



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

James Fenton

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

Budget

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

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 °C – 3Q Yr 3 Go/No Go

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 $f(\text{RH}, T, \text{Prep. Procedure})$ [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)

Task 7. Meetings and Activities of HTMWG

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

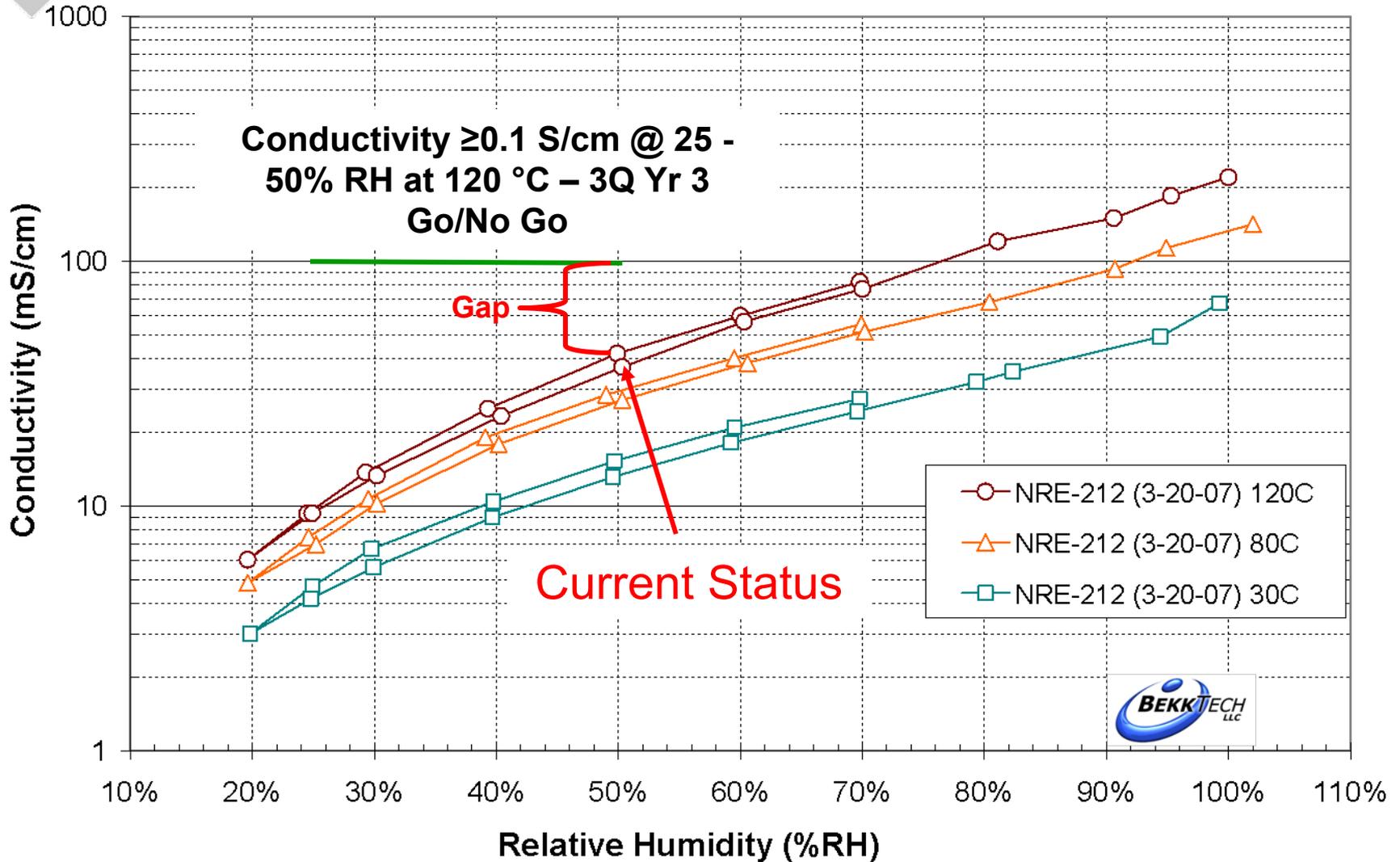


