E-TEK

DOE Cooperative Agreement

"Integrated Manufacturing for Advanced MEAs"

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

June '03 through May '04

DE-FC04-02AL67606

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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

- Develop membrane which operates at 120 °C and 25% RH
  - Water vapor pressure of 7 psi
- Membrane resistance ≤ 0.1 ohm cm^2
  - Nafion N112 has 0.7 ohm cm^2 @ 120 C, 25% RH
- Hydrolytic, oxidative, mechanical stability in FC at 120 °C
  - 5K/40K hrs auto/stationary
- No leachable components
- H_2 (or MeOH if DMFC) fuel permeation ≤ than 5 mA/cm^2
- Cost ≤ Nafion®

2003/2004 Objectives

- **1A1**: cited performance at 0.4mg/cm^2 using fg-ELAT/new catalyst
- **1A2**: ID polyelectrolyte within specifications
- **1A3**: stack baseline testing set up, prelim scale-up of 1A1 component,testing

1A3: MEA Fab for Stack Scale

- Take advances from 1A1 and/or 1A2 and integrate into pilot manufacturing
- Deliver 1-5kW stack with performance consistent with objectives of 1A1 or 1A2

Budget

Program/Co.	In $000s		
Total (4yr)	Cost Share	DOE	Total
1A1: DN	1,355	4,675	6,030
1A2: DP	1,497	4,491	5,988
1A3: DN	1,492	2,770	4,261
1A3N: NFC	1,331	2,492	3,823
total	5,675	14,428	20,102
FY03 1A1: DN	248	995	1,243
1A2: DP	316	910	1,264
1A3: DN	551	1,095	1,576
1A3N: NFC	293	532	825
total	1,408	3,532	4,909

Technical Barriers/Targets

- DOE Technical Barriers

O. Stack Material and Manufacturing Cost

P. Durability

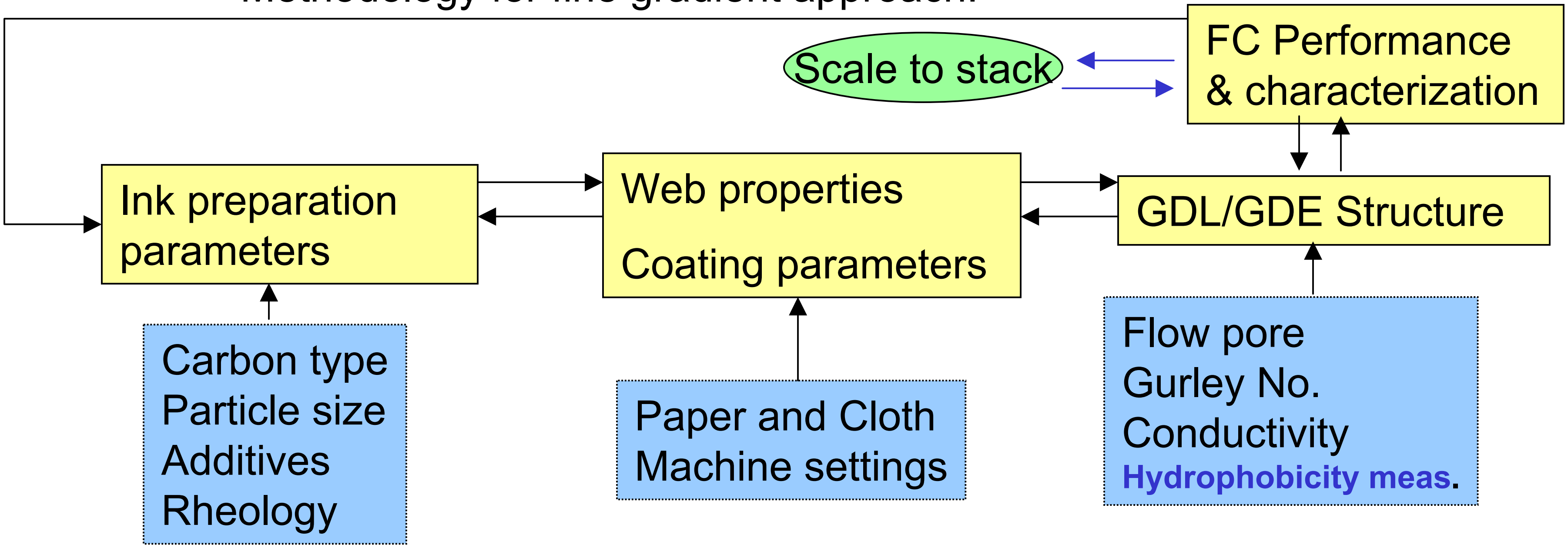
Q. Electrode Performance

R. Thermal and Water Management

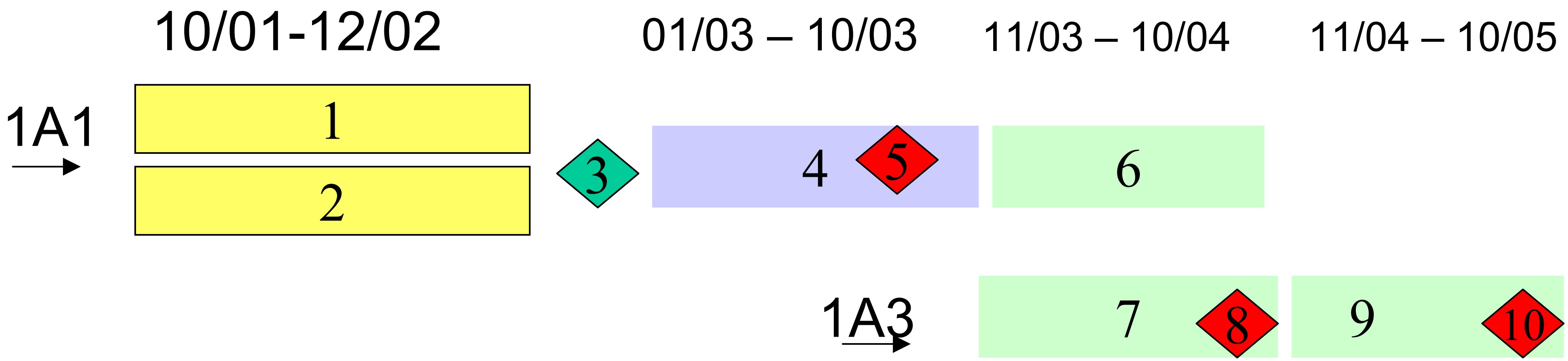
- DOE Technical Targets
- (consistent with FreedomCar)
- PM loading 2005: 0.6g/ rated kW
- PM Loading 2010: 0.2g/rated kW
- >2000 hrs life (2005)
- >5000 hrs life (2010)
- Target achieved using method amenable to Mass manufacture: <$125/kWe 2005; <$45/kWe 2010
- High Temperature Membrane
  - All of the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

