Development of High Temperature Membranes and Improved Cathode Catalysts

DOE contract DE-FC04C-02-Al-67608

2003 DOE Funds: 2.7 M$

DOE Merit Review

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UTC Fuel Cells

UTC Fuel Cells
A United Technologies Company

May 19, 2003

Outline

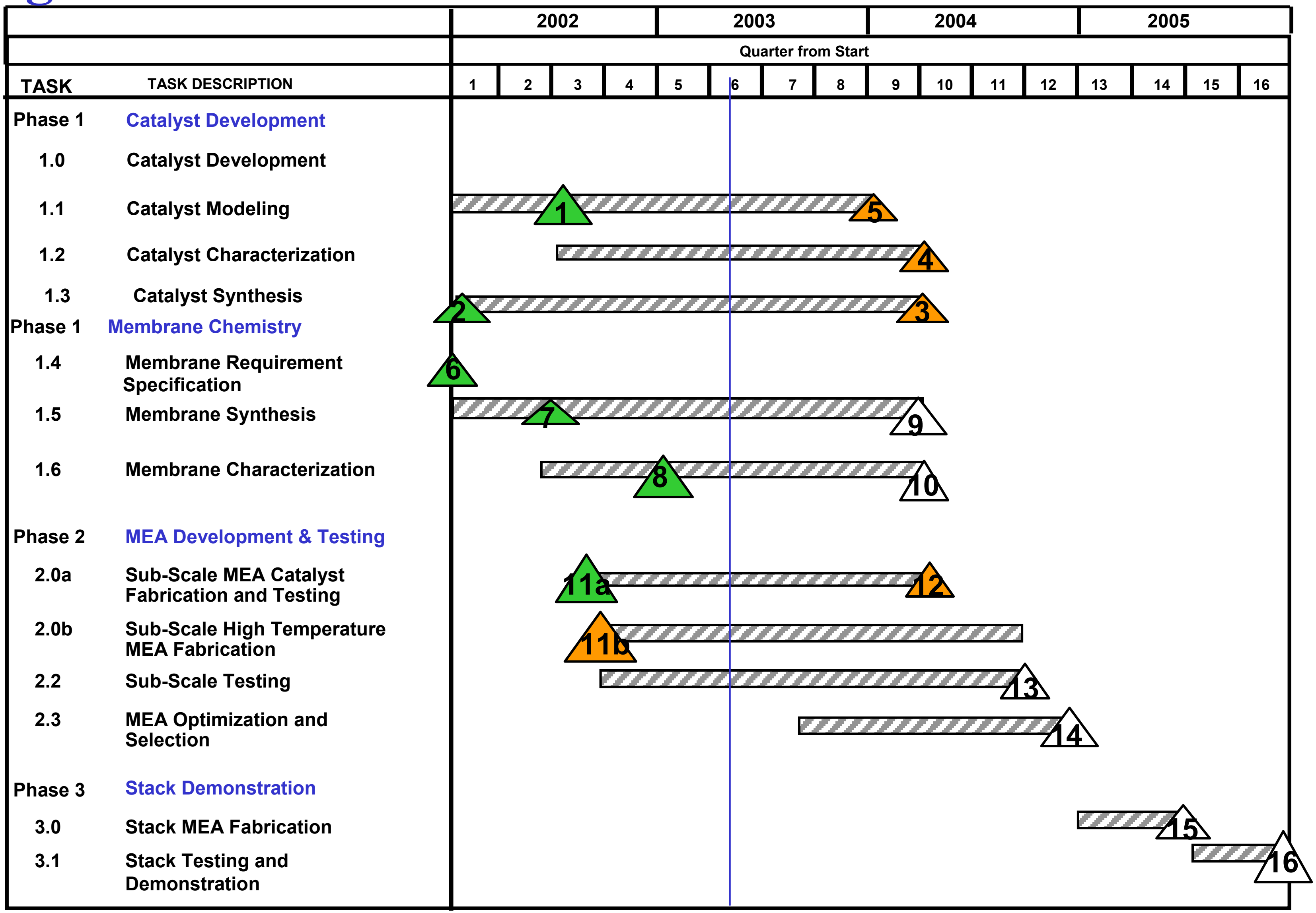
- Objectives
- Approach
- Project timeline
- Technical highlights:
  - High-temperature membrane (HTM)
  - Advanced cathode catalysts
- Future work

Objectives and Approach

- **High temperature proton exchange membranes**
  - Develop membranes capable of satisfying DOE targets. Operating conditions: *120*°C -150°C and 1.0-1.5 atm.
  - Collaboration with leading polymer chemists to develop new membrane systems.

- **Advanced cathode catalysts**
  - Develop high concentration Pt-alloy catalyst systems with improved activity.
  - Utilize the higher activity, reduce catalyst-layer thickness and achieve reduced precious-metal loading (DOE goal of 0.05 mg/cm^2).

Program Timeline



Milestone Schedule

PHASE	MILESTONE #	MILESTONE
Phase 1 Membrane Chemistry and Catalyst Development	1	Preliminary model completed
	2	Begin alloy synthesis
	3	Complete alloy synthesis
	4	Complete characterization and down-selection
	5	Complete modeling + correlation
	6	Membrane specification to team members
	7	Initial sample membrane
	8	Characterization of initial membrane samples
	9	Synthesis of final membrane samples
	10	Select membrane for Phase 2
Phase 2 MEA Development and Testing	11a	Initial electrode fabrication (catalyst)
	11b	Initial electrode fabrication (HTM)
	12	Complete subscale testing for cathode catalyst and down-select catalysts
	13	Complete subscale testing for membranes and down-select membrane(s)
	14	Select optimum catalyst-membrane combination for Phase 3
Phase 3 Stack Demonstration	15	Complete test and assembly of 2-20 cell stacks.
	16	Complete stack verification test

