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

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UTC Power

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

2006 DOE Hydrogen Program Review
May 13-16, 2006
Arlington, VA

ID# FC20

Objectives and Approach

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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 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, Budget, Team

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- ## Technical Barriers
  - P. Durability
  - Q. Electrode Performance
  - R. Thermal and Water Management

•Budget

Year	Total $M	DoE $M	UTC $M
Overall 2002-2005	9.500	7.600	1.900
Received in 2005	1.875	1.500	.375

•Program Team at Closing

- **UTC Power** (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): membrane development, MEA fabrication, HT fundamentals

Program Schedule

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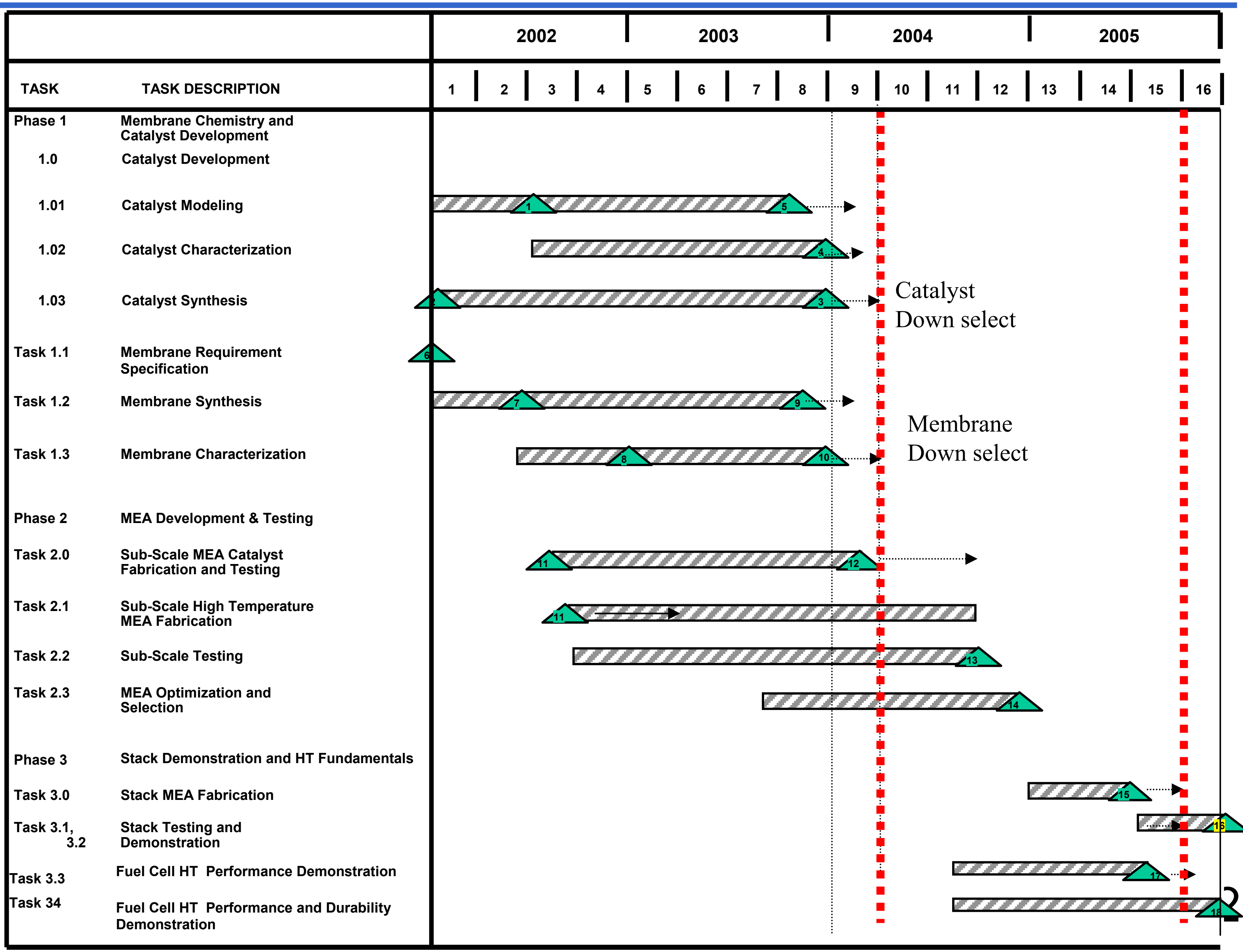

Membrane Development Approach

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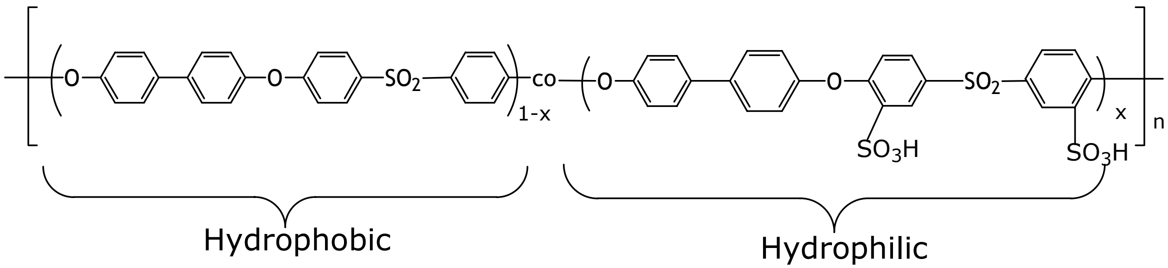
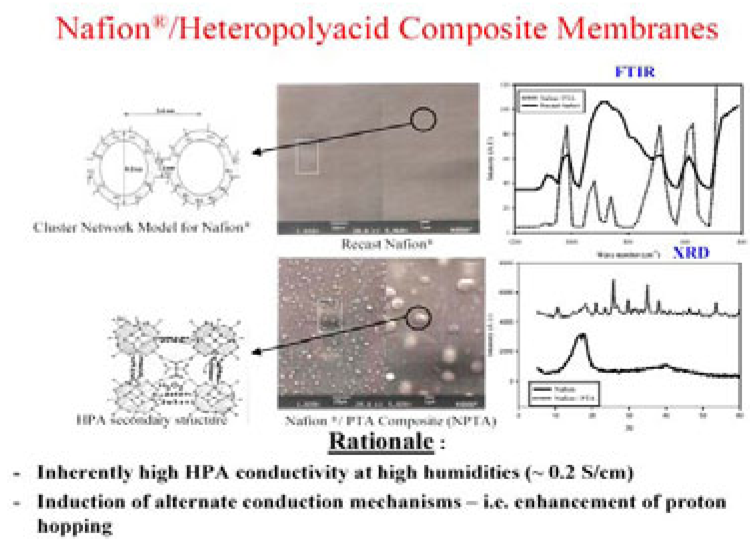
VaTech approach – sulfonated biphenole-sulfones



