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

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UTC Power

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Program Manager – Amy Manheim

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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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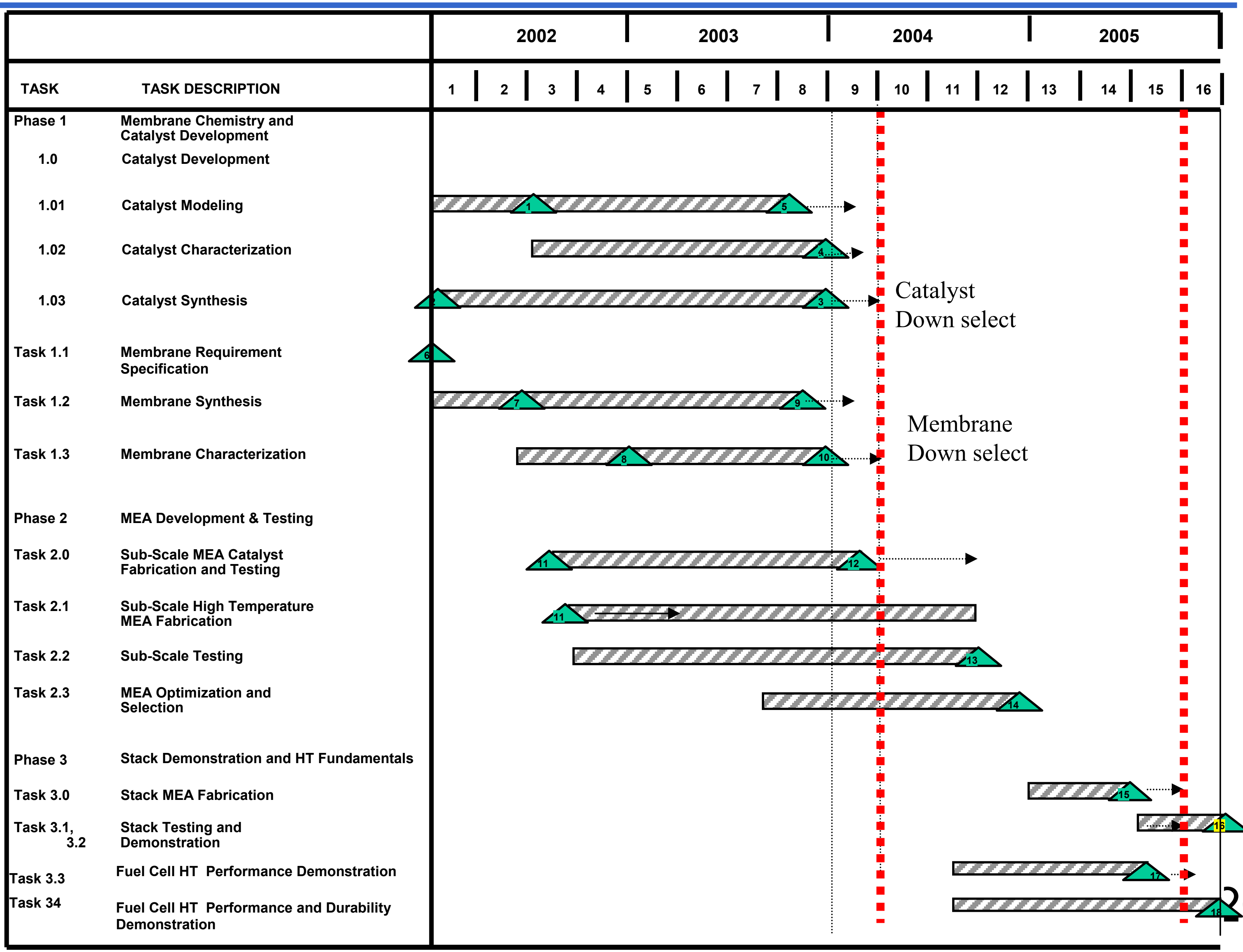

Membrane Development Approach

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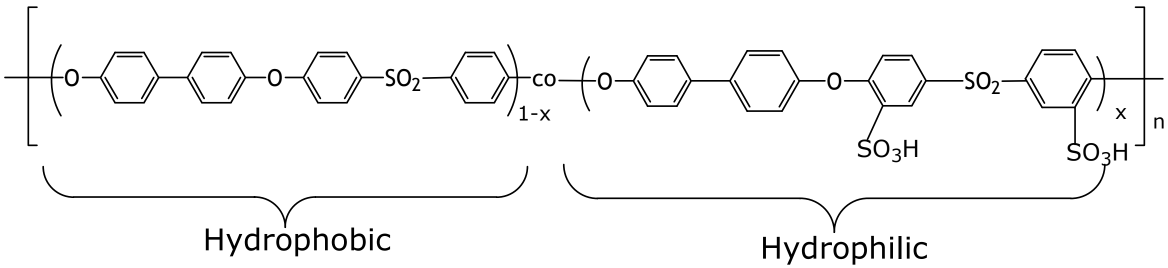
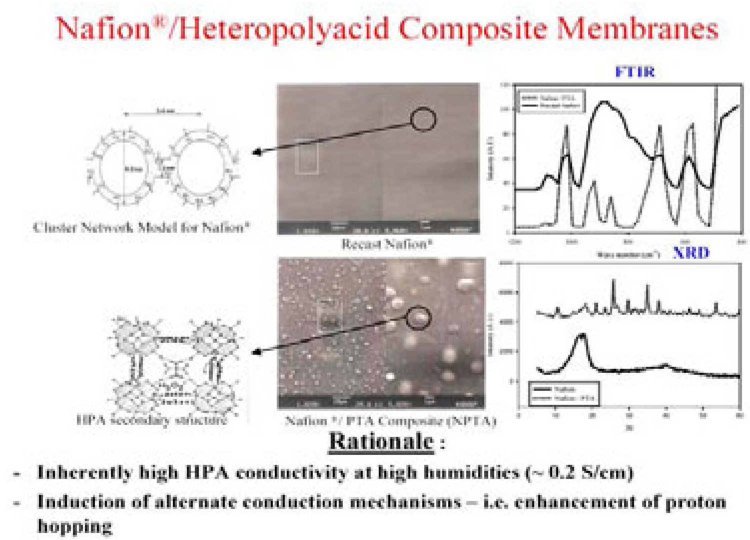
VaTech approach – sulfonated biphenole-sulfones



