Approved for Public Release

High performance PEFC electrode structures

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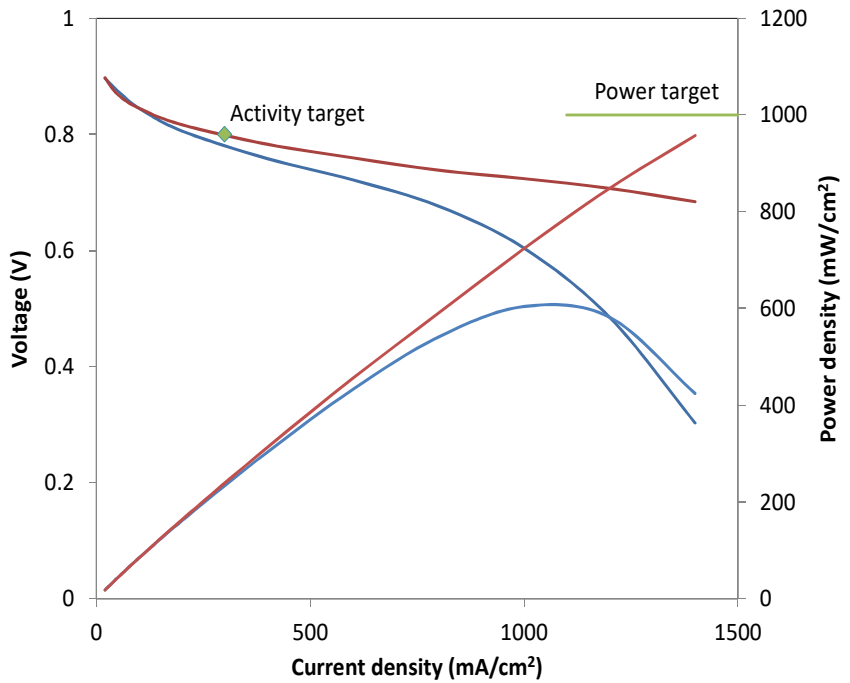
United Technologies Research Center

April 30, 2019



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

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

FC PAD Consortia Project

Project ID: **FC157**

DE-EE0007652

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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-2 End Date: June 30, 2019
Project End Date: June 30, 2020

Budget

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

Total Funds Spent*: $1,571K
Total Funds for BP-1 & 2: $1,991K

*** as of 2/28/2019**

Key Barriers

- Achieve DOE's 2020 Targets for

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

Ion Power

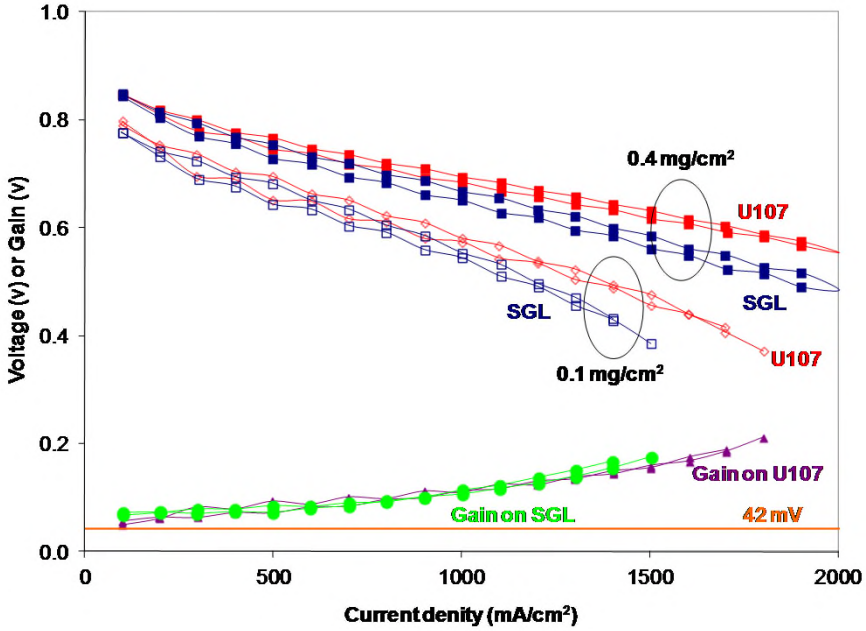
FCPAD FUEL CELL PERFORMANCE AND DURABILITY

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

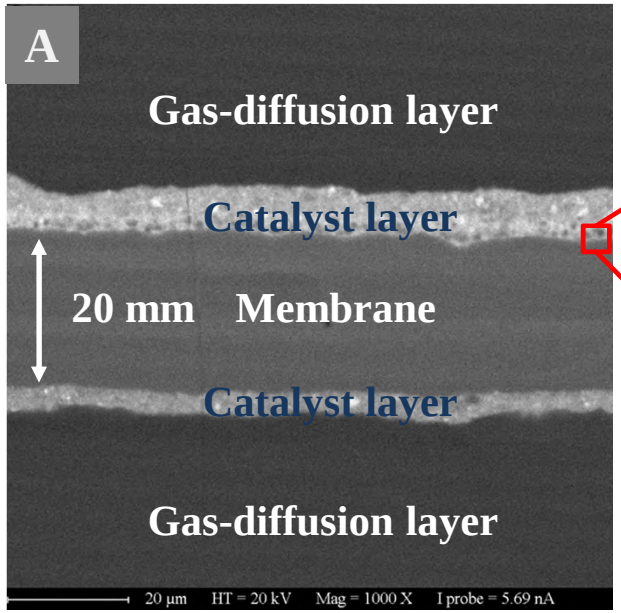


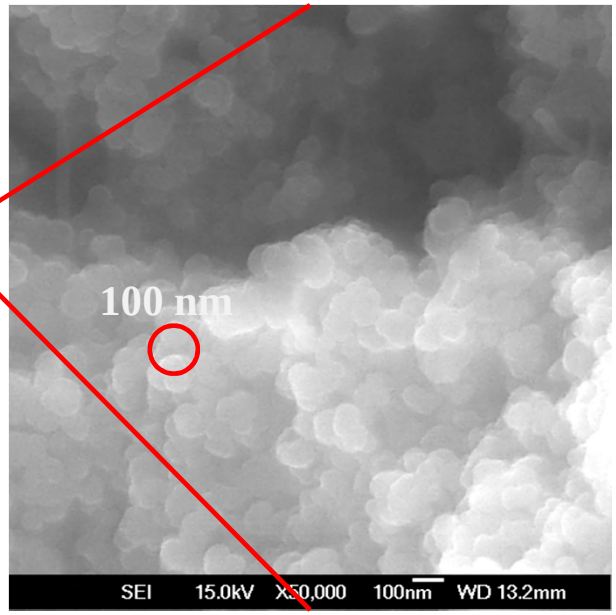
- **Need to reduce transport losses in MEAs with ULCLs**
  - ***First step is to determine actual root-cause mechanisms*** (*e.g.*, not CCL thickness)
  - Fundamental understanding lacking (***previous models did not agree w/ data***)

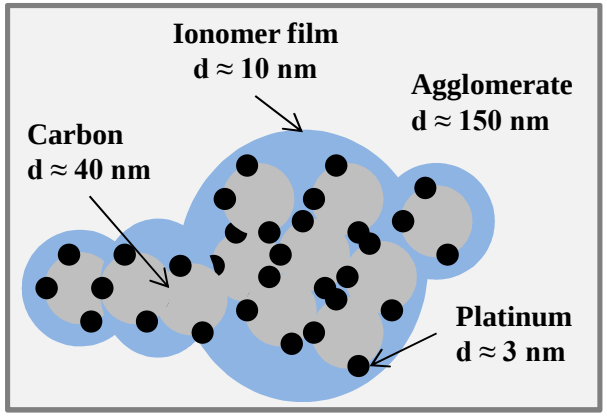
Improved understanding of transport losses in PEMFCs with ULCLs is needed