Technical Accomplishments/ Progress/Results

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



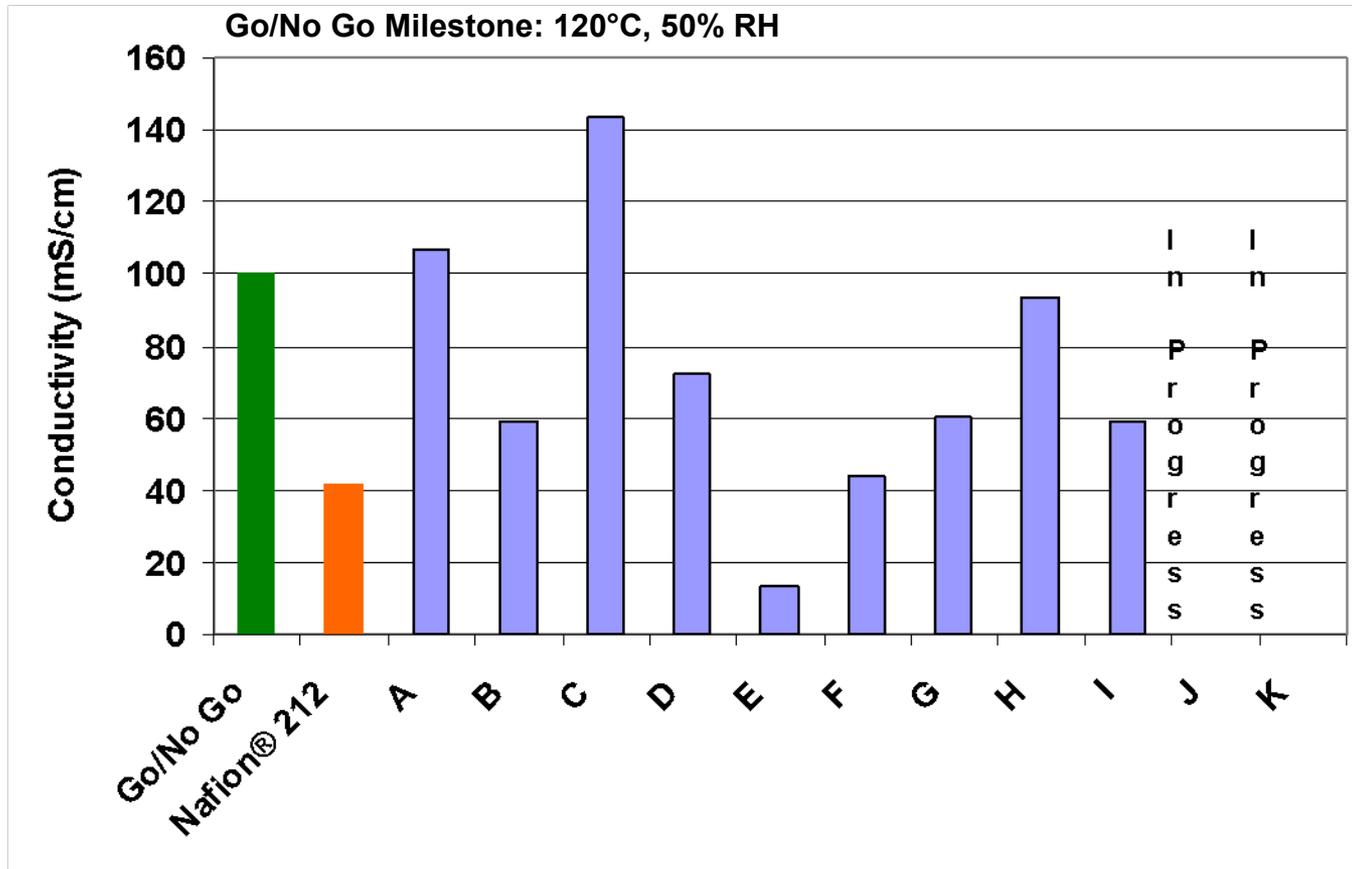
In-Plane Conductivity Measurements



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



Conductivity of Funded Project Membranes



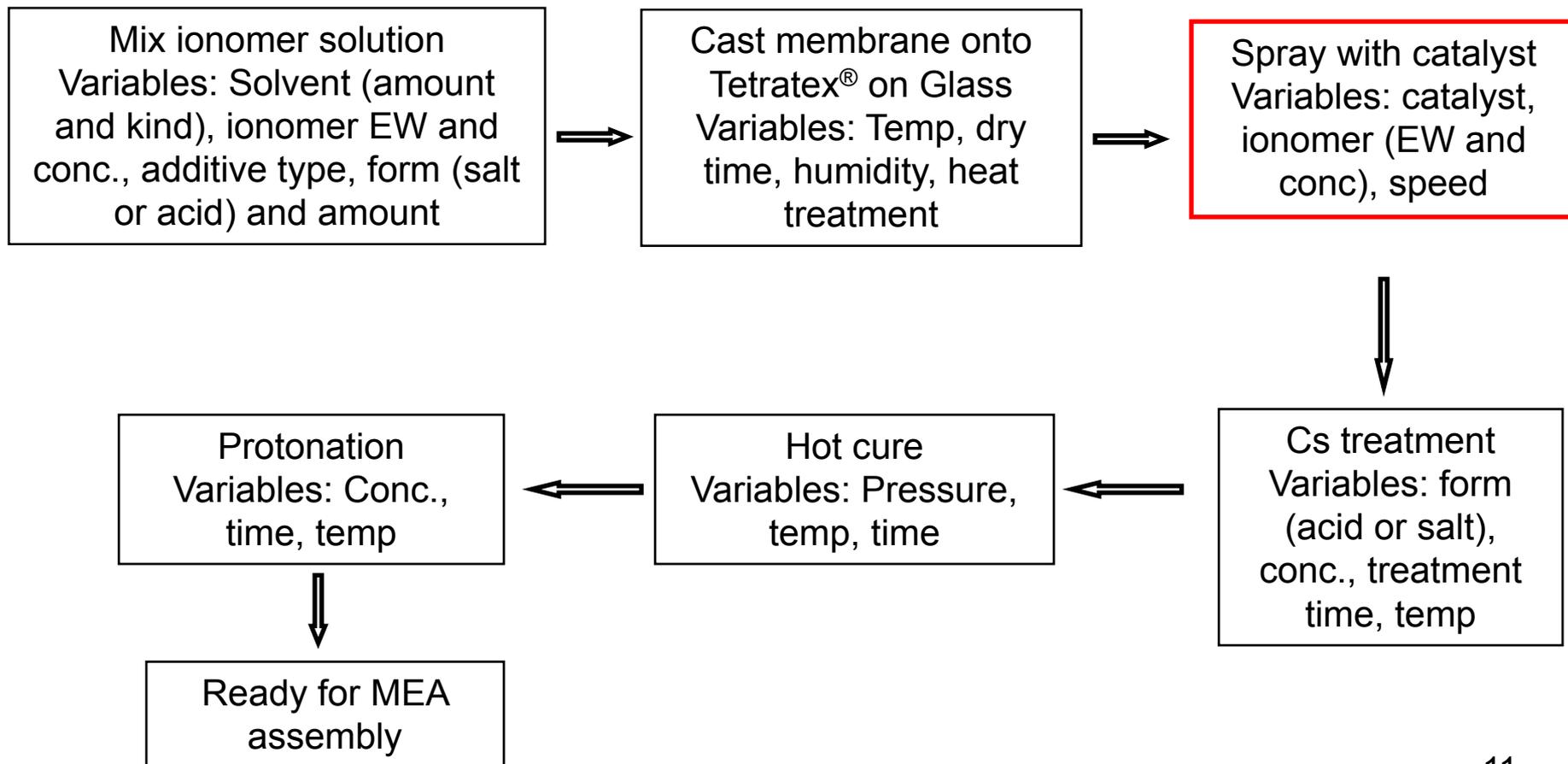
❖ Most team membranes are better than Nafion® 212. Some exceed target 10



FSEC CCM Manufacture

Catalyst: 45.5 wt% Pt/C

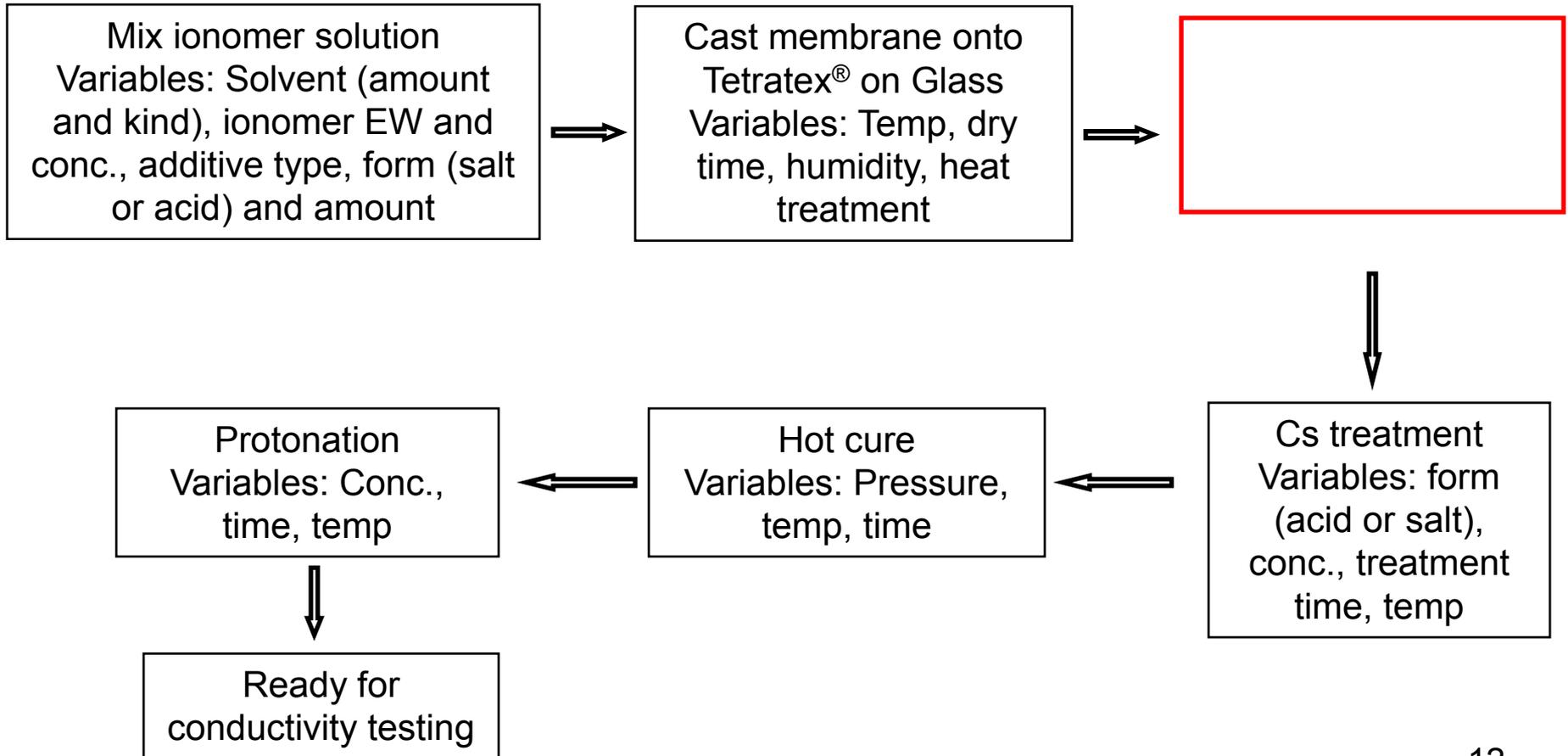
Loading = 0.4 mg Pt/cm² on both anode and cathode





