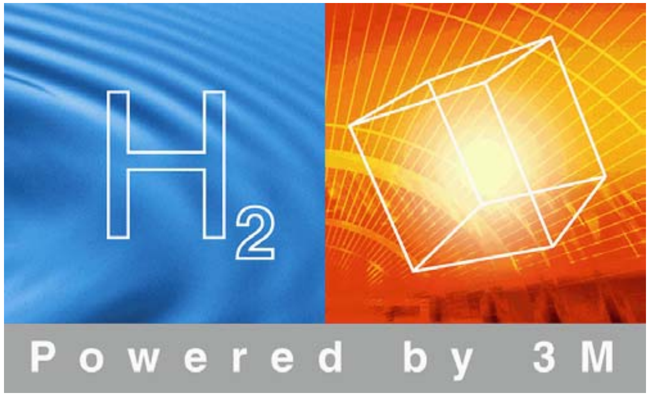
2003 DOE HYDROGEN, FUEL CELLS, AND INFRASTRUCTURE TECHNOLOGIES PROGRAM REVIEW MEETING
May 19-22, 2003
Berkeley, CA

Advanced MEA's for Enhanced Operating Conditions, Amenable to High Volume Manufacture



3M/DOE Cooperative Agreement

No. DE-FC04-02AL67621

Technical Goals and Objectives

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Development of high performance, lower cost membrane electrode assemblies (MEA's) qualified to meet demanding system operating conditions of higher temperature and little or no humidification, with less precious metal catalysts, and higher durability membranes than current state-of-the-art constructions.

Technical goals include development of:

- Durable MEA's at $85 < T < \sim 120^{\circ}C$, operating on low humidification with PFSA based ionomer and lower cost materials and catalysts
- Development of MEA's for $120 < T < 150^{\circ}C$, based on non-aqueous proton conduction mechanism, lower cost materials and fabrication processes
- Matched MEA materials and processes scaleable to high volumes

Work Plan Summary

Task 1 is directed at advancing the state-of-the-art in cathode structures and durable PFSA based membranes to stretch the limits of current MEA technology toward more stability at hotter, drier operating conditions ($85 < T < 120$ºC) with lower cost materials and high volume compatible processes.

Subtasks include:

- Development of advanced cathode catalysts: Pt ternaries, combinatorial methods, others
- Modified membranes based on 3M's non-Nafion™, PFSA ionomers
- Matching 3M MEA and air management operating conditions
- Advanced modeling for flow field and gas diffuser optimization
- Optimization of catalyst coated membrane assemblies and GDL's
- Short stack testing

Work Plan Summary (continued)

Task 2 focuses on development of very high temperature PEM membranes that do not rely on water for H^+ transport, stable catalysts and supports with matching gas diffusion and flow field components to take the MEA into an operating range of $120 < T < 150°C$ and nearly dry operation.

Subtasks include:

- Development of a high temperature electrolyte membrane and appropriate catalysts;
- Optimization of the catalyst membrane interfaces;
- Advanced materials characterization and modeling with subcontractors; and
- Short stack testing

Task 3 is directed at the scale-up and optimization of MEA component fabrication processes amenable to high volume, high quality, low cost production for selected components from Tasks 1 or 2.

Subtasks include:

- Scale-up and optimization of the fabrication processes for membrane, catalyst, CCM, GDL
- MEA's characterized in full-scale short stacks.

Relevance to Overall DOE Objectives, Technical Challenges, Commercialization Barriers

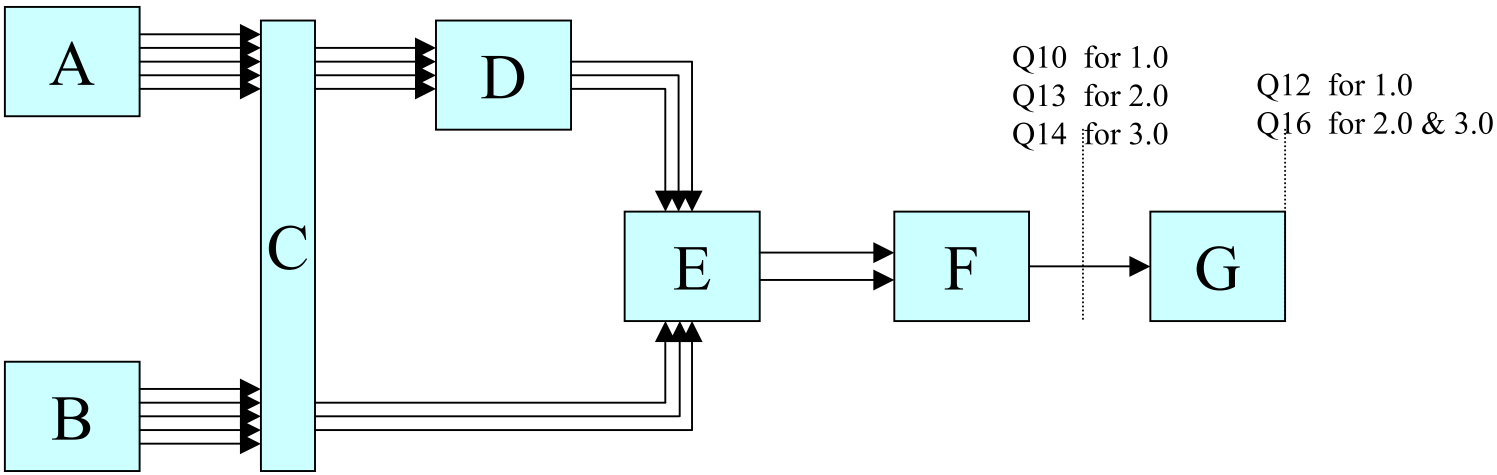
Transportation and/or Stationary Issue:	**Contributing Solution from 3M Approach**
Thermal management, size and weight	Higher T(C) operation giving - more effective heat transfer - smaller radiators, condensers, coolant flow rates
Water management	Sub-saturation operation for T < 120ºC Dry operation for T > 120ºC
Lower cost	Less precious metal catalysts Lower cost membrane and GDL materials High volume manufacturable MEA's Simpler balance of plant from high T(C) and reduced humidification requirements
High volume capacity	Roll-good manufactured MEA components