Acronym: BPSH-XX Bi Phenol Sulfone: H Form

Good mechanical and thermal properties (T_g>>120°C), monomers commercially available (low cost)

UCONN approach – composite membranes based on Nafion® and solid proton conductor – retain conductivity at low RH%



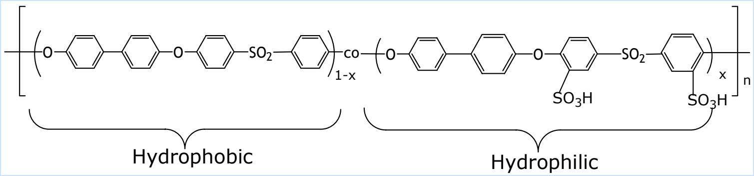
Technical Accomplishments:
HT Membrane

2 different approaches for HT membrane development were 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



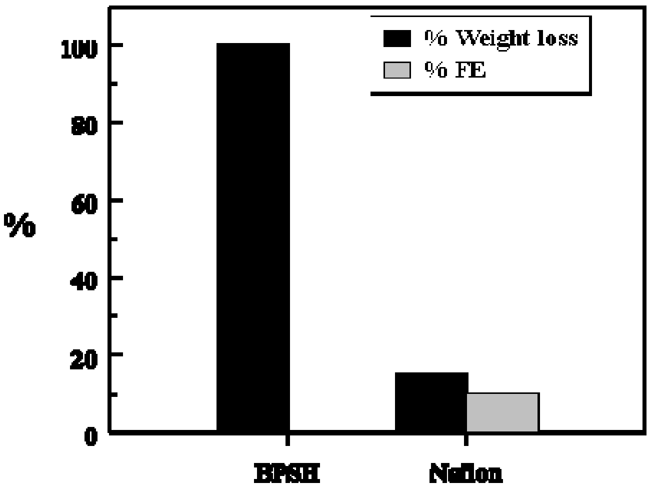
  - *Second generation*: BPSH-XX with high molecular weight, partially fluorinated, increased acidity of functional group
  - *Third generation*: multiblock copolymers

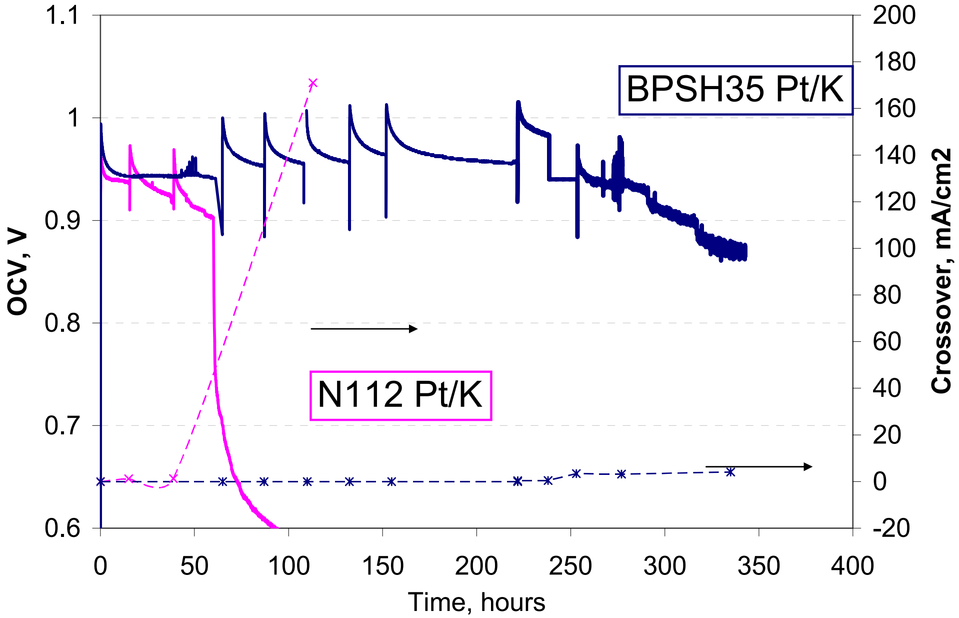
VaTech

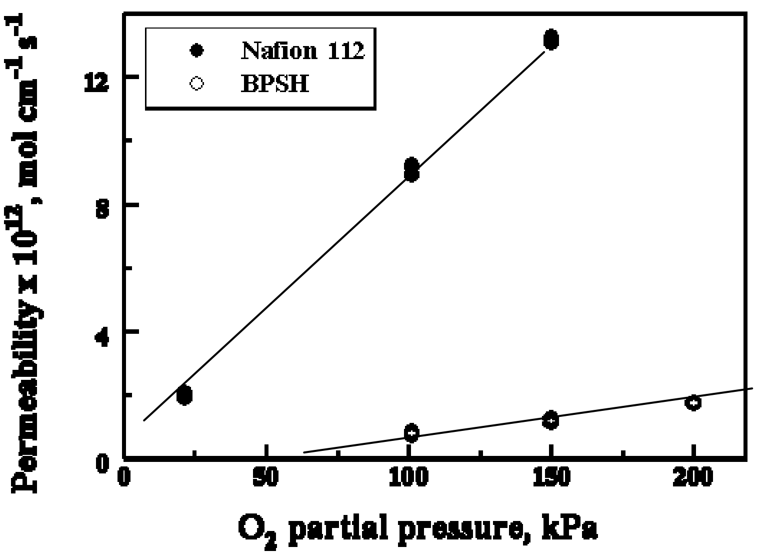
Technical Accomplishments:
BPSH Membrane

Chemical Stability in OCV Test

1. Fails Fenton test
2. Low O_2 permeability
3. Outstanding durability at OCV hold conditions

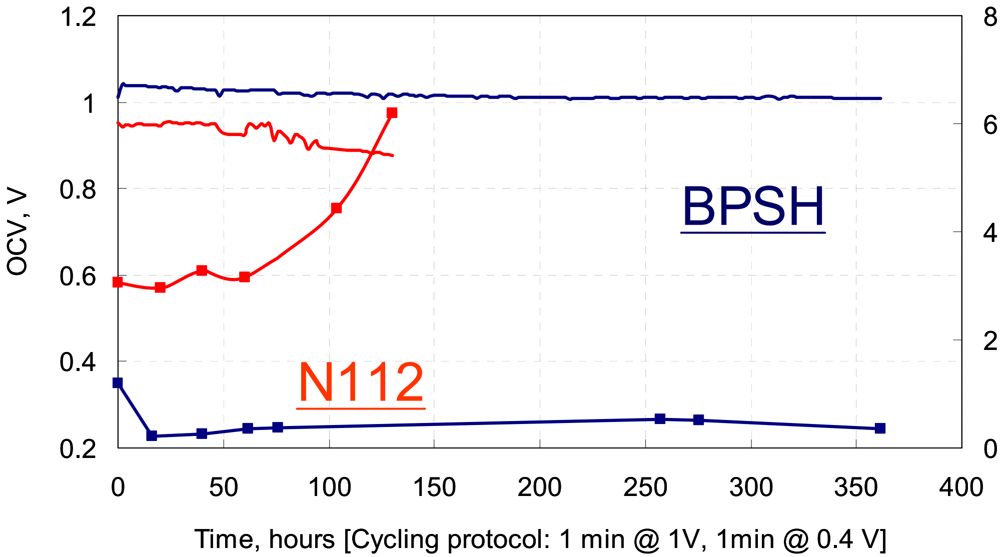






Technical Accomplishments:
BPSH Membrane

PEM198-BPSH Cycling Results - OCP Decay & Hydrogen x-over Current
100 C, 25% RH, 150 kPa, 0.5SLM H2 [Anode], 1.0 SLM O2 [Cathode]



