



FC-PAD

Fuel Cell – Performance and Durability

FC139 – Modeling, Evaluation, Characterization

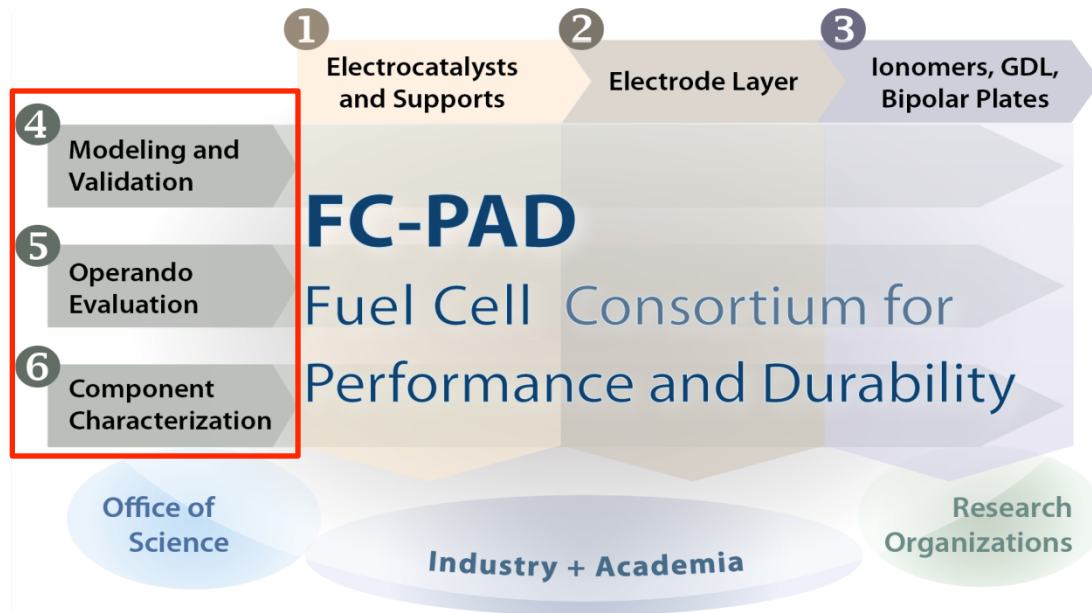
Presenter : Rangachary Mukundan

June 8th, 2016



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FC-PAD Overview & Cross cutting thrusts



Objective of Thrusts 4-6

- Develop and implement characterization techniques and models to improve performance and durability of fuel cells
 - Highly integrated into Thrusts 1-3
-
- Operando evaluation and durability is focus of this presentation
 - Supported by modeling and characterization not specific to individual components

FC-PAD contributors to this presentation



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Current Collaborators

- GM/W. L Gore (SOA MEAs)
- IRD, Ion Power (MEAs)
- Umicore (Catalyst)
- SGL Carbon (GDLs)
- National Physical Laboratory (Reference electrode)

Partners to be added by DOE DE-FOA-0001412



Overview - Relevance

Timeline

Project start date: 11/20/2015

Project end date: 09/30/2020

National Labs

- ANL, LANL, LBNL, NREL, and ORNL

External Collaborators

- IRD, New Mexico
- Umicore, Germany
- GM, USA
- W. L. Gore, USA
- Ion Power, USA
- Tanaka Kikinzoku Kogyo (TKK), Japan
- National Physical Laboratory, United Kingdom

Barriers

- Durability of PEMFC stacks, which must include tolerance to impurities and chemical and mechanical integrity, has not been established
- Sufficient durability of fuel cell systems operating over automotive drive cycles has not been demonstrated
- Development and implementation of accelerated stress tests (ASTs) are needed to shorten the time required to address durability issues
- MEA Targets:
 - 300mA @ 0.8V
 - 1W/cm² @ rated power
 - 5000 hour durability

Overview - Approach (Operando Evaluation/Durability)

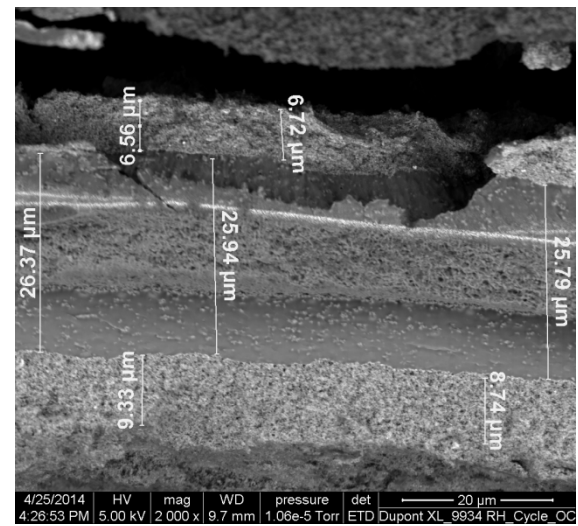
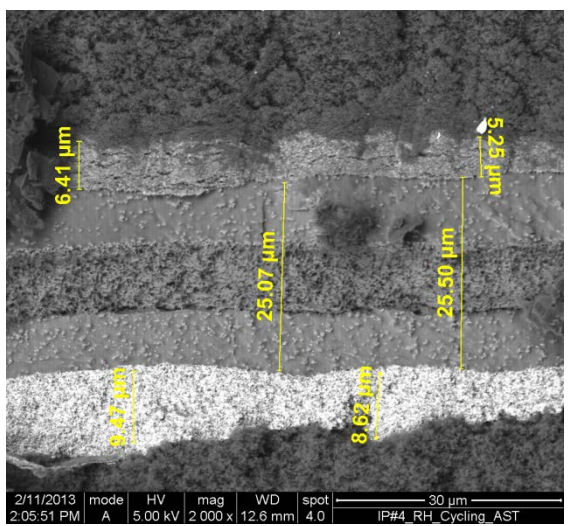
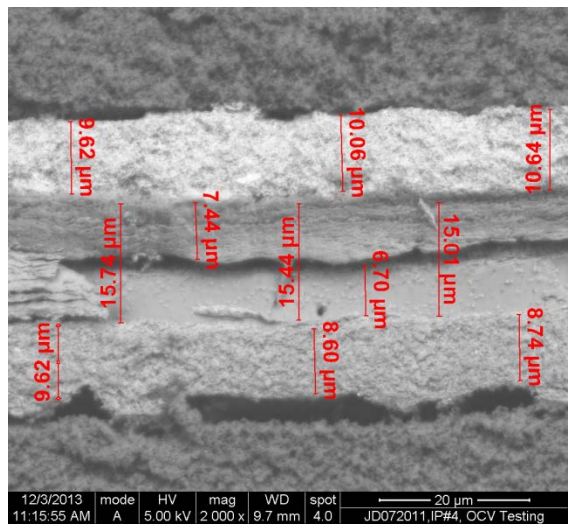
- Refine ASTs
 - Proposed new membrane and electrocatalyst ASTs
- Evaluate durability of Pt-alloy catalyst based MEAs and propose methods to improve durability
 - Operando evaluation, Characterization and Modeling
- Impurity effects on fuel cell performance
 - Reversible/Recoverable degradation (membrane degradation fragments)
 - Sulfate anion poisoning
- Benchmark SOA MEA
 - Obtained MEA with membrane from Gore and SOA catalyst from GM
- Develop/Apply advanced electrochemical characterization techniques
 - Reference electrodes

Accomplishments : Adoption of Membrane AST

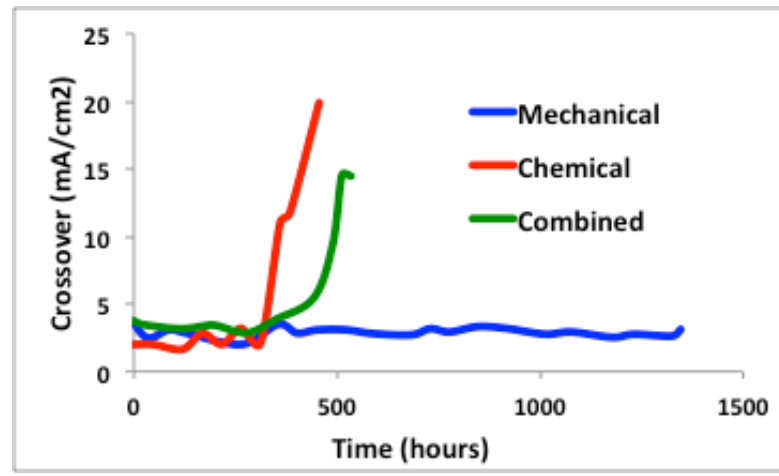
Severe degradation of DuPont XL[®] after 307 hours @ OCV

No degradation of DuPont XL[®] 20098 RH Cycles

Degradation of DuPont XL[®] 9934 RH Cycles in OCV



- 30sec wet and 45sec dry cycles in H₂/Air
- Similar RH stresses as determined by HFR
- Cycling time needs to be adjusted based on HFR