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

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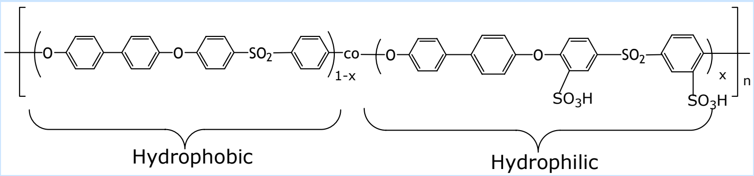
2 different approaches for HT membrane development were investigated under this program:

- 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

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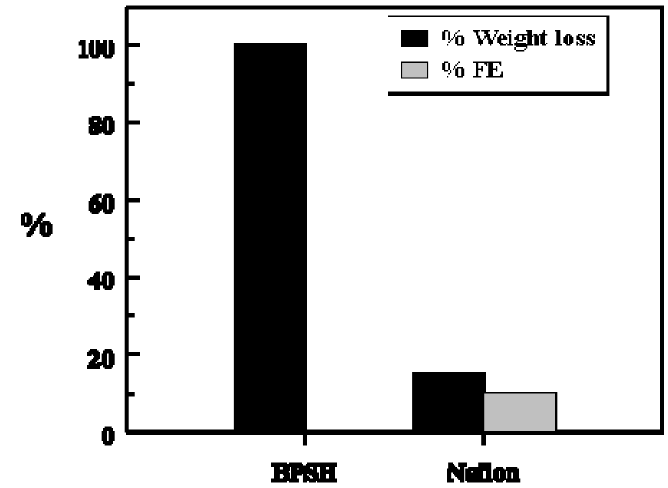
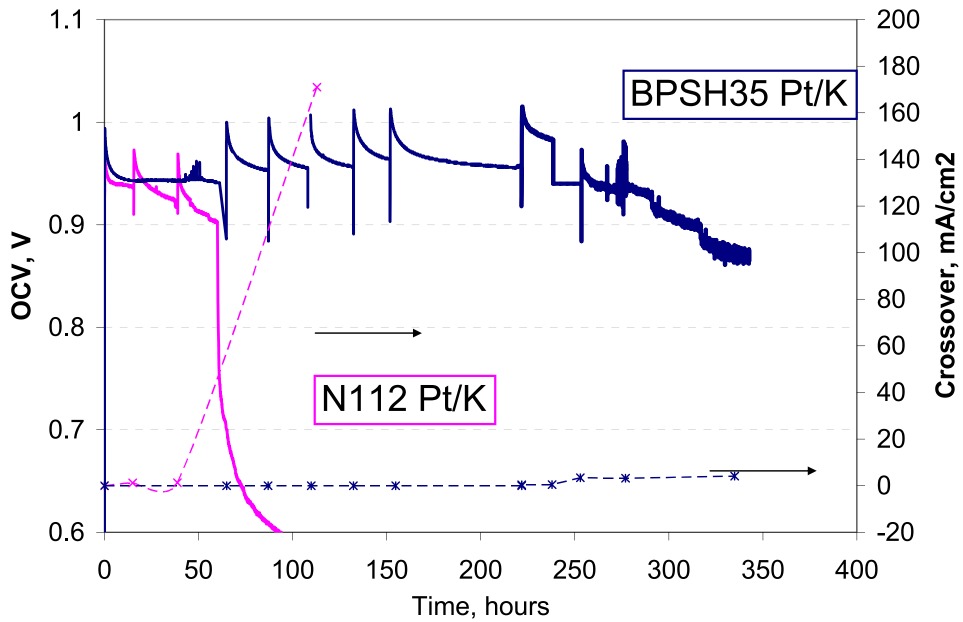
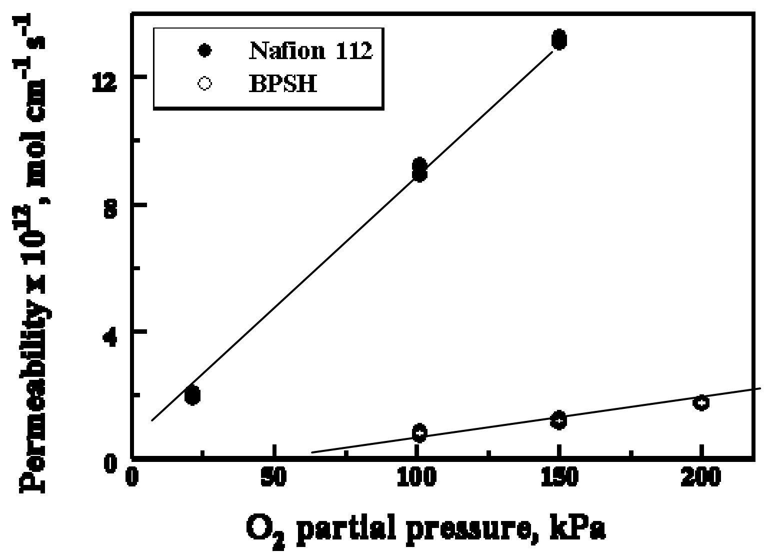
Technical Accomplishments:
BPSH Membrane

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

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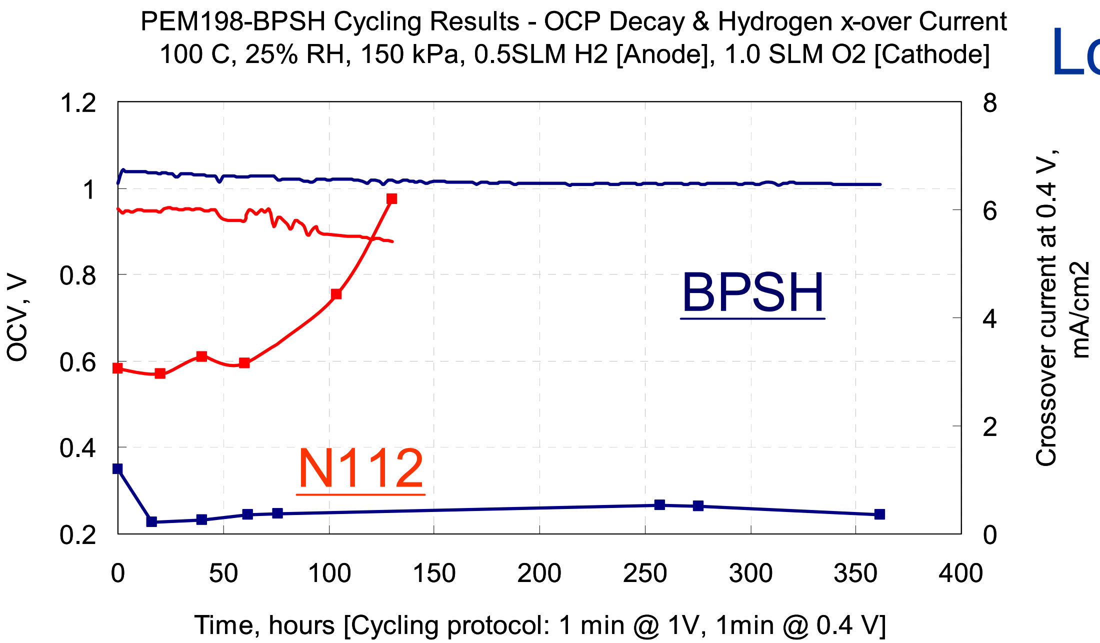