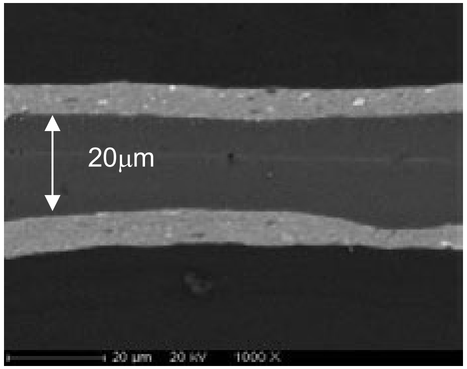
Load Cycle Test

Load cycle protocol:

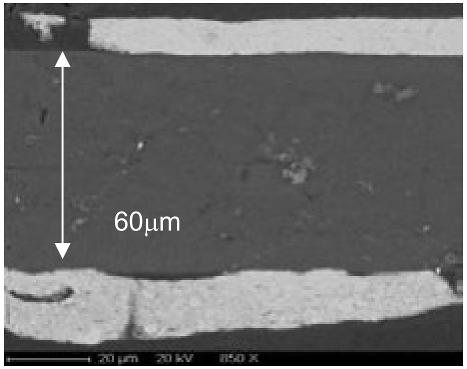
- 100°C, 25%RH
- 0.5 SLPM H_2/1.0 SLPM O_2
- 1min @ 1V, 1min @ 0.4V

EMPA post test analysis:

- BPSH retained its thickness in load cycle test



Nafion® 112



BPSH-37

Technical Accomplishments:
BPSH Membrane

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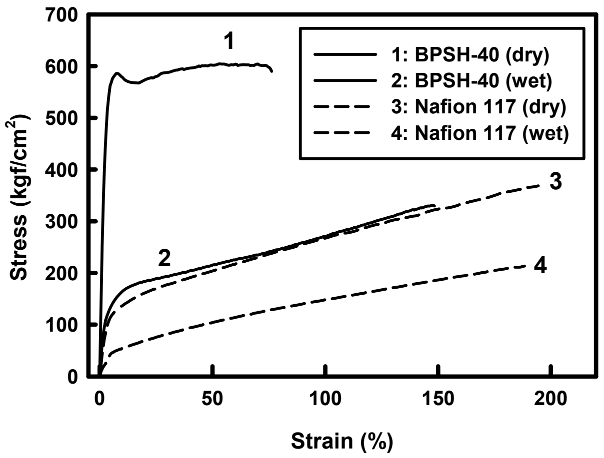
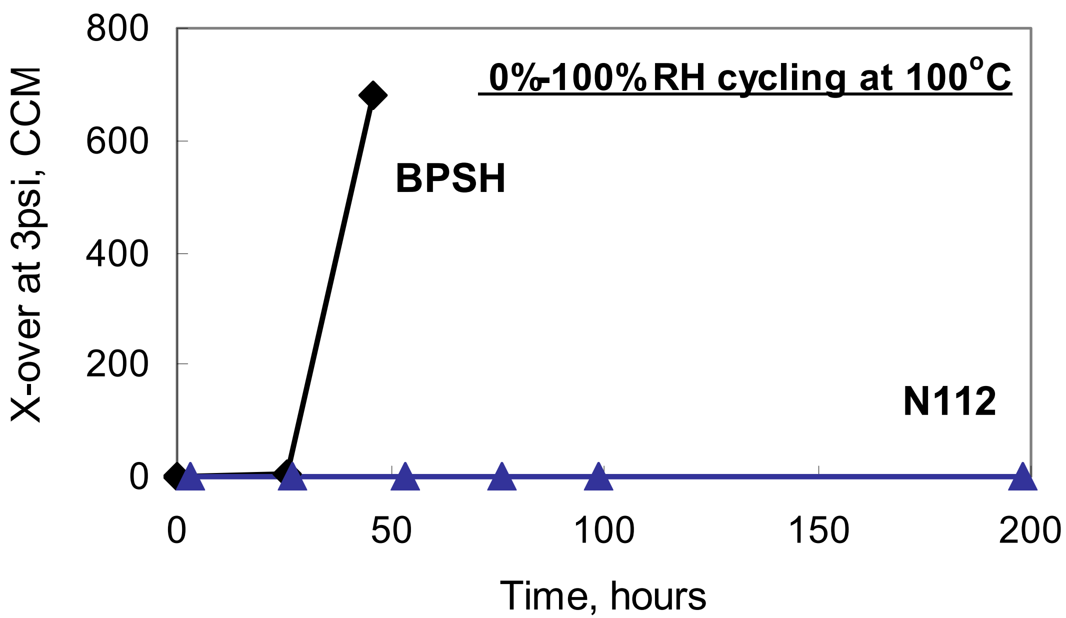
RH Cycle Test

Membrane	Linear expansion x-direction, %	Linear expansion y-direction, %	Swelling (boiling), %
BPSH	25	15	41.2
N112	10	3.1	11.4