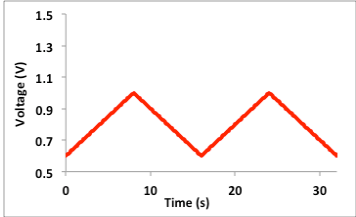


Mechanical : RH cycling @ 80 °C, Air (saturated = 2mins, dry = 2mins)
 Target = 1333 hours (20,000 cycles)
 Chemical: OCV hold at 90 °C, 30%RH
 Target = 500 hours
 Combined : RH cycling @ 90°C; H₂/Air (saturated = 30s, dry = 45s)
 Target = 500 hours (24,000 cycles)

See additional slide for FCTT adopted AST

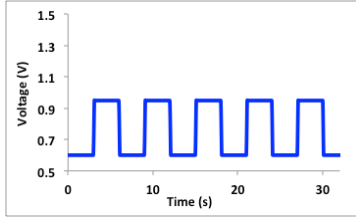
Accomplishments : Adoption of Electrocatalyst AST

0.6 to 1.0V cycles



Target = 133 hours

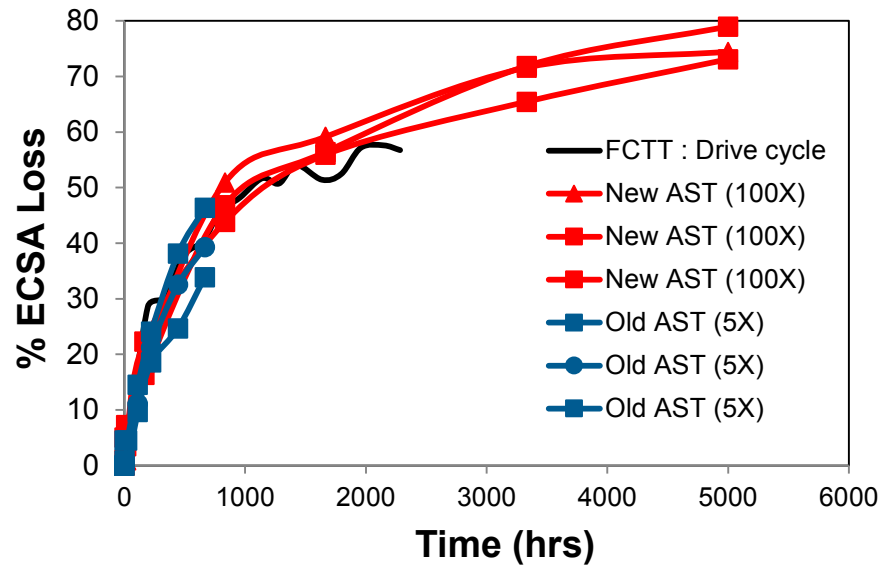
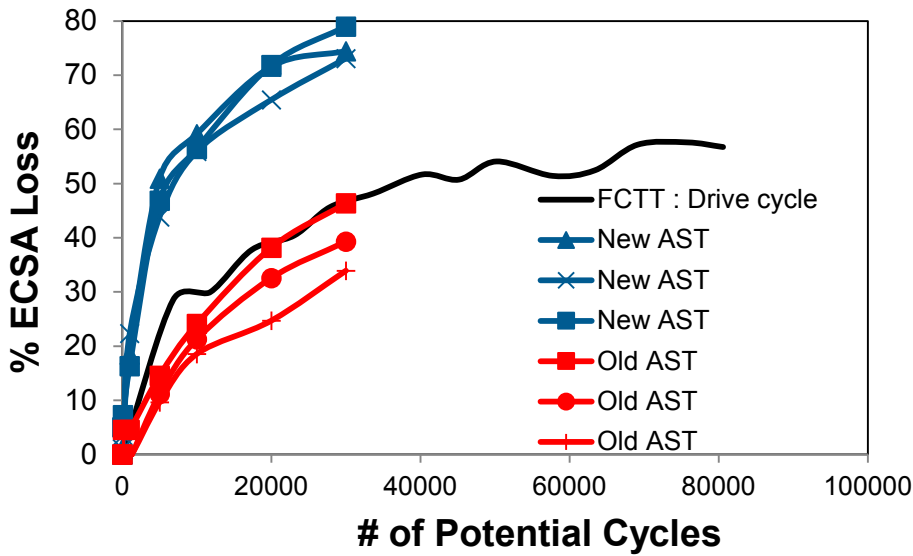
0.6 to 0.95V cycles



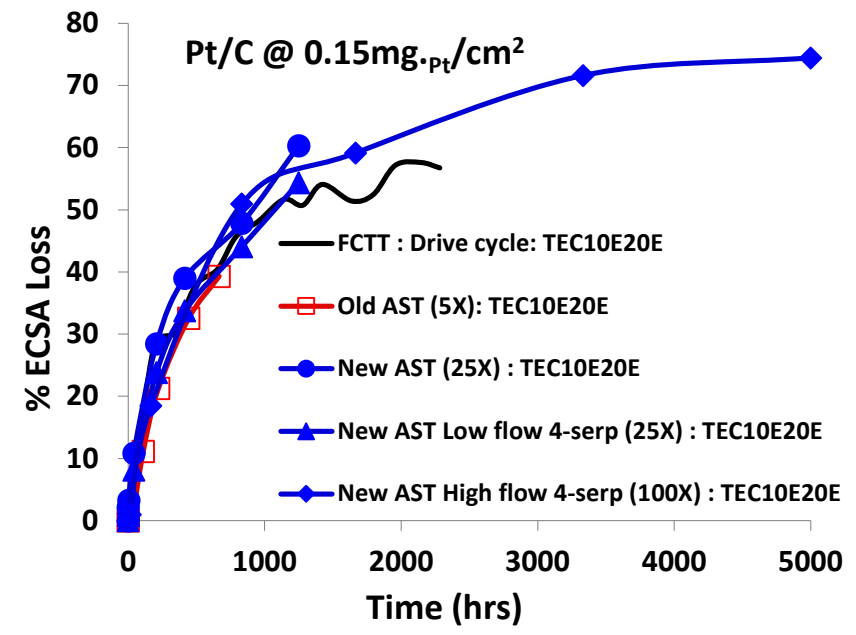
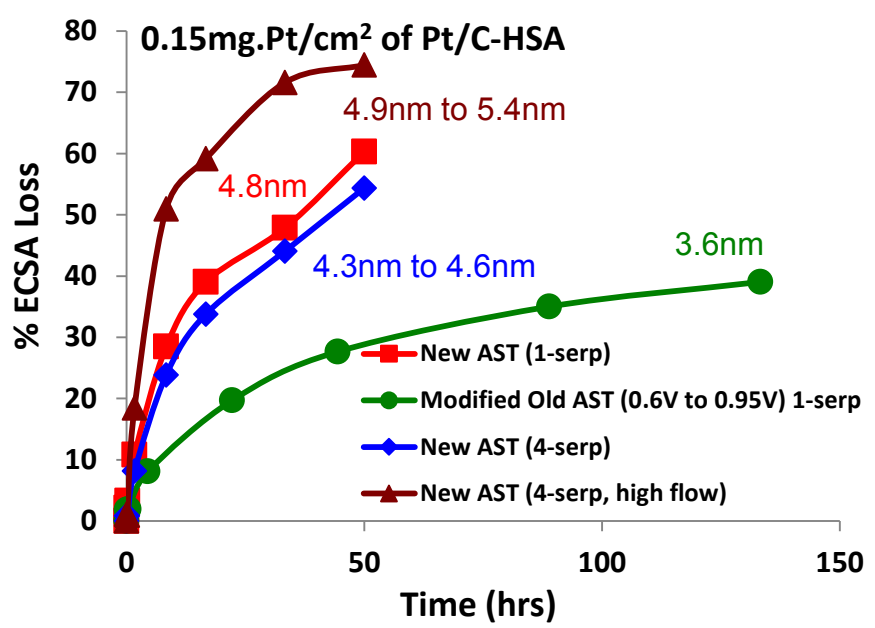
Target = 50 hours

- **New AST 20X faster than old AST and 100X faster than FCTT durability protocol**

Higher N₂ flow rates (200sccm vs 75sccm)

