High performance PEFC electrode structures

P.I.: Mike L. Perry

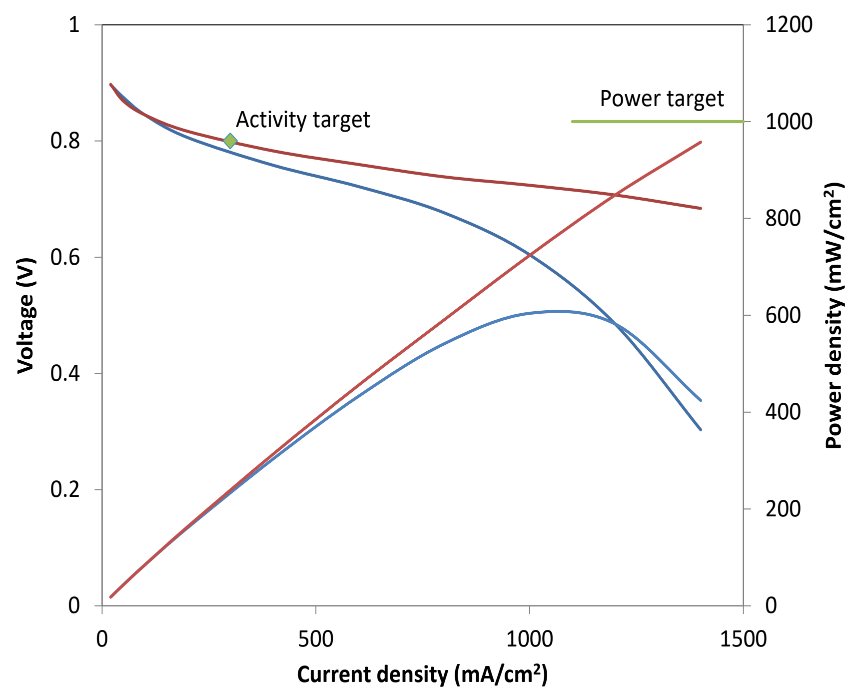
United Technologies Research Center

FC PAD Consortia Project

Project ID: **FC157**

DE-EE0007652

June 14, 2018



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

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

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

Overview

Timeline

Project Start: October 2016
Actual Start: Jan 2017
Project Duration: 45 months (with no-cost extensions)
BP-1 End Date: June 30, 2018
Project End Date: June 30, 2020

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

Budget

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

Total Funds Spent*: $748K
Total Funds for BP-1: $972K

*** as of 3/31/2018**

Partners

FCPAD FUEL CELL PERFORMANCE AND DURABILITY

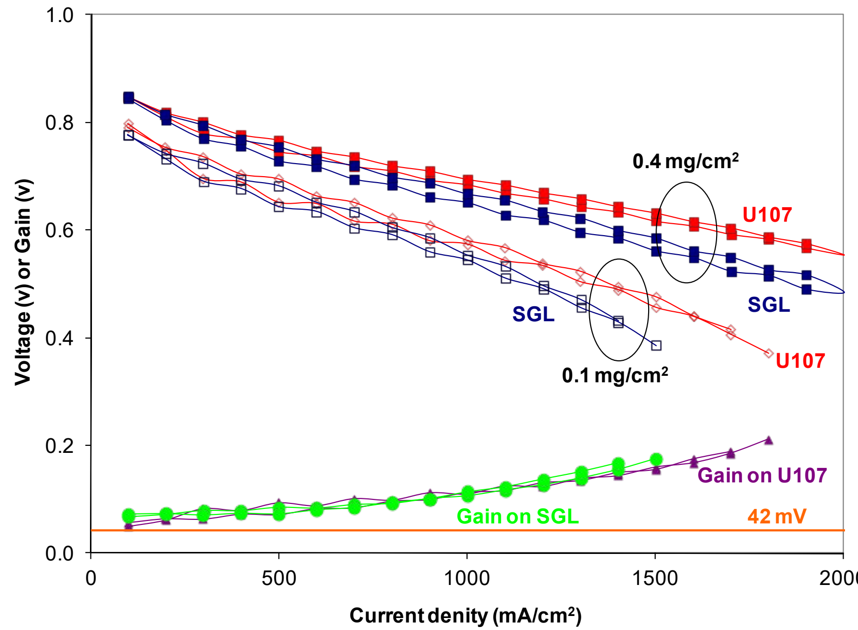
Ion Power

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

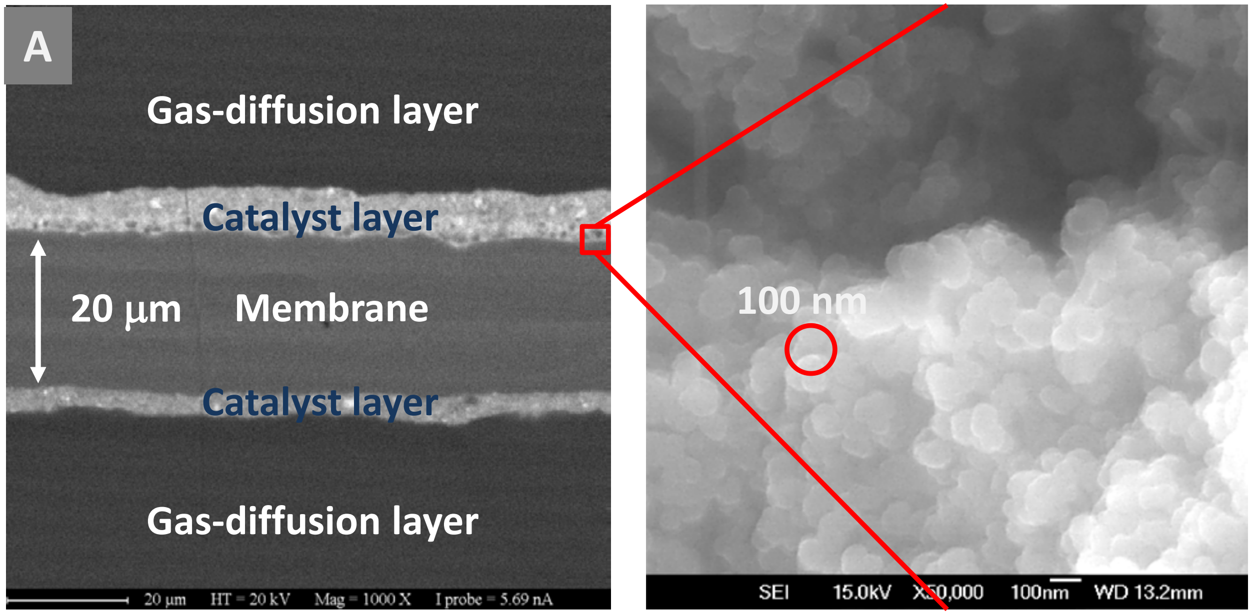


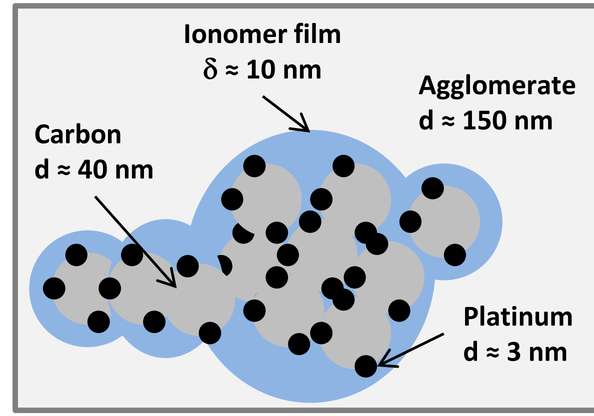
- **Need to reduce transport losses in MEAs with ULCLs**
  - ***First step is to determine actual root-cause mechanisms*** (*e.g.*, not CCL thickness)
  - Fundamental understanding lacking (***previous models did not agree w/ data***)