Technical Accomplishments:
BPSH Membrane

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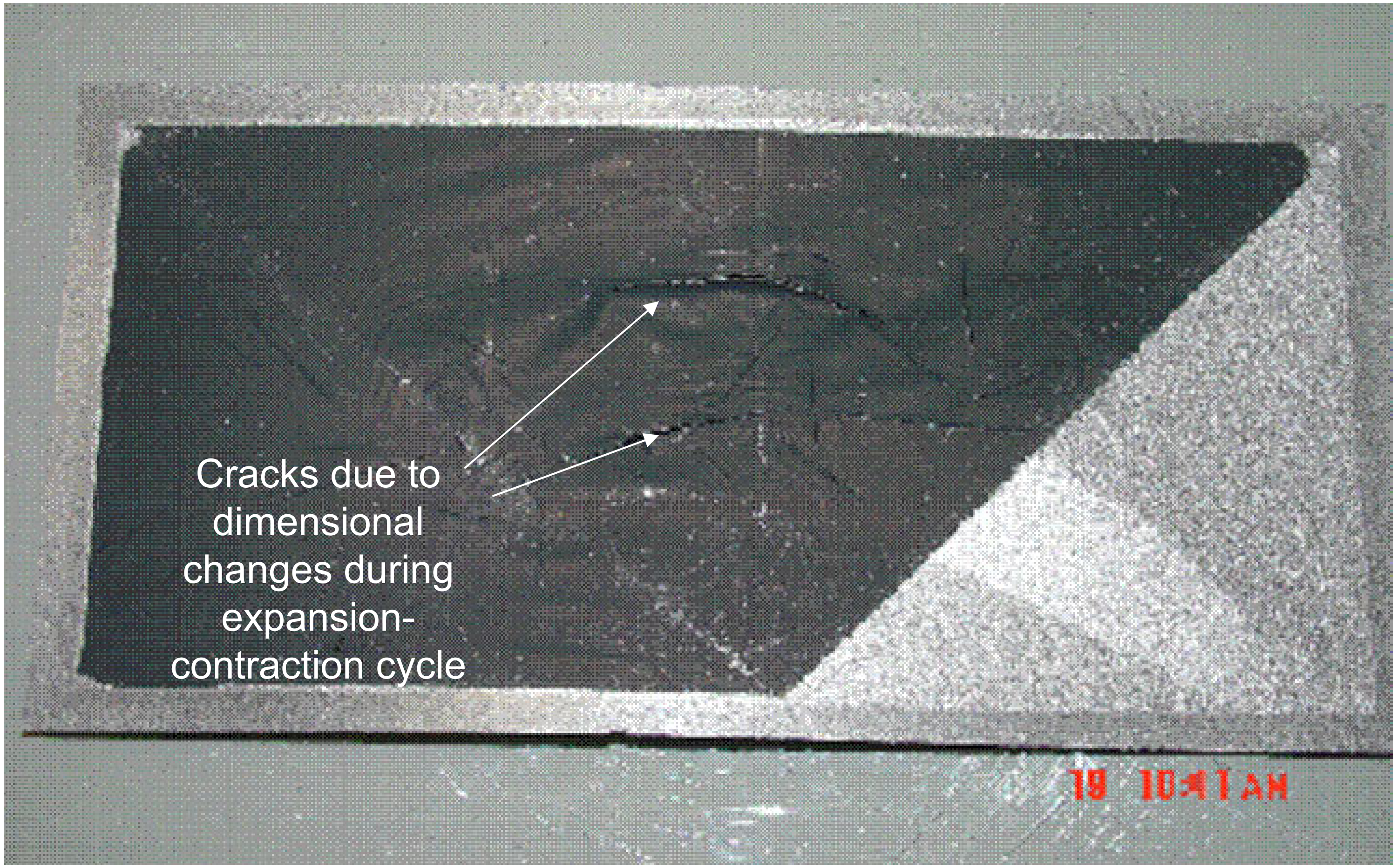
Unitized Electrode Assembly



Technical Accomplishments:
NTPA-Cs Membrane

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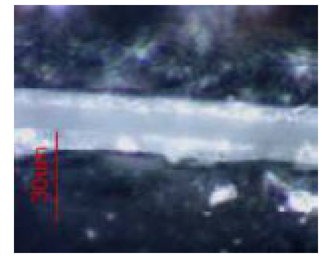
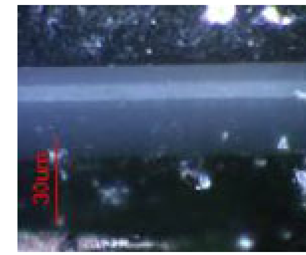
- Composite membranes based on Nafion® and solid proton conductor – retain conductivity at low RH%
  - Nafion®-Teflon®-phosphotungstic acid (NTPA) (Na-form)- Series II membrane
  - Nafion®-Teflon®-phosphotungstic acid (NTPA) (Cs-form) – Series IV membrane
    - Smaller uniform particle size
    - Solid acid proton conductor is precipitated in-situ
    - Cs-form is insoluble
    - Processed at higher T°C

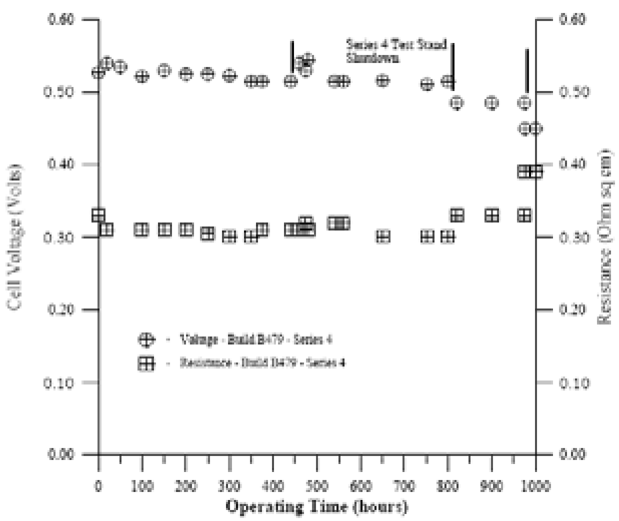
      – durability +

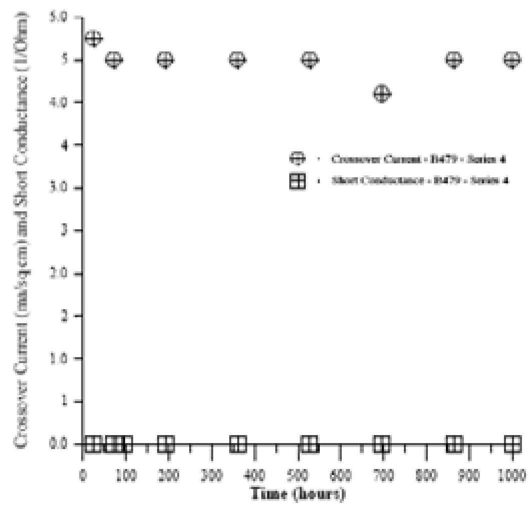


Series II



Series IV





1000 hrs demonstrated at 100°C, 25%RH;