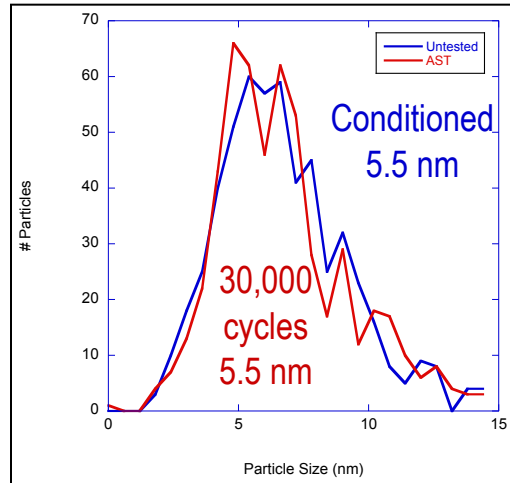
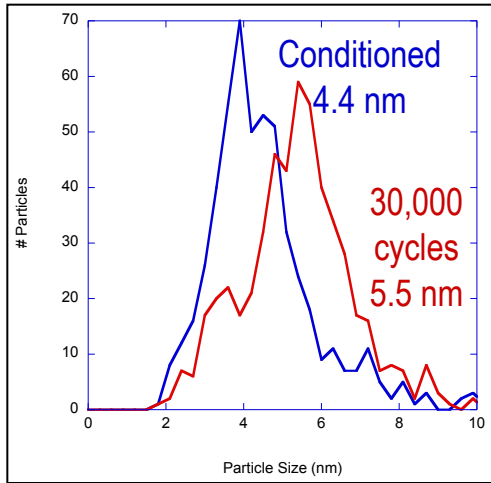
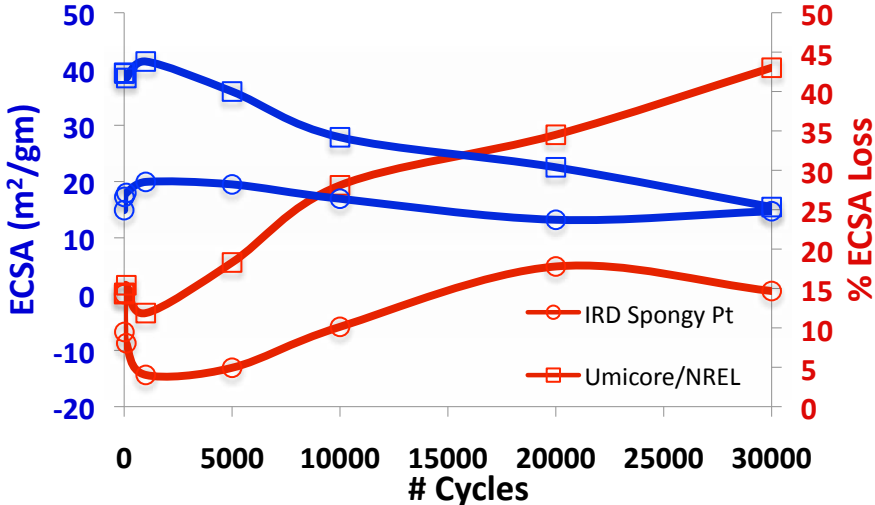


Accomplishments : Refined catalyst AST



- Acceleration factor can be increased with increasing N₂ flow rate
- High N₂ flow (200 sccm) results in 100X acceleration while low N₂ flow (75 sccm) results in 25X acceleration
- Spatial variation in degradation is greater at the higher flow rate
- Use 75sccm N₂: 5X acceleration over old AST

Accomplishments : Alloy catalyst durability

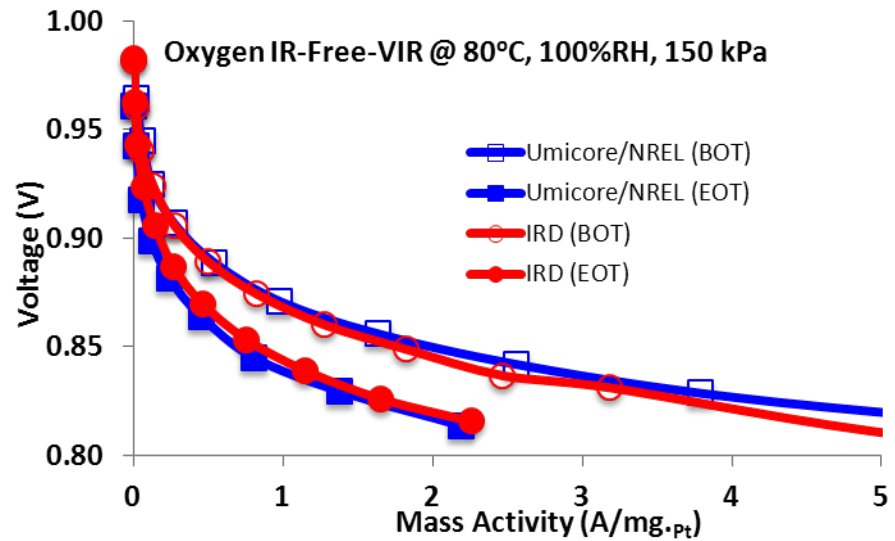
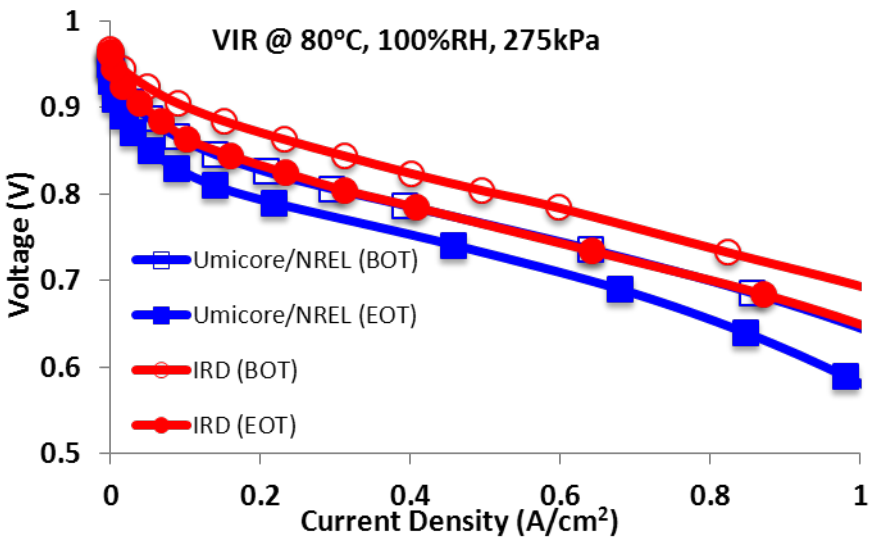


- The 3 alloy catalysts tested met the BOL mass activity criteria (Thrust 2)
- Surface area and beginning catalyst particle sizes are different
- The smaller particle size catalysts grew from 4.4nm to 5.5nm
- The larger particle size catalyst showed no increase (5.5nm) after AST
- ECSA loss of 40% can be met by starting with larger catalyst particle (> 4.5 nm)