Improved understanding of transport losses in PEMFCs with ULCLs is needed

Technical Approach

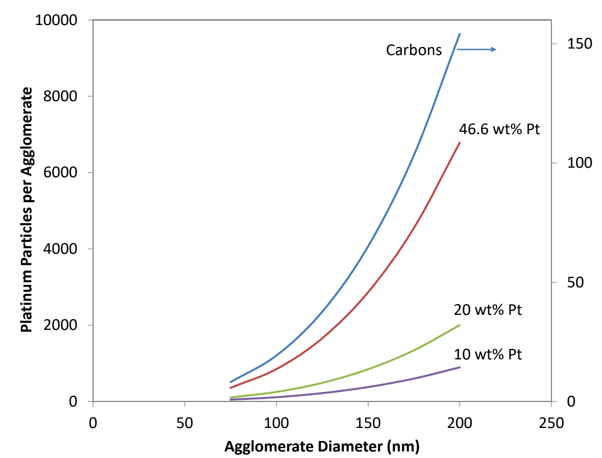
Develop Detailed Geometric (*i.e.*, microstructure) Model of CCL





Cathode catalyst layer (CCL) *contains multiple length scales*

1) Develop realistic microstructure model to help discern key mass-transport limitations in MEAs with ULCLs
2) Valid microstructure CCL model with experimental data
3) Use validated CCL model to determine how to potentially mitigate transport losses
4) Develop & demonstrate MEAs with ULCLs with reduced transport losses



Multiple possible transport-limiting mechanisms within CCL

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Approach & Collaborations

With key FC-PAD Consortia roles, to date

Ion Power

Make electrodes to probe model

MEAs that exceed DOE's BOL Performance Targets

Durability Testing (ASTs)

Los Alamos NATIONAL LABORATORY

United Technologies Research Center

BERKELEY LAB

Build increasingly sophisticated electrode model

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

Characterize electrodes

OAK RIDGE National Laboratory

United Technologies Research Center

- ***FC PAD Consortia can potentially assist with every task shown here***

Non conventional catalysts

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Improve electrode design

Cell diagnostics that highlight different losses

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Iterative process enables both improved understanding & cell performance

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Accomplishments & Progress

- Four major Quarterly Milestones have been successfully completed since the 2017 AMR meeting
  - Project is currently on-schedule (revised from original)
  - Subsequent slides show key results for the last 3 milestones
- ***Go/No-Go Milestone*** was validation of UTRC's new CCL Model
  - Model agrees well with in-cell performance data, using CCL geometric parameters measured by a variety of methods
    - This has been successfully completed using both the team's data AND with others' data

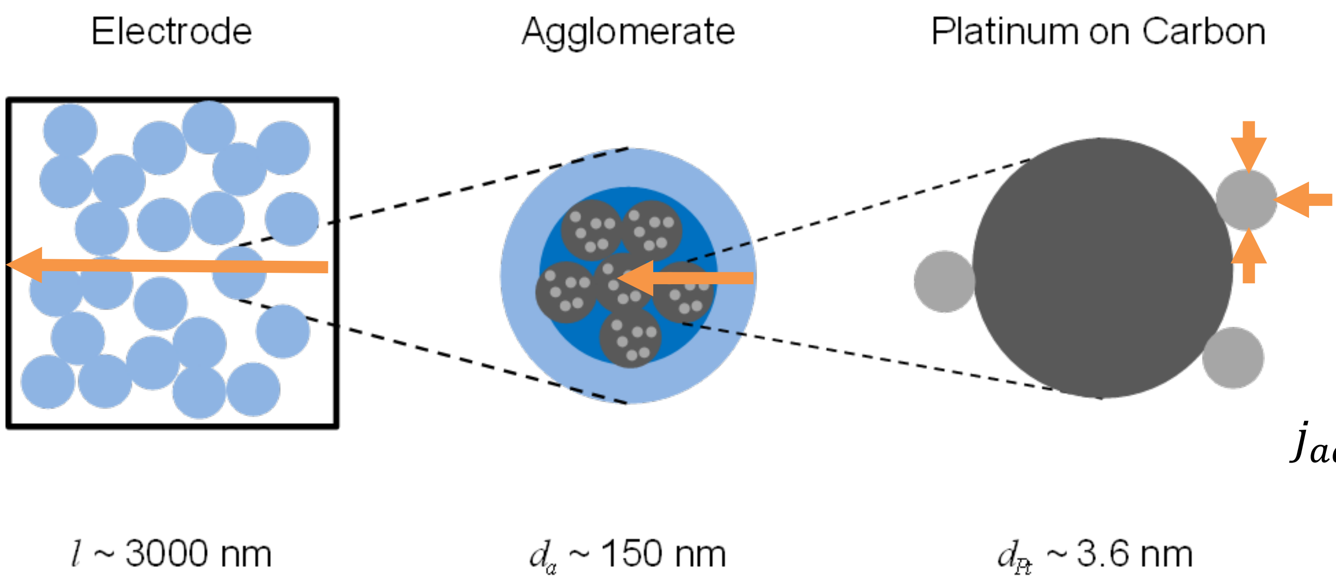
Milestone I.D.	Tasks	Task Title	Milestone Description and Status
2	3, 4	Carbon-supported MEA Fabrication	Team has demonstrated SOA performance Pt-only catalyst (Pt loading ≈ 0.1 mg/cm^2) with Ion Power MEA.
3	2	Model development and validation	UTRC's microstructural electrode model provided to LBNL and this model has been implemented in FC-PAD's PEFC model.
4 Go/No-Go	2	Model development and validation	UTRC's microstructural electrode model has been validated with SOA MEA data, both with Ion Power MEAs and with others' data.
5	6	Novel catalyst MEA Fab	Successfully fabricated a MEA (w/ 12.5-cm^2 cell active area) using thin-film catalyst deposited by UALR on GDL and tested by UTRC.

Technical Progress

UTRC has developed new Hierarchical Model of the CCL

UTRC's cathode-catalyst layer (CCL) Model is differentiated from previous models by:

- Explicit treatment of diffusion at two different length scales
  1) Agglomerates, and
  2) Platinum nano-particles



$$j_d = \frac{D(c_\infty - c_s)}{r}$$

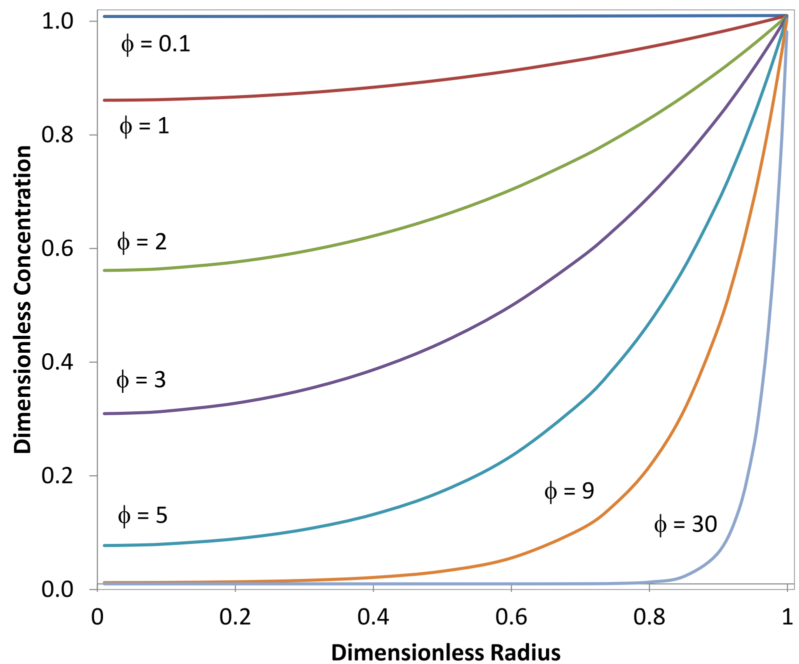
$$j_{ads} = k_{ads}(c_s - c_o)$$

UTRC CCL model includes transport losses at three different length scales

Technical Progress

UTRC model accounts for extremely large fluxes to limited catalyst surface area in CCLs with ultra-low Pt loading

- Model treats agglomerates with Thiele modulus-effectiveness factor approach
  - Thiele modulus, ϕ, is ratio of kinetic and diffusion rates
  - With ultra-low loadings, diffusion dominates and ϕ is large
  - At ϕ = 30, 90% of agglomerate is inactive and reaction is confined to a narrow surface region of the agglomerate
- ***Significant transport losses occur at length scales of the catalyst particles***
  - Use Modified Thiele modulus and effectiveness factor
  - Also modify the "reaction" rate constant to include slow adsorption and local diffusion at scale of Pt particles
  - Relationship between effectiveness factor, η, and ϕ remains the same because overall process is 1st order in oxygen



