E-TEK

DOE Cooperative Agreement

"Integrated Manufacturing for Advanced MEAs"

Topics 1.A.1 and 1.A.2

January '02 through May '03

DE-FC04-02AL67606

National Laboratory Review

Lawrence Berkeley National Laboratories

May 2003

DUPONT The miracles of science™

Northeastern UNIVERSITY

DE NORA NORTH AMERICA, Inc.
GRUPPO DE NORA
Durantes Vincunt

Objectives

1A1

- 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

- 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/cm2
- Cost ≤ Nafion®

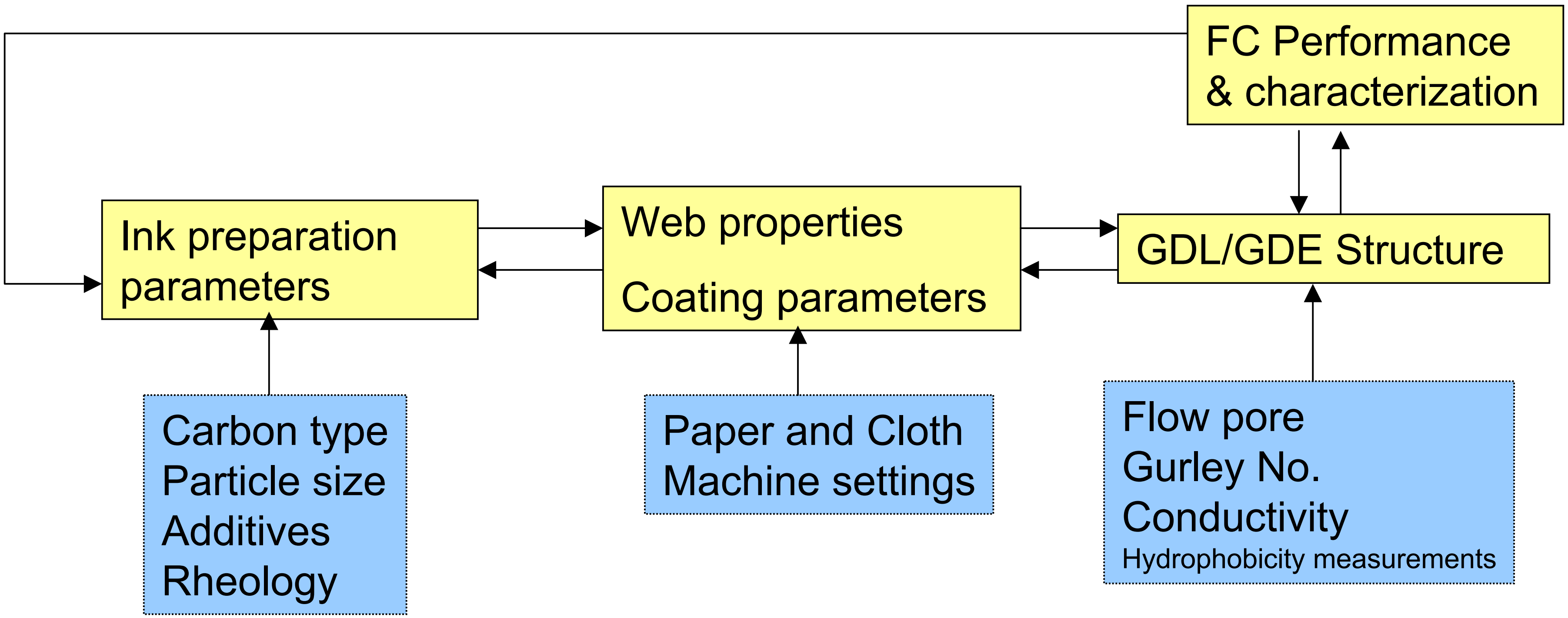
“Success” in 1A1 or 1A2 leads to 1A3: Advanced MEA Fabrication, and further reduction of metal load

Approach: Catalyst

- Technical Approach is to explore new methods of catalyst formation, identify those methods capable of controlling relative crystal face population, and using that method to create an abundance of the desired faces
- We will explore four new areas for manipulating catalyst formation chemistry : “organic precursors”, “controlled environment,” “low temperature formation,” “new carbon supports”: with NU evaluate structure with Reitveld analysis of XRD, XAFS, and XANES
- In general, the goal is to create catalysts that combine the high specific activity of highly loaded preparations (~40-50% Pt/C) with the very high surface area of low loaded preparations (~10% Pt/C).

