DOE Hydrogen and FC Program Review

"Integrated Manufacturing for Advanced MEAs"

Topics 1.A.1, 1.A.2 and 1.A.3

June '04 through May '05

DE-FC04-02AL67606

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FC2

Overview

Timeline

- Project start: 1 Oct '01 (2 Jan 02)
- Project end: 30 June '06
- Hi T membrane extended Oct 05
- Percent complete ~75%

Budget

- Total project funding:$19.5M
  - DOE : $14.5M
  - Contractors: $5M
- Funding FY04:$2.73M
- Funding for FY05:$4.64M

➢ DOE Technical Barriers

O. Stack Material and Manufacturing Cost
P. Durability
Q. Electrode Performance
R. Thermal and Water Management

➢ DOE Technical Targets

➢ (consistent with FreedomCar)

- PM loading 2005: 0.6g/ rated kW
- PM Loading 2010: 0.2g/rated kW
- >2000 hrs life (2005)
- >5000 hrs life (2010)
- Target achieved using method amenable to Mass manufacture: <$125/kWe 2005; <$45/kWe 2010
- High Temperature Membrane
  - All of the above and
  - Contributes significantly to achieving System efficiency targets

Objectives

1A1: catalyst and structures

- New cathode alloys and ELAT structures that allow an overall cell performance of greater or equal to 0.4A/cm^2 at 0.8V or 0.1A/cm^2 at 0.85V operating on hydrogen/air with precious metal loadings of 0.3mg/cm^2 or less and scales to mass manufacturing technology.
- Support 1A2 with high temp interface and/or GDL structure.

1A2: Hi T Membrane

- Operates sub-ambient to 120 °C and 25% to 100% RH
- Memb. resistance ≤ 0.1 ohm cm^2
- Hydrolytic, oxidative, mechanical stability in FC at 120 °C
- No leachable components
- H_2 fuel permeation ≤ than 5 mA/cm^2
- Cost ≤ Nafion®

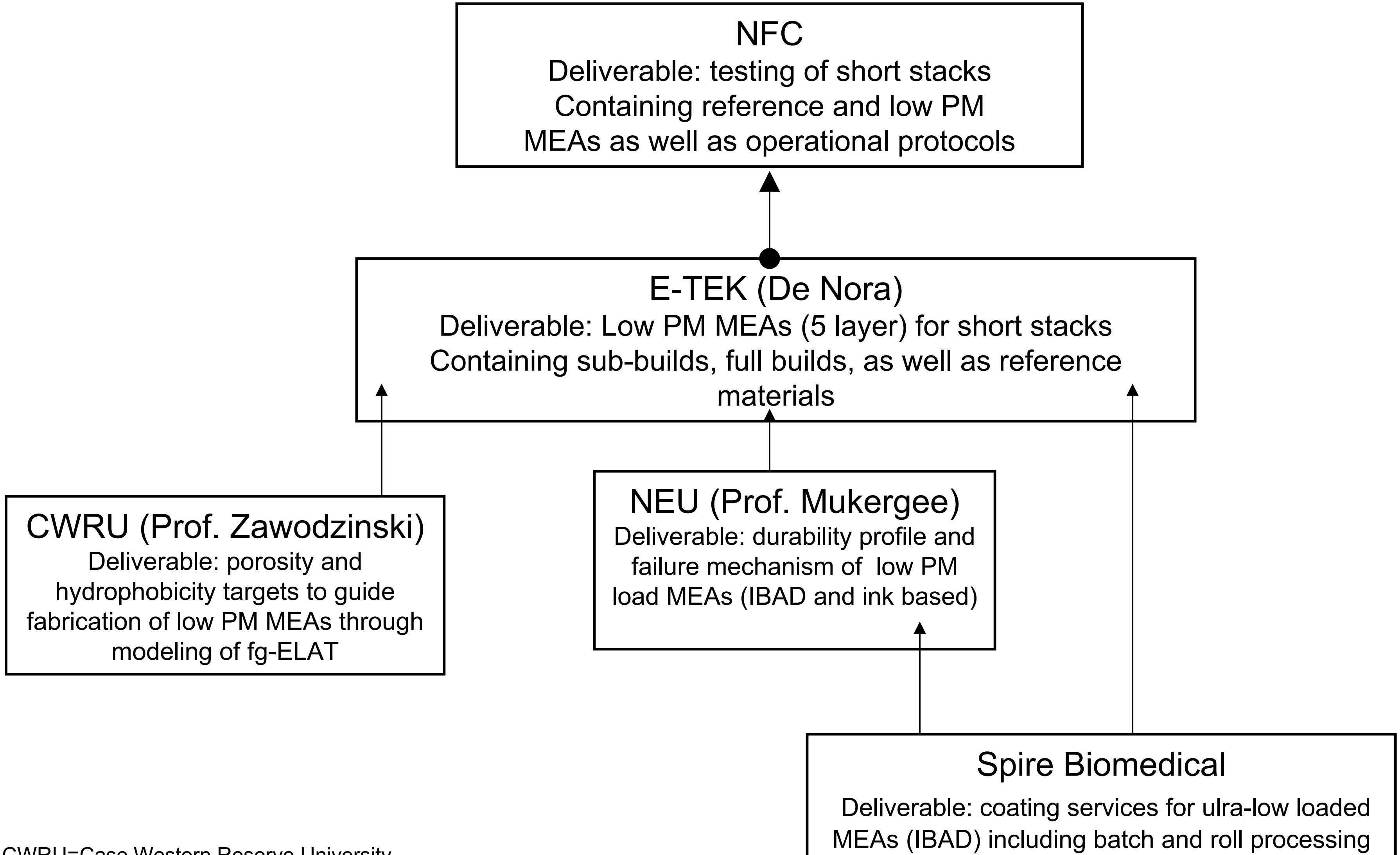
2004/2005 Objectives

- **1A1**: cited performance at 0.4mg/cm^2 using fg-ELAT: transfer to machine fabrication: continue to lower PM, develop high temp interface for A2 materials
- **1A2**: single cell testing of HT membrane, evaluate properties at <0^{o}C, begin scale up of advanced membranes
- **1A3**: scale-up of 1A1 components; testing at stack scale

1A3: MEA Fab for Stack Scale

- Take advances from 1A1 and/or 1A2 and integrate into pilot manufacturing
- Demonstrate stack scale elements operating with performance consistent with objectives of 1A1 or 1A2

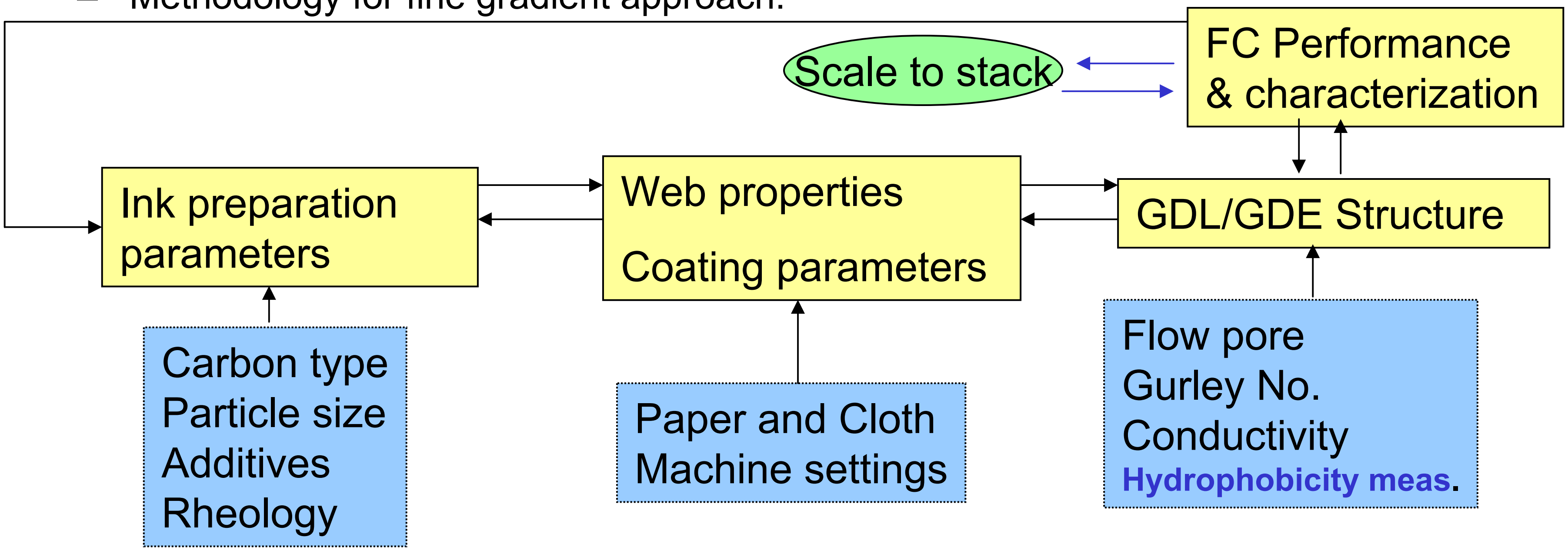
Team Members responsible for objectives of low precious metal MEAs:



CWRU=Case Western Reserve University
NEU=Northeastern University
IBAD=Ion Beam Assisted Deposition

