DOE Hydrogen and FC Program Review

"Integrated Manufacturing for Advanced MEAs"

June '05 through May '06

DE-FC04-02AL67606

Yu-Min Tsou

E-TEK division,

PEMEAS Fuel Cell Technologies

(Formerly of De Nora N.A., Inc.)

May 2006

This presentation does not contain any proprietary or confidential information

FC18

Overview

Timeline

- Project start: 1 Oct '01 (2 Jan 02)
- Project end: 30 August '06
- Hi T membrane extended Oct 05
- Percent complete ~95%

Budget

- Total project funding:$19.5M
  - DOE : $14.5M
  - Contractors: $5M
- Funding Received FY05: $3.35M + $1.53M **cost share**
- Funding for FY06: $1.61M + 0.86M **cost share**

- **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®

2005/2006 Objectives

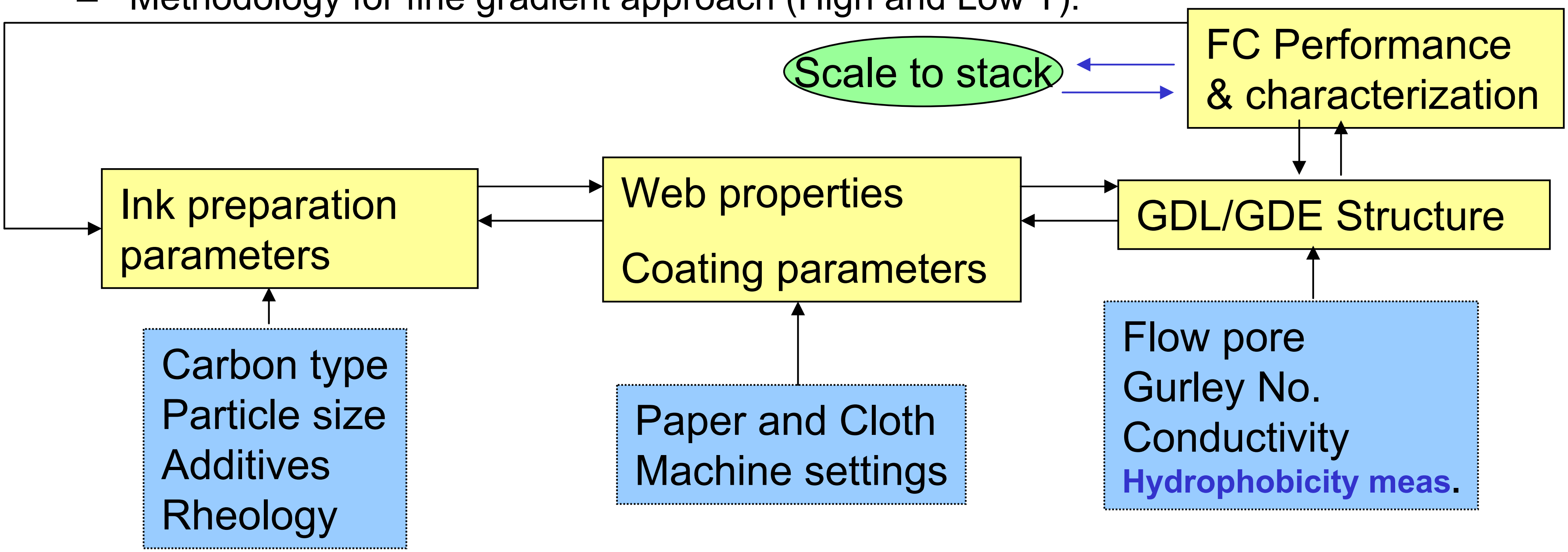
- **1A1**: cited performance at 0.4mg/cm^2 using fg-ELAT: transfer to machine fabrication: continue to lower PM, develop high temp interface for A2 materials
- **1A2**: single cell testing of HT membrane, evaluate properties at <0°C, scale up of advanced membranes
- **1A3**: scale-up of 1A1 components;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

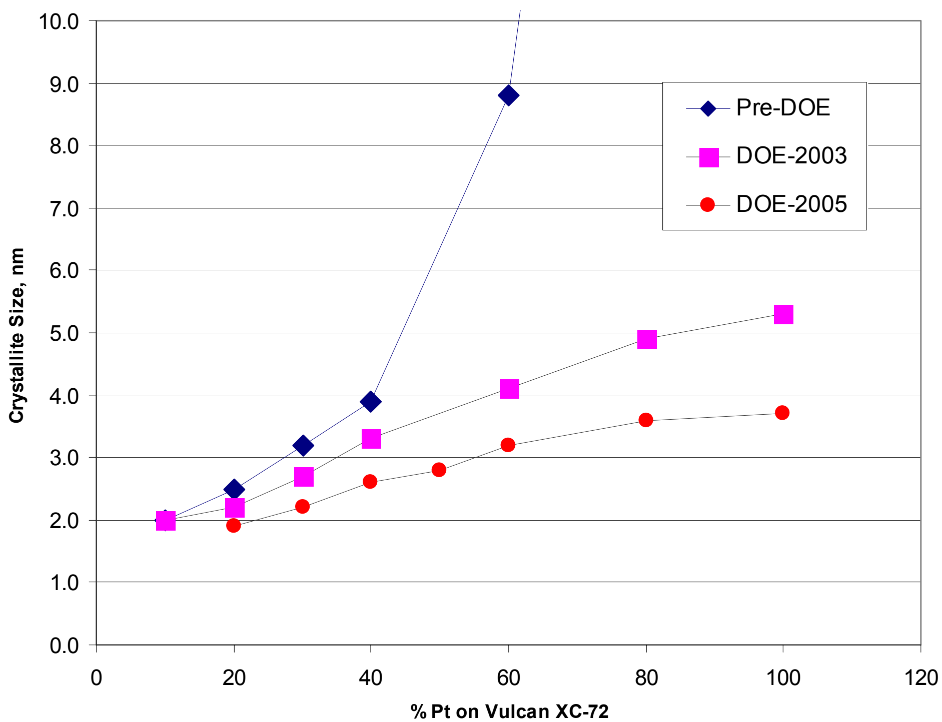
Approach: Catalyst and Fine Gradient ELAT®

- Catalyst: create structure-function relationships supported by Reitveld analysis of XRD patterns; develop/optimize new prep methods for catalysts and alloys: scale-up complete Oct 2005
- 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 lowering PM loading, designing structures for high temperature membranes and low RH
  - Methodology for fine gradient approach (High and Low T):