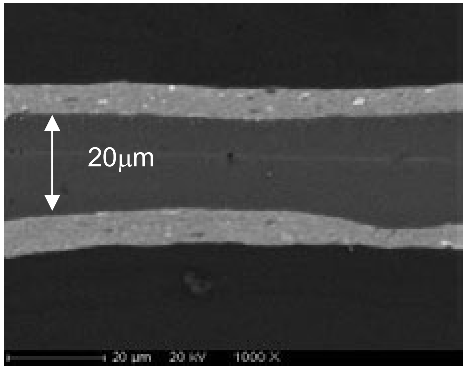
Load Cycle Test

Load cycle protocol:

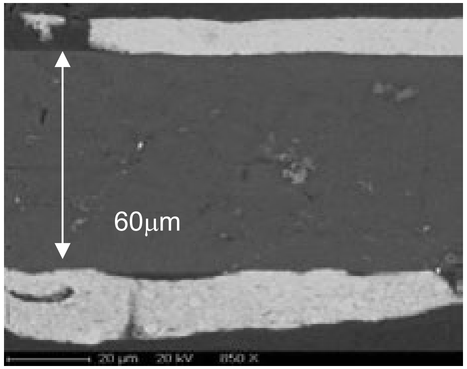
- 100°C, 25%RH
- 0.5 SLPM H_2/1.0 SLPM O_2
- 1min @ 1V, 1min @ 0.4V

EMPA post test analysis:

- BPSH retained its thickness in load cycle test



Nafion® 112



BPSH-37

Technical Accomplishments:
BPSH Membrane

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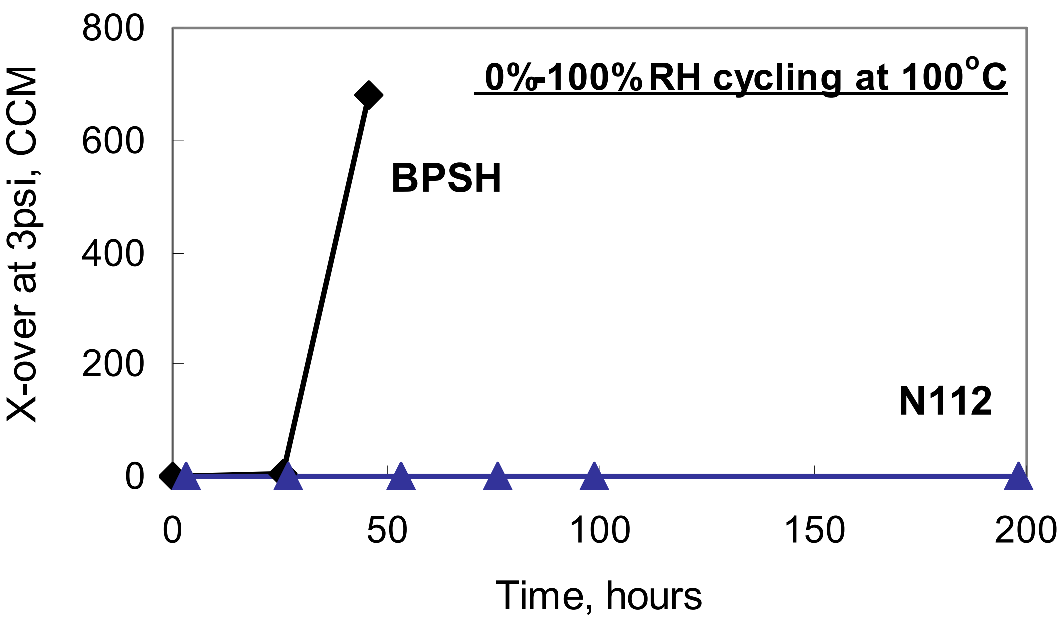
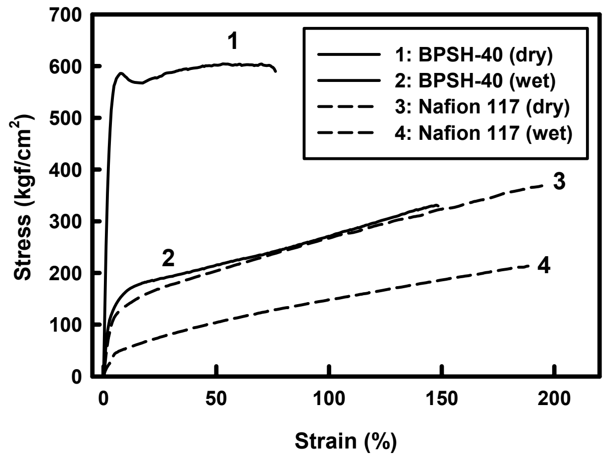
RH Cycle Test