Relevance to Overall DOE objectives, Technical Challenges, Commercialization Barriers

Transportation / Stationary Issue:	Contributing Solution from 3M Approach
Durability	Improved membrane durability (lower F^- at T < 120ºC) More stable catalysts (less loss of catalyst performance, surface area) More oxidation-stable catalyst supports Optimized electrode structures (uniformity of current density) Flow field/GDL optimized for uniformity of mass flow Integrated MEA seals/gaskets
Impurity tolerance	High temperature operation
Efficiency	Higher activity cathode catalysts, i.e. higher operational voltage Higher performance from matched component MEA's Reduced balance of plant parasitic power loss from - flow field/GDL optimized for lower stoichiometric flow - improved thermal management

Approach - General

MEA and Component Development Path



A = PEM new materials
B = Catalyst new materials
C = Critical property measurements of new materials
D = Membrane formation, treatment methods
E = CCM/MEA fabrication with integrated components and fuel cell screening
F = Full high temperature testing of selected MEA's w/comprehensive diagnostics
G = Stack development and testing

Approach – A: New PEM Materials, 85ºC < T < 120ºC

* Based on 3M's non-Nafion perfluorinated sulfonic acid ionomeric membranes
    - less fluoride generation than Nafion
    - longer lifetimes in accelerated durability testing than Nafion
    - improved mechanical properties
    - existing scaled-up processing

* Incorporation of functionalized additives to 3M membrane:
    - facilitate peroxide decomposition for better oxidative stability
    - enhance water retention for higher conductivity under low humidification
    - powders, nanoparticles, polyoximetallates, sol-gels, acid modification

Target: Develop an advanced membrane which can operate stably for > 2000 hours under sub-saturation at 85 < T< 120ºC and provide excellent catalyst interfacial kinetics.

Approach – A: New PEM Materials, T > 120ºC

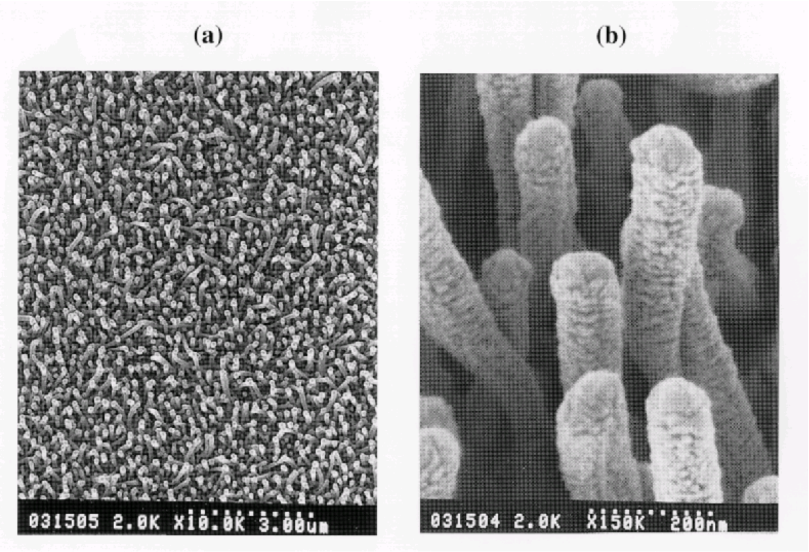
* Replace liquid water as the proton conductor
- 3M fluorinated liquids as proton conducting components
- inorganic proton conductors

* Incorporation into polymer matrices
- casting mixed dispersions of polymer with dispersions of the inorganic, or
- *in situ* synthesis of the inorganic phase in the polymer film
- incorporation into microporous media

* New polymer matrices
- acid functional polymer, such as 3M ionomer, or
- non acid containing polymer (such as PBI)
- incorporation of inorganics or fluorinated liquids
- microporous film technology

Target: Develop an advanced membrane which can operate stably for > 2000 hours under dry conditions at 120 < T< 150ºC and provide good catalyst interfacial kinetics.

Approach – B: New Catalysts



Pt coated nanostructured whisker supports (0.25 mg/cm^2), at 10,000 X plan view (left) and 150,000 X 45^o view (right).

* **Extension of 3M nanostructured thin film multi-element catalyst development: PtABC**
- Unique electronic features, increased surface area,
- catalyst specific activity is 2x pure Pt
- roll-good processing established
- enhanced oxidative stability of support whiskers

* **Combinatorial approach (w/ Dalhousie U.)**
- same catalyst deposition processes employed
- wide latitude of PtAB material compositions over 50-cm^2 areas
- full materials fabrication and spatial characterization (XRD, e-µProbe)
- novel 3M combinatorial screening methods for catalyst activity
- most promising combinations reproduced for fuel cell evaluations

* **Conventional dispersed catalysts**
- improved oxidatively stable carbon supports