Approach: Catalyst and Fine Gradient ELAT®

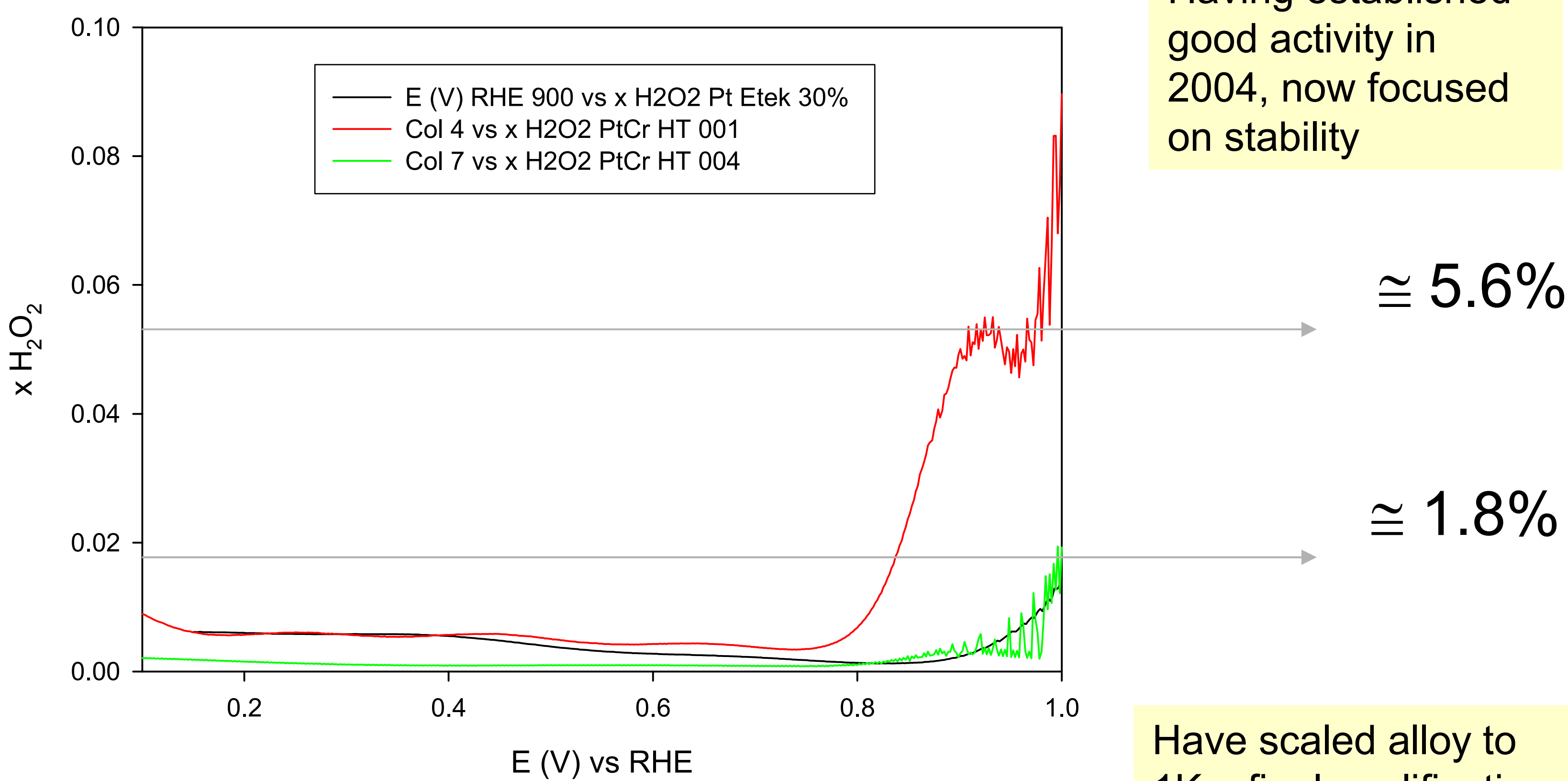
- Catalyst: create structure-function relationships supported by Reitveld analysis of XRD patterns; develop/optimize new prep methods for catalysts and alloys: now in scale-up and durability phase
- GDL/GDE: Develop a new ELAT gas diffusion layer and/or electrode structure based on fine gradients of hydrophobicity and porosity using developmental coating machine
  - Current focus on machine implementation, and extending approach w machine
  - Methodology for fine gradient approach:



Catalyst Activities: Durability and scale up

Impact of alloy structure and H_2O_2 production
(Rotating Ring Disk Electrode to detect H_2O_2 formation)

Peroxide Yield Comparison Pt Etek 30% vs Pt Cr in Sulfuric Acid



Having established good activity in 2004, now focused on stability

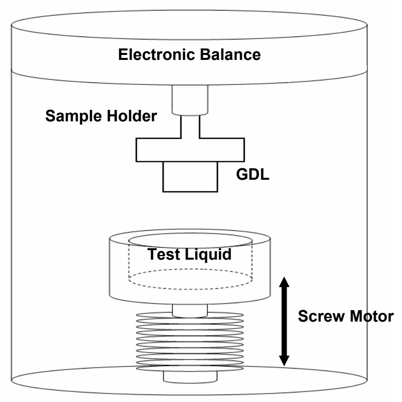
Have scaled alloy to 1Kg, final qualification goal is 3Kg

Tools to help build the fine gradient: Method to measure Hydrophobicity -

Contact angle and solid surface energy being developed at CWRU

Cobb Titration at E-TEK division

Krüss Processor Tensiometer

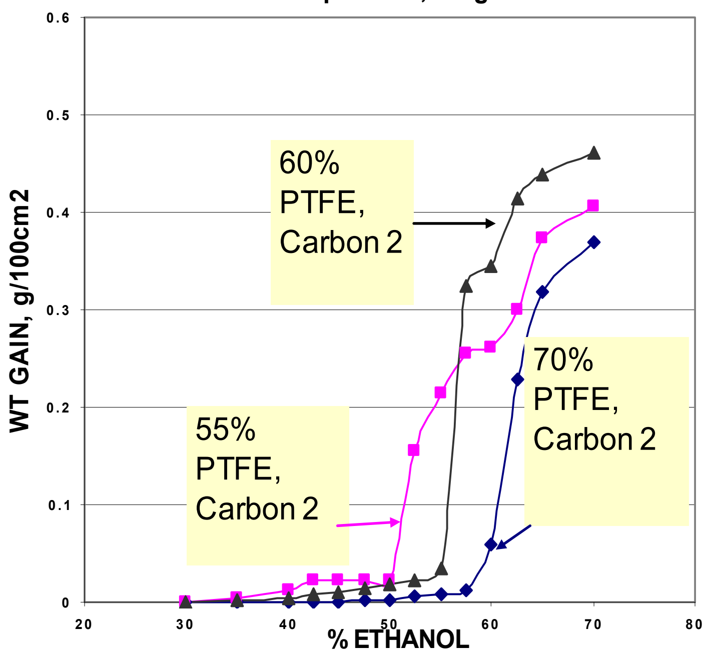


- CWRU uses Washburn method with hexane (wetting) and water to measure internal contact angle and surface energy

Internal Contact Angle to Water theta H_2O, GDL Surface Energy gamma s, and its Dispersive and Polar Components gamma s^d and gamma s^p

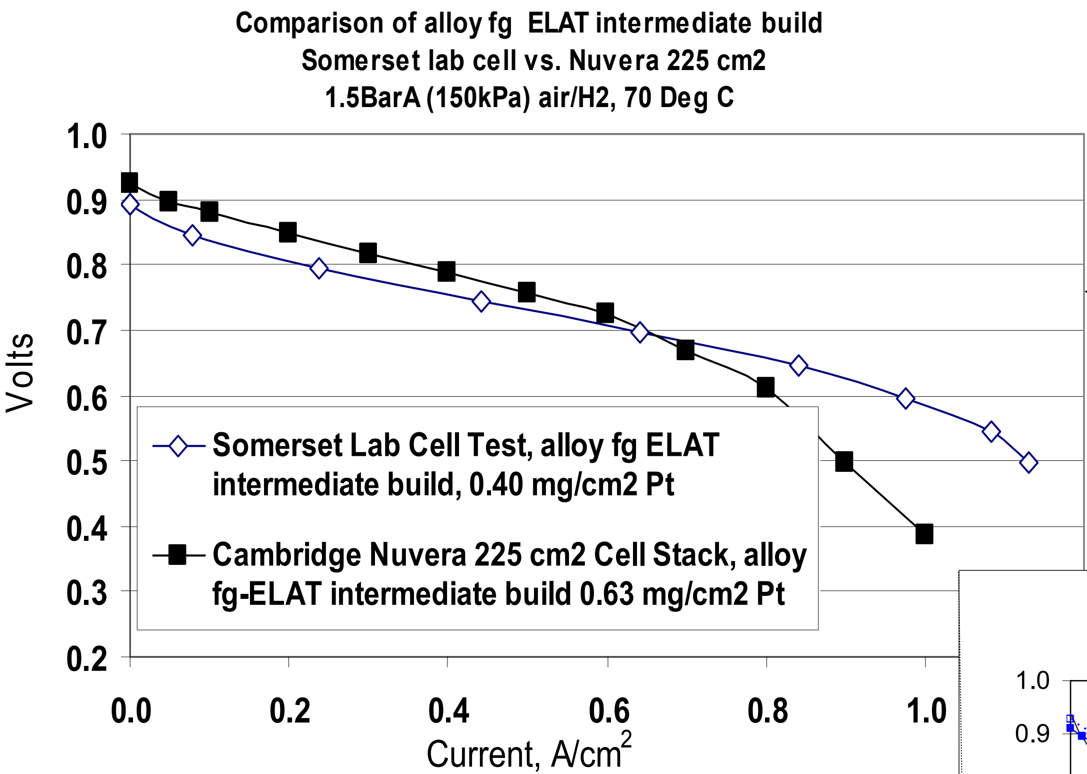
Sample	theta$_{H2O}$	gamma$_s$	gamma$_s^d$	gamma$_s^p$
30% PTFE, carbon 1	89 ± 3	21 ± 2	13 ± 1	8 ± 2
70% PTFE, carbon 1	101 ± 3	17 ± 1	13.8 ± 0.8	3.1 ± 0.8
30% PTFE, carbon 2	88 ± 7	22 ± 4	14 ± 2	8 ± 3
70% PTFE, carbon 2	96 ± 7	19 ± 3	14 ± 2	4 ± 2