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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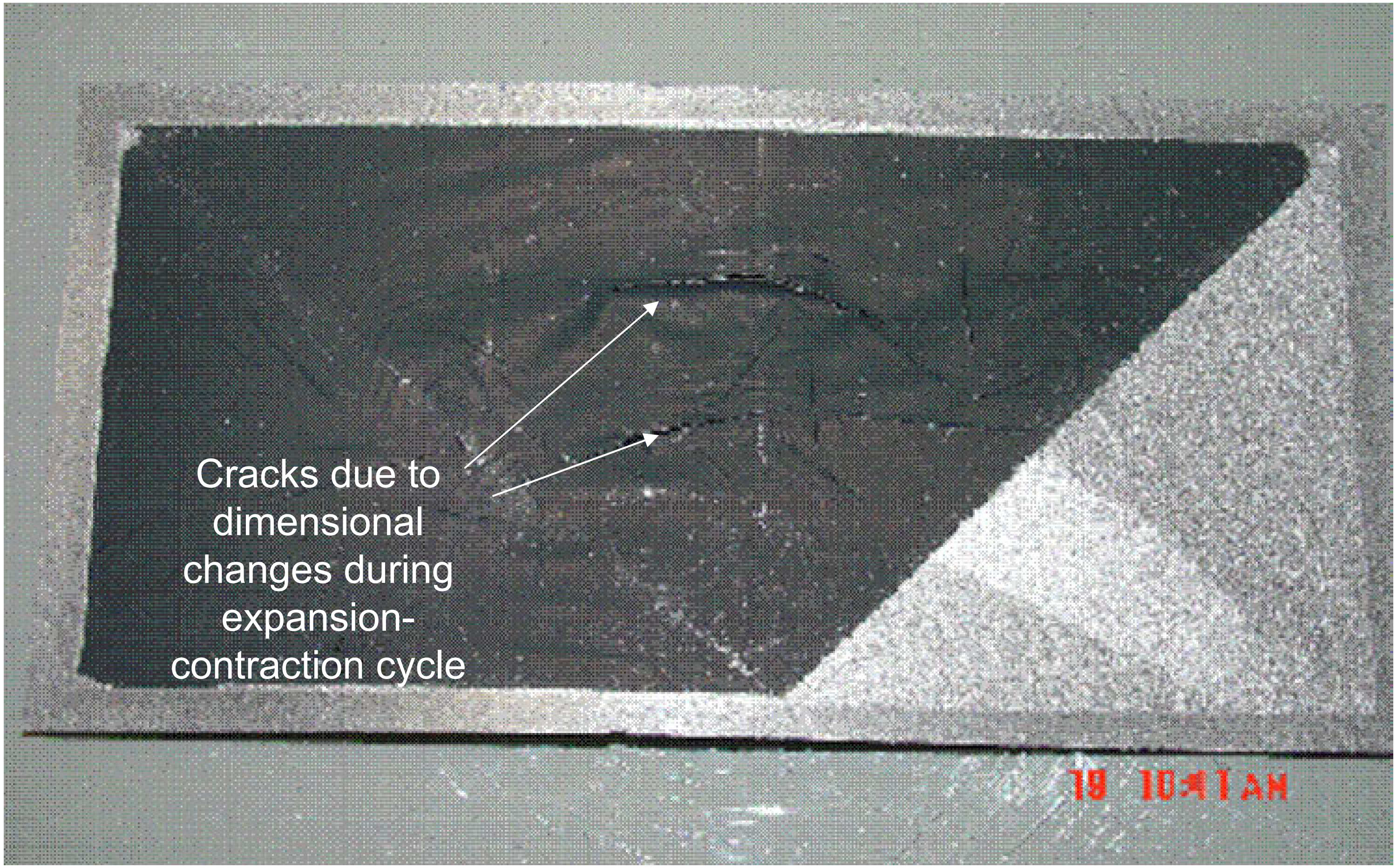
Unitized Electrode Assembly



Technical Accomplishments:
NTPA-Cs Membrane

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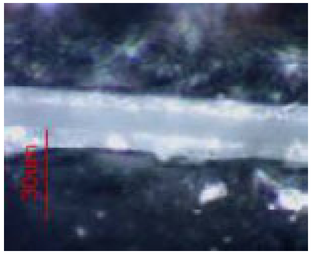
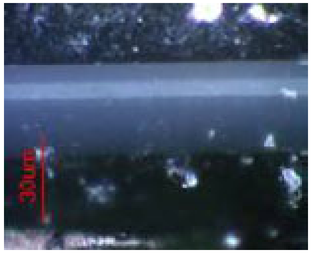
- Composite membranes based on Nafion® and solid proton conductor – retain conductivity at low RH%
  - Nafion®-Teflon®-phosphotungstic acid (NTPA) (Na-form)- Series II membrane
  - Nafion®-Teflon®-phosphotungstic acid (NTPA) (Cs-form) – Series IV membrane
    - Smaller uniform particle size
    - Solid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

