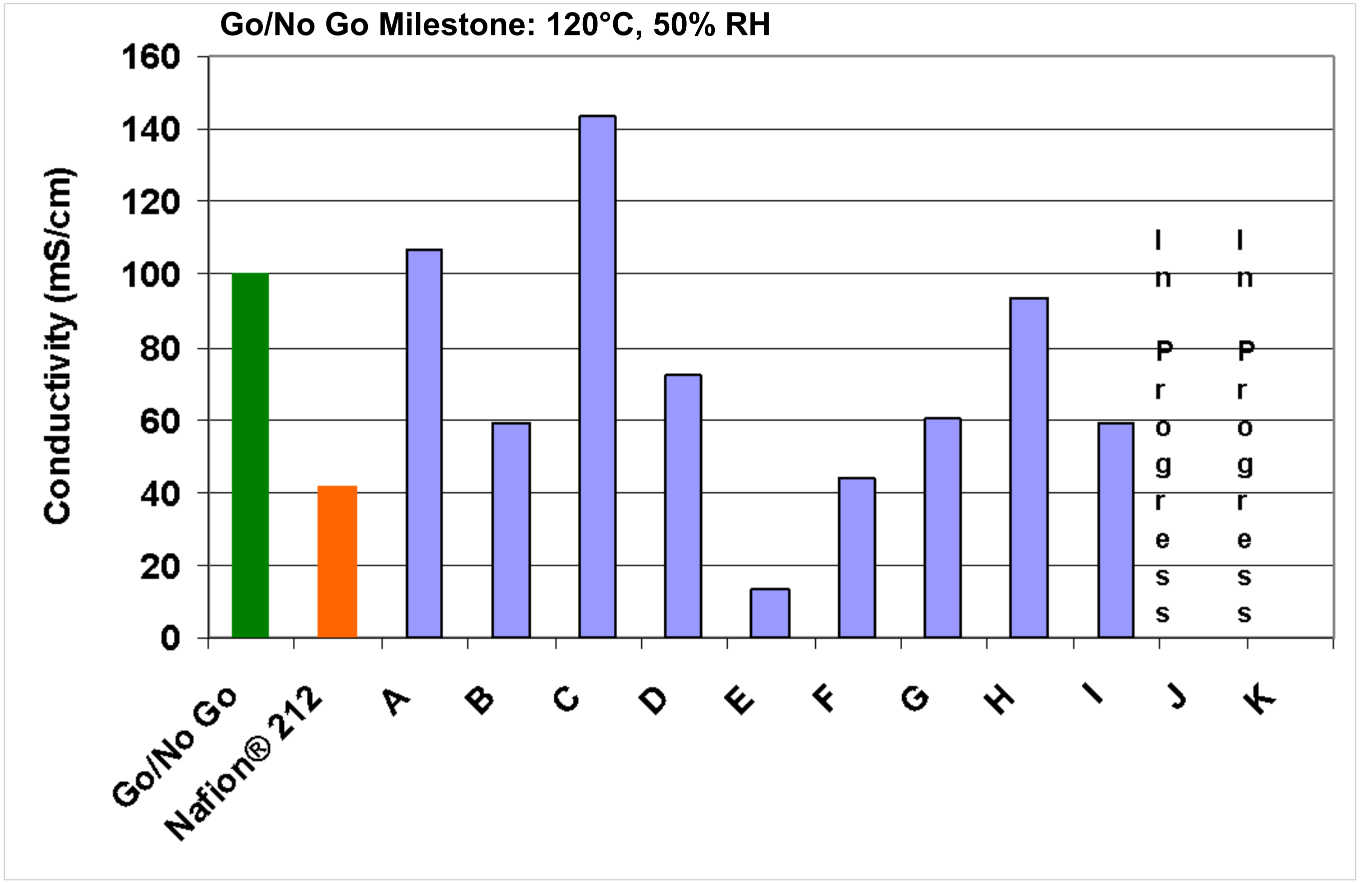
- Conductivity of Team Member Membranes
- FSEC Membrane Improvements
- MEA Test Protocols
  - Performance
  - Durability

In-Plane Conductivity Measurements



- Standard Bekktech conductivity measurements show that NRE-212 is below the target

Conductivity of Funded Project Membranes



- Most team membranes are better than Nafion® 212. Some exceed target

FSEC CCM Manufacture

Catalyst: 45.5 wt% Pt/C
Loading = 0.4 mg Pt/cm^2 on both anode and cathode

Mix ionomer solution
Variables: Solvent (amount and kind), ionomer EW and conc., additive type, form (salt or acid) and amount

⇒

Cast membrane onto Tetratex® on Glass
Variables: Temp, dry time, humidity, heat treatment

⇒

Spray with catalyst
Variables: catalyst, ionomer (EW and conc), speed

⇓

Cs treatment
Variables: form (acid or salt), conc., treatment time, temp

⇐

Hot cure
Variables: Pressure, temp, time

⇐

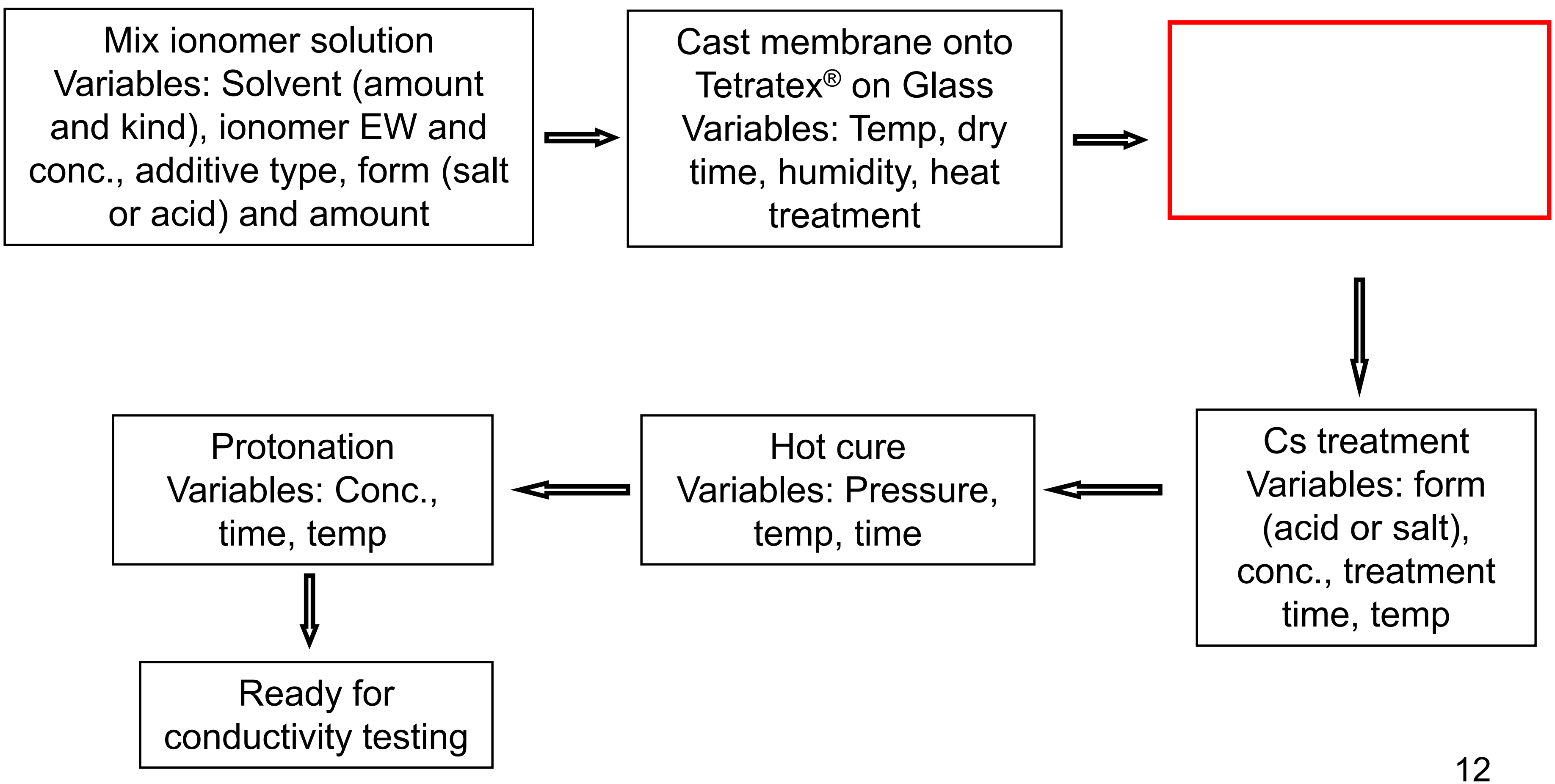
Protonation
Variables: Conc., time, temp

