Development of High Temperature Membranes and Improved Cathode Catalysts for PEM Fuel Cells

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UTC Fuel Cells

DoE Agreement DE-FC04C-02-A1-67608
Program Manager – Amy Manheim

Project ID#: FC4

Objectives and Approach

Improved Cathode Catalysts

- Goals:
  - To improve power density
  - Lower cost, $/kW
- Approach:
  - Higher activity cathode catalyst systems: binary and ternary alloys. High loading of noble metal to decrease electrode thickness and achieve mass transport benefit

High Temperature Fundamentals and Membrane Development (100-120 C, 1.0-1.5 atm):

- Goals to improve:
  - Anode CO tolerance
  - Anode and cathode kinetics
  - System heat management
- Approach:
  - Collaboration with leading polymer chemists to develop new membrane systems: poly(arylene ether sulfone), PEEK, multiblock polymers and inorganic solid conductor filled Nafion®
  - Fundamental understanding of HT operation limitations and possible solutions through modeling and experimental work

Technical Barriers and Targets

- DoE Technical Barriers for Fuel Cell Components
  - P. Durability
  - Q. Electrode Performance
  - R. Thermal and Water Management

- DoE Technical Targets for Catalyst Coated Membranes

Characteristic	Units	Calendar Year		
		2002	2005	2010
Membrane Areal Resistance in cell, operating temperature	Ω-cm^2	0.1	0.1	0.1
Cost	$/kW	200	100	10
Operating Temperature	^oC	80	120(100)	120(100)
Durability	hours	1000	>4000	>5000
Total catalyst loading (both electrodes)	mg/cm^2	0.8	0.4	0.1
Performance @ 0.25 power (0.8V)	mA/cm^2 mW/cm^2	125 100	250 200	400 320
Performance @ full power	mW/cm^2	400	800	1280
Extend of performance degradation over lifetime	%	10	10	10

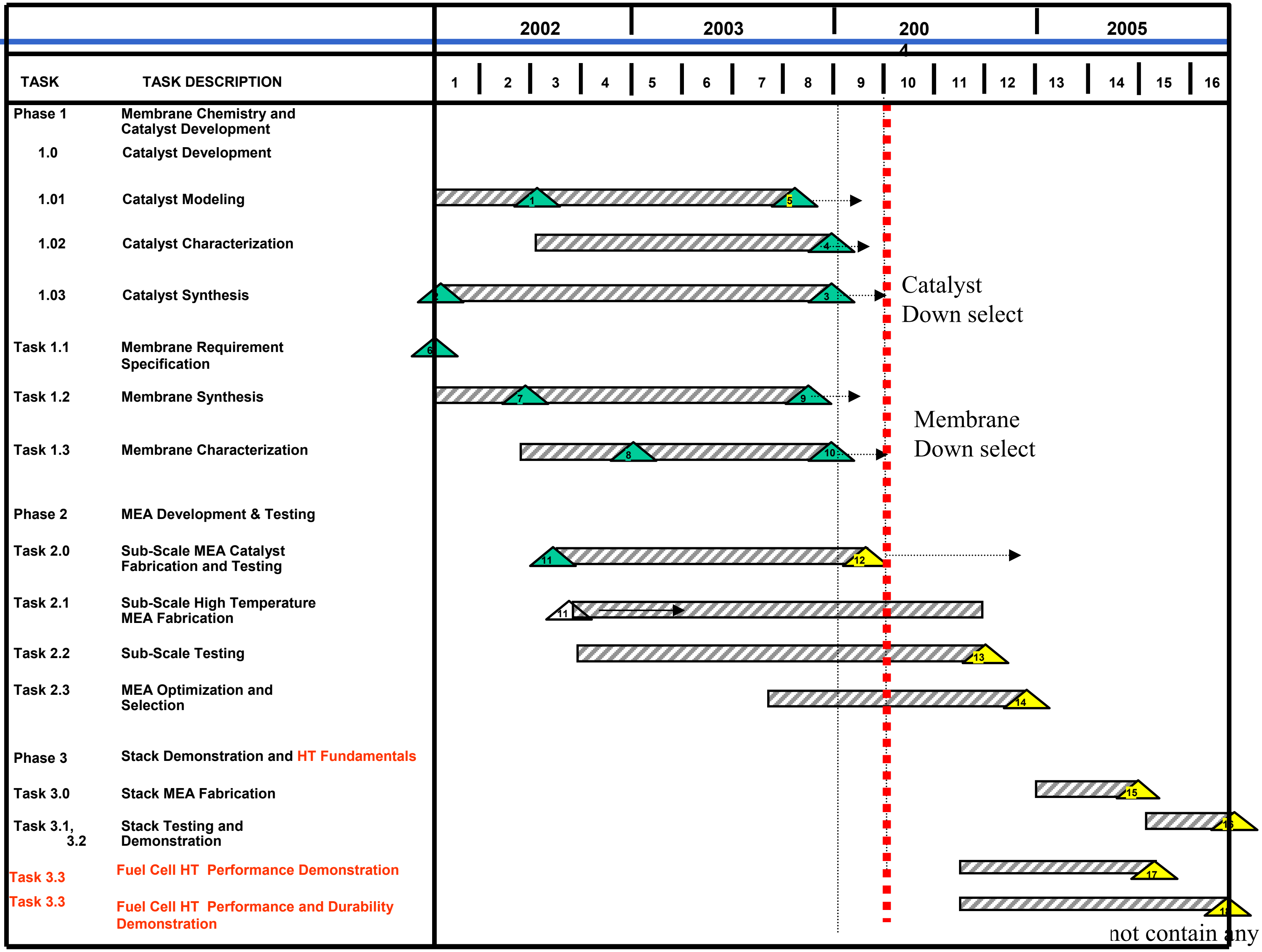
Budget and Partners

Year	Total $M	DoE $M	UTC $M
Overall Program 2002-2006	9.500	7.600	1.900
FY04 (actual)	2.983	2.387	.593
FY05 (planned)	1.875	1.500	.375

Program Team:

- **UTC FC** (Dr. L.Protsailo): general coordination, catalyst development, modeling, fuel cell testing, fundamentals and stack development
- **UTRC** (Dr. N.Cipollini): MEA optimization and fabrication
- **VaTech** (Prof. J. McGrath): membrane development, fundamentals of membrane architecture
- **UCONN** (Prof. J.Fenton/R.Kunz): membrane development, MEA fabrication, HT fundamentals
- **NorthEastern University** (Prof. S. Mukerjee): catalyst development, durability studies

Program Schedule



Program Milestones

PHASE	MILESTONE #	MILESTONE
Phase 1 Membrane Chemistry and Catalyst Development	1 2 3 4 5 6 7 8 9 10	Preliminary model completed Begin alloy synthesis Complete alloy synthesis Complete characterization and down-selection Complete modeling + correlation Membrane specification to team members Initial sample membrane Characterization of initial membrane samples Synthesis of final membrane samples Select membrane for Phase 2
Phase 2 MEA Development and Testing	11 12 13 14	Initial electrode fabrication Complete subscale testing for cathode catalyst and down-select catalysts Complete subscale testing for membranes and down-select membrane(s) Select optimum catalyst-membrane combination for Phase 3
Phase 3 Stack Demonstration and High Temperature Fundamentals	15 16 17 18	Complete stack and test stand assembly Complete stack verification test Fuel cell demonstration of the best performing high temperature materials Fuel cell demonstration of performance and durability best MEA materials for HT operation