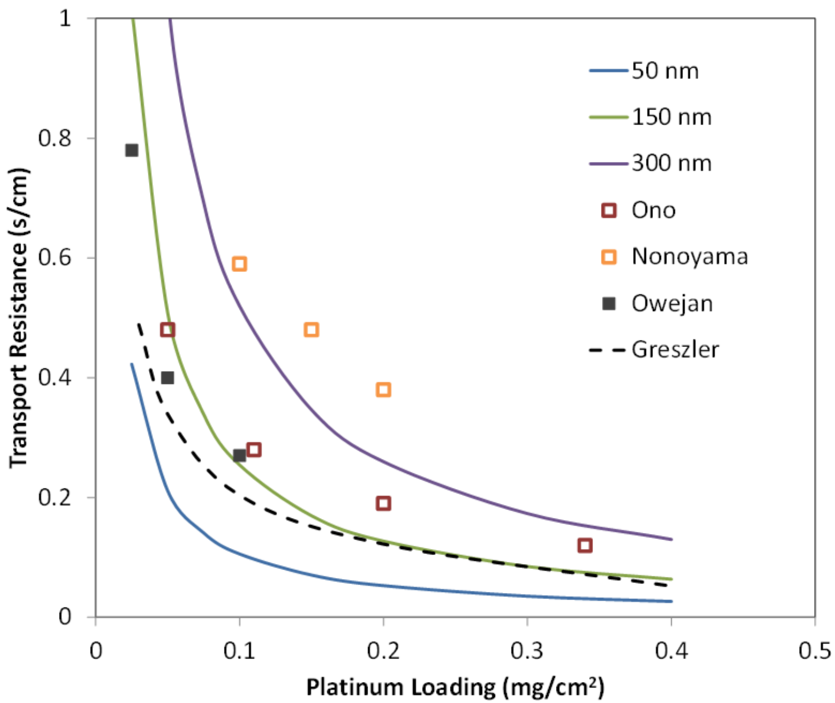
$$j_{Pt} = \frac{i_{Pt}}{n_e F} = \frac{c_\infty}{\frac{1}{k_r} + \frac{d_{Pt}}{D} + \frac{1}{k_{ads}}} = \frac{k_r c_\infty}{1 + \frac{k_r d_{Pt}}{D} + \frac{k_r}{k_{ads}}} = k_* c_\infty$$

Including transport losses at Pt-particle length scales results in i_{lim} α Pt loadings

Technical Progress

UTRC's CCL model has been validated using literature data

- Model validated using:
  - Experimentally measured agglomerate & platinum sizes
  - CCL Transport Resistances reported by GM and TMC



- 300-nm curve is close to the result for ***E-type carbon*** from TMC
- 150-nm curve is close to the result for ***Vulcan carbon*** from GM & Nissan
- 50-nm curve is close to the result with only local losses

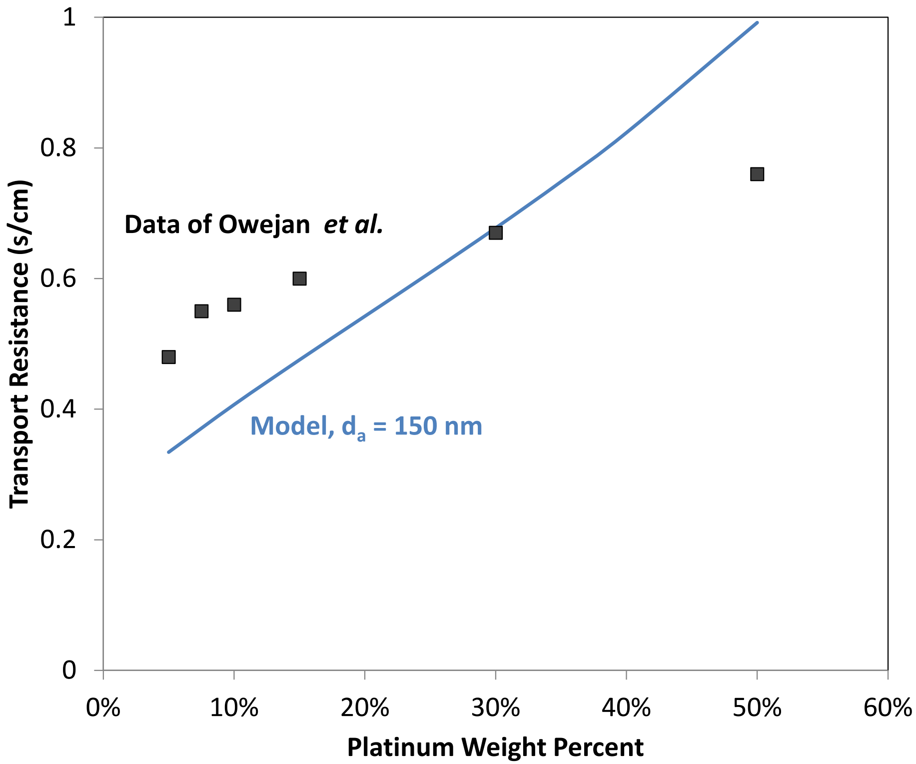
Data sources:
Nissan: ***Ono, Y., et al.*** *2010, ECS. Trans.* ***28****(27), p. 69*
TMC: **Nonoyama, N,** ***et al.***, 2011, *JECS* **158**, p. B416
GM: ***Owejan, J. P., et al.,*** *2013, JECS* ***160****, p. F824.*

UTRC model explains why O_2-transport resistance increases as Pt content decreases

