FC-PAD

Fuel Cell – Performance and Durability

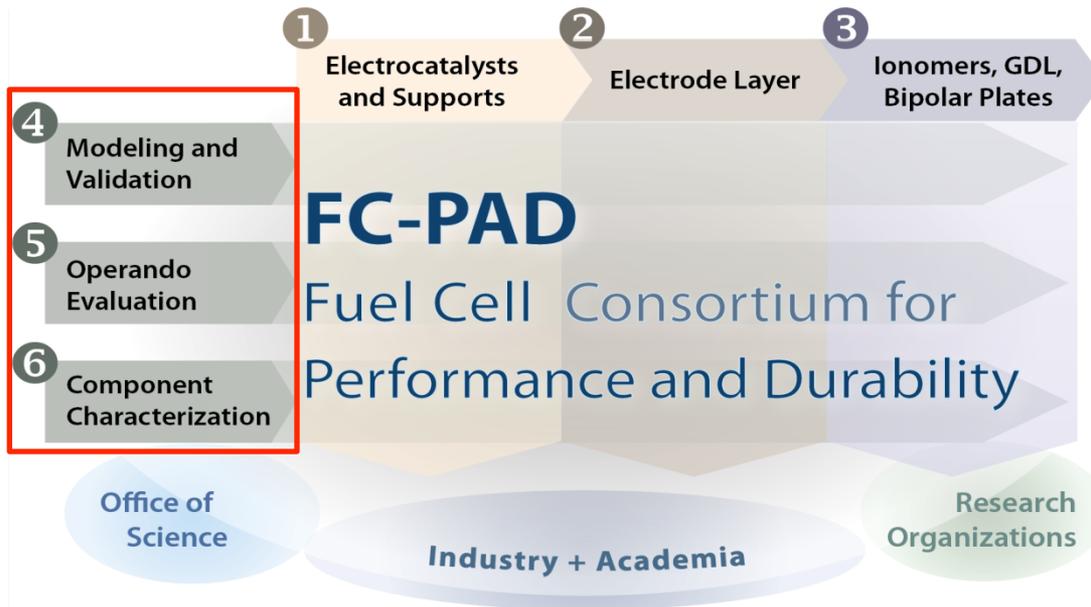## FC139 – Modeling, Evaluation, Characterization

Presenter : Rangachary Mukundan

June 8th, 2016

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

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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BERKELEY LAB

Los Alamos NATIONAL LABORATORY

NREL NATIONAL RENEWABLE ENERGY LABORATORY

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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-OOO1412

fCPAD FUEL CELL PERFORMANCE AND DURABILITY

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/cm^2 @ 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
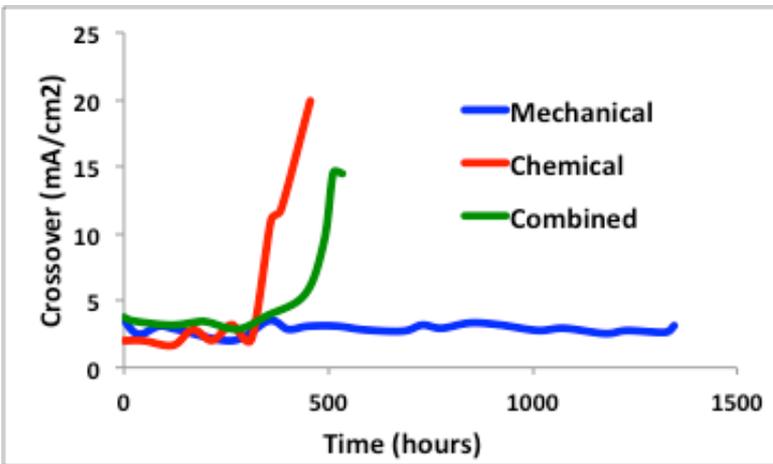
Accomplishments : Adoption of Membrane AST

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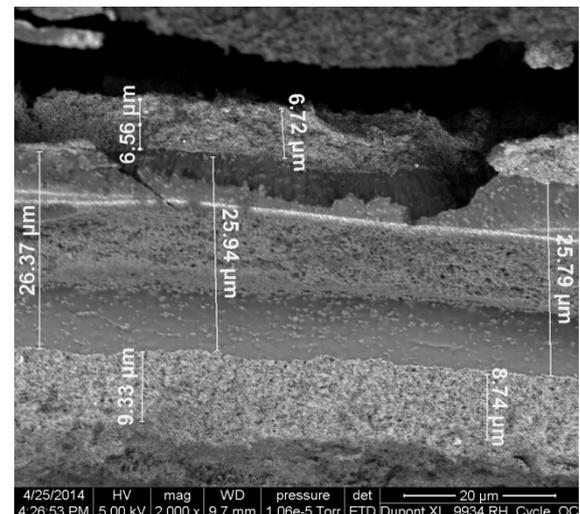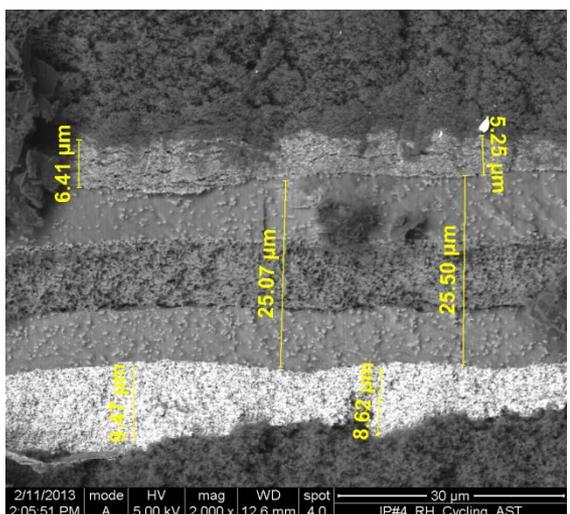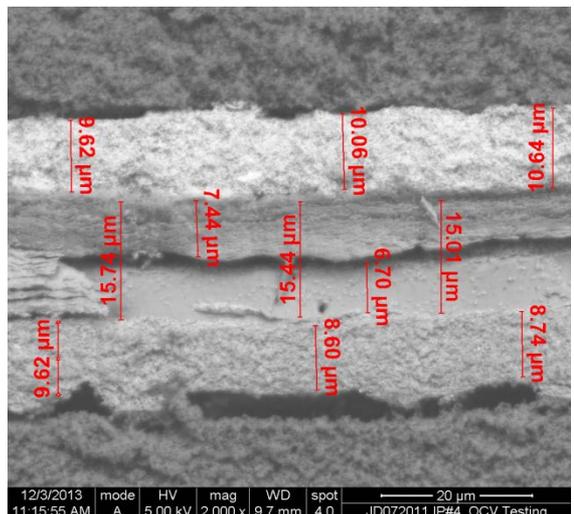
- **30sec wet and 45sec dry cycles in H²/Air**
- **Similar RH stresses as determined by HFR**
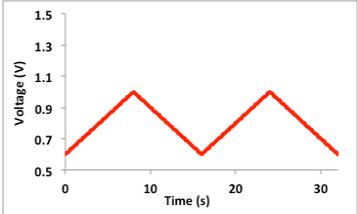- **Cycling time needs to be adjusted based on HFR**

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; H_2/Air (saturated = 30s, dry = 45s)
Target = 500 hours (24,000 cycles)