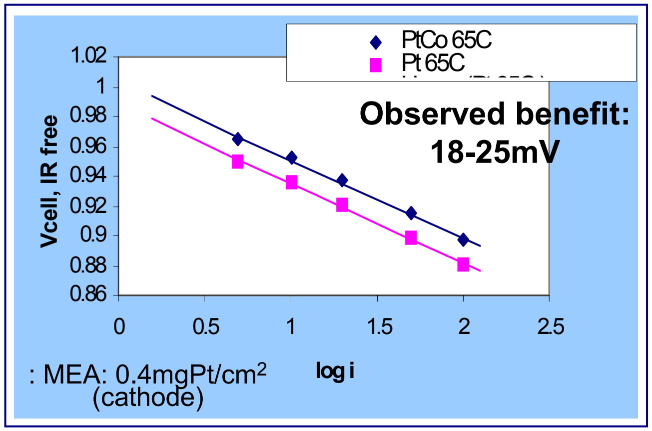
Project Safety

- Safety reviews of test equipment design and of test processes
  - Codes and Standards, Hazard Analysis, FTA, HAZOP
  - Readiness reviews required for major changes, new equipment and chemicals
- New Catalyst Preparation
  - Only low environmental impact reagents and materials are used = greater level of safety from reduction of chemical hazards and procedures
- Tests Safety
  - All testing is done in well-ventilated automated test stands
  - Hydrogen detection and emergency stop capabilities
  - Alarms
  - All test hardware for the program has been tested and evaluated in contractor safety review process
- No unusual safety issues have been encountered to date on this project

Responses to Previous Year Reviewers' Comments

- Q1. Insufficient emphasis on lower RH% requirements for HT operation
  - Emphasis is put on lower %RH. New design point 100^oC, 25% RH. Short excursions to 120^oC required.
- Q2. …research areas require more fundamental work
  …not direct sufficient fundamental analysis to each material regarding failure modes.
  - Significant emphasis has been put on fundamental analysis and understanding of HT operation issues – program re-scope in August 2004.
  - Direction toward fundamental analysis of failure modes - post-test analysis backed up by modeling work. Post tests include EMPA, XRD, fuel cell exhaust water analysis, post test of failed membranes – GPC, viscosity measurements, etc.
- Q4. The catalyst loading of alternative catalysts is not clear….Catalyst shows greater activity but Pt/C not plotted on durability or performance plots.
  - Direct comparison of alternative catalysts to pure Platinum with the emphasis on reduced loading benefit
- Q5. Need to investigate durability of alloys catalysts
  - Large emphasis on durability aspect of alternative catalyst – including electrode durability and its implications on membrane durability for wide range of operating conditions

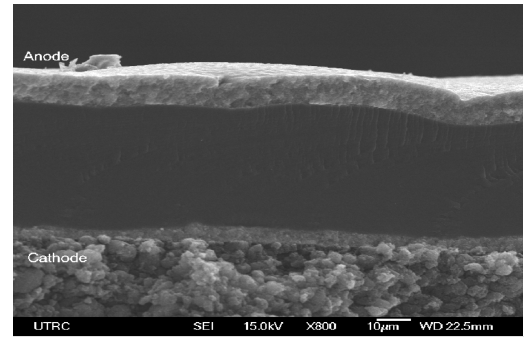
Technical Accomplishments:
Pt Alloys for Improved Performance PEM FCs

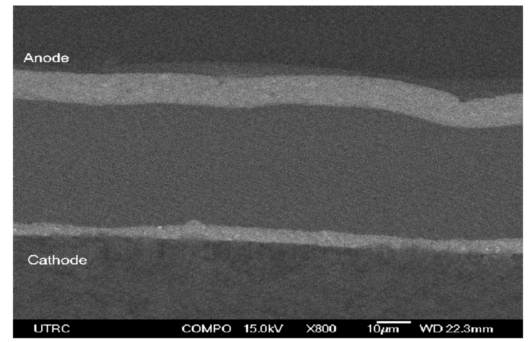


- **FC performance improvement**
  - Expected performance improvement for for $Pt_{75}Co_{25}/C$ and $Pt_{50}Ir_{25}Co_{25}/C$ systems (assuming TS=70 mV/decade):

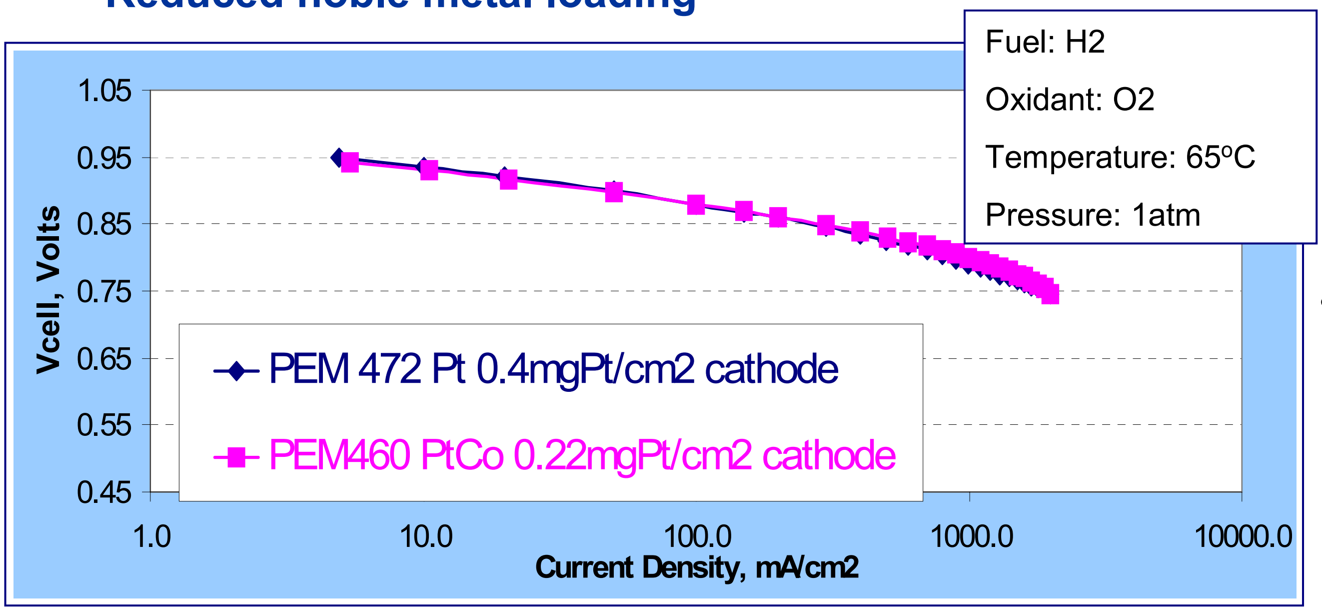
    PtCo – 20-28mV

    PtIrCo – 12-20mV





- **Reduced noble metal loading**



- ½ of Pt loading without sacrifice in performance is allowed with $Pt_{75}Co_{25}/C$ system