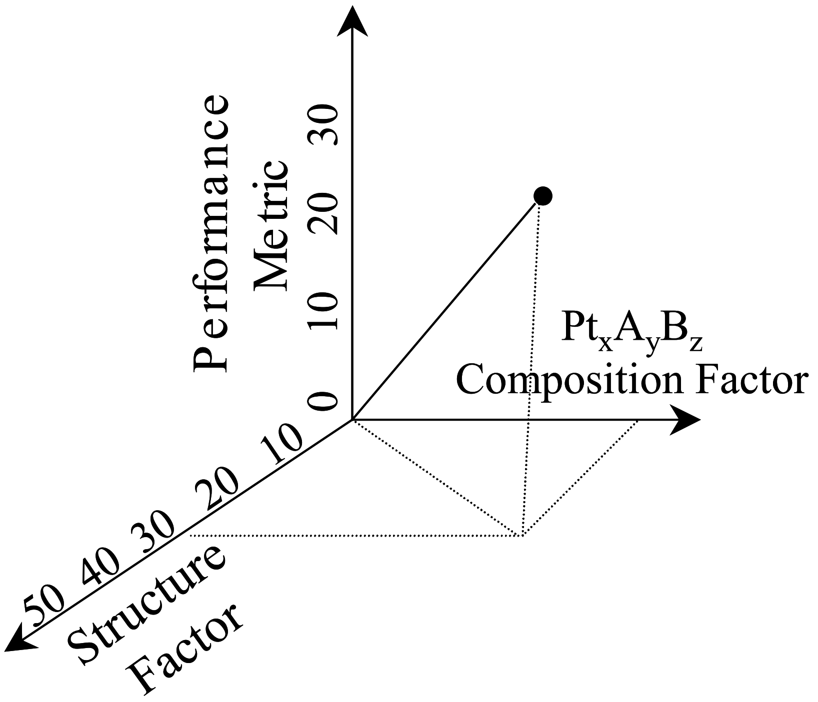
Approach – B: New Catalysts

Material Variation :
- PtCB,
- PtDB,
- PtABC, and
- relative amount of element B.

Structural Variation:
- atomic element ratios,
- physical structure, process conditions
- surface finish

Fabrication methods:
- roll-good based
- high volume manufacturability

Exploration Grid for PtAB Ternary Catalysts



Target: Develop cathode catalysts/supports requiring < 0.6 g of precious metal catalysts total per rated kW, and which are stable under enhanced operating conditions for > 2000 hours.

Approach – C: Critical Property Measurements

- **PEM, Ionomer Conductivity**
  - In-plane 4 point probe
    EIS up to 80ºC, 20 % to 95% RH or up to 200ºC, dry, ambient pressure.
  - Through-plane 5-cm^2 fuel cell
    EIS, DC (H_2/H_2) up to 200ºC, 0% to 100% RH, up to 60 psig.
  - DC conductivity – H^+ versus ionic

- **Permeability**
  - H_2O- "cup test" or fuel cell.
  - H_2- crossover (cyclic voltammetry).
  - O_2 – fuel cell test under development.

- **Chemical Stability**
  - Water boil – leachable components
  - Peroxide boil – 50 ppm Fe
  - Fluoride ion generation

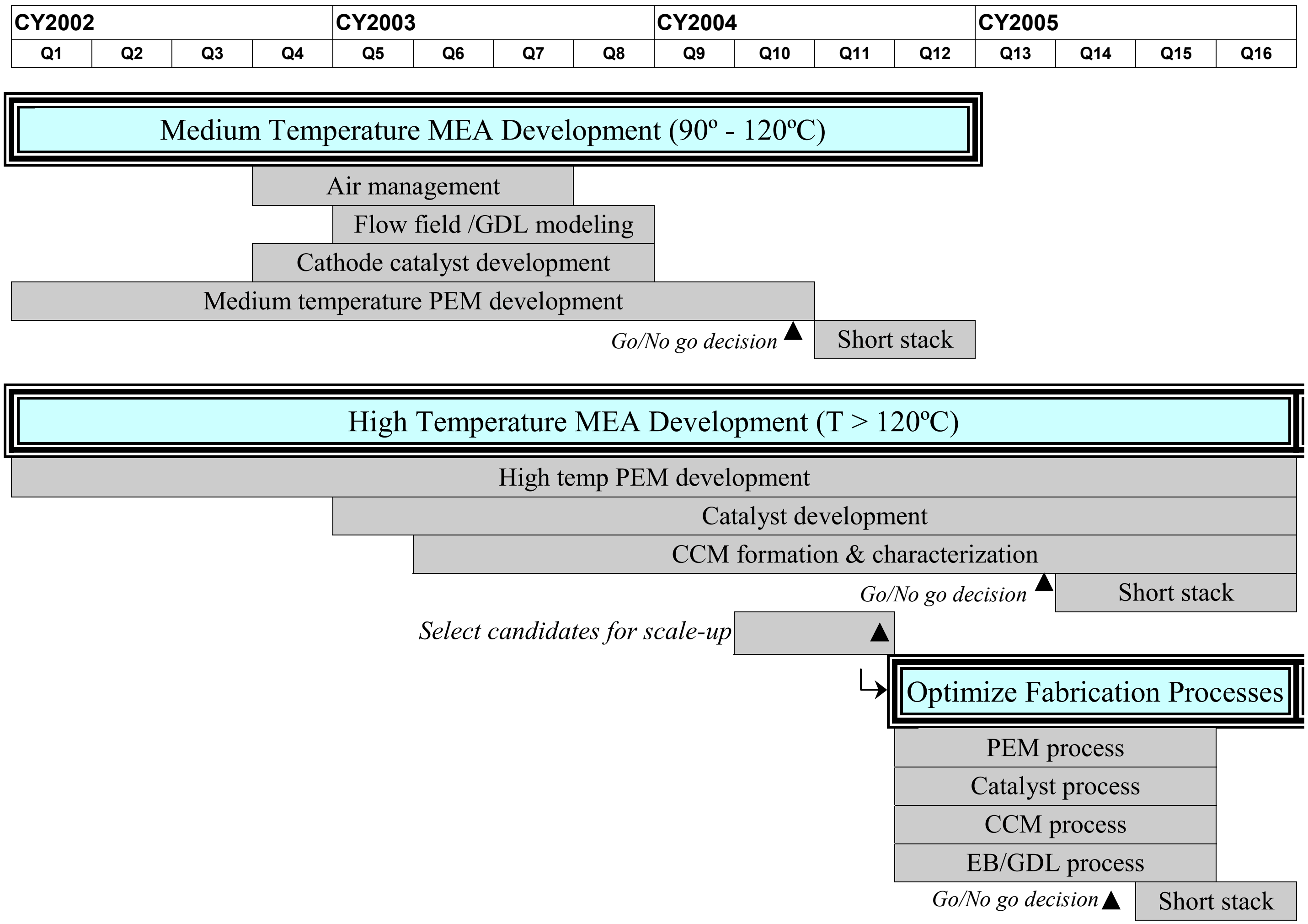
- **Water Absorption**

- **PEM Physical/Mechanical Properties**
  - Puncture resistance
  - Tensile, Creep (controlled RH up to 90ºC, dry up to 150ºC)