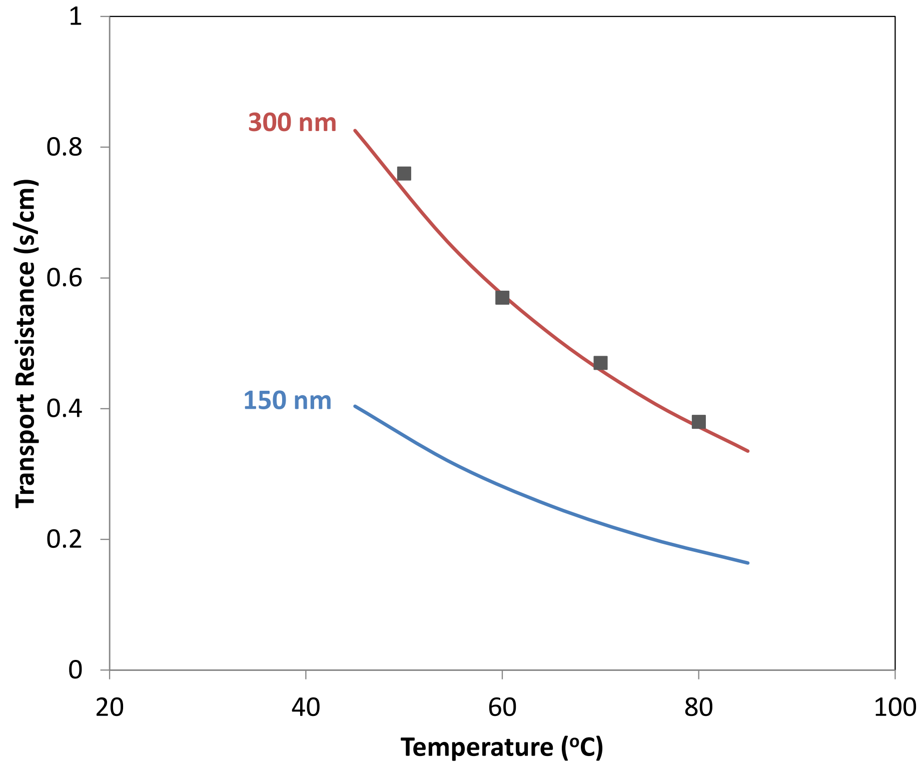
Technical Progress

Model is commensurate with key operating parameters

- Good agreement with experimental sensitivities to both Pt wt% and *T*



***Owejan, J. P., et al.**, 2013, JECS **160**, p. F824*

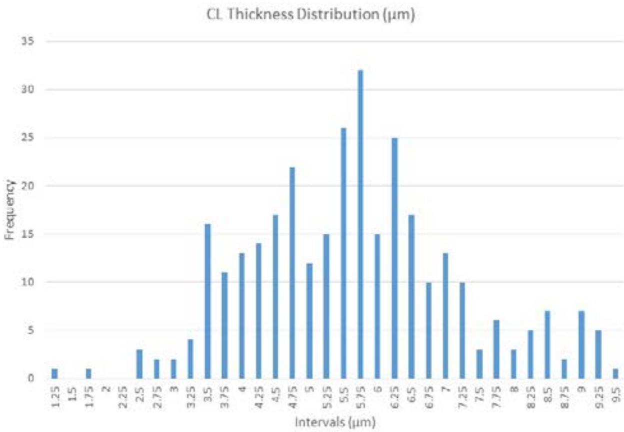


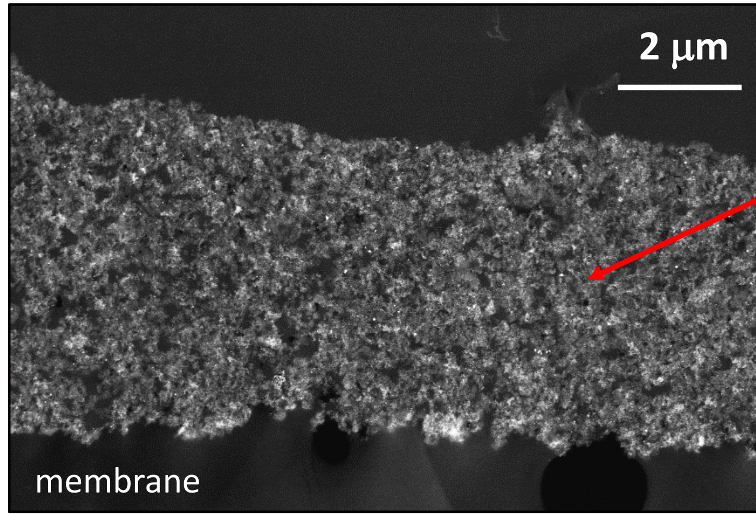
Nonoyama, N, *et al.*, 2011, *JECS* **158**, p. B416

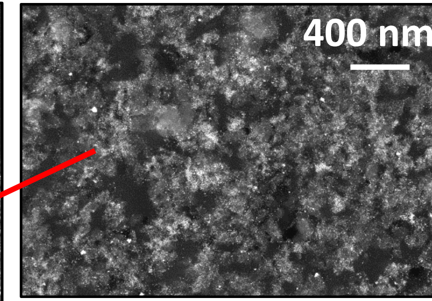
Manuscript on UTRC's Hierarchical Model has been submitted for publication

Technical Progress

Ion Power MEAs characterized in collaboration with FC PAD







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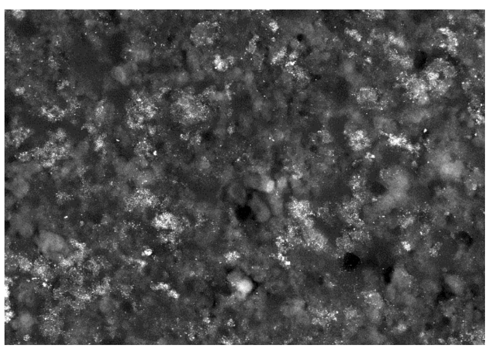
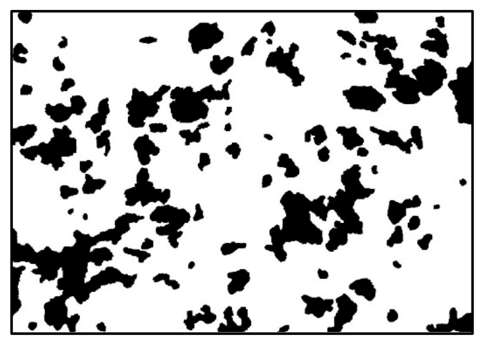
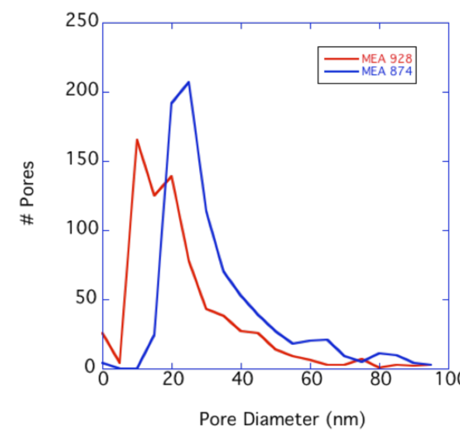




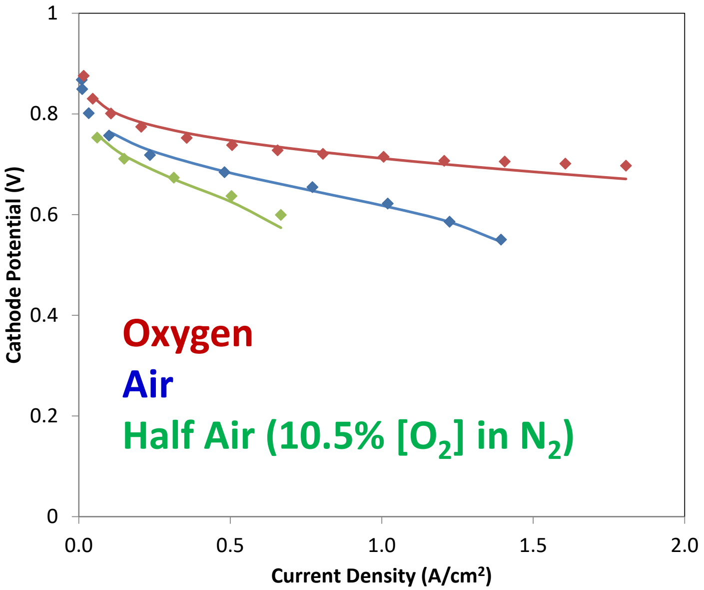


UTRC model explains why O_2-transport resistance increases as Pt content decreases

Technical Progress

UTRC's CCL model has been validated using team's data

- Model validated using:
  - Key CCL parameters measured by UTRC and FC-PAD Consortia, including (and method):
    - Pt Loading (XRF)
    - Ionomer Loading (TGA)
    - Electrode Porosity (multiple measurements)
    - Meso-porosity of Catalyst (from supplier)
    - Agglomerate Diameter (multiple measurements)
    - Ionomer Film thickness (calculated)
  - Catalyst and ionomer properties reported in the literature
  - Isolate GDL transport losses
    - Allows calculation of $[O_2]$ at the GDL-CCL interface
  - Isolate membrane resistance losses
    - *In-situ* measurements



Comparison of model to data obtained by UTRC on *Ion Power* MEA with Pt loading of approximately 0.1 mg/cm^2

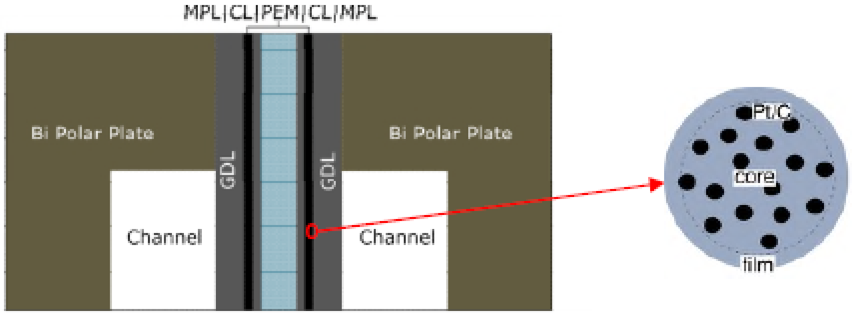
Activity on air and half air are increased 31% relative to oxygen and air, respectively, to fit low current data. No other parameters fit.