Technical Accomplishments:
Pt Alloys for Improved Durability of PEM FCs

- **Electrode Cyclic Durability: normal and HT operating conditions**

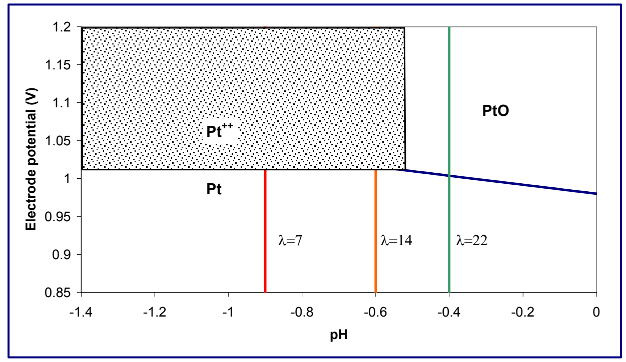
MEA performance in subscale fuel cell

Potential cycling test between 0.87V and 1.2V (1.05V for HT) for 2800cycles

Evaluate the performances/ ECAs every 400cycles

Tear down and do **EMPA and XRD analysis**

Pt stability in fuel cell environment

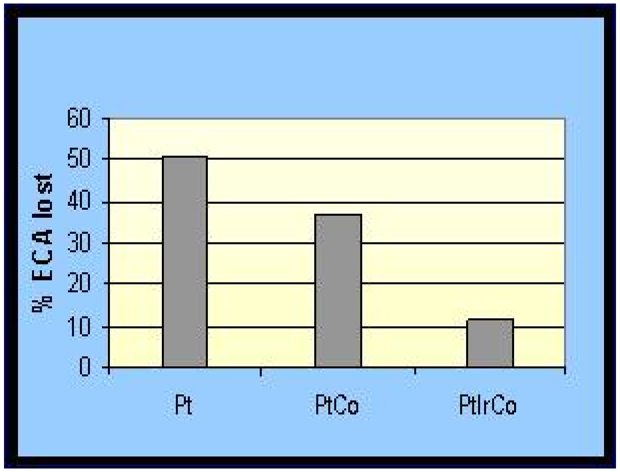


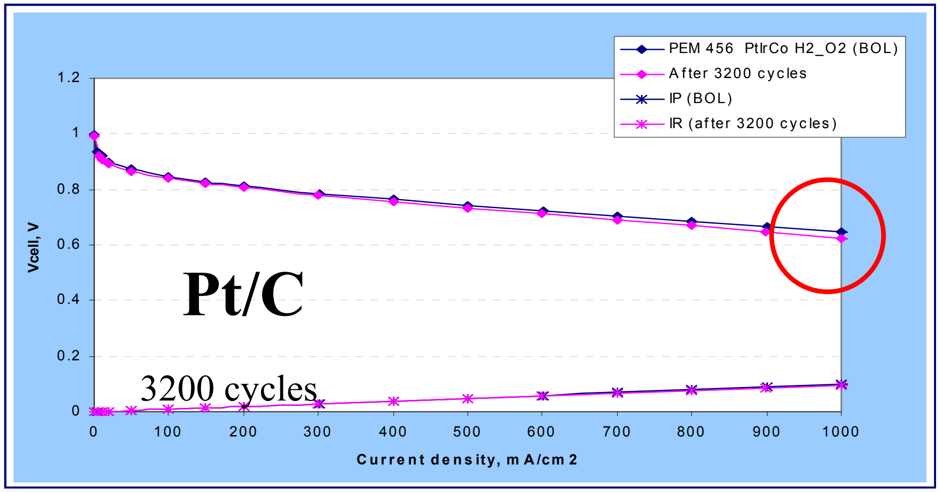
Pourbaix diagram [Pt++] = 10^{-6} M

- Membrane: Nafion® 112
- Anode: ~46% Pt/C, $0.4 mg_{Pt}/cm^2$
- Cathode: 45-49% Pt (Pt / $Pt_{75}Co_{25}$ / $Pt_{50}Ir_{25}Co_{25}$) supported on high surface area carbon (BET~$800 m^2/g$)

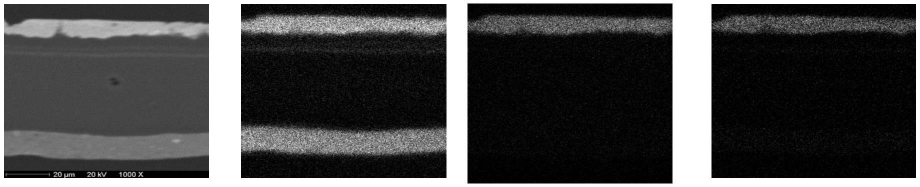
Technical Accomplishments: Pt Alloys for Improved Durability of PEM FCs – Catalyst Dissolution (65°C)