- **Catalyst Properties**
  - Electrochemical surface area
  - Specific activity
  - PtA_xB_y composition
  - PtA_xB_y structure
  - Loadings

- **Fuel Cell Characterization**
  - Continuous H-pump
  - Fourier Transform Electrochemical Impedance Spectroscopy under load
  - Tafel plots for catalyst activity
  - Standard polarization type scanning

Timeline


CY2002
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Q13
Q14
Q15
Q16
Medium Temperature MEA Development (90º - 120ºC)
Air management
Flow field /GDL modeling
Cathode catalyst development
Medium temperature PEM development
Go/No go decision
Short stack
High Temperature MEA Development (T > 120ºC)
High temp PEM development
Catalyst development
CCM formation & characterization
Go/No go decision
Short stack
Select candidates for scale-up
Optimize Fabrication Processes
PEM process
Catalyst process
CCM process
EB/GDL process
Go/No go decision
Short stack

Accomplishments – Membranes, 85 < T < 120ºC

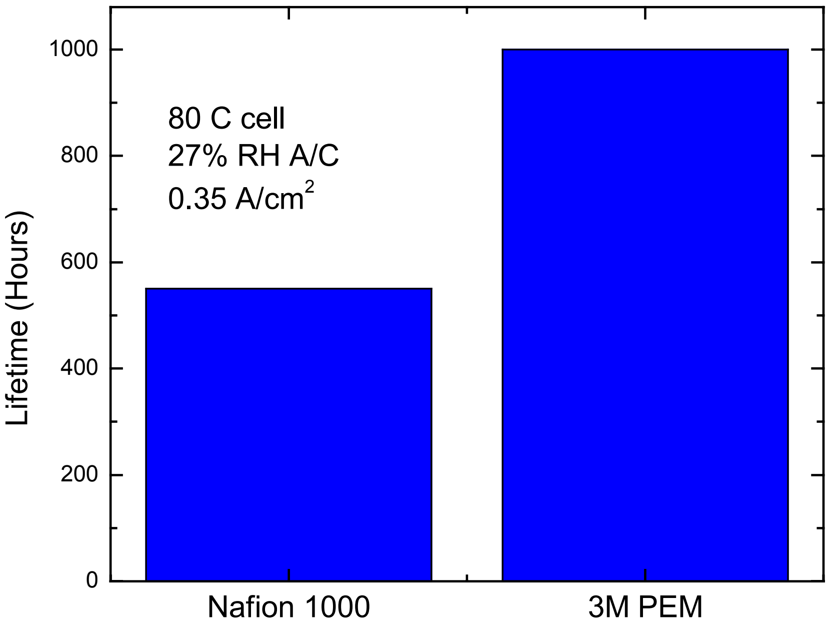
3M's non-Nafion perfluorinated sulfonic acid ionomeric membrane shows reduced F^- ion generation and longer lifetime under accelerated testing:

* 80% lifetime increase for 30 µm membrane at 80ºC, 60%/60% RH

* 5 to 10 fold decrease in F^- ion in effluent under several temperatures (up to 120ºC) and different operating conditions

* Improved mechanical properties

Incorporation of functionalized additives to the 3M membrane should further enhance these properties.

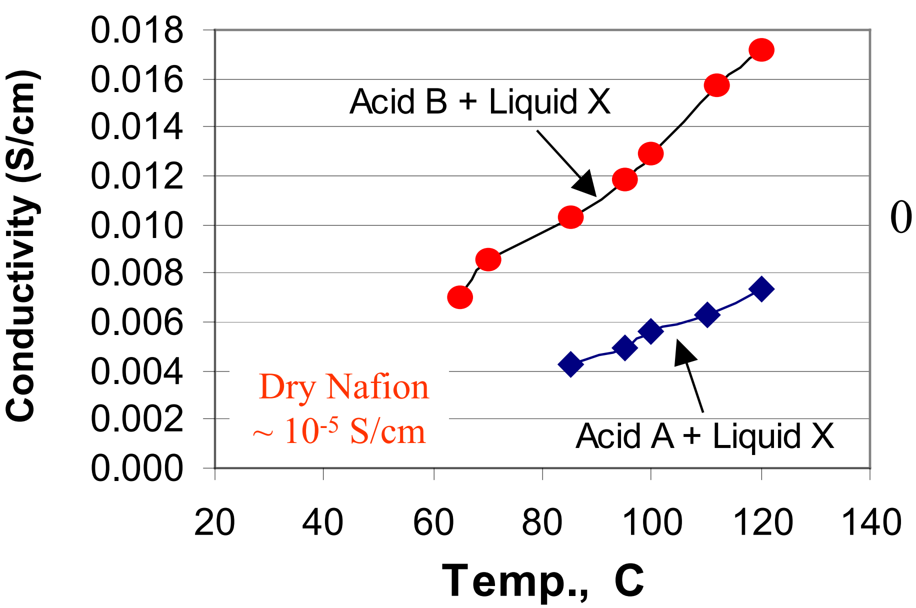


Accomplishments – Membranes, 120 < T < 150ºC

* Technique developed to measure the proton conductivity of ionic liquids and acids:
- in addition to ionic conductivity from AC impedance
- a "liquid H-pump" technique