Model predicts performance on oxygen and air using minimal fitting parameters

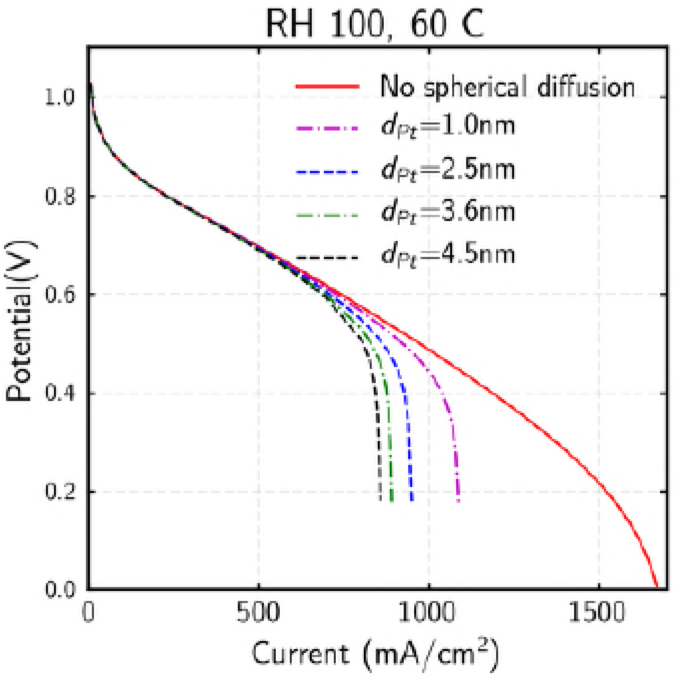
Inclusion of Spherical Diffusion near Pt Particles in MEA Model

- Full scale 2-D MEA simulation model in COMSOL
- Multi-component diffusion, electronic conduction, protonic conduction, water transport
- Butler-Volmer kinetics for HOR in anode
- Tafel kinetics for ORR in cathode with agglomerate model

- Local spherical diffusion effects near Pt particles included
  - Modified Thiele modulus
  - Modified effectiveness factor



- Cell performance is highly sensitive to size of Pt particle
- No spherical diffusion corresponds to $d_{Pt} = 0$
- Bigger Pt particles induce stronger local diffusion effects, and therefore lower performance



Technical Progress: Non-Conventional Catalysts

Pt Thin-Film (TF) electrocatalysts with different microstructures

Tansel Karabacak's Group, University of Arkansas at Little Rock

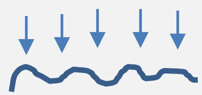
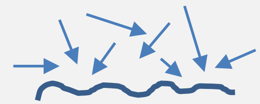
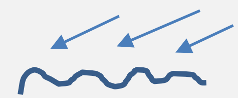
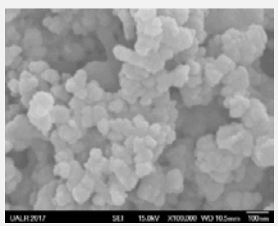
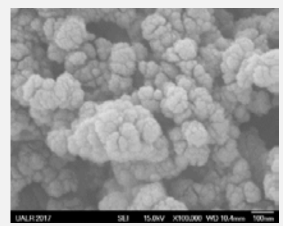
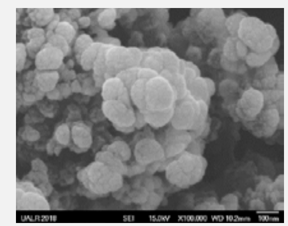
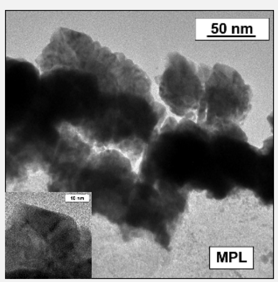
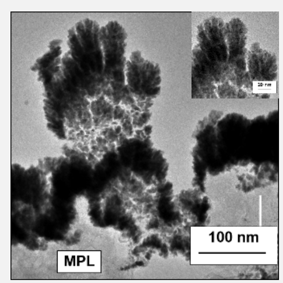
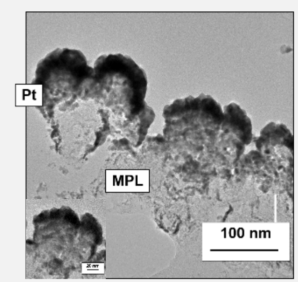
Collaboration with LANL, ORNL, and ANL

University of Arkansas at Little Rock

Goal: Producing Pt thin film electrocatalysts with various microstructures and investigate their ORR activity and MEA performance.

Approach:

- Deposit Pt thin film catalysts onto MPL with different sputter growth approaches to control the microstructure (e.g. see SEM and TEM images below).
- Microstructure of the Pt layers deposited on a flat surface (e.g. glassy carbon) and rough surface (MPL) are quite different. Therefore, we are currently developing an in-situ method to obtain CV and RDE profiles of these GDEs, which will be more comparable with MEA tests.

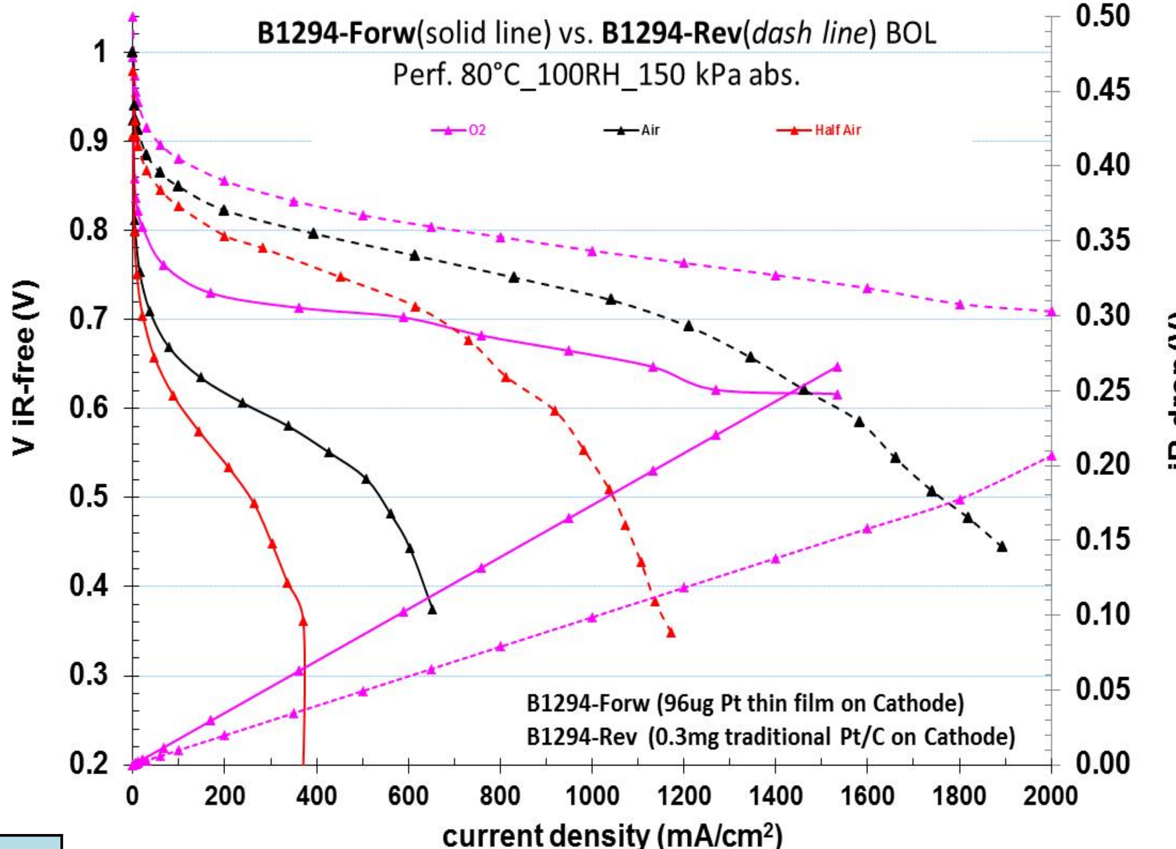
	Normal Angle Deposition (NAD)	High Pressure Sputtering (HIPS)	Glancing Angle Deposition (GLAD)
			
SEM Images (top-view)			
TEM (Oak Ridge National Laboratory)			
	▪ Densely packed fibrous structure consistent with the zone-T in structure zone model[1] of sputtered thin films ▪ Dense Pt layer thickness on MPL surface ~20-50nm. Weight loading ~0.1 mg_{Pt}/cm^2. ▪ Pt grain size >10 nm	▪ Cauliflower-like fractal nanocolumnar structure formation consistent with the shadowing effect modeling work[2] ▪ Thickness of Pt surface layer ~20-50nm . Weight loading ~0.1 mg_{Pt}/cm^2. ▪ Pt grain size (columnars) <10 nm	▪ Enhanced side growth and globular structure formation consistent with the shadowing growth simulation work[2] ▪ Thickness of Pt surface layer >~50 nm. Weight loading ~0.1 mg_{Pt}/cm^2. ▪ Pt grain size >10 nm

1) http://draftugentbe.webhosting.be/index.php?p=124&m=82

2) Karabacak, T., J. P. Singh, Y-P. Zhao, G-C. Wang, and T-M. Lu. "Scaling during shadowing growth of isolated nanocolumns." *Physical Review B* 68, no. 12 (2003): 125408.