ECA reduction during potential cycling

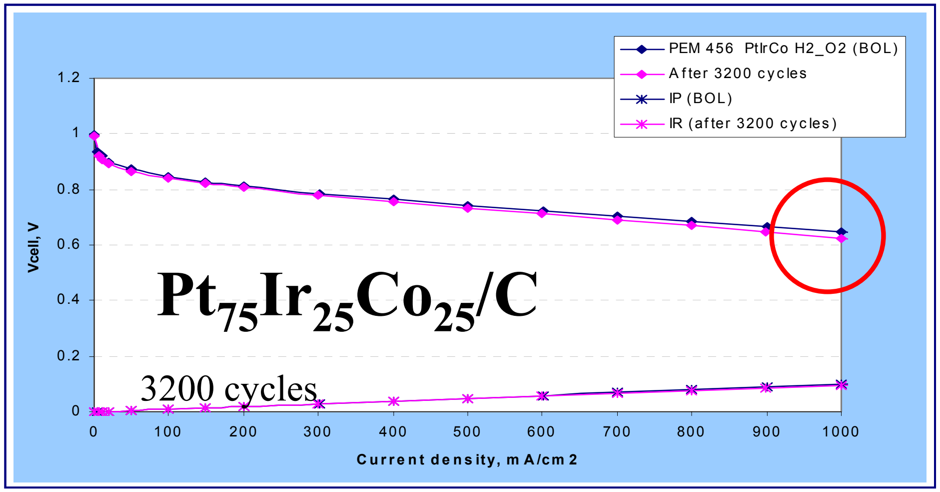




PtIrCo improves cathode durability **5x** that of Pt

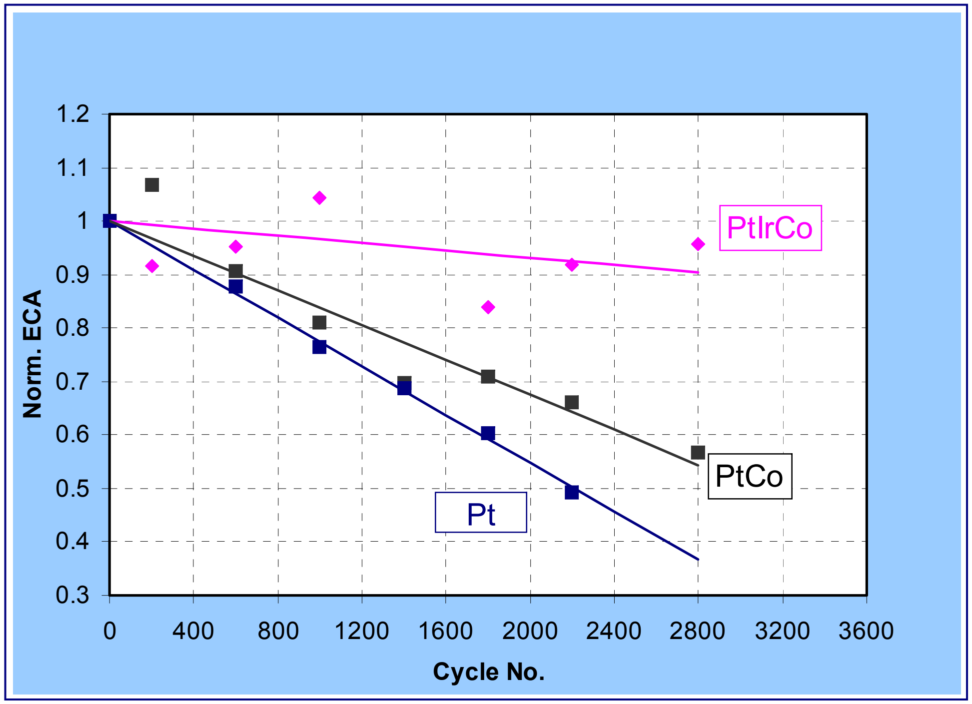


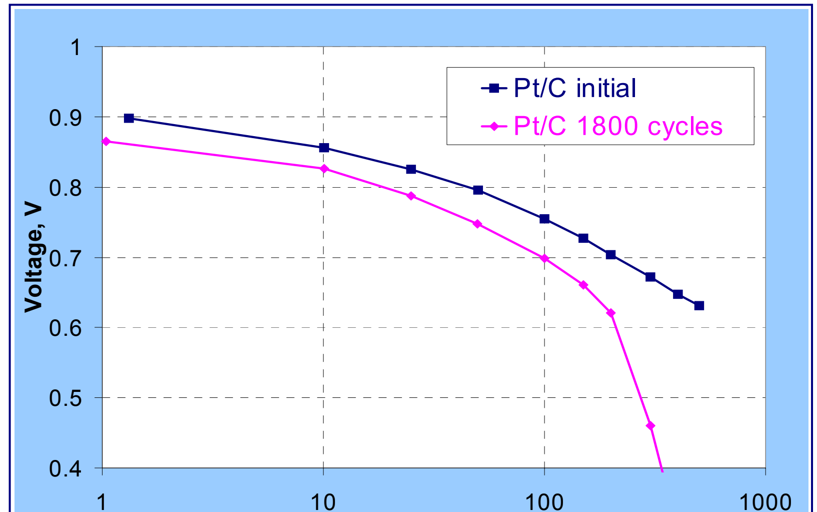
Pt Co Ir



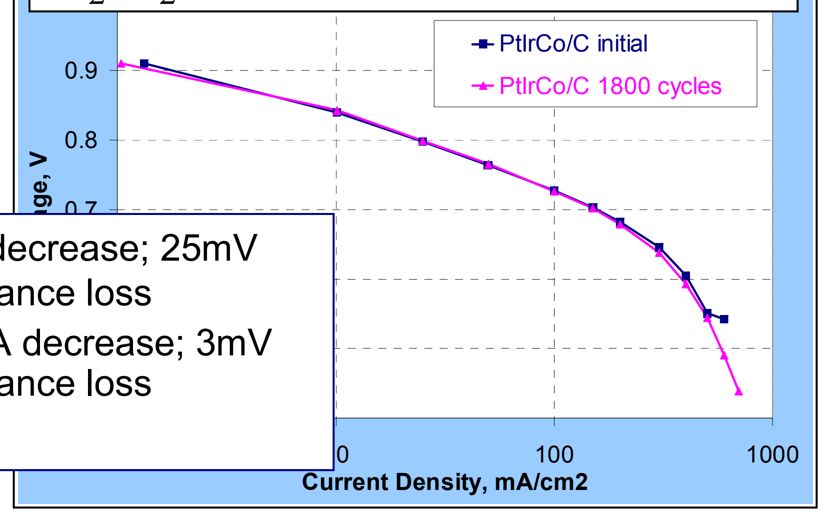
- EMPA shows no evidence of Co or Ir in the membrane and/or anode.

Technical Accomplishments: Pt Alloys for Improved Durability of PEM FCs - Catalyst Dissolution at HT





H_2/O_2, 120°C°C, 50%RH, 1.5atm.



Potential cycling conditions:

120°C, 50%RH;

2800 cycles; H_2/N_2

0.87-1.05V vs RHE;

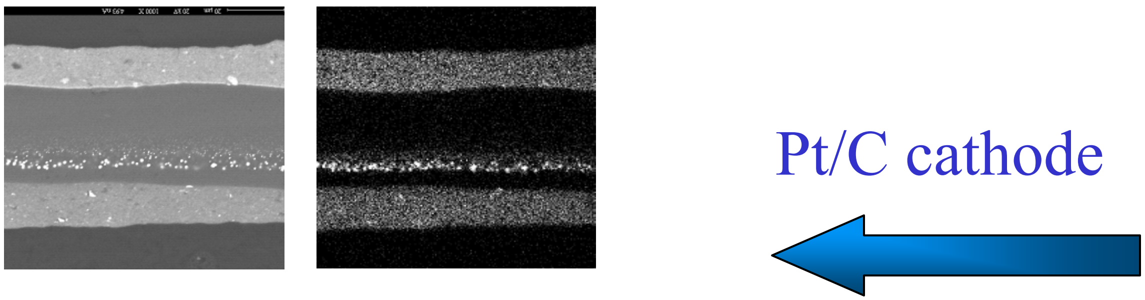
Diagnostic tests every 400 cycles: ECA, H_2/Air, H_2/O_2

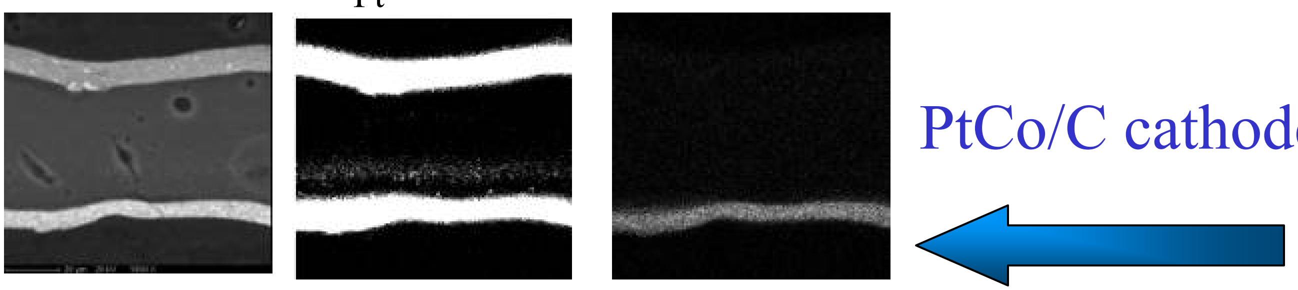
Pt/C: ~ 45% ECA decrease; 25mV performance loss