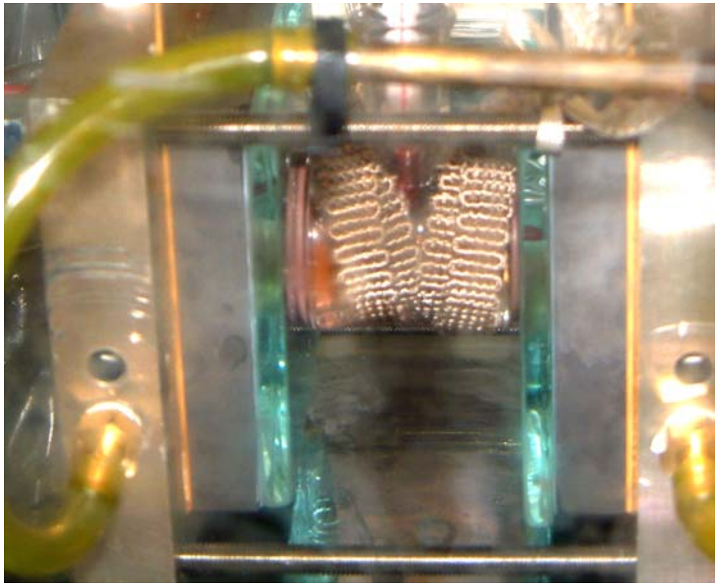
* 3M proprietary perfluorinated acids plus liquid additives show proton conductivities with 0 mole % water strongly dependent on acid type and temperature.

Proton Conductivity of Acids + Liquids as a Function of Temperature under H_2



0 % H_2O

Liquid, Proton Conductivity Cell

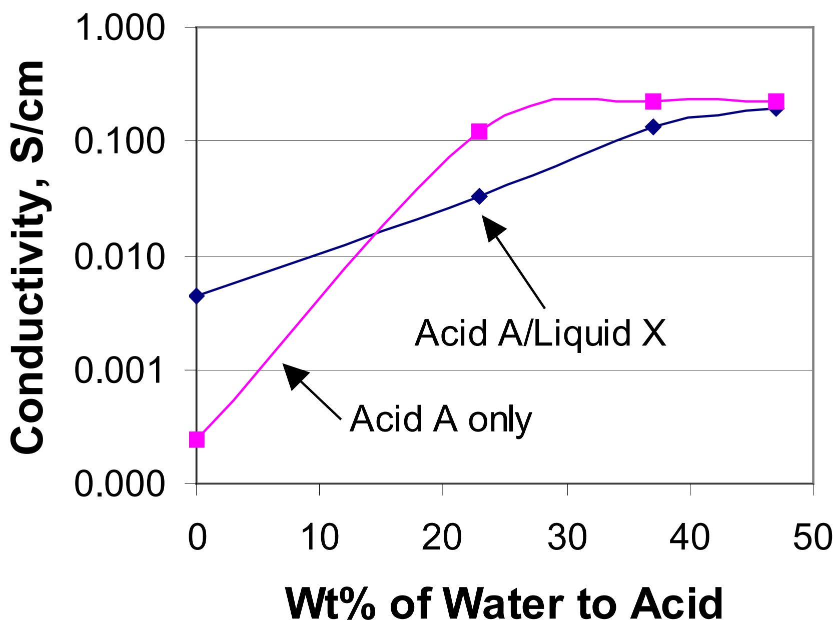


Accomplishments – Membranes, 120 < T < 150ºC)

* With very small weight % of water, the combined acid A and liquid additive show significant increase in proton conductivity.

* Acid B plus Liquid X to be measured yet. Could increase proton conductivity to target range of 0.025 to 0.1 S/cm.

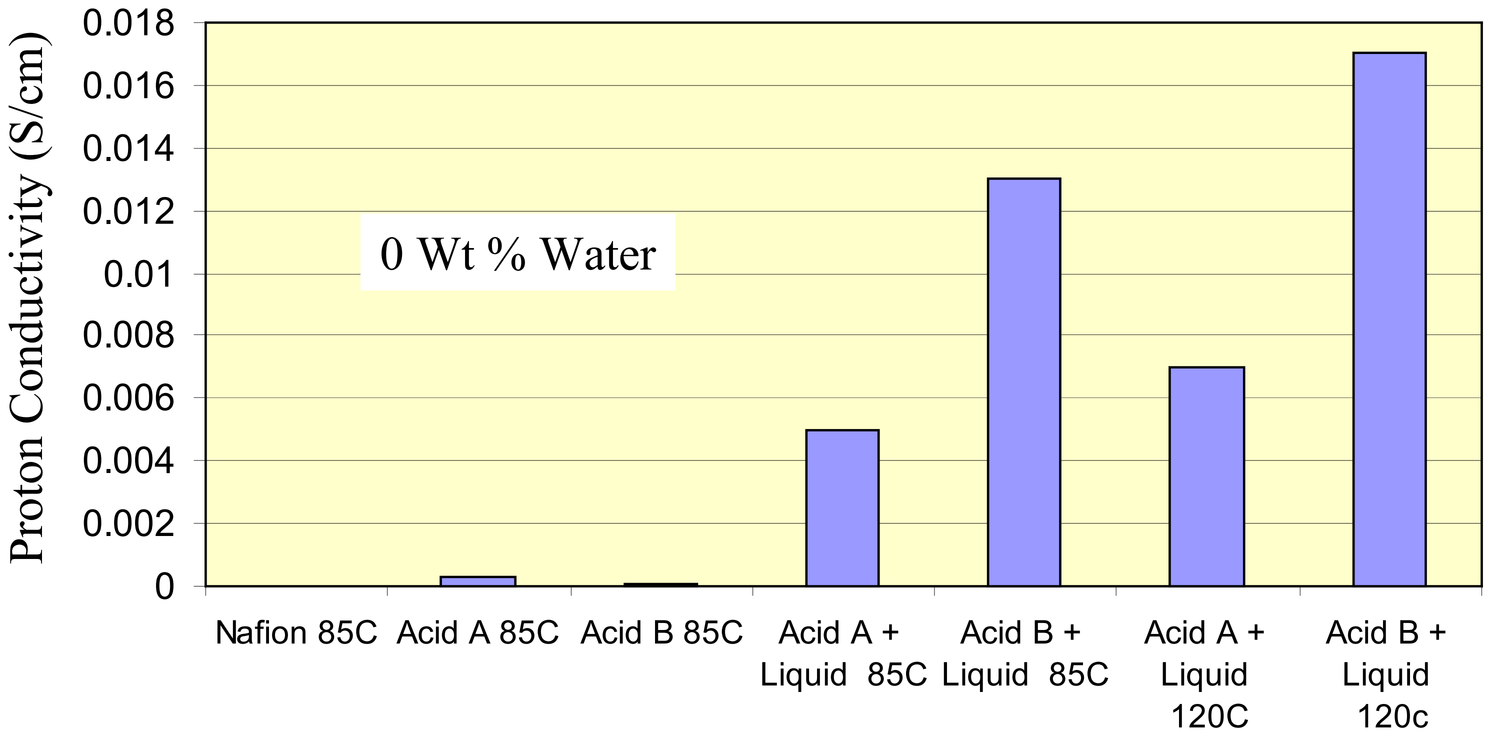
Proton Conductivity of Acid A vs. Acid A / Liquid X as a function of water conc. at 70^{o}C / H_2