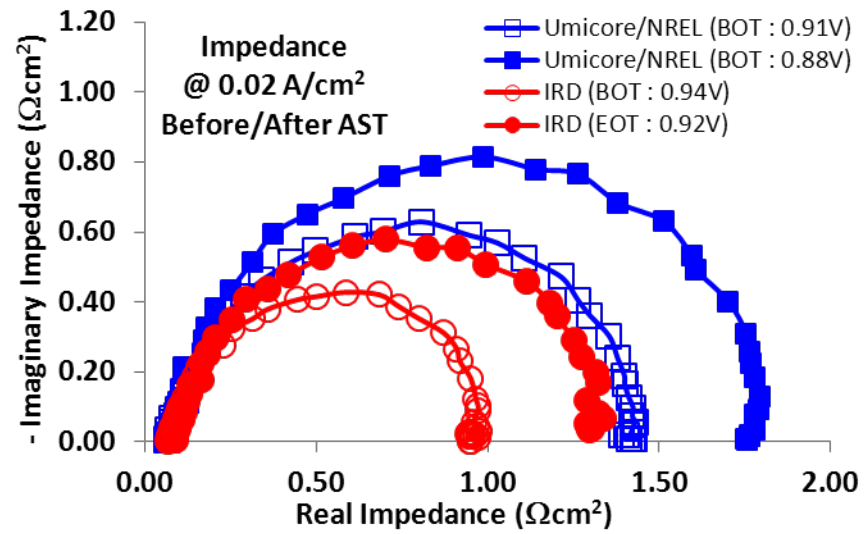
Note: Loading not identical

IRD = 0.21mg_{Pt}/cm² and Umicore/NREL = 0.1 mg_{Pt}/cm²

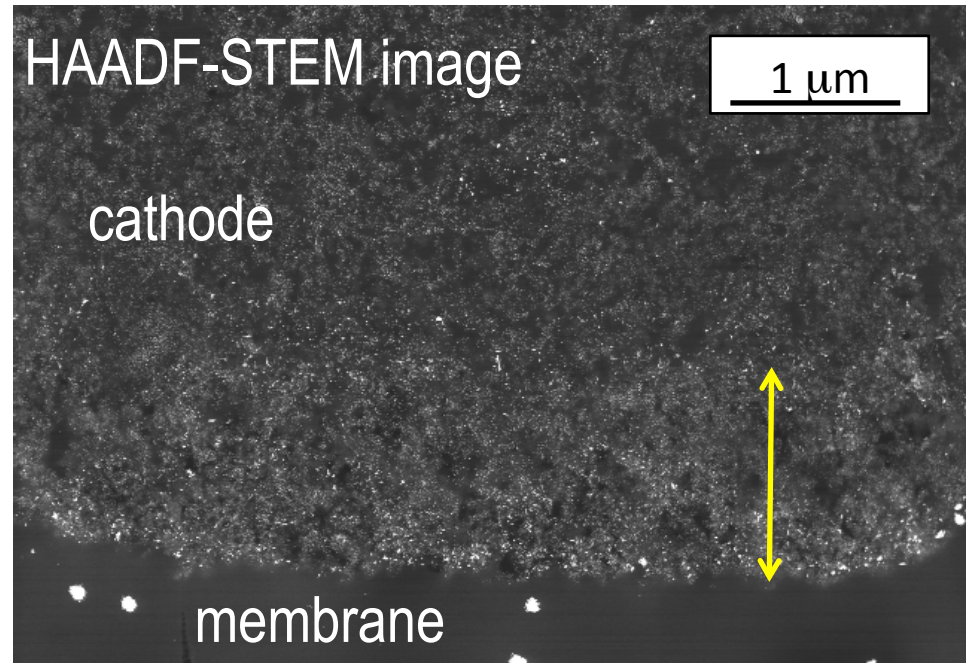
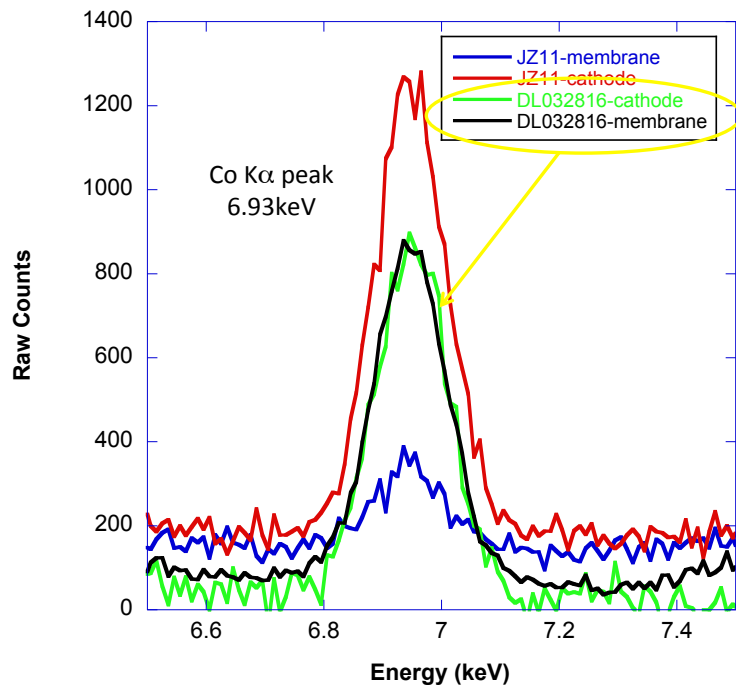
Accomplishments : Alloy catalyst durability



- Fuel cell performance decreases even though ECSA can be constant
- Kinetic losses observed and seem to be independent of ECSA losses
- Losses > 30mV @ 0.8 A/cm²

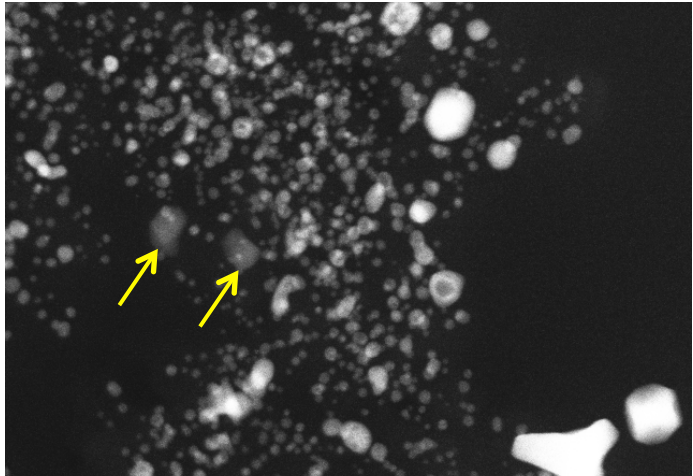
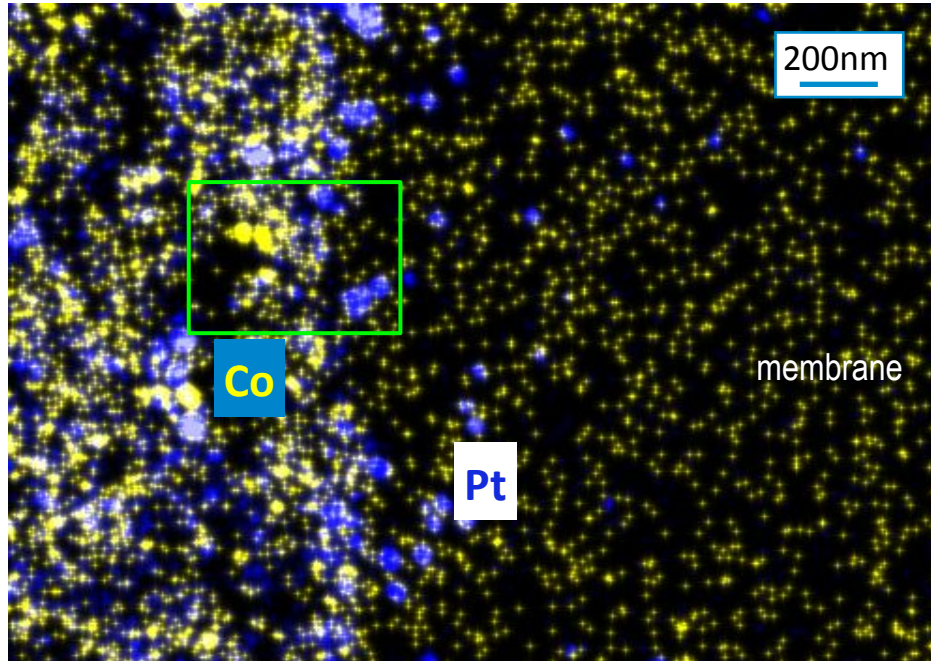
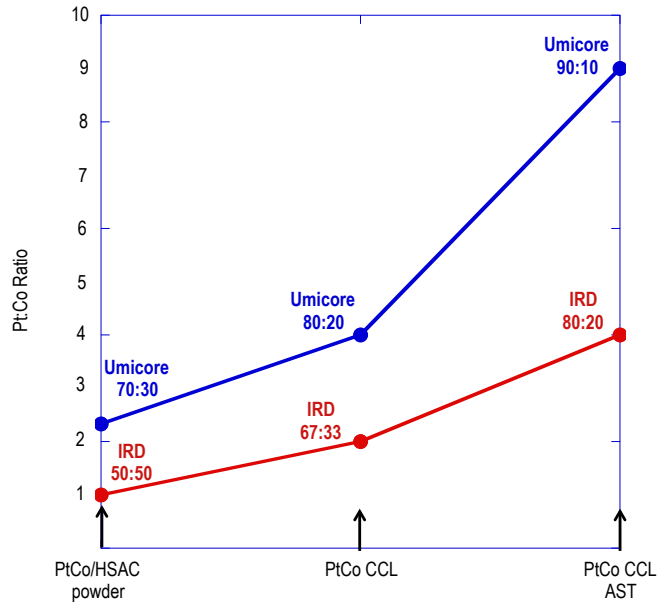


Accomplishments : Alloy catalyst durability



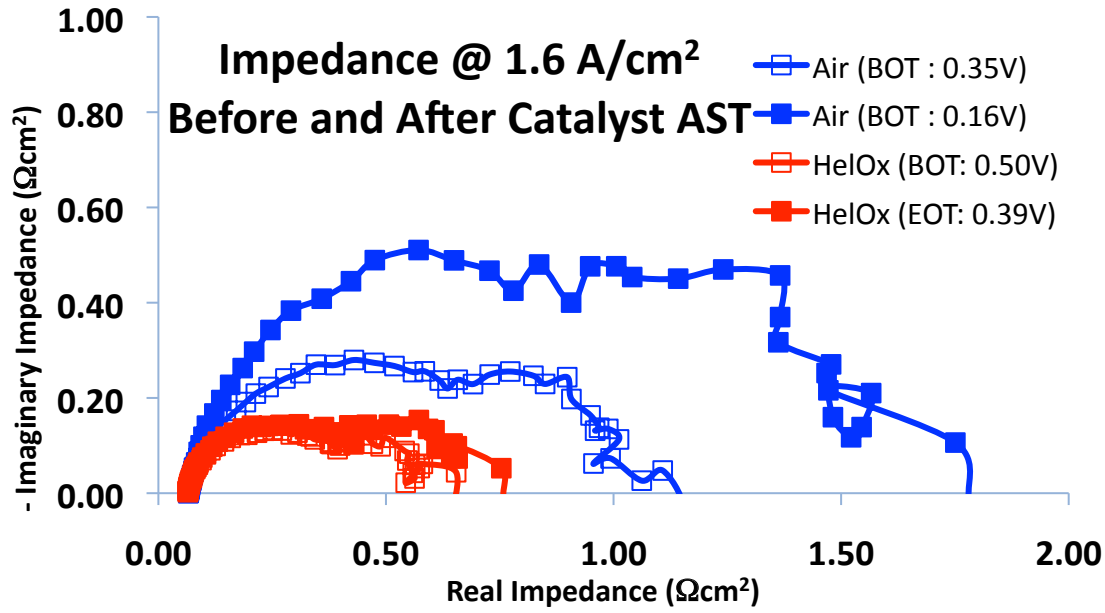
- Loss in fuel cell performance mainly due to de-alloying of Co from the PtCo electrocatalyst
- Significant and uniform Co present across entire membrane thickness (no Co in anode)
- Pt enrichment at Cathode Catalyst Layer(CCL)/membrane interface (1.5 μm in CCL) and large Pt particles form in the membrane