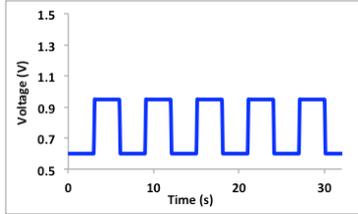See additional slide for FCTT adopted AST

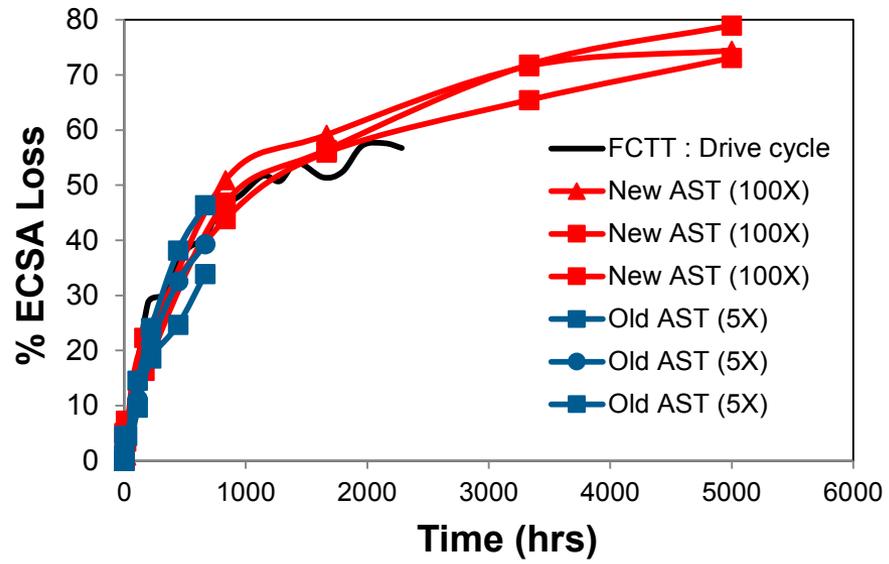# Accomplishments : Adoption of Electrocatalyst AST
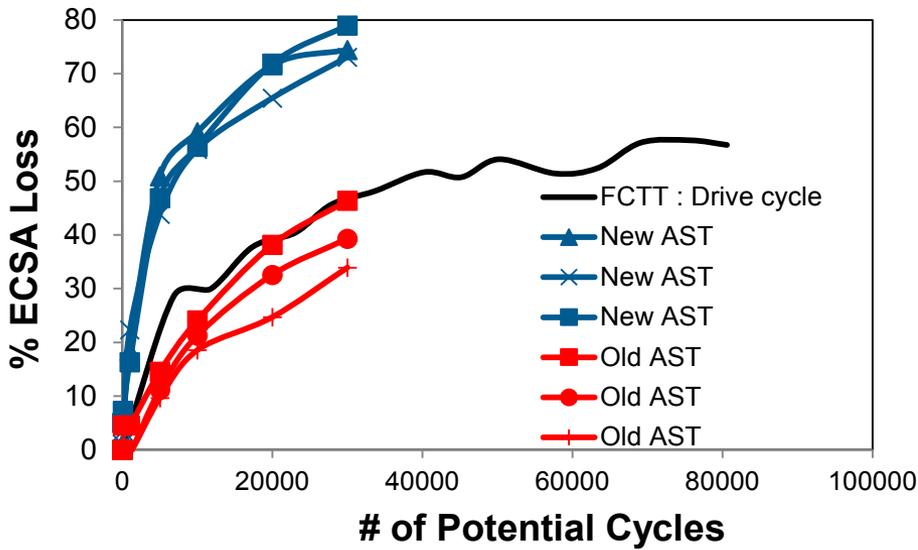
0.6 to 1.0V cycles
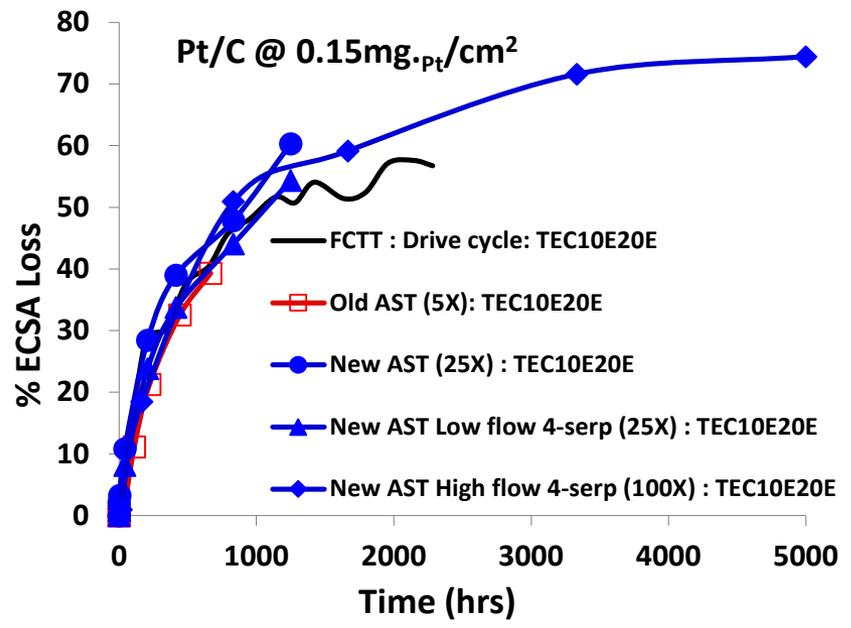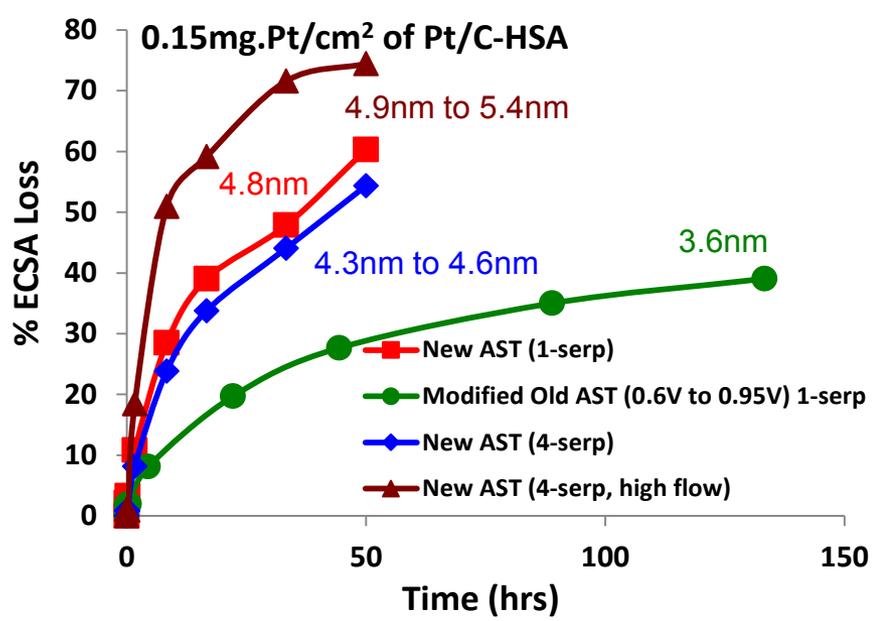
0.6 to 0.95V cycles

Target = 133 hours

Target = 50 hours

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

Higher N_2 flow rates (200sccm vs 75sccm)