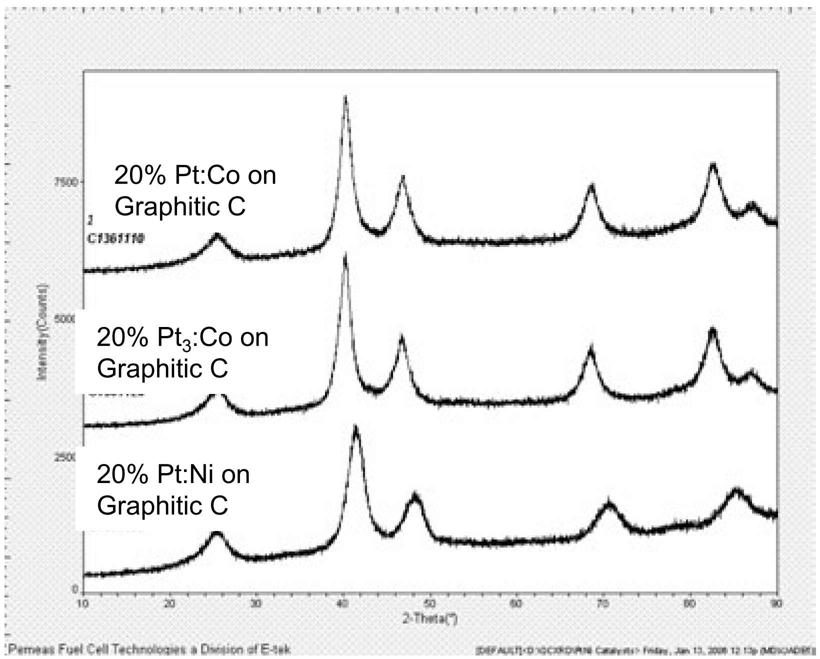
Catalyst Activities: Optimize Chemistry & Scale Up

Pt on Vulcan XC-72

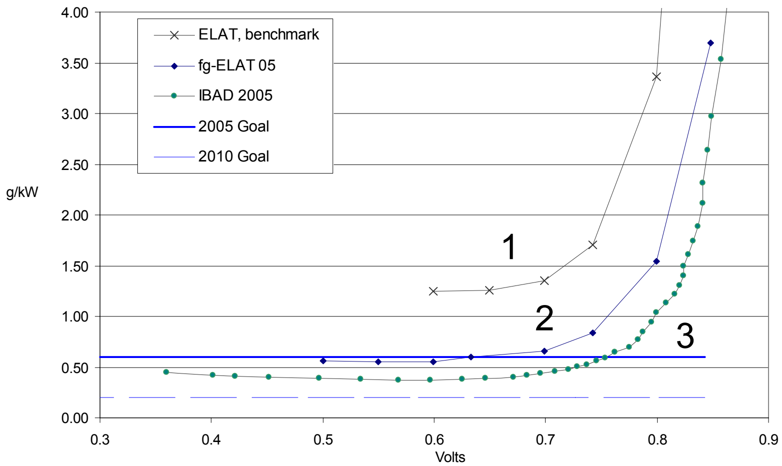


- On the path to scaling up alloys, we optimized the chemistry and can now produce smaller Pt crystallites – essential for creating uniform alloys that typically need high temperatures to form
- This feature may be useful in future efforts to make more durable alloys on graphitic lower surface area supports

Alloys on 80m²/g graphitic carbon
Crystallite range 3.0-4.5nm



Fine Gradient ELAT: Summary of Progress



Total Pt loading
ELAT benchmark (1): 1mg/cm^2
fg-ELAT(2): 0.39mg/cm^2
IBAD/ELAT(3): 0.17mg/cm^2

Overview 01--04

Have demonstrated FG approach to realize alloy activity over wide range of operating currents

Confirmed the approach for reducing PM load while maintaining power, for example 0.05mg/cm^2 Pt on anode w/o voltage loss at stack scale

Have shown scaling to stack level

Have created FG structures with continuous coating machine

This Period 05--06

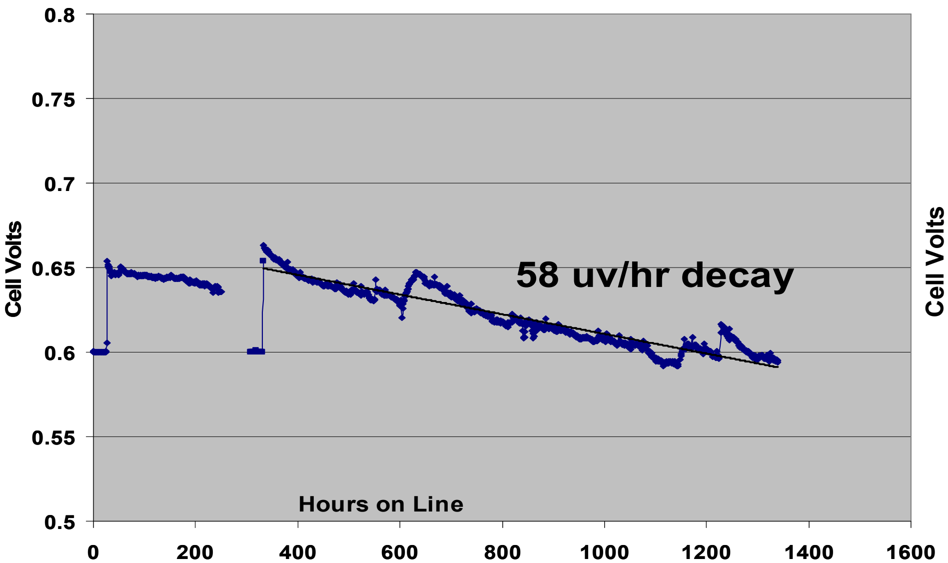
Have modified designs to decrease performance degradation due to flooding

Have investigated structures that show improved performance over lower %RH (part of high temperature goal)

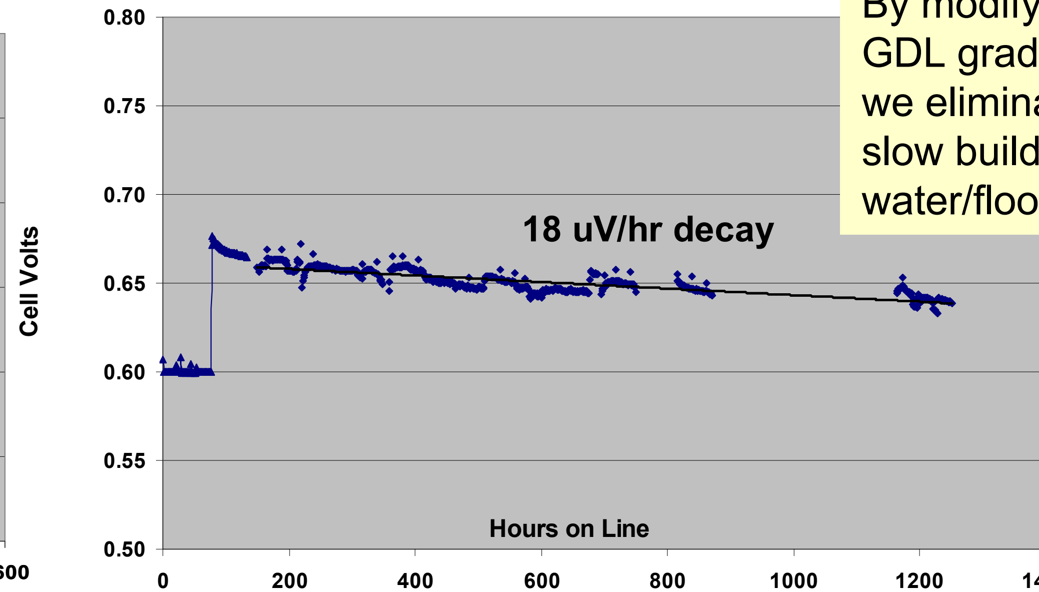
Machine-made stack scale components with 0.35 mg/cm^2 total PM have been submitted to Nuvera for testing (Program end-goal)