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
- 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
  - In 2002/03 focus was on GDL; current focus is on electrode
  - Methodology for fine gradient approach:



Project Timeline (1A1, 1A3)



1A1

1. Identify Catalyst Prep/approach that is a pathway for highly active Pt or alloy
2. Demonstrate proof-of-principle of fine gradient ELAT
3. Check-point: show approach capable of decreasing PM load and/or incr. power
4. Combine catalyst and fg-ELAT advances into MEA; develop new structures/catalysts
5. Go/no go: interim goal of 0.4mg/cm^2 tot PM, 0.85V @ 0.1A/cm^2, 0.8V @ 0.4A/cm^2
6. Transfer methods to MEA fabrication team/refine approach to reduce PM to 0.3mg/cm^2

1A3

7. Scale 1A1 results to stack size
8. Go/no go: show interim goal at stack scale
9. Develop MEA fabrication methods: compare ink to ion beam methods. Durability tests
10. Achieve 0.3mg/cm^2 tot PM/power at stack scale: deliver short-stack with best of low T/Hi T advances made with Pilot Process

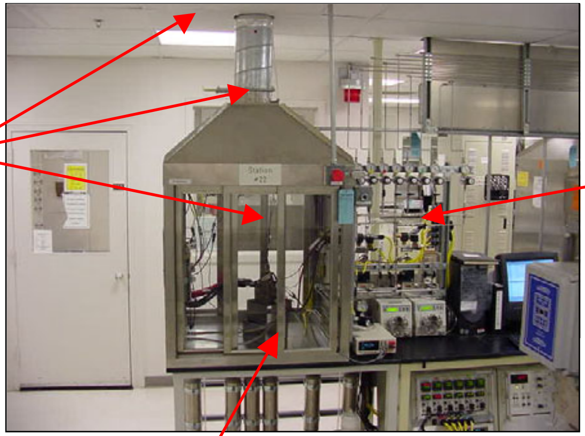
Project Safety

1A1 - Adv. Cathode

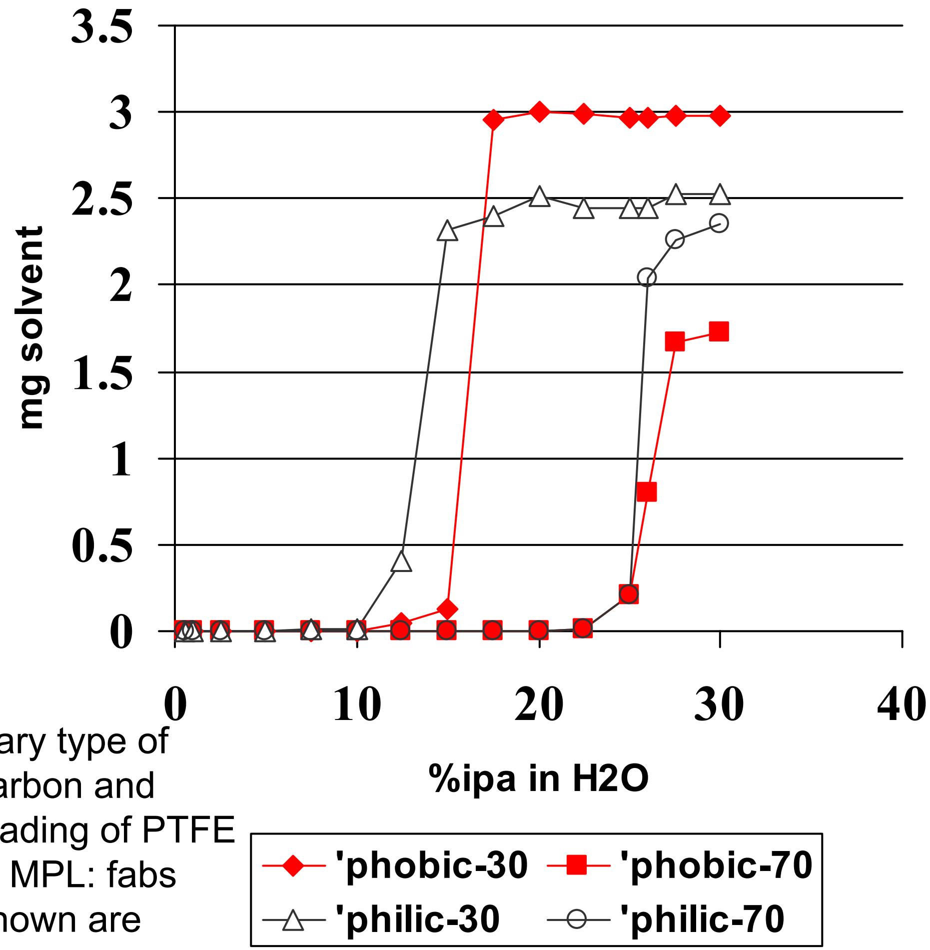
- Management of Change: New Catalyst Prep/reagents
  - Although catalyst activity is key design criteria, lower cost to convert from Pt to Pt/C or alloy is important
  - One route to lower cost is lower environmental impact
  - Lower environmental impact = greater level of safety from reduction of chemical hazards and procedures
- Management of Change: New Catalyst Prep/Activity
  - New highly active catalysts sometimes burst into flame upon first exposure to air
  - Modifications taken prior to scale-up; detailed examination of processes that trigger combustion; modifications of those processes

1A2 - HT Memb.

- Process Safety Management program emphasizes analysis of hazards for new or changed procedures and rigorous incident investigations.
- HT memb. synthesis
  - One incident involved bromine leaking from a plastic bottle - use of incompatible container material.
- HT Fuel Cell testing
  - Stations in ventilated enclosures with 3 levels of hydrogen detection & interlocks.
  - No hydrogen fires to date.