See additional slide for FCTT adopted AST

Accomplishments : Refined catalyst AST

- **Acceleration factor can be increased with increasing N$_2$ flow rate**
- **High N$_2$ flow (200 sccm) results in 100X acceleration while low N$_2$ flow (75 sccm) results in 25X acceleration**
- **Spatial variation in degradation is greater at the higher flow rate**
- **Use 75sccm N$_2$: 5X acceleration over old AST**

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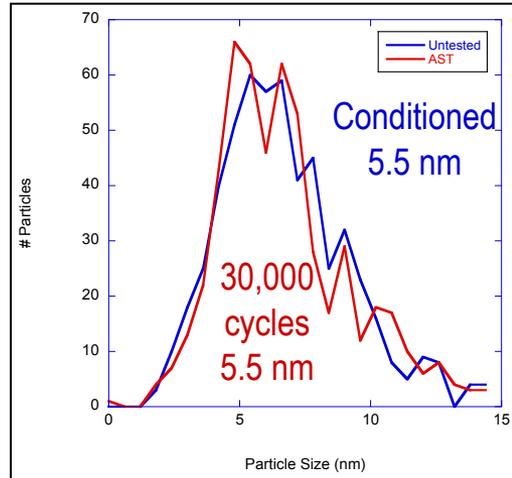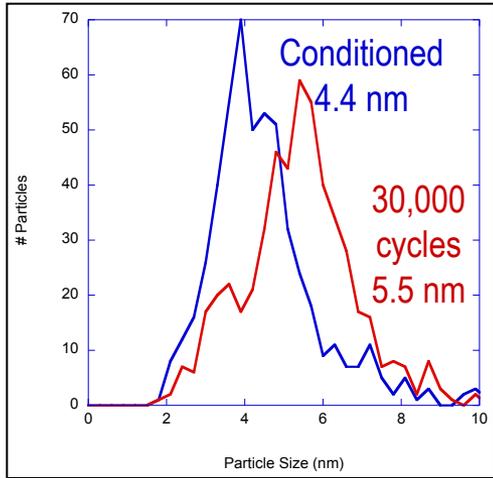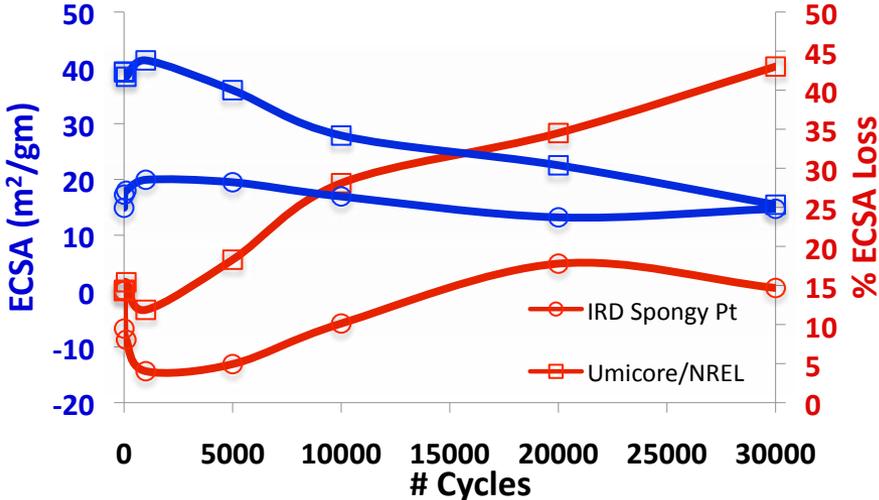
- **The 3 alloy catalysts tested met the BOL mass activity criteria (Thrust 2)**
- **Surface area and beginning catalyst particle sizes are different**
- **The smaller particle size catalysts grew from 4.4nm to 5.5nm**
- **The larger particle size catalyst showed no increase (5.5nm) after AST**
- **ECSA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

Note: Loading not identical
IRD = 0.21mg$_{Pt}$/cm^2 and Umicore/NREL = 0.1 mg$_{Pt}$/cm^2

Accomplishments : Alloy catalyst durability

VIR @ 80°C, 100%RH, 275kPa

- Umicore/NREL (BOT)
- Umicore/NREL (EOT)
- IRD (BOT)
- IRD (EOT)

Oxygen IR-Free-VIR @ 80°C, 100%RH, 150 kPa

- Umicore/NREL (BOT)
- Umicore/NREL (EOT)
- IRD (BOT)
- IRD (EOT)

Impedance @ 0.02 A/cm² Before/After AST

- Umicore/NREL (BOT : 0.91V)
- Umicore/NREL (BOT : 0.88V)
- IRD (BOT : 0.94V)
- IRD (EOT : 0.92V)
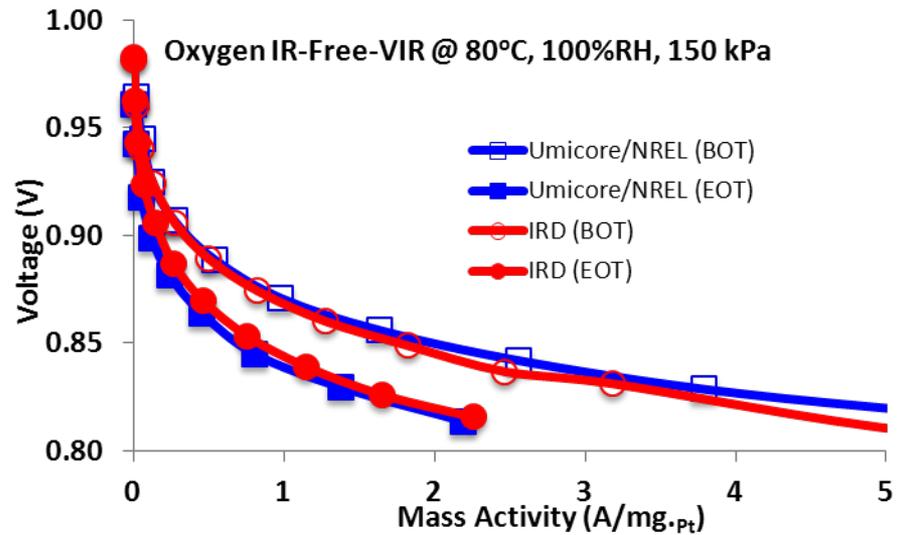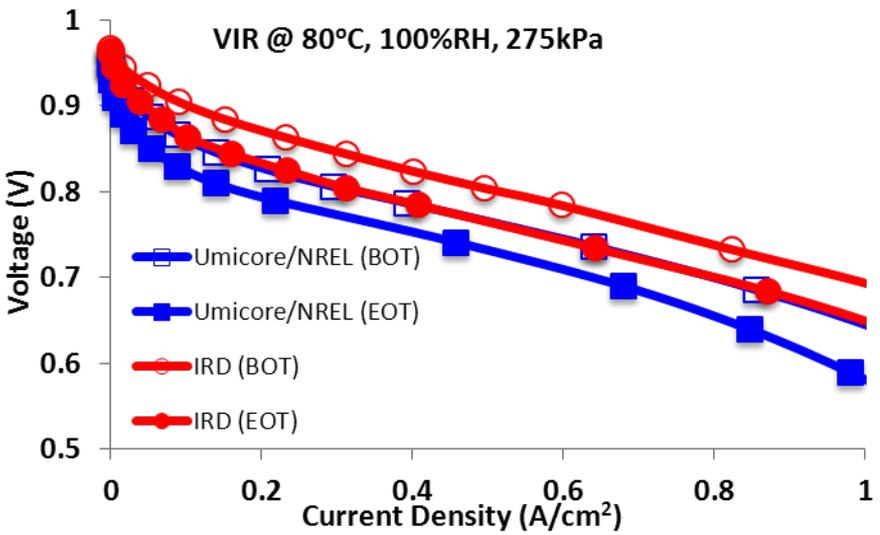
- **Fuel cell performance decreases even though ECSA can be constant**
- **Kinetic losses observed and seem to be independent of ECSA losses**
- **Losses > 30mV @ 0.8 A/cm²**