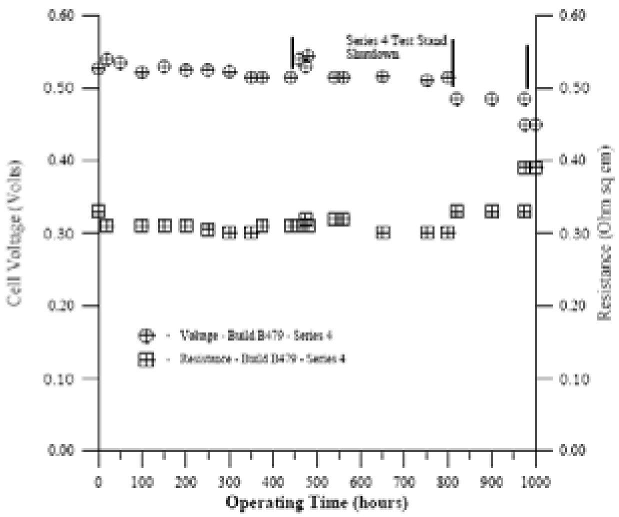
      – durability +

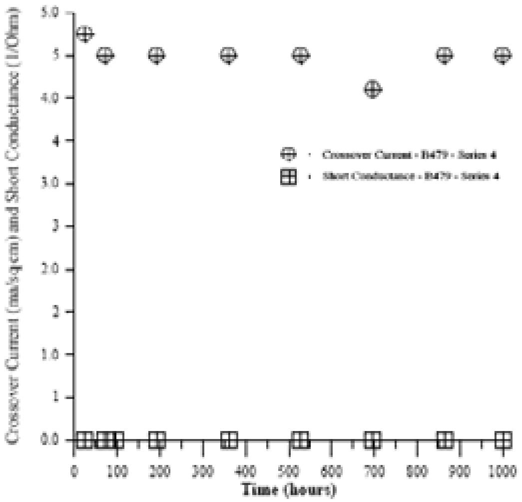


Series II



Series IV





<u>1000 hrs demonstrated at 100°C, 25%RH;</u>

No membrane failure observed @ 1000 hours

HT/Low RH Operation Modeling

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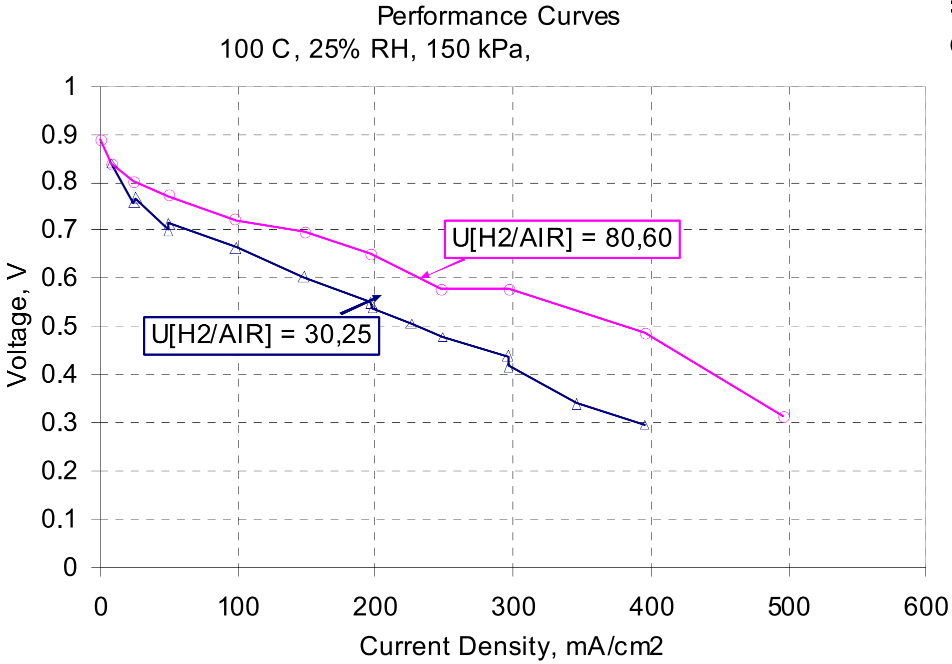
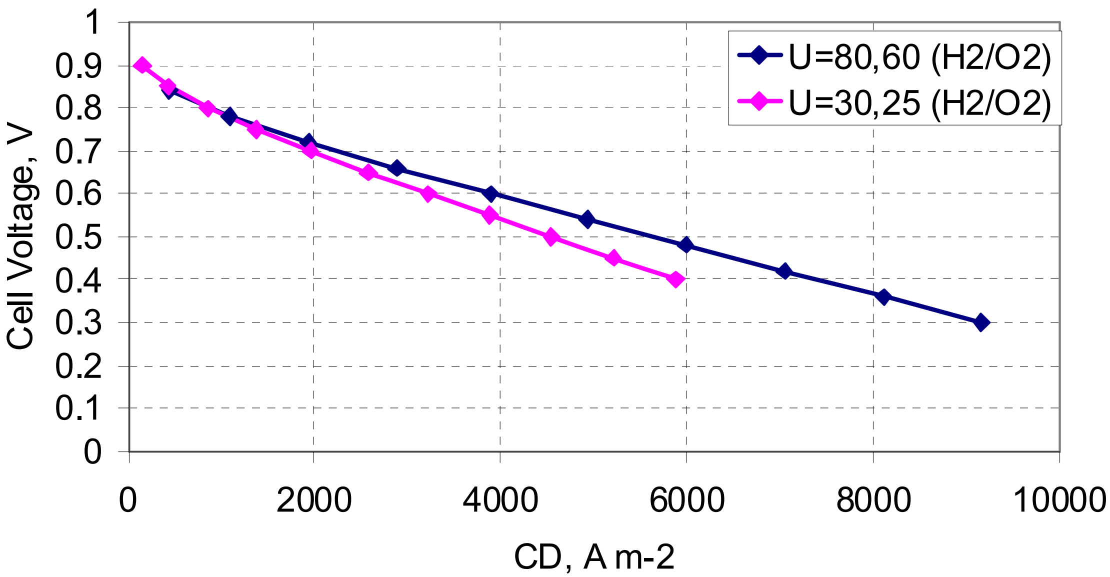
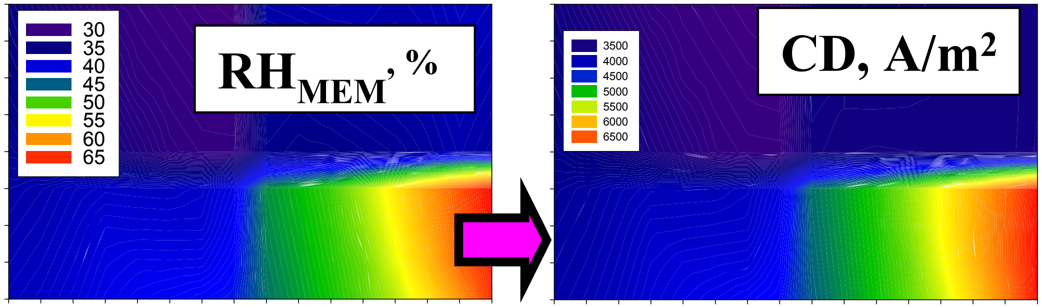
- Performance improves at higher utilizations
  - RH&Conductivity DOMINATE PERFORMANCE over O_2 concentration