Approach

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

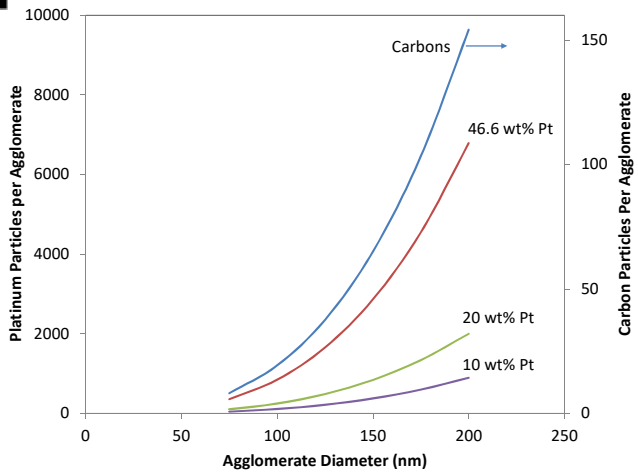






Cathode catalyst layer (CCL)
contains multiple length scales

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

Approach & Collaborations

With key FC-PAD Consortia roles, to date

Ion Power

Durability Testing (ASTs)

Make electrodes to probe model

United Technologies Research Center

Los Alamos NATIONAL LABORATORY

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

University of Arkansas at Little Rock

Improve electrode design

Cell diagnostics that highlight different losses

United Technologies Research Center

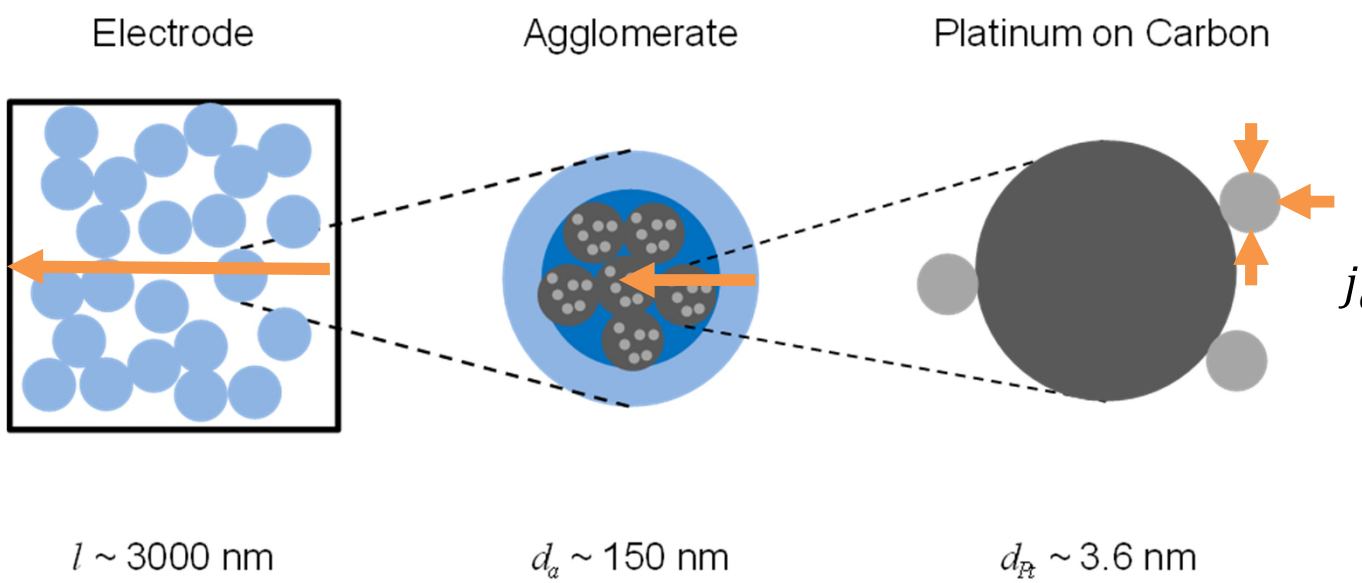
United Technologies Research Center

Iterative process enables improved understanding, CCL model, & cell performance

UTRC's Hierarchical CCL Model

- Our approach is discriminated from previous models by:
  - Explicit, analytical treatment of diffusion at three length scales:
    - Electrode, Agglomerate, and platinum Nanoparticle
  - Experimentally validated agglomerate and platinum sizes
  - Bulk transport properties with reasonable corrections for porosity and tortuosity
  - Model validated with two different datasets last year (see slide 25 in Back-Up)
  - Model was incorporated into LBNL's full-scale MEA model last year (see slide 26)

UTRC CCL model includes transport losses at three different length scales



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

R. M. Darling, "A Hierarchical Model for Oxygen Transport in Agglomerates in the Cathode Catalyst Layer of a Polymer Electrolyte Fuel Cell," *JES*, **165** (2018) F571

CCL Models of Transport Resistance

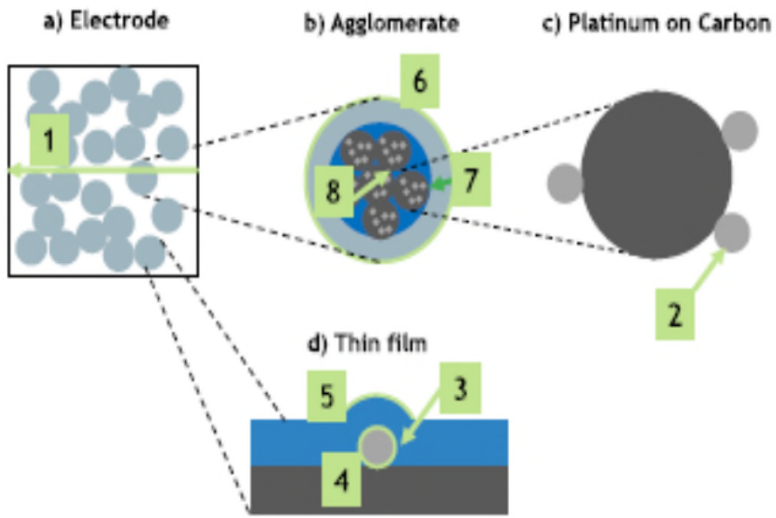


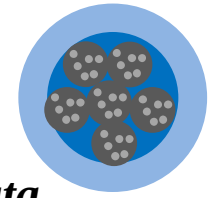
Figure 3. Schematic depictions of the various transport resistances at the (a) electrode, (b) agglomerate, (c) platinum, and (d) thin-film scales. The agglomerate and thin-film idealizations represent alternative descriptions of the fine structure of the catalyst layer.

Case	Transport through
1	Through electrode thickness
2	To isolated catalyst nanoparticles
3	Diffusion through thin ionomer film
4	Adsorption onto Pt from ionomer
5	Dissolution, primary carbon particles
6	Dissolution, agglomerates
7	Diffusion in film around agglomerates
8	Diffusion inside agglomerates
9	Agglomerate core + shell
10	Agglomerate core + shell + nanoscale

- Eight different single-effect models (labeled in figure)
- Two different multi-effect models:
  - Agglomerate core + shell = 8 + 7
  - Agglomerate core + shell + nanoscale = 8 + 7 + 2

R. M. Darling, "A Comparison of Models for Transport Resistance in Fuel-Cell Catalyst Layers," *JES*, **165**, F1331 (2018)

Model Comparison Summary



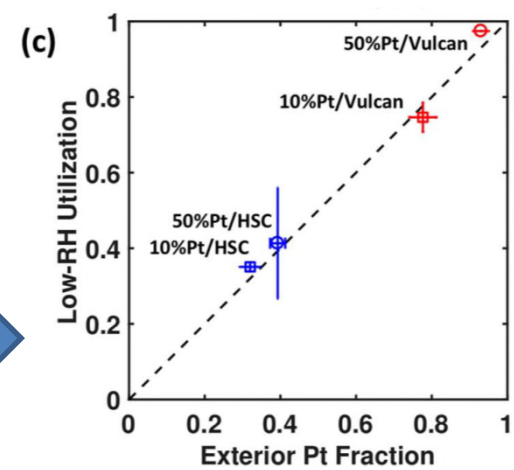
Including nanoparticle + core + shell diffusion is key to matching experimental data

Table IV. Qualitative comparisons of model to experiment.