Fine gradient ELAT: lifetime and operation at low %RH

Baseline Gradient

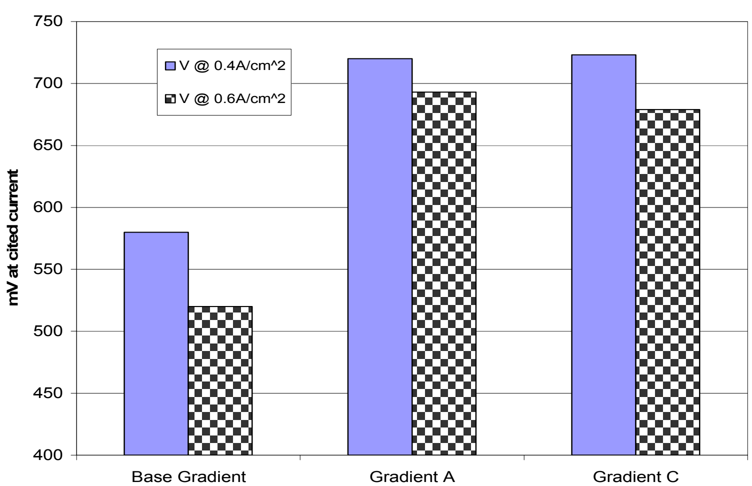


Modified Gradient



By modifying GDL gradient, we eliminated slow build-up of water/flooding

1) Constant current (0.6A/cm²), 70 deg C, 150kPa (1.5ATM A), fully humidified
2) 1mg Pt/cm² total
3) "slow accumulation of water: inferior water elimination from GDL"
4) Changing GDL gradient increased water ejection

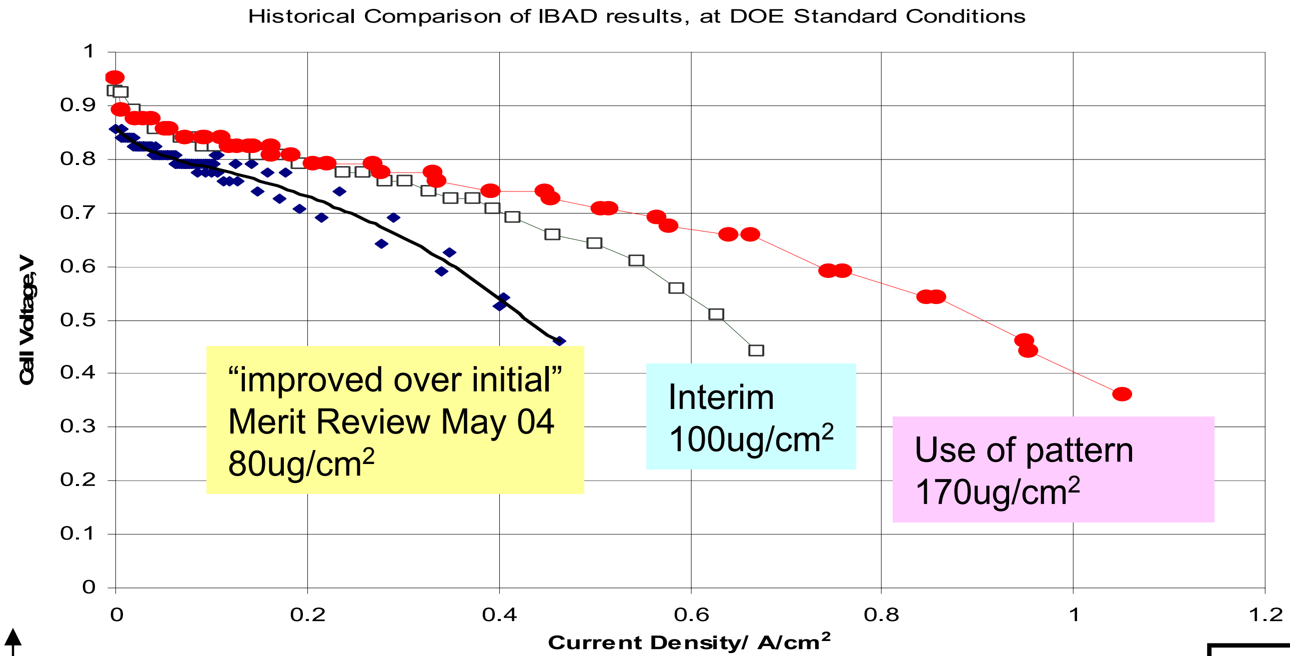


Development of GDEs for DuPont high temperature membranes: operation at lower %RH (interim results)

Have modified gradient to retain water in the electrode layer. Improvement of ~>100mV under test conditions

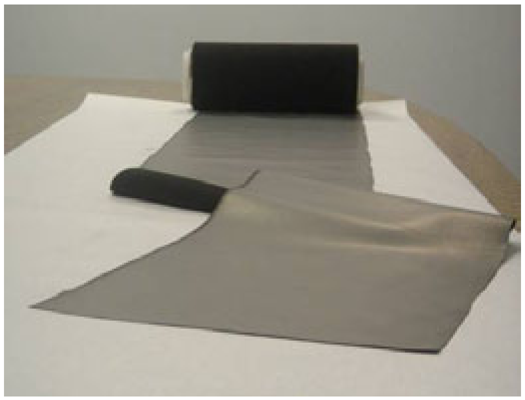
[70 deg.C, inlet %RH=50 at anode and cathode, H_2/air, 1.5/2.0 stoich, 1mg/cm² total Pt, Nafion® 112]

IBAD: ion beam assisted deposition



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

Significant gains in performance realized through new cathode structures created by using a pattern approach and the ion beam.



