High performance PEFC electrode structures

P.I.: Mike L. Perry

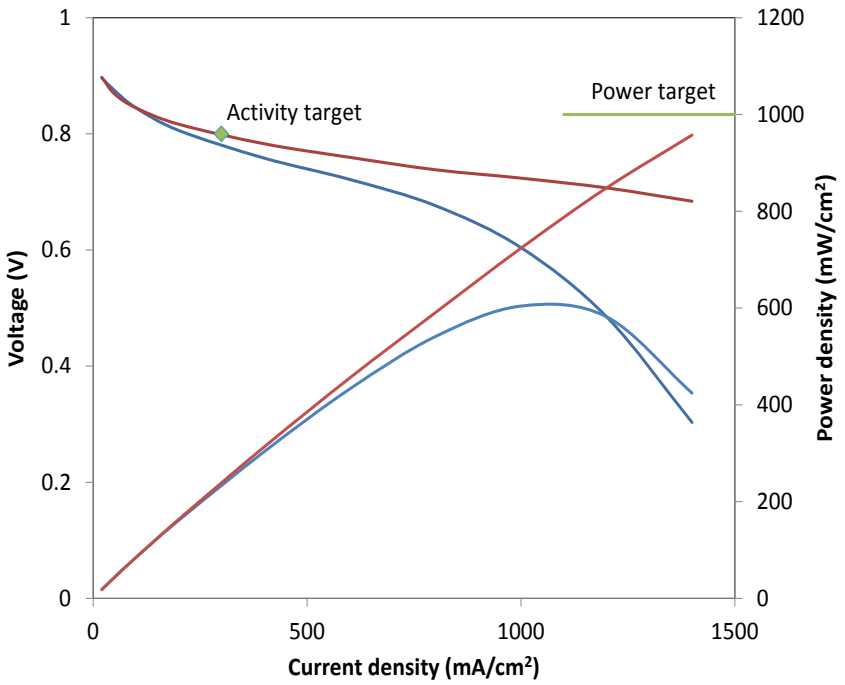
United Technologies Research Center

FC PAD Consortia Project

Project ID: **FC157**

DE-EE0007652

June 6, 2017



Polarization curve for an ultra-low-loaded PtNi/C cathode

- Raw in **blue**,
- Transport-corrected in **red**.

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This presentation does not contain technical data subject to the EAR or the ITAR.

Overview

Timeline

Project Start: October 2016
2016Q4 = "Q0"
Project Q1: Jan-March 2017
Project End: December 2019
39 months

Budget

Total Project Budget: $3,019K
- Federal Share $2,415K
- Cost Share (20%) $604K

Total DOE Funds Spent*: **$23K**

* **as of 3/31/2017**

Key Barriers

- Achieve DOE's 2020 Targets for MEAs

Characteristic	Units	2015 Status	2020 Targets
Platinum-group metal (PGM) total loading (both electrodes)	mg PGM /cm^2	0.13	≤ 0.125
Performance @ 0.8 V	mA/cm^2	240	300
Performance @ rated power (150 kPa$_{abs}$)	**mW/cm^2**	**810**	**1,000**

Partners

FCPAD FUEL CELL PERFORMANCE AND DURABILITY

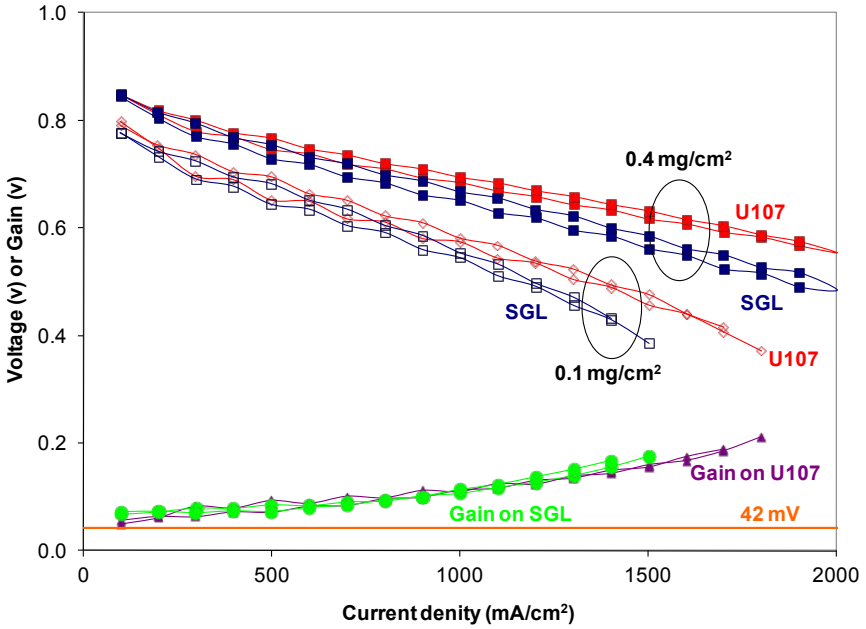
Ion Power

UALR University of Arkansas at Little Rock

Relevance

Objective: Develop *improved fundamental understanding of transport limitations* in a SOA MEA and use this know-how to ***develop and demonstrate high-performance MEAs with ULCLs***

- High-activity ORR catalysts have been developed & demonstrated
  - **MEAs with ultra-low catalyst loadings (ULCLs) can meet activity targets**
  - ***Transport losses are major barrier***
    - Flux rate per catalyst site is increased
      - Transport losses increase
    - MEAs with ULCLs cannot yet meet power density (high current) targets