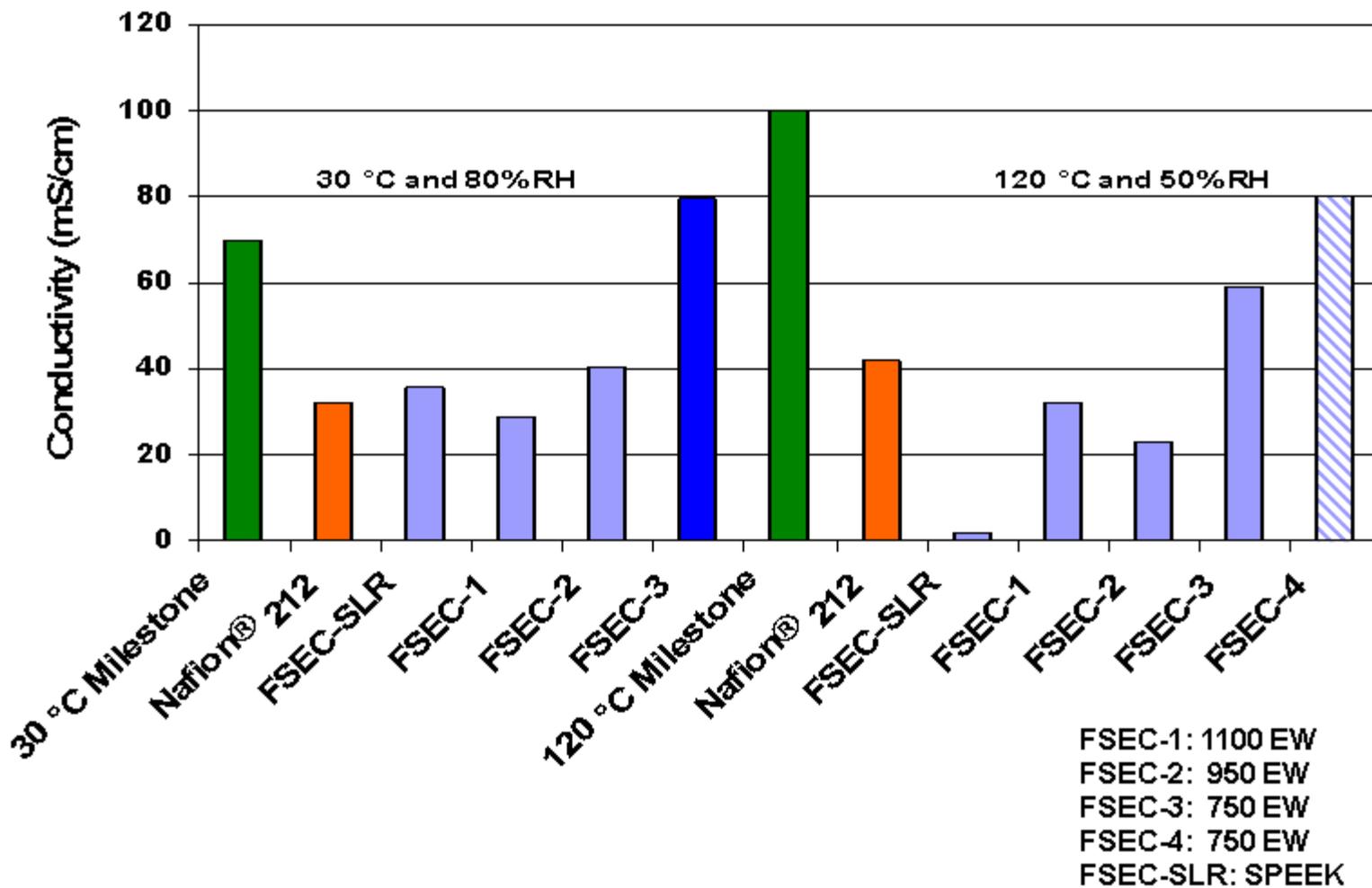
FSEC Membrane Manufacture

Membrane: PFSA ionomer on Tetratex[®] support, with HPA



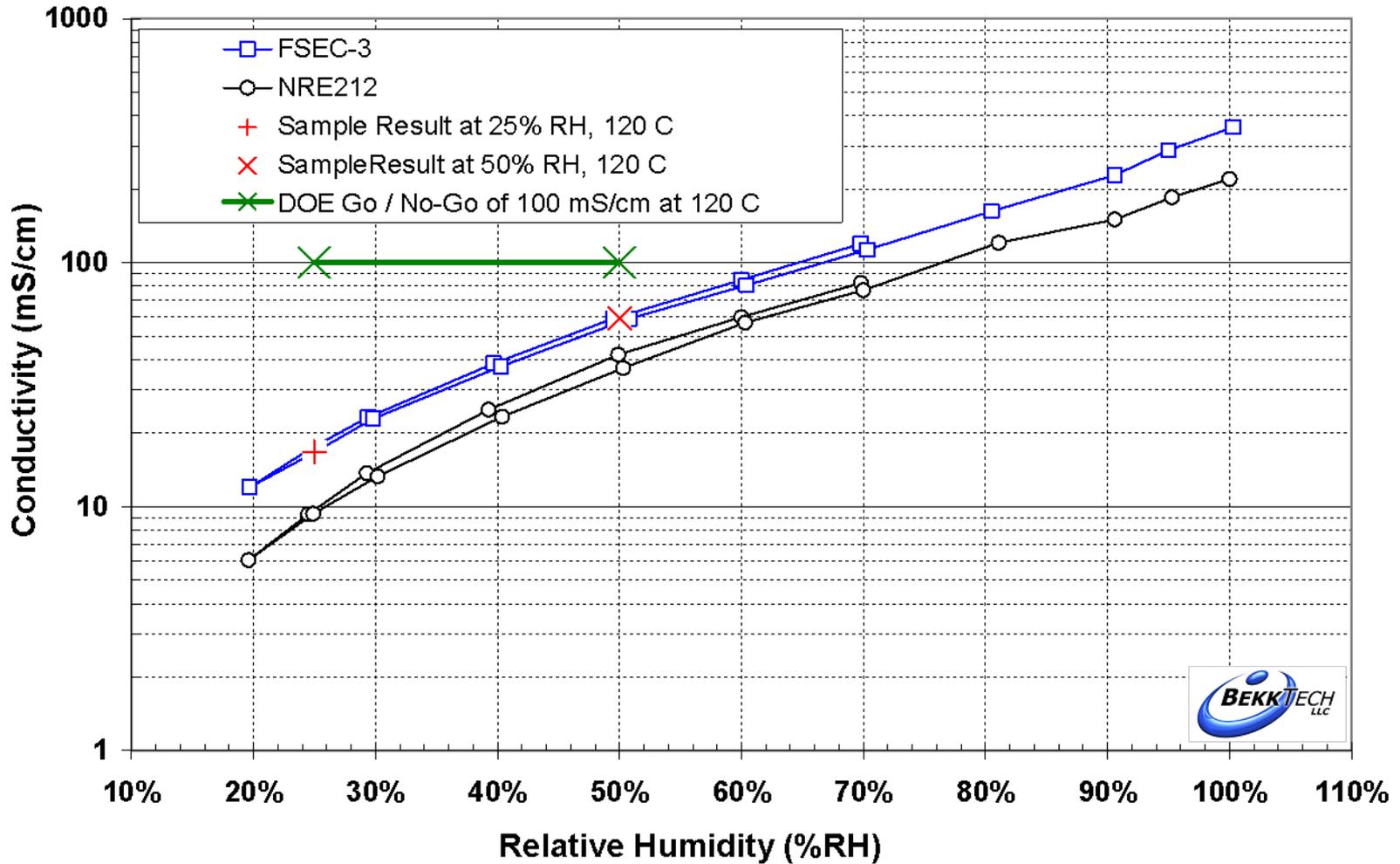


FSEC Membrane Progress





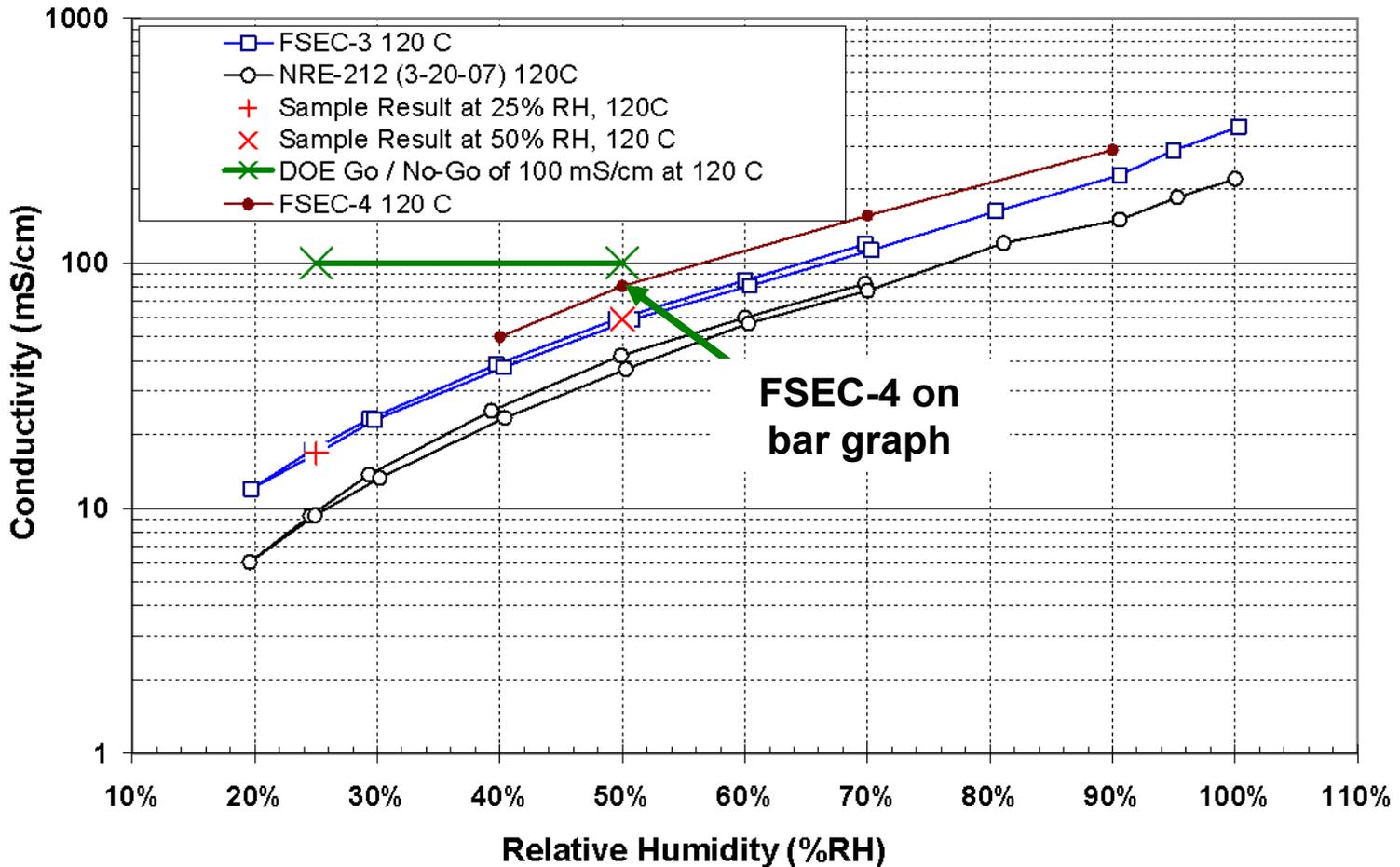
Conductivity of FSEC-3