Technical Progress: Results obtained with a *UALR-fabricated MEA*

- This cell was fabricated by:
  - UALR used GDL as substrate to deposit TF catalyst
  - UTRC built a PEMFC by integrating this UALR-catalyzed GDL with a "half MEA" (membrane with conventional Pt/C catalyst on one side), plus a non-catalyzed GDL
- UTRC ran cell in both Forward and Reverse configurations



	Anode ("forward")	Cathode ("forward')
Pt Loading	0.3 mg/cm^2	0.096 mg/cm^2
GDL	SGL25BC	SGL25BC
Membrane = Nafion®212	Active area = 12.25 cm^2	

- These results show that **UALR's TF-electrode makes a good Anode** with ≈ 0.1 mg Pt/cm^2
- Cathode performance is poor, but this is a good result for ***first-of-its-kind* MEA**

Successfully demonstrated that MEAs can be fabricated from UALR's thin-film catalysts

Collaboration & Coordination Summary

Continued collaboration with Project Partners:

- A variety of custom MEAs, and other materials, were provided by ***I.P.*** for testing and characterization purposes
- Both UTRC and LANL have tested MEAs fabricated from **UALR** catalyst (and "½-MEAs" provided by ***Ion Power***)

<u>UTRC has expanded our collaborations with FC PAD Consortia</u>

- CCL characterization done in a collaboration with:
  - **LANL** (*e.g.*, SEM, XRF, TGA, MIP, and BET)
  - **ORNL** (*e.g.*, TEM of MEAs, CCLs, & catalyst)
- Continue to collaborate with **LBNL** on modeling work

5 significant collaboration partners on this project, to date

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Proposed Future Work

Major goals for the next year of this project:

- Use improved understanding of mass-transport loss mechanisms to improve CCLs & fabricate MEAs with improved performance
- Continue to make improvements to Pt/C-catalyst model
- Develop new microstructure-CCL model with thin-film (TF) catalysts

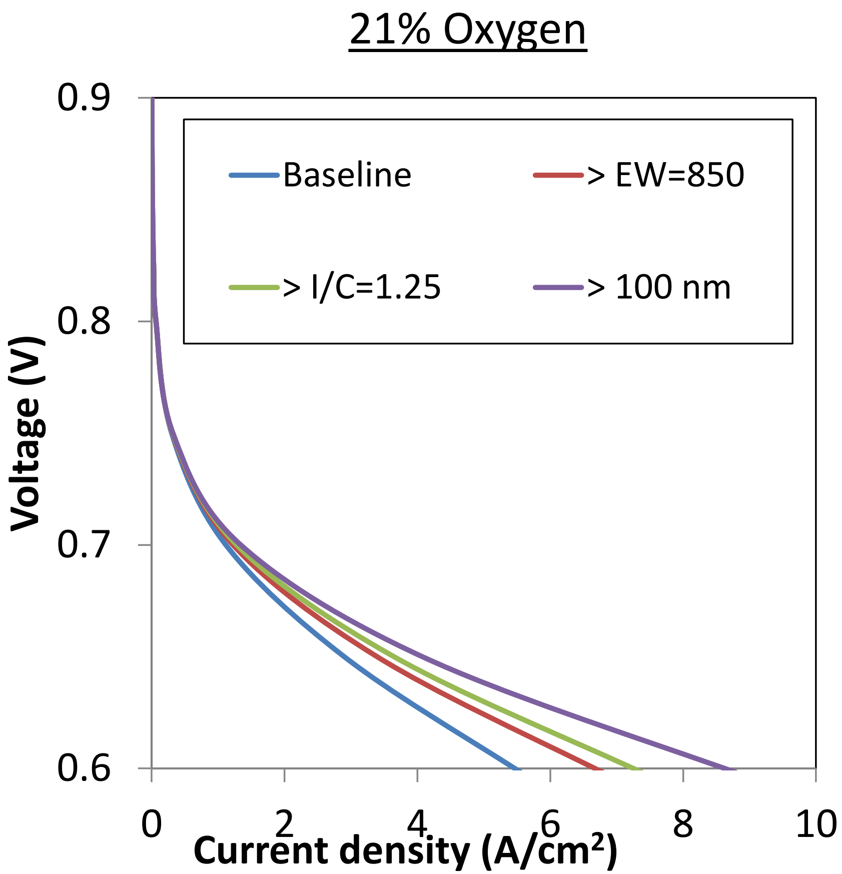
Milestone I.D.	Tasks	Task Title	Brief Milestone Description
6 (4Q2018)	3, 4	Carbon-supported MEA Fabrication	Demonstrate MEA that can meet 2020 performance targets with high stoichiometric flow rates (*e.g.*, ≥ 1 W/cm^2 at rated power).
7 (1Q2019)	2	Model development and validation	Initial thin-film catalyst CCL structure model completed and incorporated into complete PEFC model that can generate polarization curves with requisite cell operating parameter inputs.
8 Go/No-Go (2Q2019)	2, 3, 4, & 5	Model validation and C-supported MEA performance	Validate microstructural model with improved accuracy, and demonstrate MEA with significantly improved transport-limited performance (*e.g.*, ≥ 905 mW/cm^2 at rated power measured using the specified polarization curve protocol in FCTO's MYRDD.

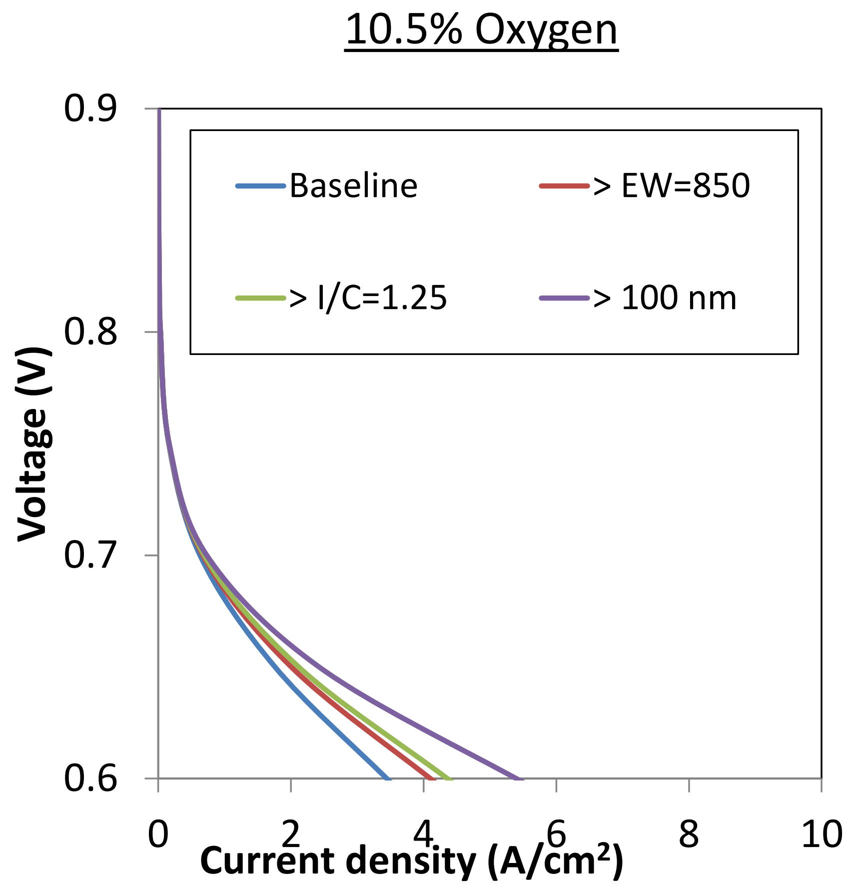
Major focus will be on demonstrating improved MEAs/CCLs with conventional catalysts

Any proposed future work is subject to change based on funding levels

Projected Improvements with Pt/C MEAs

Use UTRC's Hierarchal Model to predict optimal CCL composition





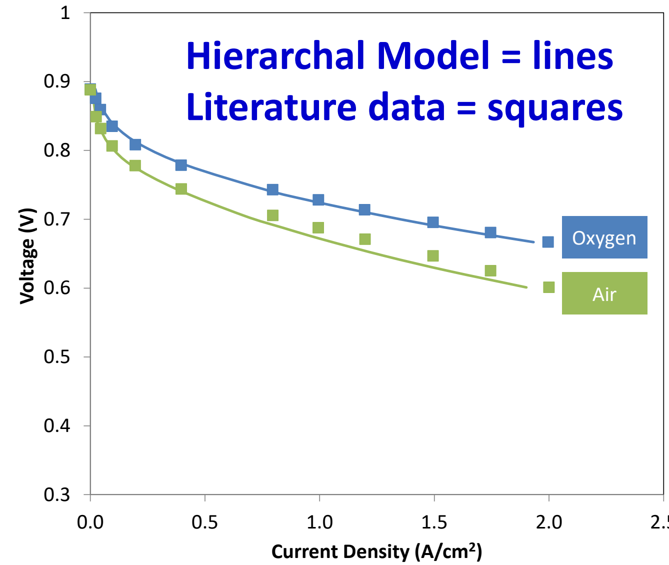
Key changes: Lower EW, slight increase in I/C, smaller agglomerates.