Accomplishments – Membranes, 120 < T < 150ºC

* DC method of proton conductivity in liquid form of mixed proprietary 3M perfluorinated acids and liquids

* Liquid mixtures show increased proton conductivity over anhydrous acids by factors of 100-1000 times with no added water.



Accomplishments – Advanced Cathode Catalysts - Background

Previous 3M/DOE Contract (12/02): Final stack testing of 3M roll-good fabricated MEA's with 3M nanostructured thin film catalysts:

* **Utilized roll-good fabricated Nano-MEA's with ~ 0.34 mg Pt/cm^2 total.**
* **14 cells, 200 cm^2**
* **Demonstrated operation at automotive conditions for H_2/air):**
  - within 11 mV of target of 680 mV at 0.8 A/cm^2
  - pressurized per automotive compressor curve
  - sub-saturation (dry cathode) operation
  - excellent cell-to-cell uniformity (23 mV spread, 6 mV std. dev. @ 1 A/cm^2
  - excellent fuel and air utilization (max of 95% H_2 and 77% air at 0 psig)
  - 400 hours of operation with no substantial change in performance
* **Exceeded peak power design specifications:**
  - Obtained - 1.9 kWe + 2.25 kW heat at 62% air utilization
  - Targeted - 1.4 kWe + 1.9 kW heat at 45% air utilization

* **0.34 mg Pt/cm^2 and 1.9 kW meets DOE 2005 target of 0.6 g Pt/peak kW**

Accomplishments – Advanced Cathode Catalysts

* 46 PtM_1M_2 ternary catalyst compositions and structures fabricated and evaluated
  - All have constant loading of Pt of 0.1 mg/cm^2
* High pressure oxygen performance (Tafel) metric
  - Most ternaries are significantly better than the Pt control
  - Improvements over PtAB used in previous 3M/DOE contract.

Mixed Metal Catalysts Evaluated

Previous 3M/Contract :

PtM binaries – numerous

PtAB – 16 compositions/structures

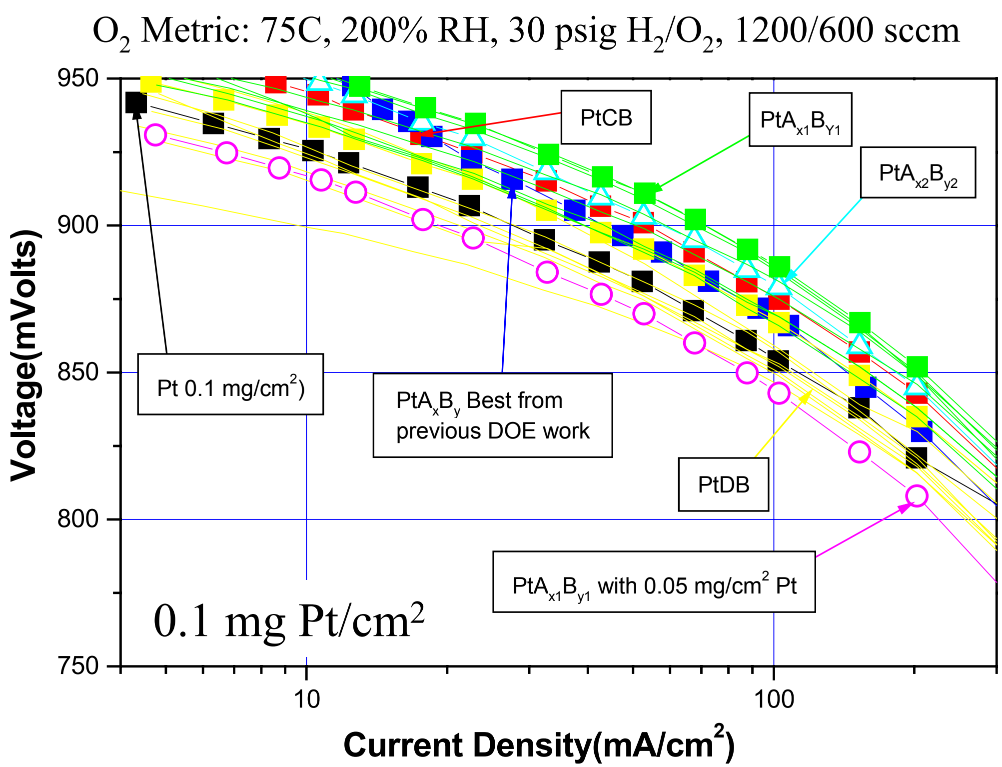
This contract to date :