Roll-to-roll ion beam coating of Pt on ELAT GDL, standard gradient

0.08mg/cm², 30 linear meters, Pt variation <+/-3%

Summary 01-04

- Demonstrated lowest level of Pt for MEAs, approaching 2010 g Pt/kW goals
- Identified the pattern approach to substantially decrease mass transport losses in cathode, although needs further improvement
- Established feasibility of using thin films of Pt and cobalt to create catalytic surfaces

Summary this Period

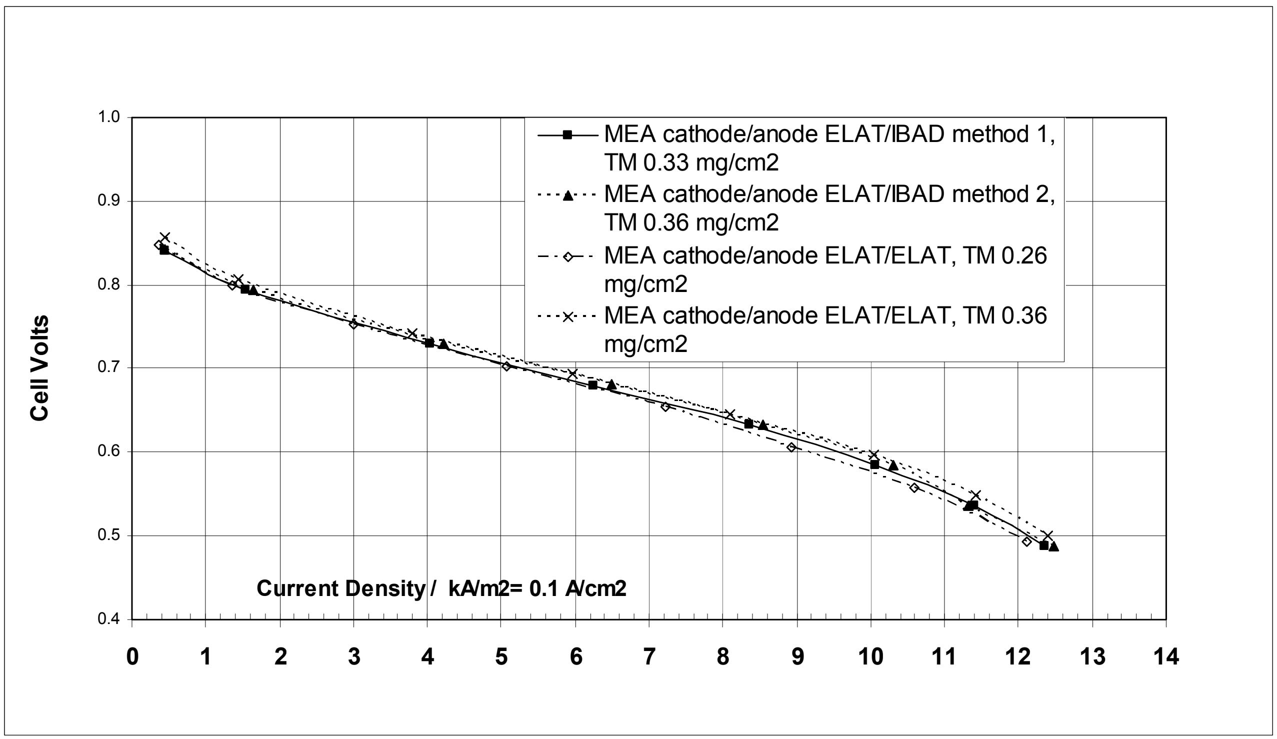
- Analytical (XANES) characterization indicates IBAD Pt or Pt:Co more stable than supported catalysts
- Membrane damage studies show IBAD structures produce less degraded membrane compared to supported catalysts
- Demonstrated roll-to-roll ion beam coating
- Showed feasibility for operating IBAD assemblies at 120 °C
- Established IBAD Pt anode operating in Nuvera FC Stack with good durability

IBAD: kinetics and use as anode

MEA Assembly	Total PM mg/cm²	A/mg Pt at 900mV	uA/cm² at 900mV
IBAD250	0.08	0.894	2,250
IBAD550	0.16	0.748	2,946
IBAD750	0.32	0.702	3,154
DOE 2005(stack)	0.7	0.3	600
DOE 2010(stack)	0.3	0.44	720

(O_2, >10 stoich, 80 deg C, Cat. Surf. Area via H_2 wave, 900mV IR free)

- IBAD assemblies show good ECSA, ranging from 22m²/g to 40m²/g
- Have demonstrated excellent activity: key challenge is to decrease mass transport limitations on cathode

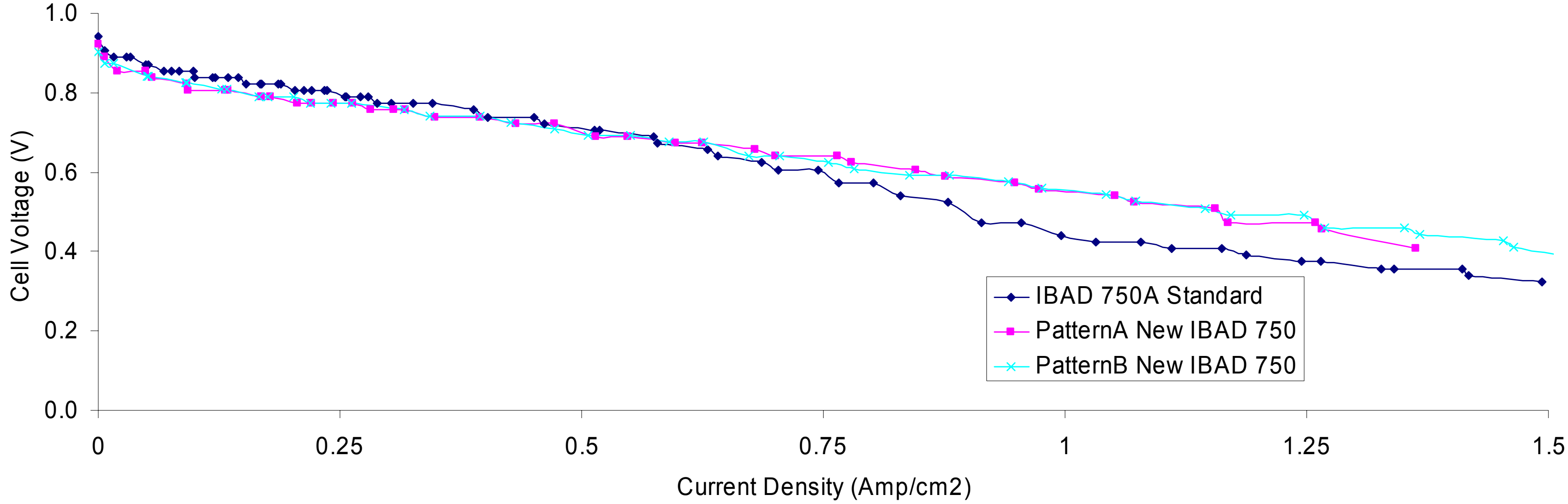


Polarization Curves for MEAs with IBAD (method 1 and 2) as anode and E-TEK ELAT as cathode. 70 deg C air/H_2 0.5/0.5 bar a

IBAD anode/conventional cathode
MEA configuration is a viable candidate for future MEA with durability

Pathway to achieve low PM and Hi T MEA

IBAD750 (~0.32mg/cm^2 total) or IBAD Pattern A/B (~0.24mg/cm^2) 120deg C, saturated, 250kPa (2.5atm) Nafion® 112