No membrane failure observed @ 1000 hours

HT/Low RH Operation Modeling

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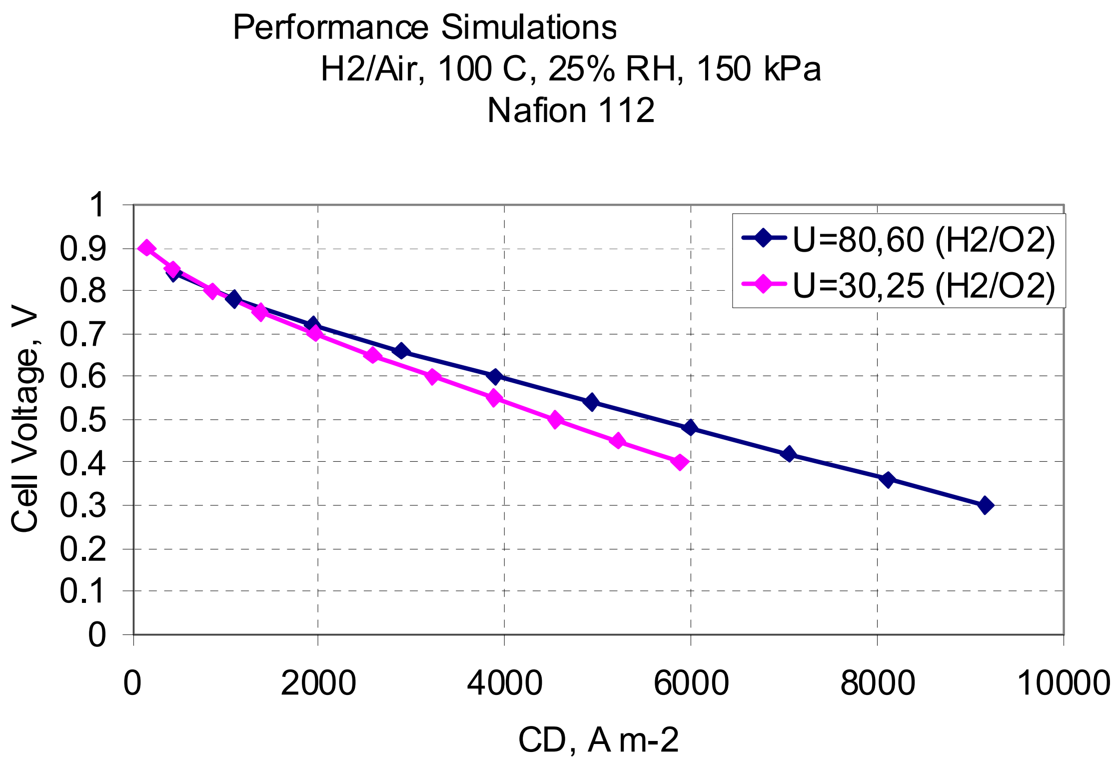
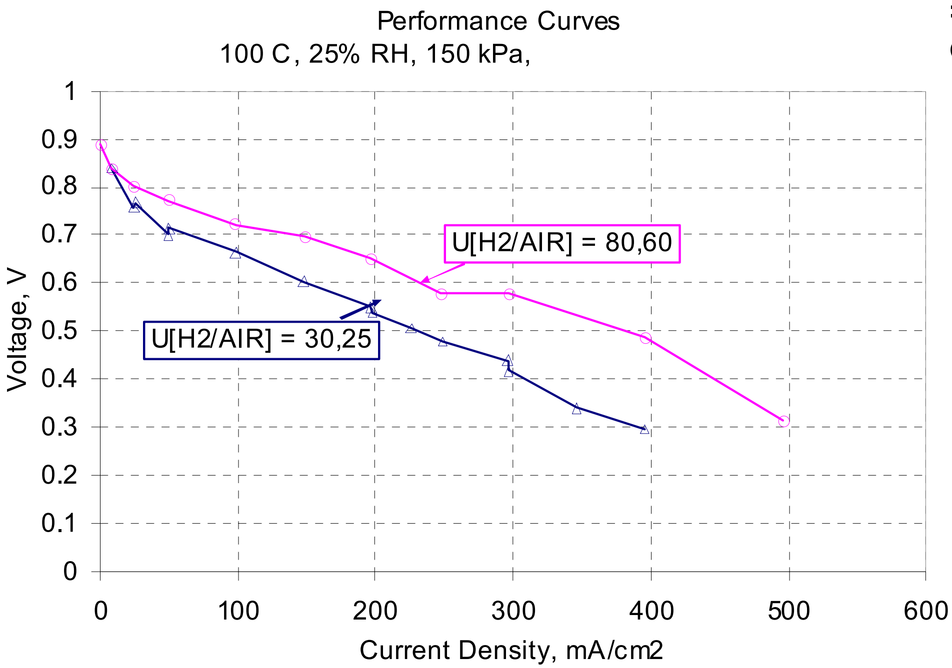
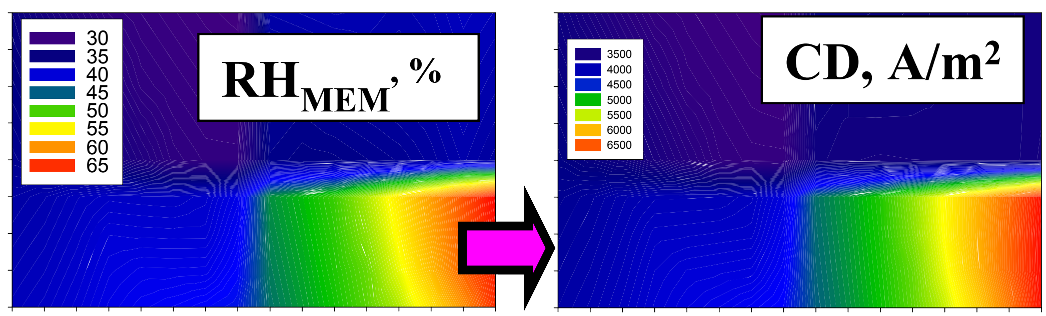
- Performance improves at higher utilizations
  - RH&Conductivity DOMINATE PERFORMANCE over O_2 concentration