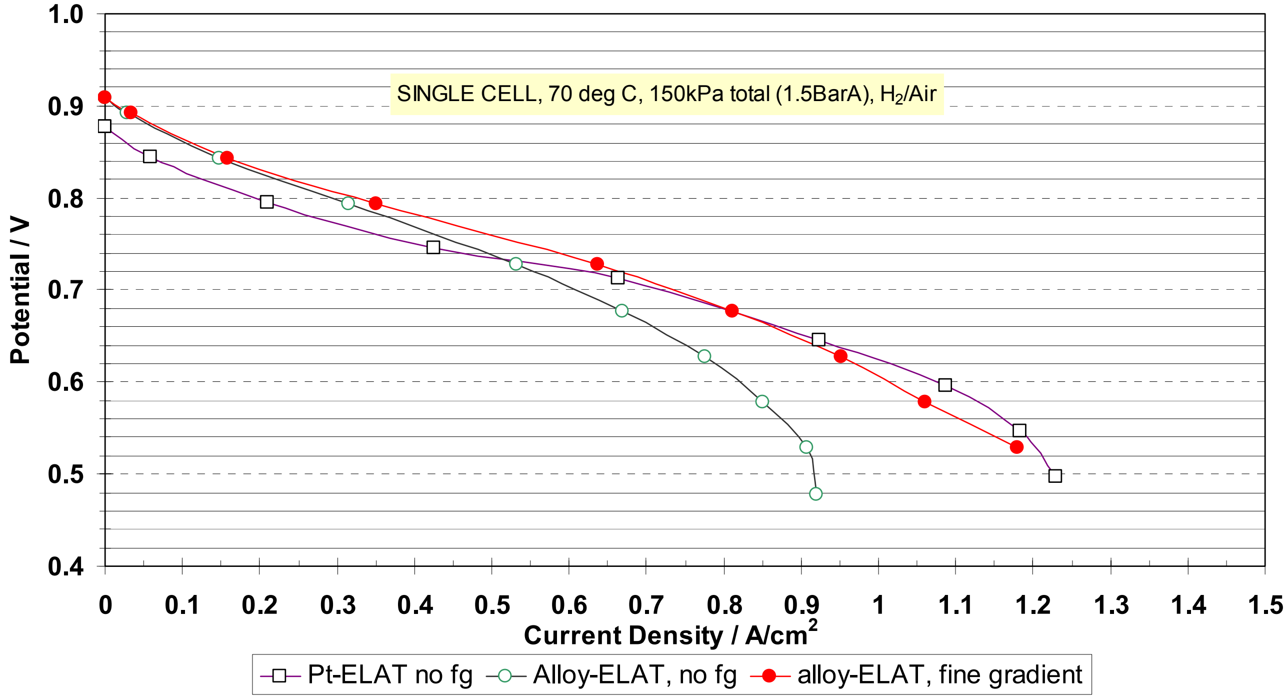
Tools to help build the fine gradient: Method to measure Hydrophobicity - "Cobb Titration" being developed with CWRU



Vary type of carbon and loading of PTFE in MPL: fabs shown are homogenous – no gradients

- Last year discussed CFP for pore-size distribution/gradient construction
- Cobb titration derived from methods for developing absorptive media: measure wt. of mixed solvent absorbed internally
- Provides relative, qualitative data on hydrophobicity and porosity
- *Unable to differentiate small differences*
- CWRU will investigate more thoroughly as well as evaluate two other potential methods

Development of fg-ELAT



Summary: extending "fg" approach to electrode

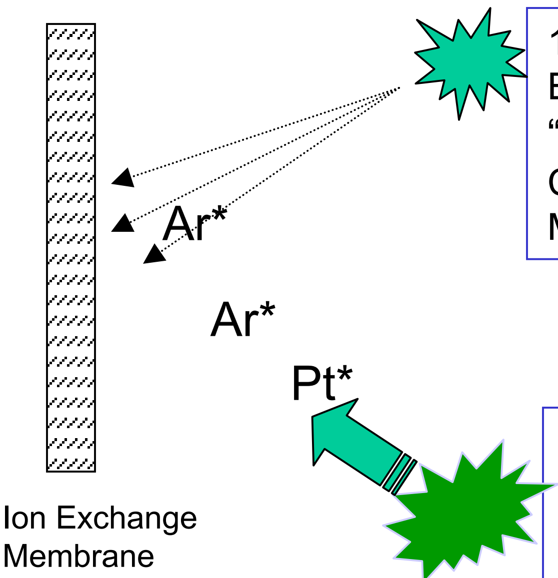
- Compares standard gradient Pt, standard gradient alloy (Pt:Cr), and a tuned fg-ELAT alloy (Pr:Cr)
- Pt Standard ELAT: good gas transport, limited proton transport; Alloy-ELAT: mass transport limitations, even at lower currents; alloy fg-ELAT: balance of transport mechanisms
- Pt and alloy ELAT all machine fab; alloy fg-ELAT is partially machine fab
- All fabrications ~0.5mg/cm^2 total metal on cathode

Building the fg-ELAT:

- Extensive characterization of ionomer dispersions prior to use
- Controlling the final ionomer structure with process variables
- Extensive porosity characterization correlated with EIS
- Qualitative hydrophobicity measurements
- Local environment of alloy must be different than Pt

Trend confirmed on NFC stack: alloy "super scales" but not over whole curve

IBAD :background



1) Low energy
E-beam
“atomically”
Cleans or roughens
Membrane surface(100-400ev)

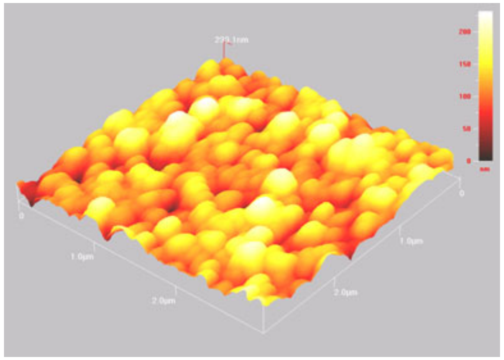
2) Higher energy
E-beam moves
ionized Pt to
membrane
substrate: implants Pt
(1000-2000ev)

Conductivity, S/cm at RT

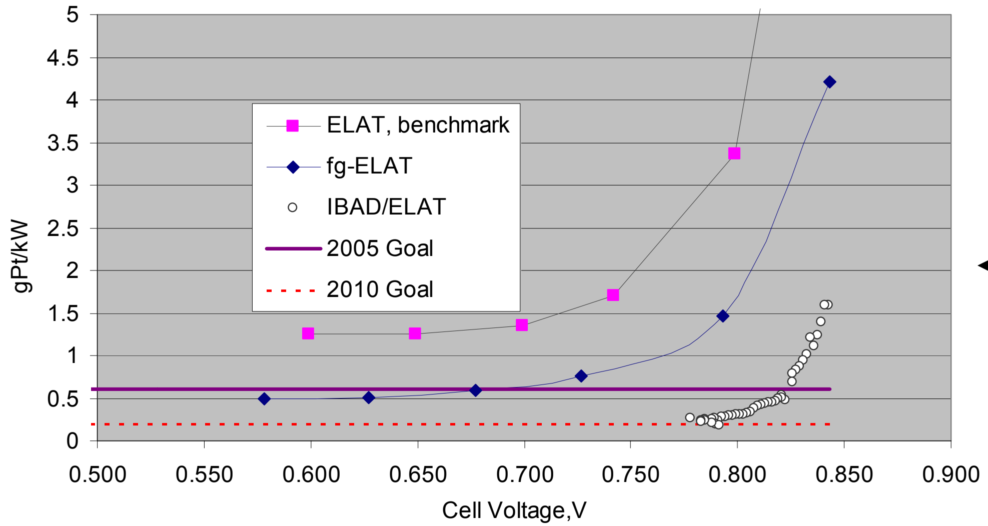
Low E-beam power	Development Membrane	Nafion ® 112
0X	**0.217**	**0.167**
1X	0.211	0.164
3X	0.208	0.161
6X	**0.192**	**0.159**