Case	How does R_{Pt} respond to increases in:	L_{Pt}	ω	γ	U-V	Match	R_{Pt}
-	Experiment	↔	↑	↑	↔	-	12
1	Through electrode thickness	↑	↓	↑	↓	×	2.3
2	To isolated catalyst nanoparticles	↔	↔	↔	↔	×	2.2
3	Diffusion through thin ionomer film	↔	↓	↑	↔	×	0.76
4	Adsorption onto Pt from ionomer	↔	↔	↔	↔	×	12.0
5	Dissolution, primary carbon particles	↔	↑	↔	↔	×	0.04
6	Dissolution, agglomerates	↔	↑	↓	↔	×	0.16
7	Diffusion in film around agglomerates	↔	↑	↑	↔	√	4.6
8	Diffusion inside agglomerates	↔	↑	↔	↓	×	0.02
9	Agglomerate core + shell	↔	↑	↑	↔	√	1.2
10	Agglomerate core + shell + nanoscale	↔	↑	↑	↔	√	15.0

- Most common models do not qualitatively match experimentally observed trends with loading, platinum mass fraction, ionomer to carbon ratio, and voltage
- Only one single-effect model, thick film around empty core, gives qualitative match
  - However, ECA(RH) behavior expected for this construct does not seem to reconcile with data

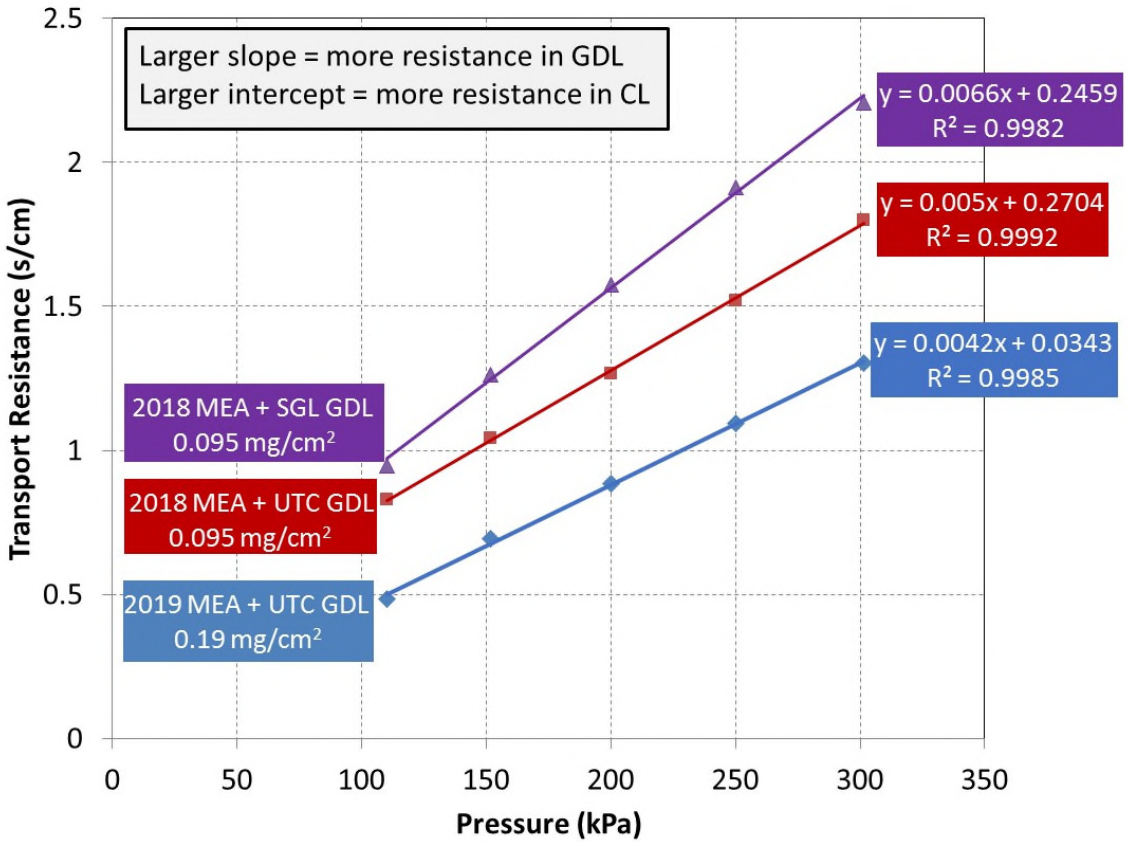
R. M. Darling, *JES*, **165**, F1331 (2018)



Padgett, *et. al.*, *JES*, **165** (2018) F173

Improved MEA Performance

Key changes recommended by hierarchal CCL Model:
1) Lower EW, 2) slight increase in I/C, and 3) smaller agglomerates.

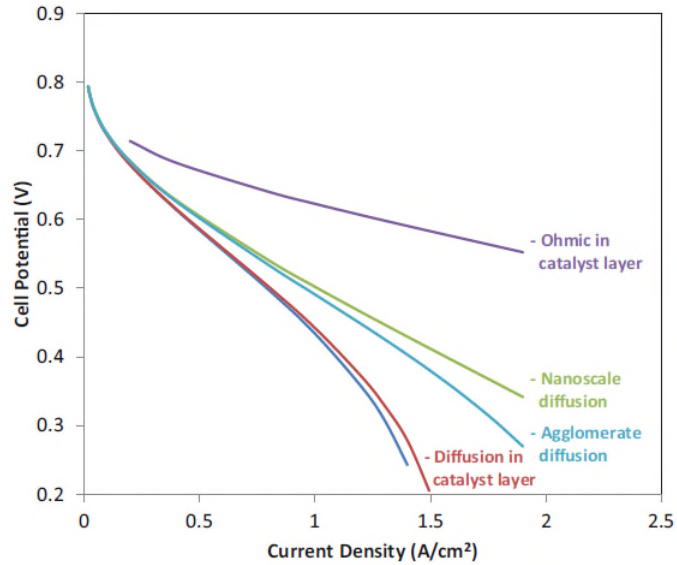


Best reported by G.M. is $R_{T,CL} \approx 0.25$ s/cm (pressure-independent value) at 0.1 mg/cm^2 Pt [S. Kumaraguru, FC-156, AMR (2018) slide 17], and $R_{T,CL} \approx 0.2$ s/cm at 0.2 mg/cm^2 Pt [Owejan, *et.al.*, *JES*, **160** (2013) F824]

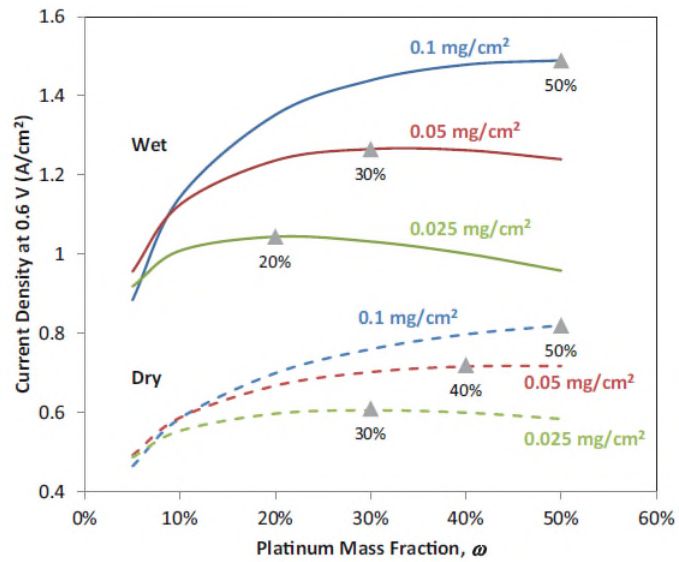
Model Summary

Incorporating oxygen transport at multiple length scales is key to matching experimental data