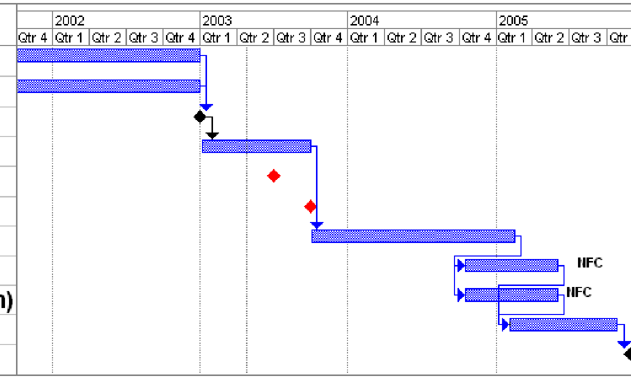
Approach: Fine Gradient ELAT®

- Develop a new ELAT gas diffusion structure based on fine gradients of hydrophobicity and porosity using developmental coating machine
- Methodology:



Project Timeline:
Milestones and Success Criteria

ID	Task Name
1	Identify catalyst prep. approach that is a pathway for highly active Pt or alloy
2	demonstrate proof of principle for the fine gradient ELAT® ("fg-ELAT")
3	Criteria: show FC Single Cell incr. power and/or decr. PM over standard
4	Create a fg-ELAT/ catalyst system that is a pathway to interim Program targets
5	Go/No Go:cat./ fg-ELAT that approaches DOE Power/PM targets-0.4mg PM/sq cm
6	Go/No Go: Scale Best System to 225 cm^2 and validate performance at NFC
7	Program (1A3):MEA Fab. with PM loading decrease (to 0.3mg/sq cm total PM)
8	Scale-up/Validate: MEA fg-ELAT/catalyst(>4 stack elements,225 sq cm)
9	Scale-up/Validate: MEA Hi Temp. fg-ELAT/membrane (>4 stack elements,225 sq cm)
10	Pilot manuf./optimized components either <100 deg C and/or >120 deg C
11	*Deliverable: Stack(s) w Performance validated 1-10KW (Hi T and/or Cathode)*



Key Success Criteria is short stack verification of improvements by team partner Nuvera Fuel Cell

Final Deliverable (1A3): 1-10KW NFC Stack with successful MEA From either Program 1A1 or 1A2

New Method for Pt/C

Comparison *Crystallite Size* (XRD, nm) on Vulcan XC-72

%Pt/C	Stnd	New
10	2.0	-
20	2.5	2.2
30	3.2	2.5
40	3.9	2.8
60	8.8	3.7
80	25	4.9

Comparison *ECSA* (CO stripping, m^2/g)

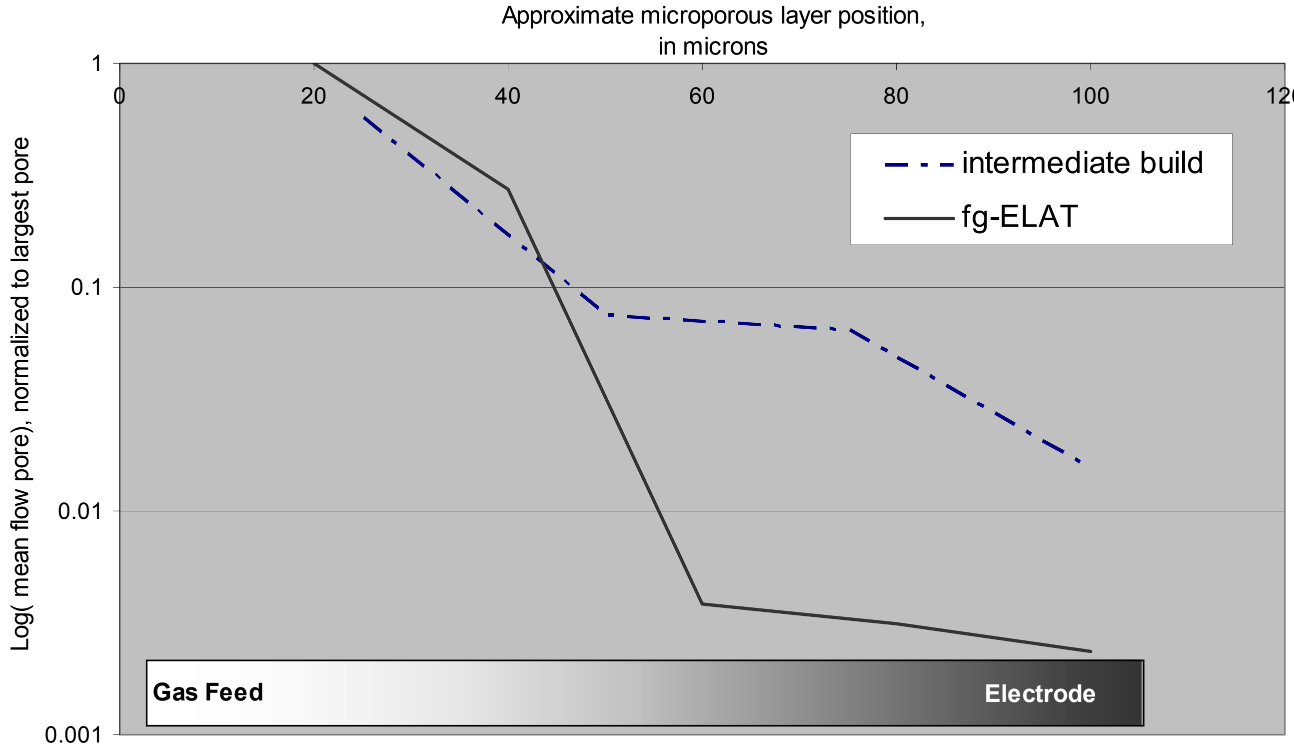
%Pt/C	Stnd	New
30	32	53
40	-	39
60	-	28
60*	-	52

*(new carbon)

- New chemistry/ reduced sulfur levels – no Cl^-
- Lower Processing Costs
- Have scaled 30%Pt/C to 2Kg batch