Accomplishments : Alloy catalyst durability

Co Kα peak
6.93keV

Legend:
- JZ11-membrane
- JZ11-cathode
- DL032816-cathode
- DL032816-membrane

Y-axis: Raw Counts
X-axis: Energy (keV)

HAADF-STEM image

1 μm
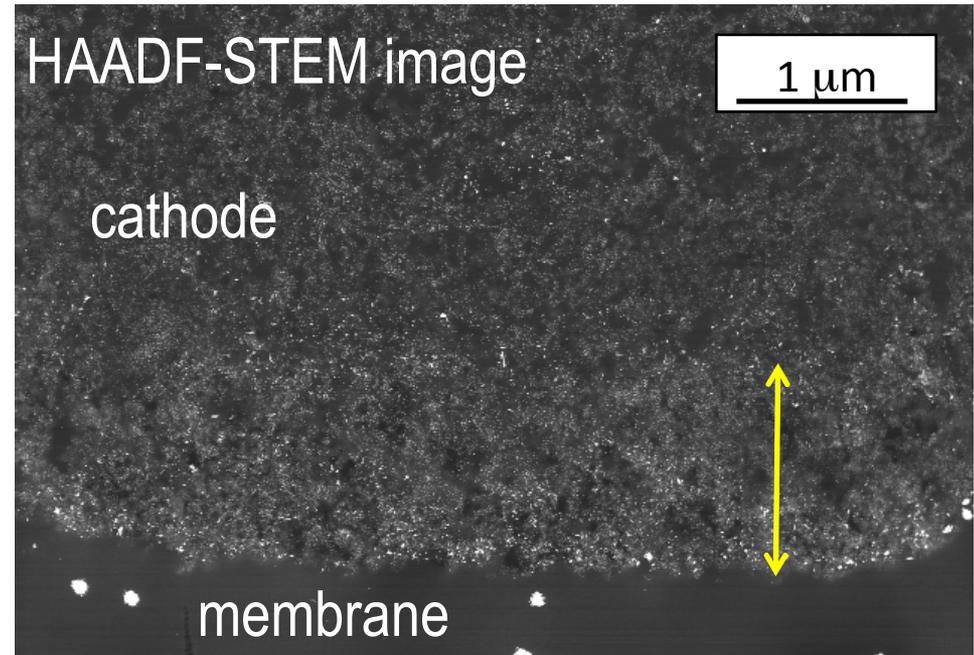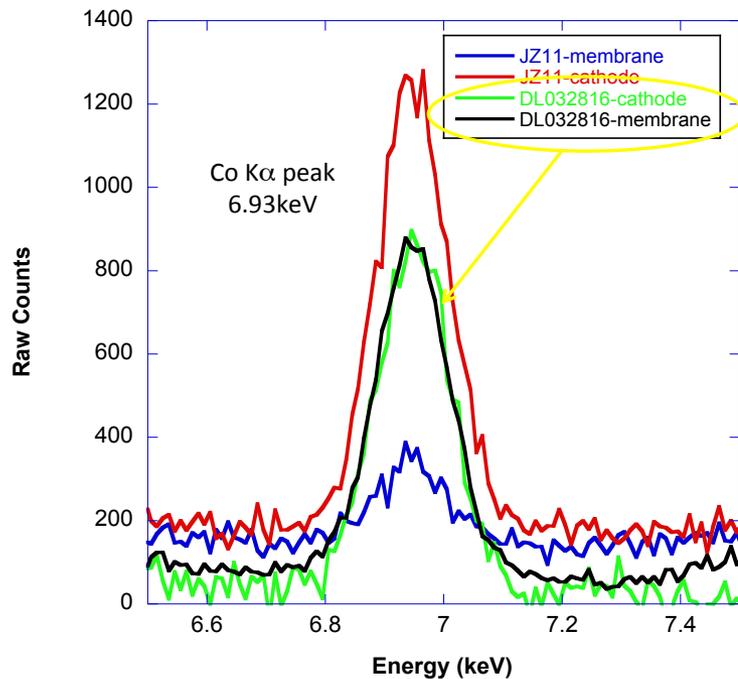
cathode

membrane

- **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**

FUEL CELL PERFORMANCE
AND DURABILITY

Accomplishments : Alloy catalyst durability

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

Accomplishments : Modeling

Impedance @ 1.6 A/cm²
Before and After Catalyst AST

- Air (BOT : 0.35V)
- Air (BOT : 0.16V)
- HelOx (BOT: 0.50V)
- HelOx (EOT: 0.39V)

Y-axis: - Imaginary Impedance (Ωcm^2)
X-axis: Real Impedance (Ωcm^2)
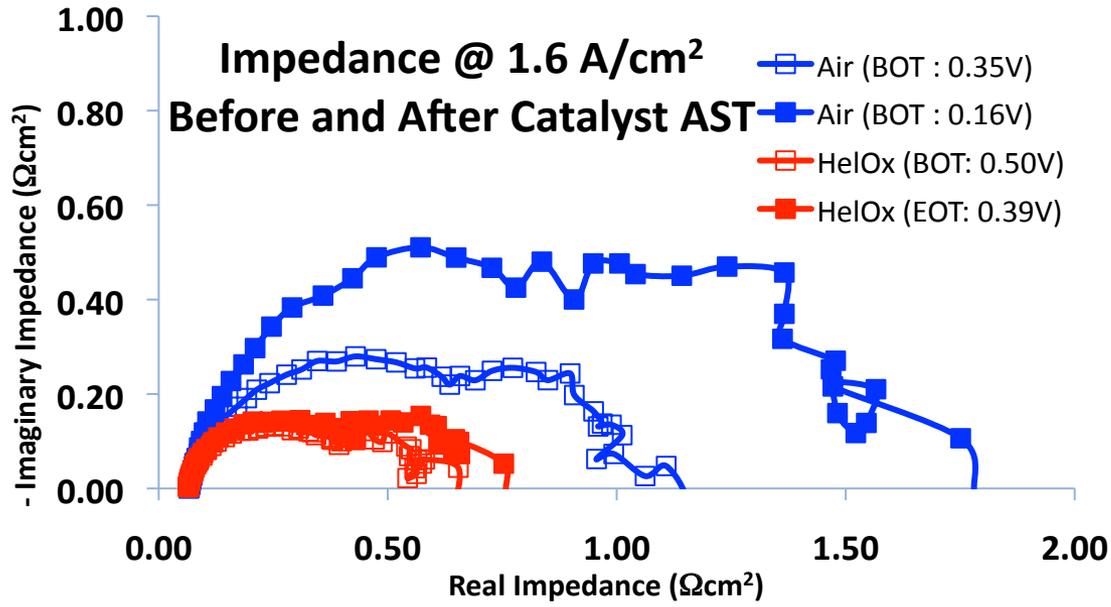
Cathode half-cell model extending from gas channel to CCL