High-Temperature Membrane Team

DOE Program Management

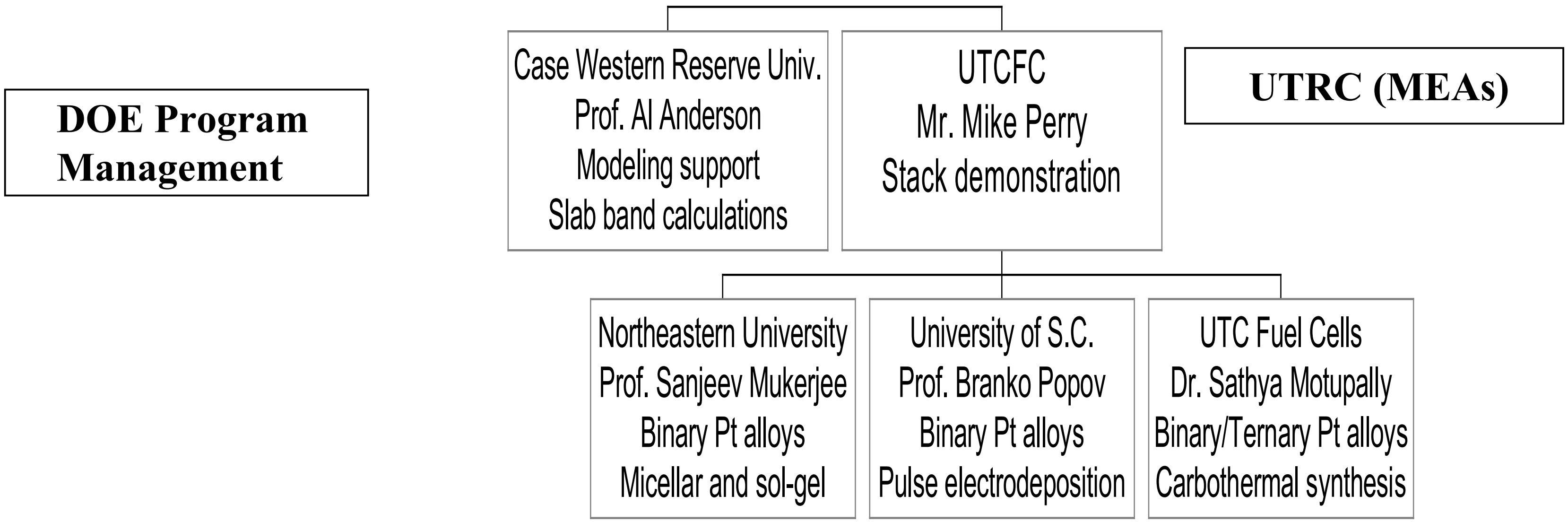
UTCFC
Mr. Mike Perry
System optimization
Stack demonstration

UTRC (MEAs)

Virginia Tech.	Stanford Research Institute	Penn State	Ionomem	Princeton University
Prof. Jim McGrath	Dr. Susanna Ventura	Prof. Digby MacDonald	Mr. Len Bonville	Prof. Andrew Bocarsly
Poly arylene ethersulfones	Modified polyetheretherketone	Poly ethersulfones	Nafion* w/ heteropoly acids	Modified Nafion*

- Collaboration with leading polymer chemists to develop new membrane systems.
- Systems include non-Nafion® and also modified-Nafion® membranes.

Advanced Cathode Catalyst Team



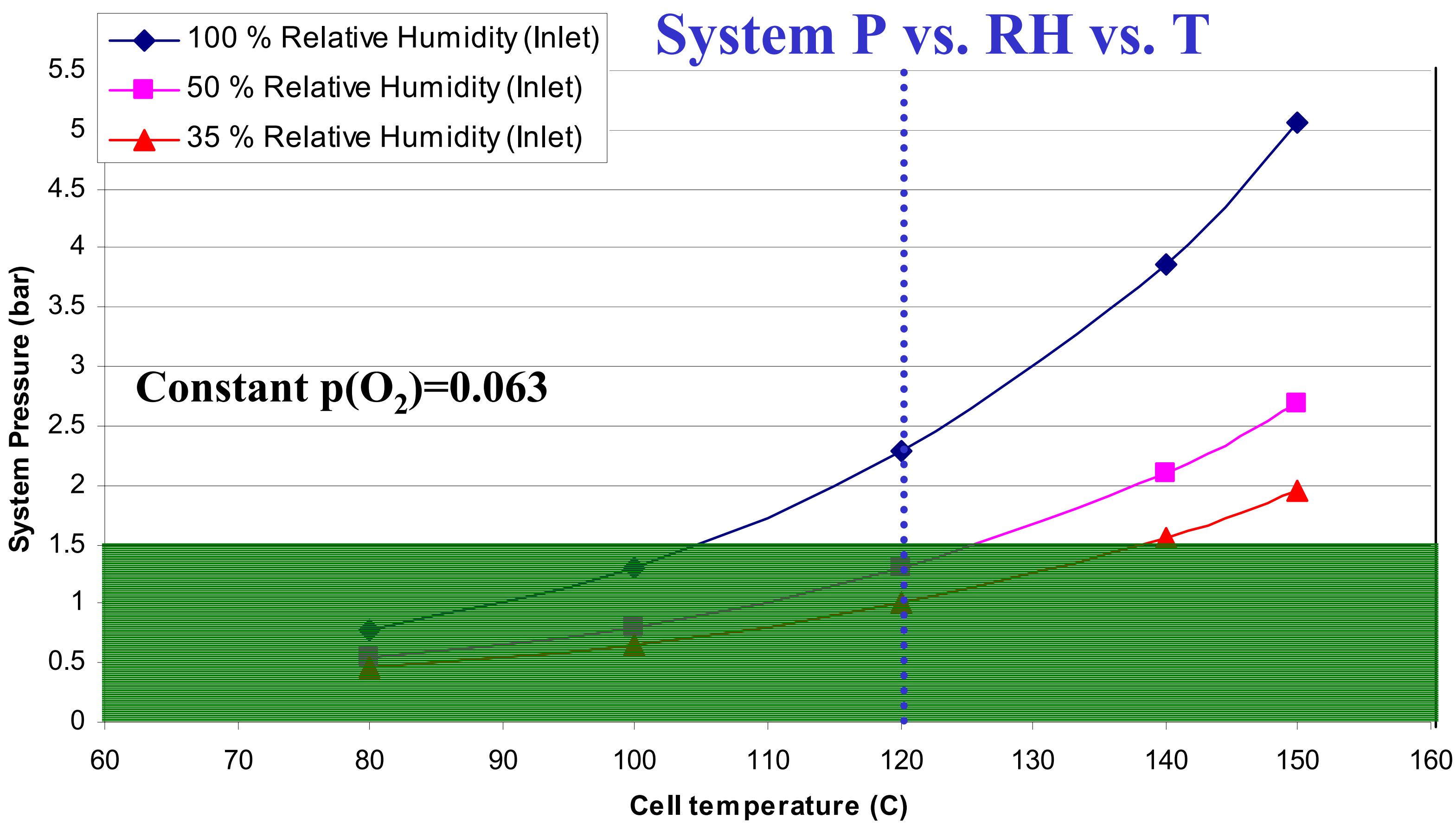
- Collaboration with leading electrochemists to develop higher activity catalyst systems.
- Systems include binary and ternary Pt alloys.
- Various deposition routes being investigated.

High-Temperature Membranes

Summary of Technical Achievements

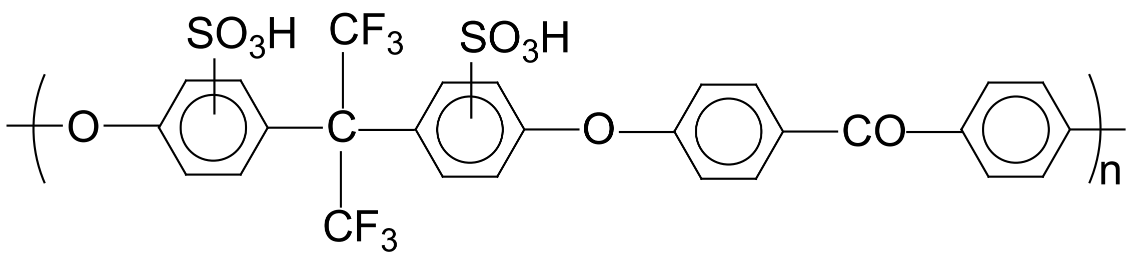
- 4 membrane systems with proton conductivity on the order of 10 mS/cm at 120 C and 50% RH synthesized.
  - BPSH from Va. Tech
  - Modified S-PEEK from SRI
  - FPES from Penn State and
  - HPA filled Nafion® from IONOMEM
- Majority of membranes synthesized date on the program require hydrophilic fillers to conduct at reduced RH.
- IONOMEM has established a baseline for HTM performance of 0.6 V at 0.4 A/cm^2 (120 C, 30% RH).