Accomplishments : Alloy catalyst durability

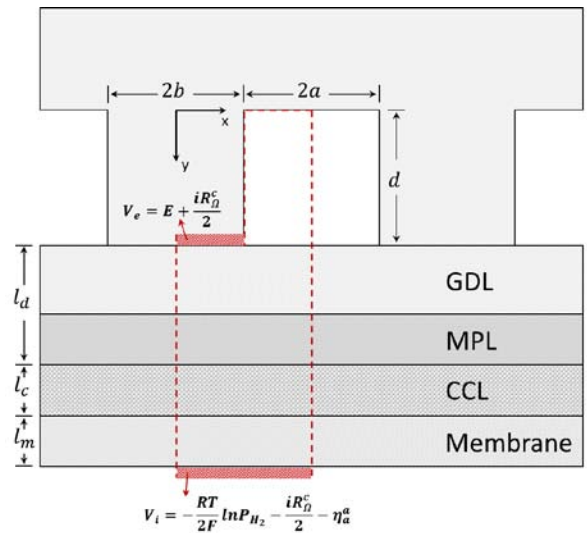


- Co loss uniform across CCL thickness
- Average Co content in CCL decreases by \approx 60-70%
- Separated Pt and Co formed in the CCL during AST
- Significant and separate Pt and Co present in membrane

Accomplishments : Modeling

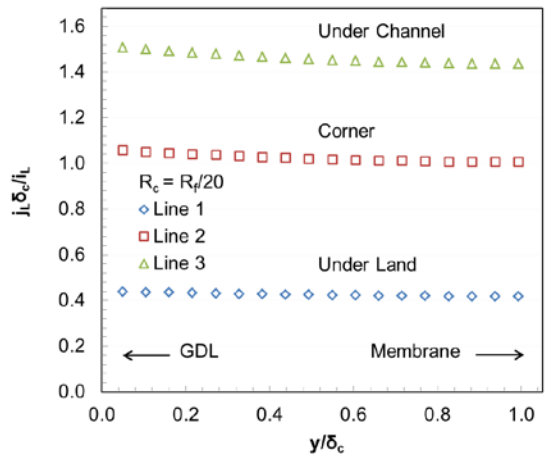


Cathode half-cell model extending from gas channel to CCL

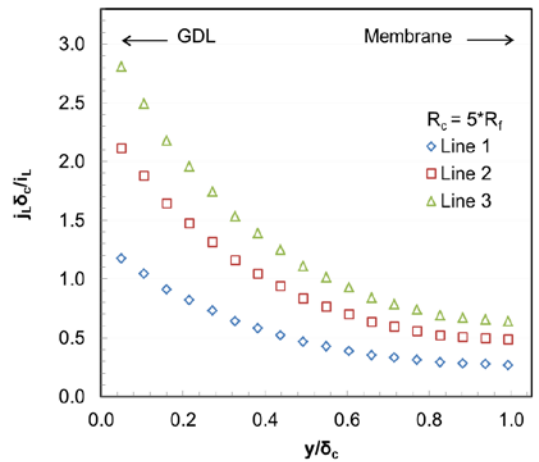


3-D Differential Cell Model

- Model Parameters to be Determined from Limiting Current Density**
- GDL resistance to O₂ transport
 - CCL pore resistance to O₂ transport
 - Ionomer film resistance to O₂ transport



Nearly uniform ORR flux in CCL for $R_c / R_f = 0.05$



Non-uniform ORR flux in CCL for $R_c / R_f = 5$

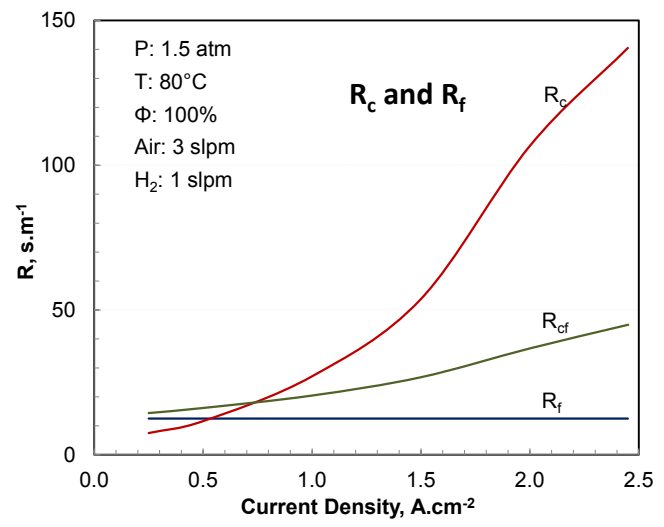
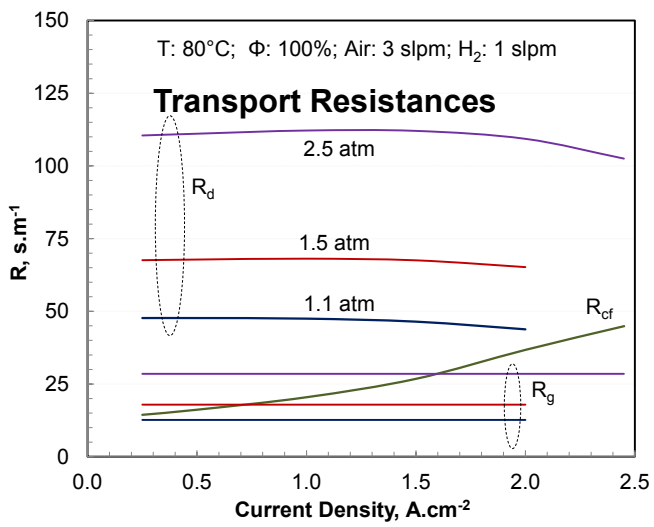
Accomplishments : Modeling

O₂ Transport Resistances in Saturated Alloy catalyst

- R_g : Gas channel resistance
- R_d : GDL resistance
- R_{cf} : Combined resistance of CCL pores and ionomer
- R_c : CCL pore resistance
- R_f : ionomer resistance

Assumptions

- O₂ transport in GDL is by molecular diffusion: diffusivity is inversely proportional to pressure
- O₂ transport in 20-100 nm CCL macros is by Knudsen diffusion: diffusivity weakly dependent on P
- O₂ transport in ionomer film and micro pores is independent of pressure
- Water breaks through GDL because gas channel RH is 100%: $R_d = R_d(P, i)$
- Ionomer is saturated with water and CCL pores contain liquid water : $R_{cf} = R_{cf}(i)$



Cathode catalyst layer pore resistance and GDL resistance are primary contributors at high current density (100% RH)

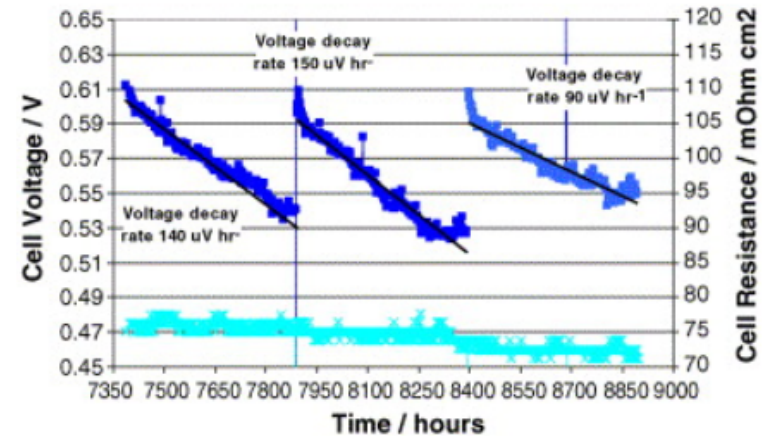
Recoverable Degradation

- From various developers and notable #'s of presentations (e.g. ECS), interest is increasing in understanding recoverable degradation
- Losses noted during long periods of un-interrupted operation^{1,2}