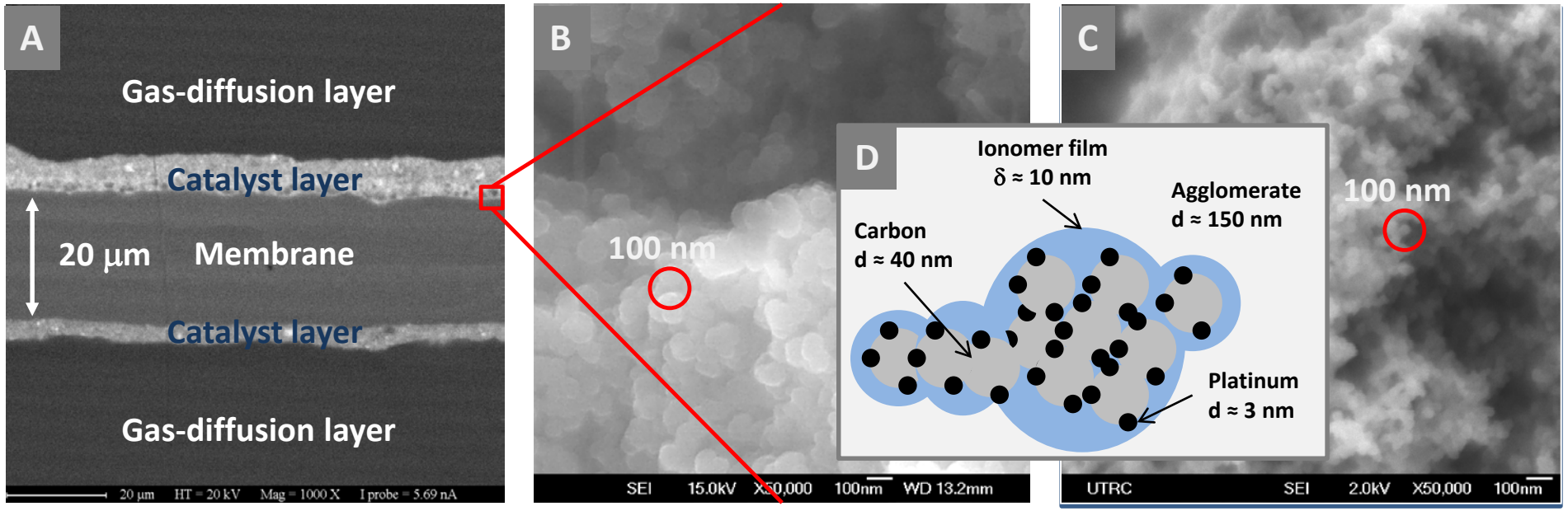


- **Need to reduce transport losses in MEAs with ULCLs**
  - ***First step is to determine actual root-cause mechanisms*** (*e.g.*, not CCL thickness)
  - Fundamental understanding is currently lacking

New electrocatalysts require new MEA architectures to realize their full potential

Technical Approach

Develop Detailed Geometric (*i.e.*, microstructure) Model of CCL



- Cathode catalyst layer (CCL) contains multiple length scales
- Agglomerates in CCL probably contain more than one carbon particle
- If there is an ionomer shell around agglomerates, then need to determine:
  - Thickness of ionomer shell and number of carbon (and catalyst sites) per agglomerate
- **Different transport-limiting mechanisms result in different limiting currents**
  - Use microstructure model to help discern different transport limitations
  - Make CCLs that can help to probe these differences, as guided by model

Multiple possible transport-limiting mechanisms within CCL

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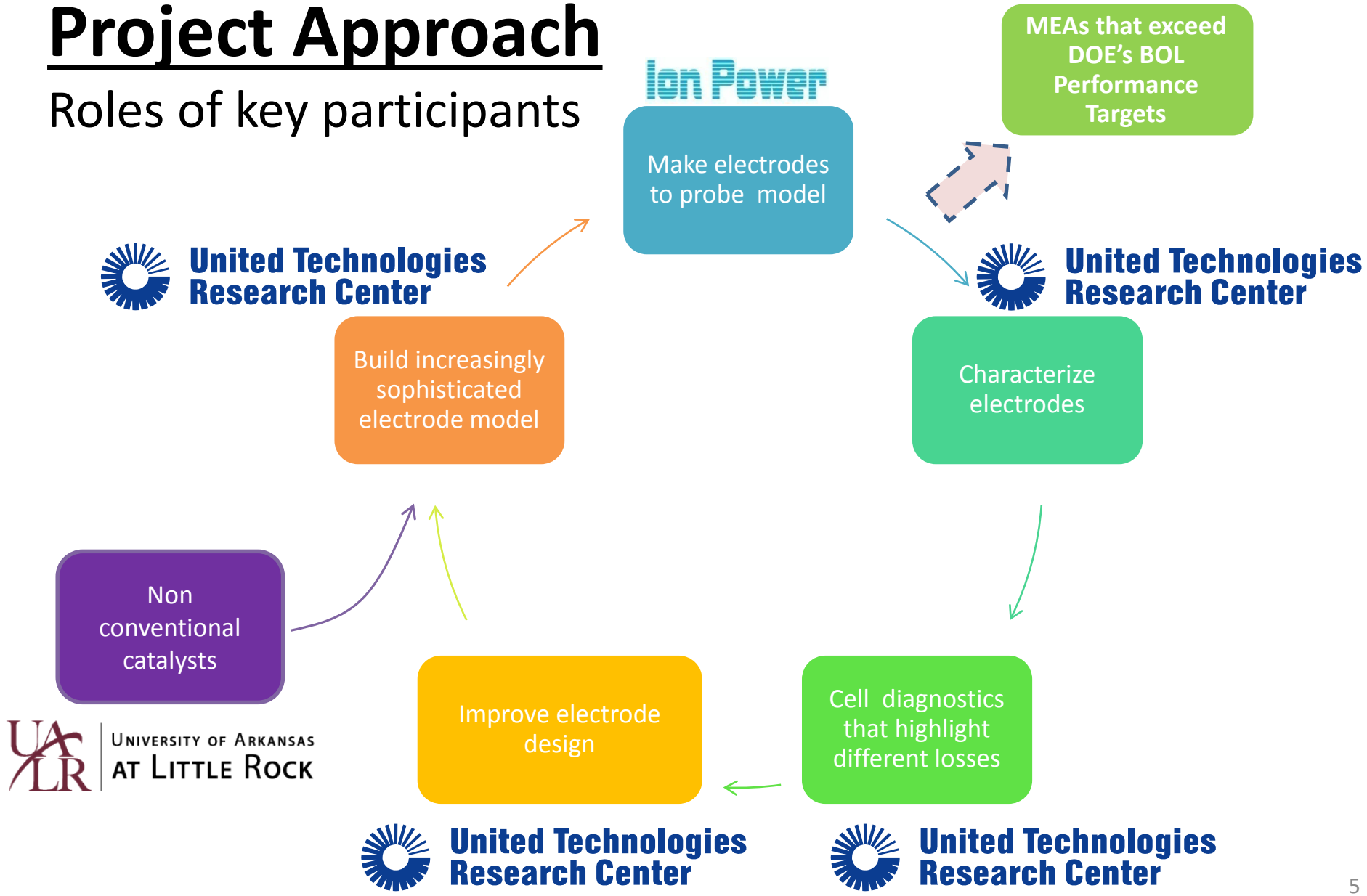
Project Approach