⇓

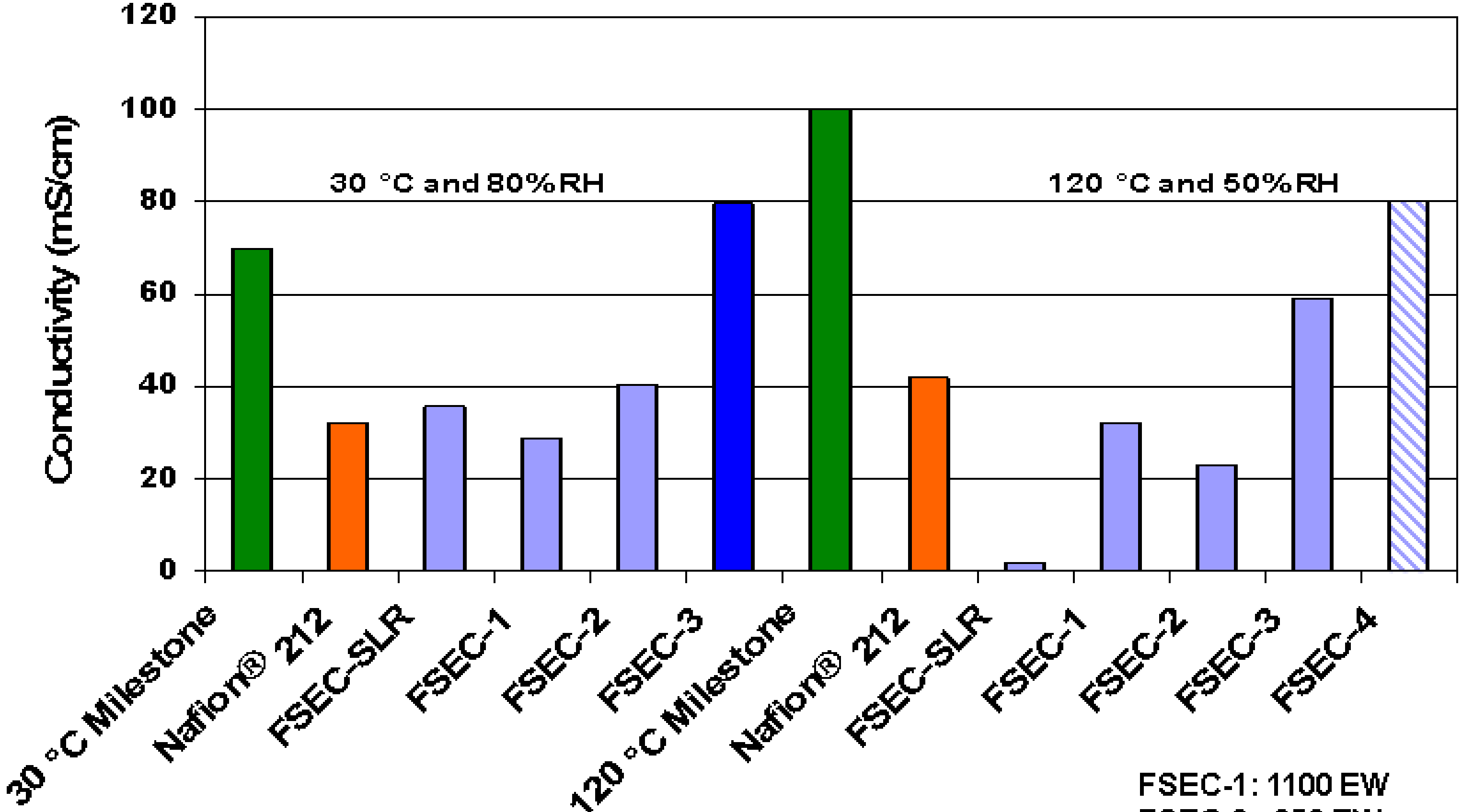
Ready for MEA assembly

FSEC Membrane Manufacture

Membrane: PFSA ionomer on Tetratex® support, with HPA

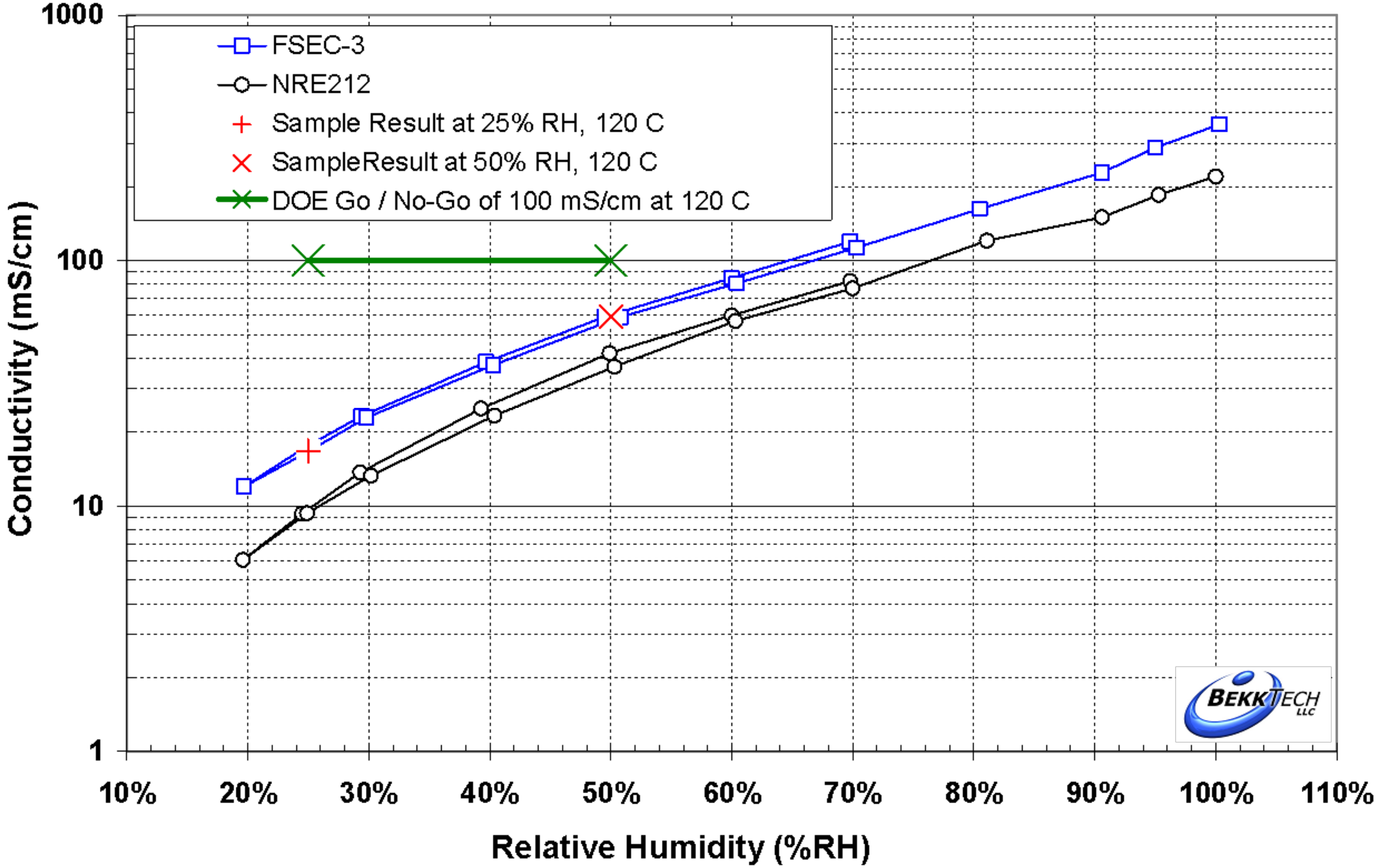


FSEC Membrane Progress



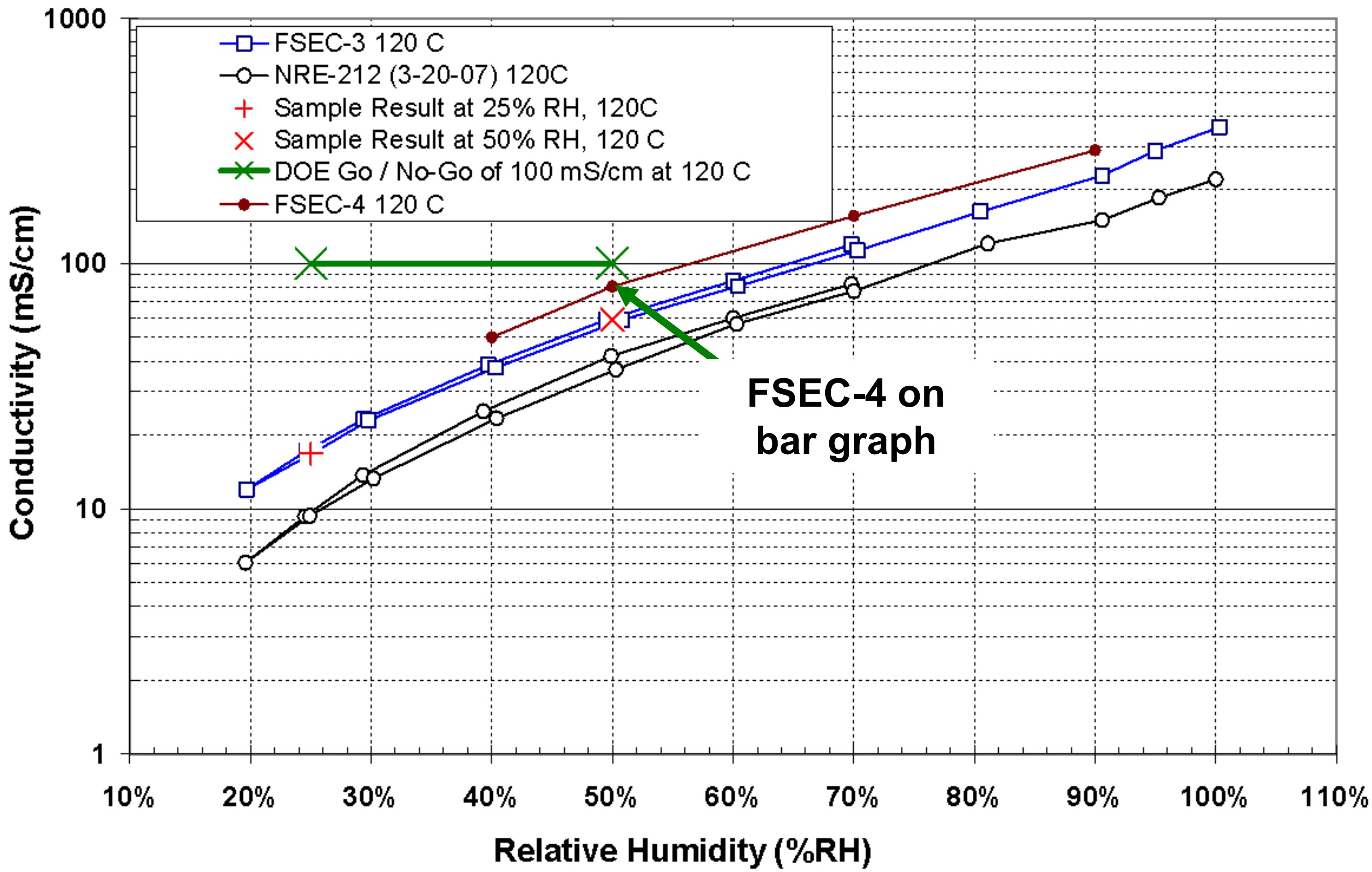
FSEC-1: 1100 EW
FSEC-2: 950 EW
FSEC-3: 750 EW
FSEC-4: 750 EW
FSEC-SLR: SPEEK

Conductivity of FSEC-3



- FSEC-3 is significantly above NRE 212

In-House Measurement of FSEC-4



- FSEC-4 approaches the target

Variables in FSEC Membrane Manufacture

Membrane: PFSA ionomer on Tetratex® support, with HPA

Mix ionomer solution
Variables: **Solvent (amount and kind), ionomer EW and conc.**, additive type, form (salt or acid) and amount

→

Cast membrane onto Tetratex® on Glass
Variables: Temp, dry time, **humidity**, heat treatment