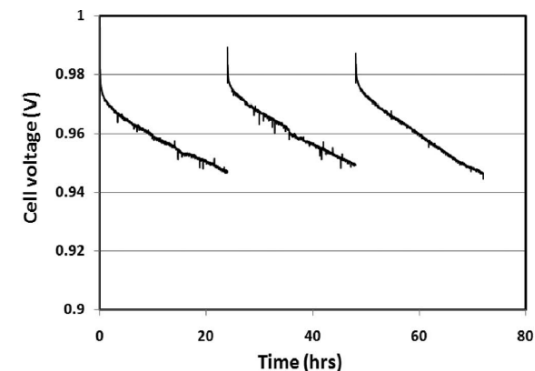
Known and suggested mechanisms:

- Pt-Ox formation and Pt reduction
 - (e.g. Pt-Ox have reduced kinetics)^{1,2}
- Adsorbed species
 - Cathode^{1,3} – SO_x / membrane fragments
 - Anode¹ – CO or other adsorbed species
- Transport
 - Flooded catalyst layer/GDL¹

Fuel Cell Test¹



OCV Test³



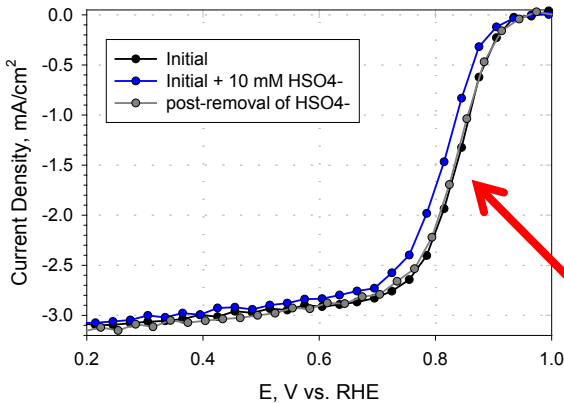
¹S.J.C. Cleghorn, et al, Journal of Power Sources, **158**, 1, 2006, 446–454

²T. D. Jarvi, et al, **Recoverable Performance Losses in PEM Fuel Cells**, Abstracts of ECS (2003)

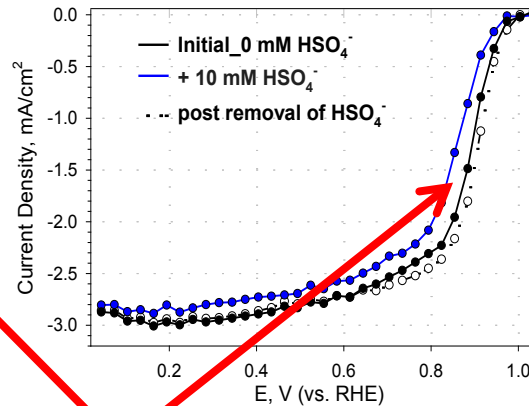
³J. Zhang, B. A. Litteer, F. D. Coms, and R. Makharia, *J. Electrochem. Soc.*, **159**(7), F287-F293 (2012)

Accomplishments – Sulfate ORR Inhibition (Ex situ)

20% Pt-Vulcan

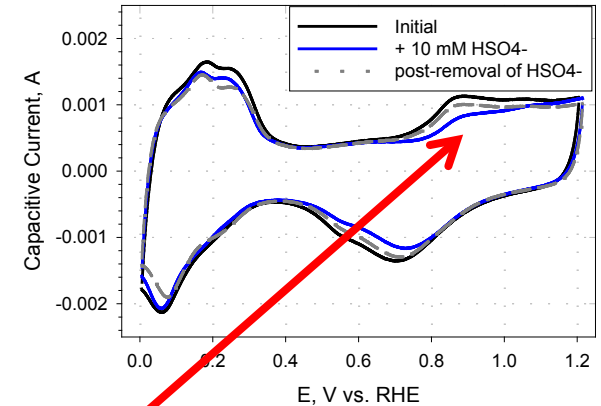


20% PtCo-Vulcan



ORR inhibition
and recovery

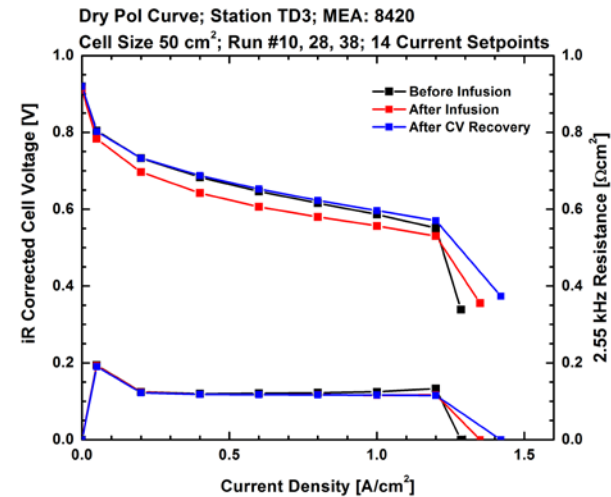
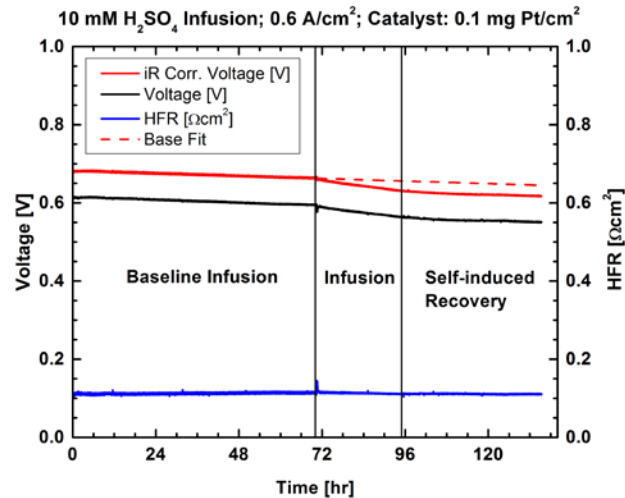
20% Pt-Vulcan



Shift in onset of Pt-Ox

- Noticeable poisoning effect by sulfates in RDE
- PtCo alloy catalyst shows a larger decrease in performance with sulfate anions
 - 10 mV shift for Pt/C ; 30 mV shift for PtCo/C
- Pt and PtCo alloy catalyst show full recovery after removal of the anions
- Onset of OH ads. shifts to higher potentials
- ORR inhibition affected by scan rate and direction (anodic vs cathode scan)

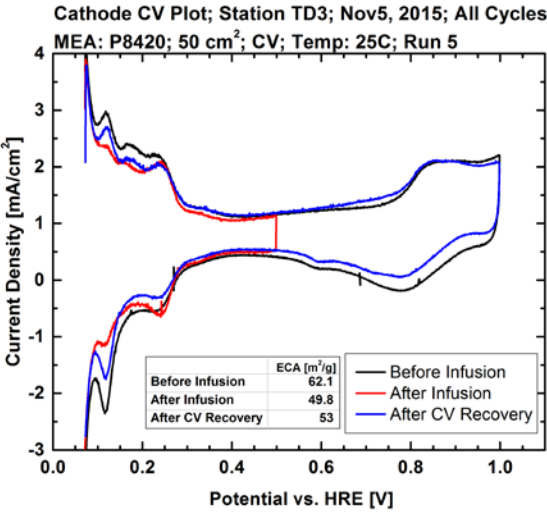
Accomplishments – Sulfate Anion Contamination (In situ)



- Sulfate infusion causes degradation in fuel cell performance at 0.6 A/cm² when the cathode loading is 0.1 mg_{Pt}/cm² (no effect at 0.2 A/cm² and 0.4 mg_{Pt}/cm²)
- The adsorption of sulfate anions on the cathode catalyst resulted in performance loss of $\Delta V_1 = 24$ mV
- Membrane resistance (HFR) was not affected by sulfate contaminant
- Voltage loss not recovered when infusion was stopped ($\Delta V_2 = 28$ mV).
- Sulfate caused degradation appears to be reversible after potential cycling recovery step.
- Low voltages and high RH's have been reported to result in recovery

Accomplishments – Sulfate Anion Contamination (recovery)