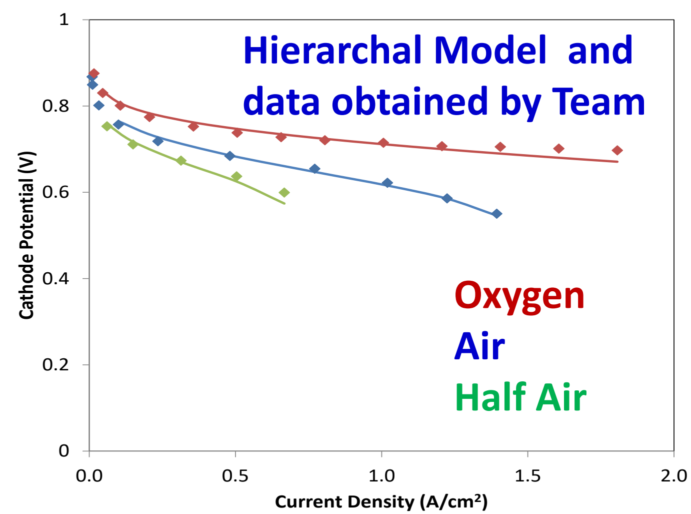
Any proposed future work is subject to change based on funding levels.

Summary

United Technologies Research Center

- Major barrier to meeting *DOE's 2020 MEA Targets* are mass-transport losses in cathode-catalyst layers (CCLs)
- Hierarchal CCL Model incorporates mass transport at multiple length scales and has been validated with two data sets
- Hierarchal CCL Model accurately predicts limiting currents that are proportional to Pt loading, and other trends (*e.g.*, *T*, wt%)
- Hierarchal Model predictions shall be used to develop advanced MEAs with reduced transport losses
- Project includes both conventional (Pt/C) and thin-film (TF) catalysts
- TF-based MEAs have been successfully fabricated and tested





Best path to MEAs with reduced transport losses is accurate CCL model

Acknowledgements

- Rob Darling
- Zhiwei (J.V.) Yang
- Chris Shovlin

Project Partners

Ion Power

- Stephen Grot

University of Arkansas at Little Rock

- Tansel Karabacak
- Busra Ergul
- Mahbuba Begum

FC PAD Partners

Los Alamos National Laboratory

- Rod Borup
- Sarah Stariha
- Natalia Macauley

Oak Ridge National Laboratory

- Karren More

Berkeley Lab

- Adam Weber
- Lalit Pant

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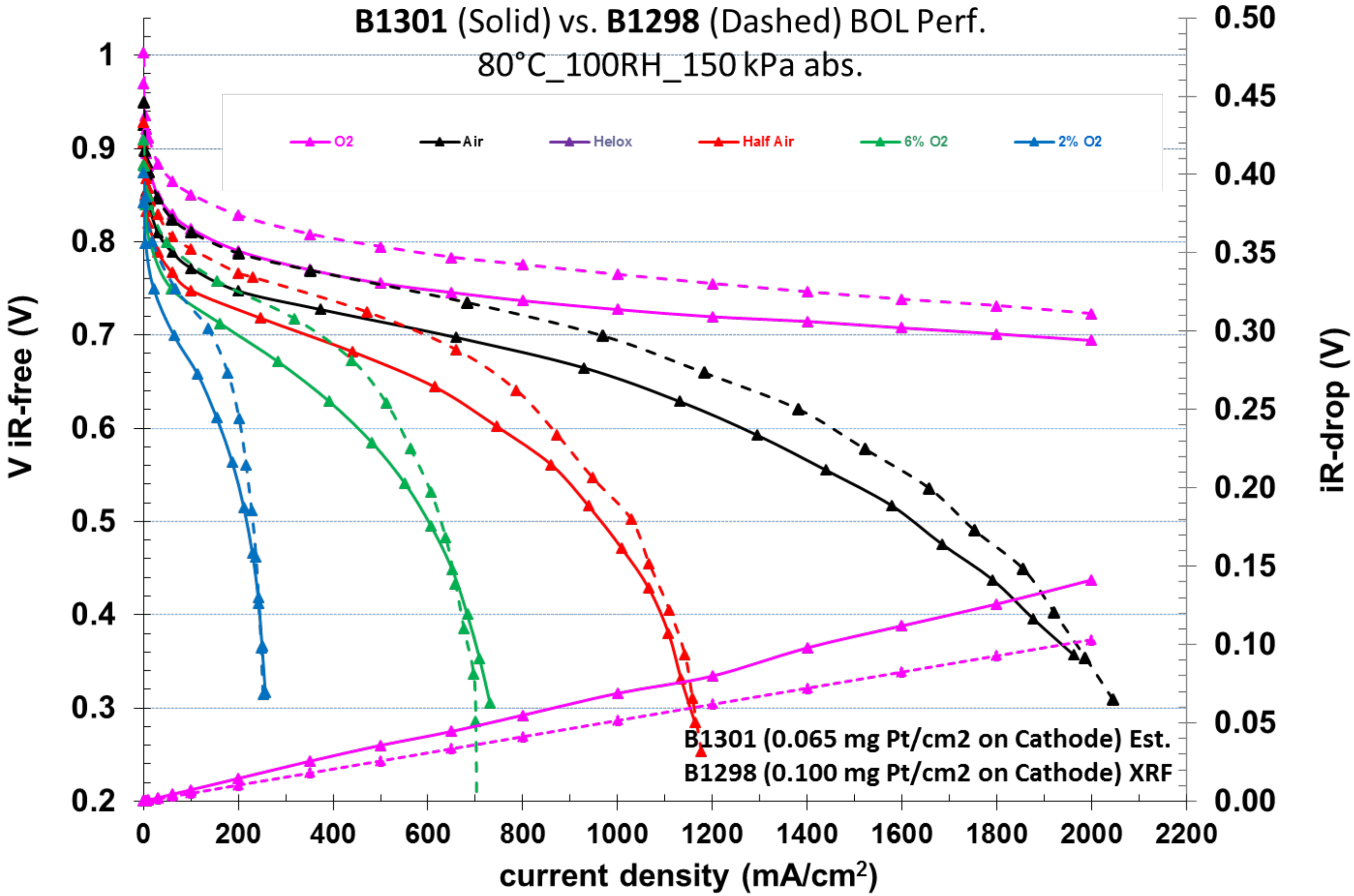
TECHNICAL BACK-UP SLIDES

UTRC Cell Performance with Ion Power MEAs

1) Cell B1298: SGL25BC/ I.P.-MEA /SGL25BC, 12.25-cm^2_SP-triple serpentine, co-flows.
2) Cell B1301: Same as B1298, with similar I.P.-MEA (with presumably lower Pt loading)
   - Same components, except "smooth" *vs*. "wavy" electrodes