1) Membrane temperature remains 35-65 deg C
2) Have shown very stable coatings: 4% loss of Pt on Nafion 115 in hot conc. HCl vs. 92% loss of Pt from 20% Pt/c
3) Key objective for Cathode is to create 3-D depositions

Use AFM to measure surface roughness:
250Å Pt on Nafion® 112



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



Total Pt loading

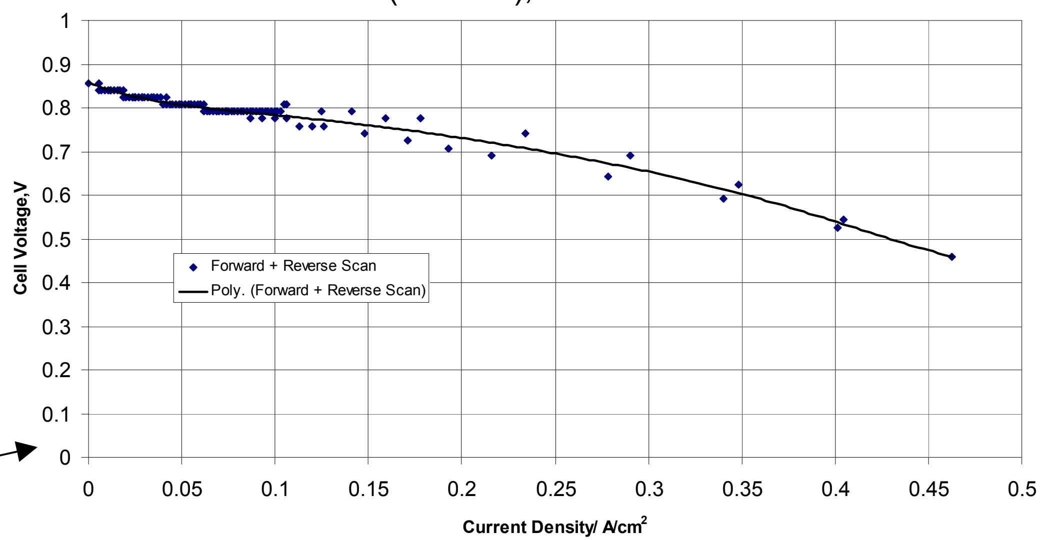
ELAT benchmark: 1mg/cm²

fg-ELAT: 0.39mg/cm²

IBAD/ELAT: 0.12mg/cm²

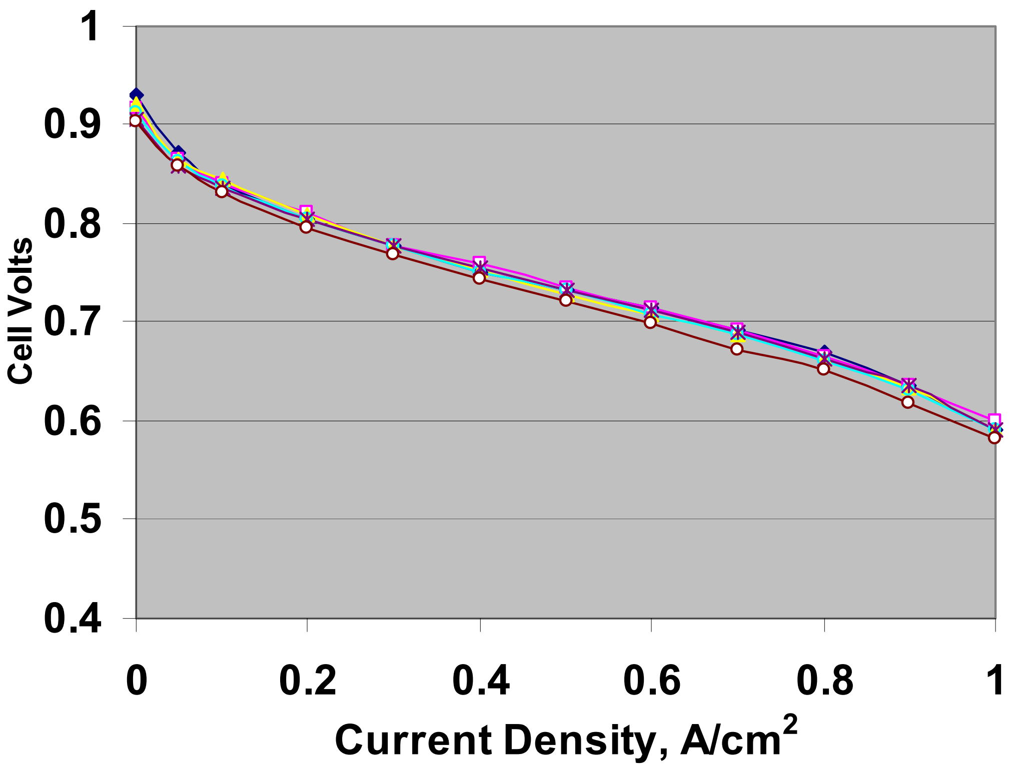
gPt/kW at 80°C, 250kAa total (2.5BarA), H_2/Air

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



While the power density is low, 0.5V at 0.4A/cm² with ultra-low loaded cathode represents a significant advance for ’03/’04: team barely realized a voltage at 0.4A/cm² at program beginning

Scale-up to Stack: Order of magnitude reduction in anode load confirmed at NFC (~10 cell short stack, 0.5 to 0.05mg Pt/cm^2)



- Using structures derived from fine gradient experience on cathode, developed low-loading anode
- Assembly is a gas diffusion electrode laminated to Nafion® 112: catalyst is on GDL
- Ahead of plan for 1A3: demonstration of capabilities for machine-based coating
- Loading confirmed with XRF as well as mass balance during coating process