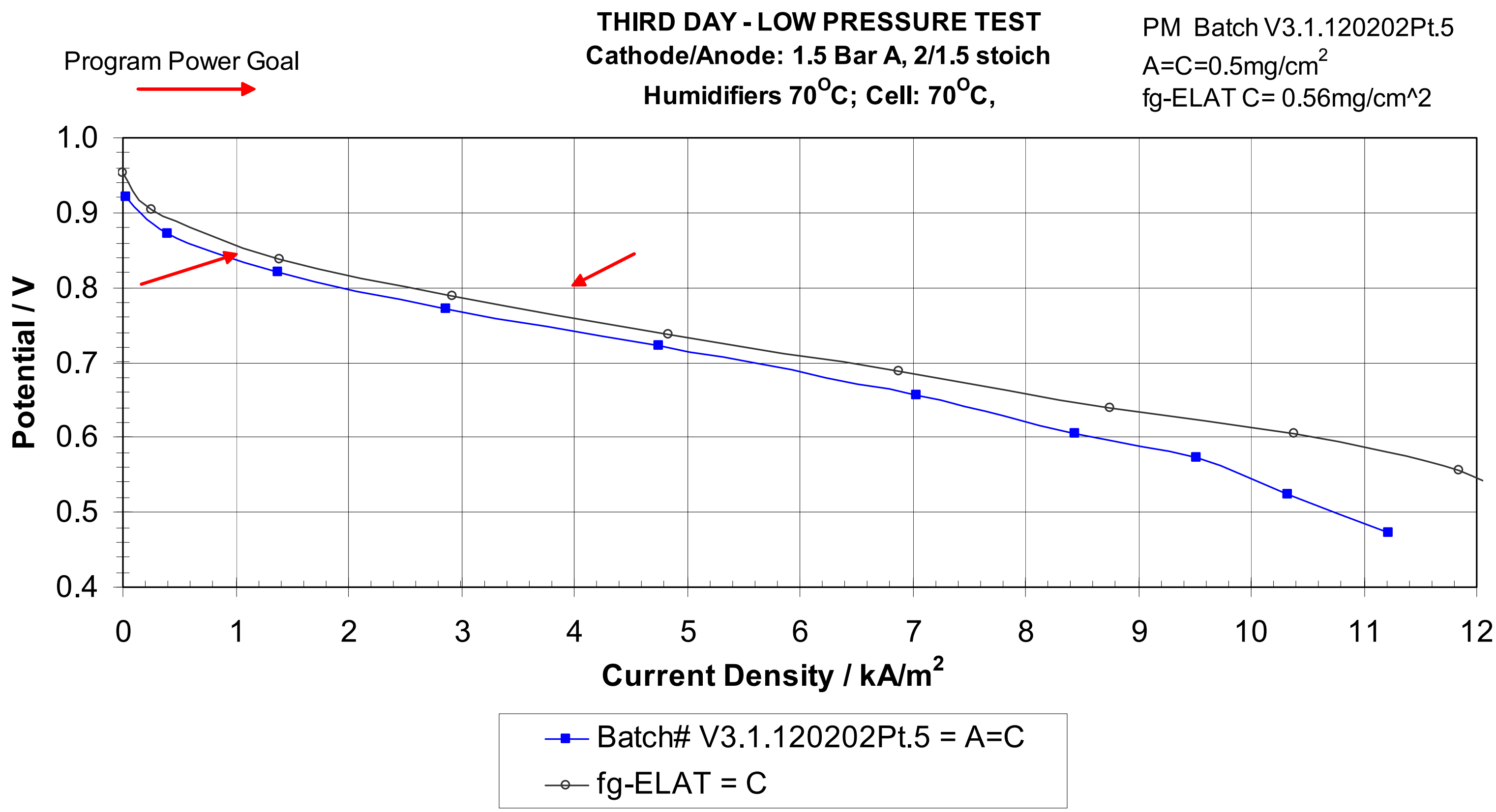
Porosity Gradient: Mean Flow Pore Comparison

Capillary Flow Porometry



The equivalent plot for hydrophobicity is missing

fg-ELAT: Proof-of-Concept



Impact of Web and More Facile Control of Gradient

Platinum Power Density

	Cathode	Cathode	Total PM	Total PM
	$1kA/m^2$	$4kA/m^2$	2005	2010
Cloth Web	g/Kw	g/Kw	g/Kw	g/Kw
Standard (st. Pt/C)	6.40	1.80	0.6	0.2
Type 1 (st. Pt/C)	3.73	1.29		
Type 2 (new Pt/C)	3.11	0.89		
Type 3 (st. Pt/C)	6.69	2.50		

(70^oC, 1.5B A ,A/C 1.5/2 stoich. Nafion® 112)

Accomplishments/Progress

- *Met Dec milestone for both catalyst prep and fg-ELAT: achieved 50% reduction in platinum power density*
- *Have submitted samples to NFC for verification (ahead of schedule)*
- *Have created low temperature process (<200 deg c) for alloy formation: scaled best Pt/C prep to 2Kg (ahead of schedule)*
- *NU high temperature simulations (RDE) indicate that there may not be an "alloy effect" under low water conditions (Introduced at Asilomar Conf 2/03, ECS Paris 4/03)*
- *"High temperature" GDE interface evaluated at Du Pont: at NU Inorganic gel additives can improve conductivity at lower RH in the reaction layer*