$$V_e = E + \frac{iR_{\Omega}^c}{2}$$

GDL
MPL
CCL
Membrane

$$V_i = -\frac{RT}{2F} lnP_{H_2} - \frac{iR_{\Omega}^c}{2} - \eta_a^a$$

3-D Differential Cell Model

Model Parameters to be Determined from Limiting Current Density

- GDL resistance to O_2 transport
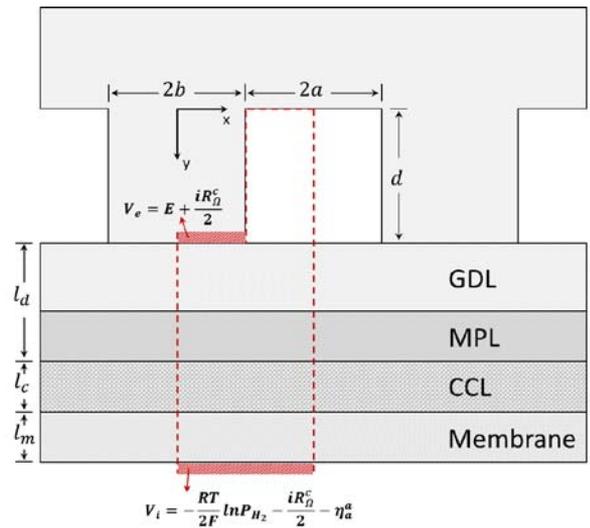- CCL pore resistance to O_2 transport
- Ionomer film resistance to O_2 transport

Under Channel
Corner
$R_c = R_f/20$
- Line 1
- Line 2
- Line 3
Under Land
GDL → Membrane
Y-axis: $j_L\delta_c/i_L$
X-axis: y/δ_c
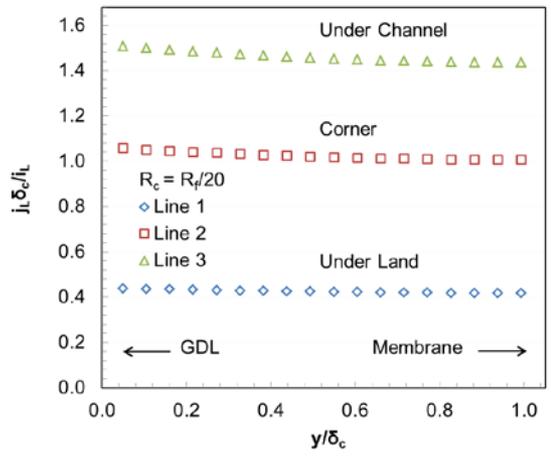
Nearly uniform ORR flux in CCL for $R_c/R_f = 0.05$

GDL → Membrane
$R_c = 5*R_f$
- Line 1
- Line 2
- Line 3
Y-axis: $j_L\delta_c/i_L$
X-axis: y/δ_c
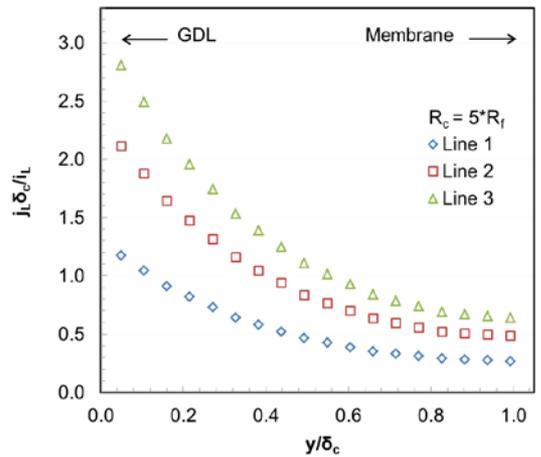
Non-uniform ORR flux in CCL for $R_c/R_f = 5$

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

- O_2 transport in GDL is by molecular diffusion: diffusivity is inversely proportional to pressure
- O_2 transport in 20-100 nm CCL macros is by Knudsen diffusion: diffusivity weakly dependent on P
- O_2 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 : $R_{cf} = R_{cf}(i)$
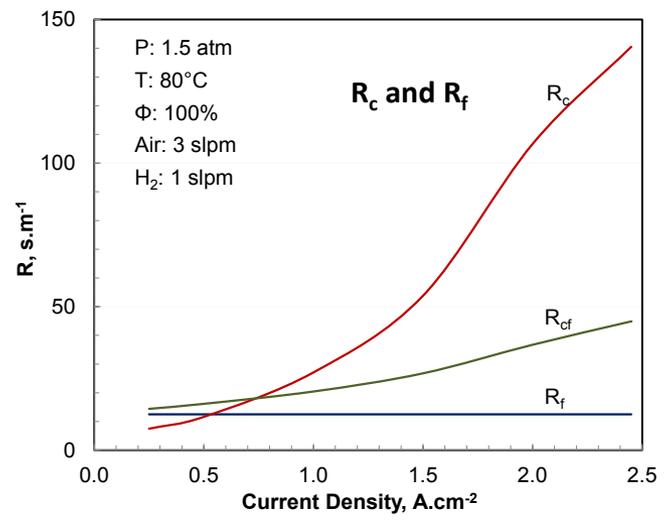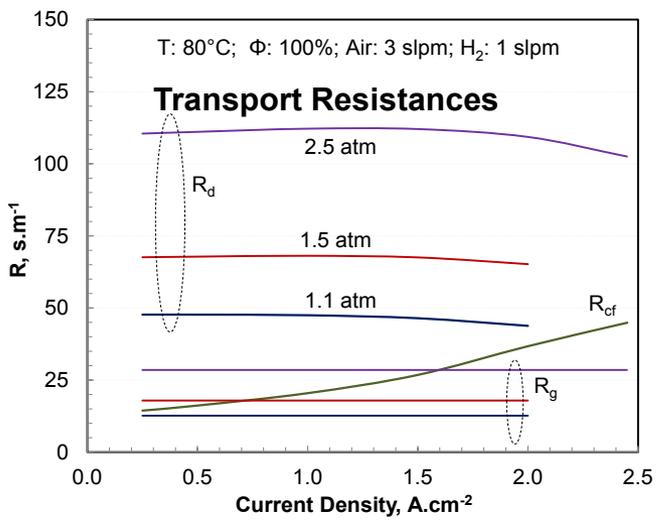
Cathode catalyst layer pore resistance and GDL resistance are primary contributors at high current density (100% RH)

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] – SOx / membrane fragments
  - Anode[1] – CO or other adsorbed species
- Transport
  - Flooded catalyst layer/GDL[1]