→

↓

Cs treatment
Variables: form (acid or salt), **conc.**, treatment time, temp

←

Hot cure
Variables: Pressure, temp, time

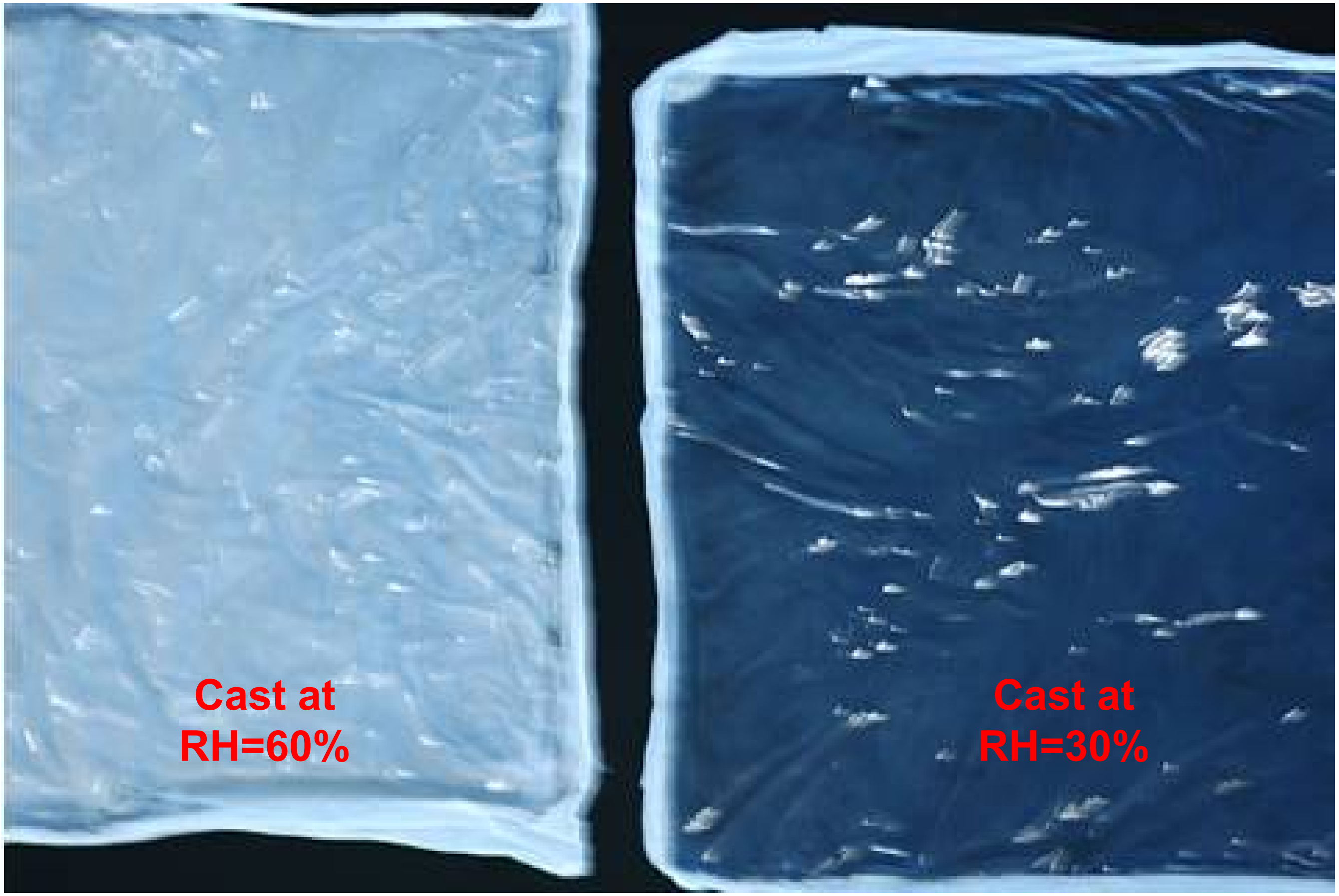
←

Protonation
Variables: Conc., time, temp, **PTA retention**

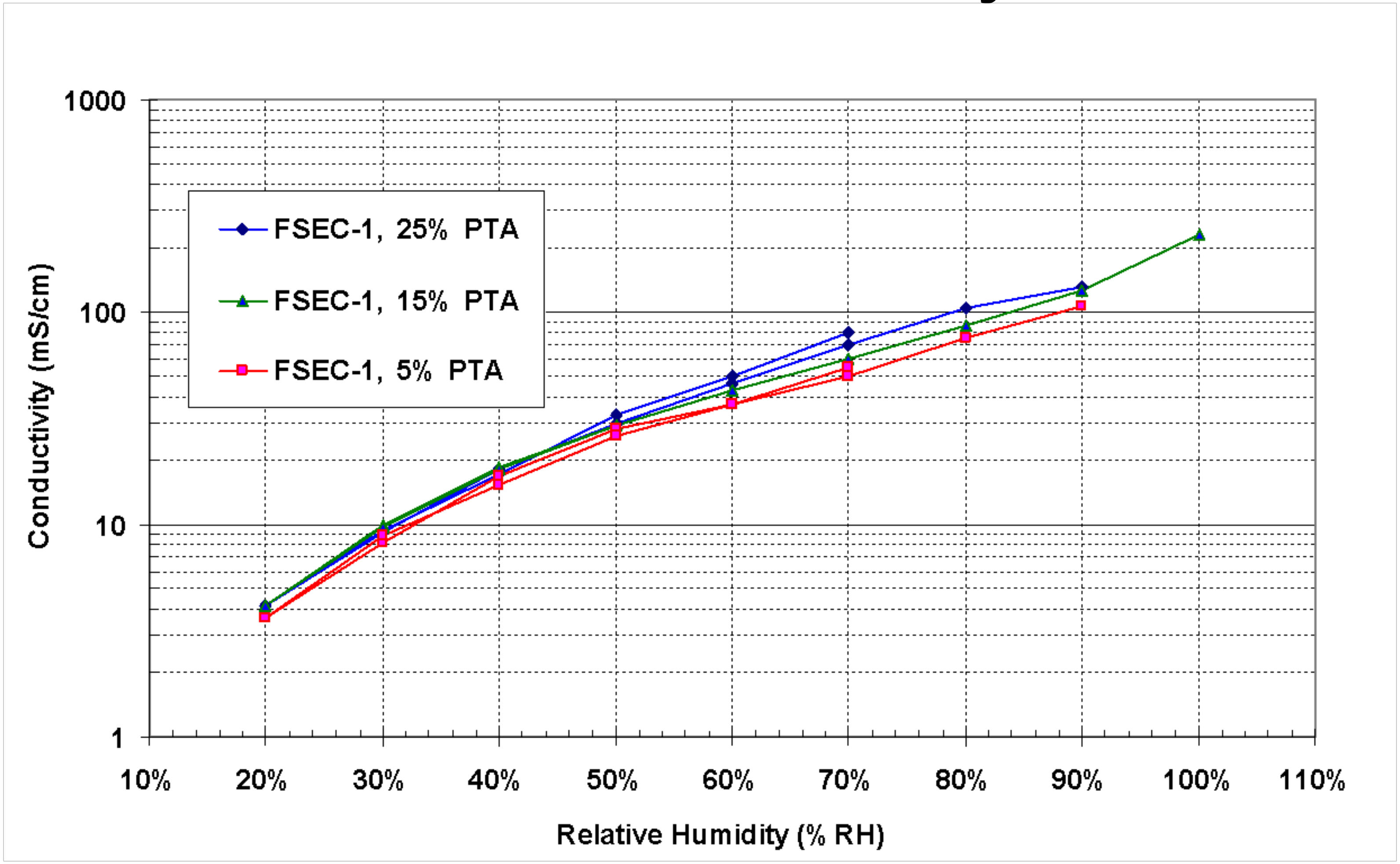
↓

Ready for conductivity testing