- Confirmed that low precious metal IBAD MEAs can approach DOE goals at higher temperatures
- *Since IBAD assemblies do not use ionomer in the interface, they are especially well-suited to high temperature membranes*
- Will be mating IBAD assemblies to the high temperature membranes of the Du Pont program in going forward
- Will also continue to develop electrodes that operate over lower RH, and mate these to Du Pont membranes

Nuvera Fuel Cell: program revised to shift team resources to membrane development

Nuvera role in the program:
Validate innovative components in full area stacks to meet DOE performance and longevity targets

- **Reduce efforts to design and deliver fuel cell stacks**
  - Focus on fundamental materials and qualification needs
- **Emphasize development of qualification test methodology**
  - To support accelerated life testing, a key industry priority
- **Program execution timeline is extended throughout Q3 / 2006.**

NUVERA SHORT STACKS WITH ETEK MEAs

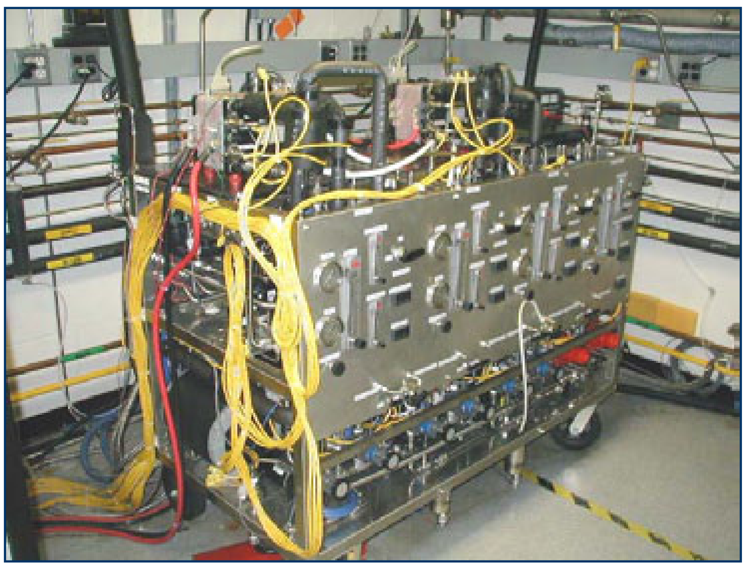
Stack # in the order of testing	Production date	ETEK materials utilized	Number of cells in the stack	Total test hours
1	April, 2003	Nafion based, Std. Elat, New catalyst, new cloth, new config/structure	20	284
2	October, 2003	std MEA,LA-MEA, Comp-MEA, CompLL2A-MEA, CompLL-MEA, CompACR-MEA, CompLL2B-MEA,	19	24
3	April, 2004	std MEA 0716, CompAC, MEA-SBK, LA-MEA0716, CompILML(1B)-MEA, MEA-SP1118, CompILML(1B)-LA_MEA, LCLA-MEA	21	299
4	July, 2004	standard MEAs	4	10
5	July, 2004	LA1HMEA1118	7	40
6	July, 2004	LA3LMEA1118	7	34
7	Jan, 2005	Nafion based MEA	5	1116
8	Dec,2004	ABL-1104-LA-MEA-0429	2	164
9	Oct, 2005	MEA0905std230	4	
10	Oct, 2005	MEA0905AB Low Pt loading MEAs	4	1324
11	Nov, 2005	MEA0905AB	4	40
12	Feb, 2006	Std S12, Alloy, IBAD, FG	8	24
			Total	3359

- 12 stacks assembled and tested for performance
- 5 stacks tested for longevity
- 2 stacks passed 1000 hr durability test
- Low Platinum loading stack passed 1300 hr durability test

STACK TESTING INFRASTRUCTURE

Full active area single cell and short stack testing facility

Electrochemical diagnostic cart

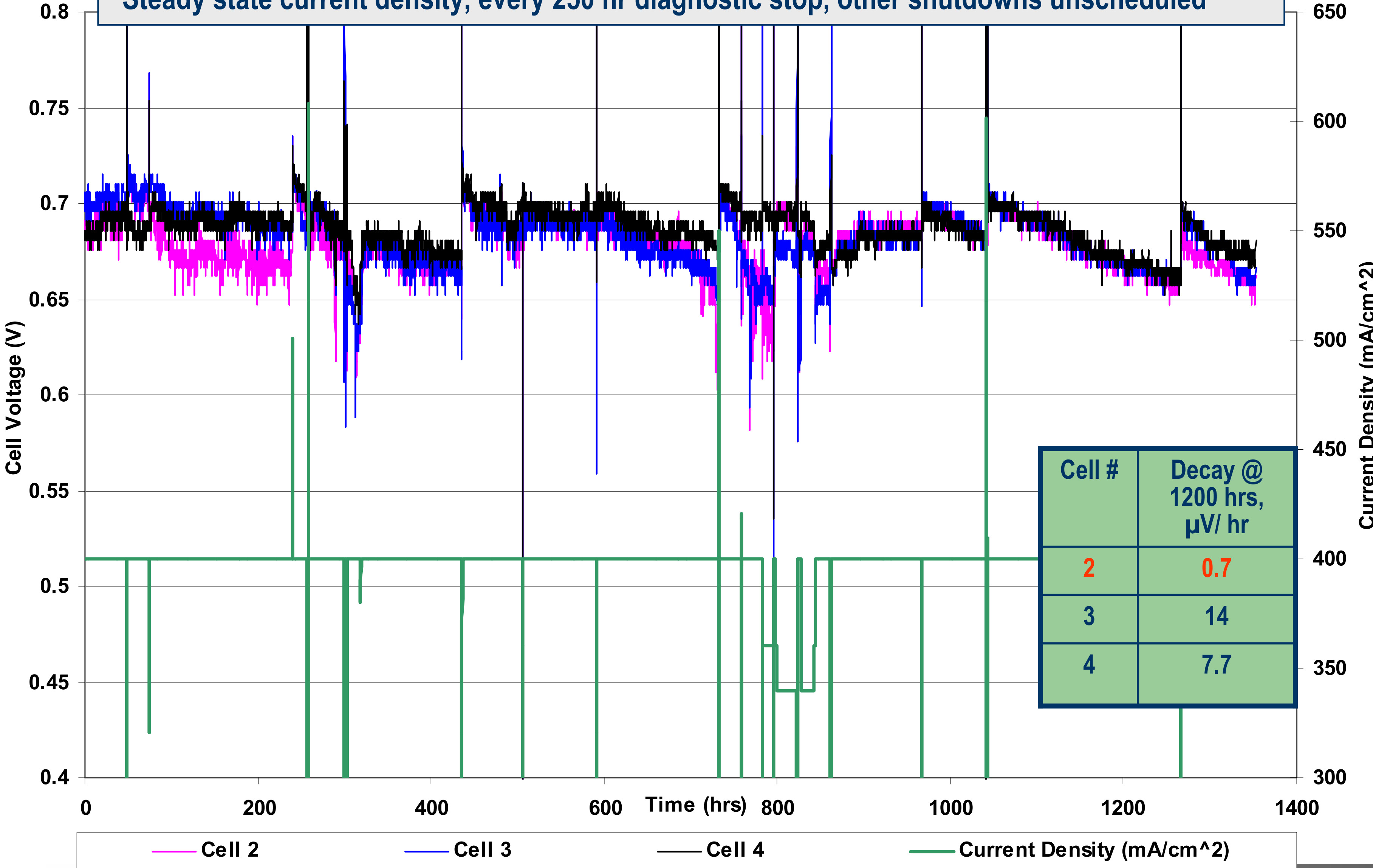


Multi Channel Test Stand : Short Stack Testing

Low Platinum Loading Stack Durability

XDS technology by Nuvera. 2.5 ata, 70 C, 2.5/2.5-3.5 AS/CS. Points every 10 minutes.