Open markers: three machine-made anodes (0.05 mg Pt/cm^2)
Solid markers: three machine-made 30% Pt/C (0.5 mg/cm^2)
All as anodes in Nuvera 225 cm^2 Cell Stack 150kPa total (1.5 barA), 70^o C (one cell 20mV worse)

Accomplishments/Progress

- *Current Best: 0.78V at 0.4A/cm^2, 0.85V at 0.1A/cm^2, 0.39mg/cm2 total PM loading (have achieved power target with 0.5mg/cm^2)*
- *Built up significant understanding for how to build fg-ELAT for alloy and realizing the potential of alloys at higher currents*
- *Program 1A3 ahead of plan: 50 ug/cm^2 Pt at anode shown at stack scale: trends for fg-ELAT cathodes reproduced at stack scale*
- *Starting to create "3-d" structures via IBAD for cathodes: 60 ug/cm^2 cathode, 120ug/cm^2 total PM loading very encouraging*
- *Baseline model for fg-ELAT established at CWRU – starting verification phase*

Responses to Reviewers

- Need to understand catalyst/GDL interactions better
  - *This became a focus area for this reporting period: the ability to tune the fg-ELAT architecture for the alloy demonstrated an increased understanding of these interactions*
- fg-ELAT: current methodology is empirical, need better basis to guide structure designs
  - *Started a subcontract with CWRU to model fg-ELAT whereby the output of model is specific measurable structural properties to guide construction efforts. We anticipate a benefit of this approach is further reduction of metal loading in a refined fg-ELAT structure*
- Need more information on possible advancements in Catalyst/alloy work
  - *While we have significantly advanced Pt/c (detailed '03) based on the structure-function approach, improvements made to the alloys were not realized in FC testing until this reporting period. We now anticipate additional advancements for the alloys based on an improved understanding of the electrode structure needed for the alloys*

Interactions and Collaborations: Technology Transfer

Technology Transfer/Lessons Learned

- Goal of catalyst program is to improve activity and lower cost of transformation: Pt/c and alloys
  - Lessons learned in identifying processes that have lowered cost/improved activity have been transferred to Pt/C catalyst line
  - Have been able to keep price increases moderately low while Pt spot metal prices have increased almost 40% since start of work
- One challenge of "fg-ELAT" is producing detailed microporous layers with very low variations.
  - "Methods learned" have been applied to increasing yield during traditional machine ELAT production
  - Result is decrease of price for GDL/GDE products and higher quality