- Model also includes ohmic losses and both kinetic and charge-transfer effects
- Model correctly predicts observed trends with: Pt loading, Pt mass fraction, & *RH*
- Ohmic losses scale with electrode thickness
- O_2-transport resistance is significant at all 3 scales: nanoparticle, agglomerate, & electrode
- Model can be used to project optimal CCL configurations; one example shown here:
  - Optimal Pt mass fraction of a Pt/C catalyst decreases as total Pt loading is reduced
    - Larger ohmic loss due to thicker electrode is offset by improvement in intra-agglomerate oxygen transport



Predicted sources of overpotential in a CCL with 0.025 mg/cm^2 and 50 wt.% Pt.



Predicted current densities at 0.6 V *vs.* Pt mass fraction at wet (100% *RH*) and dry (65% *RH*).

R. M. Darling, "Modeling Air Electrodes with low Platinum Loading," *JES*, **166** (2018) F3058.

Agglomerate Size is a key CCL parameter

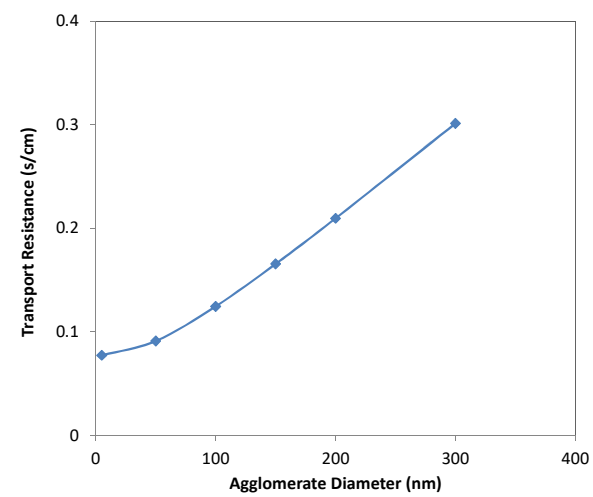
- Determining agglomerate size is very important to support modeling
  - Agglomerate diameters in PEFC models have range from 100 to 10,000 nm!
  - ***Reconciling results obtained via different characterization techniques is necessary***

Some methods for determining agglomerate size:

- SEM – difficult to interpret images of coated agglomerates in catalyst layer, images of isolated carbon agglomerate more amenable to analysis
- Microprobe (Pt) analysis of catalyst layers with Pt/C catalyst diluted by carbon
- BET – surface area from N_2 adsorption on coated agglomerates should return diameter if ionomer coverage is complete. Sensitivity looks poor at expected agglomerate diameters.
- Porosimetry – an older less commonly encountered analysis of breakthrough pressures in beds of spheres can be used determine agglomerate diameter if porosity is known.

Technique	Particles	Diameter (nm)	BET (m^2/g_C)	Source
Electron microscopy of colloidal carbon aggregates	**79**	149	34	Medalia (summary in Kinoshita)
BET of ionomer covered agglomerates	200	204	**25**	Soboleva
Microprobe of Pt covered C in diluted catalyst layer	56	**133**	38	Owejan, GM
Mercury intrusion of catalyst layer, assuming 60% porosity	36	**115**	44	Yu + Carter, GM
Mercury intrusion of catalyst layer, assuming 42% porosity	330	**241**	21	Yu + Carter, GM

Red = measured value



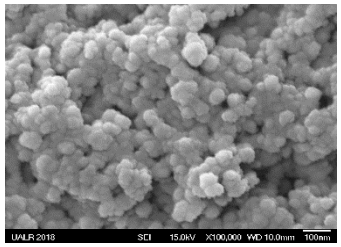
Technical Progress: Non-Conventional Catalysts

Nanocolumnar Pt Thin Film Electrocatalyst

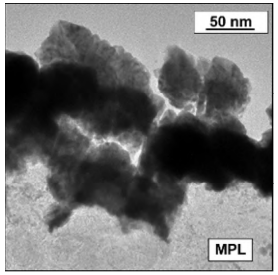
Tansel Karabacak's Group, University of Arkansas at Little Rock, collaboration with LANL, ORNL, and ANL

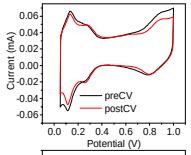
- Nanocolumnar Pt thin films were deposited on an MPL-like surface composed of carbon particles in order to mimic the catalyst coated gas diffusion layer (gas diffusion electrode, GDE) in a MEA. Benchtop CV and RDE measurements were performed.
- With this approach, catalyst performance obtained by benchtop tests can be more accurately related to MEA results.
- MEA tests are currently under progress at LANL.

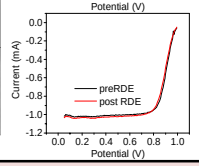
Conventional dense Pt thin film



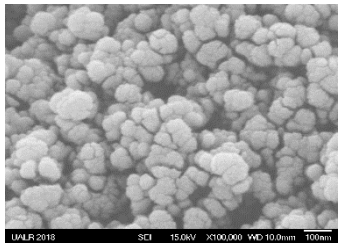
- Normal angle deposition
- Densely packed fibrous structure
- Weight loading ~0.1 mg_{Pt}/cm^2



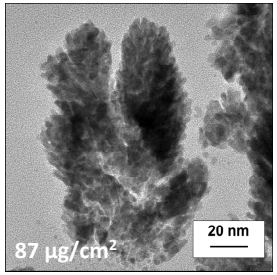


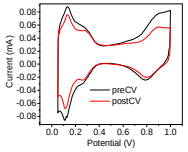


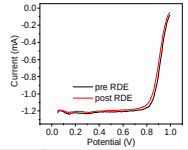
Nanocolumnar Pt thin film



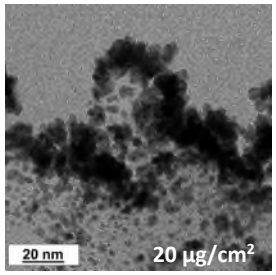
- High pressure sputtering
- Cauliflower-like columnar structure
- Weight loading ~0.1 mg_{Pt}/cm^2

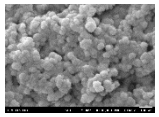




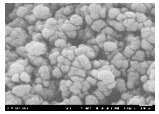


Ultra low loadings: Isolated nanocolumns





Sputtering pressure increase



Pt loading (μg/cm²)	Pressure (mbar)	ECSA (m²/g)		SA (μA/cm²)		MA (A/mg)	
		pre	*post*	*pre*	*post*	*pre*	*post*
101	3.71×10^{-3}	10	9	639	555	0.06	0.05
103	1.13×10^{-2}	12	9	666	565	0.08	0.05
107	1.57×10^{-2}	14	10	517	508	0.07	0.05
104	2.00×10^{-2}	15	10	587	564	0.09	0.06
100	2.97×10^{-2}	15	10	766	688	0.11	0.07
87	3.92×10^{-2}	19	14	667	593	0.13	0.08
52	3.92×10^{-2}	22	15	528	484	0.12	0.07
21	**3.92×10^{-2}**	**32**	**25**	**822**	**617**	**0.26**	**0.15**
11	**3.92×10^{-2}**	**42**	**33**	**646**	**607**	**0.27**	**0.20**