System Pressure Requirements



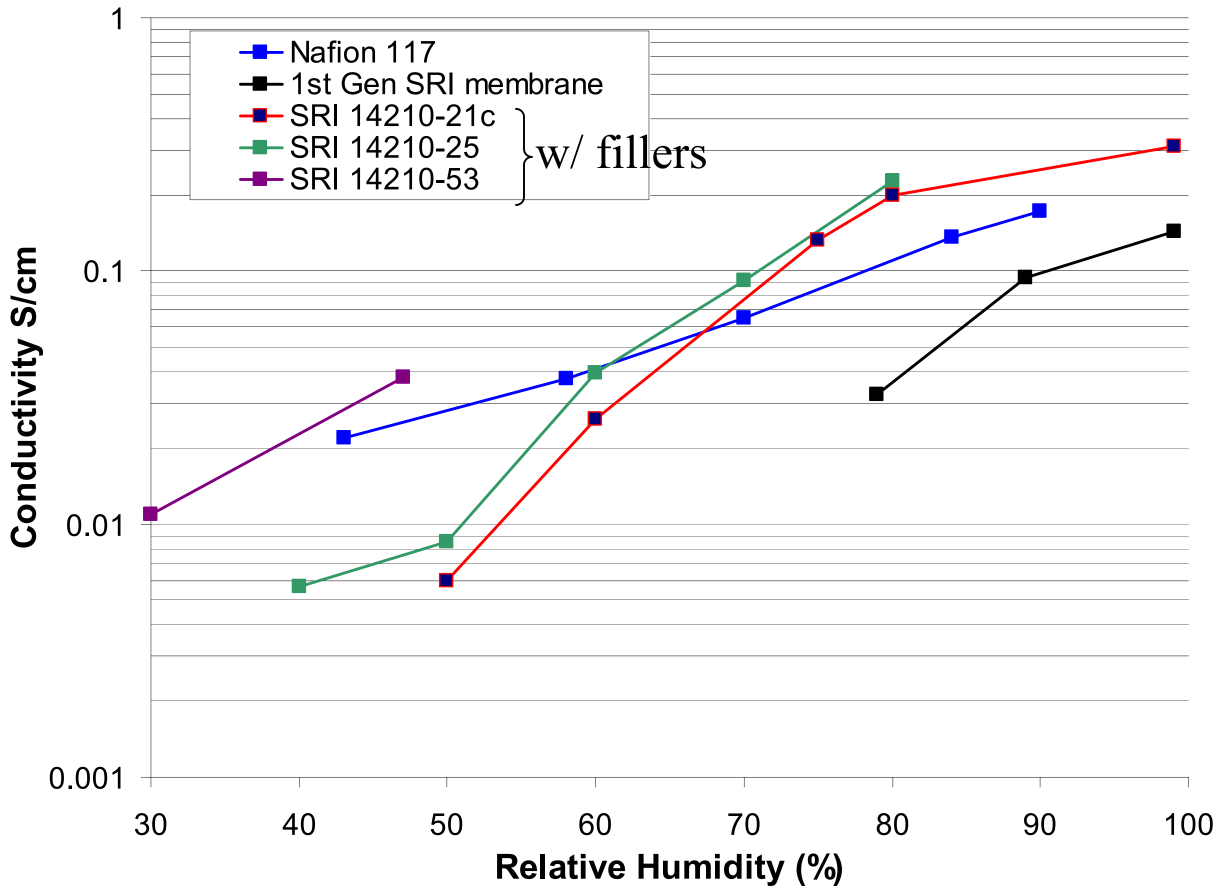
SRI Approach

- SRI polymer membrane is based on sulfonated liquid crystalline polymers crosslinked to produce dimensionally stable and flexible membranes.



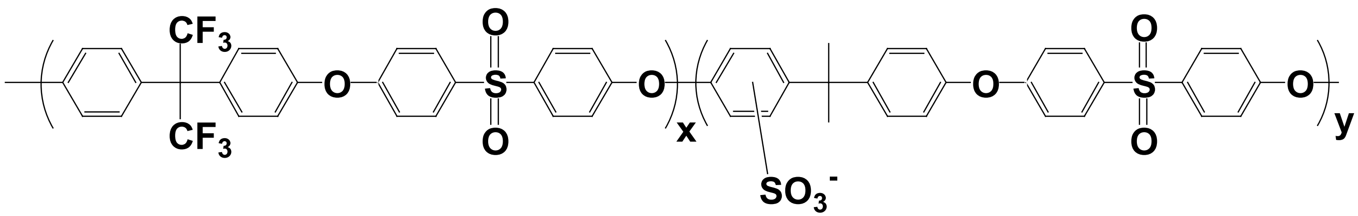
  – Hydrophilic polymers designed to retain water of hydration are added to the membrane to aid in conductivity at reduced RH.

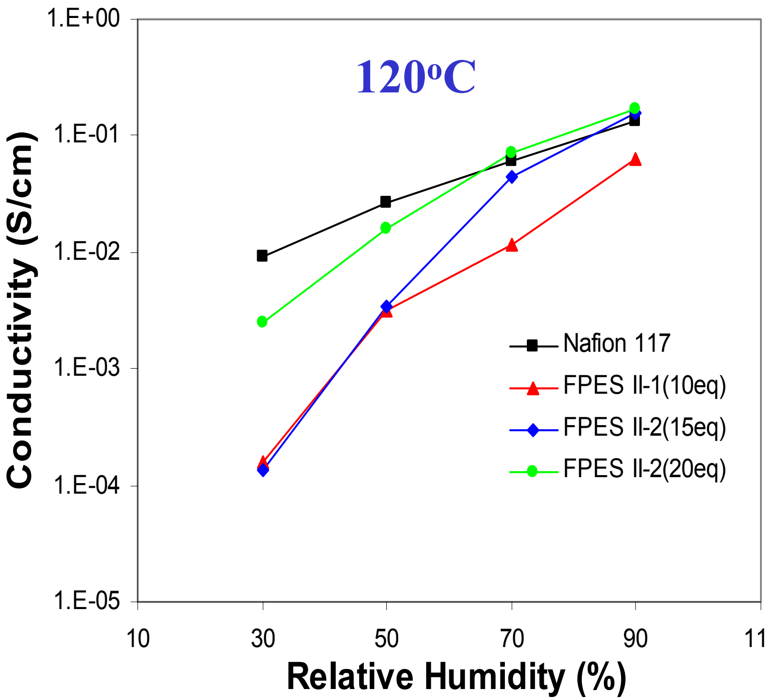
Membrane Conductivity at 120^{o}C vs. RH