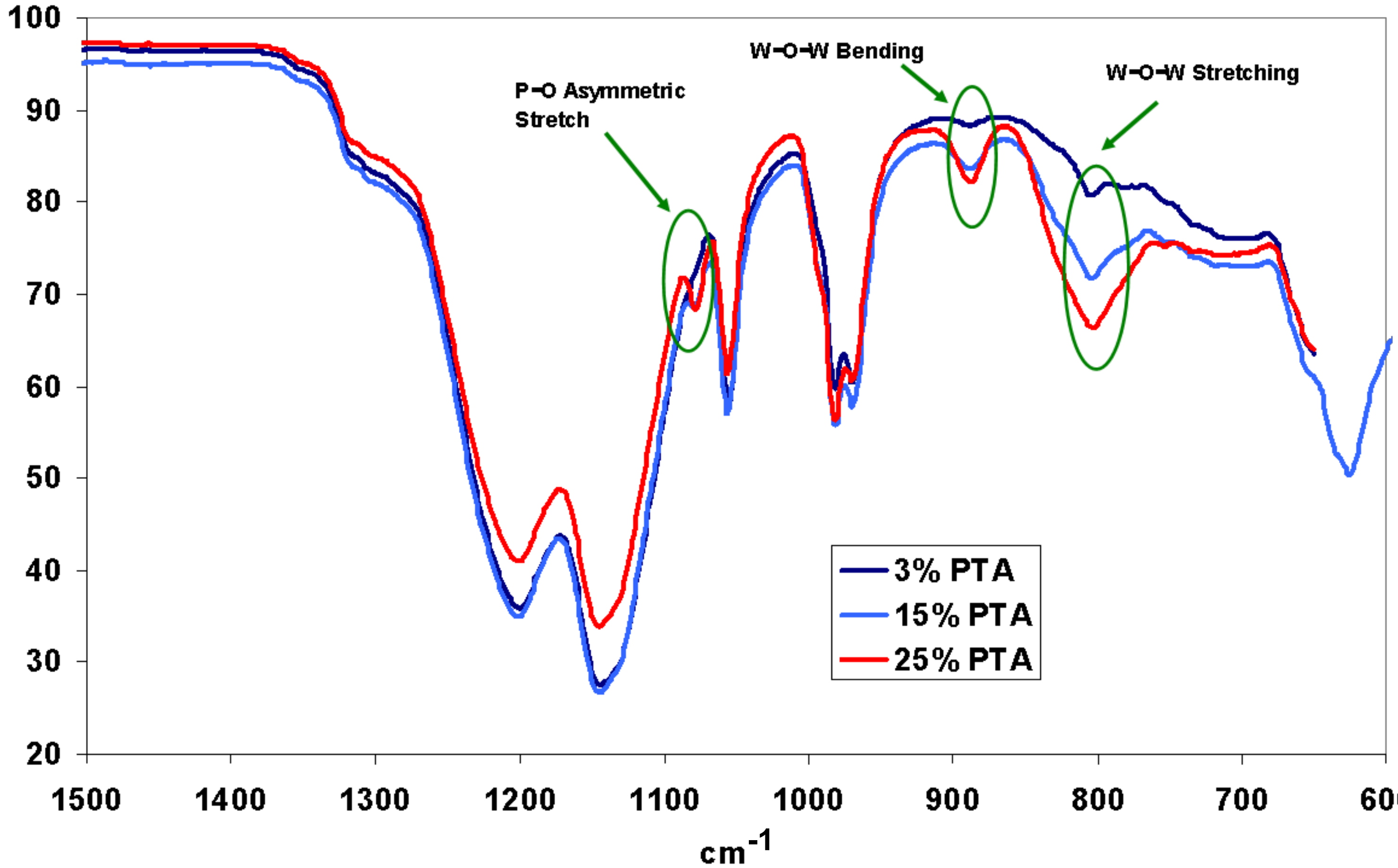
RH Influence During Casting



Influence of PTA on Conductivity

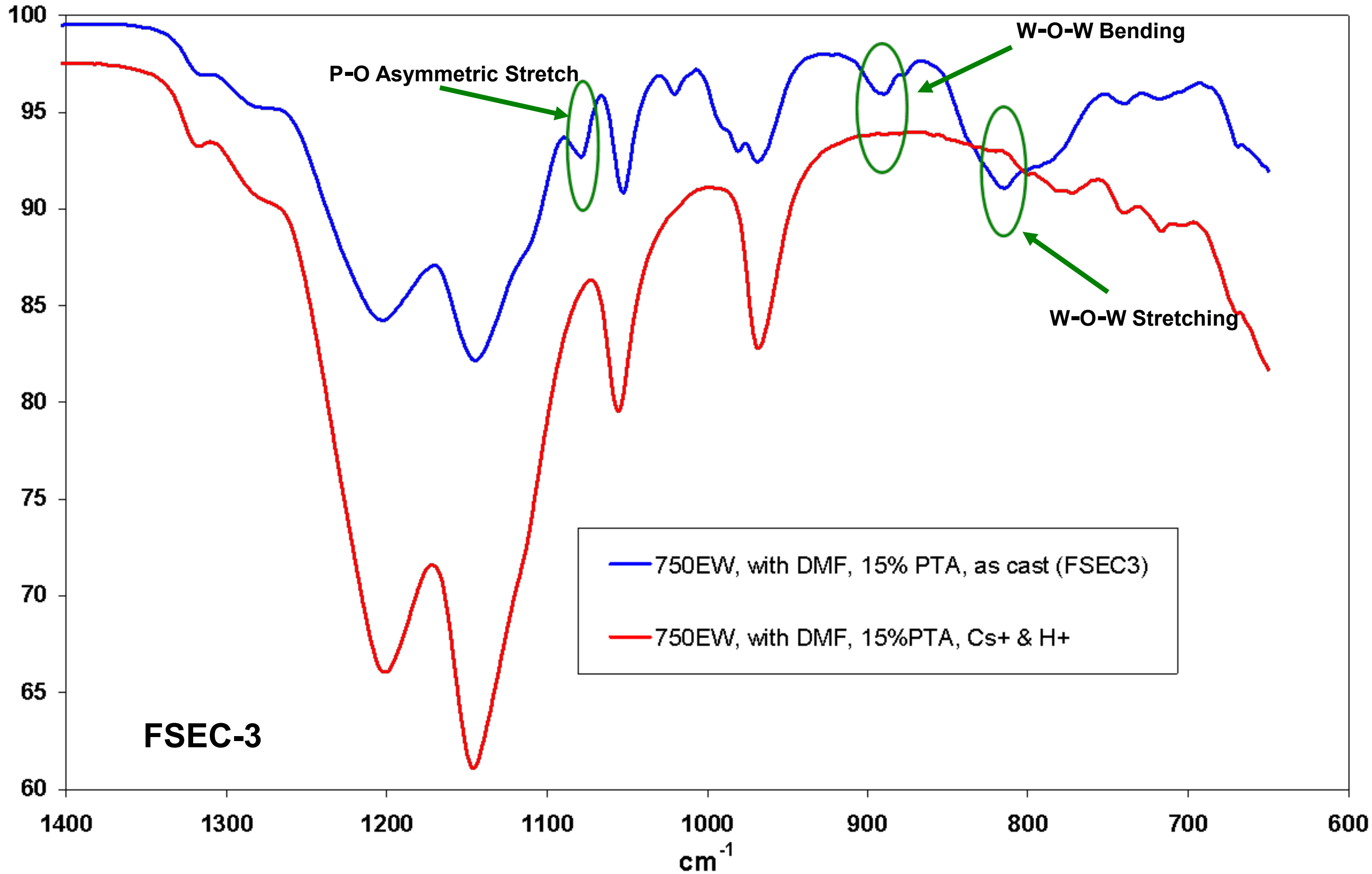


FTIR Analysis Shows Presence of PTA in FSEC-1



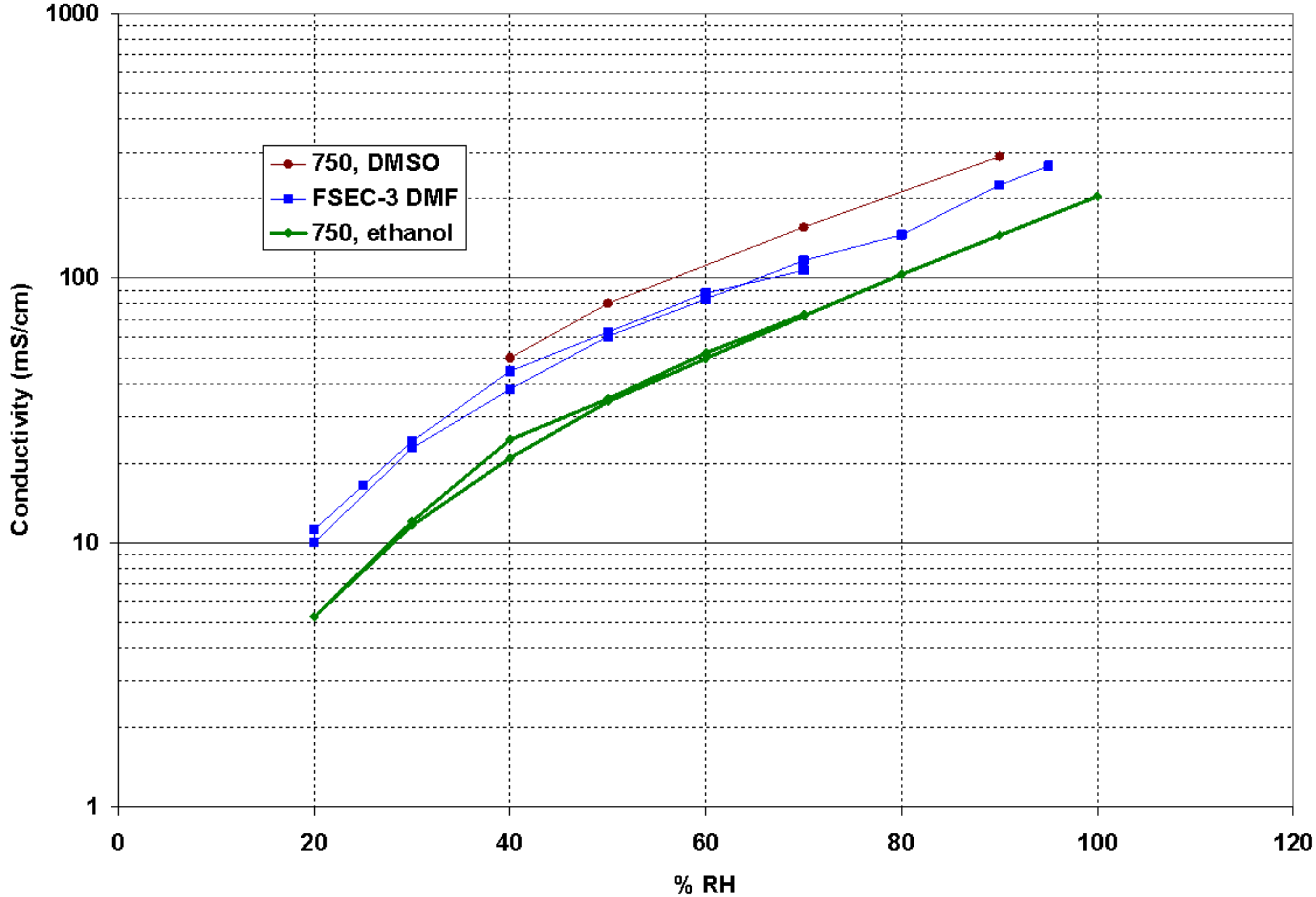
- FTIR confirms PTA presence in Membrane