Steady state current density, every 250 hr diagnostic stop, other shutdowns unscheduled



Cell #	Decay @ 1200 hrs, μV/ hr
2	0.7
3	14
4	7.7

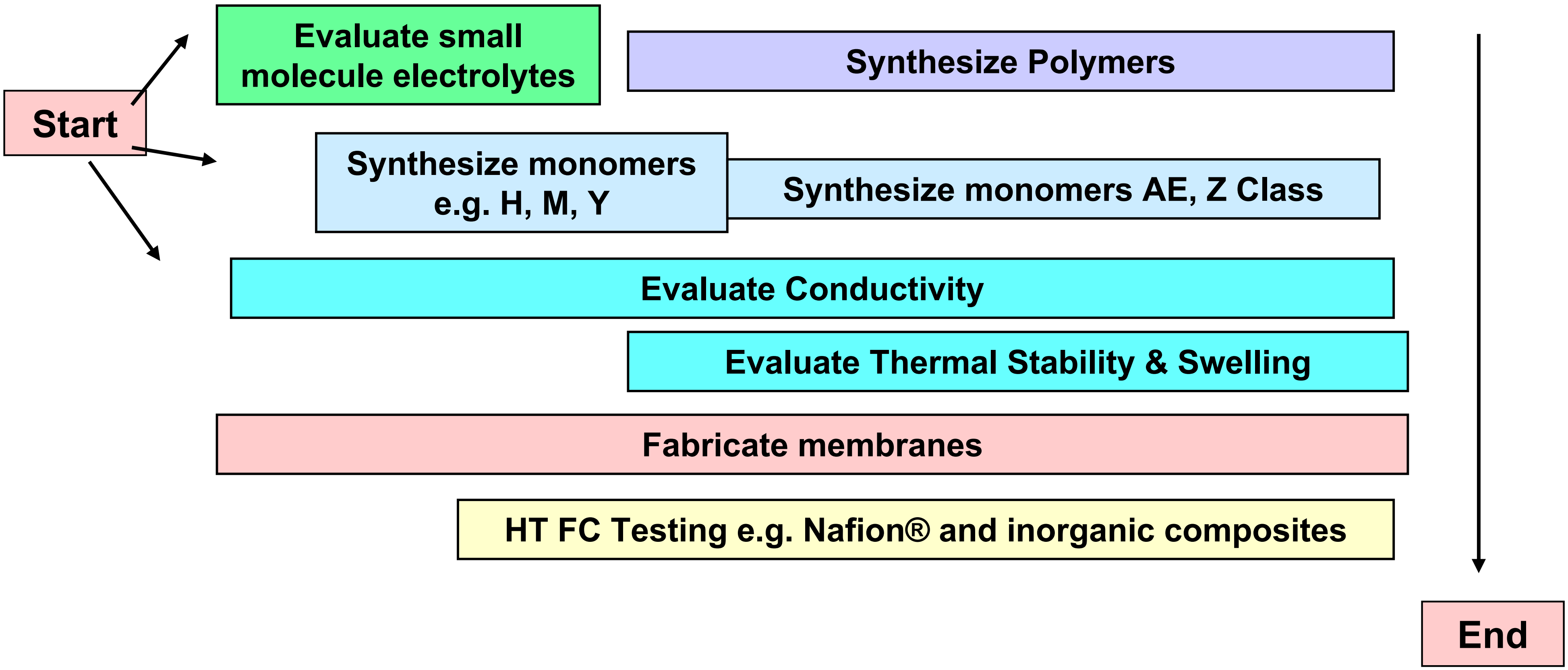
Cell 1 is excluded due to low performance

NUVERA

SUMMARY

- Nuvera evaluated ETEK innovative fuel cell components in 225-, 250- and 500-cm^2 active area stacks both for performance and durability.
- LA1H and LA3L MEA1118 materials by ETEK achieved DOE target voltage 0.85V at 100 mA/cm^2 current density in Nuvera 225cm^2 short stacks.
- Low Platinum Loading MEAs by ETEK demonstrated low decays in 1300-hr durability test in Nuvera short stack.
- Stability of ETEK catalyst is confirmed by in-situ electrochemical diagnostics and by post-mortem analysis.
- Advanced testing, accelerated and diagnostic infrastructure and protocols are developed by Nuvera within the program scope.

Program 1A2: High Temperature Membrane General Approach



Program ended Dec 2005: next generation materials have been sent to E-TEK for making into MEAs and testing at high T/ low RH

AE (& Derivative)-Type Polymer Electrolytes

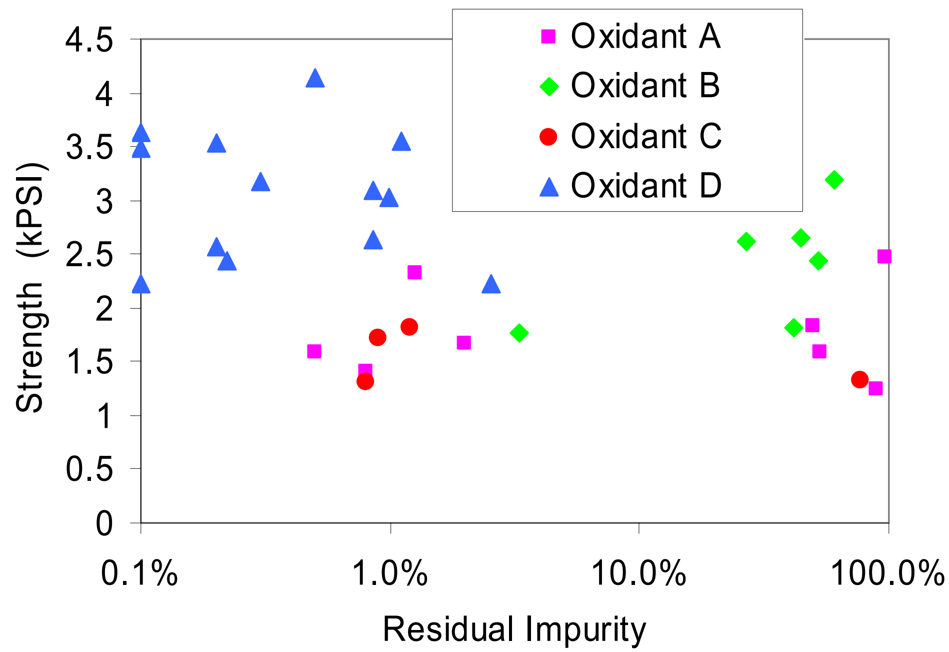
- New polymerization chemistry for AE-type electrolyte
  - Film forming M_W finally obtained with three new polyelectrolytes synthesized in 2Q05-4Q05.
- Thermal stability only with BP
- Initial results: Low-RH conductivity is anisotropic, but higher than Nafion® in the desired direction.
- DuPont continuing to work towards lowering the swelling and further increasing conductivity.