Other Notable Progress

Patents

- Two Patent Applications pertaining to fg-ELAT
- Two Patent Applications on new catalyst preparation methods (low temp Alloys, new Platinum prep)

Publications

- A systematic investigation of the shift in water binding energy and its effects on the on-set Oxygen Reduction. (in preparation; Andrea F. Gullá, Robert J. Allen and Sanjeev Mukerjee)
- Electrocatalysis and Charge Transfer in Proton Conducting Membranes Operating at Elevated Temperatures. (in preparation; Sanjeev Mukerjee, R. Craig Urian, Chengsong Ma, Lei Zhang and Andrea F. Gullá)
- Investigation on the kinetics of Pt based alloys using Rotating disk (RDE) and Fuel Cell data; effect of synthesis procedures and the effect of water binding. (in preparation; Andrea F. Gullá, Robert J. Allen, Vivek Srinivasamurthy and Sanjeev Mukerjee)

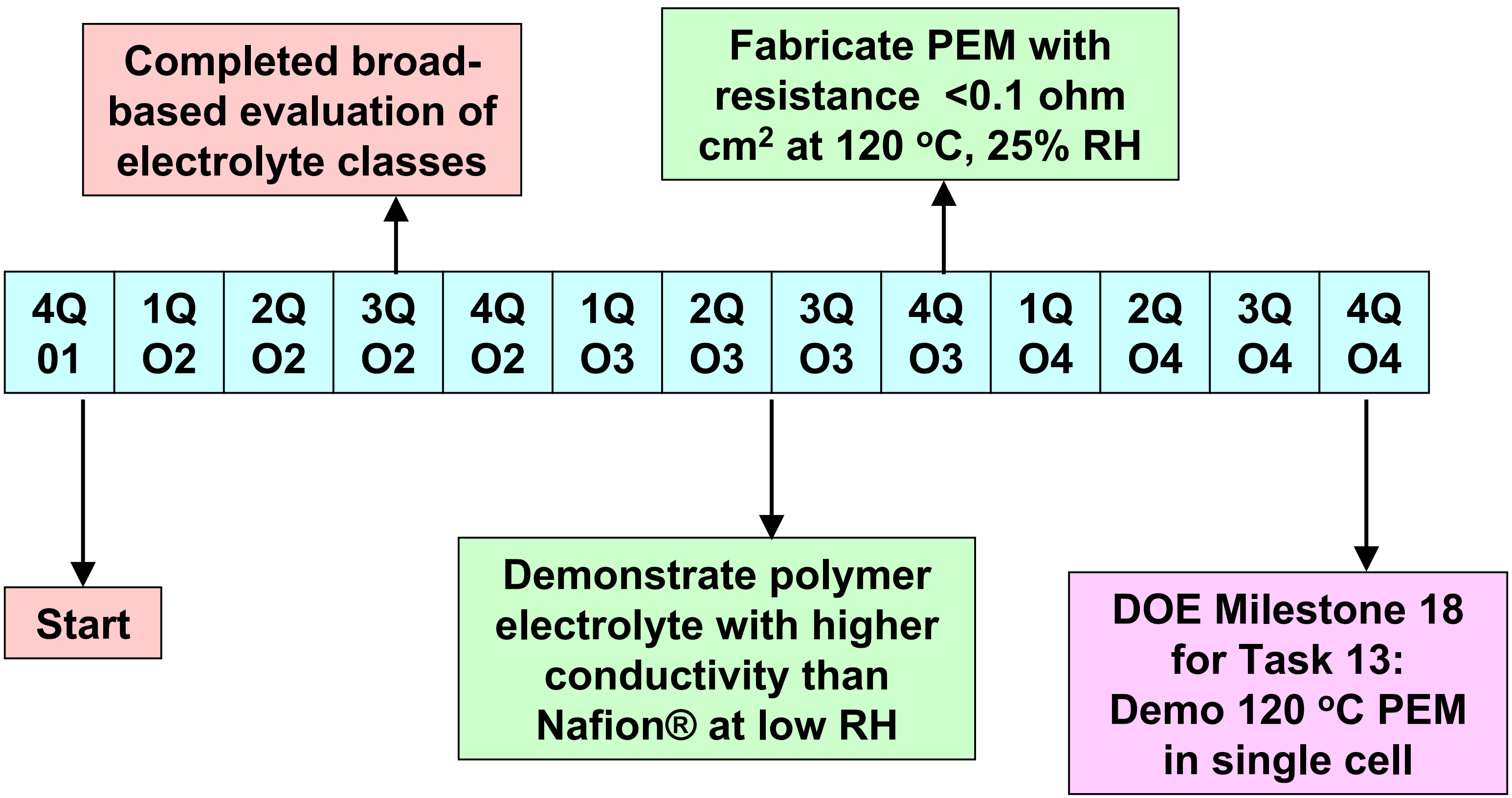
Going Forward

- Achieve lower total PM loadings by “jump-starting” limited Ion Beam Assisted Deposition (IBAD) on membrane for low loaded anodes (Program 1A3)
- Use increased coating control to lower metal load in GDE: continue with improvements in Nafion/GDE structure
- Use morphological characteristics of carbon cloth/paper and different carbon gas diffusion layers (“fg-ELAT”) to build structure of GDE to designed for DOE power targets
- Develop quantitative methods to measure hydrophobicity during builds (will pursue with CWRU)