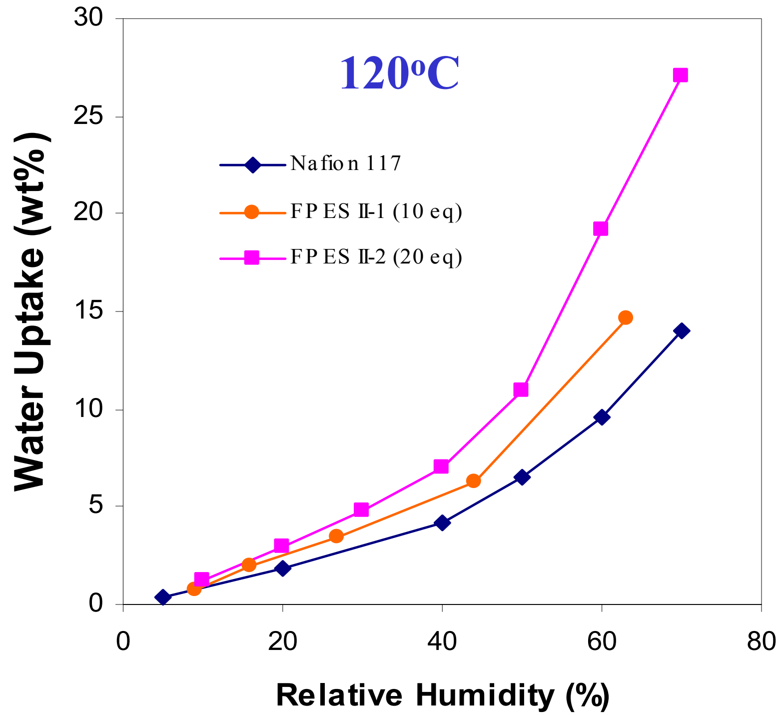


- Conductivity of 0.011 S/cm at 120^{o}C@ 30% relative humidity and 0.038 S/cm at 120^{o}C@ 47% relative humidity.

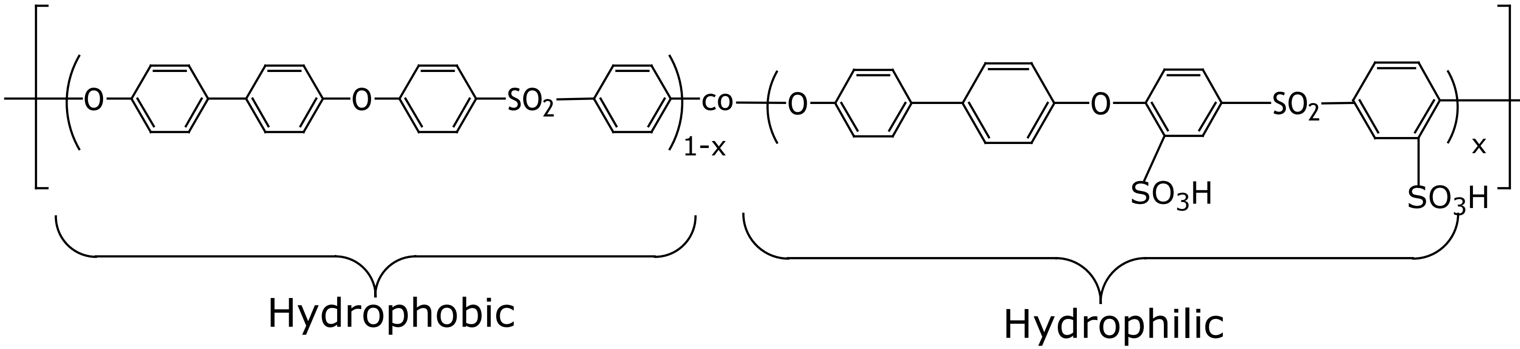
F-PES Membrane (Penn State)