Candidate	M_w	Solubility	Thermal Stability; Rate of wt. loss @150 °C %/hr	Conductivity at 120 °C or at 80 °C denoted with*			
				in-plane		through-plane	
				95%RH	25%RH	95%RH	25%RH
AE	est 8,000	Soluble at 22 °C	0.025			700	73
BL	100,000	Insoluble 22 °C, Soluble 100 °C	0.47	440-460*	0.2*	360-400*	17* 16
BN	62,000	Soluble at 22 °C	0.41	390	0.2		
BP	84,000	Insoluble 22 °C, Soluble 100 °C	0.0084	450	5*	405	16* 5

BA Membrane: front runner new material

outstanding conductivity for dry and sub-freezing conditions

- Previous
  - Synthesis requires oxidation of a functional group
  - High thermal stability for BA membrane only obtained for polymer with low levels of un-oxidized residual impurity.
- 2nd half 2005
  - Investigated alternative oxidants
  - Desire a better combination of activity and selectivity.
- Membranes using Oxidant D delivered to E-TEK
- DuPont is pursuing this membrane on their own
  - Lower-cost fabrication process
  - Demonstrate/Improve durability



Membrane Program Accomplishments

Candidate	Conductivity @120C, 25%RH (mS/cm)	Thermal Stability; Rate of wt. loss @150C %/hr	Water Swell
NR111	11	0.007	50%
AE	73	0.025	soluble 22 °C
AK	156	2.3	soluble 22 °C
BL	16	0.47	insoluble 22 °C, soluble 100 °C
BN	0.2	0.41	soluble 22 °C
BP	5-16	0.008	insoluble 22 °C, soluble 100 °C
AO	17-31	16.	70%
BG	0.4	0.056	25%
BA	15-30	0.009	55%
AF	40	0.31	soluble 22 °C
BB	80	30.	soluble 22 °C

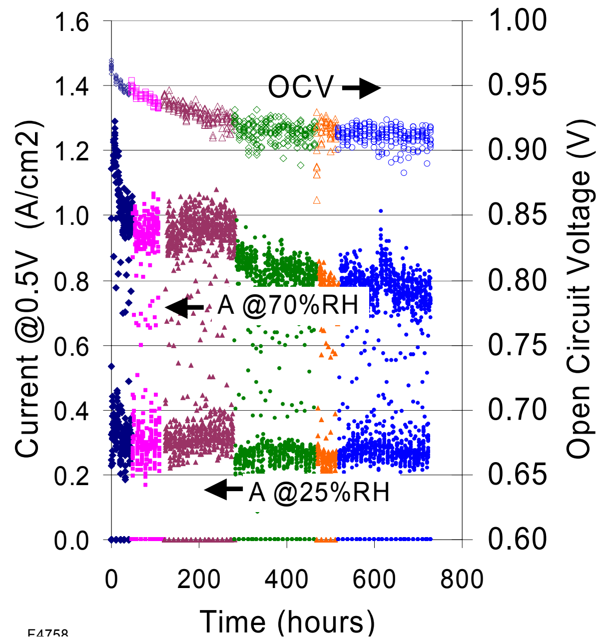
Status at start in 2001: No PEM (except PBI/PA) has low-RH conductivity above Nafion®. Limited durability @120 °C.

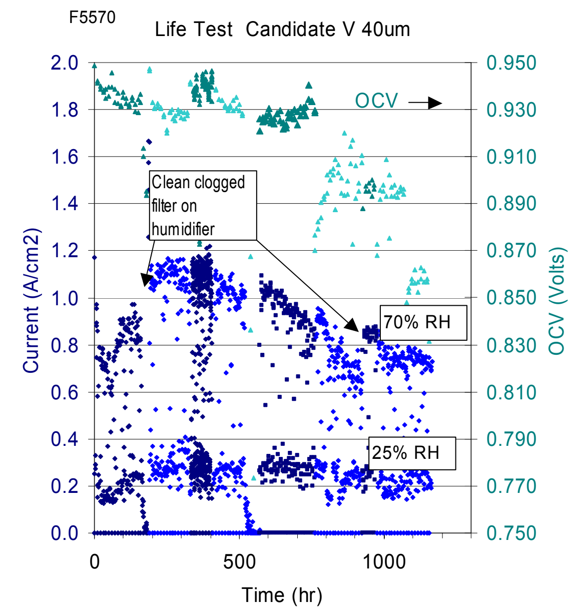
Record(?) conductivity for polymer electrolyte with covalently bound acid.

Two new polymer electrolytes also have thermal stability similar to Nafion®. These are being developed further.

High Temperature Durability

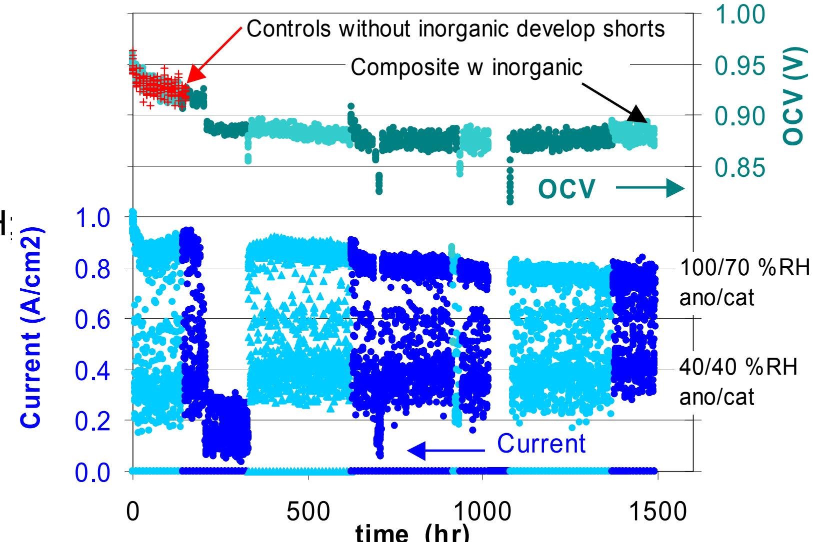
- Candidates V and AV are Nafion®/inorganic composite membranes
- Properties similar to Nafion®:
  - Conductivity, strength, swelling, H_2 permeation
- Properties superior to Nafion®:
  - Fenton test chemical stability
  - Lifetime in FC
- **Demonstrated 700 to 1500 hr at 120 °C, including cycling to only 25% RH.**