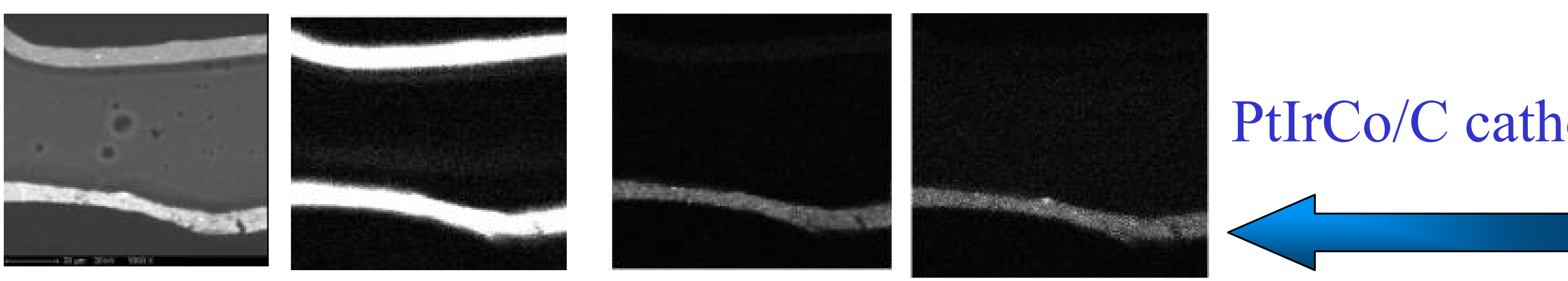
PtIrCo/C: ~ 6% ECA decrease; 3mV performance loss

Technical Accomplishments: Pt Alloys for Improved Durability of PEM FCs - Catalyst Dissolution at HT

MEA Post-Test: EMPA Analysis





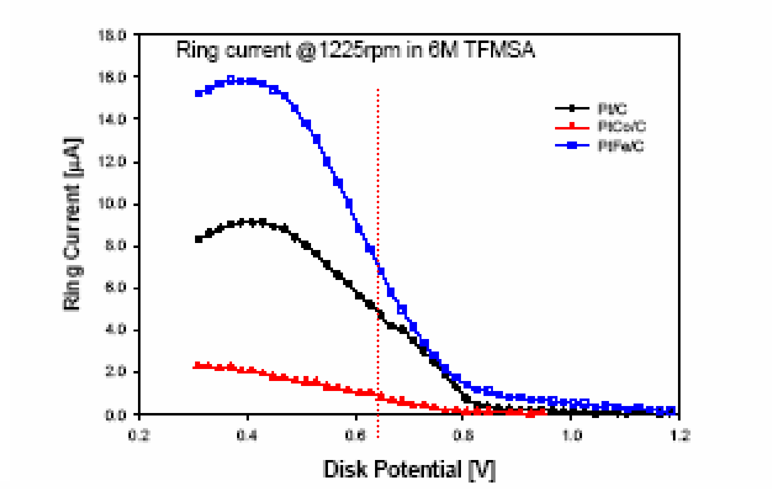


- The electron microprobe analysis shows no evidence of Co or Ir in the membrane and/or anode.
- The absence of Co/Ir migration demonstrates a benefit of PtCo and PtIrCo alloy systems – will not poison membrane.

Technical Accomplishments: Pt Alloys for Improved Durability of PEM FCs – Peroxide Formation

RRDE experiments

Rate of H_2O_2 formation:
- Pt > PtCo
- Low RH% >> High RH%



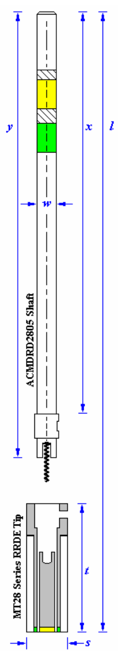


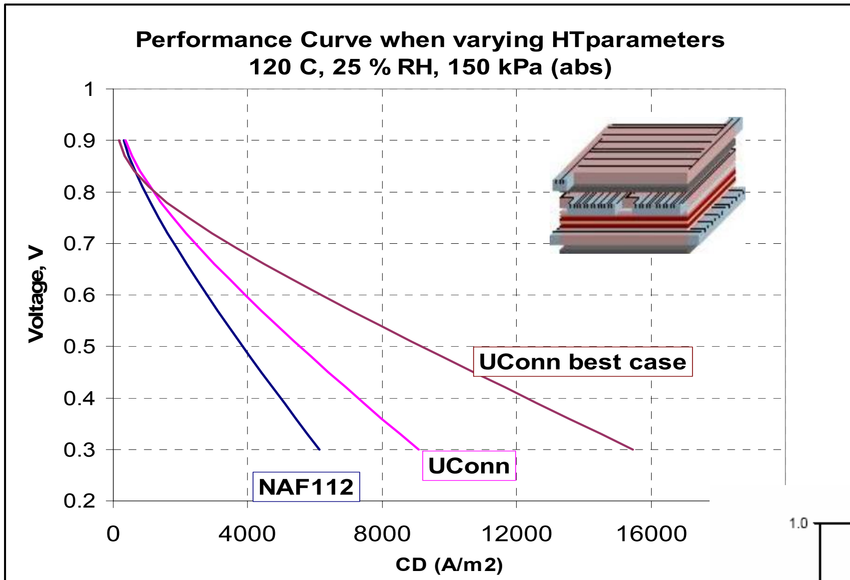
Table 1. Comparison of mole fraction of peroxide formed for the Pt and Pt alloy catalysts at 0.7 and 0.6 V from RRDE experiments at 1225 rpm, room temperature.

Catalyst	%H_2O_2, 1 M TFMSA [@0.7 V]	%H_2O_2, 6 M TFMSA [@0.7 V]
Pt/C	0.114	0.416
PtFe/C	0.147	2.387
PtCo/C	0.151	0.301

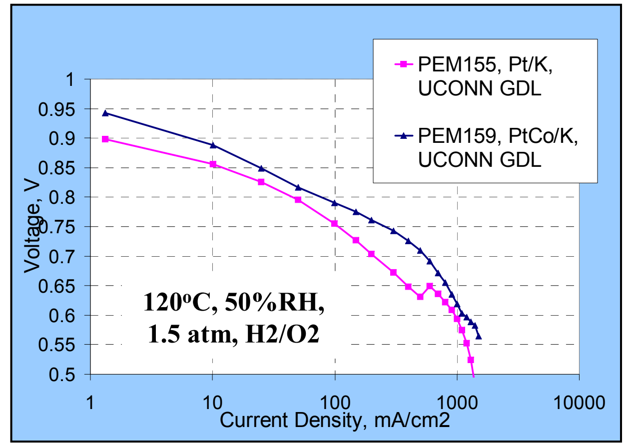
Technical Accomplishments: HT operation – performance improvements

Modeling

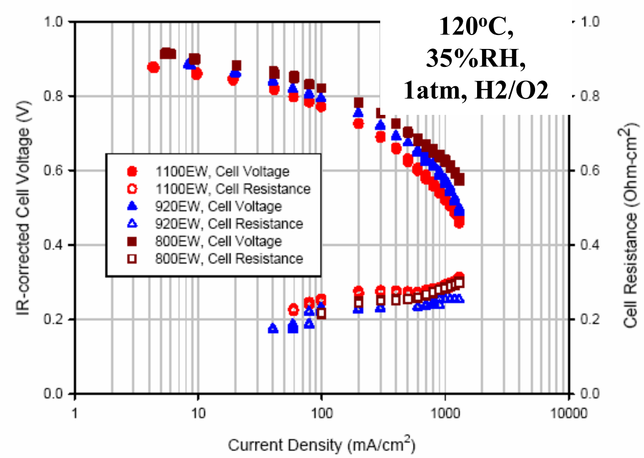
Experimental Verification



40mV activity enhancement with PtCo at 120°C



- Re-optimize cathode
  - More ionomer
  - More conductive ionomer
  - Thinner
  - More active catalyst
- Thinner membrane, more conductive
  - UConn has 25 micron membrane
  - Good Conductivity