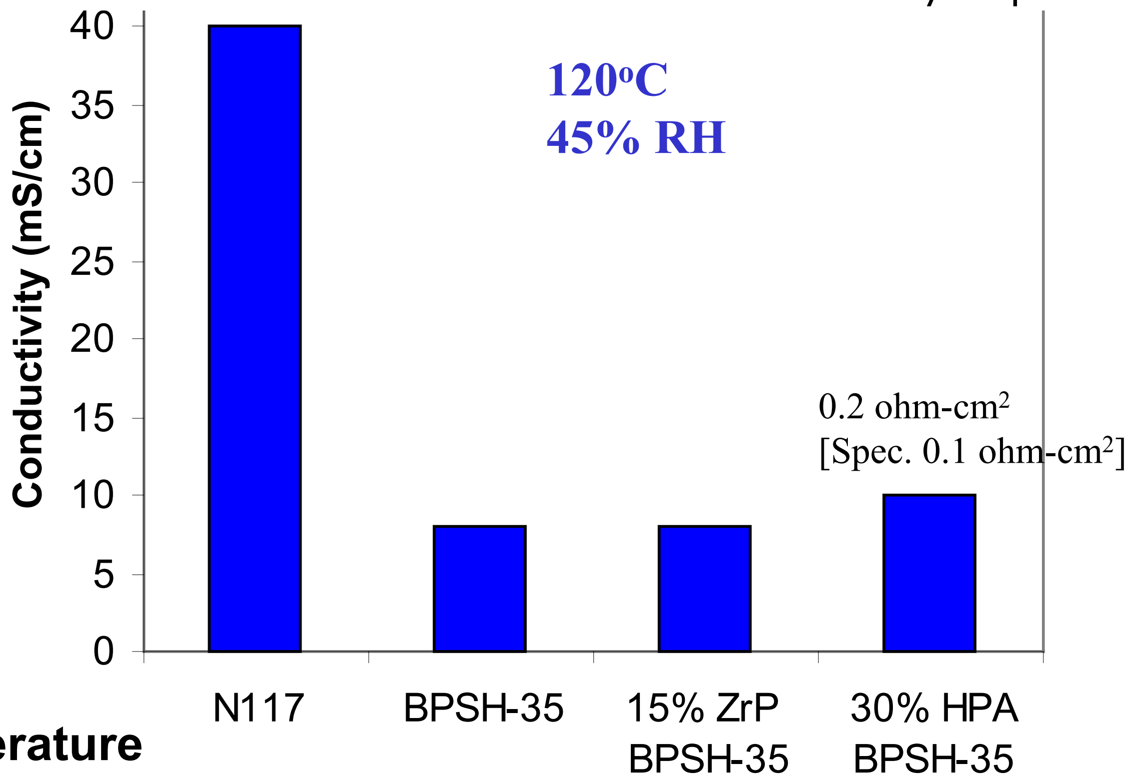




BPSH Membrane Virginia Tech



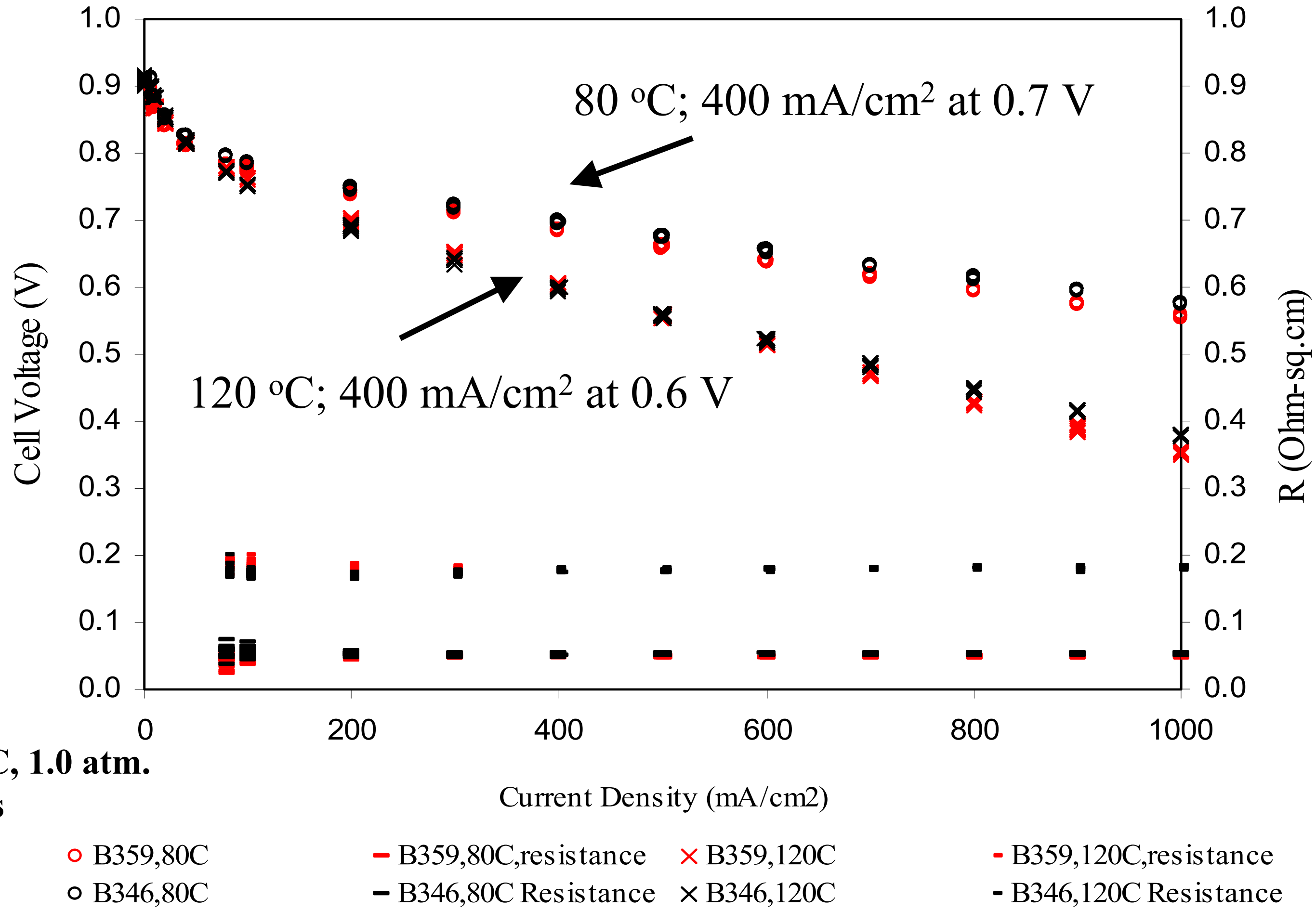
Bi-phenyl sulfones



Upper use temperature fully - hydrated T_g **99°C** **135°C**

Nafion®-HPA Composite Membranes (IONOMEM)

Nafion®-Teflon®-phosphotungstic acid (HPA)



80 °C and 120°C, 1.0 atm.
H_2/air reactants
3.3/4.0 Stoich.

Future Work (2003)

- Further optimization of membrane systems and/or fillers required to improve conductivity at practical RH.
- Develop a generalized stability template for HTMs.
- Initiate HTM down-select process.
- Initiate HTMEA fabrication and optimization.

Advanced Cathode Catalyst

Summary of Technical Achievements

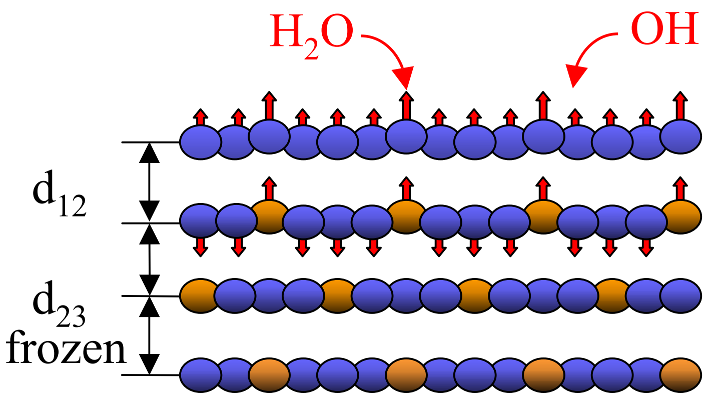
- Slab band calculations using VASP program have provided insight into binary alloy skin effect.
- Higher activity and more stable binary Pt alloys synthesized using the colloidal-sol, carbothermal, and pulse electrodeposition routes.
- Reproducible and SOA CCMs fabricated using the decal transfer process.

VASP Modeling (Case Western)

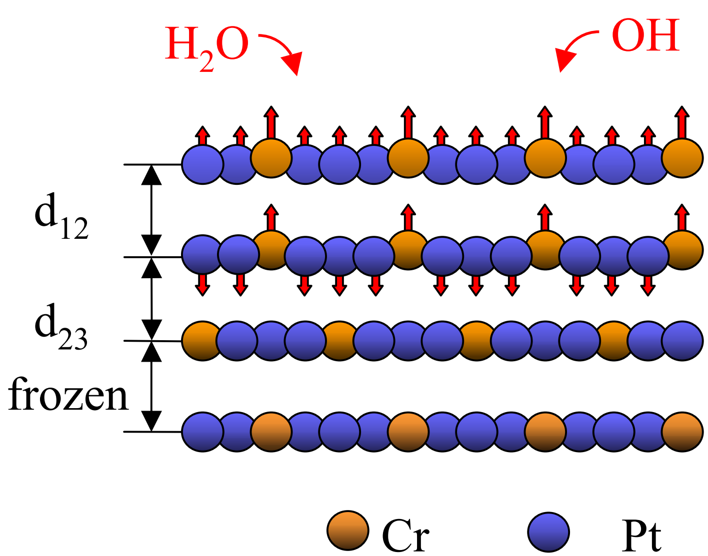
$\Delta U^{o} = U^{o}(\text{alloy}) - U^{o}(\text{Pt}) =$

$[\ (D_0(OH)_{Pt}\ - D_0(OH_2)_{Pt}\ ] - [D_0(OH)_{alloy} - D_0(OH_2)_{alloy}\ ]$