"Cobb Titration"



- Team verified earlier Cobb results with tensiometer
- However, previous Cobb method unable to discriminate a delta of <10% PTFE
- Modified the solvent: can measure <5% delta PTFE
- *Plan to extend method to gdl durability tests*

Fine gradient ELAT

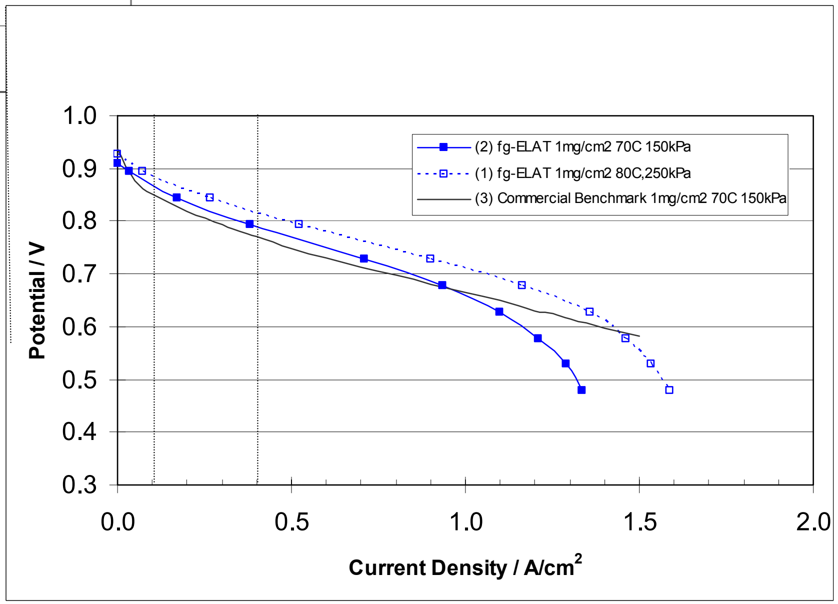


Stack scale fg-ELAT constructed by machine and hand steps: supper-scaling at under $0.6 A/cm^2$

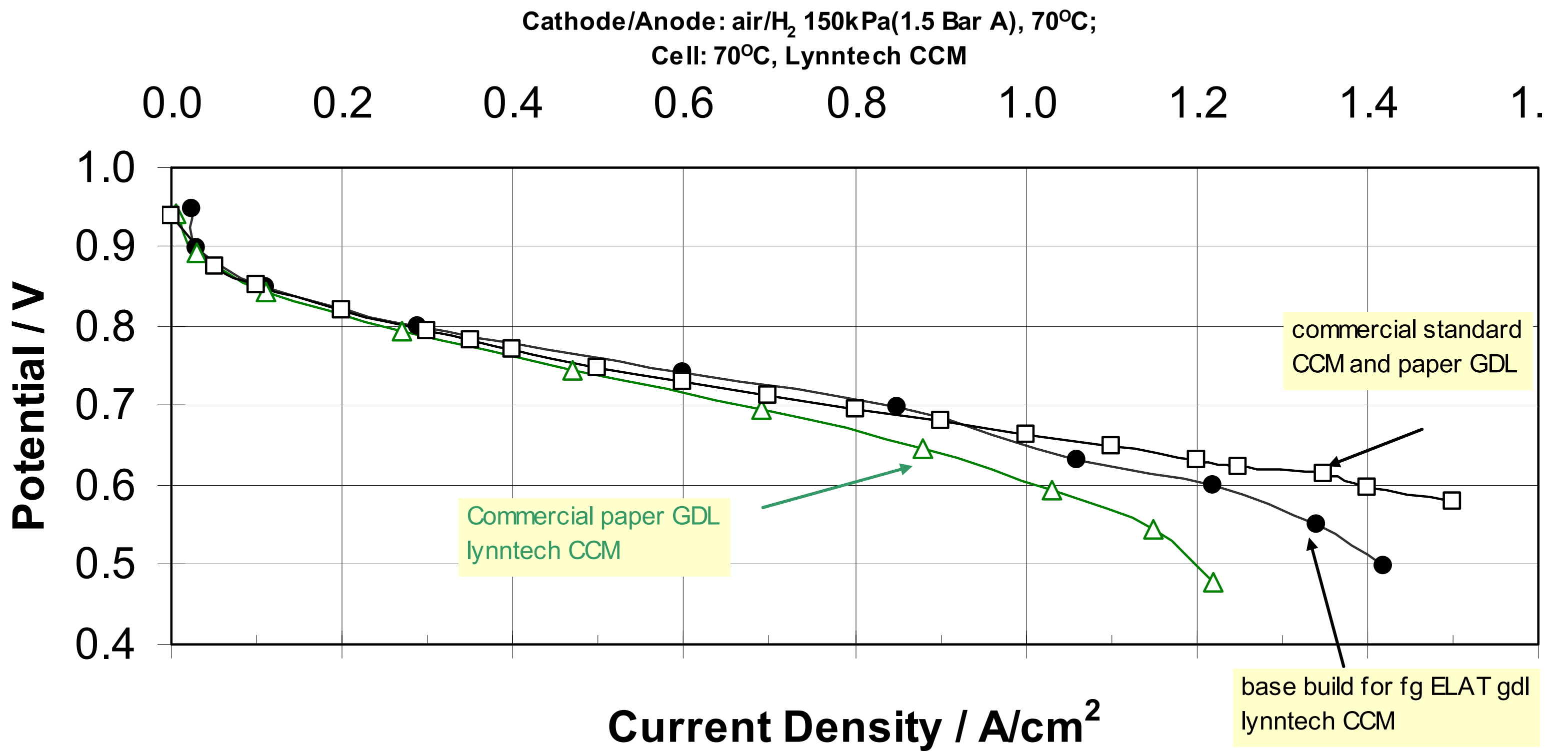
fg-ELAT, *all machine*

1) fg-ELAT MEA DOE T and P, $1 mg/cm^2$ PM
2) fg-ELAT MEA 70 deg C, $1 mg/cm^2$ PM
3) Commercial MEA 70 deg C, $1 mg/cm^2$ PM

fg-ELAT MEA at DOE T and P with $0.39 mg/cm^2$ PM (0.28mg Pt cat. alloy, 0.11mg Pt anode) results in 0.86V at 0.1A/cm2 and 0.8V at $0.4 A/cm^2$ – *interim goal achieved*

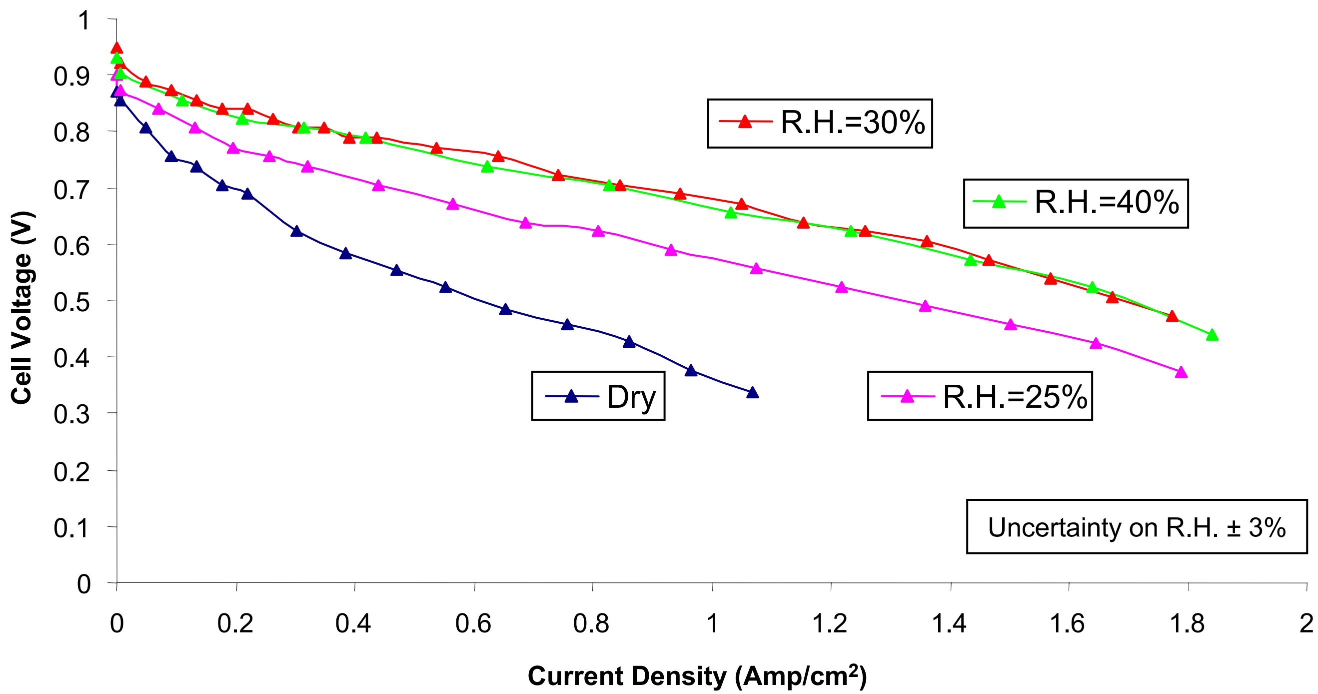


Summary of “paper” progress to date: started base build



- All “standard” 3rd party electrode (CCM) structures
- All PM loadings are high (~1mg/cm² total PM)
- Very encouraging performance for fg sub build
- Accomplished through extensive changes in formulation and coating variables compared to carbon cloth woven web