800EW ionomer in electrode shows up to 45mV improvement at low current densities compared to 1100EW

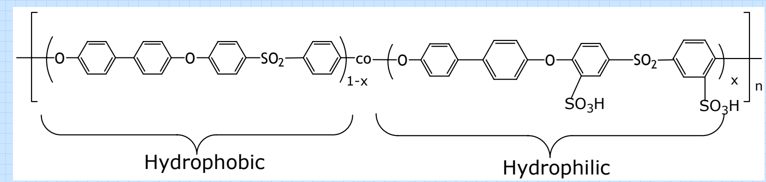
Technical Accomplishments: HT Membrane Development

2 different approaches for HT membrane development are currently investigated under this program:

- Approach A
  - *First generation*: Series II solid acid doped reinforced Nafion-like membrane
    - Nafion®-Teflon®-phosphotungstic acid (NTPA) (Na-form)- Series II membrane
  - *Second generation:* Series IV Cs form in-situ doped reinforced Nafion-like membrane

UCONN

- Approach B
  - *First generation*: BPSH-XX



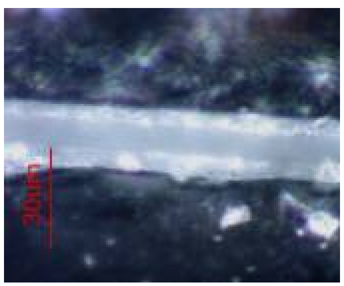
  - *Second generation*: BPSH-XX with high molecular weight, partially fluorinated, increased acidity of functional group
  - *Third generation*: multiblock copolymers

VaTech

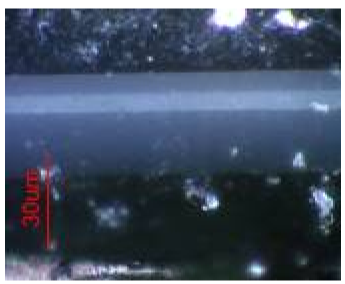
Technical Accomplishments: HT Membrane Development - Approach A

❖ Composite membranes based on Nafion® and solid proton conductor – retain conductivity at low RH%

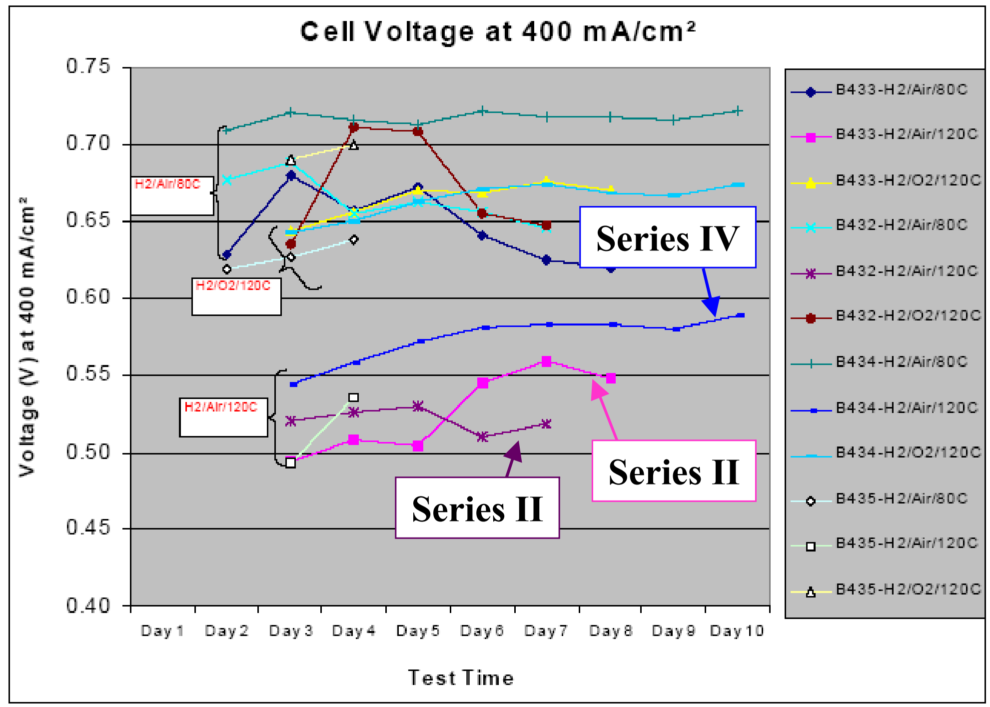
- Nafion®-Teflon®-phosphotungstic acid (NTPA) (Na-form)- Series II membrane
- Nafion®-Teflon®-phosphotungstic acid (NTPA) (Cs-form) – Series IV membrane
  - Smaller uniform particle size
  - Solid acid proton conductor is precipitated in-situ
  - Cs-form is insoluble
  - Processed at higher T°C
    - – durability +



Series II Membrane



Series IV Membrane

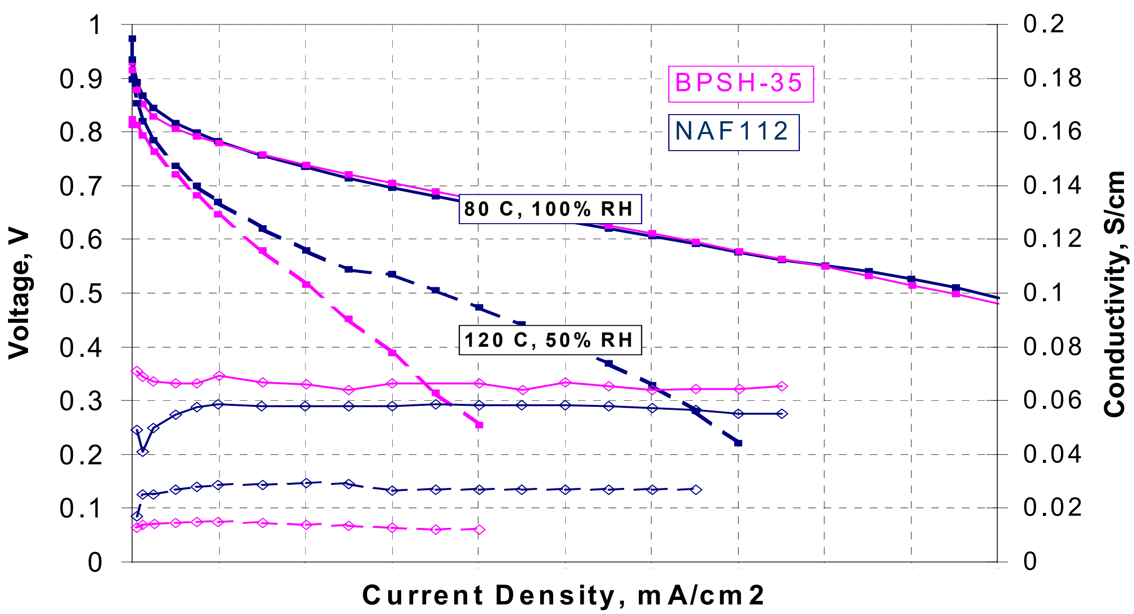


Technical Accomplishments: HT Membrane Development Approach B

❖Sulfonated Biphenyl Sulfones (BPSH)