*pre = initial
*post = after 3000 cycles of stability test

Higher ECSA, SA, and MA at lower Pt loadings

CCL Models with Thin-Film (TF) Catalysts

Summary of key figures of merit for five frameworks

Description	Water film	Water filled	Ionomer filled	Ionomer film	Ionomer, flooded
Effectiveness at 0.65 V	0.98	0.073	0.091	0.98	0.05
Thiele Modulus	0.02	13.7	11	0.02	17.7
Resistance (Ω-cm2)	17.8	17.8	0.1	0.55	0.55

$$\textit{Effectiveness Factor} = \frac{\textit{Current density limited by transport \& kinetics}}{\textit{Current density limited by kinetics only}}$$

Key model inputs:

- **Pt loading = 0.1 mg/cm^2**
- D_{O2} **= 5.7e-7 cm^2/s**
- k_{ORR} **= 0.053 cm/s (at 0.65V)**
- $\sigma_{ionomer}$ **= 89 mS/cm**

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Accomplishments & Progress

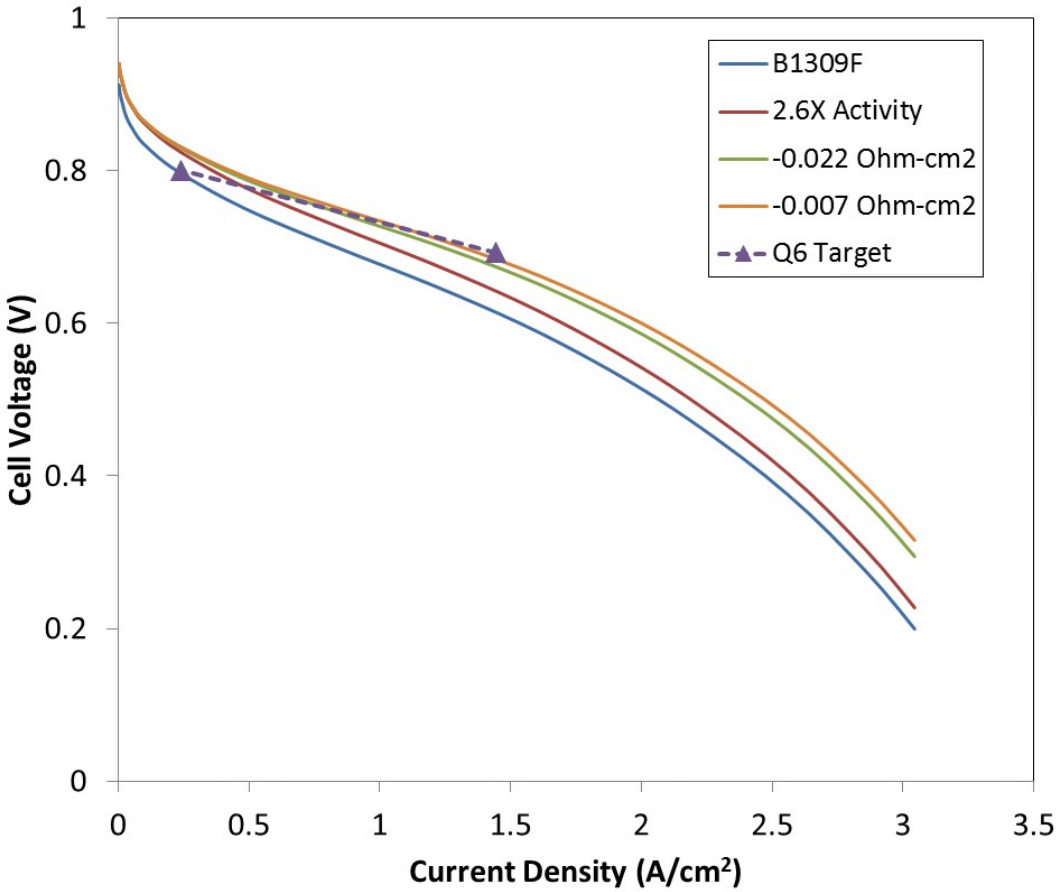
- All Year-1 (BP-1) Milestones were successfully completed by 6/30/2018
- Project that all BP-2 Milestones can be successfully completed by 6/30/2019
  - Project is currently behind schedule on MEA-performance targets
    - MEAs have excellent transport losses (as shown in slide 10)
    - Need to improve other aspects (Membrane, Pt alloys)
  - Subsequent slide shows projected path to meeting MEA-performance target

Milestone	Task Title	Milestone Description (w/ additional details)	Status
Q5	Novel MEAs w/ UALR's thin-film (TF) catalysts	Successfully fabricate MEAs (with 12.5-cm^2 active area) using TF catalysts, which have been tested by both LANL and UTRC.	**100%**
Q6	C-supported MEA fabrication & performance	Meet DOE's 2020 MEA performance targets with high stoichiometric flow rates, *e.g.*, $\geq$ 1 W/cm^2 at rated power	**80%**
Q7	Model development	Initial microstructural electrode model for CCL with thin-film catalysts complete	**100%**
Q8 G/No-Go	Model validation & MEA performance	New CCL model successfully validated with SOA MEA pol curve data; AND MEA performance $\geq$ 240 mA/cm^2 at 0.8 V and $\geq$ 905 mW/cm^2 using pol-curve protocol	**100%** and **80%**

Projected Performance Gap Closure

Three key improvements required to meet Q8 Performance Target:

1. Use Pt-alloy catalyst: Activity ratio = **2.6X** (550 *vs.* 210 μA/cm^2 for leached PtCo vs. HSA Pt[A])
2. Close HFR gap between UTC and GM cell (with Pt/V & 18 μm membrane[B]) = **24 mW-cm^2**
3. Additional **7 mW-cm^2** gain by using 10-μm membrane with 950 EW (*vs.* 18-μm membrane)



A. H. Gasteiger, *et.al.*, *Applied Catalysts B: Environmental,* **56** (2005) 9-35
B. Owejan, *et.al.*, *JES*, **160** (2013) F824-F833.

United Technologies Research Center

Collaboration & Coordination Summary

UTRC continued our 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 continue to test MEAs fabricated from **UALR** catalyst (and "½-MEAs" provided by ***I.P.***)

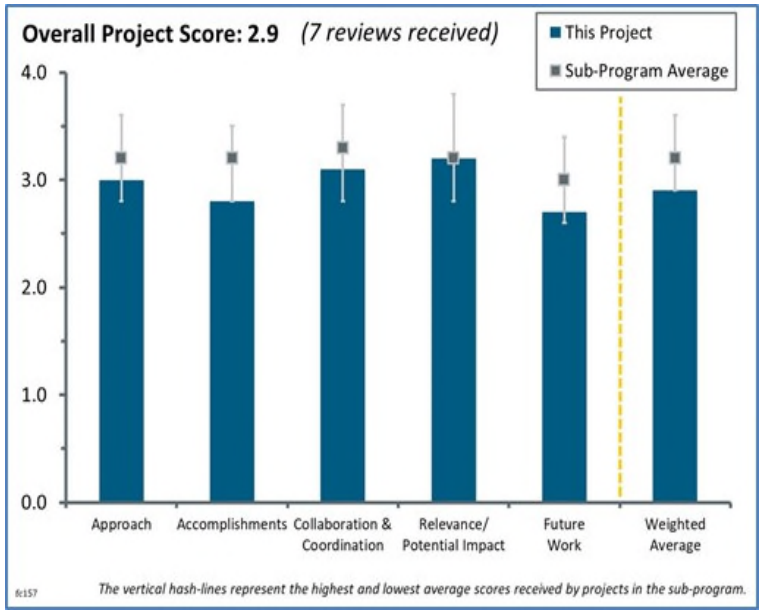
Continued to expand our collaborations with FC PAD Consortia

- Continued CCL characterization in a collaboration with:
  - **LANL** (*e.g.*, SEM, XRF, TGA, MIP, and BET)
  - **ORNL** (*e.g.*, TEM of MEAs, CCLs, & catalyst)
- Continuing collaborate with **LBNL** on modeling work
  - Treating different carbon supports for Pt/C model
- Advice & characterization of UALR's TF catalysts from **ANL**
  - Plan to use nano-CT capabilities going forward

6 significant collaboration partners on this project, to date

Reviewer's Comments and Brief Responses

- The most critical Comments, and Scores, were on:
  - Accomplishments & Future Work
  - Closer to average scores in the other categories



Comments expressed by multiple reviewers:

- Concerns about the lack of model details making it "difficult to judge," and doubts about whether the model will have a significant impact on development of CCLs

The team has now published details of the Hierarchal Model, as well as a detailed comparison of the various CCL models in the literature. Performance improvements have been realized by the team using the model as guidance.