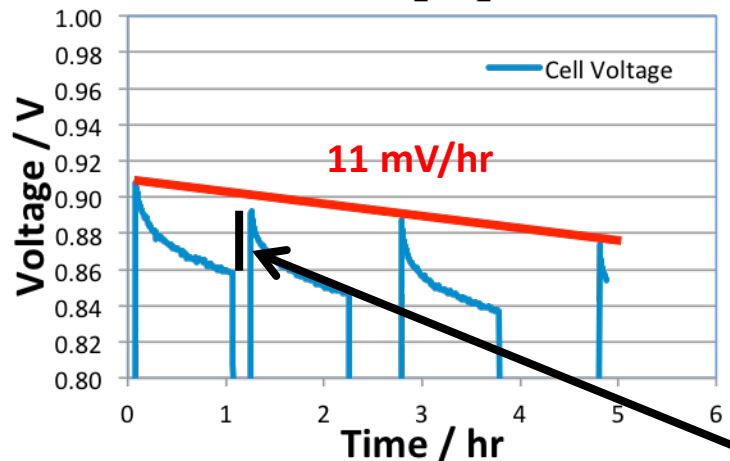
Infusion recovery



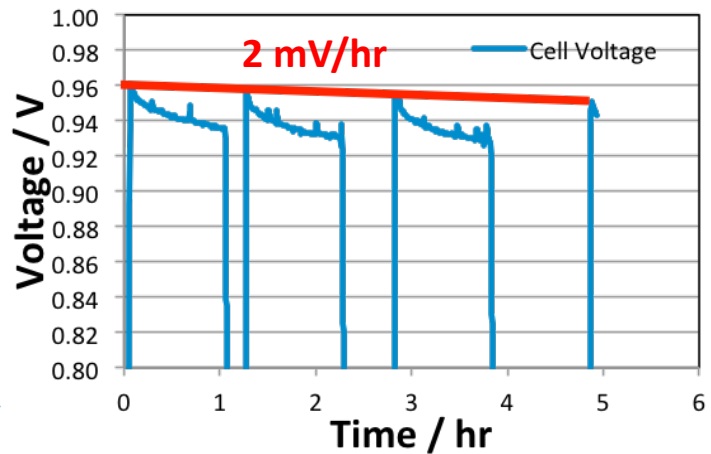
- After infusion, Pt CV shows a decrease in ECSA
- After several CVs from low (0.085V) to high (1V) potentials, ECSA was partially recovered and performance almost fully recovered
- Recovery potential needs to be $\leq 0.3V$ for sulfate anions
- Cathode environment irrelevant between: N₂ or Air
- Liquid water injection observed to hurt recovery

OCV tests

Recovery in H₂-N₂ at 0.4V

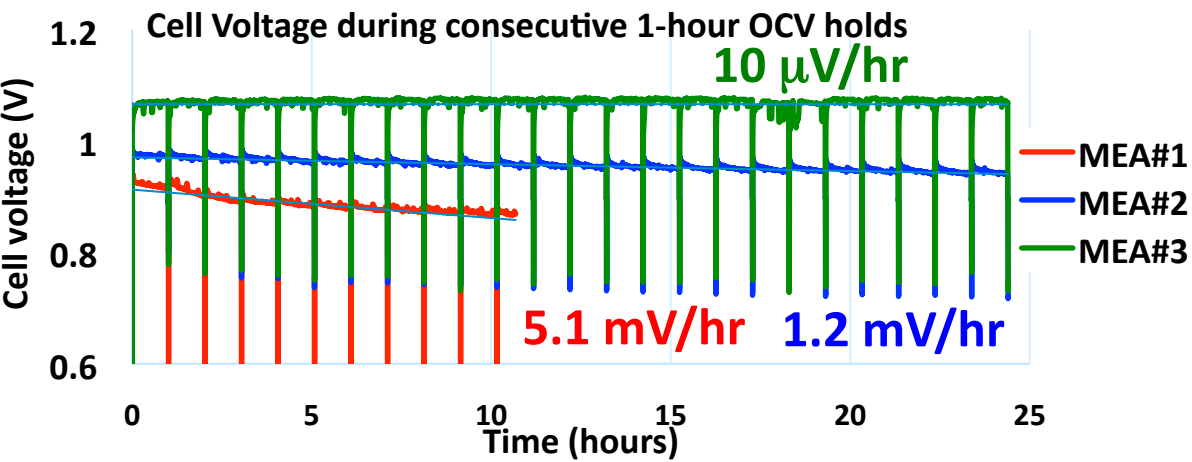


Recovery in H₂-N₂ at 0.2V



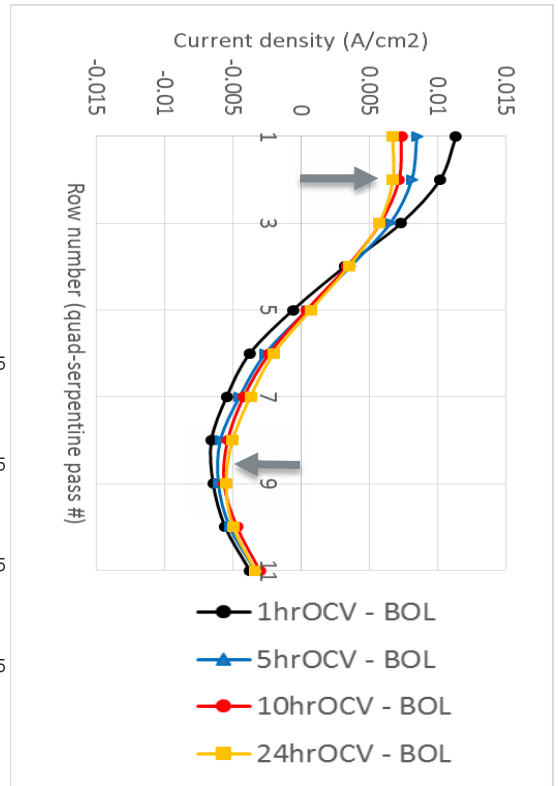
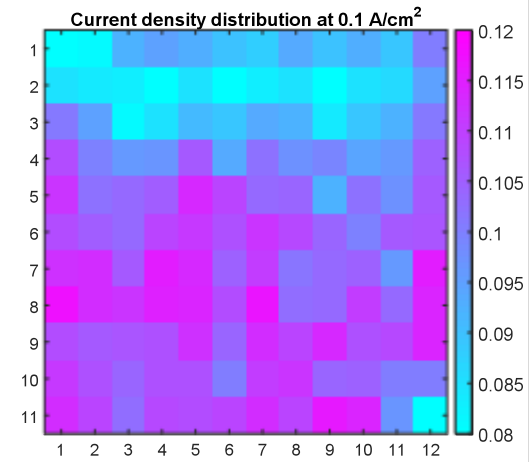
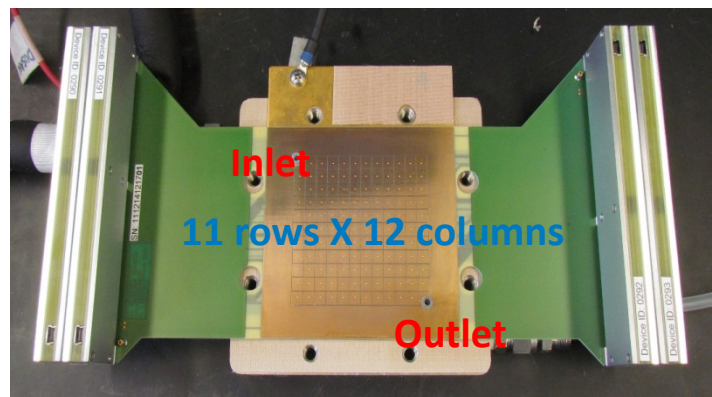
Recovery of Pt-Ox

Accomplishments –Recoverable Degradation



- Degradation effect decreases with increasing levels of membrane chemical stabilization and cathode catalyst loading
- Greater effect at outlets

MEA 1: Membrane with no additives : $\approx 0.04\text{mg}_{\text{Pt}}/\text{cm}^2$
 MEA 2: Membrane with no additives : $0.4\text{mg}_{\text{Pt}}/\text{cm}^2$
 MEA 3: Chemically stabilized membrane : $0.4\text{mg}_{\text{Pt}}/\text{cm}^2$