Cathode Catalyst Development Approach

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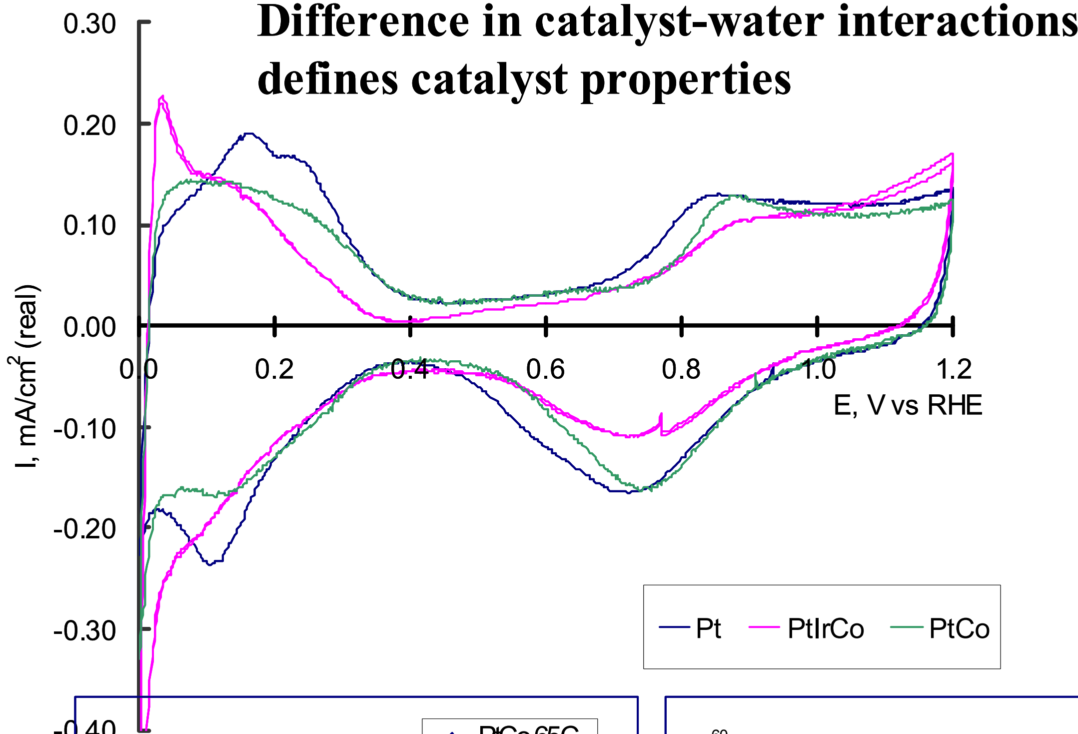
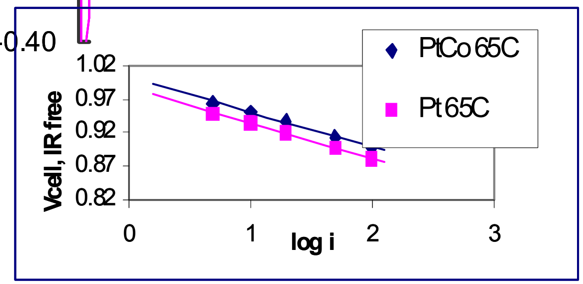
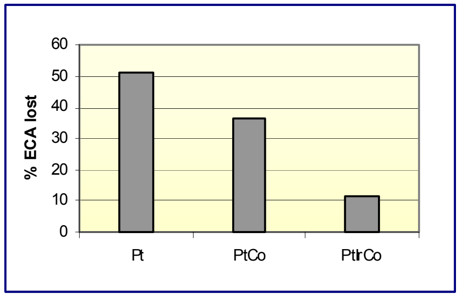
- Higher activity cathode catalyst systems: binary and ternary alloys
  - Carbothermal synthesis
  - PtCo and PtIrCo leading systems
- High loading of noble metal to decrease electrode thickness and achieve mass transport benefit







MEA Optimization

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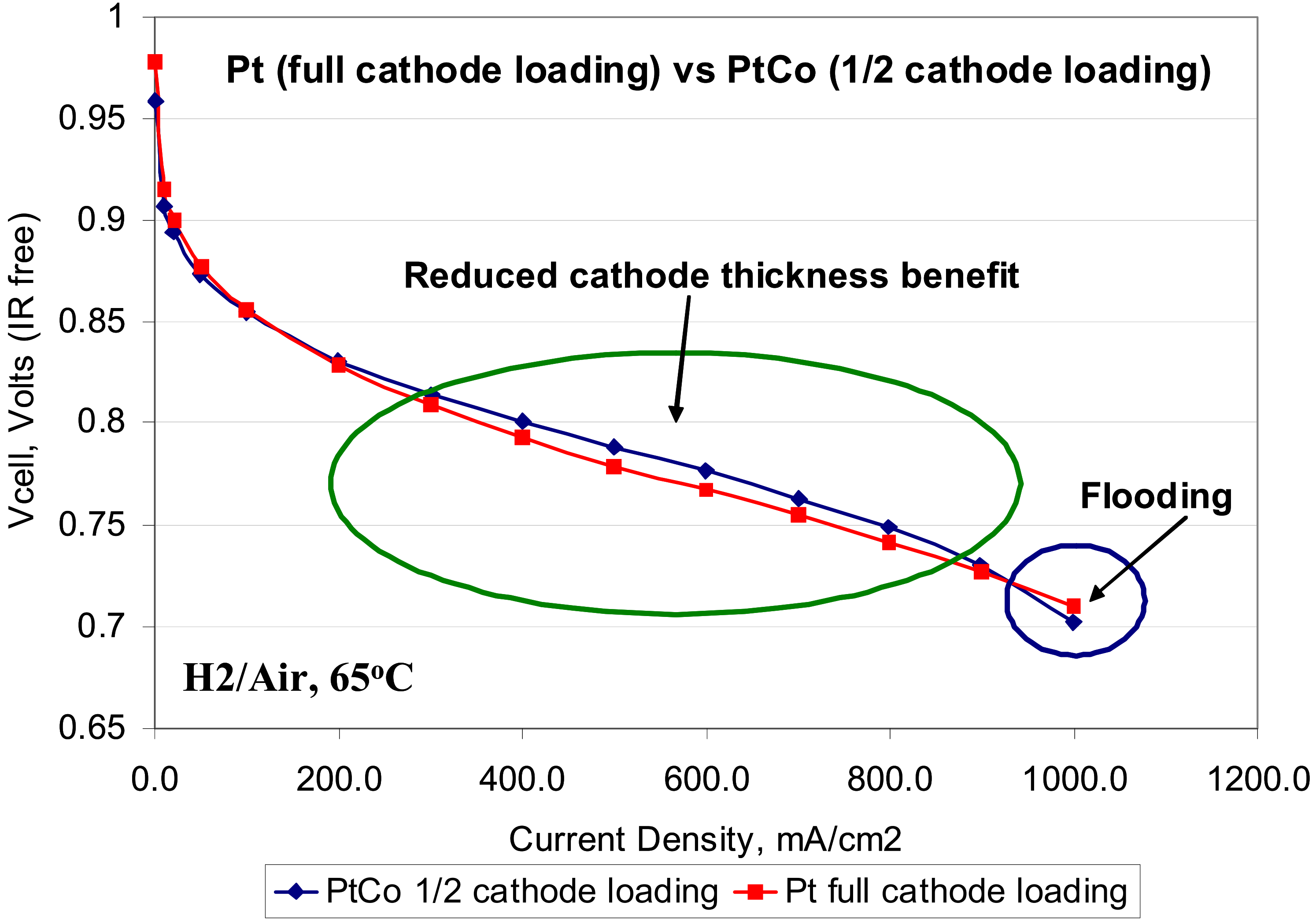