❖ FSEC-3 is significantly above NRE 212



In-House Measurement of FSEC-4

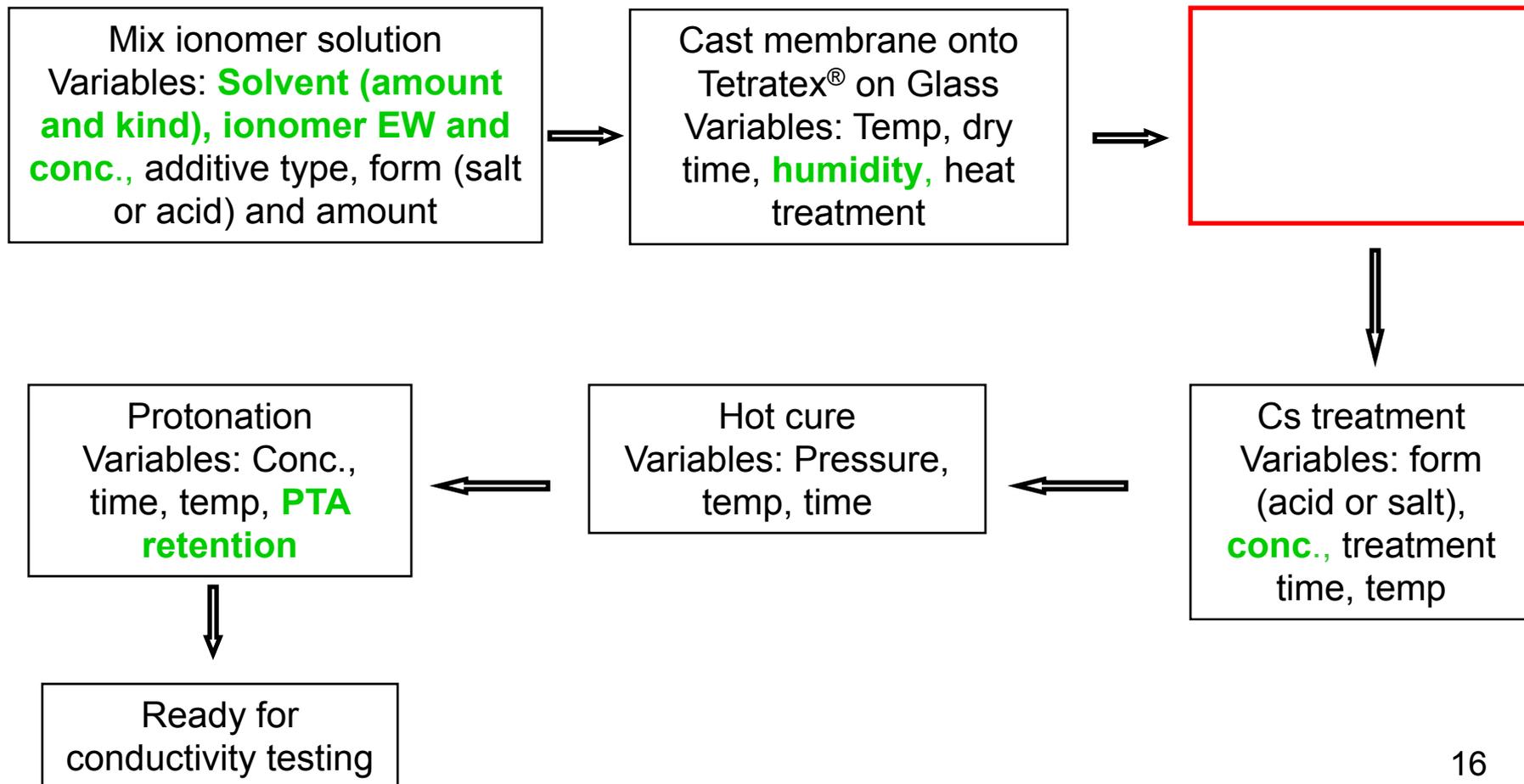


❖ FSEC-4 approaches the target



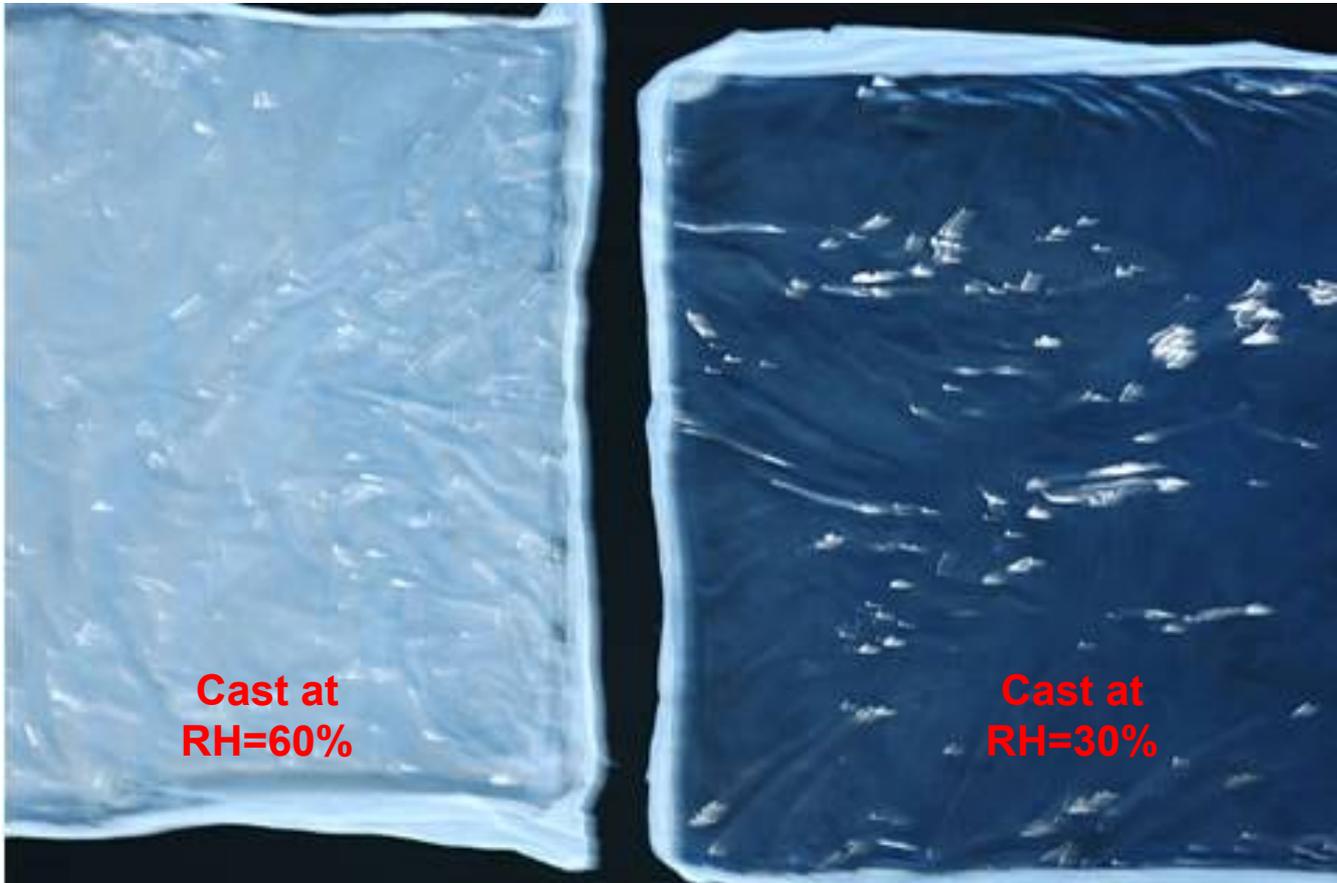
Variables in FSEC Membrane Manufacture

Membrane: PFSA ionomer on Tetratex[®] support, with HPA