Effect of Protonation on PTA Content of FSEC-3



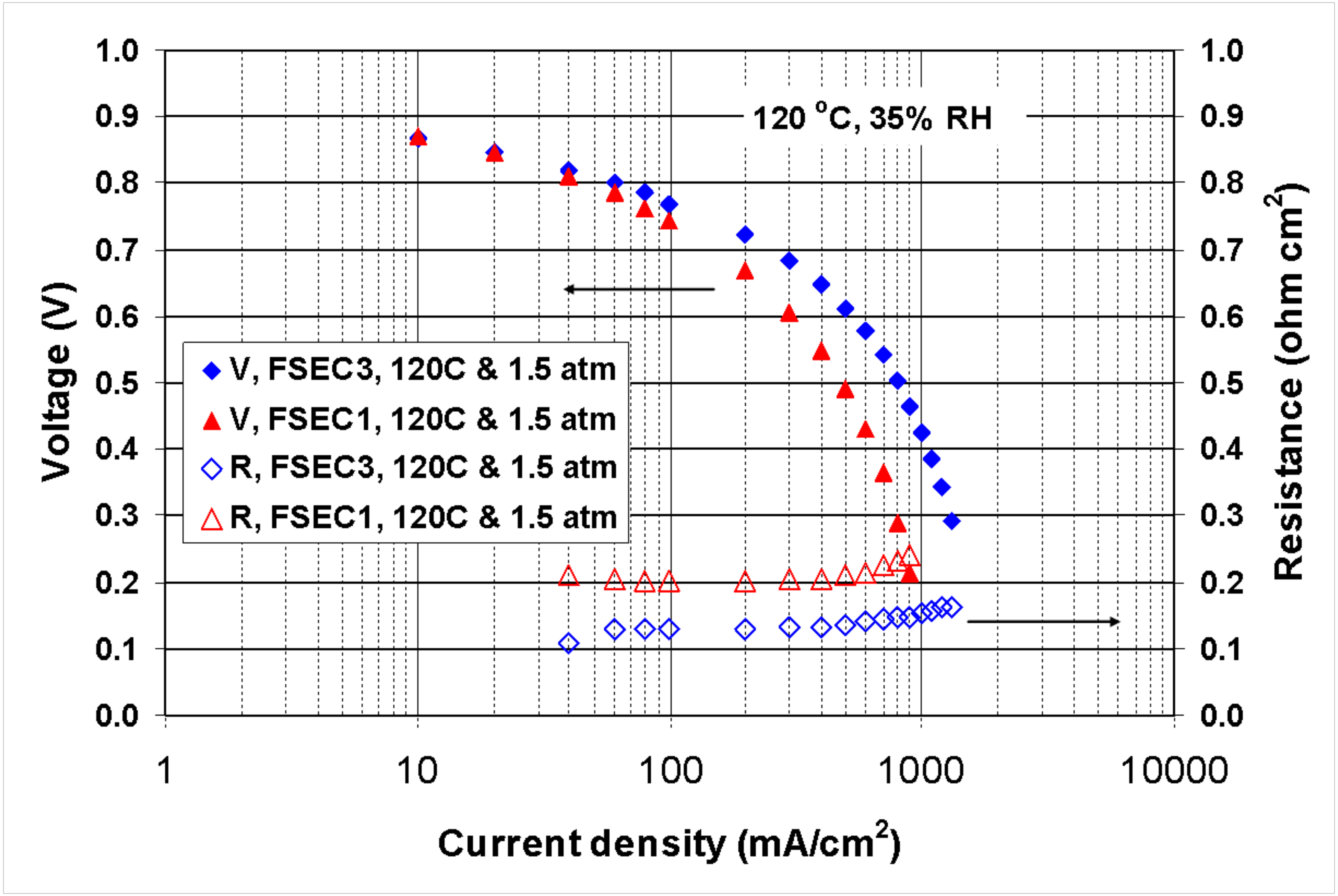
- PTA can be lost during protonation of FSEC-3

Influence of Casting Solvent on Conductivity of FSEC Low Equivalent Weight Membranes



- Solvent choice strongly effects conductivity

FSEC-3 has Improved Cell Resistance and Performance Compared to FSEC-1



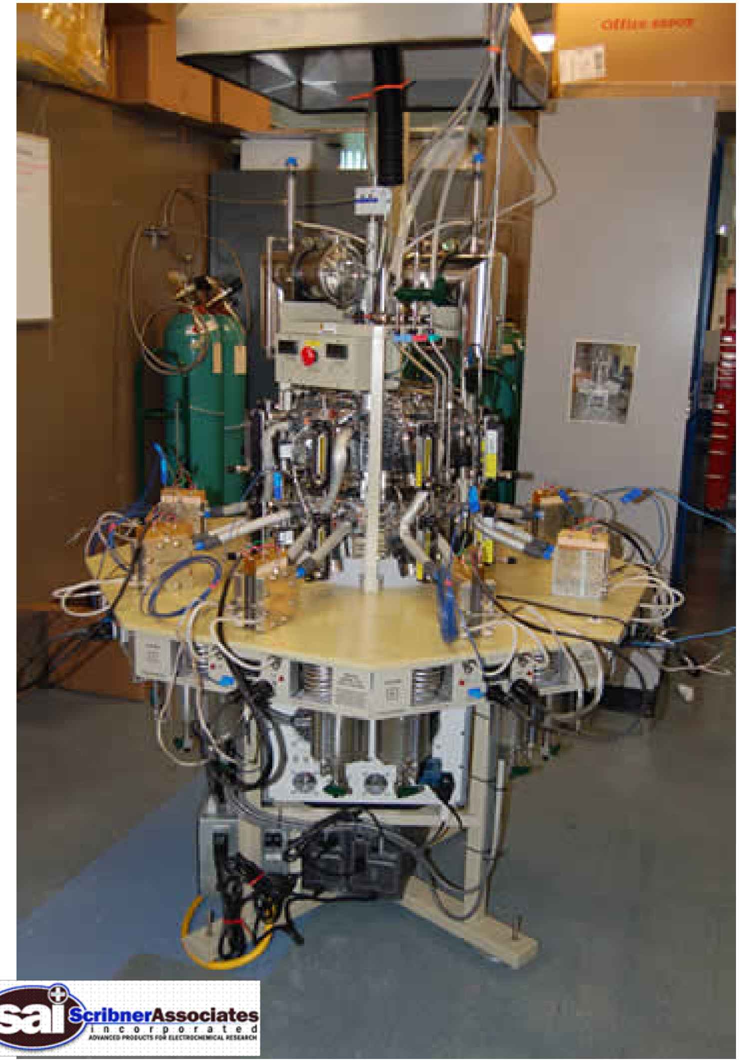
Meeting Area Specific Resistance Targets

- ASR is <u>not</u> an intrinsic property
- Generate formal definition of ASR
- Generate ASR testing procedure
  - Define pre-test membrane conditioning
  - Define test hardware and test procedure
  - Define analysis procedure
  - Verify test results

Factors pertinent to ASR targets are shown in supplemental slides

MEA Durability System

- 8 MEA testing
- Open circuit and load accelerated durability
- Hydrogen crossover, ECA and resistance
- Condensate collection for analysis
- Samples for post-test mechanical durability



❖ Throughput of durability testing increased 8-fold and test stands freed for performance testing

Future FSEC Membrane Work

Membrane: Various PFSA ionomers on Tetratex® support, with HPAs

Mix ionomer solution
Variables: Solvent (**amount and kind**), ionomer **EW,** (**manufacturer** and conc.), additive **type**, form (**salt or acid**) and amount

→

Cast membrane onto Tetratex® on glass
Variables: Temp, dry time, **humidity**, **heat treatment**

→

↓

Cs treatment
Variables: Form (**acid or salt**), concentration, **treatment time**, **temp**

←

Hot Cure
Variables: Pressure, **temp, time**, and **humidity**

←

Protonation
Variables: Concentration, time, temp

↓

Ready for conductivity testing

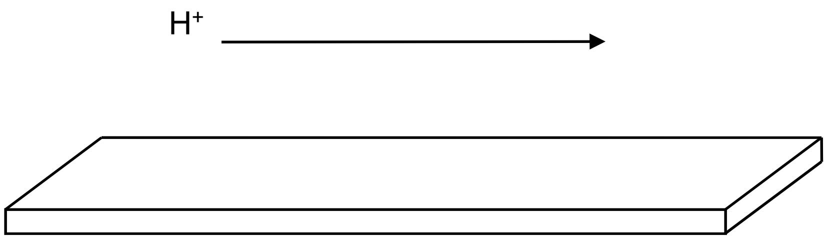
Summary

- **Relevance**
  - New membrane material is needed with improved conductivity at high temperature(120 °C) and low RH
  - Accurate and reliable conductivity measurement is required for DOE program
- **Approach**
  - Develop and demonstrate new materials for membranes
  - Define and apply new tools and procedures for membrane conductivity testing
- **Tech. Accomplishments /Progress**
  - FSEC membranes approach conductivity target of 0.10 mS/cm at 50% RH and 120 ^{o}C.
  - Process optimization of membrane fabrication in progress. Developed FTIR analytical technique to measure PTA in membranes
  - Developed and presented MEA performance protocol
  - Obtained MEA Durability Testing System Capability (8 MEA testing capability)
  - Provided independent conductivity measurements for HTMWG members
    - Most membranes from team members exceeded conductivity of NRE 212
    - Some team members exceeded conductivity target
- **Collaborations**
  - Active partnership with BekkTech LLC and Scribner Associates
  - Working closely with HTMWG members to provide accurate data under standardized conditions
  - Provided protocol to HTMWG members
  - Started work with fuel cell community on defining ASR