Higher Temperature Membranes: DuPont's Approach

- Synthesize model compounds and monomers
  - Evaluate conductivity at low RH
- Make ionomers
  - Thermally, hydrolytically, oxidatively stable
  - Incorporate best functionality from model compound studies.
    - With and without additional groups supporting ionization
- Fabricate Membranes
  - Optimize equivalent weight
  - Control swelling & provide mechanical properties
    - Composite membranes
    - Crosslinking
- Examine new electrolyte functional group
- Explore ionomers with uncollapsible hydrophilic domains
  - With CWRU
- Make MEA's and test in single cells

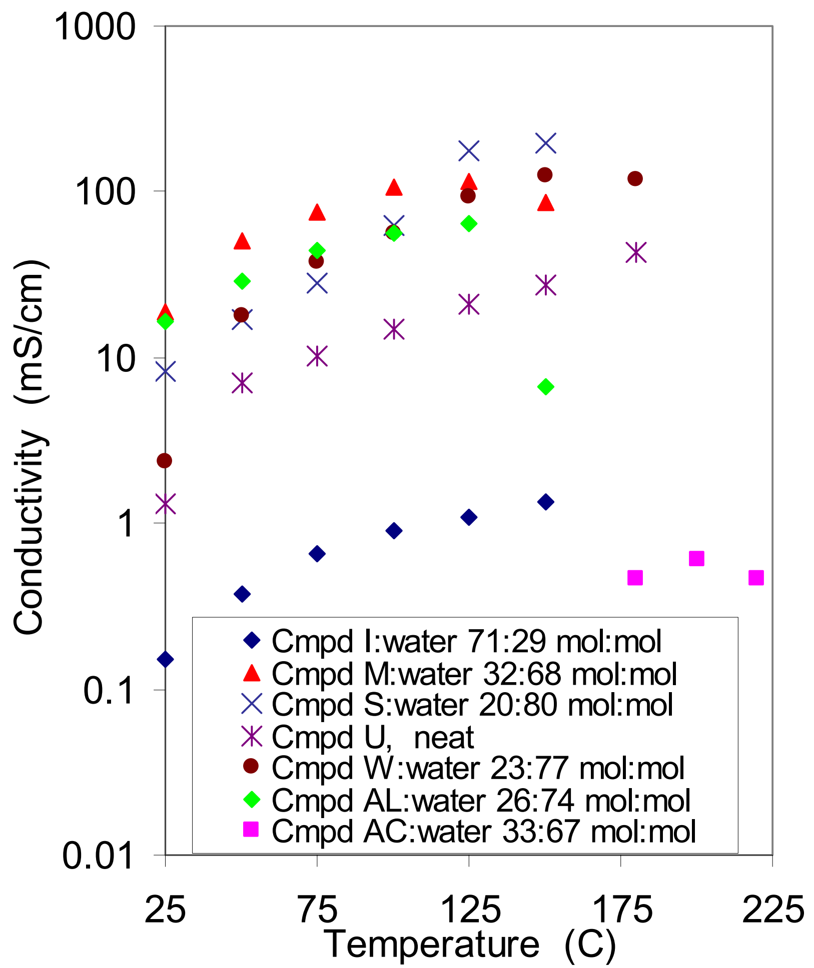
HT Membrane Timeline



Conductivity of Liquids

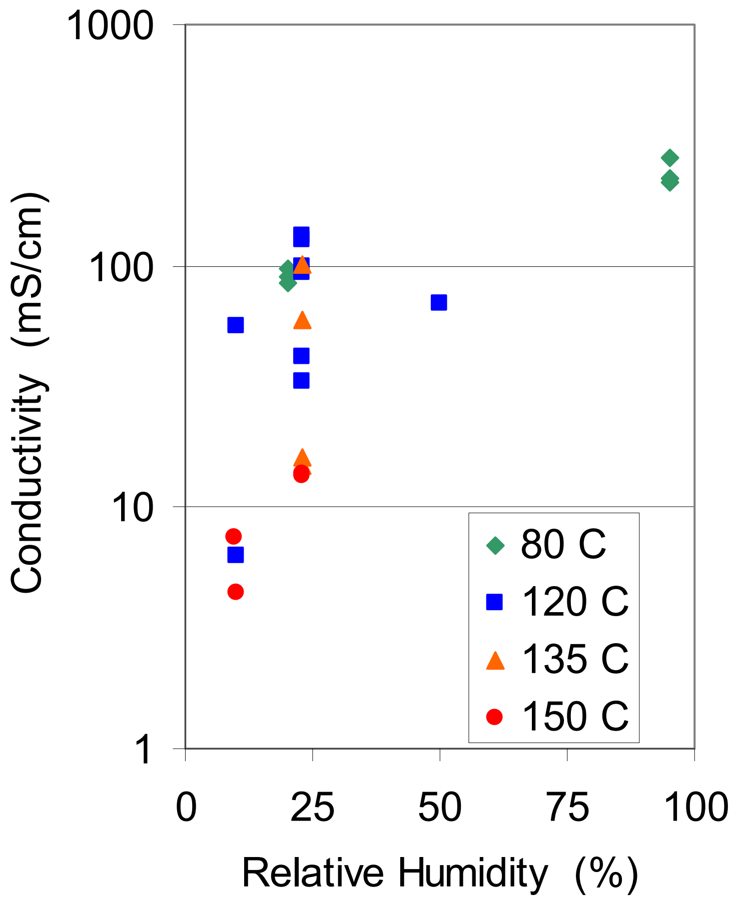
- More than 25 model electrolyte compounds and monomers synthesized
  - Which functionalities can engender conductivity at low RH?
- The water contents used are lower than required by Nafion®.
  - Cell was not pressurized.
  - Water vapor partial pressure was less than 1 atm.
- Compound U requires no water!
- Compound M is a monomer.