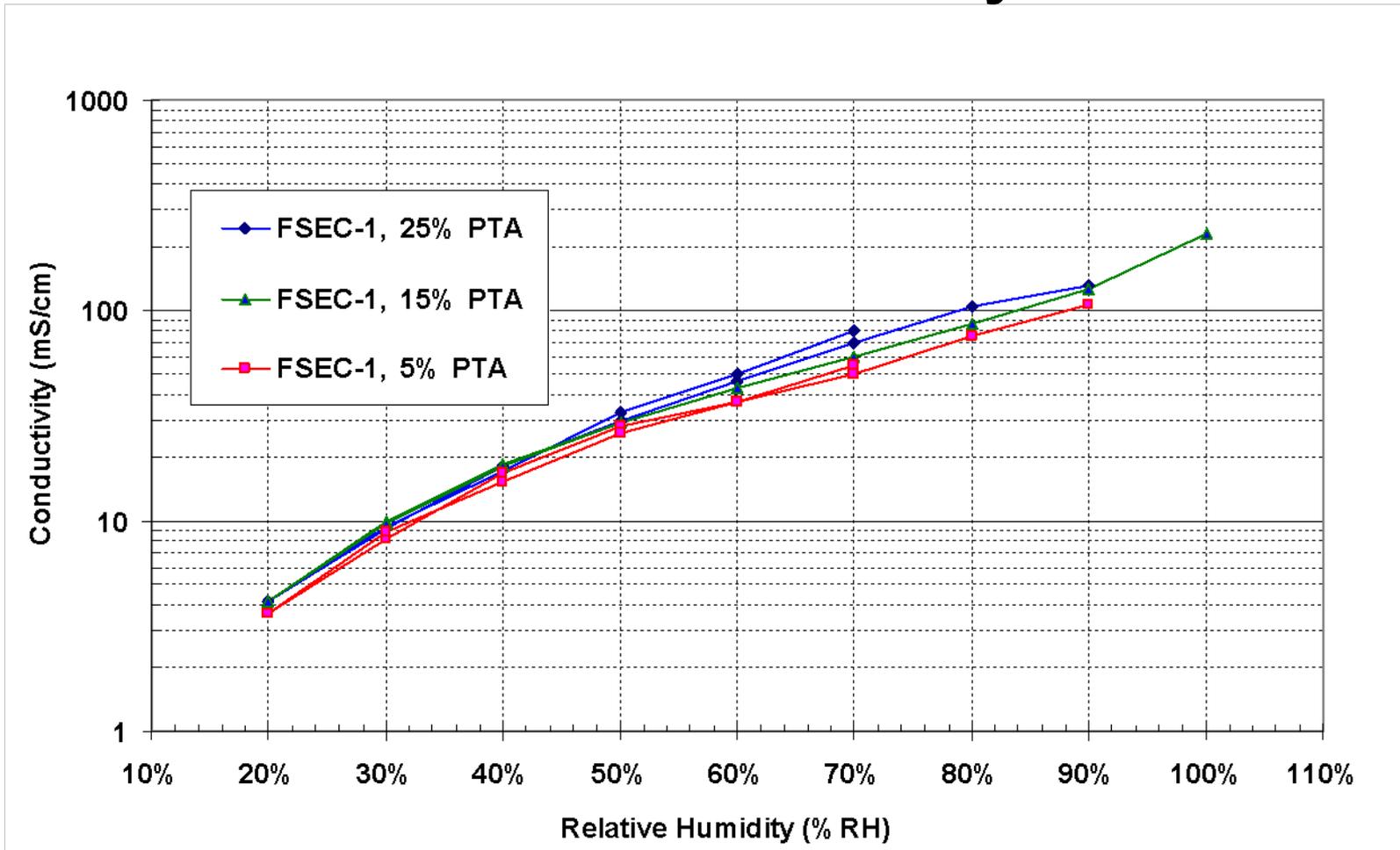


RH Influence During Casting



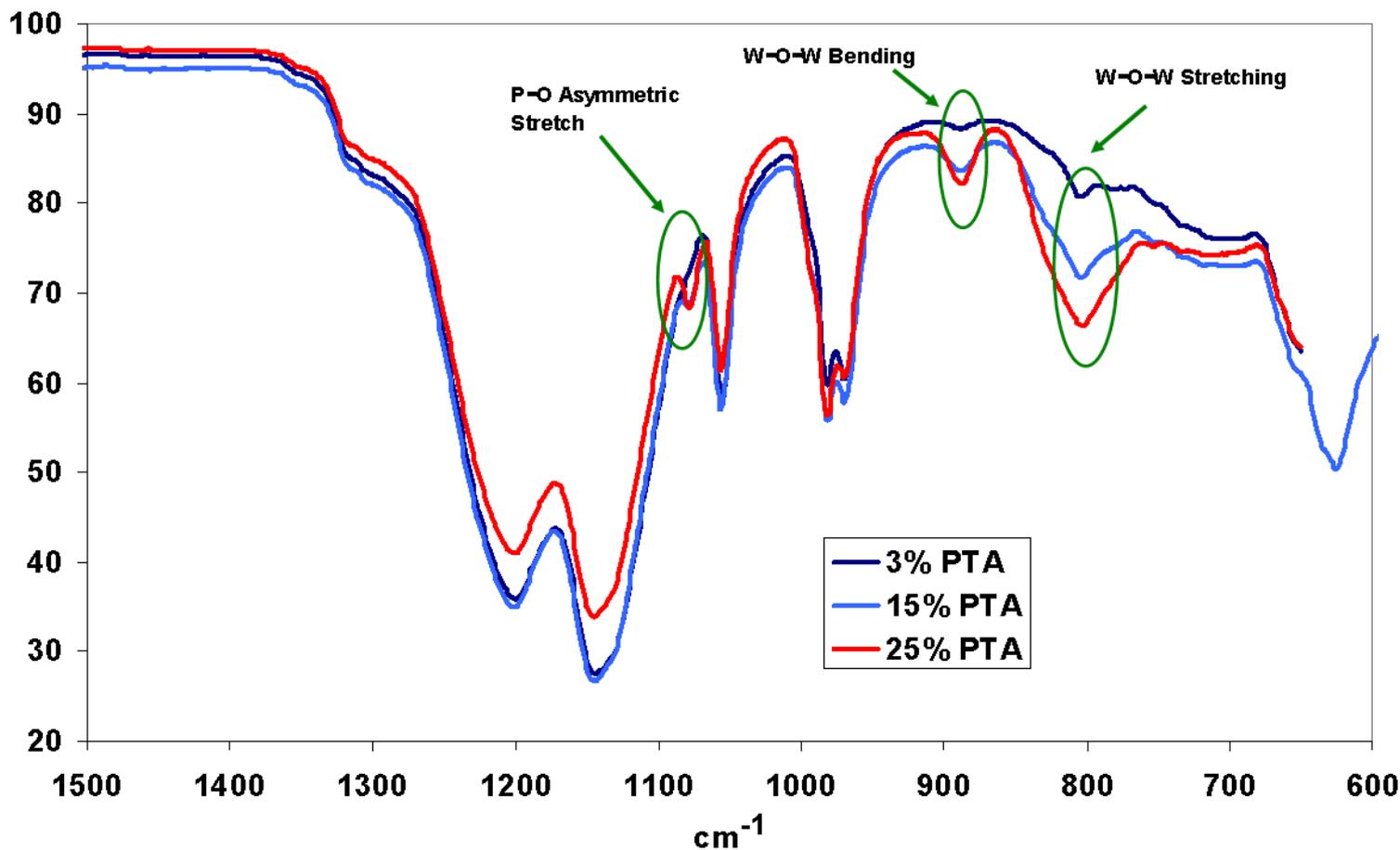


Influence of PTA on Conductivity





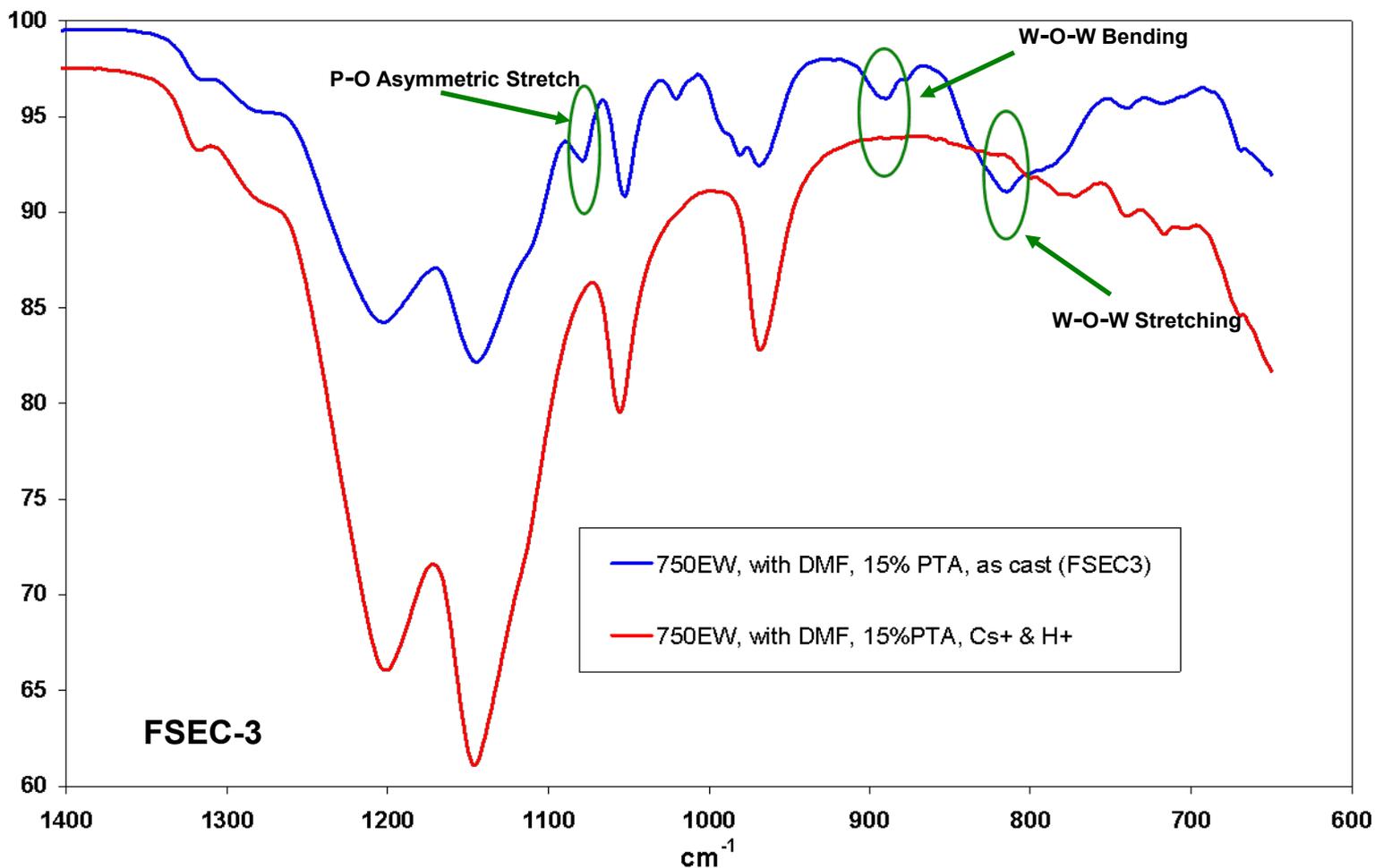
FTIR Analysis Shows Presence of PTA in FSEC-1