Pt(111)-skin on Pt_3Cr



Mixed metal surface on Pt_3Cr

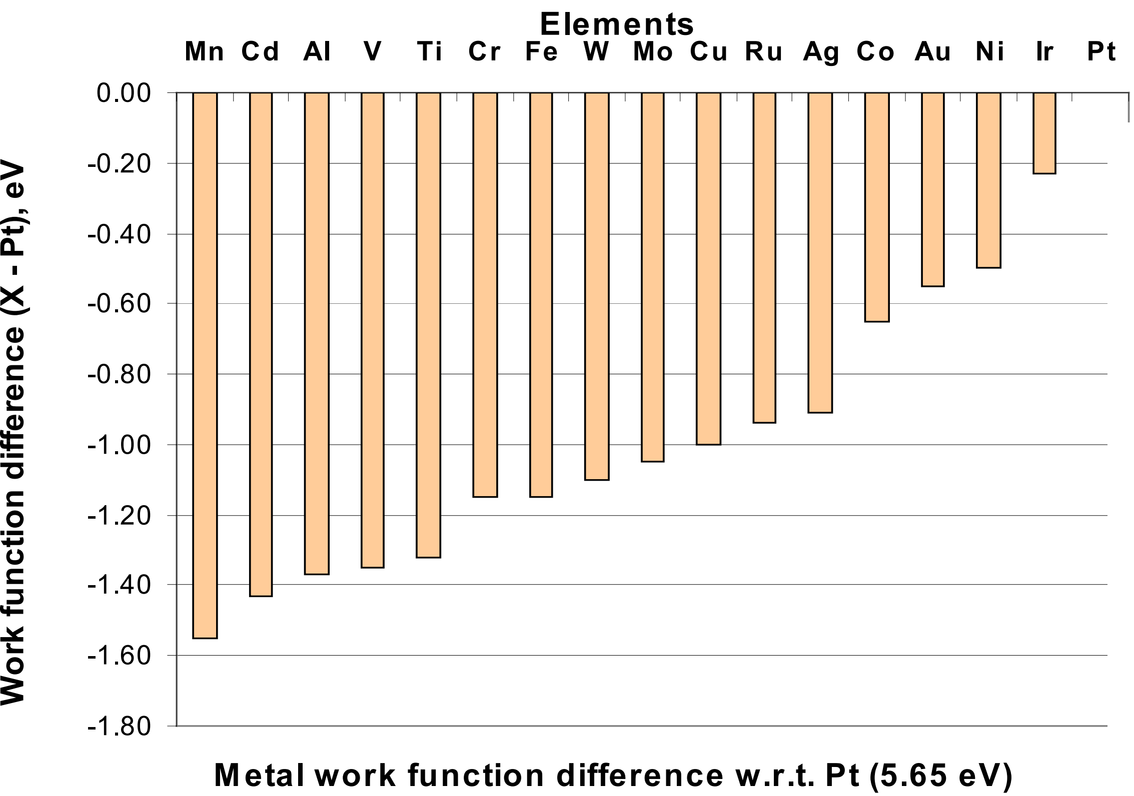


Catalyst surface	D_0(Surface-OH) eV	D_0(Surface-OH_2) eV	ΔU^{o} eV
Pt(111) (θ = 0 ML)	2.371	0.231	0
Pt(111)-skin on Pt_3Cr (θ = 0 ML)	2.241	0.210	0.11
Pt_3Cr mixed metal surface (θ =0 ML)	3.316 on Cr 2.516 on Pt	0.628 on Cr 0.204 on Pt	-0.55 -0.17

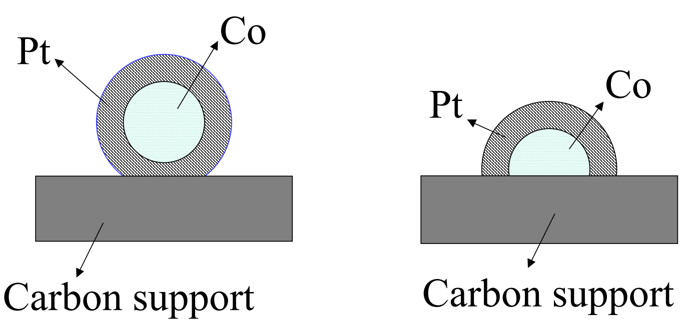
- On Pt-skin, model model predicts that charge transfers from Cr to Pt skin.

Shell-Core Structures (UTCFC)

- The model studies support the following model structures for composite catalysts based on the work-function differences.
- Current effort is focused on verifying this core-shell concept experimentally in conjunction with the theoretical modeling.