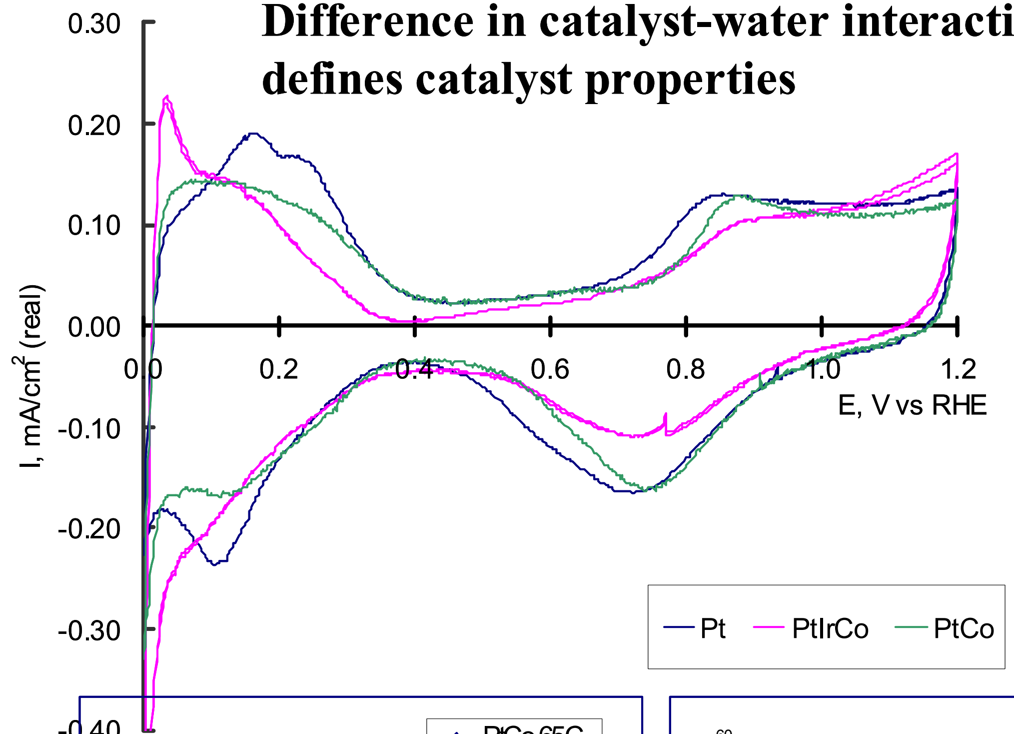


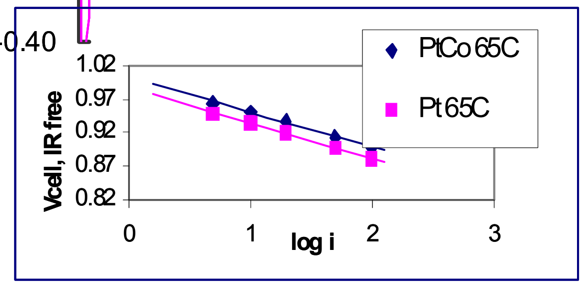


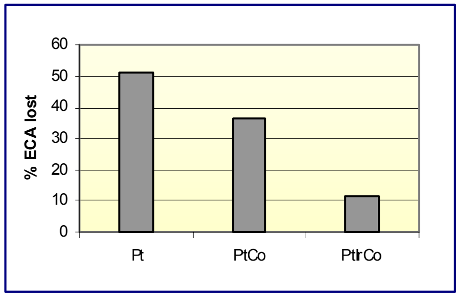
Cathode Catalyst Development Approach

- Higher activity cathode catalyst systems: binary and ternary alloys
  - Carbothermal synthesis
  - PtCo and PtIrCo leading systems
- High loading of noble metal to decrease electrode thickness and achieve mass transport benefit

Difference in catalyst-water interactions defines catalyst properties







2006 DOE Hydrogen Program Review
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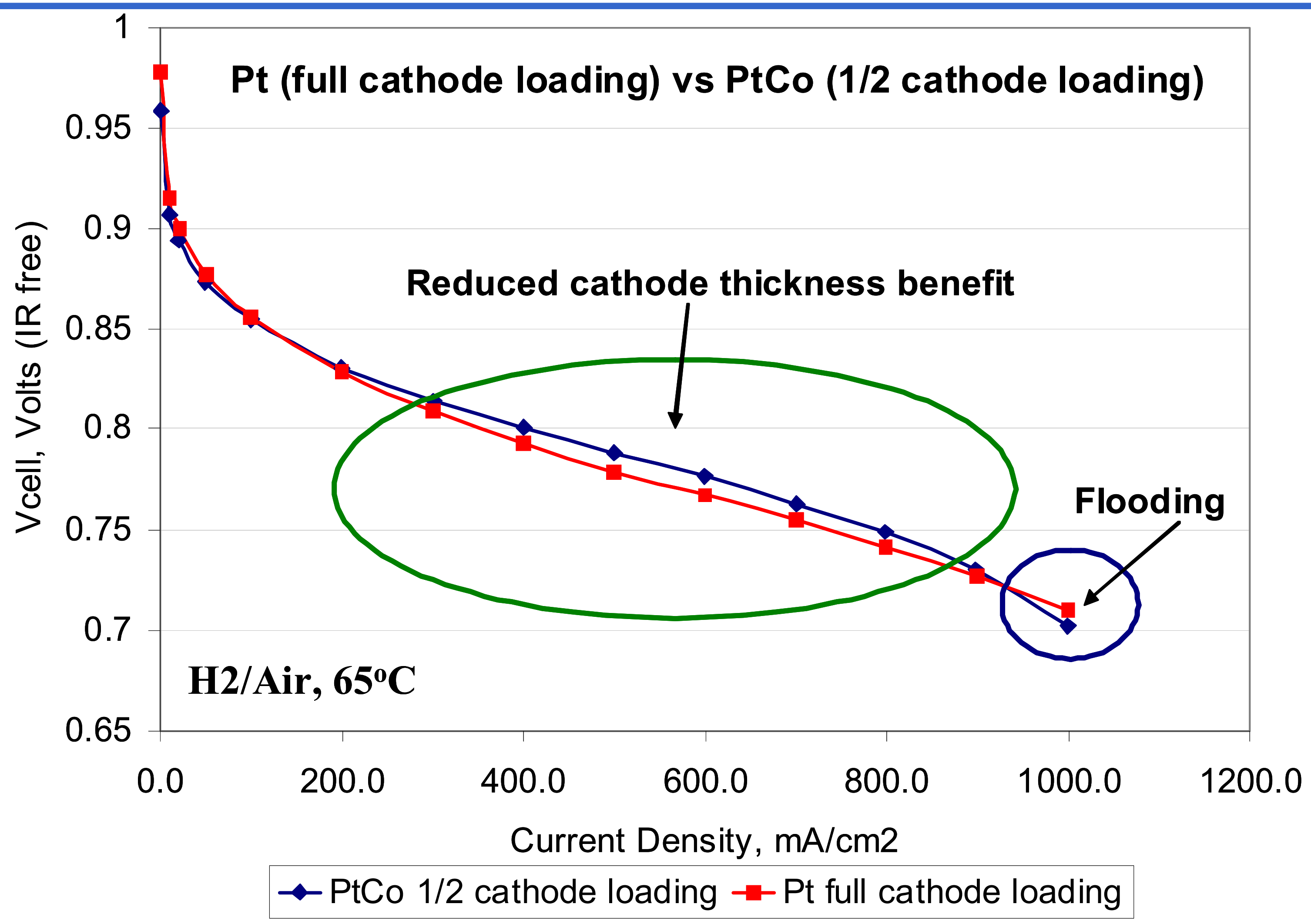
MEA Optimization



PtCo 20-Cell Stack

PtCo 20-cell stack was delivered to ANL for durability studies. Technical support is provided.