❖ FTIR confirms PTA presence in Membrane



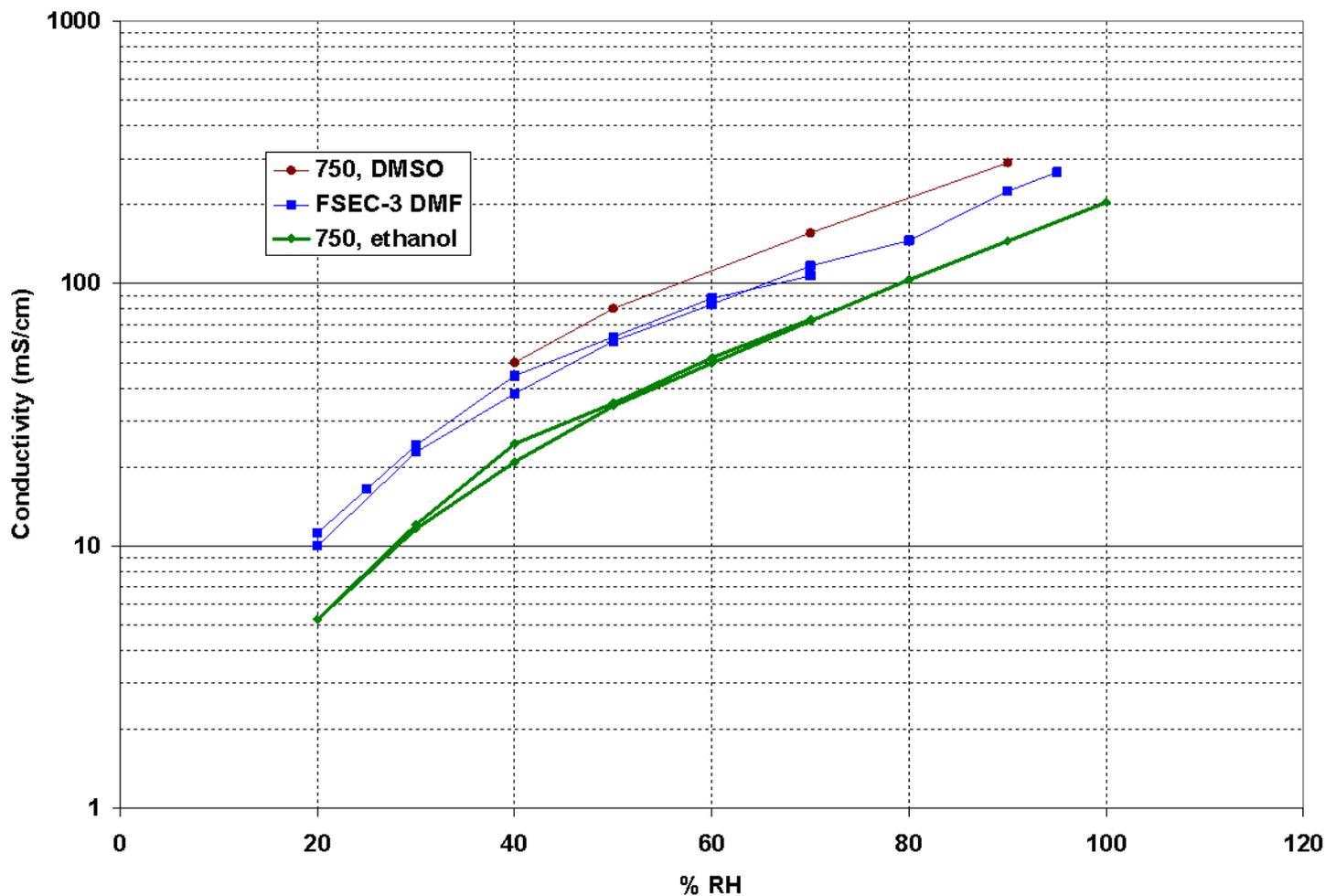
Effect of Protonation on PTA Content of FSEC-3



❖ PTA can be lost during protonation of FSEC-3



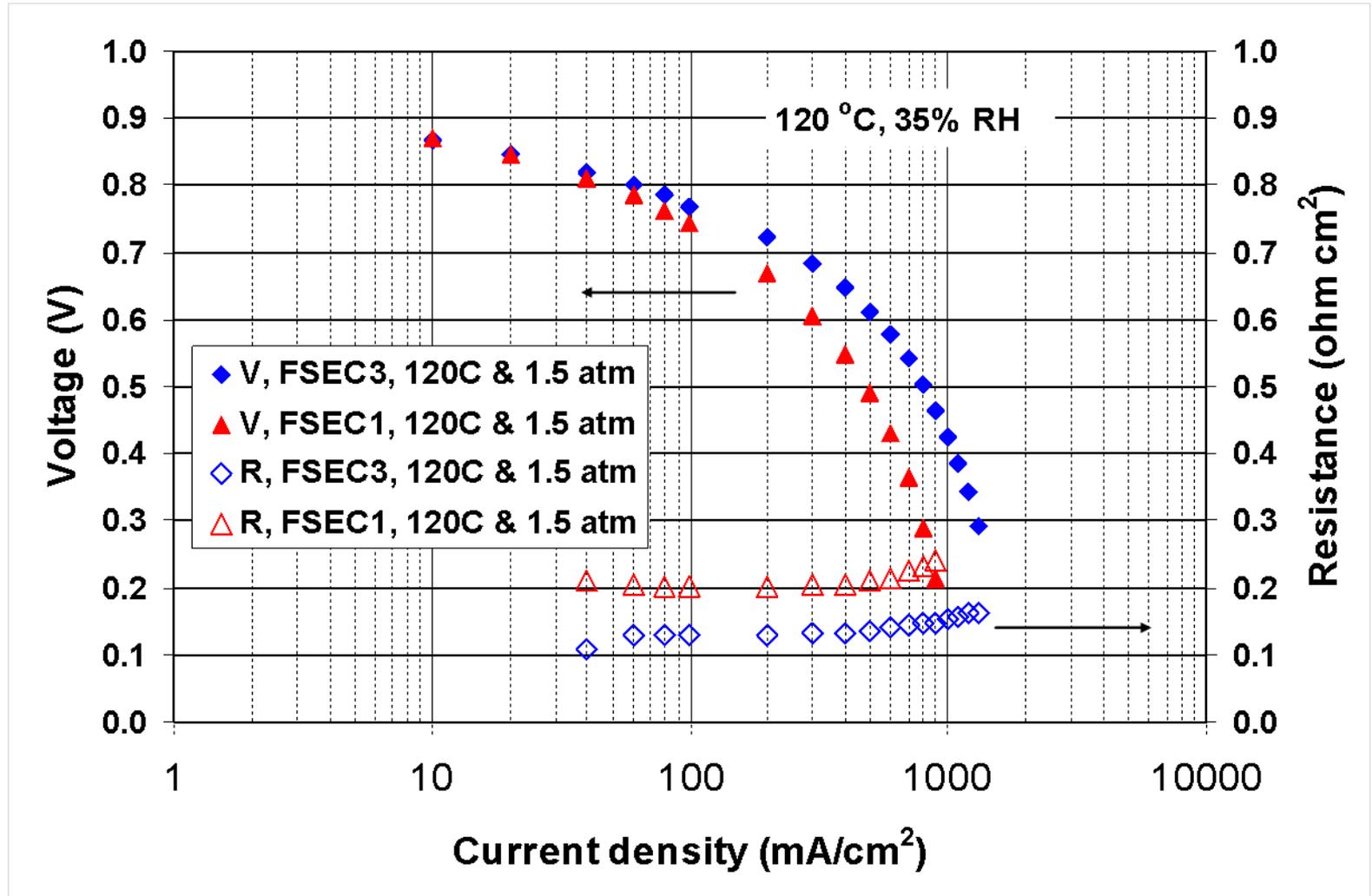
Influence of Casting Solvent on Conductivity of FSEC Low Equivalent Weight Membranes



❖ Solvent choice strongly effects conductivity



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





Meeting Area Specific Resistance Targets

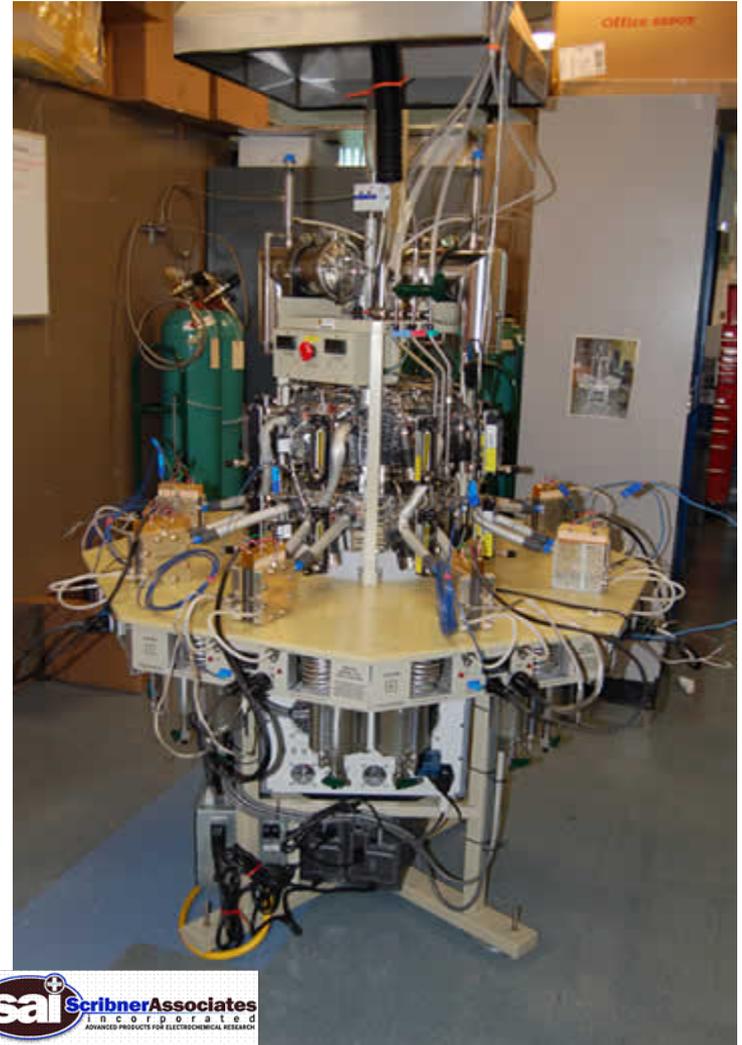
- ASR is not an intrinsic property
- Generate formal definition of ASR
- Generate ASR testing procedure
 - Define pre-test membrane conditioning
 - Define test hardware and test procedure
 - Define analysis procedure
 - Verify test results