High Temperature Interface with Membrane (V) Du Pont



- Standard Gradient/machine made
- Focused effort on formulation and fabrication variables (hand fab interface, machine GDE)
- Demonstrated >1500 hrs with membrane V under accelerated aging protocol (2003/2004)
- EXCEEDS POWER GOAL AT 30% RH

Experimental conditions:

MEA:

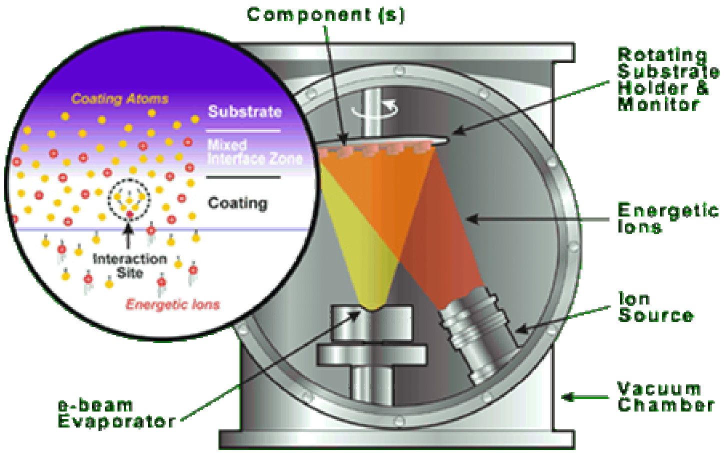
A) Total (cathode and anode) PM = 1 mg/cm^2
B) Electrode: HT140E-W
C) Ionomer Interface: Proprietary
D) Membrane: DuPont Membrane V

Cell:

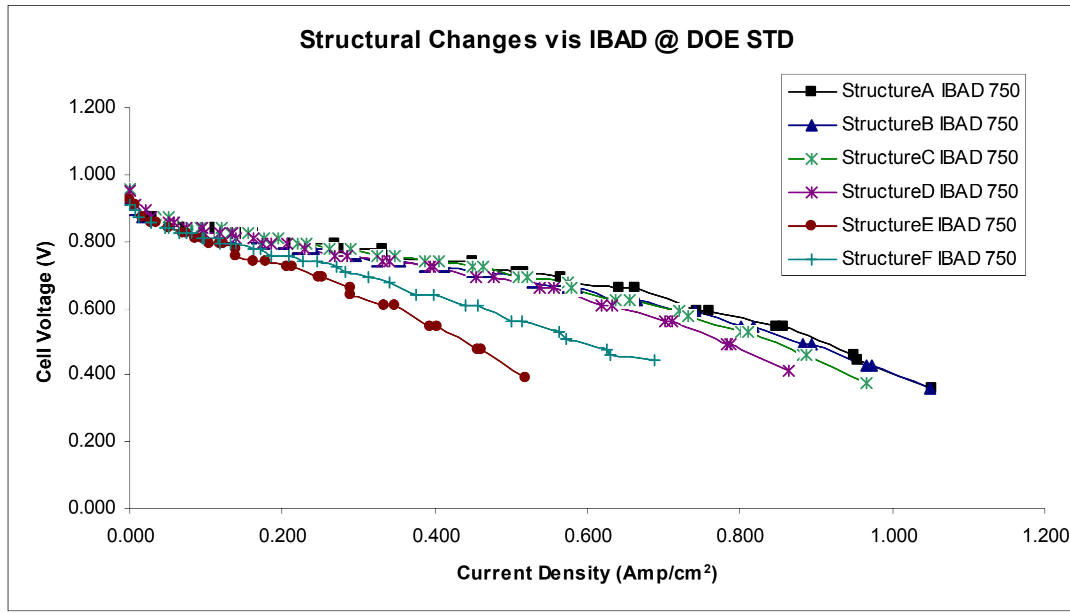
A) R.H. = 25% to 40%
B) Gases: Air (Cathode) and H_2 (Anode)
C) Cell Temperature: 120 ^{o}C
D) Total Pressure: 2.0 Atm

NOTE:
The R.H. was measured at the cathodic and anodic gas inlets using a digital relative humidity sensor (Tech-Edge, Inc.).

Dual Ion Beam Assisted Deposition



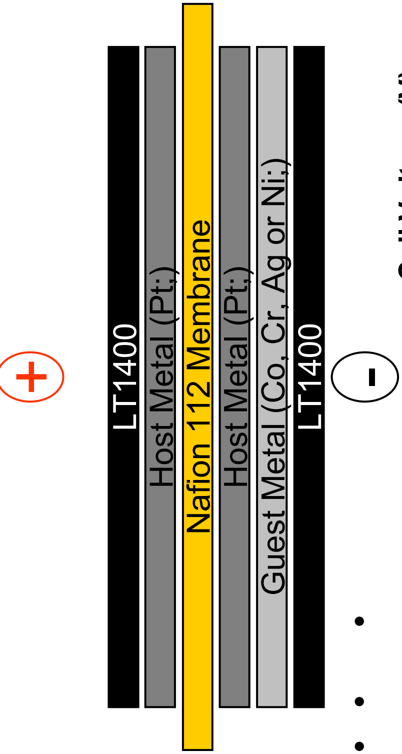
Breakthrough in approach: can make 3d structures with ion beam. Improvement in mass transport (~0.14 mg/cm^2 total Pt below)

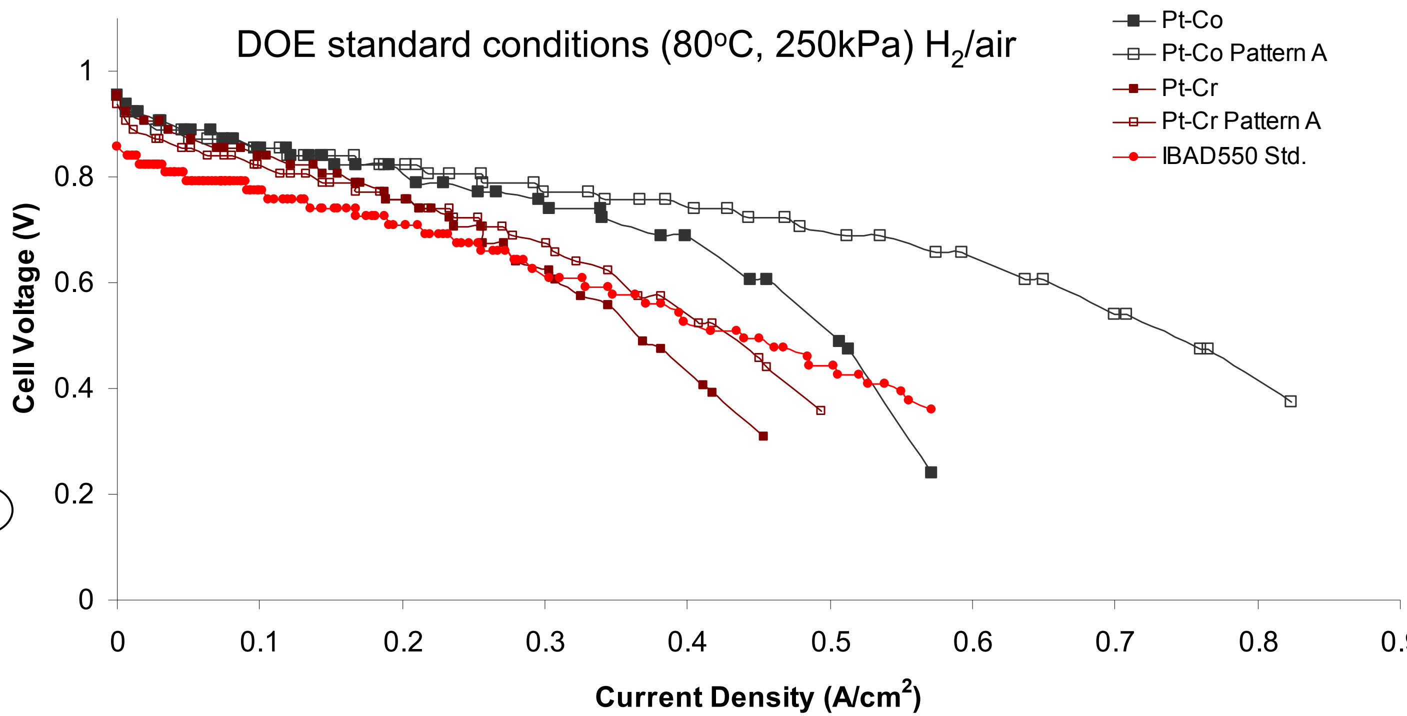


Sample	Real Surface Area (cm^2/cm^2)	Loadings (mg/cm^2)
IBAD250	26.3	**0.034**
IBAD550	23.8	**0.078**
IBAD STD 750	34.6	**0.102**
IBAD750 Structure A	70.9	**0.071**
IBAD1500 Structure A	79.6	**0.142**
LT140-E ELAT Reference	99.1	0.500