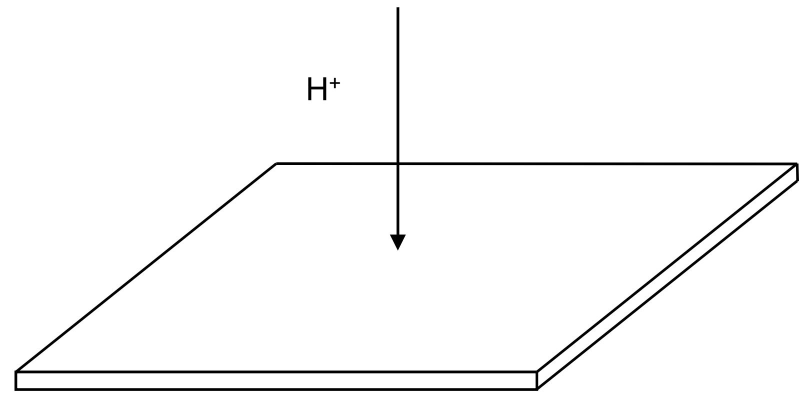
Supplemental Slides

In-plane And Through-plane Data Should Not Be Used To Estimate Membrane Area Specific Resistance (ASR)

Through-Plane vs. In-Plane



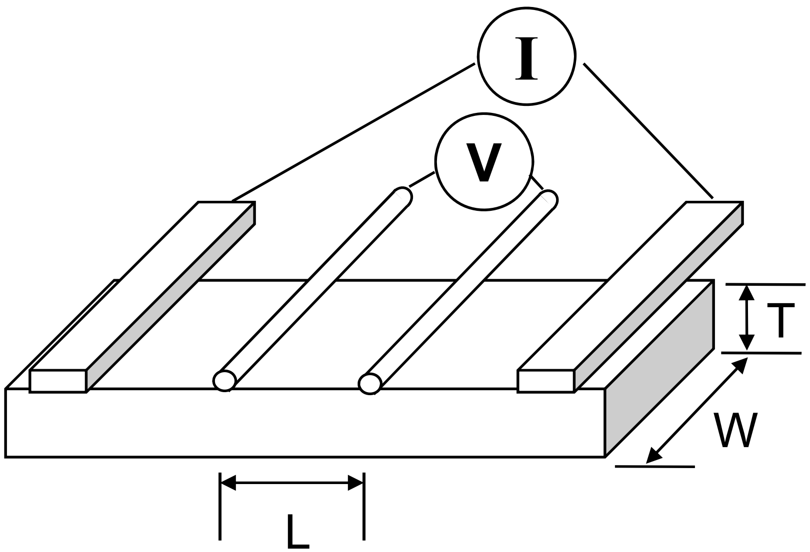
Current Conductivity
Protocol (In-Plane)



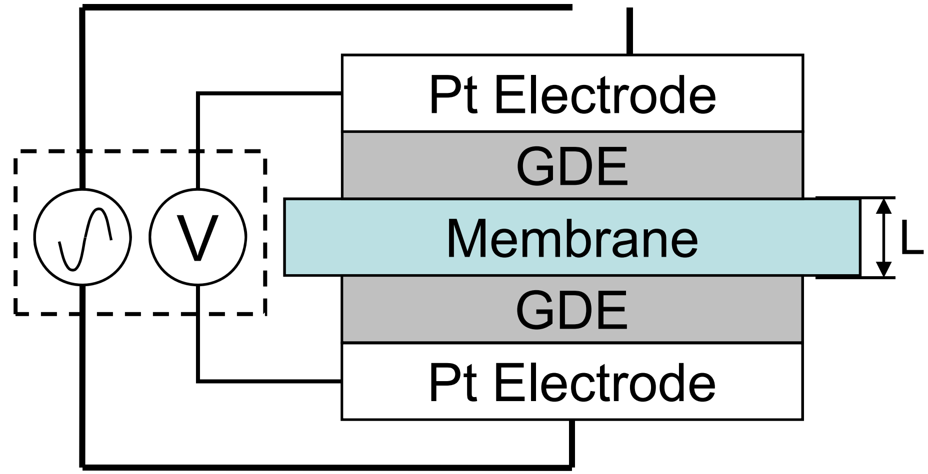
Like a Fuel Cell

(Through-Plane)

In-Plane vs. Through-Plane



4-electrode DC or AC measurement



2-electrode / 4-terminal, high frequency, AC measurement

$$A_{in-plane} = W \cdot T \neq A_{through-plane}$$

$$\sigma\left(S/cm\right) = \frac{L}{R \cdot A}$$

Through-Plane Measurement Sources of Ohmic Resistance

- Ohmic resistances that contribute to the measured high frequency resistance, R_{HF}:
  - Membrane
  - GDE/membrane interface – f(RH,T)
  - GDE
  - Pt electrode / GDE contact
  - Pt electrode

R_{cell}(T,RH)

- Must account for non-membrane ohmic resistances (R_{cell})

Scribner Associates incorporated ADVANCED PRODUCTS FOR ELECTROCHEMICAL RESEARCH

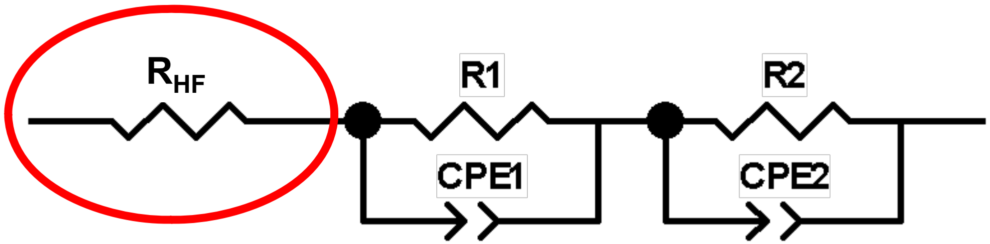
Through-Plane Measurements

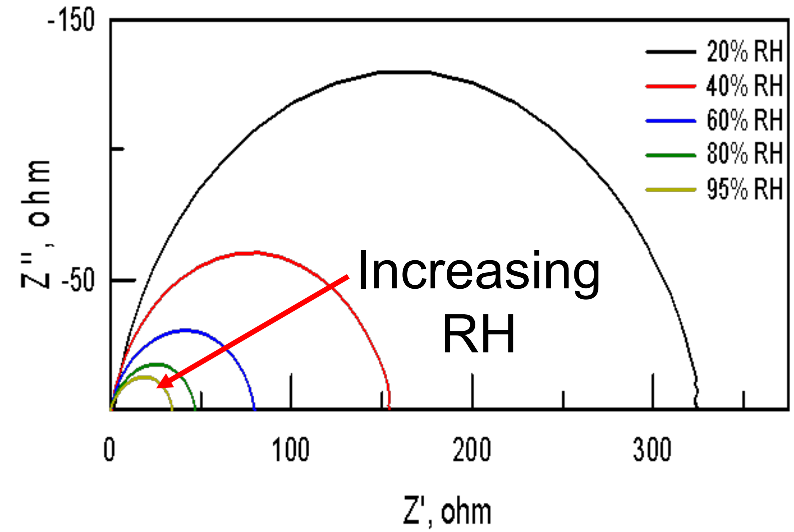
- Pros
  - Measures conductivity in the orientation of relevance to fuel cells
    - Eliminates concern about intrinsically anisotropic and/or supported membranes
  - Technique requires only a small sample of bare membrane
    - Eliminates time-consuming & costly task of CCM/MEA fabrication & fuel cell testing
  - Excludes other sources of ohmic resistance that contribute to in-cell ASR measurements (flow field, GDL, contacts, etc.)