- **Pros:**
  - Higher stability with post-sulfonation
  - High conductivity at high RH%
  - Low O_2 permeability mitigates membrane decomposition caused by peroxide attack
  - Excellent thermal stability
  - Commercially available monomers - $$$++

Copolymer	T_g	
	M1	*M2*
BPS-0	223	
BPSH-30	259	270
BPSH-40	268	272
BPSH-50	272	283



Results consistent with conductivity measurements

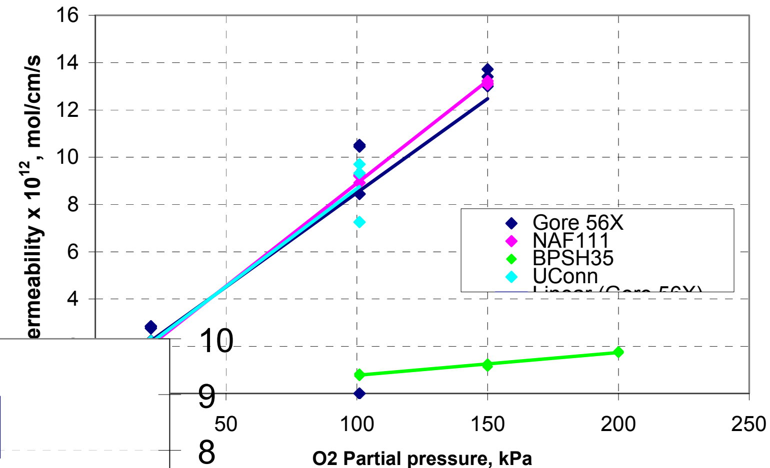
- **Cons:**
  - Improvements of conductivity at low RH% and mechanical strength improvement needed – **higher molecular weight** polymer was developed

Target Mn (kg/mol)	Cond. (mS/cm^2)
20	72
30	78
40	85
50	92
1:1 Stoich	120

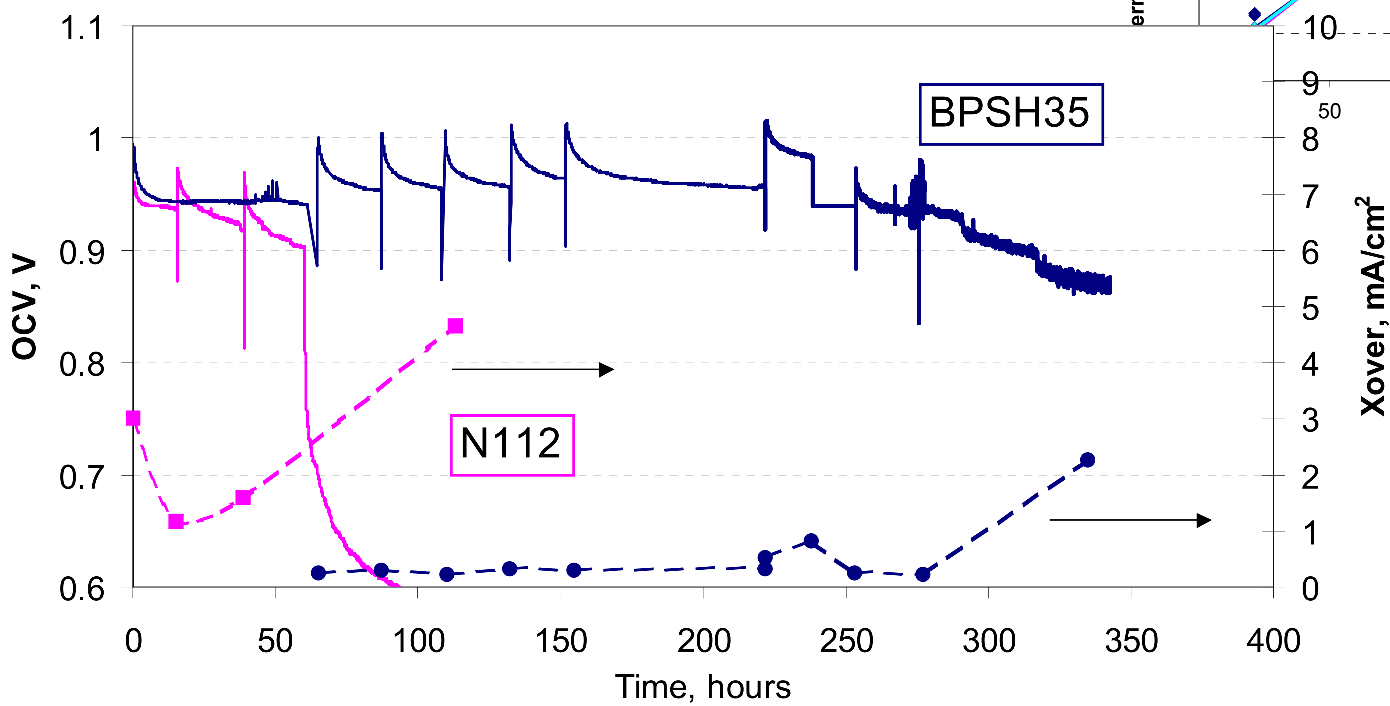
Technical Accomplishments: HT Membrane Development Approach B

- BPSH O2 permeability is 10x lower that of PSFA-like membrane - significantly increases durability

Oxygen Permeability Measurements



Accelerated Membrane Degradation Test

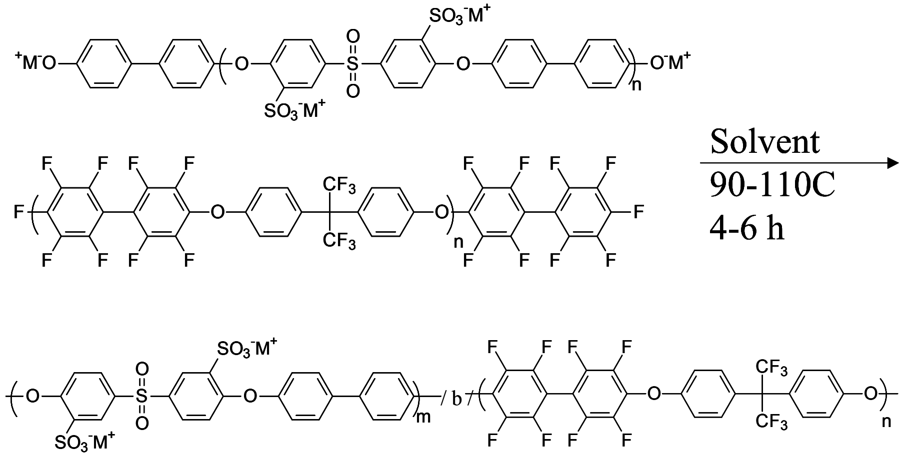


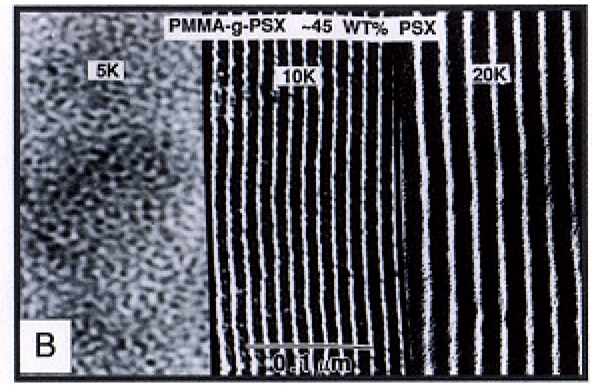
Accelerated Membrane Degradation Test Conditions:

100°C, 25%RH, 1.5atm

H2/O2

Technical Accomplishments: HT Membrane Development
Approach B – Path Forward

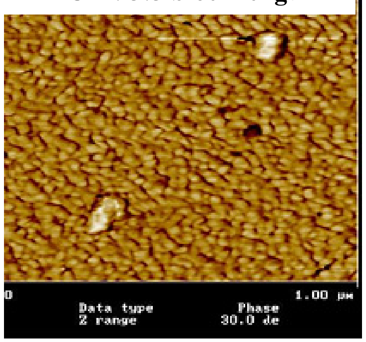




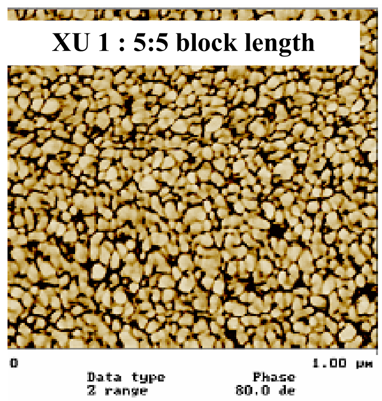
Transmission Electron Micrographs:
PMMA-*g*-PDMS Copolymer – Path to Cocontinuous Multiblocks

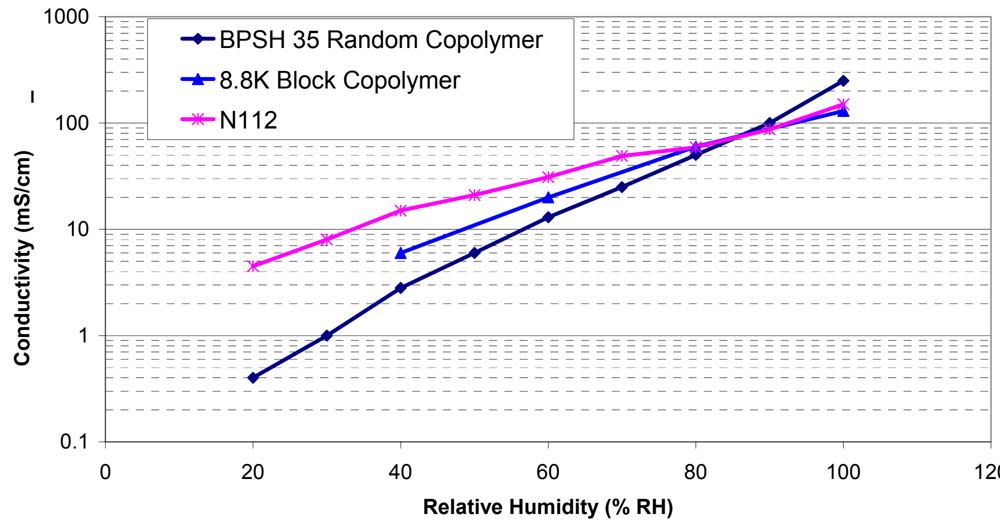
Cocontinuous multiblock polymers – path forward for HT membranes development

XU 1 : 3:3 block length



XU 1 : 5:5 block length





Summary of 05/04-05/05 Technical Achievements

- PtCo and PtIrCo showed x1.5-2.5 specific activity improvement
- PtCo MEAs were optimized and benefit of minimum 20mV was shown in-cell
- Two-fold reduction of Pt loading is achieved with PtCo without loss in performance
- Up to x5 extension of cyclic durability of electrodes was shown with PtIrCo/C cathode systems
- Durability at high temperature operation was shown to be possible through use of Pt alloy catalyst systems
- Significant membrane life extension is possible with alternative alloys due to lower peroxide generation rates
- Improved Series IV membrane was developed in UCONN – will lead to durability improvements
- High molecular weight BPSH membrane was developed and showed HT at least 5x durability improvement compared to PFSA-like membrane
- Fundamental studies showed that additional performance benefit can be obtained at HT operation through the use of advanced catalyst (PtCo) and low EW ionomer in electrodes

Going Forward

Tasks to be completed by the end of Q1 FY06:

- Pt-alloy full size single cell verification
- Pt-alloy stack demonstration: full size MEAs fabrication, stack build and testing
- Fundamental understanding of alternative catalyst stability and its implications on membrane durability
- HT operation
  - RH% effects – experimental and modeling effort
  - 100-120^{o}C 25-50%RH membrane endurance demonstration
  - Demonstration of lessons learned and the best up-to-date technology for HT operation: single cell performance demonstration

05/04-05/05 Selected Publications and Presentations

May 2004 – May 2005: Over 25 publications in refereed journals and over 35 presentations

Refereed Articles

- Si, Y., H. R. Kunz and J. M. Fenton. 2004. "Nafion®-Teflon®-$Zr(HPO_4)_2$ Composite Membranes for High-Temperature Polymer Electrolyte Membrane Fuel Cells." Journal of the Electrochemical Society, **151:4**, A623 (2004).
- Ramani, V., H. R. Kunz, J. M. Fenton. 2005. "Stabilized Heteropolyacid/Nafion® Composite Membranes for Elevated Temperature / Low Relative Humidity PEFC Operation." Electrochimica Acta, 50:5, 1181 (2005).
- Song, Y., Y. Wei, H. Xui, M. Williams, Y. Liu, L. J. Bonville, H.R. Kunz, and J.M. Fenton. 2005. "Improvement in high temperature proton exchange membrane fuel cells cathode performance with ammonium carbonate." Journal of Power Sources, 141:2, 250 (2005)
- M.A. Hickner, H. Ghassemi, Y.S. Kim, B. Einsla and J.E. McGrath, Alternative Polymer Systems for Proton Exchange Membranes, *Chemical Reviews* (2004), 104(10), 4587-4611
- K.B. Wiles, C. M. de Diego and J .E. McGrath, Poly(arylene sulfide sulfone) Copolymer Composites for Proton Exchange Membrane Fuel Cell Systems: Extraction and Conductivity, *Polymer Preprints* (American Chemical Society, Division of Polymer Chemistry) (2004), 45(1),724-25.
- Y. Li, T. Mukundan, W. Harrison, M.L. Hill, M. Sankir, J. Yang, and J.E. McGrath, Direct Synthesis of Disulfonated Poly(arylene ether ketones)s and Investigation of Their Behavior as Proton Exchange Membrane (PEM),*American Chemical Society, Division of Fuel Chemistry Preprints*, (2004), 49(2), 536-537.

Presentations

- "High Temperature Membrane Electrode Assembly Development for Proton Exchange Membrane Fuel Cells." Keynote Presentation by Dr. Fenton, 14th International Conference on the Properties of Water and Steam, Kyoto, Japan, August 29 – September 3, 2004. (L. J. Bonville and H.R. Kunz co-authors)
- "Alternative Materials for Improved Performance and Durability of PEM Fuel Cells", L.Protsailo, A.Haug, J. Meyers; Fuel Cells 2005, Pacific Grove, California , February 2005
- Advanced Polymeric Materials for Proton Exchange Membranes, J.McGrath; Gordon Research Conference on Fuel Cells, July 28, 2004.

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