Fuel Cell Test[1]
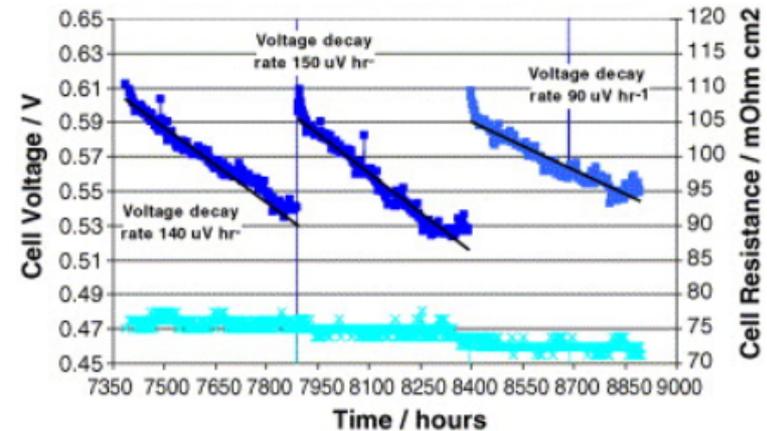
OCV Test[3]
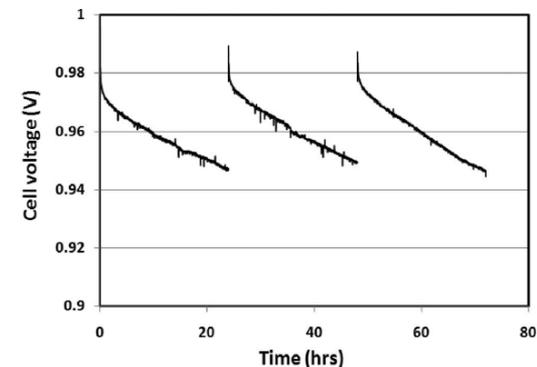
[1]S.J.C. Cleghorn, et al, Journal of Power Sources, **158**, 1, 2006, 446–454
[2]T. D. Jarvi, et al, **Recoverable Performance Losses in PEM Fuel Cells,** Abstracts of ECS (2003)
[3] J. Zhang, B. A. Litteer, F. D. Coms, and R. Makharia, J. Electrochem. Soc., **159(7)**, F287-F293 (2012)

Accomplishments – Sulfate ORR Inhibition (Ex situ)
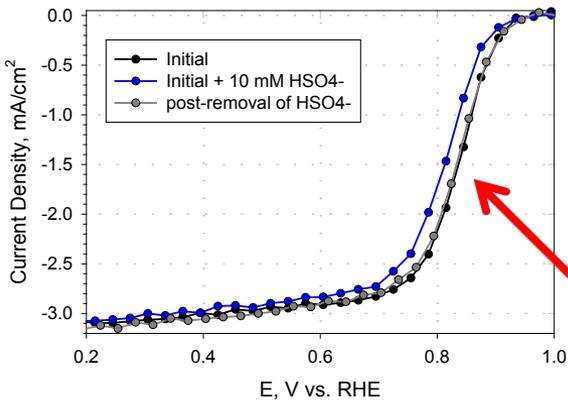
20% Pt-Vulcan · 20% PtCo-Vulcan · 20% Pt-Vulcan
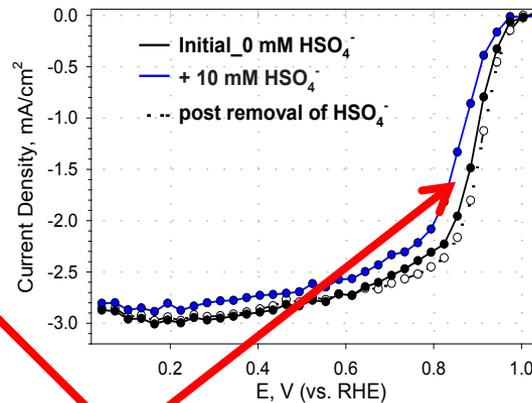
ORR inhibition
and recovery
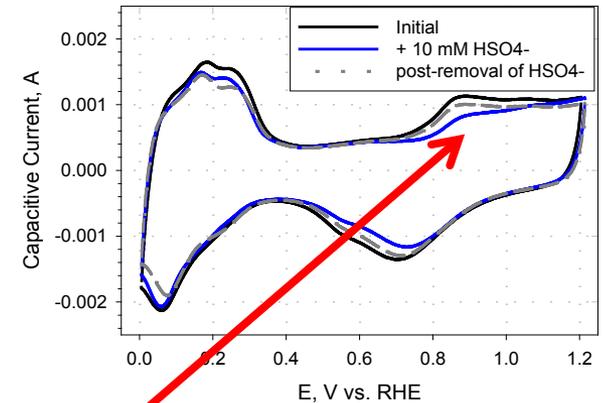
Shift in onset of Pt-Ox

- 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)

10 mM H_2SO_4 Infusion; 0.6 A/cm^2; Catalyst: 0.1 mg Pt/cm^2

Dry Pol Curve; Station TD3; MEA: 8420
Cell Size 50 cm^2; Run #10, 28, 38; 14 Current Setpoints
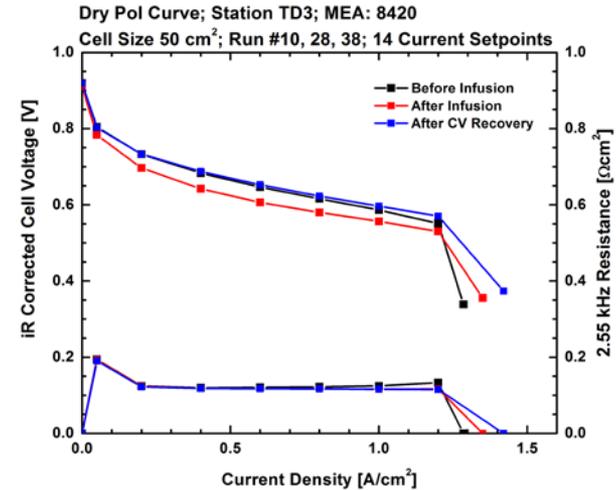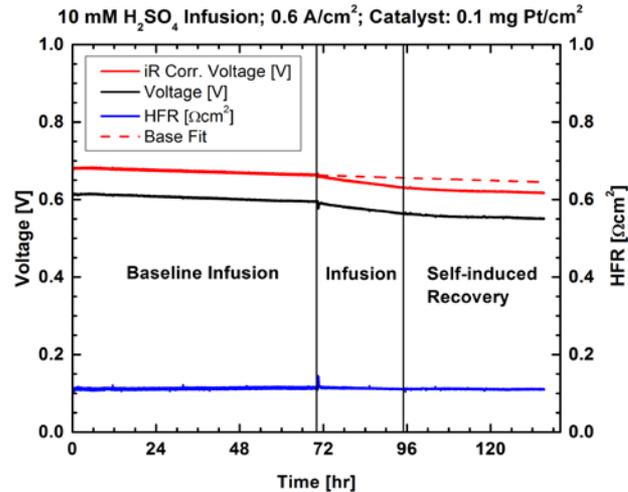
- **Sulfate infusion causes degradation in fuel cell performance at 0.6 A/cm^2 when the cathode loading is 0.1 mg$_{Pt}$/cm^2 (no effect at 0.2 A/cm^2 and 0.4 mg$_{Pt}$/cm^2)**
- **The adsorption of sulfate anions on the cathode catalyst resulted in performance loss of ΔV_1 = 24 mV**
- **Membrane resistance (HFR) was not affected by sulfate contaminant**
- **Voltage loss not recovered when infusion was stopped (ΔV_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

Cathode CV Plot; Station TD3; Nov5, 2015; All Cycles
MEA: P8420; 50 cm^2; CV; Temp: 25C; Run 5