- Doubts raised about the team being able to substantially vary agglomerate size

Agreed, this appears to be challenging, and the team does not plan to explore a variety catalyst ink solvents and mixing methods, which has already been done.

- There was a lot of skepticism about the thin-film (TF) catalyst work included here

The team has successfully fabricated and tested MEAs using UALR's TF catalysts. UALR can provide the team with variations of TF catalysts, which can be used to study and develop new CCL architectures that utilize TF catalysts.

- Multiple suggestions to use other available catalysts and/or alternative structures

Agreed, the team plans to collaborate more with others working on alternative CCLs

Proposed Future Work

***Major goals for the next year of this project* (beyond BP-2 G/NG):**

- Continue to develop improved understanding of transport losses on CCLs
  - Make improvements to both Pt/C & Thin-Film Catalyst models
- Continue to work on resolving results from multiple CCL characterization methods
  - Focus primarily on porosity and agglomerate-size distributions
- Develop modeling collaborations with others working on alternative CCL architectures, *e.g.*, Spendelow (LANL) and Pintauro (Vanderbilt University)
- More work on making, testing, and modeling other alternative CCL architectures

Milestone	Task Title	Milestone Description (w/ additional details)
Q9		Validated microstructural model for MEA with alternative catalysts
Q10	MEA Performance (w/ conventional catalyst)	Meet DOE's 2020 performance targets with C-supported catalyst
Q11	MEA Performance (w/ alternative catalyst)	Meet DOE's 2020 performance with MEA with alternative catalysts and *high stoichiometric flow rates*
Q12 G/No-Go	MEA performance (w/ alternative catalyst)	Meet DOE's 2020 performance targets with MEA with alternative catalysts

Major focus will be on developing and demonstrating high performance MEAs

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

Summary

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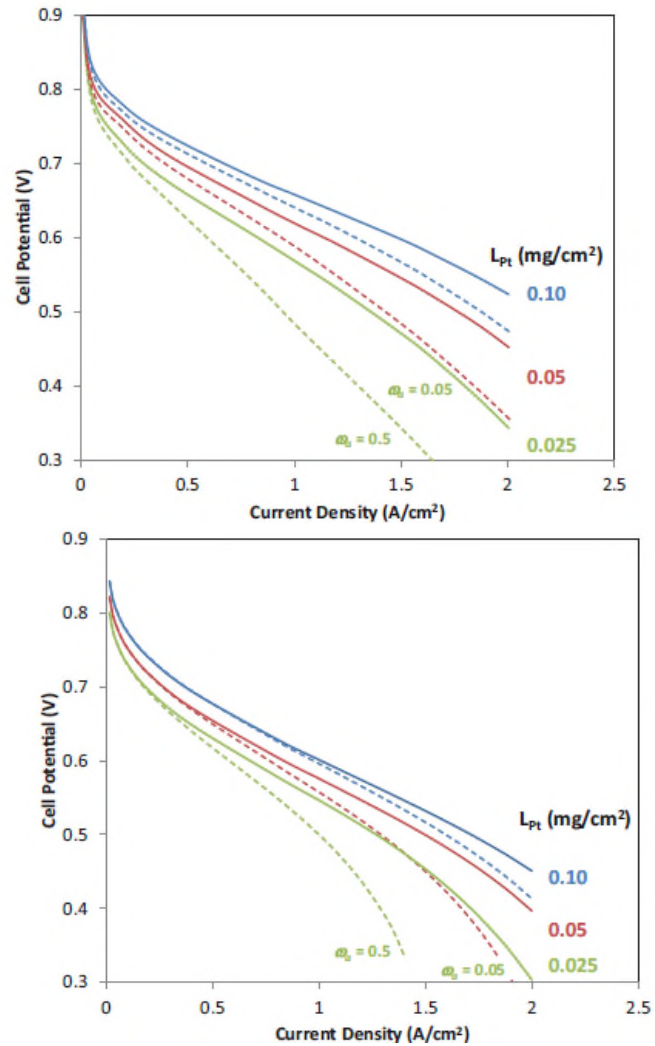
- Major barrier to meeting 2020 MEA Targets are mass-transport losses in cathode-catalyst layers (CCLs)
- UTRC's Hierarchal CCL Model incorporates transport at multiple length scales and has been validated with multiple data sets
- ❖ Comparison of various CCL Models shows that Hierarchal Model is only one that accurately predicts observed trends of CCLs with ultra-low Pt loadings
- ❖ Model predictions have been used to develop advanced MEAs with reduced transport losses
- ❖ Realistic pathway to achieving project's BP-2 performance targets has been identified
- ❖ Path to potentially reconcile key CCL parameters obtained via different characterization techniques has been formulated and is being pursued with FC PAD
- ❖ Project has begun to focus more on CCLs with thin-film (TF) catalysts; modeling multiple frameworks
- ❖ The team has also begun to collaborate with others that are developing alternative CCL structures



Pol curves on air for 3 Pt loadings with 2 Pt mass fractions for each. Top plot is experimental data [Owejan, *JES* **160** (2013) F824]; bottom is model predictions.

Most efficient path to MEAs with improved transport is accurate CCL model

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University of Arkansas at Little Rock

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- Busra Ergul
- Mahbuba Begum

FCPAD Fuel Cell Performance and Durability

Los Alamos National Laboratory

- Rod Borup
- Natalia Macauley
- Sarah Stariha
- Mike Workman

Berkeley Lab

- Adam Weber
- Lalit Pant
- Sarah Berlinger
- Anamika Chowdhury

Oak Ridge National Laboratory

- Karren More

Argonne National Laboratory

- Nancy Kariuki
- Debbie J. Myers

TECHNICAL BACK-UP SLIDES

Publications & Presentations (since last AMR)

- R. M. Darling, "A Hierarchical Model for Oxygen Transport in Agglomerates in the Cathode Catalyst Layer of a Polymer Electrolyte Fuel Cell," *JES*, **165** (2018) F571.
- R. M. Darling, "A Comparison of Models for Transport Resistance in Fuel-Cell Catalyst Layers," *JES*, **165** (2018) F1331.
- L. M. Pant, Z. Yang, M. L. Perry, and A. Z. Weber, "Development of a Simple and Rapid Diagnostic Method for Polymer-Electrolyte Fuel Cells," *JES*, **165** (2018) F3007.
  - This work was done as part of LBNL's FC PAD project, but was *not* part of UTRC's FC PAD project
- R. M. Darling, "Modeling Air Electrodes with low Platinum Loading," *JES*, **166** (2018) F3058.