Roles of key participants



Iterative process will enable improved understanding and performance

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Collaborations

Core Project Team (*i.e.*, subcontractors)

Understanding electrodes with ultra-low catalyst loadings

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- Modeling
- Cell testing
- Cell diagnostics

Mike Perry (Project)
Rob Darling (Modeling)
J.V. Yang (Experimental)

Ion Power

- SOA MEAs
  1. C-supported catalysts
  2. Novel catalysts

Stephen Grot

University of Arkansas at Little Rock

- Novel catalyst structures

Tansel Karabacak

Core team has capability to lead modeling and fabricate key materials required

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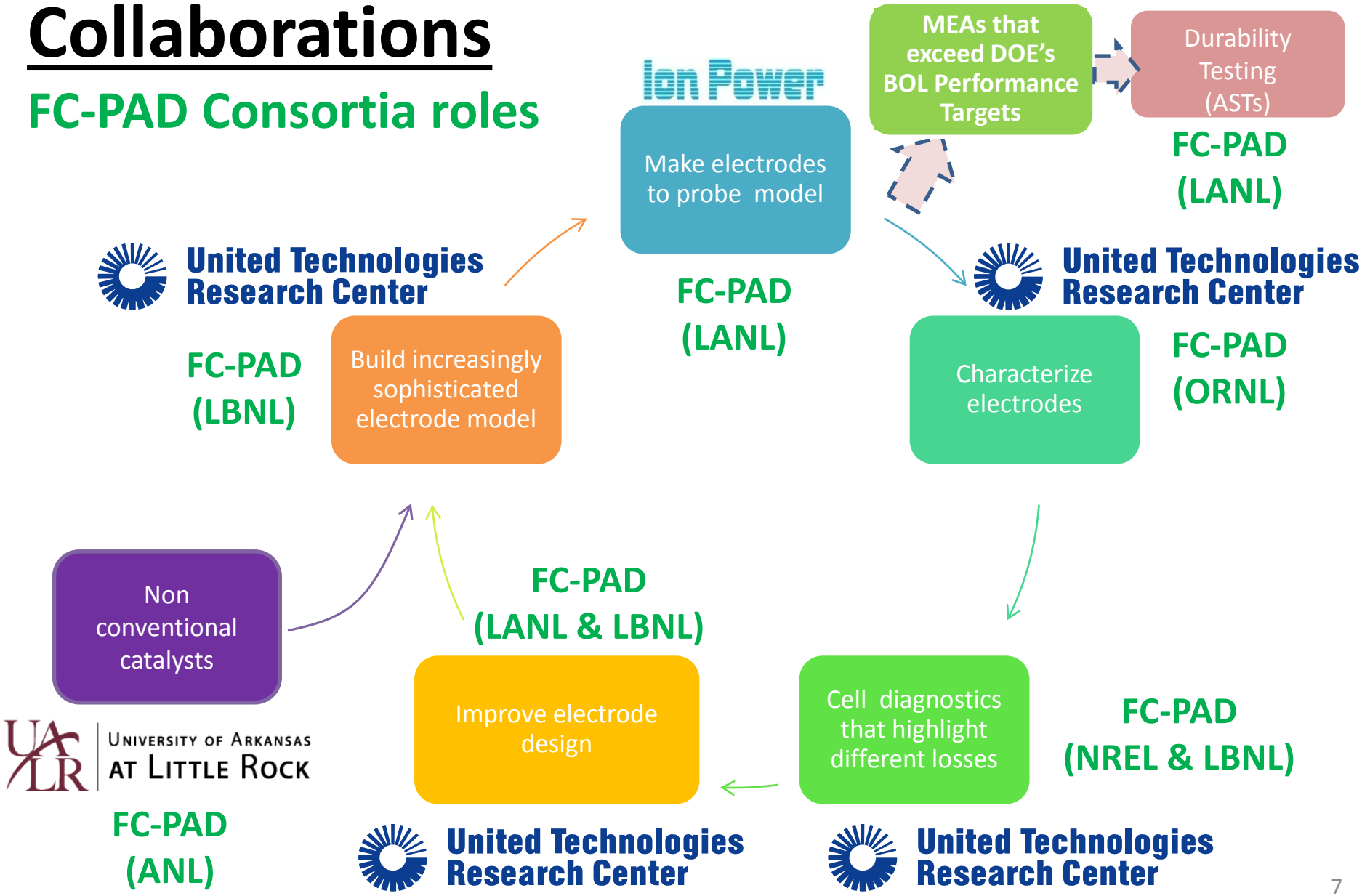
Collaborations

FC-PAD Consortia roles



FC PAD can make significant contributions on every major project task

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Accomplishments & Progress

Key Project accomplishments in Q1:

- Completed sub-contracts (both done by 4/7/2017)
- Made progress on micro-structural CCL model
- Began to assess diagnostic methods at UTRC based on model cases
- Obtain MEAs from *Ion Power* and completed initial diagnostic testing in cells at UTRC
- Prioritized catalyst-architecture options with UALR
- Begin to engage appropriate FC PAD Consortia members
  - Assigned primary contact (R. Borup, LANL)
  - Completed FC-PAD SOW for this project
  - Obtained MEAs from LANL
  - Began to work with LBNL on modeling tasks