- Cons
  - Have to account for non-membrane ohmic resistances, $R_{cell}(T,RH)$
    - non-trivial task to determine
  - Requires high-frequency (AC) measurement – more sophisticated hardware and data analysis than DC methods

Data Analysis for Conductivity

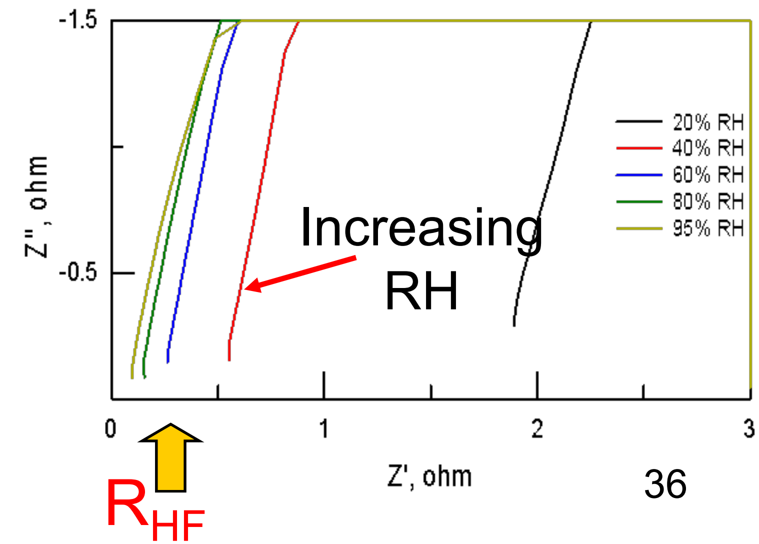
- Fit EIS spectra to equivalent circuit model → high freq. resistance, R_{HF}





- $ASR_{Total} = R_{HF} \times Area$
- $ASR_{membrane} = ASR_{Total} - ASR_{cell}$
- Conductivity: $\sigma_{\perp} = \dfrac{L}{ASR_{membrane}}$

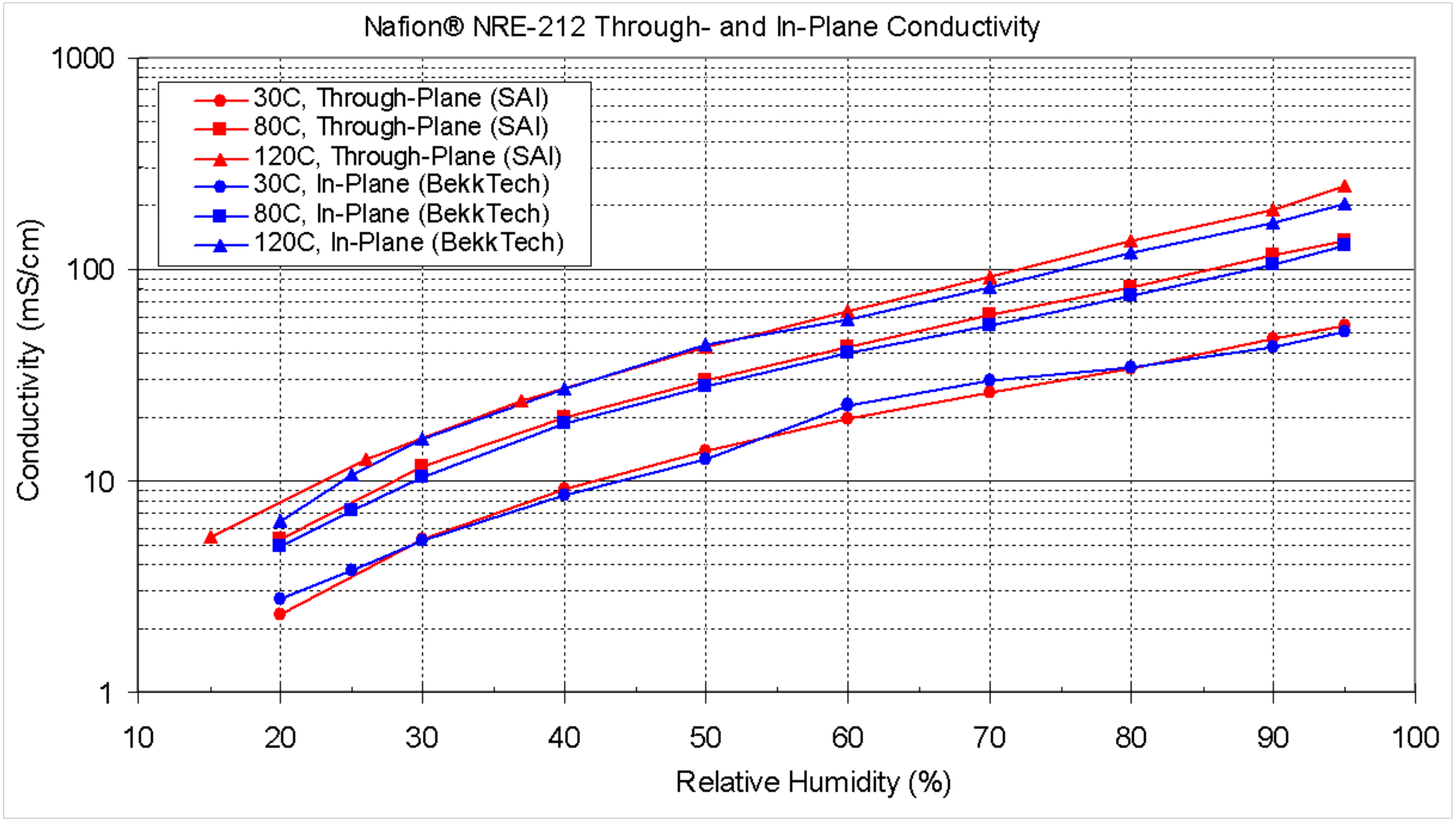
L = membrane thickness



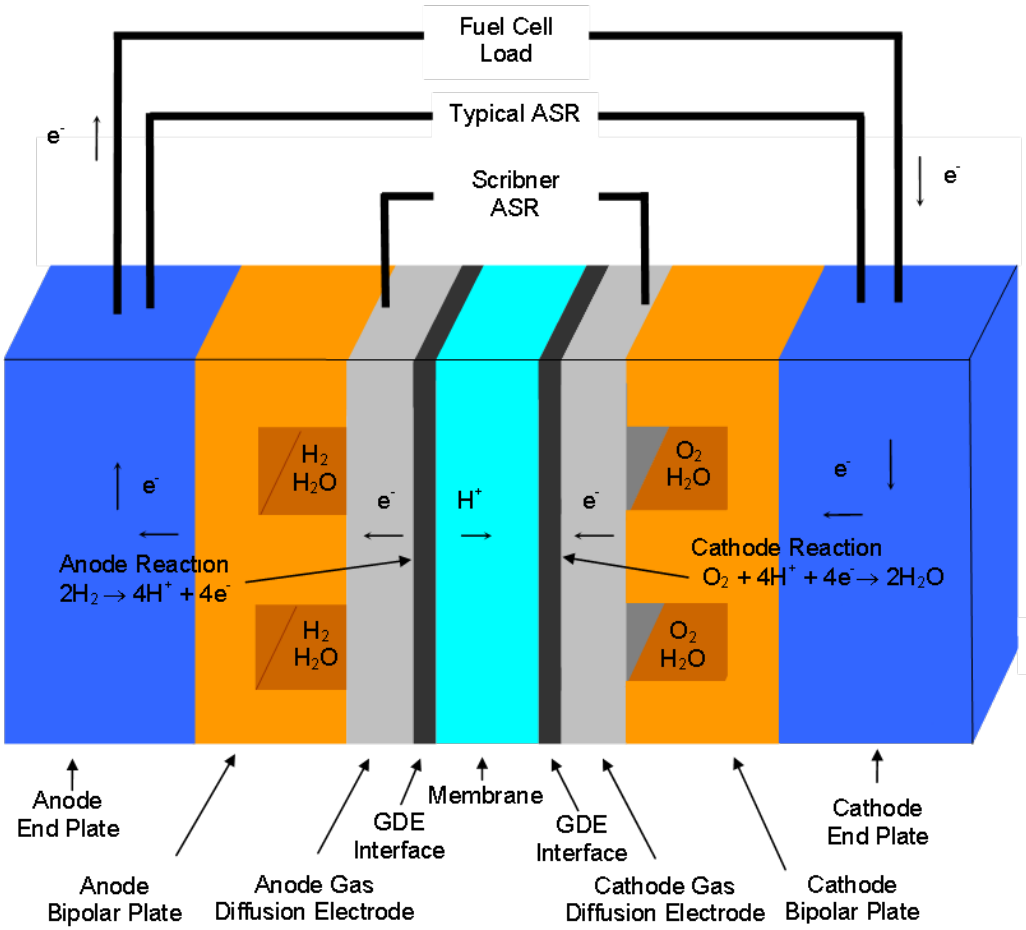
Comparing In-Plane & Through-Plane Measurement Methods

Attribute	BekkTech In-Plane	Scribner Through-Plane
Requires only small piece of membrane	Yes	Yes
Eliminates MEA Fabrication	Yes	Yes
Rapid evaluation of membrane resistance over broad range of T and RH	Yes	Yes
Measurement in orientation relevant to fuel cells	No	Yes
Measurement excludes non-membrane ohmic resistances	Yes	No
Can use AC or DC methods	Yes	No
Conductivity calculated using in-situ measured dimensions, especially thickness	No	No

In-Plane and Through-Plane Data Comparison for NRE 212



Components of a Through-Plane ASR Measurement



Component Resistance Plus Resistance at each interface