PtDB – 10

PtCB – 12

$PtAx_1By_1$ – 12

$PtAx_2By_2$ – 10



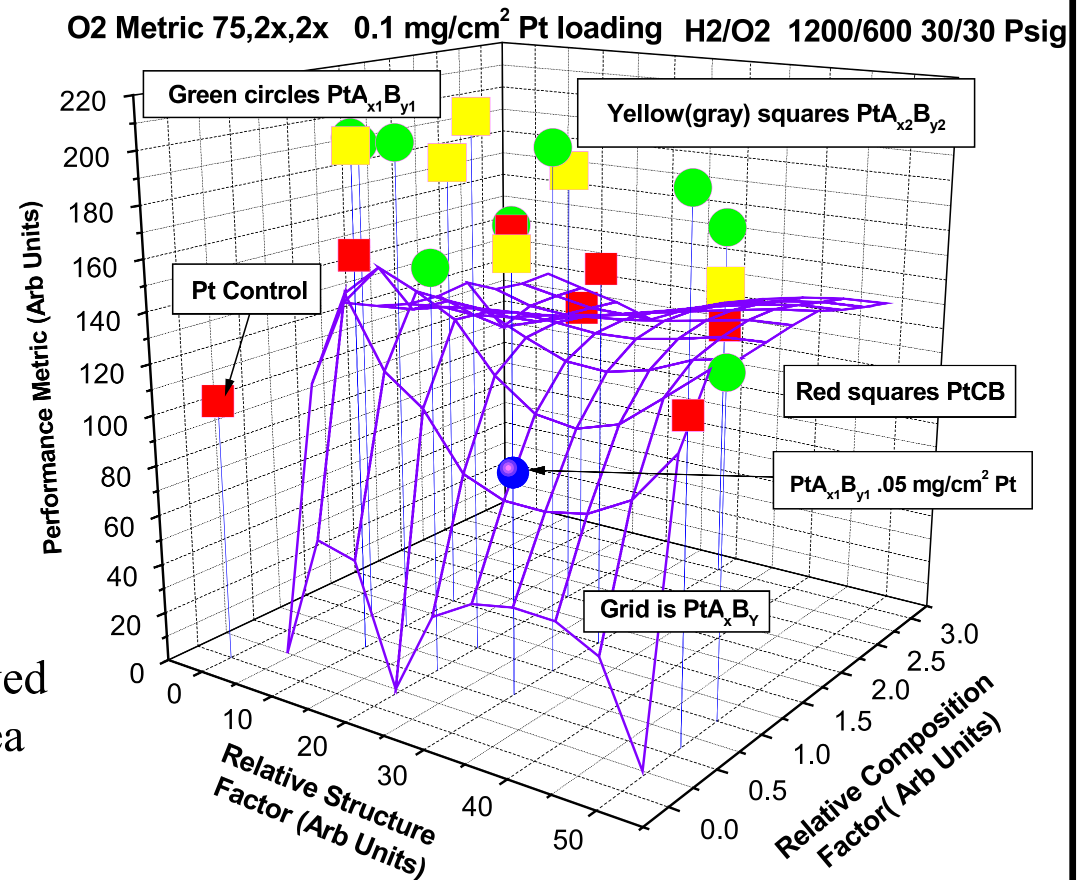
Accomplishments - Advanced Cathode Catalysts

Comparison of activities of $PtA_{x1}B_{y1}$ and PtC_xB_y ternaries against the grid of original PtA_xB_y (previous 3M/DOE contract) ternary samples.

* 3M process controls the relative metallic composition and structure of the catalysts

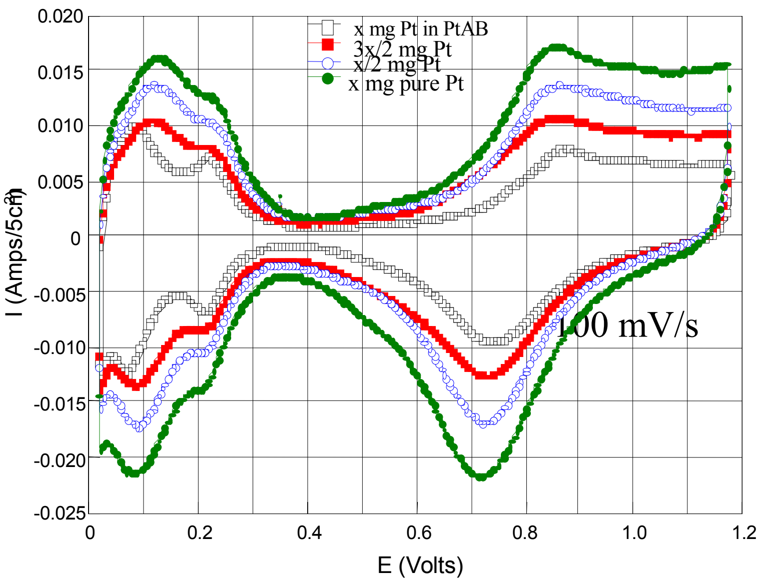
* Catalyst performance depends on the composition and structure factors

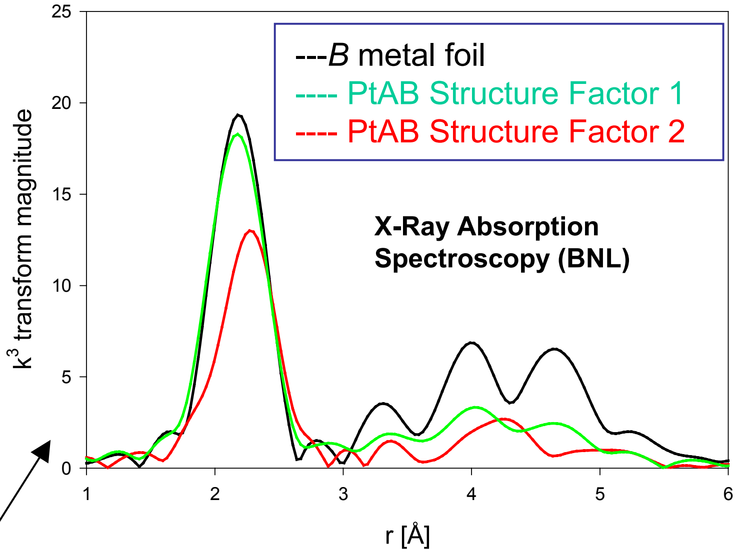
* Ternary compositions give improved performance from both surface area increases and electronic effects