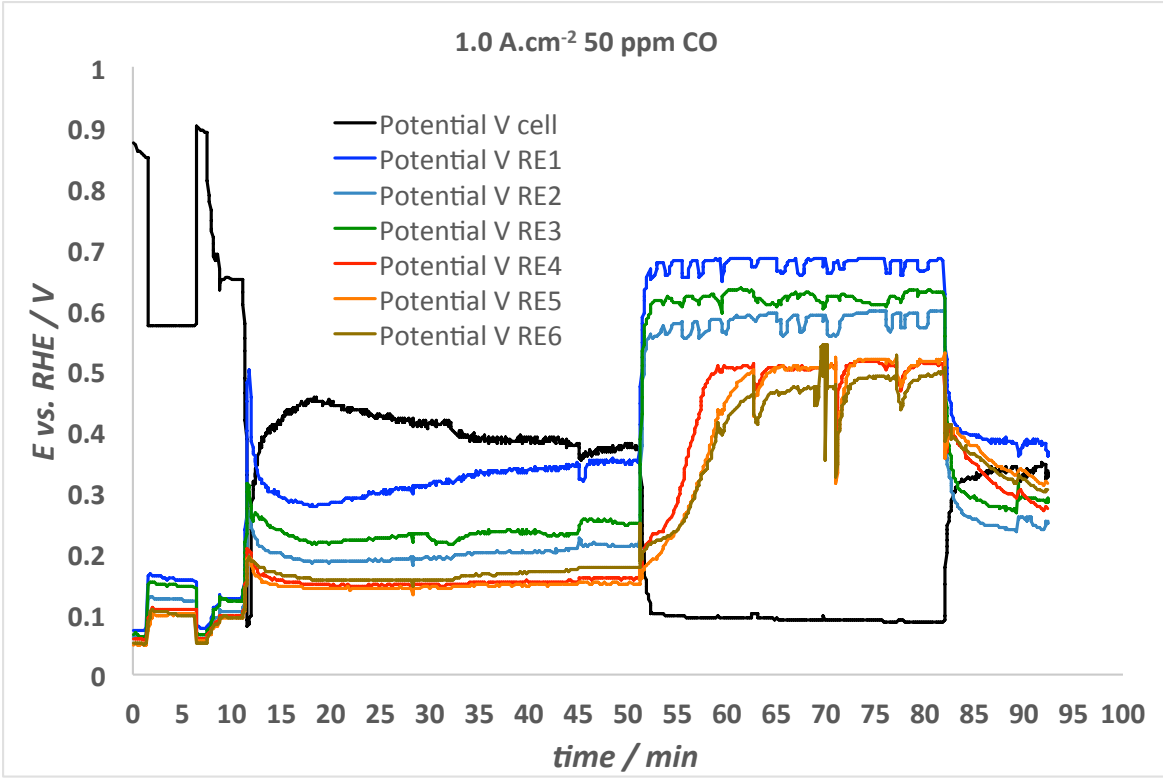
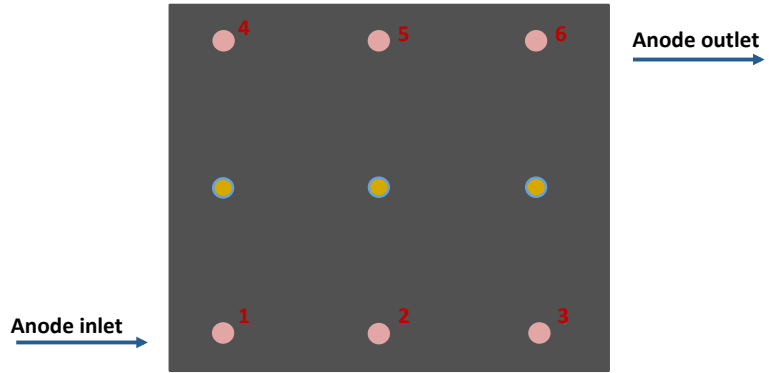
- **W. L. Gore provided 18 μm membrane to GM**
- **GM applied SOA catalyst layer of $0.1\text{mg}_{\text{Pt}}/\text{cm}^2$ @ cathode**
- **MEA meets DOE BOL Mass activity target (FC 137)**
- **Will be used in durability protocol, membrane AST protocols, and catalyst/support AST protocols to benchmark SOA MEA**

Accomplishments : Spatially distributed Reference Electrodes



Luis Castanheira, Gareth Hinds

- Nafion salt bridge contacts directly the anode catalyst layer through small holes in the GDL
- 6 of the 9 RE positions were used (numbered in direction of hydrogen flow)
- 3 unused holes were sealed with a PEEK rod (diameter 0.9 mm) inside the PTFE tubing



Collaborations

Institutions	Role
FC-PAD Consortium	ANL, LBNL, ORNL, LANL, NREL
Umicore, TKK	Supply SOA catalysts for evaluation
IRD, Ion Power	Supply SOA catalysts and/or MEAs for evaluation
GM/W.L. Gore	Supply SOA MEA for Benchmarking
NPL	Reference electrode Setup

Proposed Future Work

- **Plans for the remainder of FY16**
 - Complete durability evaluation of PtCo alloy catalyst based MEAs
 - Complete development of reference electrode setup
 - Systematically evaluate effect of sulfate infusion as a function of potential and during durability cycling protocol
 - Quantify effect of reversible degradation under durability cycling protocol
- **Plans for FY 17**
 - Evaluate durability of PtNi and advanced carbon based MEAs
 - Use segmented/reference cell to evaluate effect of operating parameters on durability
 - Model durability of MEAs under both AST and durability cycling protocols
 - Benchmark durability of SOA MEA (durability cycling , membrane AST, and support AST)
 - Adopt a differential cell for single cell durability testing
 - Evaluate effect of system contaminants on low loaded SOA MEAs

Summary

- **Relevance**: Evaluate durability of SOA MEAs, determine degradation mechanisms, propose mitigation strategies to meet DOE 2020 durability targets for MEAs that can meet the DOE 2020 Pt loading and BOL performance targets. Refine ASTs to evaluate the durability of MEAs.
- **Approach**: Our approach involves developing advanced diagnostics, modeling and characterization techniques to evaluate SOA MEAs and provide insights to improve the durability of the MEA components to meet DOE 2020 performance and durability targets.
- **Accomplishments and Progress**: 2 new ASTs have been adopted by the DOE. Durability studies of SOA MEAs meeting BOL targets have been initiated. Benchmarking of SOA MEA initiated. Reference electrode setup being developed for durability studies.
- **Future work**: Identify all degradation mechanisms in SOA alloy catalysts and quantify voltage losses (especially in the mass transport region). Develop mitigation strategies. Complete the development of advanced tools and models.



Supplemental Slides

New Catalyst AST (Square Wave)

Table A1 Electrocatalyst Cycle and Metrics

Cycle	Square wave cycle: steps between 0.6 V (3 s) and 0.95 V (3 s) with rise time of ~0.5 s or less; run polarization curve and ECSA at specified intervals. Single cell 25-50 cm ²	
Number	30,000 cycles	
Cycle time	6 s	
Temperature	80°C	
Relative Humidity	Anode/Cathode 100/100%	
Fuel/Oxidant	Hydrogen/N ₂ (H ₂ at 200 sccm and N ₂ at 75 sccm for a 50 cm ² cell)	
Pressure	Atmospheric pressure	
Metric^a	Frequency	Target
Catalytic Mass Activity^b	At beginning and end of test minimum	<40% loss of initial catalytic activity
Polarization curve from 0 to ≥1.5 A/cm²^c	After 0, 1k, 5k, 10k, and 30k cycles	<30 mV loss at 0.8 A/cm ²
ECSA/Cyclic Voltammetry	After 10, 100, 1k, 3k, 10k, 20k and 30k cycles	<40% loss of initial area

- A protocol such as the one in Table A9 should be used to recover reversible losses prior to measurement of metrics.
- Mass activity in A/mg @ 150 kPa abs backpressure at 900 mV iR-corrected on H₂/O₂, 100% RH, 80°C, anode stoichiometry 2; cathode stoichiometry 9.5. A minimum hold time of 15 min is recommended, with the mass activity calculated based on the average current during the last 1 min. Multiple points should be measured at low current, and the 0.9 V iR-free potential should be determined based on these measurements. Measured ORR current may be corrected for H₂ crossover. Based on the protocol published by Gasteiger et al., Applied Catalysis B: Environmental, 56 (2005) 9-35.
- Polarization curve per protocol in Table A6.

New Membrane AST (Combined Chemical/Mechanical)

Table A5 Membrane Chemical/Mechanical Cycle and Metrics (Test Using a MEA)

Cycle	Cycle 0% RH (30 s) to 90°C dewpoint (45 s), single cell 25-50 cm²	
Total time	Until crossover >15 mA/cm ² or 20,000 cycles	
Temperature	90°C	
Relative Humidity	Cycle from 0% RH (30 s) to 90°C dewpoint (45 s) ^a	
Fuel/Oxidant	H ₂ /Air at 40 sccm/cm ² on both sides	
Pressure	Ambient or no back-pressure	
Metric	Frequency	Target
F⁻ release or equivalent for non-fluorine membranes	At least every 24 h	No target – for monitoring
Hydrogen Crossover (mA/cm²)^{b,c}	Every 24 h	≤15 mA/cm ²
OCV^{c,d}	Continuous	Initial wet OCV ≥ 0.95 V, <20% OCV decrease during test
High-frequency resistance	Every 24 h at 0.2 A/cm ²	No target – for monitoring
Shorting resistance^e	Every 24 h	>1,000 ohm cm ²

- Step durations of 30 s dry and 45 s wet were selected in testing at LANL so that the HFR at the end of the dry step was 2.5 times the HFR at the end of the wet step, which is approximately equal to the HFR ratio that occurs when running the mechanical test (Table A4). Depending on hardware used, these step times may need to be adjusted to achieve the same HFR variation.
- Tested in MEA on H₂, 80°C, fully humidified gases, 1 atm total pressure. See M. Inaba, et. al. *Electrochimica Acta*, 51, 5746, 2006. Crossover recorded after 2 min of drying under 0% RH conditions.
- Hydrogen crossover and OCV targets should be achieved at 0 kPa pressure differential and at 50 kPa anode overpressure, providing sensitivity to global membrane thinning and to hole formation, respectively.
- A protocol such as the one in Table A9 should be used to recover reversible losses at least once every 24 h and prior to each measurement of metrics.
- Measured at 0.5 V applied potential, 80°C, 100% RH N₂/N₂. Compression to 20% strain on the GDL.