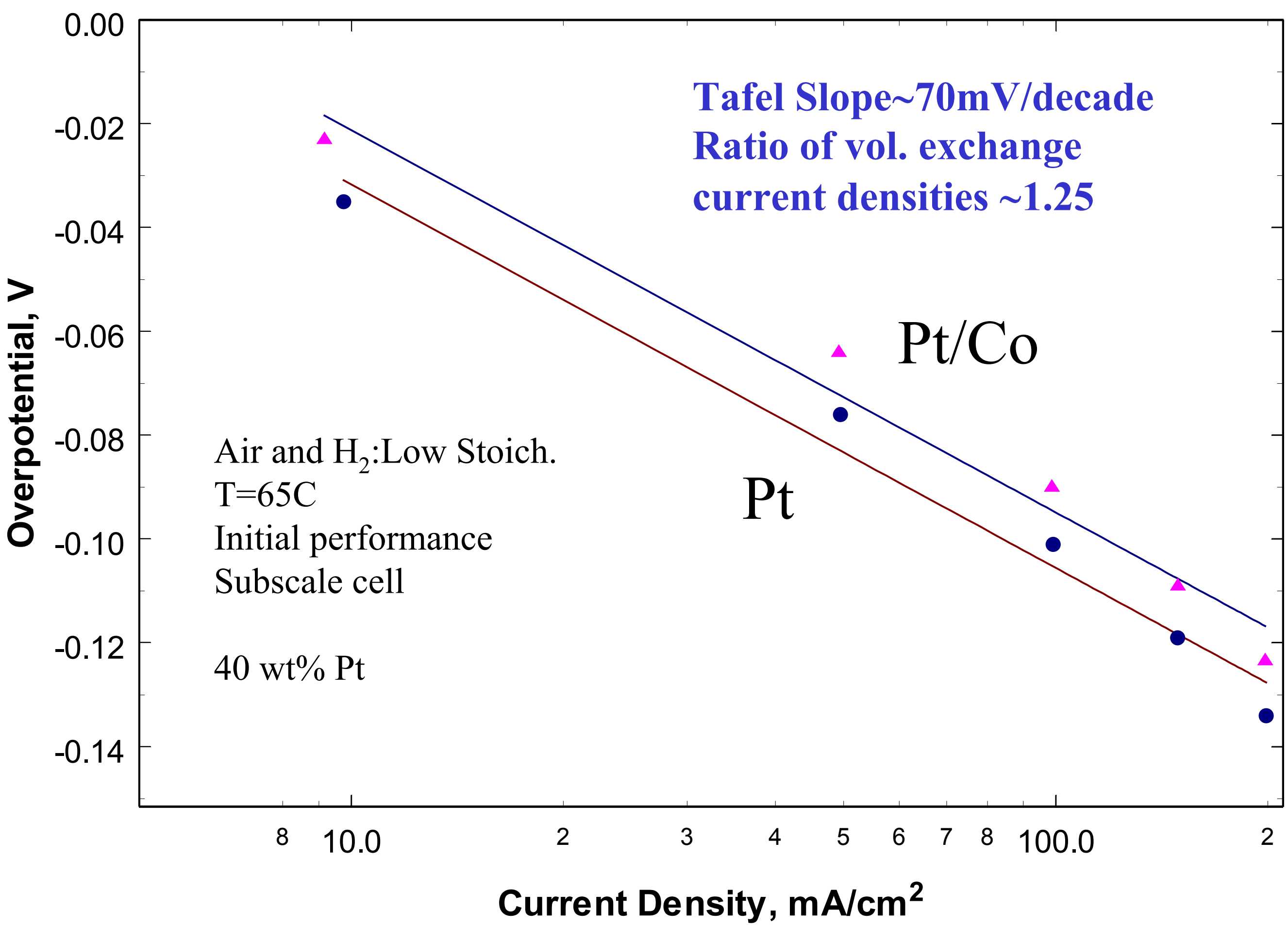


Supported $Metal_{core}$ – Pt_{shell} nanoparticles



Kinetic Enhancement with Pt-Co Binary Alloy (UTCFC)

- True catalyst activity of Pt-Co is approximately 2.2 X Pt.



$$i = p_{O_2} a.i_0 e^{-\alpha \frac{F}{RT}\eta}$$

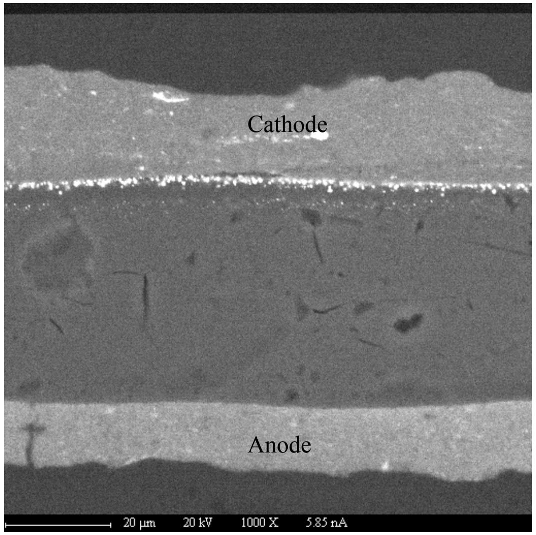
η=A+B log(i)

η=overpotential
i=current density
$a.i_0$=Exchange current density

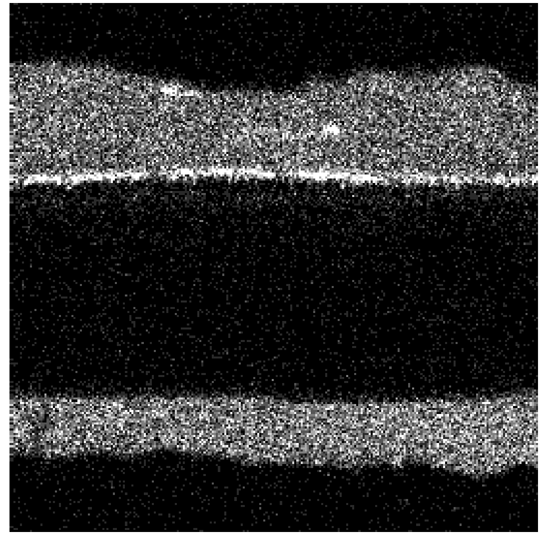
Cycling Stability with Pt-Co

(a) PtCo CCM

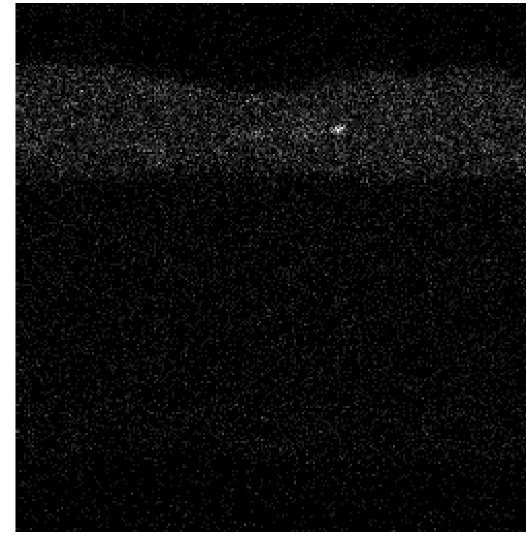
4000 Cycles
1.3 V-0.9 V



B.S.E.