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Ion Power

UALR University of Arkansas at Little Rock

FCPAD Fuel Cell Performance and Durability

UTRC has recently begun to work with all of the project partners

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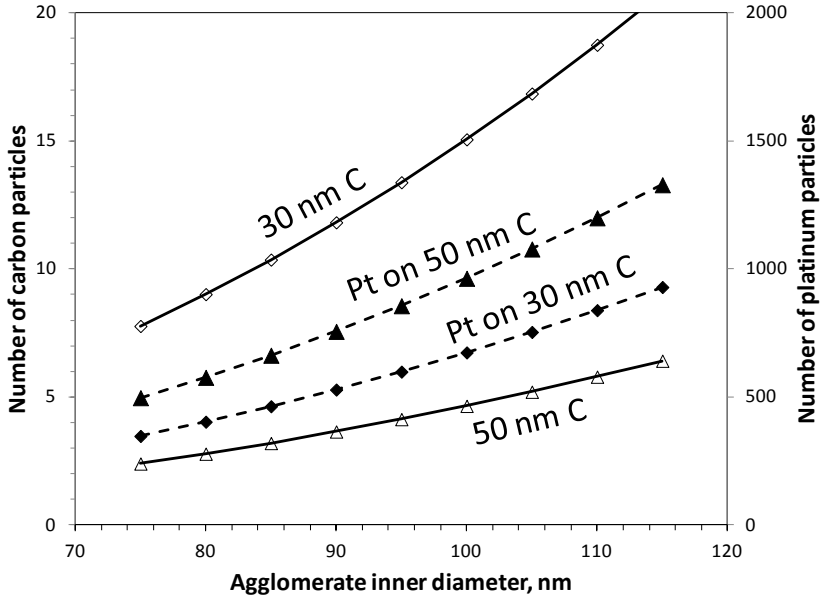
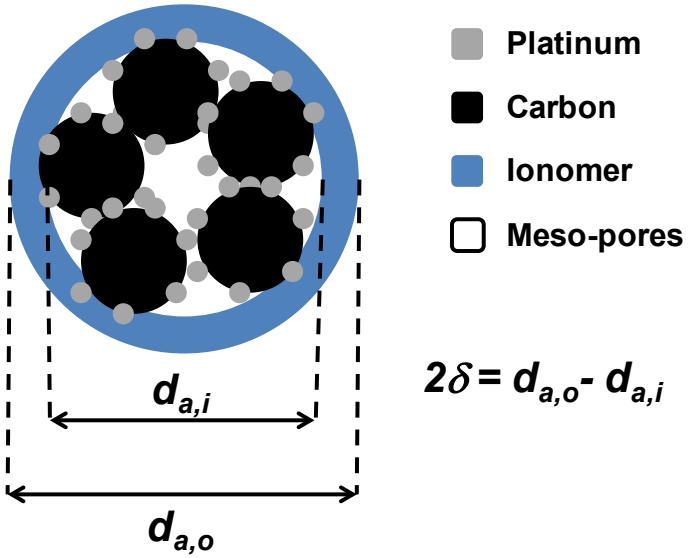
Technical Progress: Initial microstructure model has been developed

- CCL geometry depends on multiple factors:
  - Composition of the component materials (*e.g.*, Pt/C wt%, Ionomer EW, I/C ratio)
  - Arrangement of these key components (*e.g.*, agglomerate size, ionomer film distribution)



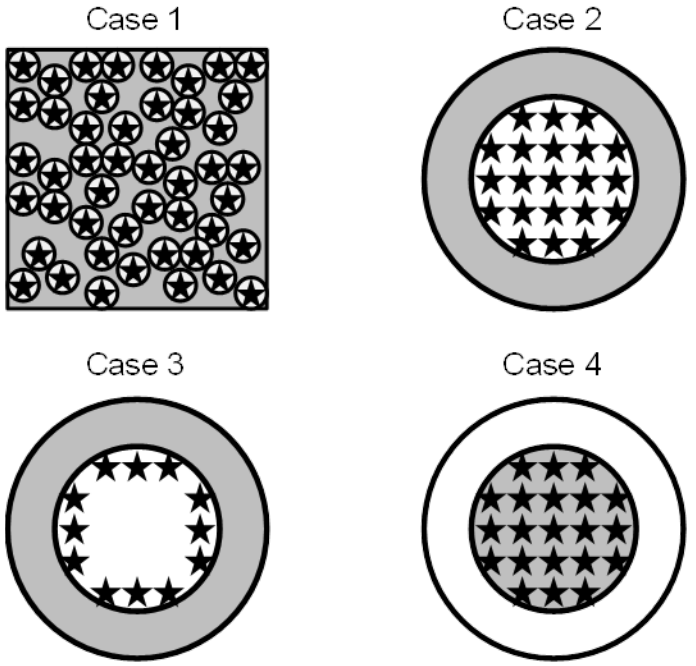


- ***One possible arrangement*** is an agglomerate structure with an outer shell of ionomer:
  - For a assumed agglomerate size, can estimate number of C and Pt per agglomerate
  - Can also estimate ionomer film and electrode thickness from I/C ratio
  - These estimates can be verified with SEM and other electrode-characterization tools

UTRC has begun to construct and verify some microstructure CCL models

Technical Progress: Some Limiting Cases have been identified

- Different transport-limiting mechanisms ***result in different limiting currents***
  - Can make CCLs that help to probe these differences



$$I_{L,1} = \frac{4F\varepsilon_b DPy}{\tau lRT} = \frac{4F\varepsilon_b(1-\varepsilon)DPy}{\tau RTL_{Pt}G(\omega,\gamma)}$$

$$I_{L,2} = I_f \mathrm{r_a} = \frac{24FDHPyL_{Pt}G(\omega,\gamma)}{\delta d_a}$$

$$I_{L,3} = I_f r_{Pt} u_{Pt} = \frac{24FHDPy}{\tau_f \delta}\frac{L_{Pt}u_{Pt}}{\rho_{Pt}d_{Pt}}$$

$$I_{L,4} = I_a r_a = \frac{48FDcL_{Pt}G(\omega,\gamma)}{d_a^2}$$

L_{Pt} = amount of platinum in electrode, mg/cm²

ω = mass fraction Pt in Pt/C catalyst

γ = ionomer to carbon ratio by mass

Case	Limiting transport through	Limiting current varies as			
		L_{Pt}^n, n=	$G(\omega,\gamma)^n$, n=	d_a^n, n=	d_{Pt}^n, n=
1	Electrode thickness in gas pores	-1	-1	0 < n < 1*	0
2	Ionomer film, uniform consumption in agglomerate	1	1	-2	0
3	Ionomer film, consumption near perimeter	1	0	-1	-1
4	Agglomerate	1	1	-2	0

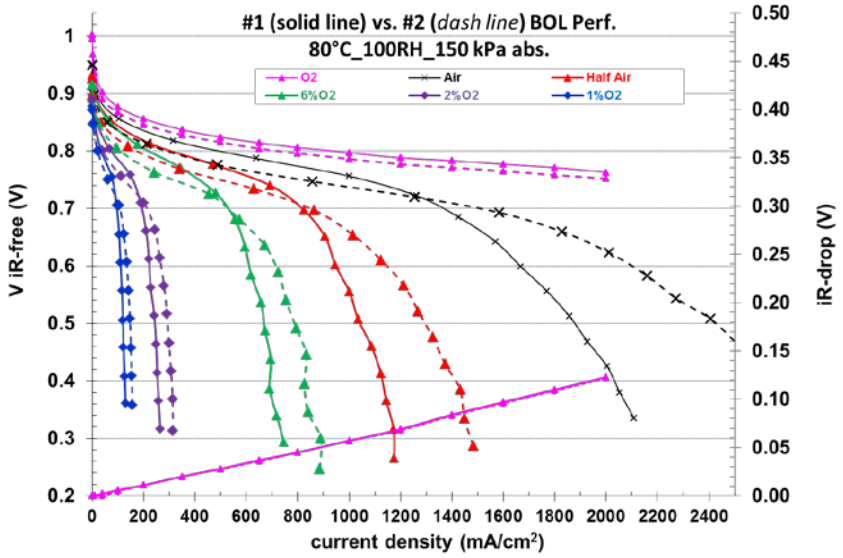
*** The diffusion coefficient increases with agglomerate diameter.**