Electrochemical Surface Area Measured with fully flooded GDEs, H_2 wave, and cyclic voltammetry

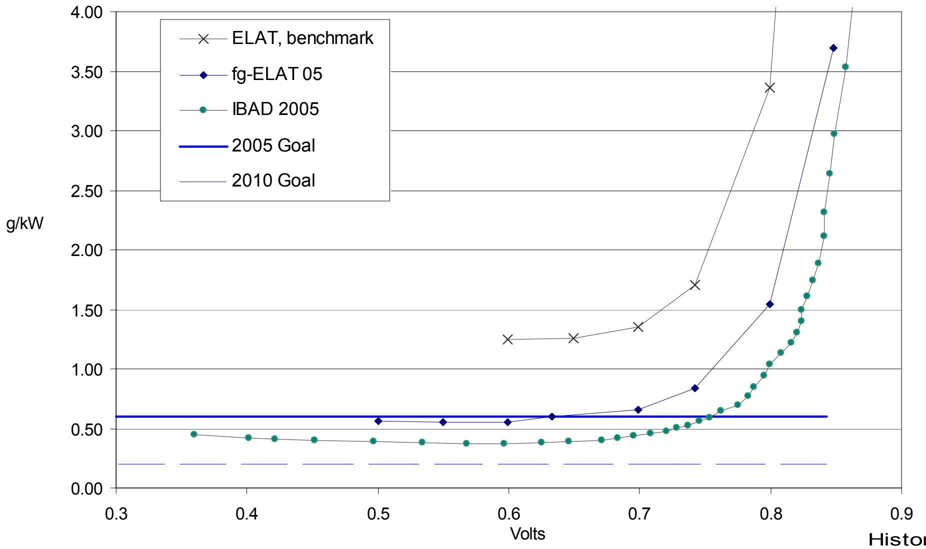
Pt Skin-effect catalysts with IBAD





- Use IBAD to create multi-layer structures such as depositing Co, Cr, Ni, or Ag first, and then covering with a thin layer of Pt (which then contacts the membrane)
- Can also use new beam-created structures on the multi-layered catalysts
- According to XRD, these are *not alloys*
- Preliminary stability acceptable: will continue detailed durability at NEU
- Pt:Co “Pattern A” total PM is 110 ug/cm^2
- Standard gradient ELAT® employed as substrate

Comparison of “IBAD”, best fg-ELAT, and start-of-program benchmark: total PM/ power vs. V in“GM” format



Total Pt loading

ELAT benchmark: $1 mg/cm^2$

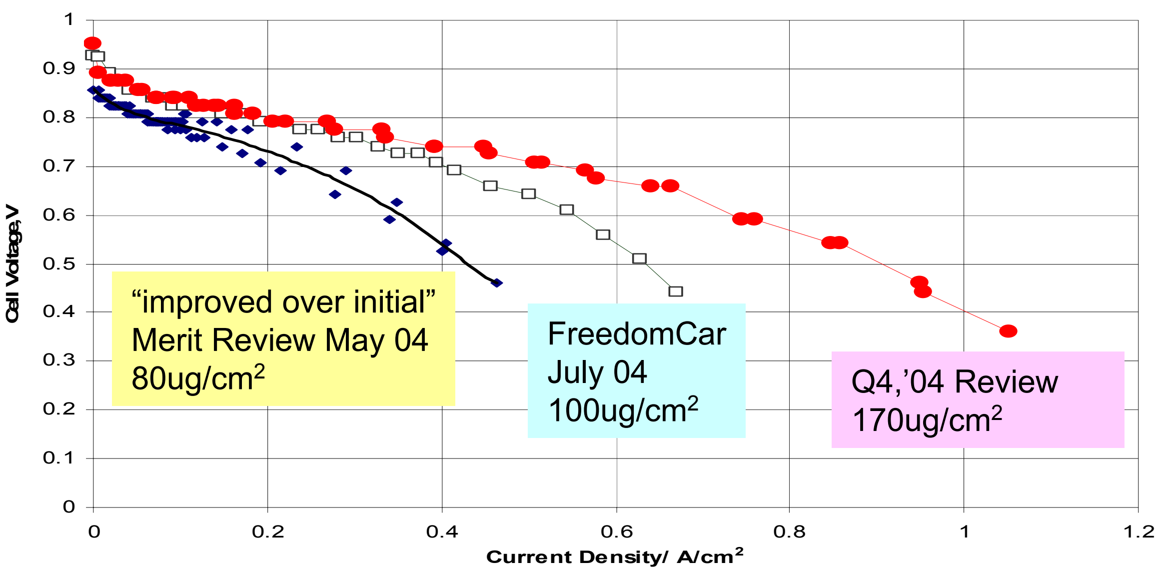
fg-ELAT: $0.39 mg/cm^2$

IBAD/ELAT: $0.17 mg/cm^2$

Pt IBAD deposition on anode and cathode Air H_2 250kPa total (2.5BarA), 80°C Nafion 112

gPt/kW at 80°C, 250kAa total (2.5BarA), H_2/Air

Historical Comparison of IBAD results, at DOE Standard Conditions



Significant gains in performance realized through new cathode structures created by ion beam. Showing capability for higher currents as well.

Responses to Reviewers

- Improvements should be benchmarked against commercially available components, not necessarily internal or start of program benchmarks
  - *Have shown some examples within this presentation, although obtaining commercial benchmark data at different operating conditions can be difficult*
  - *We have also approached third parties to provide comparative data for these new components versus commercial benchmarks. The effort is on-going.*
- IBAD approach may be limited in these assemblies' capability to achieve high current – especially beyond the quarter power goal of this program
  - *The recent breakthrough has allowed a substantial improvement in higher current operation: however, we now need to "reinvent" the GDL to respond to this unique interface for improved water management*
- Efforts on the fabrication of electrodes for the high temperature membranes of Du Pont should be increased
  - *2003/2004 saw limited quantities of samples: however, improvements by the Du Pont team in solving materials issues in making membranes has provided more material for 2004/2005. We expect some of the understanding learned from making an interface/electrode for Membrane V may be applicable to the other new materials being developed by Du Pont. Electrode assembly with new membrane materials is a key focus for 2005/2006, as well as scaling Membrane V assemblies to stack scale.*