Accomplishments – Advanced Cathode Catalysts – Fundamental Properties

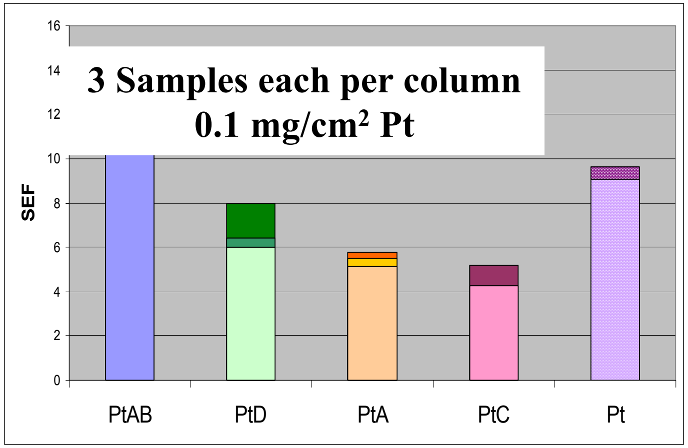
- Enhanced surface area as measured by Hydrogen adsorption over pure Pt or Pt binary catalysts.
- A shift of ~30 mV of the weakly adsorbed H compared to pure Pt.
- Local atomic environment by XAS of the noble and non-noble components depends on structure factor.





Cyclic voltammograms of Pt and PtAB show a 30 mV shift of weakly adsorbed H on PtAB, indicating a stronger adsorption than on pure Pt, => electronic structure effects.

Fourier transform at *B*-edge. The number of nearest non-Pt neighboring atoms to Pt changes from 3.5 to 6.3 in going from the Structure Factor 1 to 2.



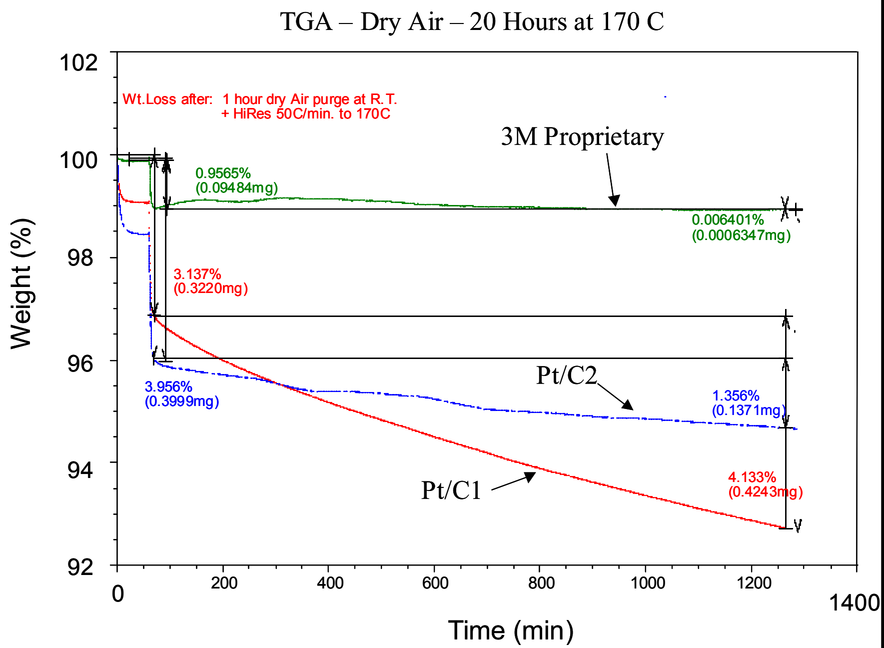
Electrochemical surface area enhancement factor (SEF) is higher for the ternary catalyst over pure Pt and various binaries compared to Pt.

Accomplishments - Advanced Cathode Catalyst Support Stability

* Oxidative chemical stability of 3M proprietary catalysts and supports are much improved over commercial carbon black supported Pt catalysts.

* Highly sensitive TGA weight-loss profiles over 20 hrs at 170ºC air
  Corrected for water desorption mass loss
  Mass loss of two Pt/C commercial catalysts vs
  3M proprietary catalyst and support system

Pt/C1: wt % loss = 4.133 %
Pt/C2: wt % loss = 1.356 %
versus
3M catalyst/support: wt % loss = 0.0064%



* 3M catalyst support appears more stable for hot (120 - 150ºC), dry operating conditions

* Fuel cell tests at 120 ºC show no loss in surface area over 90 hours of test.

Subcontractors and National Laboratory Interactions

Advanced Catalysts: Fundamental Understanding and Characterization

- U. of Illinois, Urbana (A. Wieckowski) - Subcontractor

Use electrochemical, isotope labeling, NMR and infrared spectroscopy

- Brookhaven National Laboratories (J. McBreen)

EXAFS, XANES characterization of 3M PtAB catalysts

- Lawrence Berkeley National Labs (P. Ross, N. Markovic)

Catalyst-anion interaction effects

Advanced Catalysts: Combinatorial Fabrication

- Dalhousie University (J. Dahn) – Subcontractor

Utilize existing combinatorial materials science capability at Dalhousie University to produce and characterize a wide spectrum of ternary metals for use as electrocatalysts.

Advanced Membranes: Fundamentals

- U. of Minnesota (W. Halley) – Subcontractor

Theory and simulation studies for non-aqueous membrane based proton conduction

- CWRU (T. Zawodinski) – Subcontract being established

Fundamental experimental studies of proton transport in liquid and solid proton conductors

MEA Modeling:

- U. of Miami (H. Liu) - Subcontractor

Extend existing 3M/U. of Miami developed MEA model to determine electrode, gas diffusion and flow field properties required for durable operation under enhanced operating conditions.

Air Management:

- Vairex, Inc. – Subcontractor

Understanding and development of an air management system designed for optimized performance of MEA's operating under hot, dry conditions.

Plans and Future Milestones (through 2003)

* Continue to execute the current plans for Tasks 1, 2 and 3 as discussed;
  - continue materials development and screening
  - incorporate into integrated catalyst coated membranes
  - robust fuel cell testing and evaluation
  - optimization of gas diffusion layers, flow fields and operating conditions

* Accelerate interactions with subcontractors