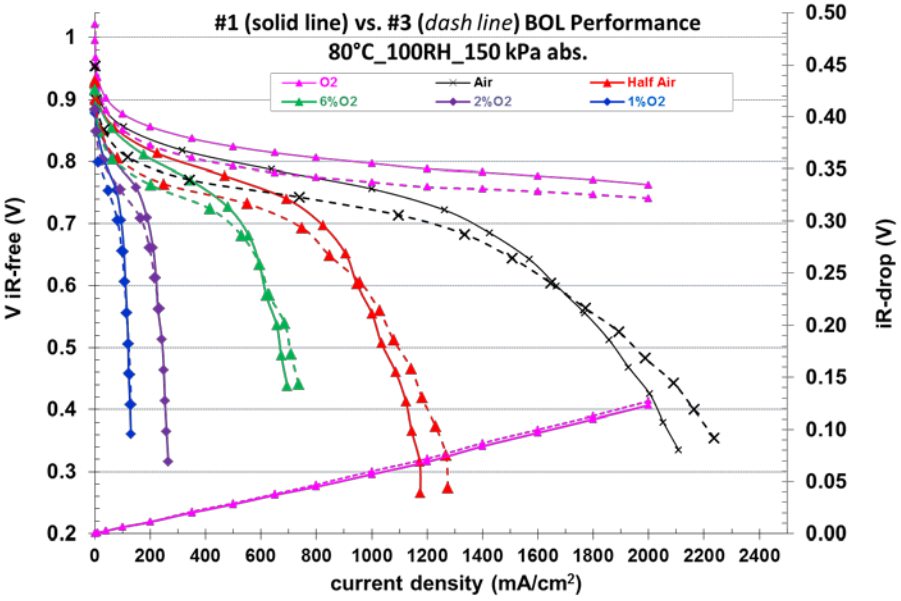
UTRC has already begun to engage FC-PAD (LBNL) on modeling work

Technical Progress: Established relevance of Pt-only MEAs

- Have utilized key results from previous DOE project to assess:
  - Best in-cell diagnostic techniques
  - **Initial MEA compositions**
- Comparison of Pt/Ni to Pt-only MEAs with ultra-low loadings:
  - Pt/C catalyst with similar catalyst-particle size as Pt-Ni/C exhibit very similar mass-transport losses
    - ***Pt-only MEAs offer simple path for initial transport studies***

BOL	#1 PtNi	#2 Pt (HSA)	#3 Pt
ECA (m^2/g-Pt)	58	82	56
Mass activity (A/mg-Pt)	0.53	0.37	0.28





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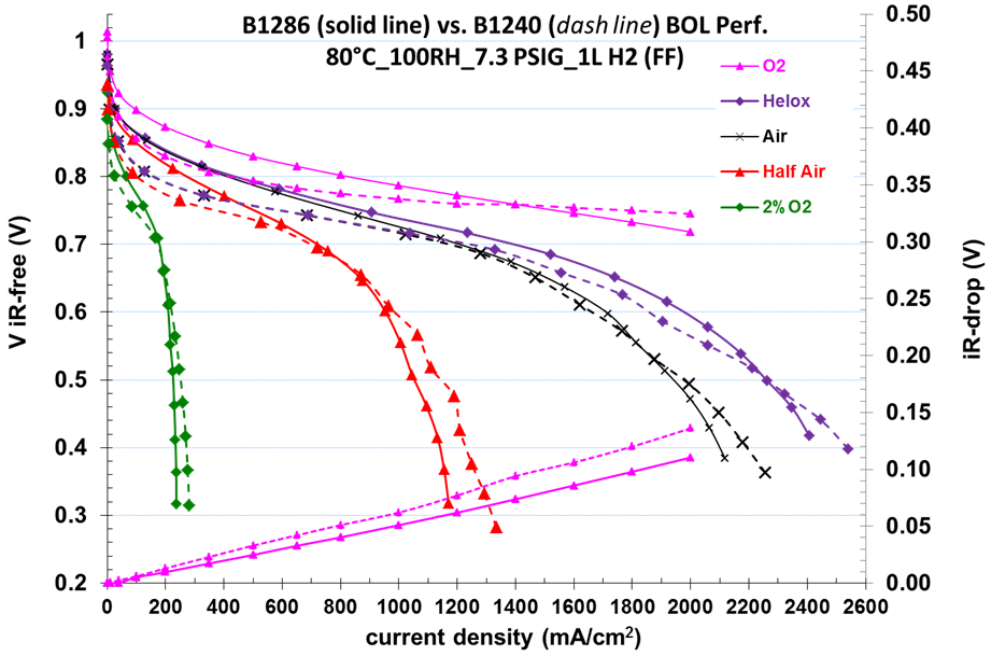
Project builds on UTRC's extensive modeling & diagnostics capabilities

Technical Progress: Initial Results with *Ion Power* MEAs

- Comparison with state-of-the-art (SOA) Pt-only MEA
- ***Ion Power*** MEA exhibited:
  - Similar Pt catalyst activity
  - Superior performance at low current densities
    - Higher catalyst loading
  - Lower *iR*-drop, but higher H2-pump resistance
    - Indicative of lower proton-conductivity in electrodes
  - Slightly lower limiting currents at low O_2 concentrations
    - Appears to indicate slightly lower oxygen-transport



BOL	B1240 SOA Baseline	B1286 IP MEA
Pt Size & Loading	5-nm Pt 0.1 mg	4-nm Pt 0.3 mg
H2-Xover	4.5 mA/cm²	3.5 mA/cm²
Mass activity	312 A/g-Pt	304 A/g-Pt
H2-pump	61 mΩ*cm²	80 mΩ*cm²

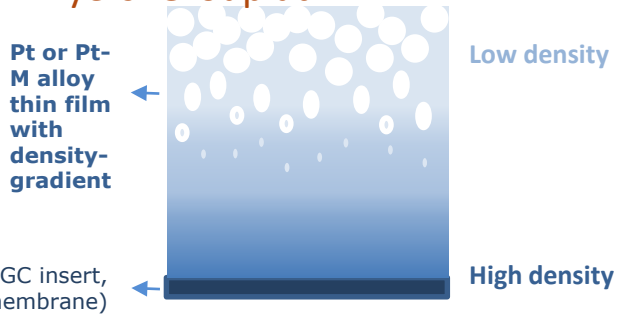
Very good initial result, some further work required to match SOA performance

Technical Progress: Non-Conventional Catalysts

Density-modulated Pt and Pt-alloy thin film electrocatalysts

Tansel Karabacak's Group, University of Arkansas at Little Rock
Collaboration with Deborah Myers' Group at ANL

University of Arkansas at Little Rock



Goal:

- Developing an ORR electrocatalyst with high performance and durability.