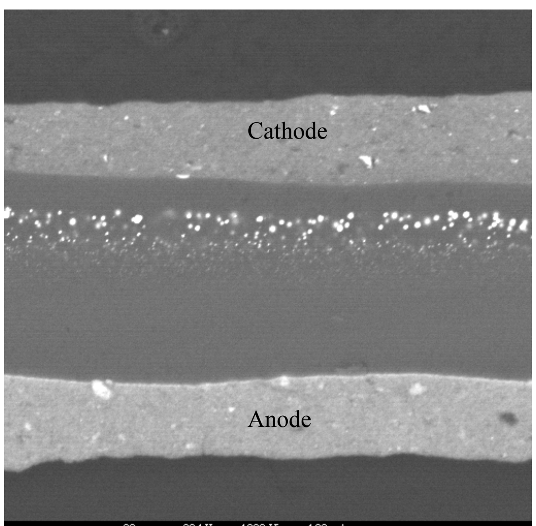


Platinum



Cobalt

(b) Pt CCM



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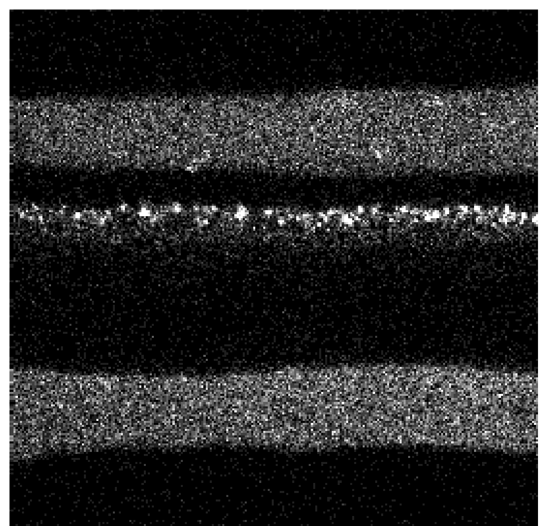
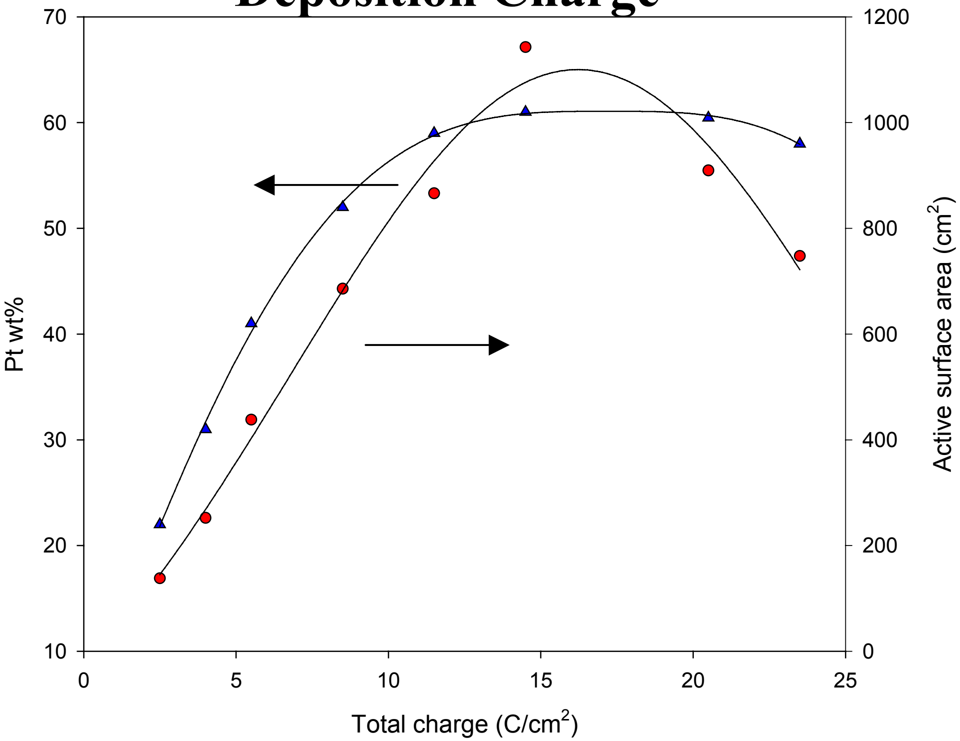


Platinum

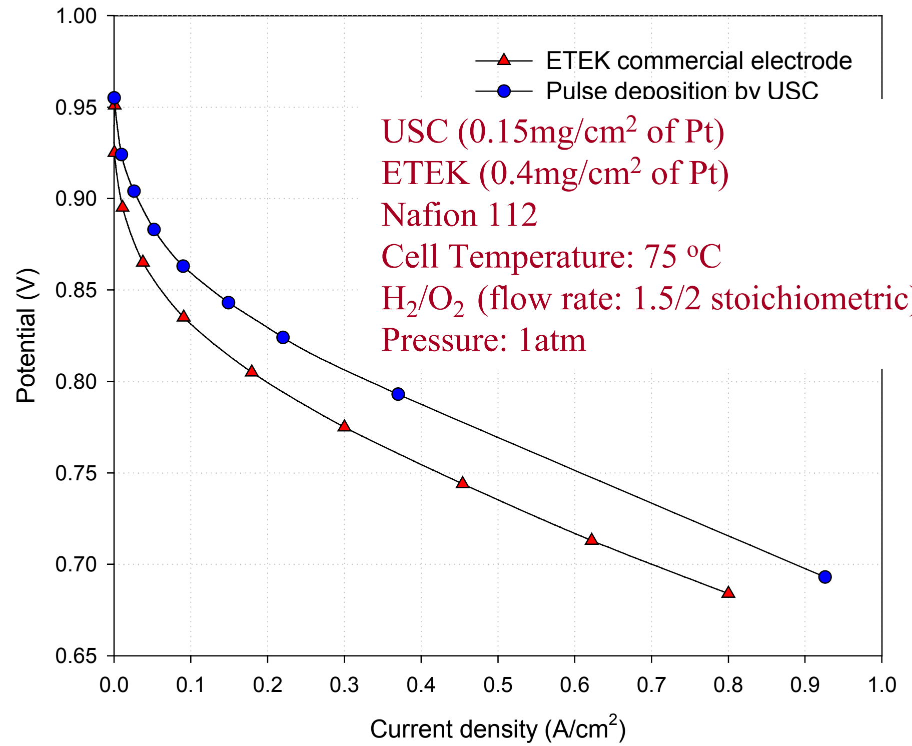
- The electron microprobe analysis shows no evidence of Co in the membrane and/or anode.
- The absence of Co migration is a strong benefit for the Pt/Co alloy system.

Pt Pulse Electrodeposition (USC)

Pt wt% vs. Surface area vs. Deposition Charge



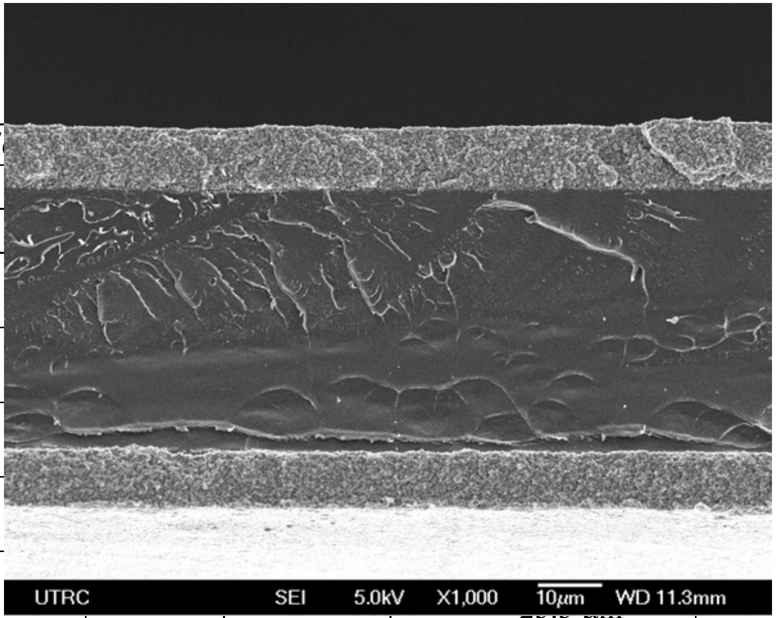
Sample Performance Curve



CCM Fabrication (UTRC)

- Reproducible and SOA CCMs currently being fabricated with decal transfer process.

HRSEM of a Freeze Fracture



Relatively Uniform Cathode Thickness, ~10 µm

CCM ID	V, mV @ 400 mA/cm		V, mV @ 100 mA/				
	H_2/O_2	H_2/Air	H_2/O_2	H_2/Air			
DOE target**	0.80		0.85				
Commercial → PEM 411***	0.824	0.786	0.885	0.			
PEM 404	0.800	0.760	0.875	0.			
PEM 413	0.795	0.757	0.879	0.			
PEM 414	0.790	0.748	0.880	0.			
PEM 415	0.810	0.767	0.887	0.			
PEM 416	0.798	0.756	0.886	0.854	69	44	Membrane thickness

** DOE targets are specified for 85%H_2/60%O_2 utilization;

*** Pt Loading on cathode side=0.4g/cm^2;

Future Work (2003)

- Investigate the feasibility of Pt/X skin effect.
- Continue Pt-alloy synthesis using the various routes and optimize for activity and stability.
- Initiate catalyst down-select process.
- Investigate several methodologies to reduce Pt loading (e.g., ionomer gradient, etc.)