	ECA [m^2/g]
Before Infusion	62.1
After Infusion	49.8
After CV Recovery	53

- Before Infusion
- After Infusion
- After CV Recovery
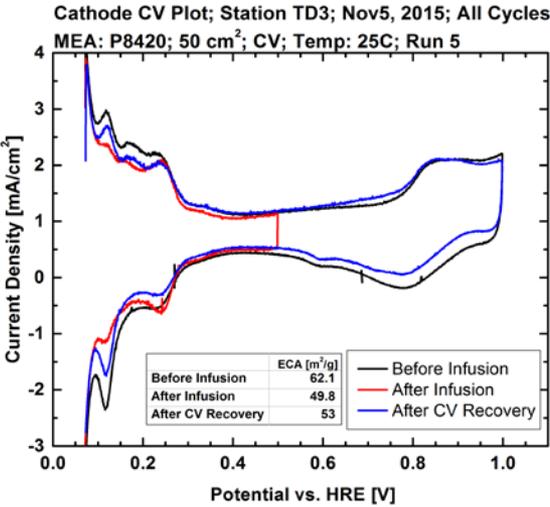
- After infusion, Pt CV shows a decrease in ECSA
- After several CVs from low (0.085V) to high (1V) potentials, ECSA was partially recovered and performance almost fully recovered
- Recovery potential needs to be <= 0.3V for sulfate anions
- Cathode environment irrelevant between: N$_2$ or Air
- Liquid water injection observed to hurt recovery

OCV tests

Recovery in H$_2$-N$_2$ at 0.4V

11 mV/hr
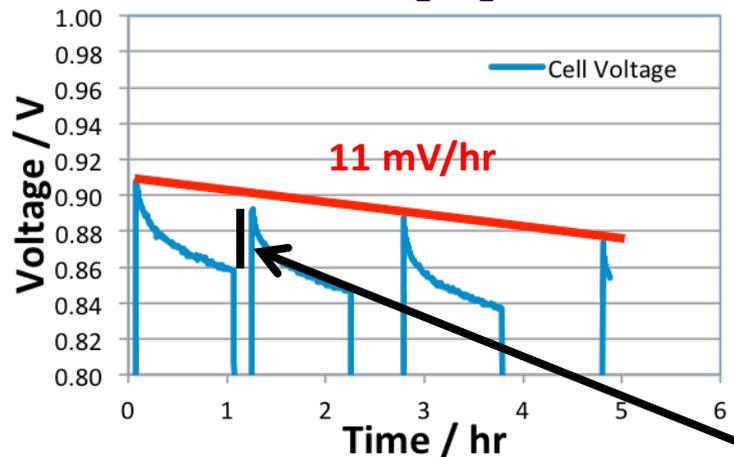
Recovery of Pt-Ox

Recovery in H$_2$-N$_2$ at 0.2V

2 mV/hr
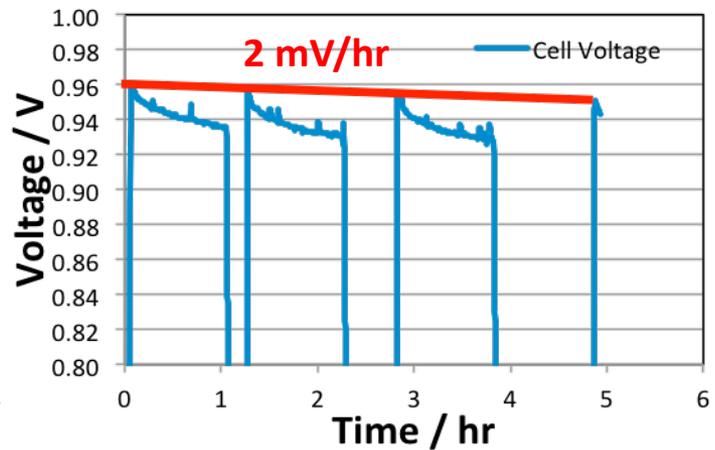
Accomplishments – Recoverable Degradation

Cell Voltage during consecutive 1-hour OCV holds

10 μV/hr
5.1 mV/hr   1.2 mV/hr

MEA#1
MEA#2
MEA#3

MEA 1: Membrane with no additives : ≈ 0.04mg$_{Pt}$/cm^2
MEA 2: Membrane with no additives : 0.4mg$_{Pt}$/cm^2
MEA 3: Chemically stabilized membrane : 0.4mg$_{Pt}$/cm^2
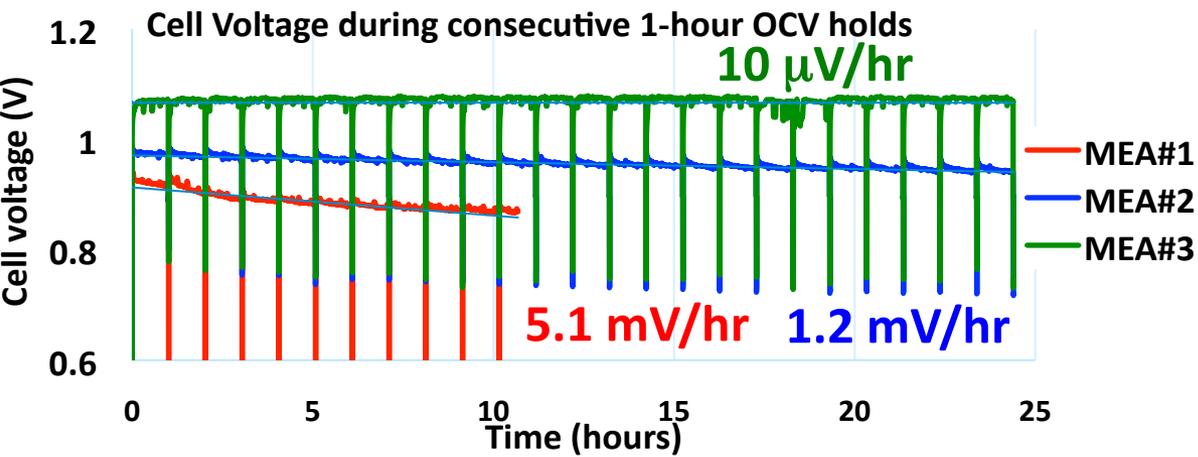
- Degradation effect decreases with increasing levels of membrane chemical stabilization and cathode catalyst loading
- Greater effect at outlets

Inlet
11 rows X 12 columns
Outlet

Current density distribution at 0.1 A/cm^2

Current density (A/cm2)
Row number (quad-serpentine pass #)