Presentations

August 2018: "Use of Modeling for Diagnostics of Polymer Electrolyte Fuel Cells"

- Presented by L. M. Pant **(LBNL)** at ISE Meeting (Providence, R.I.)
- Co-authors: M. L. Perry (**UTRC**) and Adam Z. Weber (**LBNL**)

October 2018: "Platinum Nanorod Arrays as ORR Electrocatalyst for Polymer Electrolyte Membrane Fuel Cells"

- Presented by M. Begum **(UALR)** at Fall ECS and AiMES Meeting (Cancun, Mexico)
- Co-authors: B. Ergul & T. Karabacak (**UALR**), Nancy Kariuki & Debbie J. Myers (**ANL**), & M. L. Perry (**UTRC**)

October 2018: "A Model-Based Approach to Improved Understanding & Mitigation of Transport Losses in PEFCs"

- Presented by M. L. Perry (**UTRC**) at Fall ECS and AiMES Meeting (Cancun, Mexico)
- Co-authors: Z. Yang & R. M. Darling (**UTRC**)

September 2018: "High Performance PEFC Electrode Structures"

- Presented by R. M. Darling (**UTRC**) at FCTT Meeting (Detroit, MI)
- Co-authors: Z. Yang & M. L. Perry (**UTRC**)

November 2018: Platinum Nanorod Arrays as ORR Electrocatalyst for Polymer Electrolyte Membrane Fuel Cells

- Two talks presented by B. Ergul and M. Begum at 2018 American Chemical Society (ACS) Southwest Regional Meeting (Little Rock, AR)
- Co-authors: T. Karabacak (**UALR**)

January 2019: "High Performance PEFC Electrode Structures"

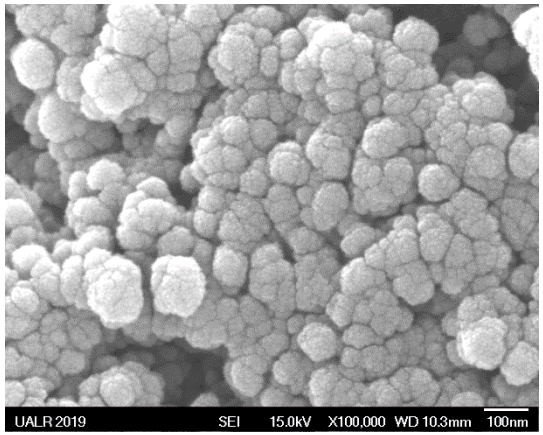
- Presented by M. L. Perry (**UTRC**) during breakout session at FC PAD Consortia Meeting (Santa Fe, NM)
- Co-authors: Z. Yang & R. M. Darling (**UTRC**)

Nanocolumnar Pt-Ni Alloy Thin-Film Electrocatalyst

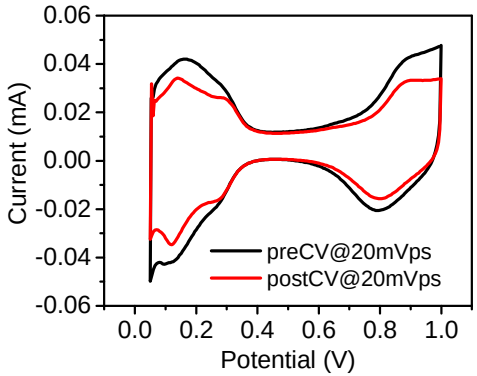
Tansel Karabacak's Group, University of Arkansas at Little Rock

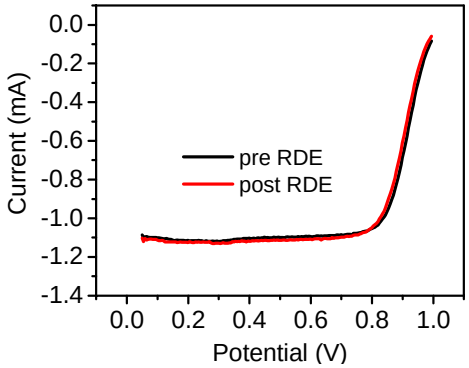
- Nanocolumnar Pt-Ni alloy thin film was deposited on an MPL-like surface composed of carbon particles in order to mimic the catalyst coated gas diffusion layer (gas diffusion electrode, GDE) in a MEA.
- CV and RDE measurements show promising ECSA, SA, and MA performance and also good stability even for a highly Ni-rich composition. MEA tests are in preparation.

Nanocolumnar Pt-Ni alloy thin film



- High pressure sputtering
- Deposited on MPL-like surface
- Cauliflower-like columnar structure
- Pt:Ni ratio is estimated to be 1:13 (Ni rich)

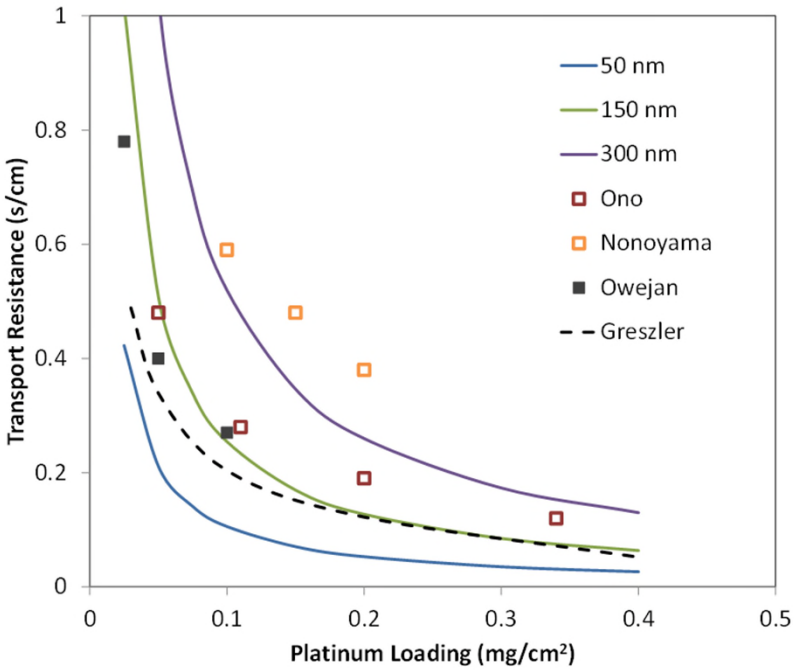


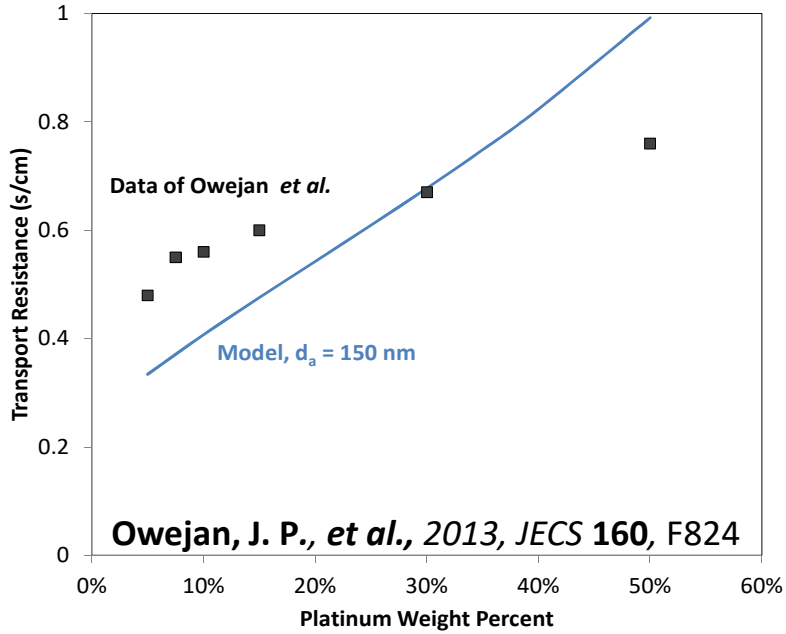


Pt loading (μg/cm²)	Pressure (mbar)	ECSA (m²/g)		SA (μA/cm²)		MA (A/mg)	
		pre	*post*	*pre*	*post*	*pre*	*post*
~15	2.90×10^{-2}	66	51	938	905	0.62	0.46