- Now pursuing ionomers based on the best functionalities from this study.



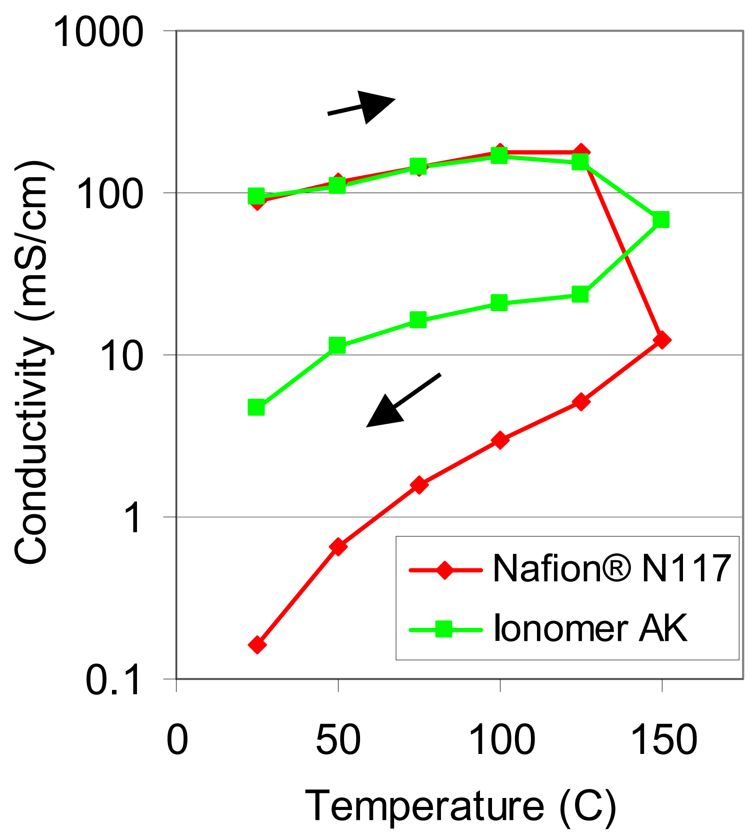
Conductivity for New Electrolyte X

- X is a small molecule model liquid compound
  - Sample for conductivity made by soaking X into ceramic paper
- Measured under controlled RH
  - Several different samples plotted with different loadings on paper
- Maintains conductivity at low RH better than several other electrolytes that have been examined



Conductivity of Polymeric Version

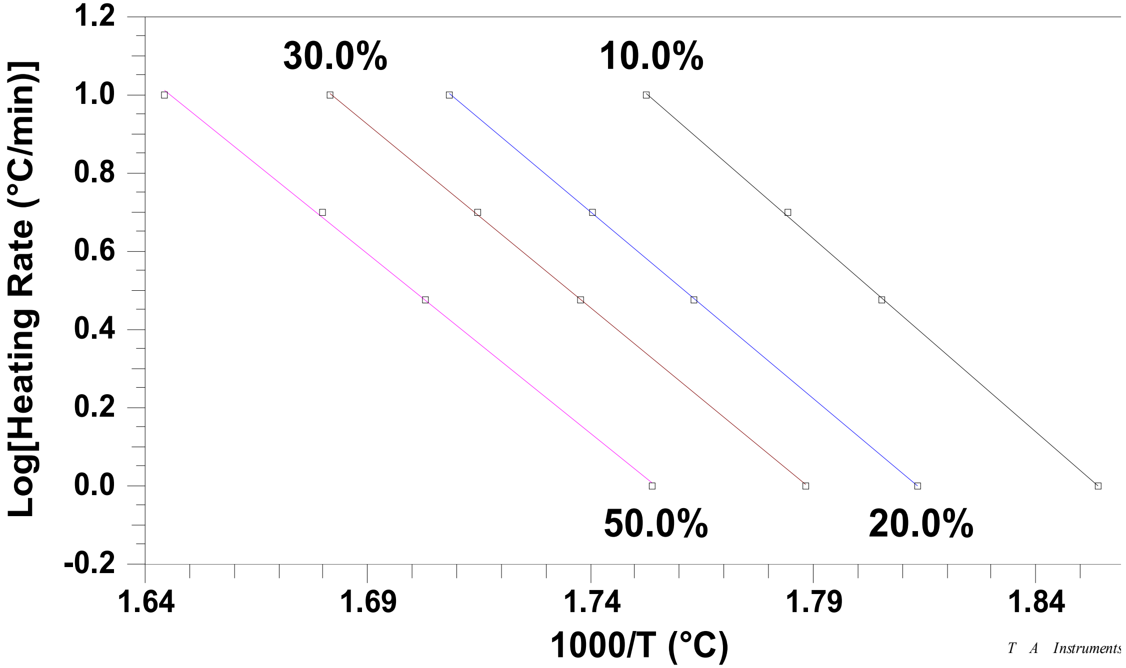
- Candidate ionomer AK
  – Polymer based on model compound X
  – Porous sample suitable for conductivity testing
- Through-plane Conductivity
  – Samples fully-hydrated at start
  – Samples dehydrate during measurement (no water added to cell)
  – Total pressure is 1 atm
  – RH ~ 25% @ 150 ^{o}C
- Maintains higher conductivity after exposure to low RH than does N117 benchmark
- Further work required to achieve thin impermeable membrane suitable for FC testing