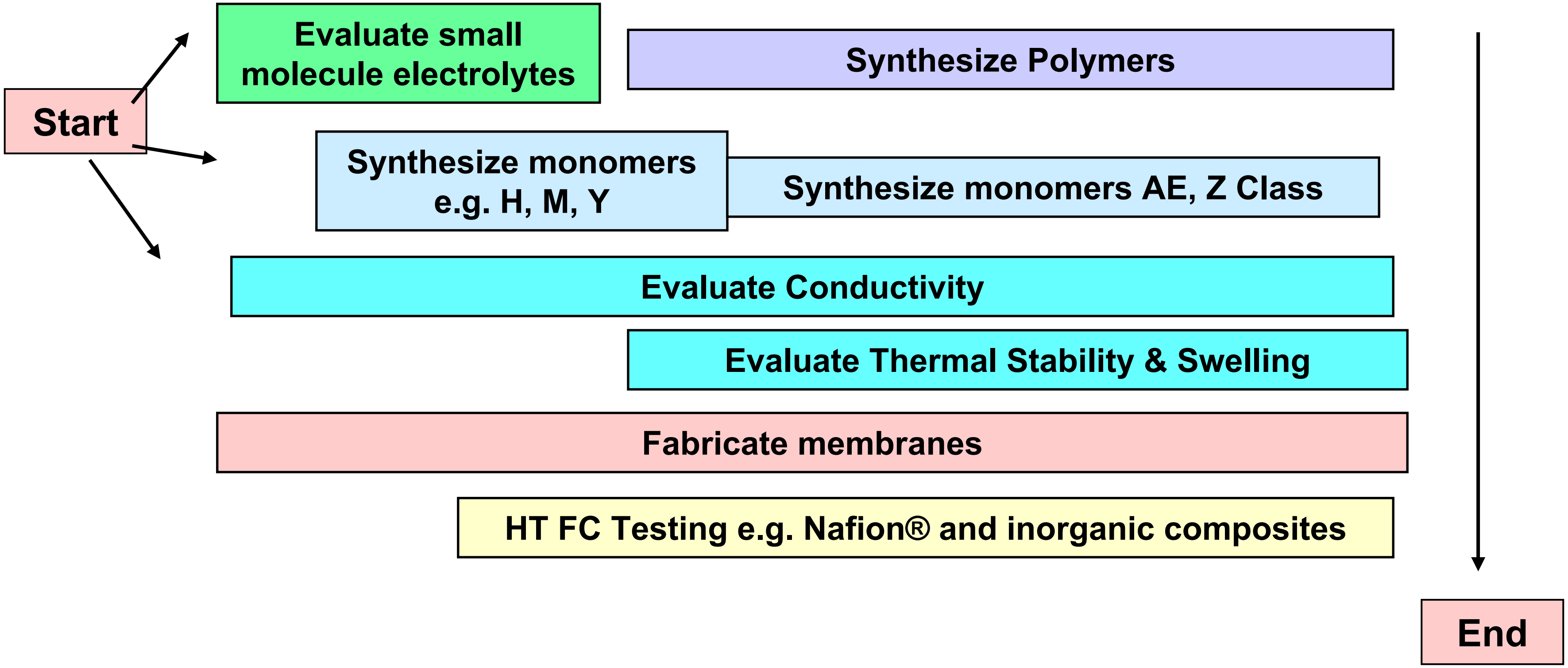
Accomplishments/Progress

- *The team continued to increase power and reduce PM loading*
  - *Met interim goal of 0.8V at 0.4A/cm^2 and greater than 0.85V 0.1A/cm^2 at DOE test conditions with under 0.4 mg Pt/cm^2 total using coating technology suitable for mass manufacturing*
- Implementation of fg-ELAT approach on non-woven materials begun: outstanding results with baseline structures may provide a path to achieving final power/PM goals
- Strategy for introducing designed structures for IBAD based fabrications continues to show improvements in power and mass transport at higher currents while approaching 2010 PM loading targets: new approach is subject to a patent application. Realized catalytic activity with layered metal structures
- Have shown first generation high temperature interface capable of approaching DOE power goal with Du Pont's modified membrane ("Membrane V")
- Developed much-needed methods to quantitatively measure hydrophobicity for GDL materials. Although initially used to design fine gradient ELAT, these methods will have utility in durability studies
- Began baseline 1,000 hr constant current durability operation

Next Steps

- **Reduce PM loading to 0.3mg/cm^2 and scale results to stack level**
  - optimize fg-ELAT approach through structure refinement and machine practices
  - develop fg-ELAT on non-woven web
  - Use next generation CWRU/CAPI modeling to guide structure design
- **Catalyst**
  - Scale up prep for improved alloys: 3Kg target
  - Continue ex-situ lifetime tests; post-mortem MEA/catalyst analysis
- **Ultra-low PM loading (IBAD)**
  - Develop new GDL structures tailored to the unique IBAD "Pt-layered" interface to realize full catalytic potential of these new materials
  - Lifetime/durability analysis of IBAD structures (at NEU)
  - Transition to continuous coating
- **Durability**
  - Develop durability protocol and methods at stack level (NFC)
    - Refine to incorporate at single cell scale at E-TEK
  - Using new hydrophobicity measurements, analyze fine gradient sub builds under forced aging regimes for change in hydrophobicity
  - Durability testing of machine made fine gradient ELAT MEAs

Program 1A2: High Temperature Membrane General Approach



Program officially ended Oct 2004: however encouraging advances in new classes of polyelectrolytes justified an extension of one year for Du Pont’s activities. Programs for the other team members were accordingly.

Team Members responsible for objectives of high temperature MEAs:

NFC
Deliverable: testing of short stacks
Containing reference and high temperature MEAs as well as operation protocol

E-TEK (De Nora)
Deliverable: High T MEAs (5 layer) for short stacks
Containing high temperature interface as well as reference materials

CWRU (Prof. Zawodzinski)
Deliverable: porosity and hydrophobicity targets to guide fabrication of high temp interface

Du Pont
Deliverable: at least two types of high temperature membranes
Enough of one for stack level testing

NEU (Prof. Mukergee)
Deliverable: 1. durability profile of "ultra low" PM load MEAs (IBAD) at Hi T
2. durability profile of High Temp Interface

CWRU (Prof. Litt)
Deliverable: High T membrane Structures and synthesis for materials fulfilling " uncollapsible hydrophilic domains"

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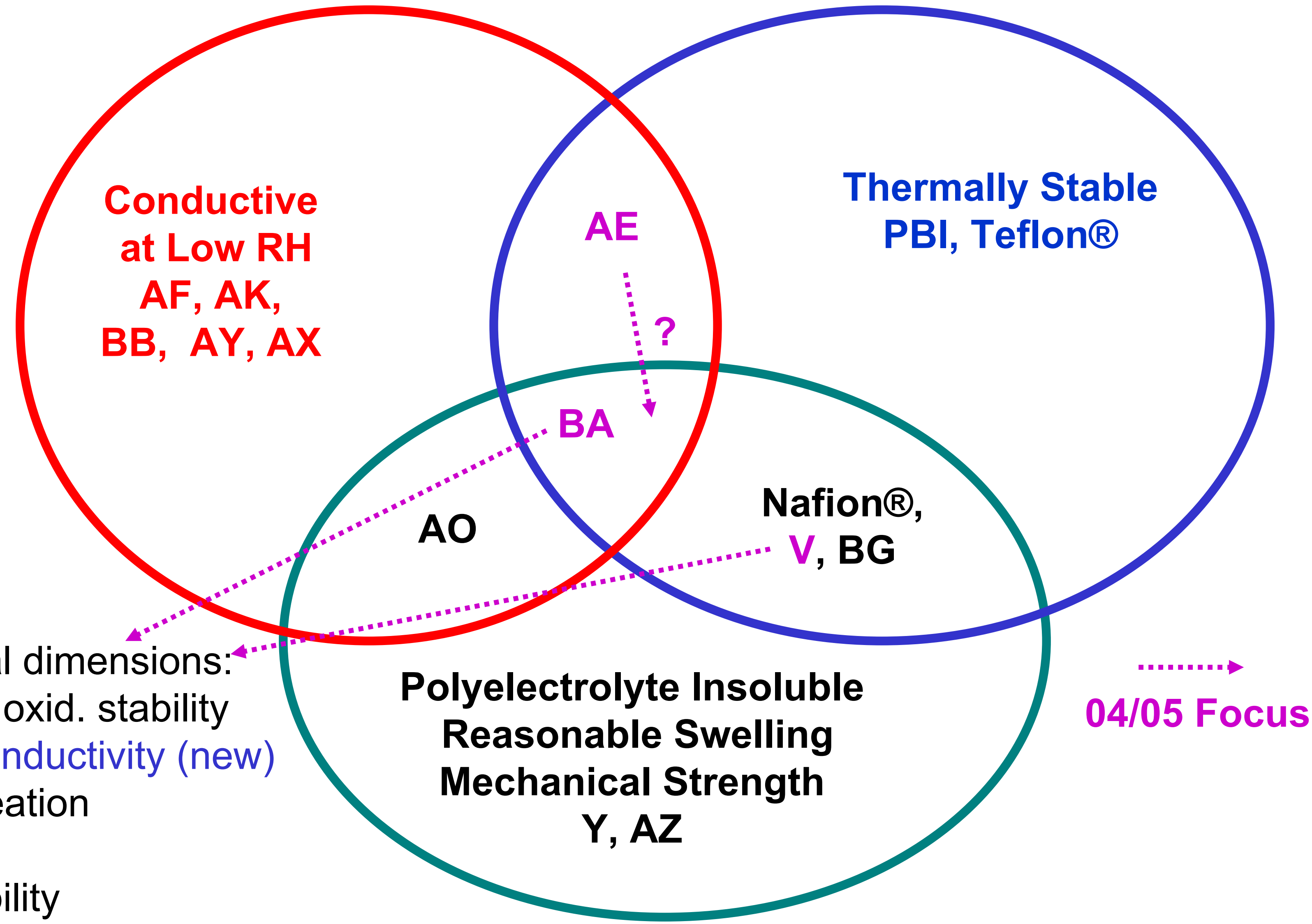
NEU=Northeastern University
IBAD=Ion Beam Assisted Deposition

1A2 High Temperature Membrane

Past year focused on 3 technology options:

Polymer	Type	Features
Candidate V	Per-fluorinated composite membrane	FC lifetime at 120 C increased vs Nafion®; similar conductivity
Candidate BA	Partially fluorinated composite membrane	Increased conductivity vs Nafion®
AE - type	AE: perfluorinated Design & synthesis of partially fluorinated polymers	AE: Best conductivity (73 mS/cm 25%RH), thermal & chem. stability. Challenge to insolubilize & strengthen