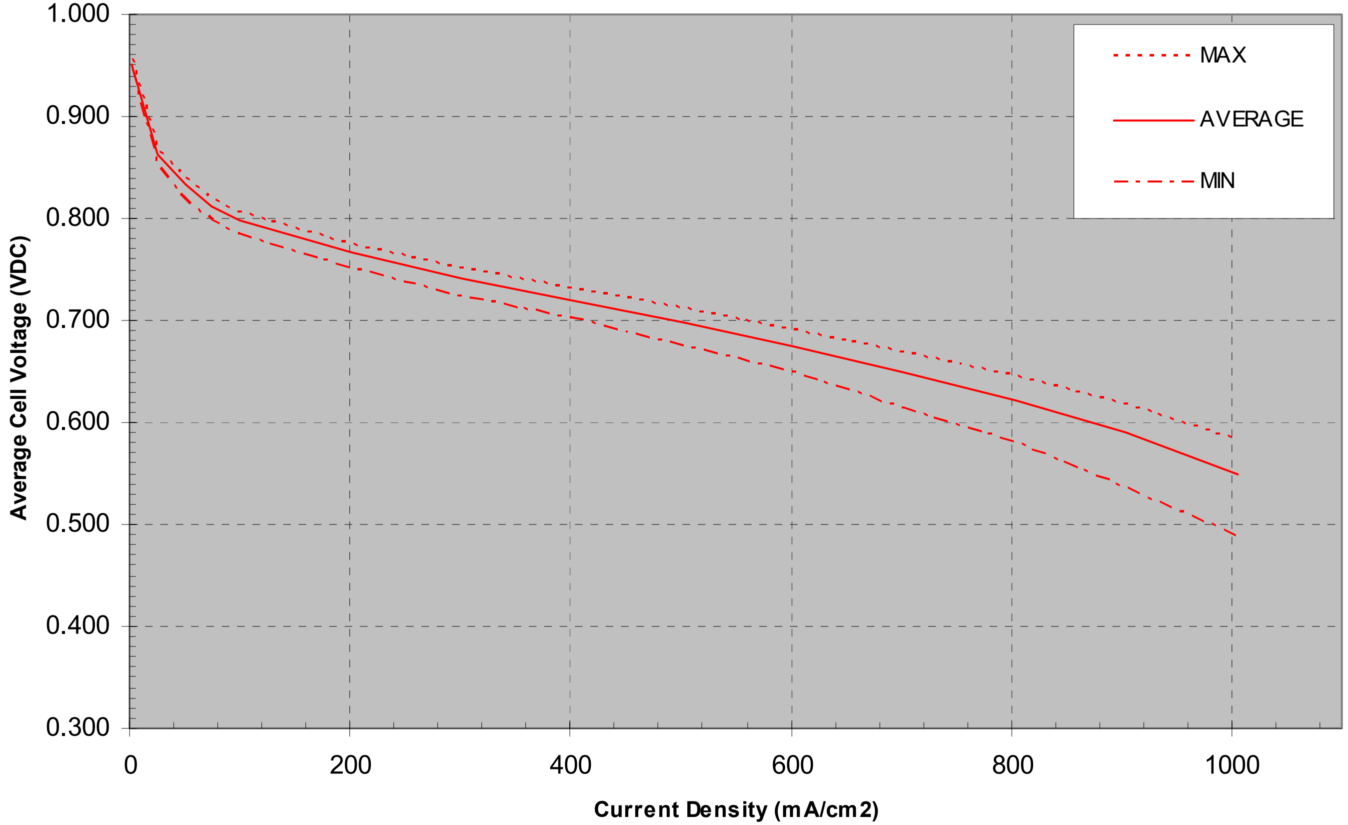
PtCo MEA specification:

0.35mgPt/cm^2

Nafion® 112

Toray GDL

UTCFC planform ($400cm^2$)



Alloy Catalyst Durability

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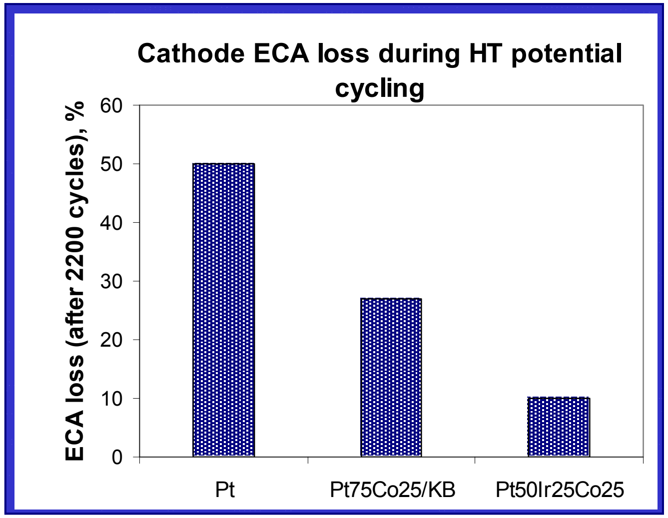


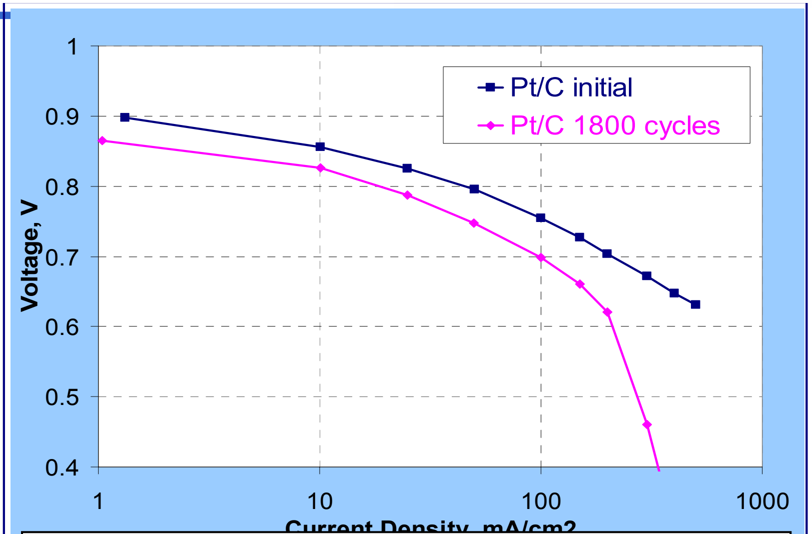
Potential cycling conditions:

120°C, 50%RH;