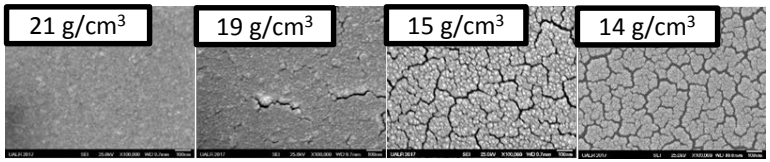
Approach:

- High pressure sputtering (HIPS) to modulate the density of the thin film (TF) catalyst. Pressure change results in a change in porosity, density, and strain.
- High density bottom: Strong adhesion to the substrate leading to enhanced physical and electrochemical stability of the TF by preventing leaching of Pt at the bottom and the detachment of large regions of TF from the substrate.
- Porous top: Effective transportation of oxygen, improved catalyst utilization, reduced Pt-loading, and enhanced ORR activity.

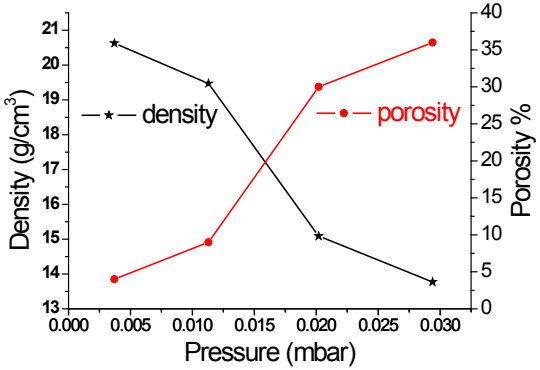
Preliminary results:

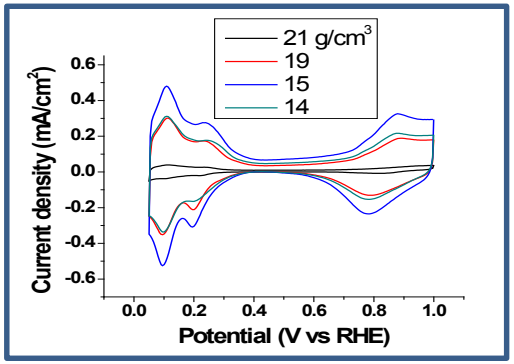
- Electrochemical activity of Pt-TFs with different densities/porosities is shown. UALR will investigate the effect of density, thickness, strain, and crystal structure on the ORR activity.

Pt TFs of different porosity/density:

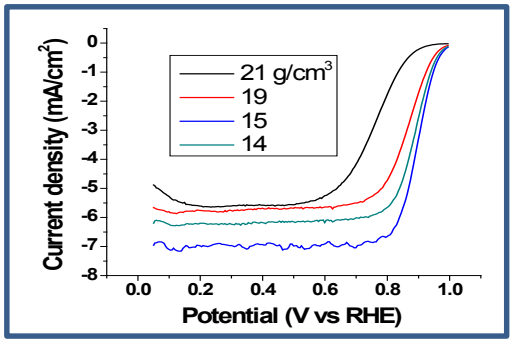


Higher porosity (lower density)

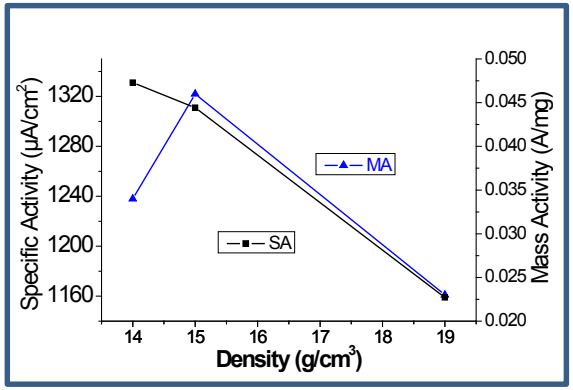




Cyclic voltammetry curves of Pt-TFs with different densities after 3000 cycling between 0.05-1 V in N_2 saturated 0.1 M $HClO_4$.



RDE profile of Pt-TFs with different densities in O_2 saturated 0.1 M $HClO_4$ at sweep rate 20 mV/s and rotation rate 1600 rpm.



Electrochemical activity of Pt-TFs with various densities
* Mass and specific activity of Pt-TFs are compared only for three films (19, 15 and 14 g/cm³).

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Proposed Future Work

Major goals for the next year of this project:

- Completion and validation of microstructural model using state-of-the-art MEAs with ultra-low catalyst loading (Pt/C)
- Use improved understanding of mass-transport loss mechanisms to improve CCLs & fabricate MEAs with improved performance