PtCo 20-Cell Stack

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

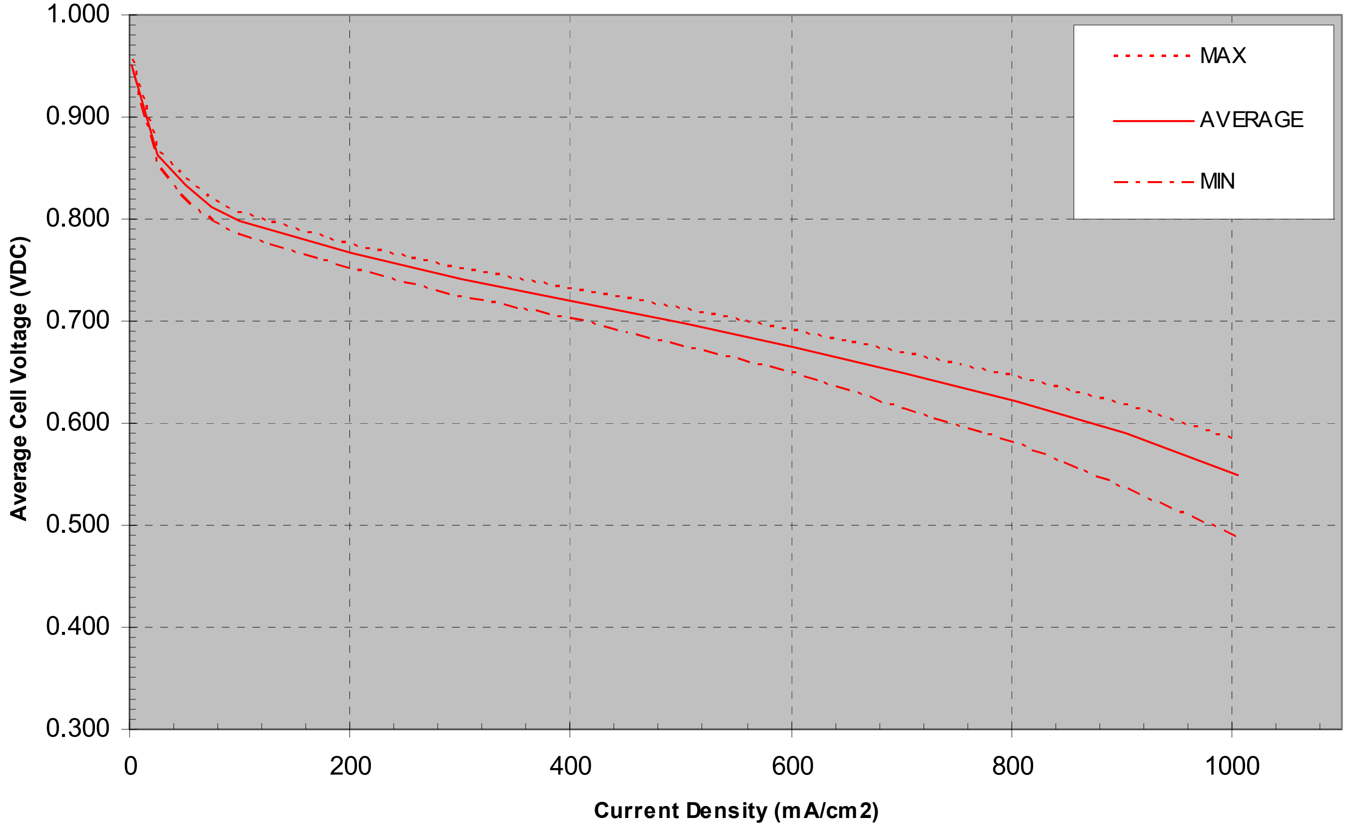
<u>PtCo MEA specification:</u>

0.35mgPt/cm^2

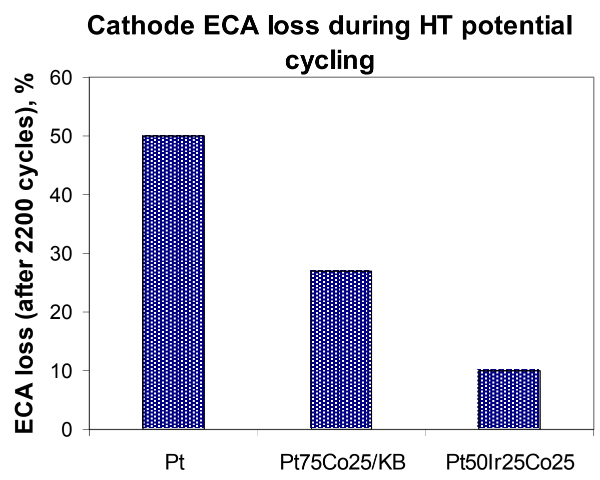
Nafion® 112

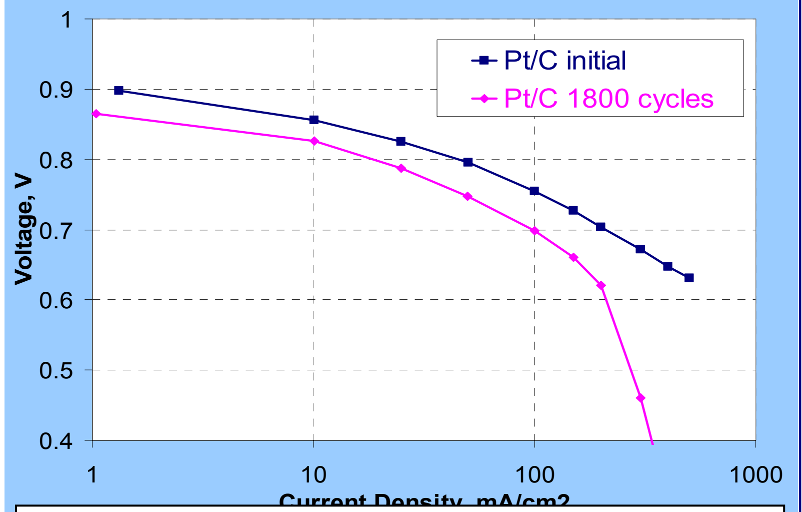
Toray GDL

UTCFC planform (400cm^2)