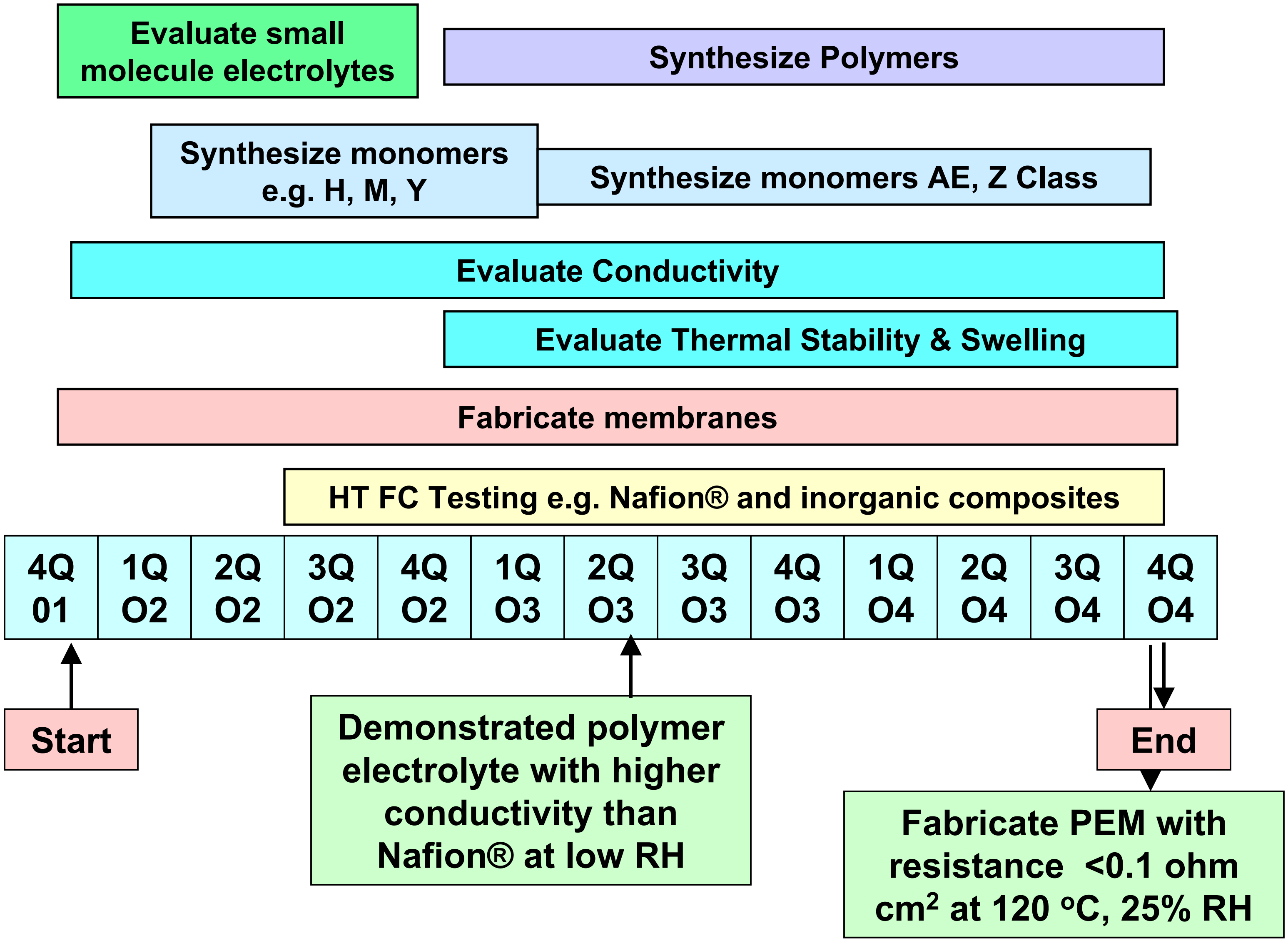
Publications

- 'Oxygen Reduction Kinetics in Low and Medium Temperature Acid Environment: Correlation of Water Activation and Surface Properties in Supported Pt and Pt Alloy Electrocatalysts' V. Srininvasamurthi, R. C. Urian and S. Mukerjee, submitted to *J. Phys. Chem.,* (February, 2004) **[Accepted**]
- 'Oxygen Reduction and Transport Characteristics at a Platinum and alternative Proton Conducting Membrane Interface' L. Zhang, C. Ma and S. Mukerjee, *J. Electroanalytical Chemistry* (**In Press**)
- 'In situ determination of O(H) adsorption sites on Pt based alloy electrodes using X-ray Absorption Spectroscopy' M. Teliska, D. Ramaker, V. Srinivasamurthi and S. Mukerjee, submitted to *J. Phys. Chem.,* (**submitted March 2004**).
- 'Effect of Water Activation on the Activation Energy of Oxygen Reduction in a Polymer Electrolyte Interface', J. Jerome, A. Anderson, V. Srinivasamurthi and S. Mukerjee, Manuscript under preparation for submission to *J. Phys. Chem.*
- 'Oxygen Reduction and Structure Related Parameters for Supported Catalysts', **S. Mukerjee** and S, Srinivasan, *Handbook of Fuel Cells: Fundamentals, Technology and Applications, Vol. 2: Electrocatalysis*, Edited by W. Vielstich, H. A. Gasteiger and A. Lamm, John Wiley and Sons (2003).
- 'In situ X-Ray Absorption Spectroscopy of Carbon Supported Pt and Pt Alloy Electrocatalysts: Correlation of Electrocatalytic Activity with Particle Size and Alloying', **S. Mukerjee**, *Advanced Nanoparticles for Fuel Cells and Electrocatalysis*, Edited by A. Weickowski, E. Savinova, and C. G. Vayenas, Marcel Dekker, (2003).

Going Forward

- **Reduce PM loading** through "ink" based methods and fg-ELAT approach
  - Use CWRU/CAPI modeling to guide structure design
  - Follow structural refinements with quantitative methods to measure hydrophobicity (will pursue with CWRU)
- **Catalyst**
  - Scale up prep for improved alloys (binary)
  - Modify alloys to assess impact of catalyst hydrophilicity
    - Modifications are designed to tune catalyst to the structural needs of the electrode – not to inherently increase kinetic activity
      - Ternary catalyst and/or alternative support
- **Scale up** performance of fg-ELAT cathode to NFC stack
  - Part of this effort is translating hand-fab steps to machine process
- **Develop IBAD**
  - Focus on effects to further 3-D depositions on cathode as well as understanding for the conditions to activate catalyst depositions
  - Develop fg-ELAT architecture matched to IBAD/catalyst interface
  - Develop cathode alloys with IBAD
  - Develop methods to verify Pt loading
- **Durability**
  - Having identified successful "fg" structures and new preparations for alloy catalysts, durability program has just begun late Q1 2004 with NFC partner

Program 1A2: High Temperature Membrane Approach & Timeline



Focus on Two Classes for HT Memb.

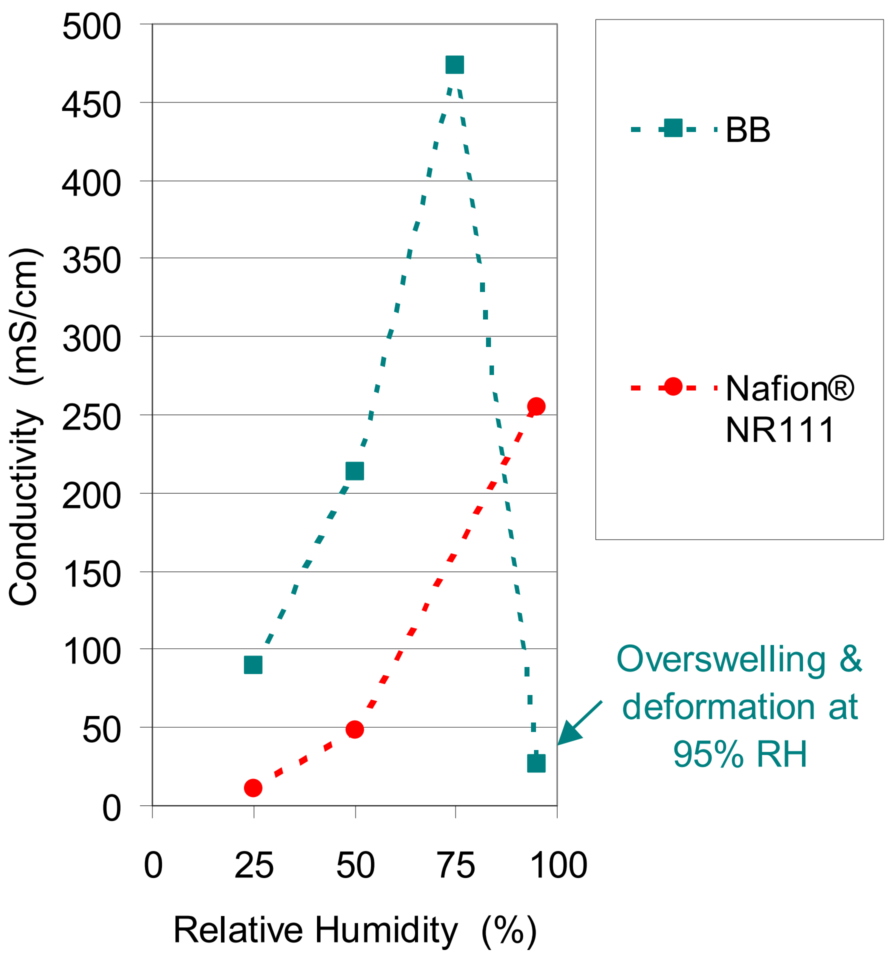
Class	Monomer or Polymer Memb.	Composite or Graft Memb.
AE	AE	BC,BD*,BE*
	AK	
Z	Z	AO
	AW	BG
	AY	AZ
	AX	BA
AF	AF	
BB	BB	
*not made yet, synthesis active		

- Four classes of polymer electrolytes have been synthesized having significantly higher conductivity than Nafion® at 25% RH.
- Due to thermal instability of AF and BB, most of the **focus** last year has been on the **AE and Z class** ionomers.
- This small group still has some chemical diversity.
  - Different acid functionalities.
  - Some are aromatic.
  - Some are perfluorinated.
  - Some are heterocyclic.