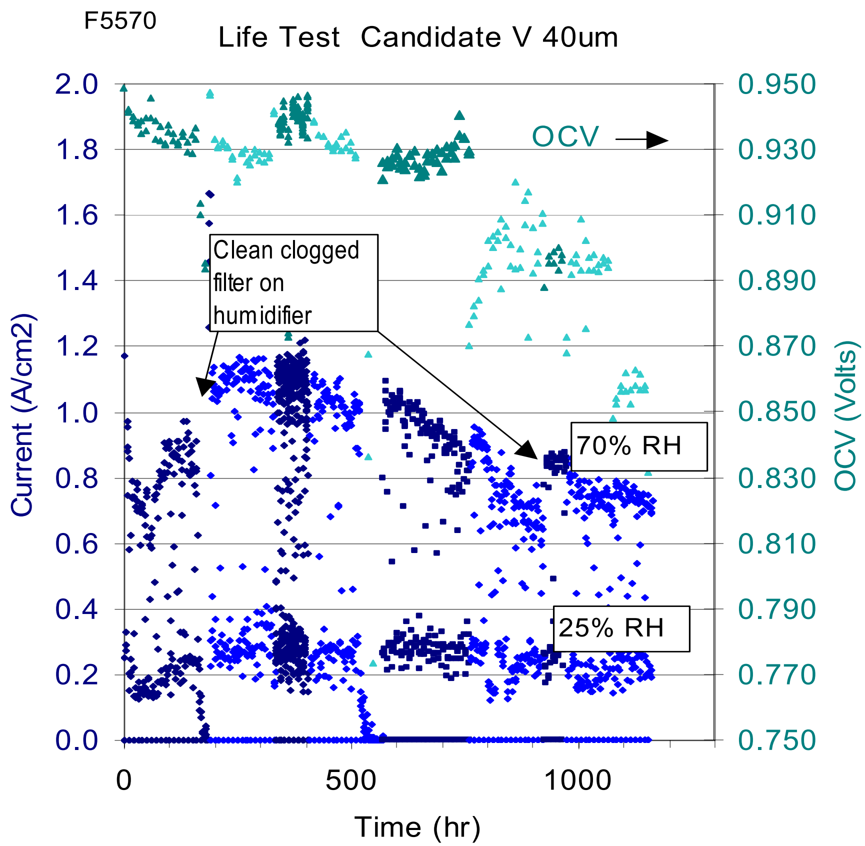
High Temperature Membrane: Focus areas for 04/05



Additional dimensions:
Chem. & oxid. stability
Low-T conductivity (new)
H_2 permeation
Cost
FC durability
….

Candidate V

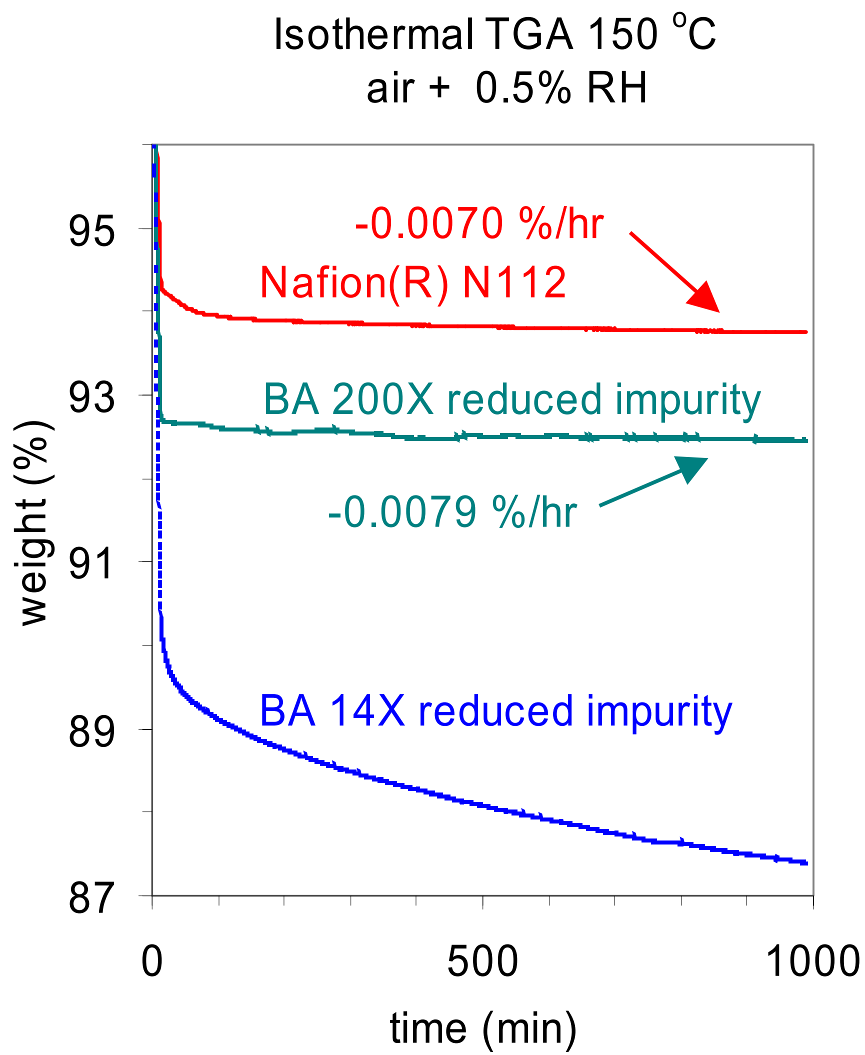
- Properties similar to Nafion®:
  - Conductivity, strength, swelling, H_2 permeation
- Properties superior to Nafion®:
  - Fenton test chemical stability
  - Lifetime in FC
- Life tests at 120 °C show cycling feeds to lower RH accelerates membrane degradation.
  - New protocol cycling to 25% RH
  - More aggressive than pervious cycling to 40% RH
  - 1000 hr life test Candidate V
- Membrane scaled-up to size for 250 cm² short stack; Delivered 17 membranes to De Nora
- Future V work: Increase strength & decrease swelling



120 °C H_2/air 21 psig 25 cm² active area
Const. flow = stoic 2/2 anode/cath. @ 1.2 A/cm²
Triple cycle: 1) 10 min OCV 70/70 %RH
2) 5hr 0.5V 70/70 %RH
3) 5hr 0.5V 25/25 %RH

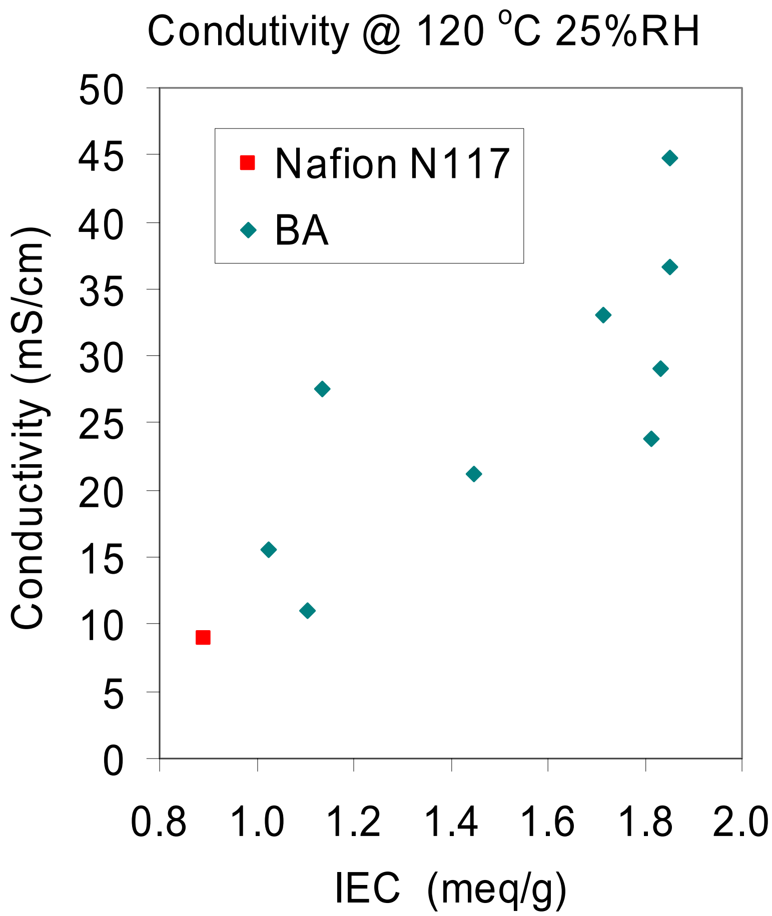
Progress BA Membrane

- Thermal stability of BA membrane significantly improved
- Thermal decomposition dominated by weak-link impurity
  - '04 Focus: Identify impurity, decrease impurity
- BA membrane with weak links decreased to 1/200 of original
  - Thermal stability similar to Nafion®