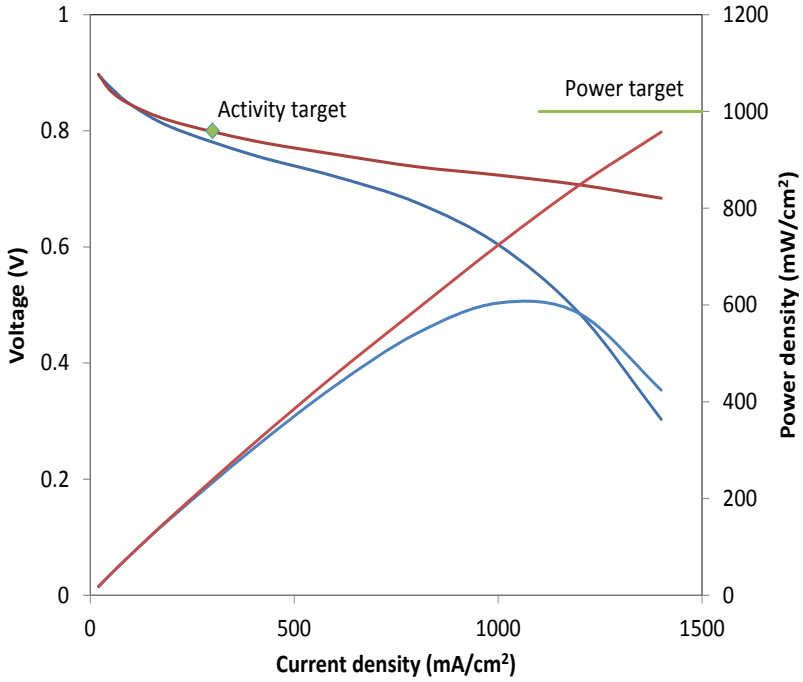
Milestone I.D.	Tasks	Task Title	Brief Milestone Description
Q1	1	Program Management	All subcontracts completed
Q2	3, 4	Carbon-supported MEA Fabrication	Demonstrate SOA performance at low PGM loading
Q3	2	Model development and validation	Microstructural electrode model framework complete
Q4 Go/No-Go	2	Model development and validation	Initial carbon-supported catalyst-layer model complete and validated with SOA MEA data
Q5	6	Novel catalyst MEA Fab	Fabricate thin-film graded catalyst
Q6 (2Q2018)	3, 4	Carbon-supported MEA Fabrication	Meet 2020 performance targets with high stoichiometric flow rates

Major focus in first year will be on MEAs/CCLs with conventional electrocatalysts

Summary

United Technologies Research Center

- *Major barrier* to meeting DOE's 2020 MEA Targets is *mass-transport losses in CCL*
- Sources of these losses are *currently not well understood*
- This project should enable improved understanding
- Utilize this understanding to develop MEAs that meet all of DOE's performance targets
- Both conventional and thin-film catalysts are included



Polarization curve for an ultra-low-loaded PtNi/C cathode

- Raw in **blue**,
- Transport-corrected in **red**.

Develop MEAs w/ ultra-low catalyst loadings & minimal transport losses

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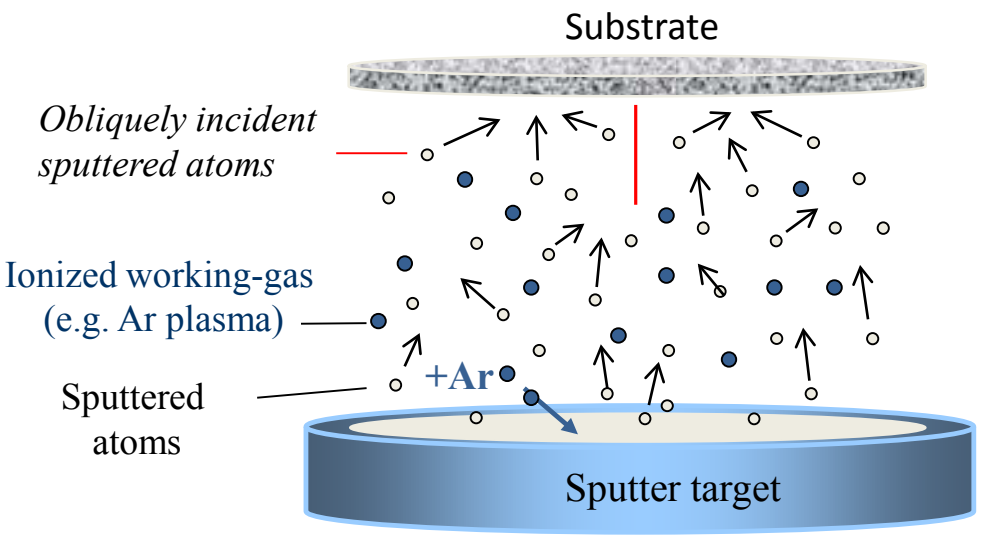
TECHNICAL BACK-UP SLIDES

Technical Background: Non-Conventional Catalysts

Fabrication Technique:

High Pressure Sputtering (HIPS)



High working gas pressure

↓

Higher number of atom-atom collisions and shorter mean free-paths

↓

Flux of source atoms with higher angular distribution: ***Obliquely incident atoms***

Enhanced Shadowing Effect: Lower density (higher porosity)

Technical Progress: Non-Conventional Catalysts

University of Arkansas at Little Rock

Summary of electrochemical activity *vs*. porosity/density

Density (g/cm^3)	Porosity %	Mass Activity (A/mg)	Specific Activity ($\mu A/cm^2$)
21	4	-	-
19	9	0.023	1159
15	30	0.046	1311
14	36	0.034	1331

Additional Preliminary results:

- Electrochemical activity of Pt-TFs with different densities/porosities.
- UALR is currently investigating the effect of density, thickness, strain, and crystal structure on the ORR activity.

Key Risk

Make electrodes to probe model

Los Alamos NATIONAL LABORATORY

NREL NATIONAL RENEWABLE ENERGY LABORATORY

- **Fabrication of CCLs** with *sufficient differentiation* to uniquely identify model parameters and/or sufficiently uniform ULCLs

FCPAD FUEL CELL PERFORMANCE AND DURABILITY

- **FC PAD Consortia** has additional capabilities that can be used here
- LANL has already provided UTRC with ULCL MEA samples
- NREL also has MEA-fabrication capabilities
  - Thrust 2: "Electrode Layers"
    Coordinator: Shyam Kocha