A Fourth Conductive Polymer Class

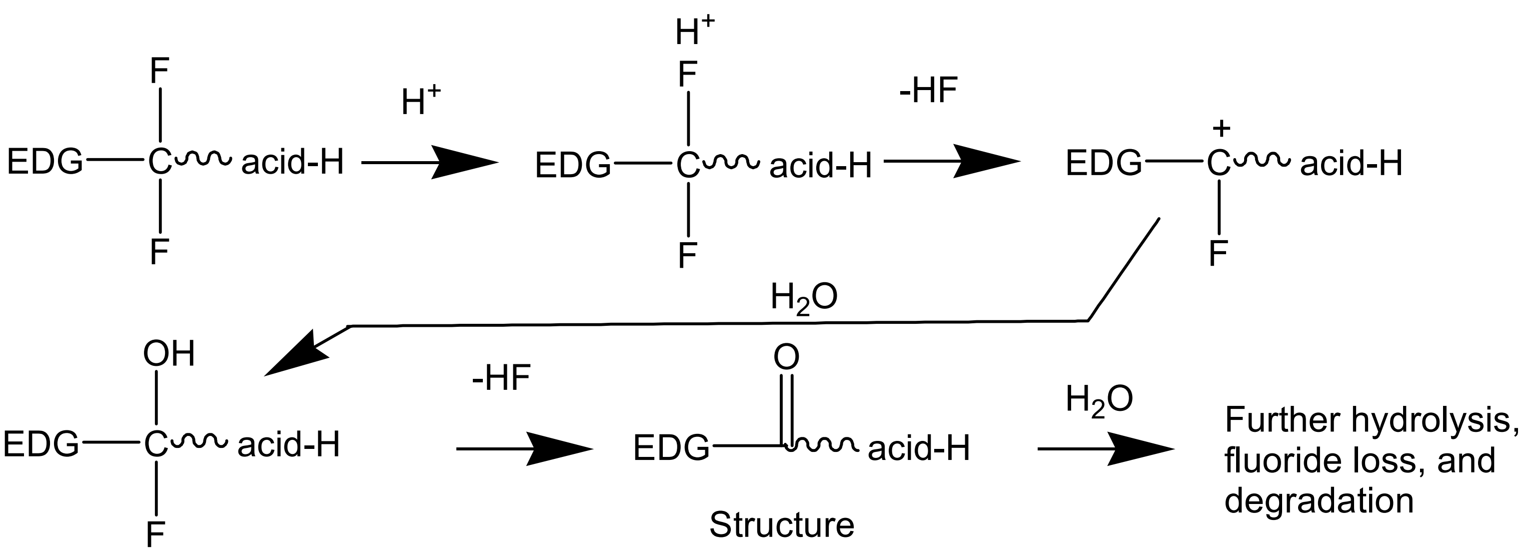
- Candidate BB is a high-MW film-forming fluorinated copolymer containing a new ionic monomer.
  - Had not been previously investigated in our project.
- Conductivity at low RH is high.
  - Confirms our optimism that it is possible to achieve conductivity significantly higher than Nafion®.
- Excessive water swelling and poor strength.
- Thermal stability is measured as only 14 hr @120 C.
  - **Do not see a path to increase thermal stability of this class - no further effort is planned.**

Conductivity 120 °C; Avg of two labs



Progress on Z-Class Ionomers

- Monomer Z scaled up to 350 grams
- AO was a composite membrane made using Z and a second high-strength polymer
  - High conductivity, reasonable swelling, low-thermal stability
- Determined the cause for the thermal instability of Z
  - Monomer Z had an electron donating group (EDG)



Structure confirmed by NMR of thermally-degraded model compound

New Z-Class Ionomers

- Decomposition work led to design & synthesis of three new co-monomers
  - AW, AX, AY All change the EDG to decrease the donation.
  - AY is an intermediate to AX; it is also a monomer in its own right.
  - Thermal stability of the original Z-monomer can be greatly increased!
  - The method of forming the composite membrane has allowed for only 66% AX so far. Believe better conductivity might be obtained.
- We are very excited about the prospects for achieving both conductivity and thermal stability with membranes based on AX.

Monomer	Quantity synthesized to date	Thermal Stability of Model Compounds in Acid Form, Vacuum Oven/NMR (Aggressive Low RH)	Thermal Stability, Upper Limit to Life of Composite Memb., est @ 120C kinetic TGA	Conductivity Composite Memb 25% RH (mS/cm)
Z	**350 g**	Starts to decompose 80 C Rapid decomposition 120 C	**5 hr**	**17-31**
AW	**150 g**	Stable 80 C Rapid decomposition 220 C	**60,000 hr**	**0.4**
AX	**30 g**	**Stable 120 C** **Unchanged 24 hr 220 C**		**14 to date**
AY	**300 g**			

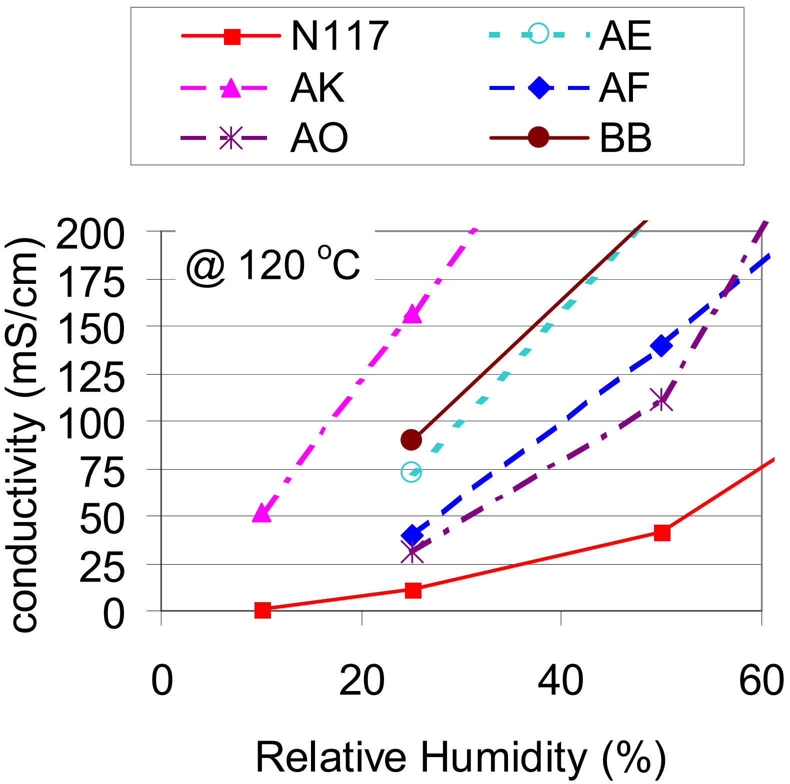
Status of AE

- AE polymer electrolyte:
  - Conductivity 70 mS/cm @ 120 C, 25%RH.
  - Thermal stability higher than Nafion®.
  - Excessive water swell and poor strength.
  - AE monomer has been synthesized in several 50 to 100 g batches.
- Approaches to reduce swelling and increase strength being investigated are composite membranes, polymerization, grafting, and crosslinking.
  - Significant effort was needed to identify and develop synthetic protocols for each of these four methods.
- Satisfactory results have not yet been obtained.
  - Both the polymerization chemistry and the immobilization chemistry are more difficult than with Z-type.
- We continue to work on this because AE has a better combination of conductivity and thermal stability than any other candidate we have tested.