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

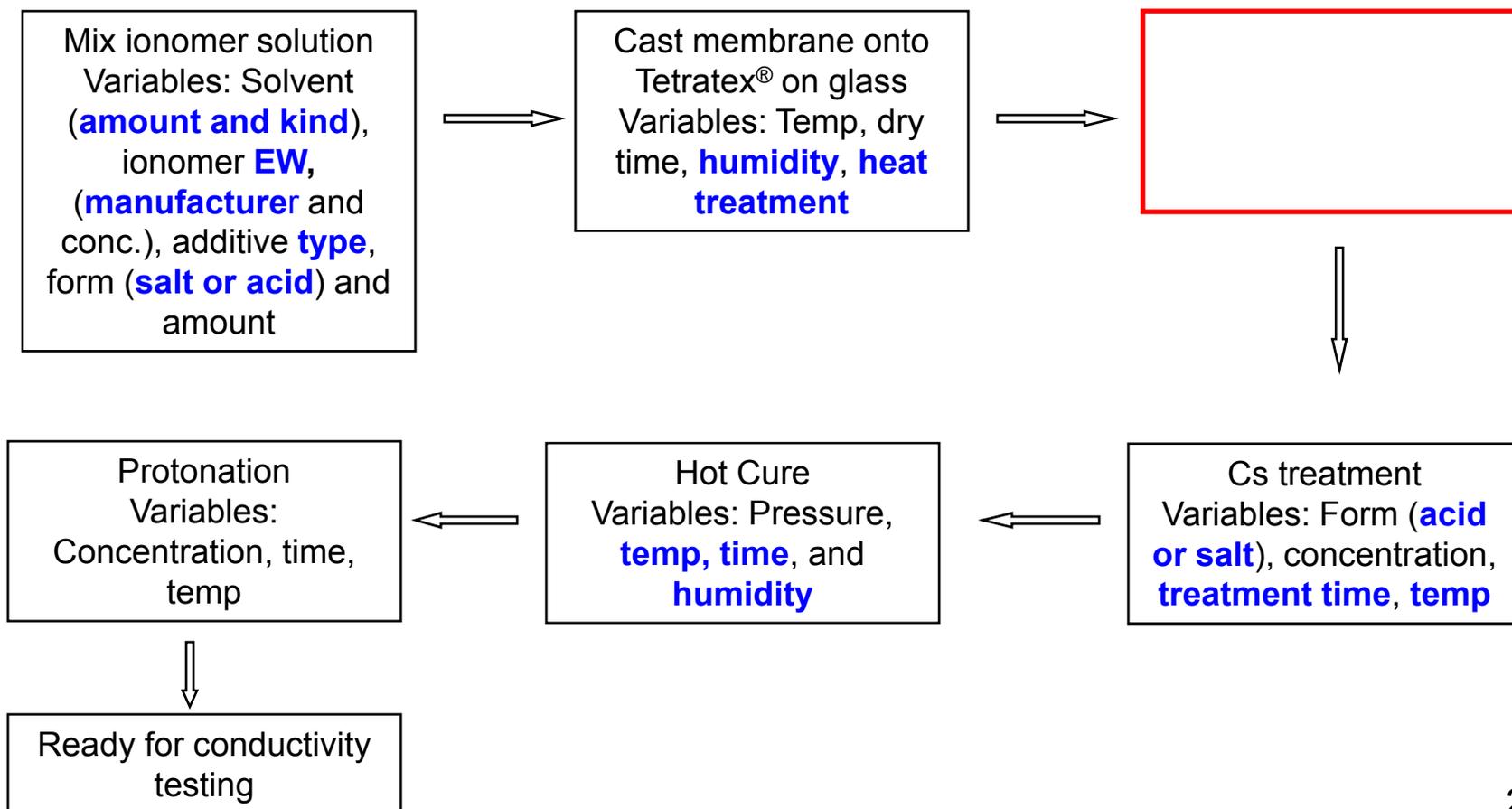


❖ Throughput of durability testing increased 8-fold and test stands freed for performance testing



Future FSEC Membrane Work

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





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 °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)



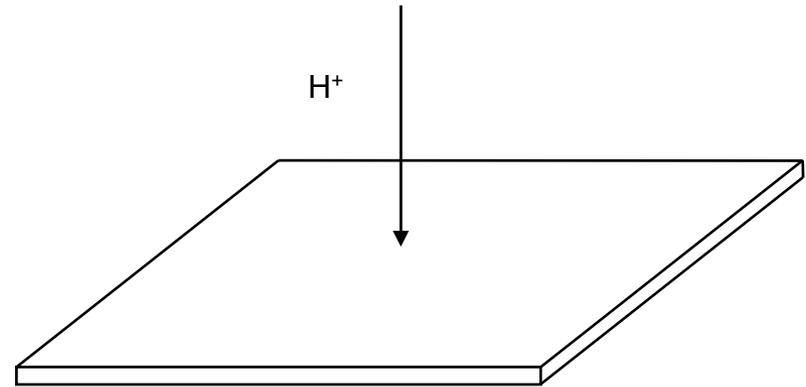
Through-Plane vs. In-Plane

H⁺ 



Current Conductivity
Protocol (In-Plane)

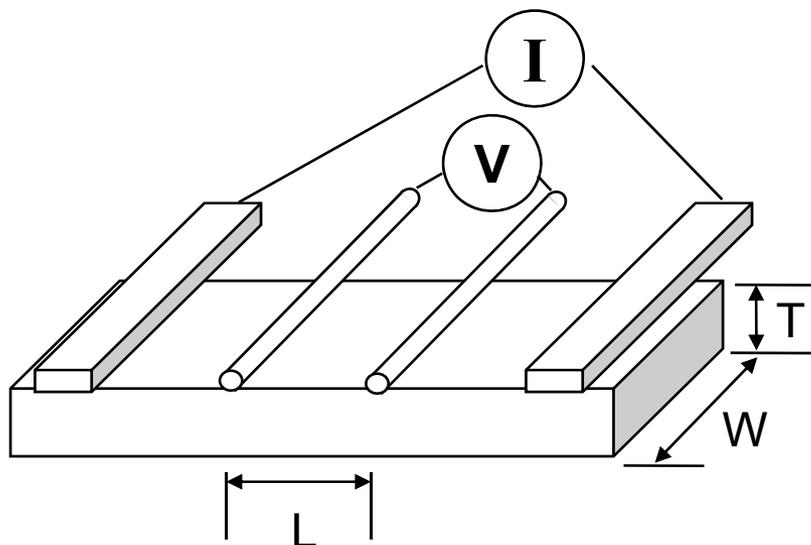
H⁺



Like a Fuel Cell
(Through-Plane)

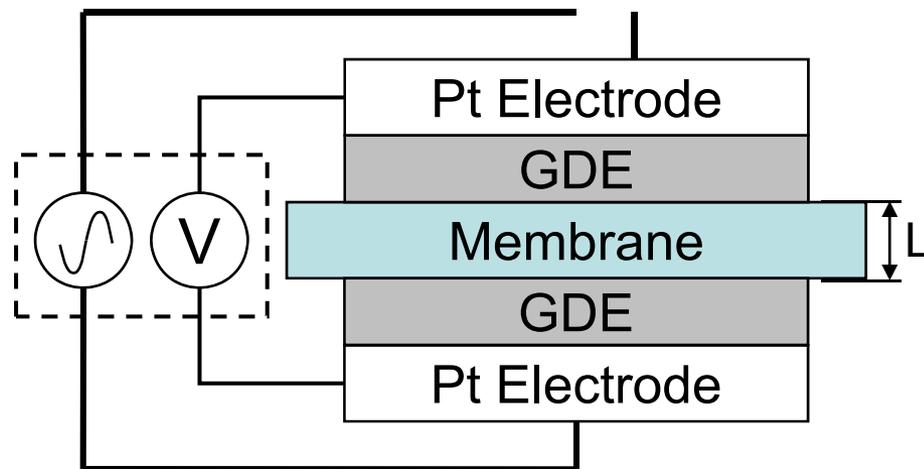


In-Plane vs. Through-Plane



4-electrode DC or AC measurement

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



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

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



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})



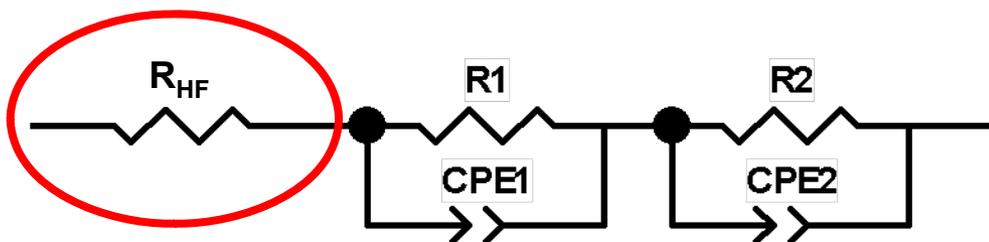
Through-Plane Measurements

- 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, $R_{\text{cell}}(T, RH)$
 - non-trivial task to determine
 - Requires high-frequency (AC) measurement – more sophisticated hardware and data analysis than DC methods