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

AV memb to right. 30 psig
2) 5hr 0.5V 100/70 %RH
3) 5hr 0.5V 40/40 %RH
Symbol color change are station restarts after „crash"



FC18 E-TEK / Du Pont / Nuvera

Future Work

- **Key Milestones have been met or exceeded during this period**
  - **We have exceeded target kinetic activities for the IBAD system, showing promise for 2010 goals**
  - **The Du Pont team has identified polyelectrolyte systems greatly exceeding Nafion benchmark at both subzero and high temperature/low RH**
- **Remaining milestones include operation of a short-stack using MEAs derived from low RH/high temperature materials or demonstration of a stack meeting DOE power goals with 0.3mg/cm^2 total PM. We will address these milestones by:**
  - **Reducing PM loading to 0.3mg/cm^2 through a combination of IBAD anodes and fine gradient cathodes;**
  - **Construct high temperature MEAs using Membrane V and Membrane BA; if Membrane V assemblies approach DOE goals, construct stack scale fabrications and submit to Nuvera for validation and additional lifetime studies**
    - **Will use fine gradient ELATs, IBAD, or a combination of both**

Summary

- *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*
  - *Assemblies approaching 0.3mg Pt/cm^2 being evaluated by Nuvera*
- The fine gradient approach has led to successes in lowering PM without a loss in power, greater ability for water elimination in the GDL, and with the proper design, greater water retention in the electrode for operation in dry conditions
- Roll-to-roll Ion beam deposition demonstrated that the technology is ready for use in commercial anode structures. There is a further cost savings in the elimination of ionomer. Preliminary data for IBAD cathodes indicates greater stability compared to supported catalyst. Our strategy for introducing designed structures ("patterns") shows a path to improve mass transport although additional work on GDL design matched to IBAD structures is needed
- Du Pont has developed several new classes of polyelectrolytes that exceed the benchmark Nafion in conductivity at low RH and high temperature: these materials represent enough of a significant advance to justify Du Pont's further pursuit of membranes with these materials beyond the term of this project

- The success of this program is due largely to close collaborations between the industrial partners (Du Pont, Nuvera, E-TEK) and academic teams providing key guidance through fundamental supporting activities (Northeastern University, Case Western Reserve University). Numerous publications and patents have resulted from this effort

Acknowledgements

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- Kartikeyan Ramamoorthi (Ph.D. candidate)

Spire Biomedical

Nadar Kalkhoran, Ph.D.
Jason Burns

NFC

Olga Polevaya
Stack Testing Team

DuPont

- Mark Roelofs, Ph.D (Project Leader)
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- Zhen-yu Yang, Ph.D.
- Rosa Ruiz-Alsop, Ph.D.
- John J. Borowski
- Robin Blackburn
- David Lilly
- Charles Wheeler

Case Western Reserve U.

- Prof. Morton Litt
- Casey Check (Graduate Student)

Responses to Reviewers

- Recommend serious focus on transition to continuous IBAD coating
  - *Have shown an example in this presentation*
- More durability work
  - *We delayed durability efforts until we identified systems that could approach DOE power/precious metal goals*
  - *We have increased our efforts, and have shown here a summary of IBAD durability, some preliminary approaches to more graphitic supported catalysts, and some efforts on changing the fine gradient to handle water ejection more effectively under flooding conditions*

Publications and Presentations

By CWRU

- V. Gurau M. Bluemle,Jr., E. S. De Castro, Y. M. Tsou J. A. Mann T. A. Zawodzinski : "**Characterization of Transport Properties In Gas Diffusion Layers for PEMFCs 1. Wettability (Internal Contact angle to water and surface energy of GDL fibers)",** *Accepted in Journal of Power Sources, 200*

By NEU

- "**High performance polymer electrolyte fuel cells with ultra-low Pt loading electrodes prepared by dual ion-beam assisted deposition**." - M. Saha, A. Gullá, R. Allen, S. Mukerjee; *Electrochimica Acta*, 2006
- "**Towards Improving the Performance of PEM Fuel Cell by Using Mix Metals Electrodes Prepared by Dual IBAD**." - A. Gullá, M. Saha, R. Allen, S. Mukerjee; *Journal of the Electrochemical Society*, 2006
- "**Dual Ion Beam Assisted Deposition as a Method to Obtain Low Loading-High Performance Electrodes for PEMFC's**." – A. Gullá, M. Saha, R. Allen, S. Mukerjee; *Electrochemical and Solid-State Letters*, 2005
- "**Enhancing the Performance of Low Pt Loading Electrodes Prepared by Dual Ion Beam Assisted Deposition in PEM Fuel Cells**." - A. Gullá, R. Allen, M. Saha, S. Mukerjee; presented at the 208th Symposium of the Electrochemical Society in Los Angeles, CA 2005
- "**Peroxide Yield on New Materials for Oxygen Reduction in Acid Media**" - A. Gullá, R. Allen, C. Urgeghe, Y. Garsany, S. Mukerjee; presented at the 207th Symposium of the Electrochemical Society in Quebec City, Canada 2005
- "**High Performance of Electrode with Very Low Pt Loading Prepared by Dual Ion-Beam Assisted Deposition in PEM Fuel Cells**" - A. Gullá, R. Allen, M. Saha, S. Mukerjee; presented at the 207th Symposium of the Electrochemical Society in Quebec City, Canada 2005

By E-TEK

- Emory S. De Castro, Yu-Min Tsou, Lixin Cao and Chien Hou **"New ELAT Interface Designs through Manufacturing Practices",** Fuel Cell Seminar, Palm Springs, Nov, 2005
- Y. Tsou, L. Cao, E. De Castro, "**Factors Affecting Activities of Nano-sized Fuel Cell Catalysts and Diagnosis Methods**", 208th ECS Meeting LA Oct , 2005, abstract# 907
- (3) Y. Tsou, E. De Castro, Chien Hou, Zhiyong Zhu, "**Impact of Machine Coating GDE/MEA on Commercialization of Fuel Cells or Electrolyzers**, 208th ECS Meeting LA Oct , 2005, abstract#1025

Critical Assumptions and Issues

- **IBAD Cathodes**: full implementation of IBAD MEAs will rest on improving mass transport for cathode side. Throughout this program, we have used standard configuration GDLs and believe efforts at designing GDLs for the unique IBAD interface can overcome this limitation
- **High Temperature Stack Operation** (100-120 deg C, low RH): We had assumed basic materials and geometries developed for low temperature MEAs could be extended to high temperature assemblies. This has been shown to be otherwise. Hi T MEA could not be safely tested until gasket/sub-gasket/hardware issues are resolved.

  Currently looking into alternative materials such as gaskets as well as developing a sub-gasket system, which are critical in operating a stack under more extreme conditions