Summary of Progress

Polymer Electrolyte	Conductivity @ 120 C, 25%RH (mS/cm)	Upper Life Limit Kinetic TGA @ 120C (khr)	Reasonable Mechanical & Swelling
Nafion 1100EW benchmark	**8**	**120**	**Yes**
AM = p-PSEPVE	27	130	No
AE	73	>1,000	No
AK	68-156	0.005	No
AO	17-31	0.005	Yes
BA	14 to date	?	Yes
AF	40	0.039	No
BB	90	0.014	No

Kinetic TGA: Flynn, J.H. and L.A. Wall, Polymer Letters, 1966. **4**: p. 323-328.



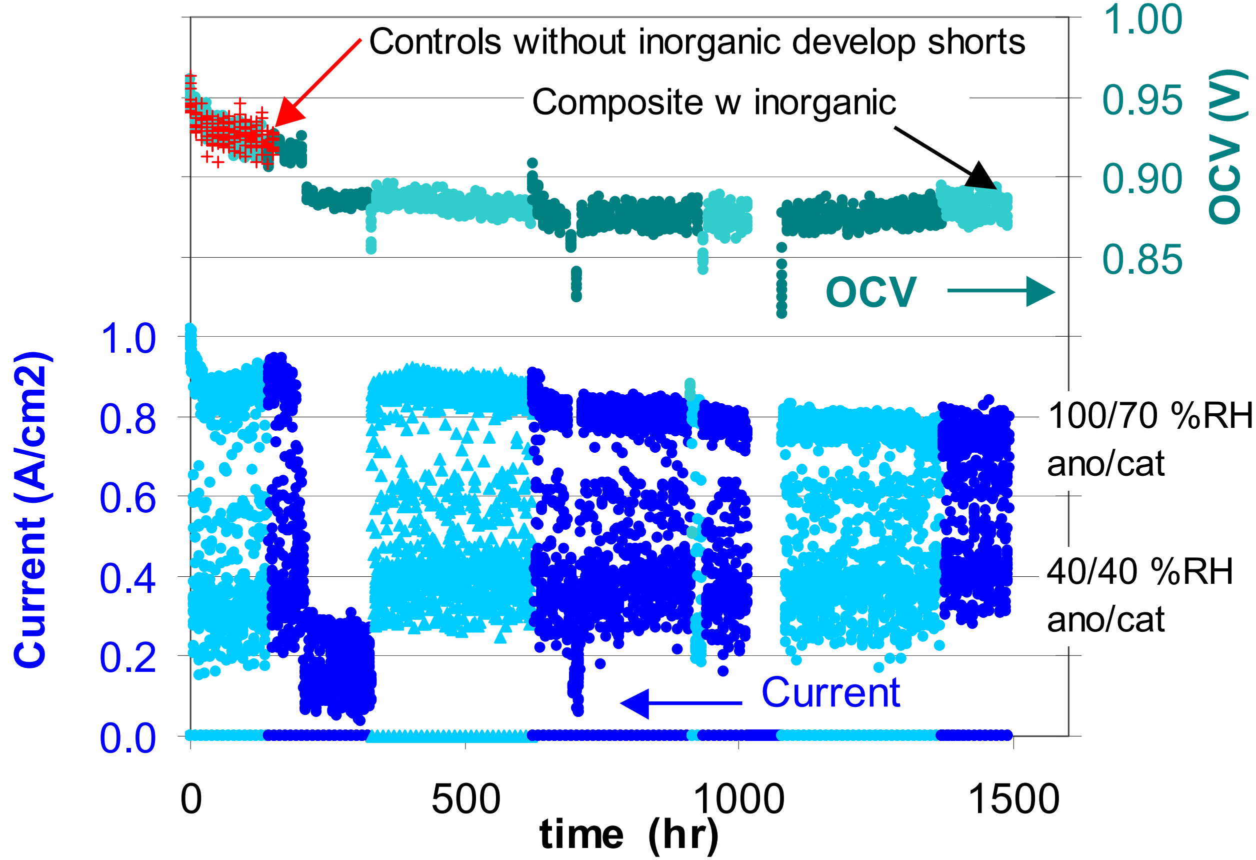
- No candidate yet meets all three requirements.
  - Several candidates achieve two of these

Reviewers Comment

- 2003: “Drop the composite approaches (inorganic fillers) because such systems (under load cycling) are prone to defect formation.”
- Response: *Admittedly, we have not obtained significantly higher conductivity at low RH with PFSA/inorganic. However, we find for one candidate evidence of increased durability under load cycling. We hope to be able to apply durability learnings to the new polymer electrolytes as they mature, and propose to pursue these tasks in parallel given the time constraint.*

GDE = HT 140E-W ELAT®
120 ^{o}C H_2/air 30 psig
25 cm^2 active area
Const. flow = stoic of 2/2
anode/cath. @ 1.2 A/cm^2
Triple cycle:
10 min OCV 70/70 %RH
0.5V 5hr 100/70 %RH
0.5V 5hr 40/40 %RH

Changes in symbol shading indicated station restarts after various hardware/software failures. Low current at 208-339 hr is from humidifier failure.



Interactions & Patents

- Sub-Sub-Contract to Case Western Reserve U. - Prof. Morton Litt
  - Synthesis has begun of hydrocarbon membranes with "uncollapsible hydrophilic domains" - retain water at low RH.
  - New approaches may avoid stability problems associated with previous versions.
- Significant interactions with a number of stationary and transportation FC developers. They provide input on membrane needs and in some cases provide feedback on performance of prototype membranes.
- 5 patent applications filed on polymer electrolytes; 3 additional in preparation.

Path Forward

- Continue to work to achieve simultaneously three properties of conductivity, thermal stability, swelling.
- AE Class
  - Develop method for immobilize AE to make membranes BD and/or BE.
- Z Class
  - Prove thermal stability of AX ionomer.
  - Work to increase the composite membranes to 70-80% AX or AY ionomer.
  - Develop methods of post-polymerization converting AY ionomers to AX ionomers.
  - If current approach fails, investigate composites with e-PTFE.
- If single-cell durability testing warrants, provide sufficient Nafion®/inorganic composite type to Nuvera for short-stack testing.

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