1hrOCV - BOL
5hrOCV - BOL
10hrOCV - BOL
24hrOCV - BOL
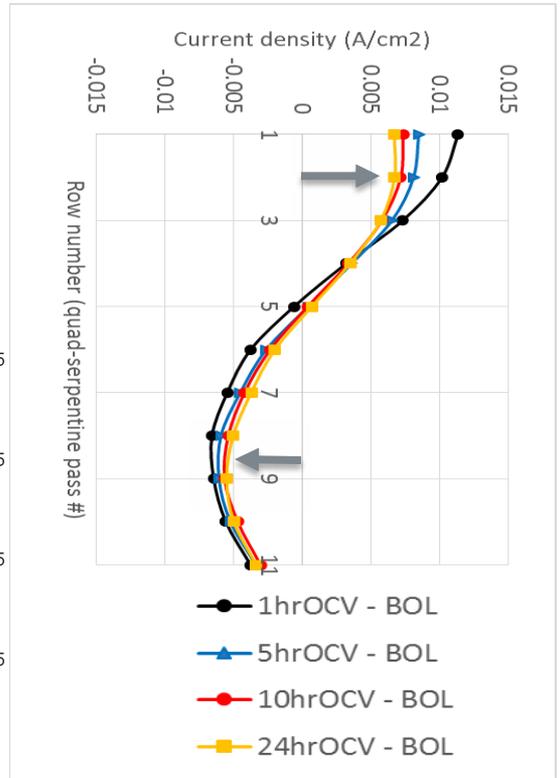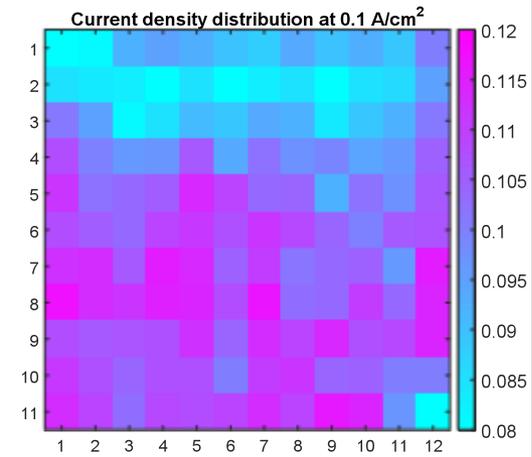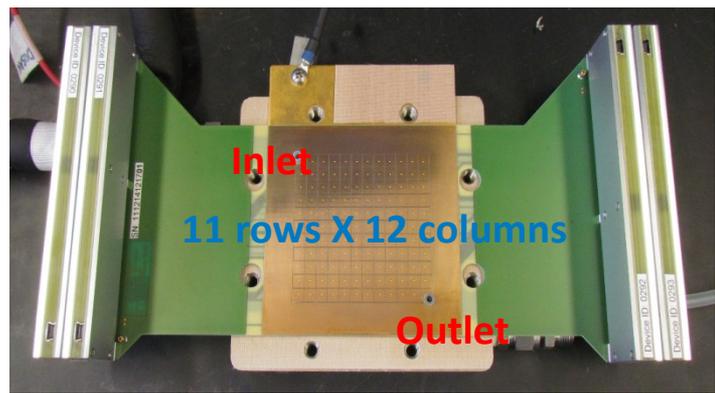
Benchmarking

- **W. L. Gore provided 18 μm membrane to GM**

- **GM applied SOA catalyst layer of 0.1mg$_{Pt}$/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**

Luis Castanheira, Gareth Hinds

o Nafion salt bridge contacts directly the anode catalyst layer through small holes in the GDL

o 6 of the 9 RE positions were used (numbered in direction of hydrogen flow)

o 3 unused holes were sealed with a PEEK rod (diameter 0.9 mm) inside the PTFE tubing

1.0 A.cm^{-2} 50 ppm CO

— Potential V cell
— Potential V RE1
— Potential V RE2
— Potential V RE3
— Potential V RE4
— Potential V RE5
— Potential V RE6

E vs. RHE / V

time / min
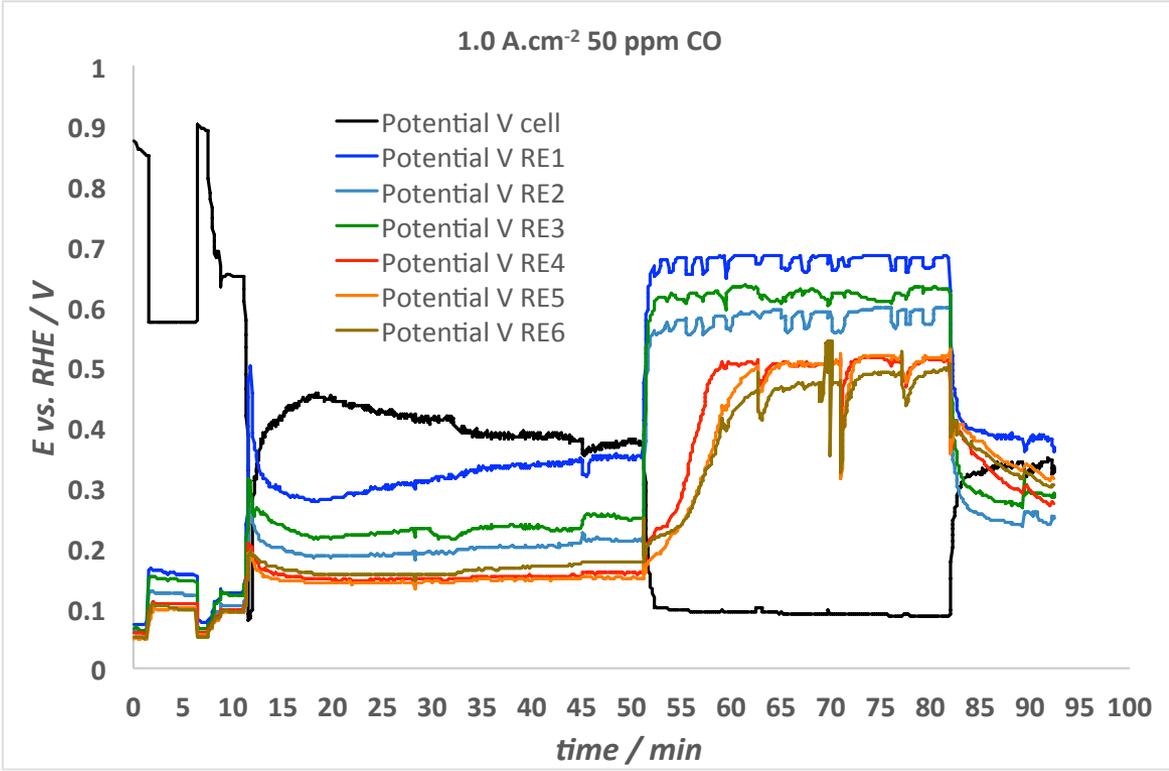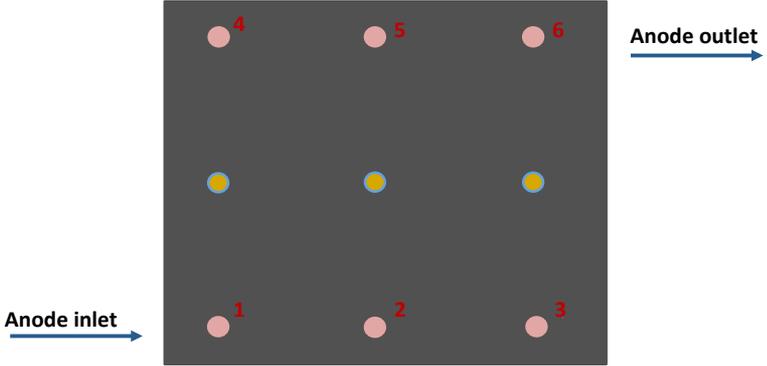
Collaborations

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

FCPAD
FUEL CELL PERFORMANCE
AND DURABILITY

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 $\geq$1.5 A/cm^{2}[c]	After 0, 1k, 5k, 10k, and 30k cycles	$\leq$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. A protocol such as the one in Table A9 should be used to recover reversible losses prior to measurement of metrics.
b. Mass activity in A/mg @ 150 kPa abs backpressure at 900 mV iR-corrected on H_2/O_2, 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 H_2 crossover. Based on the protocol published by Gasteiger et al., Applied Catalysis B: Environmental, 56 (2005) 9-35.
c. 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 cm^2	
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/cm^2)[b,c]	Every 24 h	$\leq$15 mA/cm^2
OCV[c,d]	Continuous	Initial wet OCV $\geq$ 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

a. 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.

b. Tested in MEA on H$_2$, 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.

c. 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.

d. 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.

e. Measured at 0.5 V applied potential, 80°C, 100% RH N$_2$/N$_2$. Compression to 20% strain on the GDL.