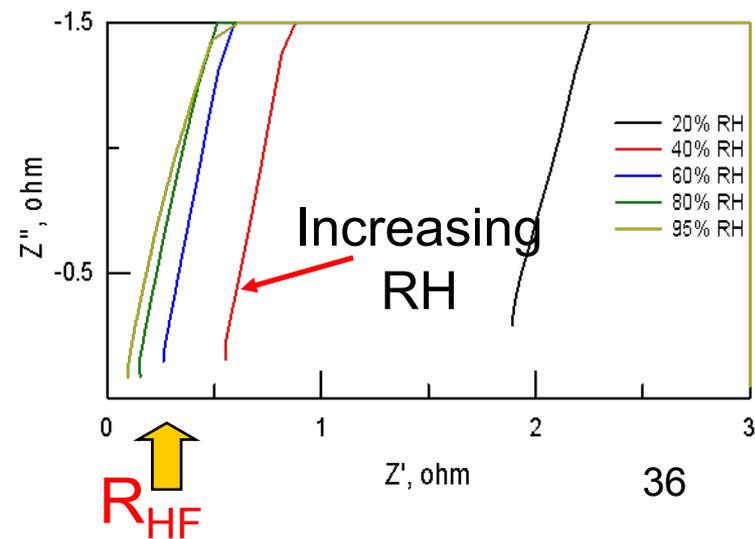
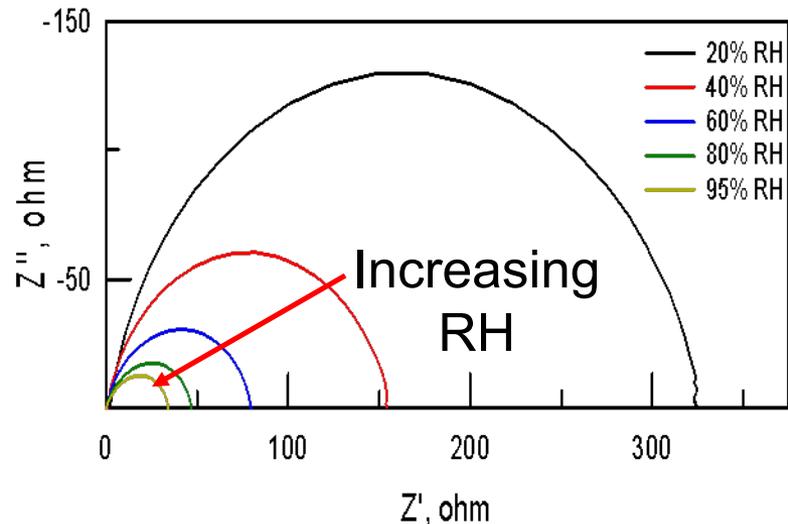
Data Analysis for Conductivity

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



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

L = membrane thickness



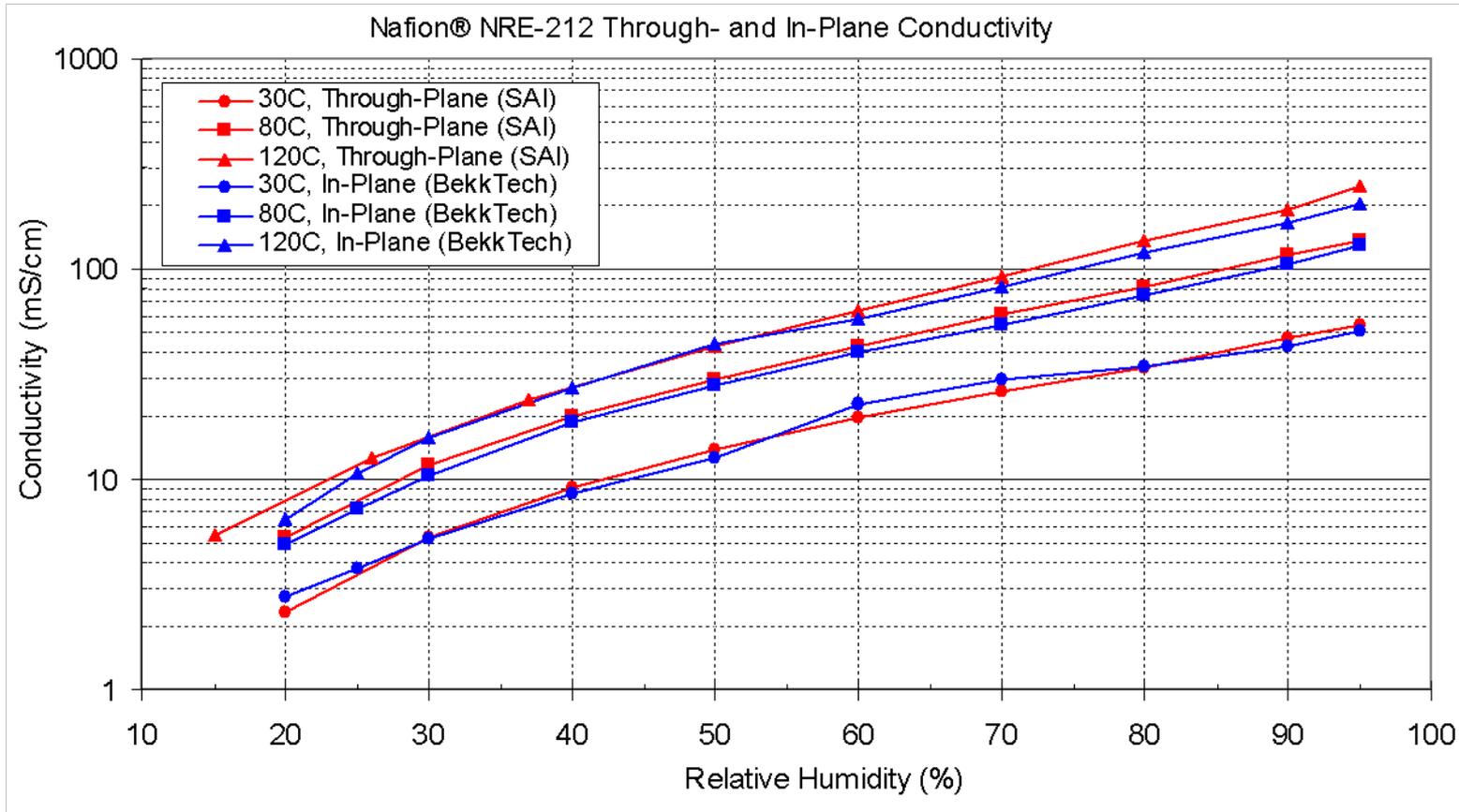


Comparing In-Plane & Through-Plane Measurement Methods

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

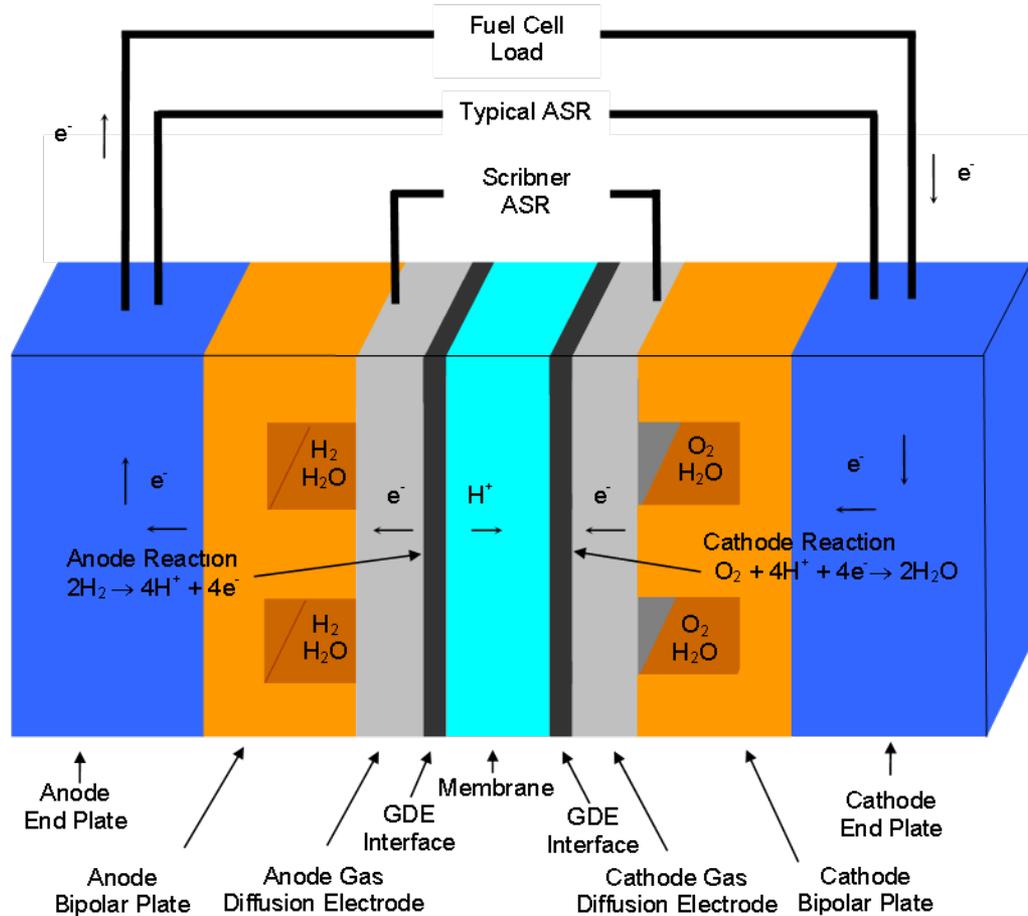


In-Plane and Through-Plane Data Comparison for NRE 212





Components of a Through-Plane ASR Measurement



Component Resistance Plus Resistance at each interface