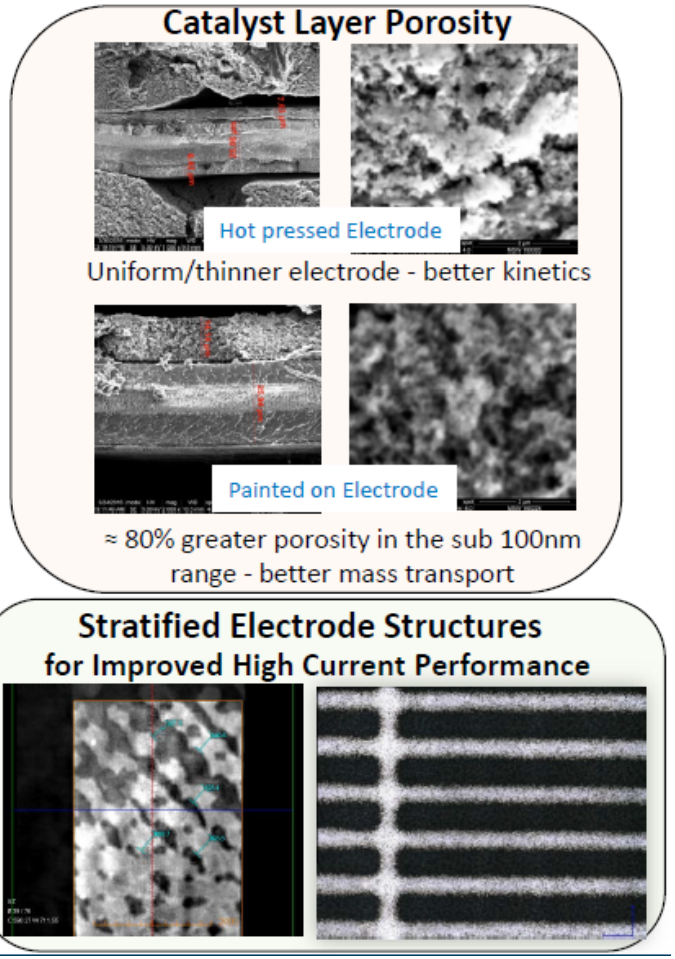


Figure from: R. Borup, 2016 AMR: "**FC-PAD Consortium Overview**" (FC135)

Key Risk

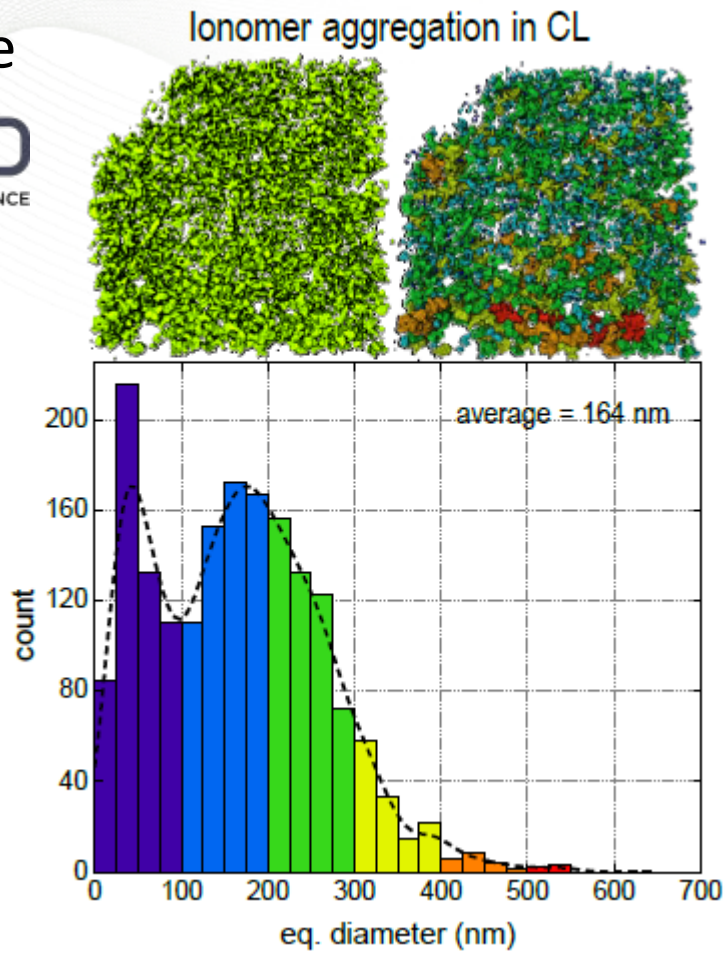
Characterize electrodes

OAK RIDGE National Laboratory

- Capability to ***adequately characterize structures*** for accurate input into the geometric models

FCPAD FUEL CELL PERFORMANCE AND DURABILITY

- **FC PAD Consortia** has world-class capabilities that can be used here
- Especially valuable in assessing:
  - Ionomer-film dimensions and primary pore sizes & volume
    - Example: HAADF-STEM
  - Pt particle sizes and pore structures in thin-film catalysts
    - Ex: Electron Tomography



Figures from: K. More, 2016 AMR Presentation (FC020) showing ionomer dispersion in CCLs

Key Risk

Non conventional catalysts

- Availability of ***sufficient quantities of alternative catalysts*** (*e.g.*, thin-film and/or nanoframe structures) to support the fabrication of MEAs by conventional techniques
- **FC PAD Consortia** has world-class capabilities that can be used here
- NREL has experience in fabricating MEAs with Thin-Film catalysts
  - Use MEA fabrication methods that work with relatively small quantities of catalysts
- **ANL** also has extensive capabilities to make alternative electrocatalysts
  - This is ***not*** part of FC-PAD Consortia, but is still a possible source of materials

"FC-PAD Consortia Overview" 2016 AMR (FC135)

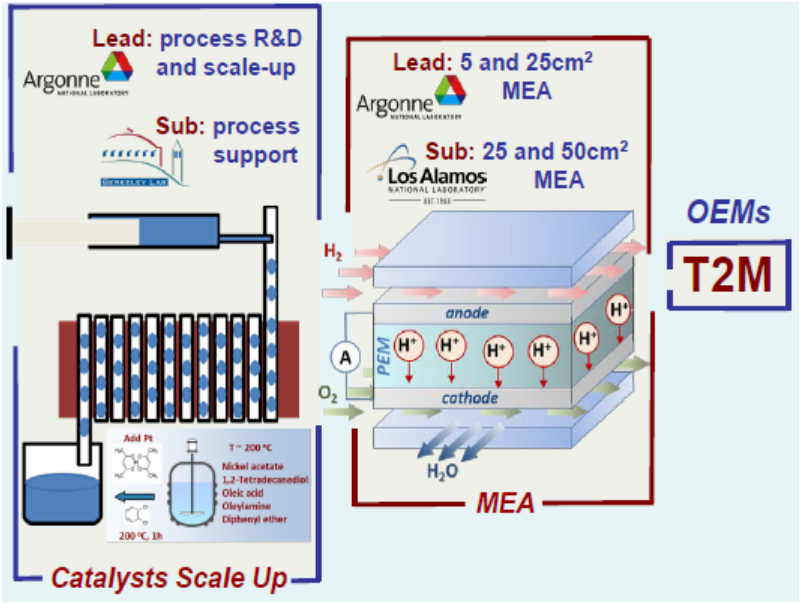


Figure from: V. Stamenkovic, 2016 AMR (FC140)