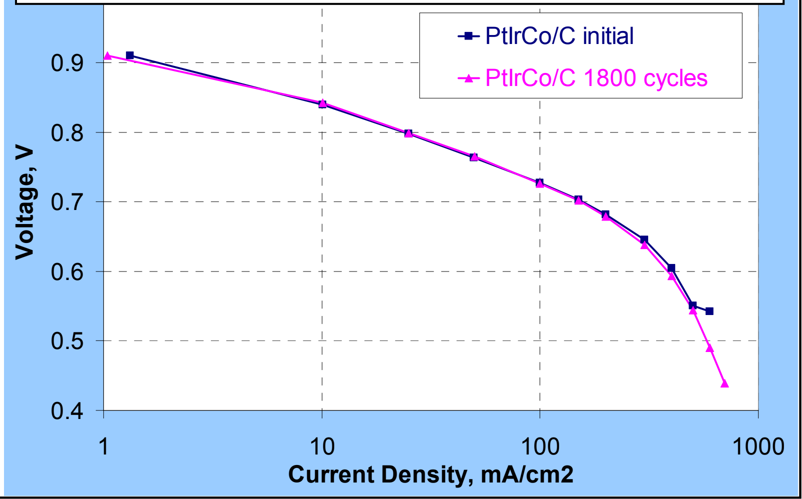


Alloy Catalyst Durability





H_2/O_2, 120ºCºC, 50%RH, 1.5atm.



Potential cycling conditions:

120ºC, 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

Alloy Effect on Ionomer Durability

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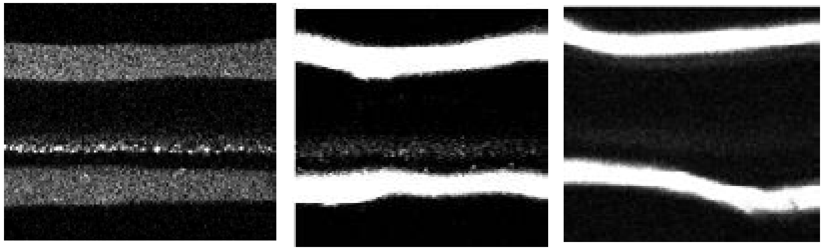
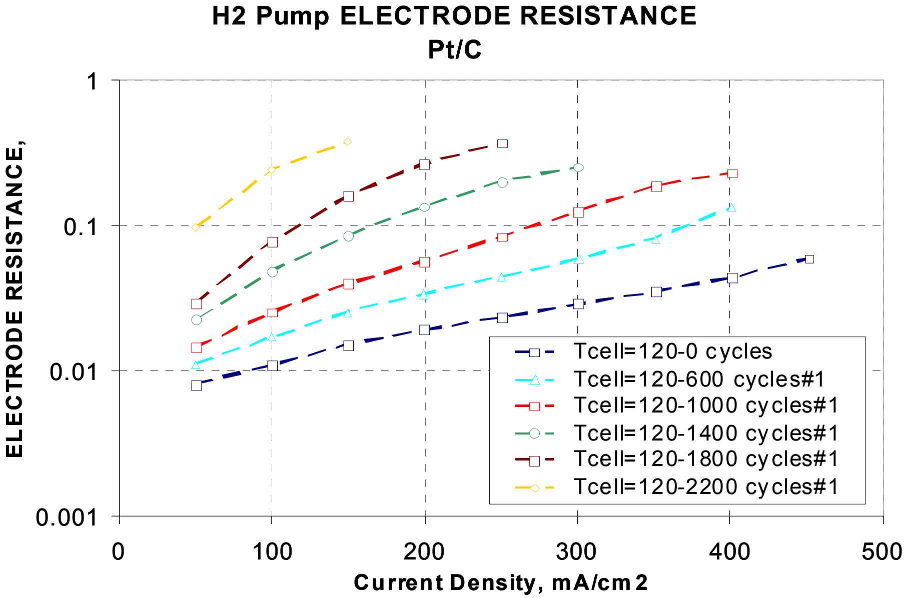
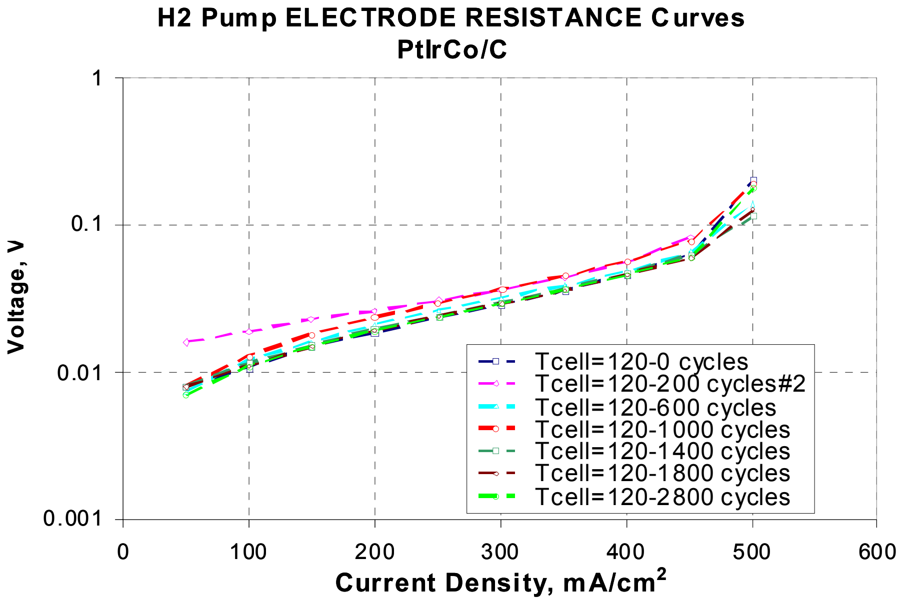
– 10 % H_2 in N_2, low utilization
– Electrode Ionic resistance changes with time
– PtIrCo cathode prevents ionomer poisoning

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.

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