Testing conditions: 80°C_100%RH_150kPa abs

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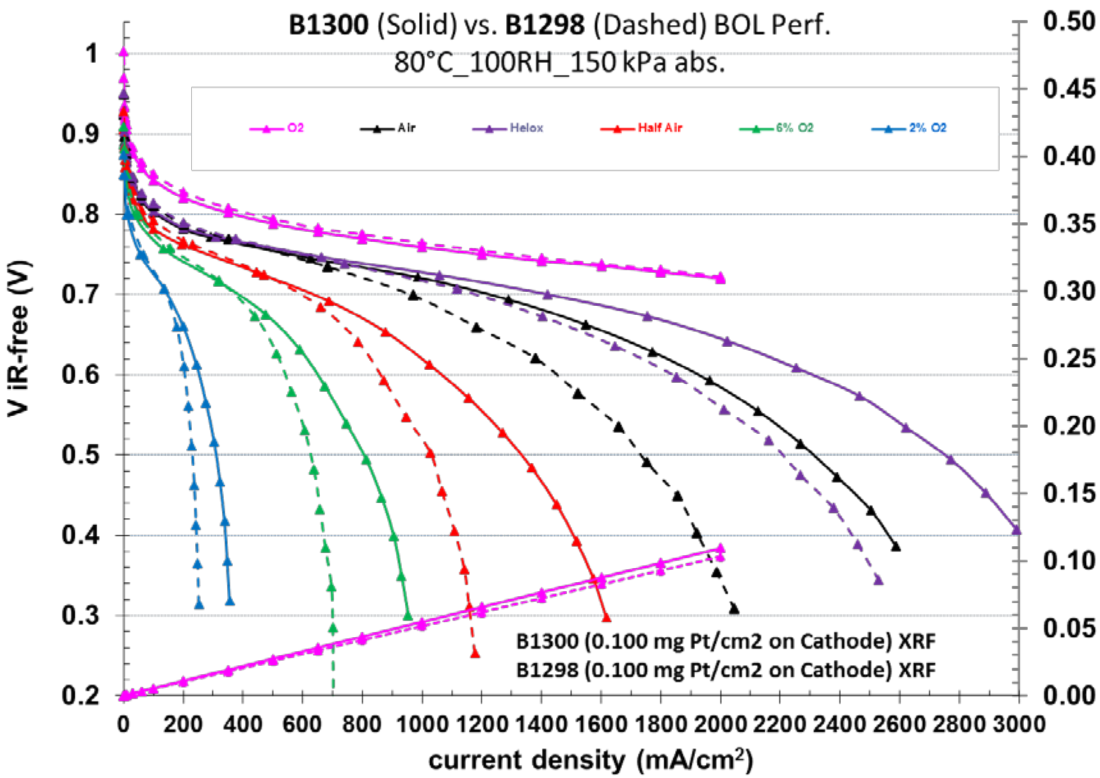
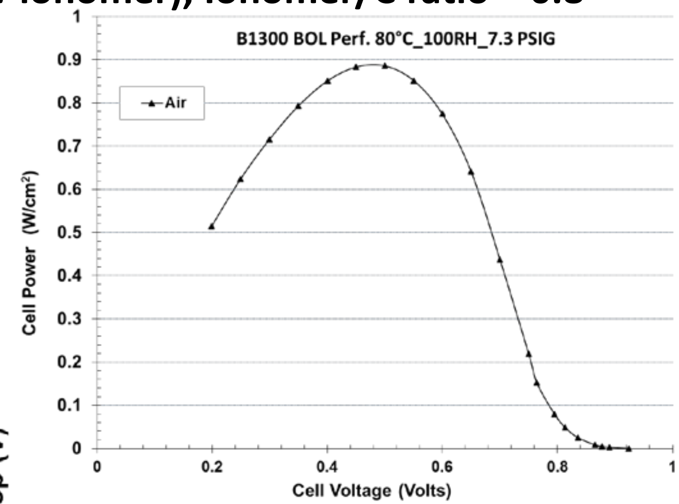
Ion Power

UTRC Cell Performance with Ion Power MEAs

1) Cell B1298: SGL25BC/ I.P.-MEA /SGL25BC, 12.25-cm^2_SP-triple serpentine, co-flows.
2) Cell B1300: SGL25BC/ I.P.-MEA /UTRC-GDL, 12.25-cm^2_SP-triple serpentine, co-flows.
- Same I.P.-MEA with TEC10V20E catalyst, I.P. ink (1100 EW ionomer), Ionomer/C ratio = 0.8





	B1300 IP MEA	B1298 IP MEA
Pt size & Pt Loading	25 A 0.10 mg (XRF)	
H2-Xover	6.9 mA/cm^2	4.6 mA/cm^2
ECA (m^2/g-Pt)	63	
Mass activity A-mg Pt	0.30	
CI @ 1A_O_2	55 mV	52 mV
H2-Pump	6.0 mOhm	6.2 mOhm

Testing conditions: 80°C_100%RH_150kPa abs

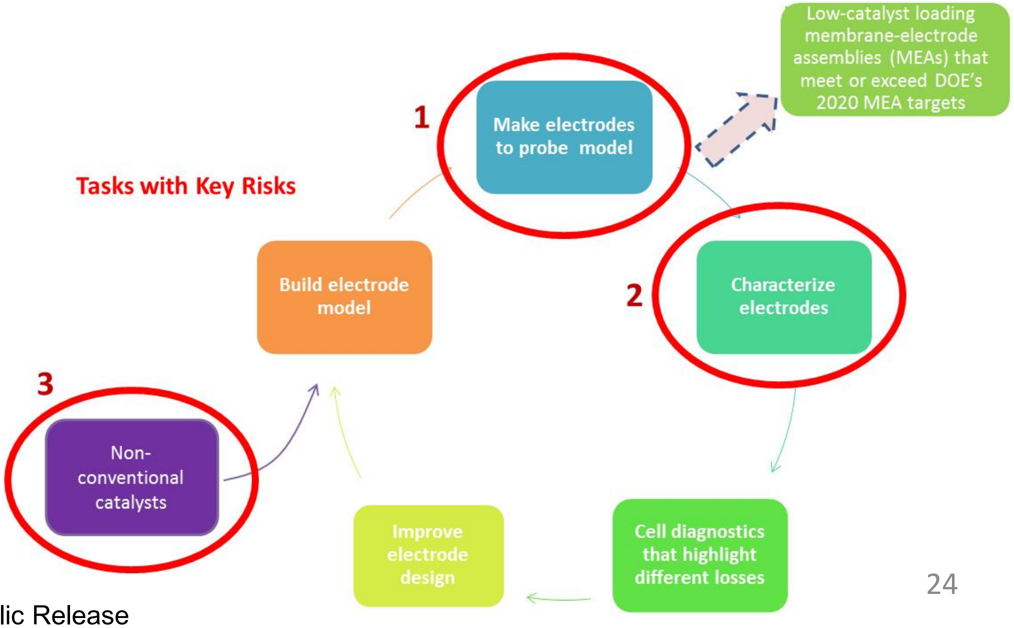
Critical Assumptions & Potential Issues

Key **technical risks** include:

1) Fabrication of CCLs with sufficient differentiation to uniquely identify model parameters and/or sufficiently uniform ULCLs
2) Capability to adequately characterize structures to provide accurate input for the geometric models.
3) Availability of sufficient quantities of alternative catalysts (*e.g.*, thin-film and/or nanoframe structures) to support the fabrication of MEAs by conventional techniques

Team has the capabilities, experience, and expertise to address these issues.

Also have FC PAD Consortia resources that can potentially help mitigate these as well.



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Supplementary Agglomerate Modeling Details

Normal Thiele modulus without spherical diffusion is defined as:

$$\phi_0 = \frac{r_{agg}}{3}\sqrt{\frac{k_c}{D_{O_2N}\epsilon_{agg}^{1.5}}},$$

where, r_{agg}-agglomerate core radius, D_{O_2N} - diffusivity of oxygen in bulk ionomer, ϵ_{agg}- fraction of ionomer in agglomerate, k_c-reaction constant.

The corrected Thiele modulus after adding spherical diffusion is defined as:

$$\phi = \frac{\phi_0}{\sqrt{1 + \varphi\, exp\left(\frac{-\alpha F}{RT}\eta\right)}},$$

where, φ is given as:

$$\varphi = \frac{d_{pt} i_0}{4F D_{O_2N}\epsilon_{agg}^{1.5} c_{O_2}^{ref}},$$

d_{pt} is the diameter of platinum particle.

Conventional effectiveness factor based on corrected Thiele modulus is given as:

$$E_r^0 = \frac{1}{\phi}\left(\frac{1}{\tanh(3\phi)} - \frac{1}{3\phi}\right),$$

The updated effectiveness factor describing diminishing of total current w.r.t. kinetic current at surface is given as:

$$E_r = \frac{E_r^0}{1 + \varphi \exp\left(\frac{-\alpha F}{RT}\eta\right)}$$