Thermal Stability

- Will the ionomers be even thermally stable for the required lifetimes at 120 °C?
- Assessing with accelerated test using Kinetic TGA Method.
  - Measure TGA at different heating rates under slightly-wet air.
  - Plot log(heating rate) *vs* 1/T for different levels of weight loss.
  - Parallel lines indicate 1st-order decomposition and give E_a.

Sample	Activation Energy E_a (kJ/mol)	Lifetime limit due to thermal decomposition @ 120 °C (khr)
Candidate AE	265	>1,000
Nafion® 1100 EW benchmark	166	260 (±70 gage repeatability)
Candidate AM	178	27
Candidate AF	180	0.42

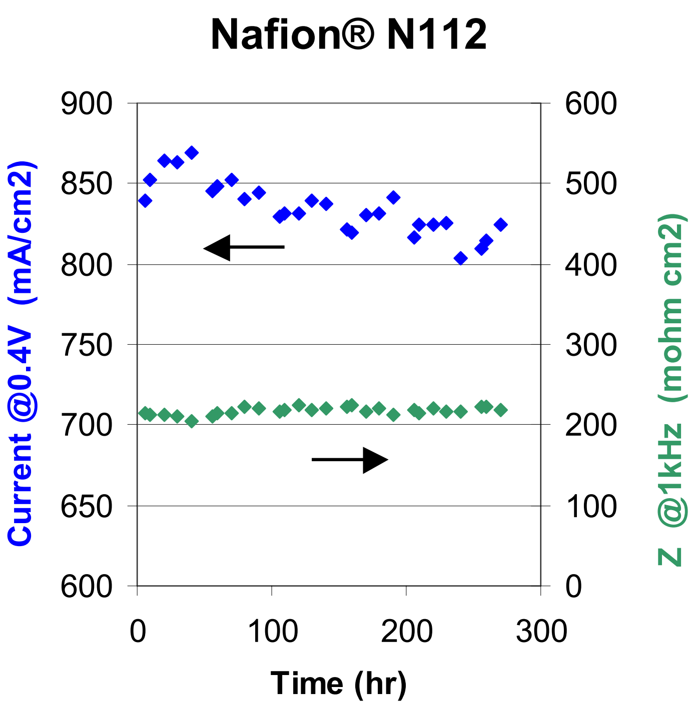


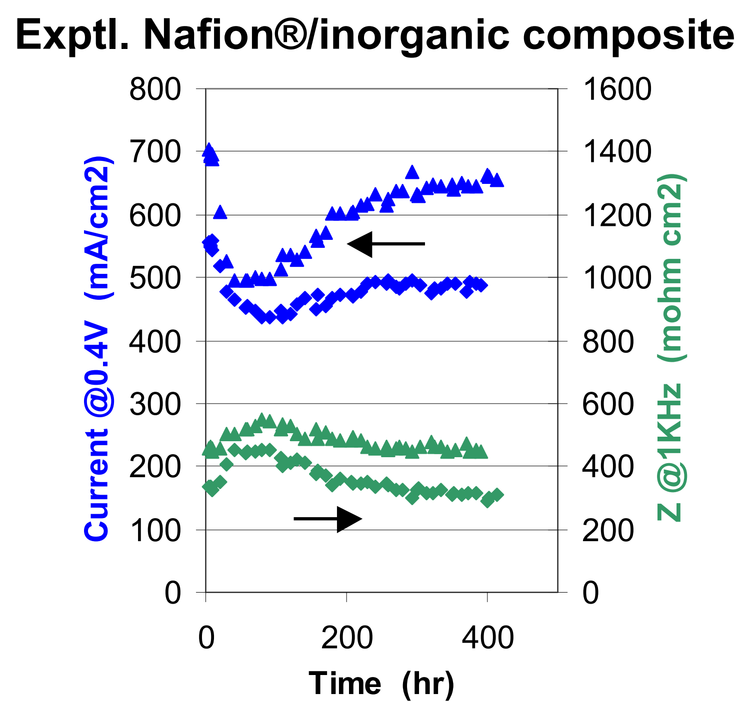
Question from the July 2002 Freedom Car Review of HT Memb. sub-Program

- Q: You have shown some preliminary results on new membranes operating at higher temperature for short periods of times. What happens after 3-5 days?
  - A: FC testing has now been carried out which shows significant degradation of performance, at least partly attributable to the membrane, after 400 hr for benchmark Nafion® and Nafion®/inorganic composite membranes.