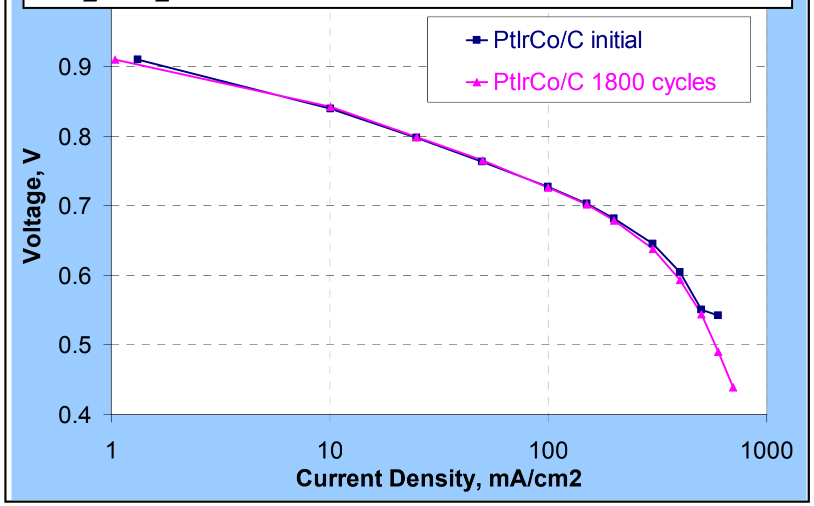
2800 cycles; H_2/N_2 30s 0.87-30s 1.05V

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

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



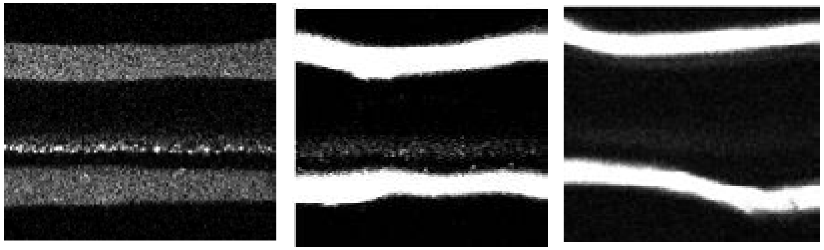
H_2/O_2, 120°C°C, 50%RH, 1.5atm.



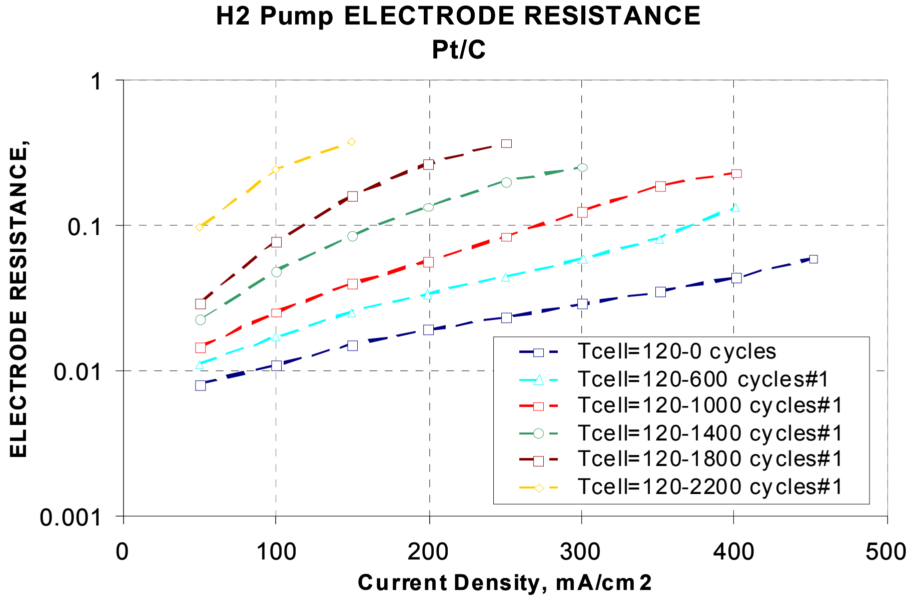
Alloy Effect on Ionomer Durability

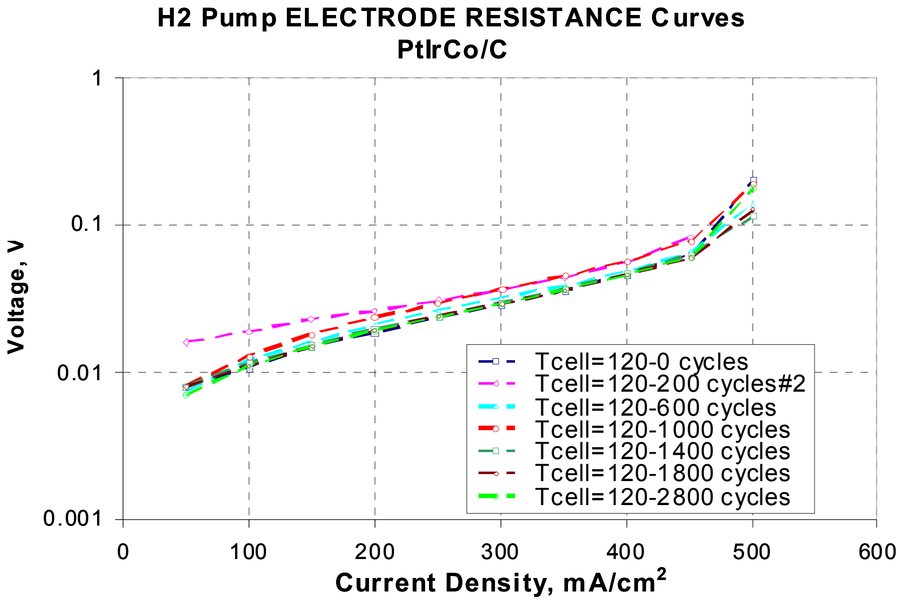
- 10 % H_2 in N_2, low utilization
- Electrode Ionic resistance changes with time
- PtIrCo cathode prevents ionomer poisoning

Pt EMPA map after cycling



Pt PtCo PtIrCo





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Summary of Program Accomplishments

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2002 - 2005

- Established the importance of cyclic durability
- Developed best in class PtIrCo alloy catalyst and demonstrated 5x cyclic durability improvement vs. Pt
- Established membrane down-select criteria
- Developed fundamental understanding of hydrocarbon membrane durability
- Demonstrated 1000 hours of operation at 100^{o}C, 25%RH

Responses to Previous Year Reviewers' Comments

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- Q1. Shows results on hydrogen/oxygen primarily
  - Initial stages of alloy work were dedicated to activity investigations (thus oxygen data are more useful). MEA optimization step operated with H2/air performance

- Q2. Membrane durability studies weak – the new materials are interesting, but durability data are limiting
  - Significant emphasis has been put on fundamental analysis and understanding of alternative membrane durability – especially hydrocarbon membranes

- Q3. Testing of new catalysts in full-size cells and a stack to compliment fundamental studies of catalyst and membrane durability is needed
  - PtCo catalyst was tested in full size cell and 20-cell stack was built and delivered for testing to ANL facilities
  - Attempt to test hydrocarbon membrane in full size cell was made. Unitizing BPSH for full-size testing is a challenging task due to dimensional instability of the membrane.

Acknowledgements

A. Haug
M. Fortin
M. Pemberton
P. Plasse
J. Meyers
S. Motupally
CSA Durability group

N. Cipollini
T. Madden
B. LeTourneau

J.E. McGrath
X. Yu
K. Wiles
A. Roy
X. Li

H.R. Kunz
J. Fenton
L. Bonville (IONOMEM)
Y. Song
V. Mittal
Y. Du
F. Kassim
Y. Liu
H. Xu
V. Ramani