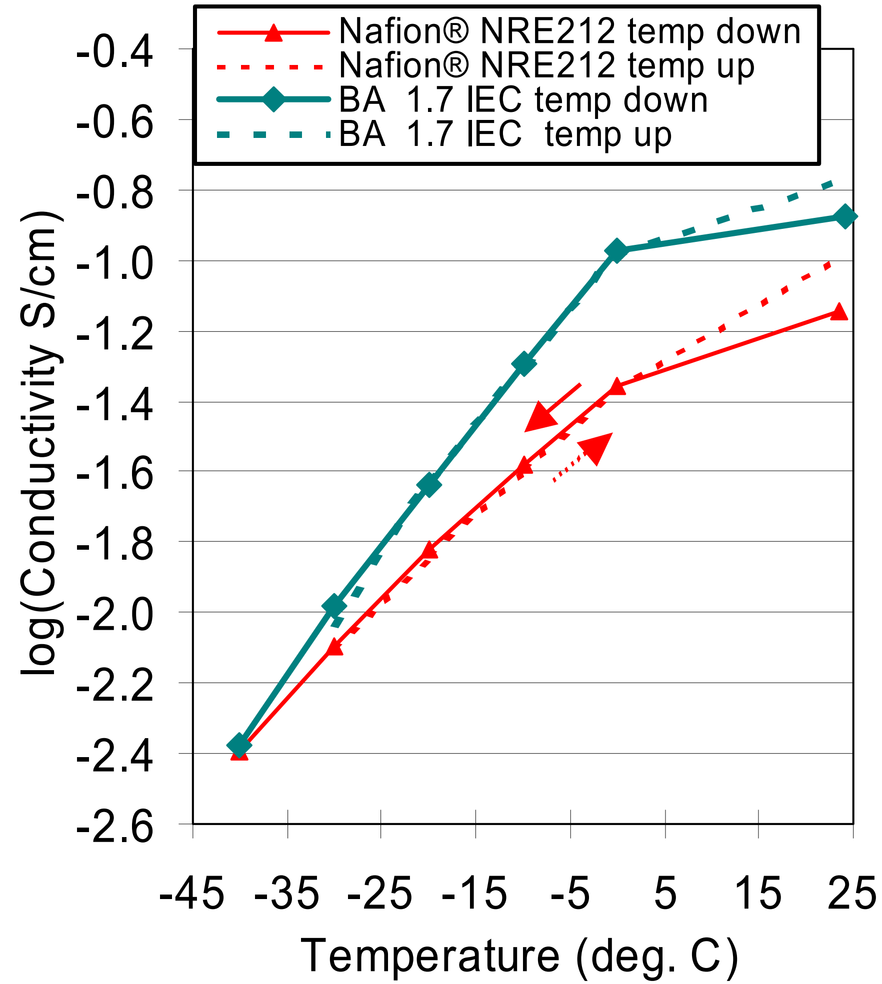
Low-RH Conductivity

- Conductivities
  - BA membranes with high IEC
  - Up to 45 mS/cm @ 120 ^{0}C, 25% RH
  - Can still be boiled in water
- Mechanical properties
  - Poor for IEC above 1.7 meq/g in current BA membranes
- IEC in the range of 1.3 to 1.6 meq/g
  - 2X to 2.5X conductivity of Nafion®
  - Maintains mechanical properties
  - Swelling 62% water uptake
    - @1.6 IEC
    - 100 ^{0}C water → 22 ^{0}C vacuum



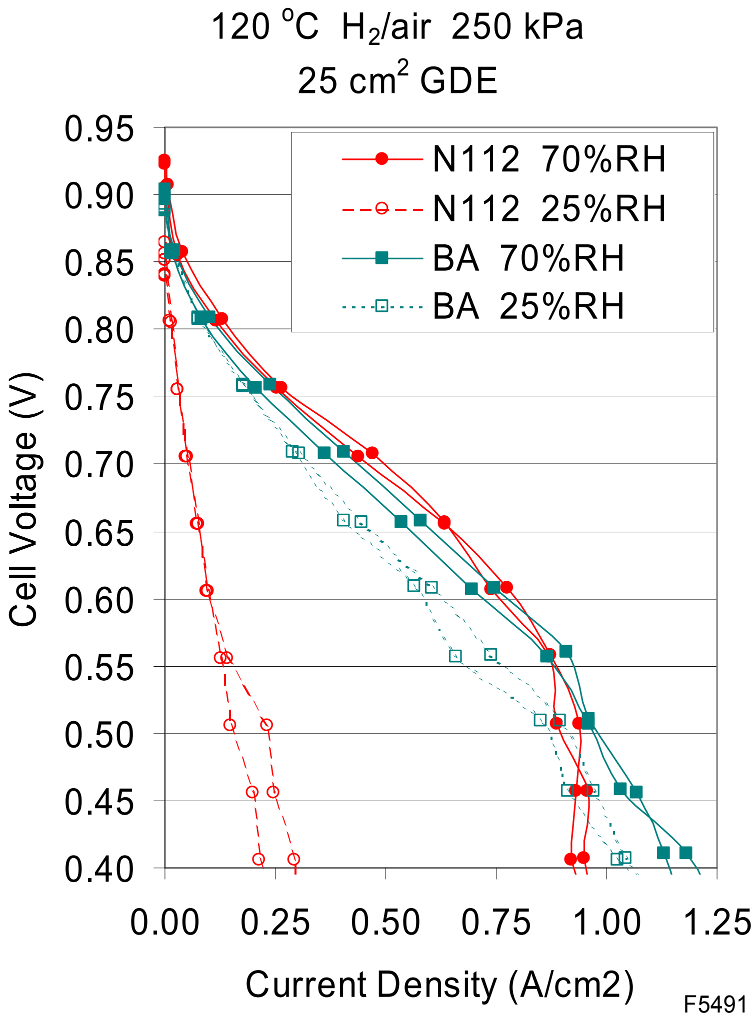
Low-Temperature Conductivity

- New measurement method gives low hysterisis between 0 ^{o}C and -40 ^{o}C
  - 4-point probe of initially-wet membrane cooled/heated in cryo GC
- BA membrane maintains significant advantage over Nafion® only to -20 ^{o}C
- At -40 ^{o}C, both membranes have similar conductivity
- Due to BA having many of the membrane properties, and good relative conductivity over a wide range of temperatures, the High Temperature Membrane Program was extended



FC Performance BA *vs* N112

- BA membrane
  - 53 μm thick
  - Similar to Nafion® N112 thickness
- Superior performance to N112 at low RH.
  - Even though electrodes are still PFSA
- Future work on BA
  - Deliver samples to De Nora
  - Reduce wrinkles & swelling
  - Increase FC durability
  - Will ultimately need also electrodes based on BA or other adv. electrolyte to deliver MEA performance



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AE Type

- Immobilization strategy identified for AE-type polymer
- New monomers and partially fluorinated copolymer synthesized - Candidate BL
  - Succeed in obtaining high MW and tough membrane
    - M_w 124,000, IV 3.5
  - Membrane is insoluble in room-temp water, soluble in hot water
    - Partially success on immobilization (make insoluble)
    - Melting of polymer, T_m 126 ^oC (76 J/g), needs to be raised
  - Monomer chemistry compromised stability & conductivity
    - Thermal stability, T_{onset} 228 ^oC (too low to be practical)
    - Conductivity 360 mS/cm @95%RH 80C, only 0.2 mS/cm @25%RH
- Future AE work: Strategies identified to increase thermal stability, melting point, and conductivity
  - Monomer syntheses begun

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- David Lilly
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Case Western Reserve U.
- Prof. Morton Litt
- Casey Check (Graduate Student)

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CASE WESTERN RESERVE UNIVERSITY

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FUEL CELLS

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UNIVERSITY

spire Biomedical

Publications and Presentations

By CWRU

- M. Bluemle, V. Gurau, J. A. Mann, T. A. Zawodzinski Jr., E. S. De Castro, Y. M. Tsou: "**Characterization of Transport Properties In Gas Diffusion Layers for PEMFCs**", *206th Meeting of Electrochem. Soc., Honolulu, Ha,* October 2-8, 2004
- M. Bluemle, V. Gurau, J. A. Mann, T. A. Zawodzinski Jr., E. S. De Castro, Y. M. Tsou: "**Permeability and Wettability Measurements for Gas Diffusion Layers for PEM Fuel Cells",** *2004 Fuel Cell Seminar. San Antonio, TX,* November 1-5, 2004

By NEU

- **'High Performance Electrode with very Low Pt Loading Prepared by Dual Ion Beam Assisted Deposition in PEM Fuel Cells'** M. S. Saha, S. Mukerjee, A. F. Gulla and R. J. Allen' Extended Abstracts for the Meeting of the Electrochemical Society to be held in Quebec, Canada, May 2005.

- **'Dual Ion Beam Assisted Deposition as a Method to Obtain Low Loading-High Performance Electrodes for Proton Exchange Membrane Fuel Cells',** A. F. Gulla, M. S. Saha, R. J. Allen and S. Mukerjee, *Electrochemical and Solid State Letters,* (Submitted)

- **'Oxygen Reduction and Transport Characteristics at a Platinum and Alternative Proton Conducting Membrane Interface'** L. Zhang, C. Ma and S. Mukerjee, *J. Electroanalytical Chemistry* 58, 273 (2004).

By E-TEK

- Hua Deng, Qingzhi Guo; Maria Cayetano; Yu-Min Tsou; Emory Sayre De Castro, "**An Investigation of Ionic Conductivity of the PEMFC by AC Impedance Spectroscopy**", *Meeting of Electrochem. Soc., Honolulu, Ha,* October 2-8, 2004
- Yu-Min Tsou, Lixin Cao, Emory De Castro "**High Performance Oxygen Reduction Catalyst For PEM and DMFC Fuel Cells"**
  Meeting of Electrochem. Soc., San Antonio, Tx May, 2004
- Emory S. De Castro, Yu-Min Tsou, Lixin Cao and Chien Hou **"Approaches for low cost components and MEAs for PEFCs: current and future directions",** Fuel Cell Seminar, San Antonio, Nov, 2004
- Emory S. De Castro, "**New Nano-Catalysts and Reduction of Component Costs for Portable Fuel Cells",** Small Fuel Cells, Arlington, Va., April 2004

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

- Testing single cells or short stacks at higher temperature with novel membrane materials
  - pinholes/cross over at the higher temperatures may lead to more catastrophic consequences

Hydrogen Safety

- Our approach to deal with this hazard is:
  - Stations in ventilated enclosures with 3 levels of hydrogen detection & interlocks.