Benchmarking 120 ^oC FC Lifetime

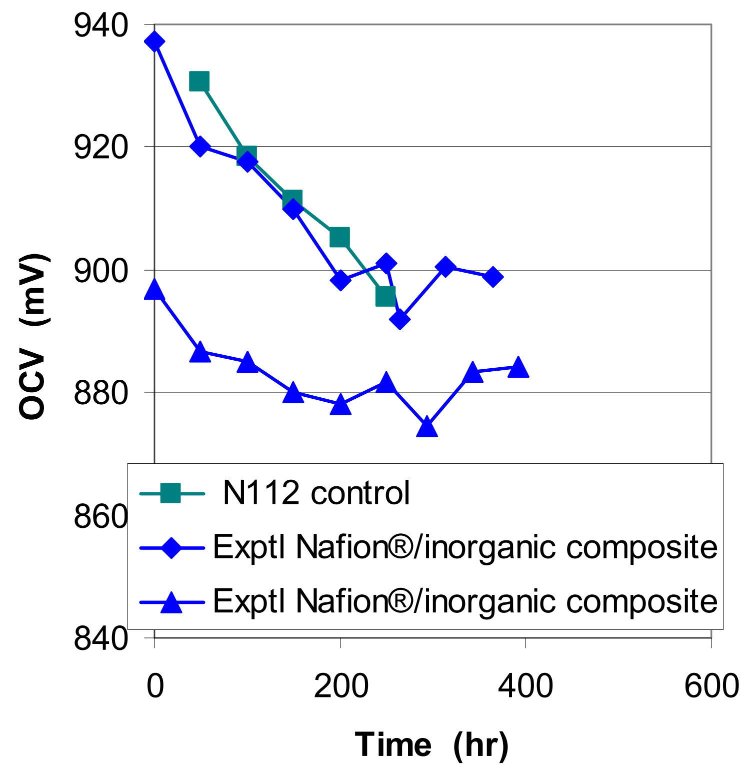
- MEA's prepared using ELAT® GDE's
- Conditions: HFC, const. 0.4 V, 120 ^oC, cathode/anode feeds 50% RH, 15 psig, stoic. 1.5/1.5 @1.6A/cm^2
- N112 lost 5% of current in first 250 hr; reasonably stable resistance
- Exptl. composite memb. shows higher resistance and instability in current and resistance attributed to decomposition of the inorganic component.





Open Circuit Voltage

- Cycle at 120 ^{o}C, 50% RH feeds
  - 49.5 hrs at 0.4 V
  - 0.5 hrs at open circuit
- Decay in OCV is believed due to increase in hydrogen crossover (membrane failure)
- Hydrogen crossover increase confirmed with voltammetric measurements on cells with feed switched to N_2 anode-side / H_2 cathode-side
- Further studies to determine causes
  - Chemical degradation
  - Mechanical failure



Responses to two Questions from the July 2002 Freedom Car Review of HT Memb. sub-Program

- Q: In designing your membranes, FreedomCAR is not only interested in high temperature membranes but those with acceptable performance over a wide range: automobiles will still have to start at sub freezing temperatures.
  - A: We have measured the temperature dependence of conductivity and acknowledge that, at constant low RH, some of our new electrolytes have a higher activation energy than Nafion® (larger decrease at lower temp.) However, at lower temperatures the FC pressure budget allows higher RH, which strongly increases the conductivity. We can only commit to keeping this requirement in mind as it is balanced against the other requirements.

Going Forward

- Develop further work on ionomer "AK" to achieve thin impermeable membrane suitable for FC testing
- Explore ionomers with uncollapsible hydrophilic domains
- Make ionomers
  - Thermally, hydrolytically, oxidatively stable
  - Carry strong acid groups
  - With and without additional basic groups supporting self-ionization
- Optimize equivalent wt., control swelling, and provide mechanical properties
  - Composite membranes
  - Crosslinking
- Continue to examine new electrolyte functional groups

Acknowledgements

De Nora N.A. E-TEK *div*

- Yu-Min Tsou, Ph.D.
- Lixin Cao, Ph.D.
- Guy Havet, Ph.D.
- Hua Deng, MS, ChE
- Michael Schneider
- Maria Cayetano
- Jeffrey Morse
- Laura Bellamy

Northeastern University

- Prof. Sanjeev Mukerjee
- Andrea F. Gullá (DNNA.), Ph.D.
- Robert J. Allen (DNNA) Distinguished Visiting Scientist
- Vivek Srinivasamurthy (Graduate Student)
- Lei Zhang (Graduate Student)
- Jillian Goldfarb (Undergraduate)

DuPont

- Mark G. Roelofs, Ph.D (Project Leader)
- Mark Teasly, Ph.D.
- Zhenyu Yang, Ph.D.
- Hongli Dai, Ph.D.
- Jayson Bauman, Ph.D.
- John J. Borowski
- Ruping Wang
- Robin Blackburn
- James I. Johnson

DE NORA NORTH AMERICA, Inc.
GRUPPO DE NORA
Durantes Vincunt

Northeastern UNIVERSITY

DUPONT The miracles of science™