*pre = initial *post = after 3000 cycles of stability test

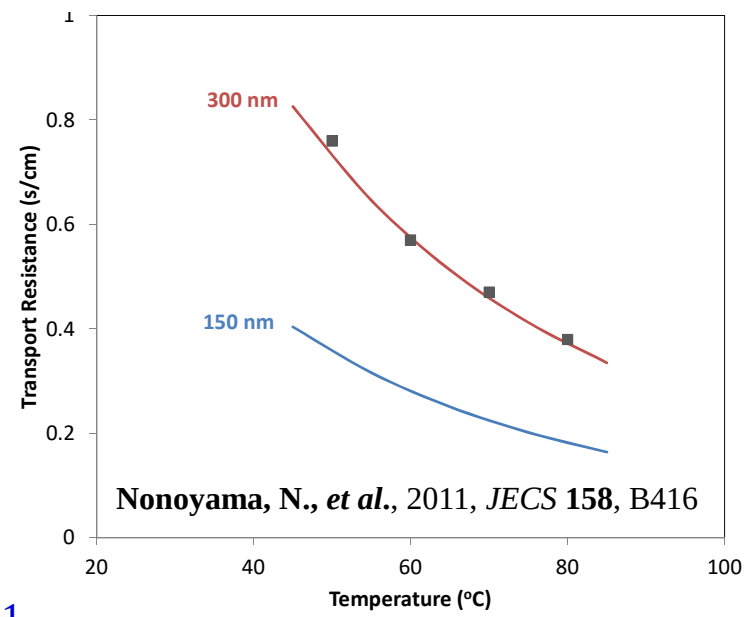
Transport Resistance Results and Model Predictions





Data from:
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.*

- 150 nm curve is close to the result for ***Vulcan carbon*** from GM
- 300 nm curve is close to the result for ***HSA carbon*** from TMC
- 50 nm curve is close to predictions for nanoparticle losses only



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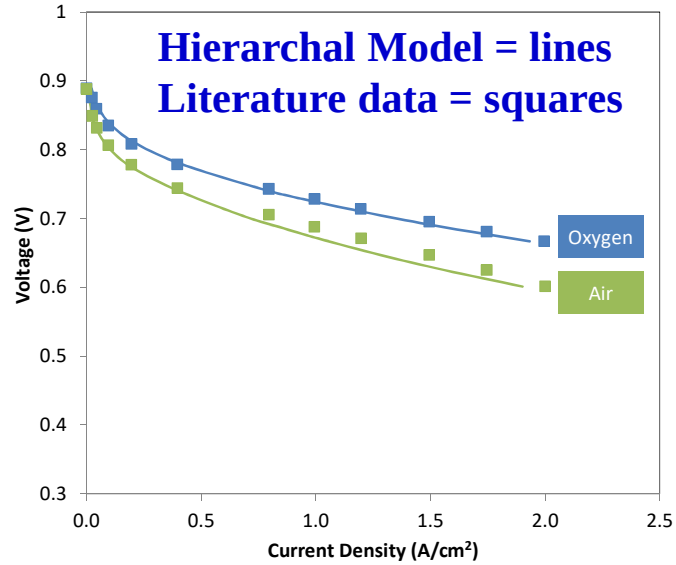
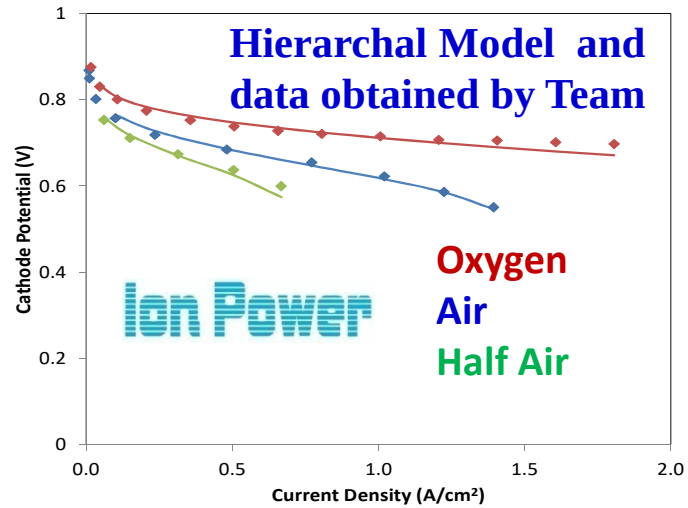
R. M. Darling, *JES*, **165** (2018) F571

UTRC's Hierarchical Model has been validated

Using both Literature and Team's data on MEAs w/ ULCL

- Hierarchal CCL Model incorporates transport at multiple length scales
  - ***Convert CCL projections to pol curves by:***
    - Isolating GDL transport losses
      - Allows calculation of [O_2] at the GDL-CCL interface
    - Isolating membrane resistance losses
      - *In-situ* measurements
  - ***Model has been successfully validated with two data sets***:
    - Data from literature (top graph)
    - Data obtained by team (bottom graph)





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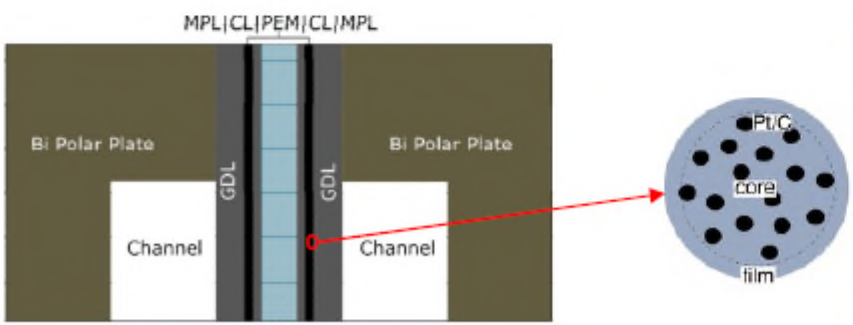
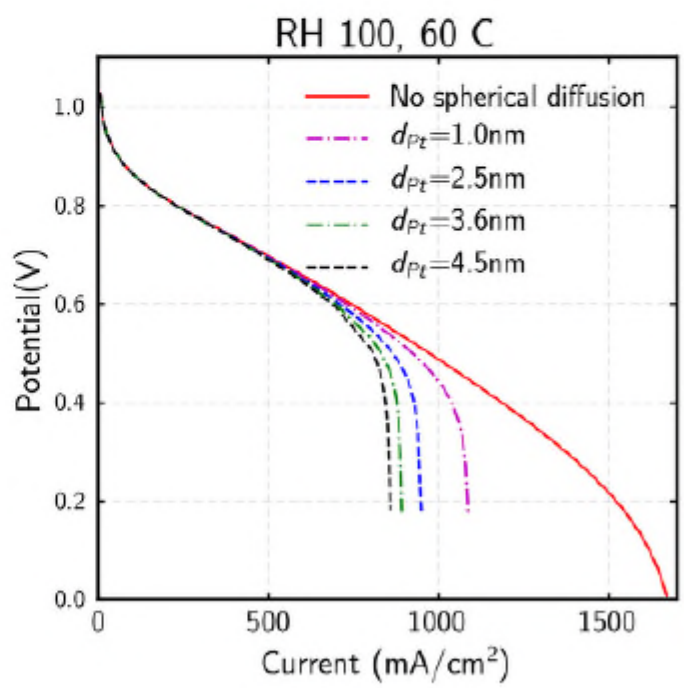
Inclusion of Spherical Diffusion near Pt Particles in MEA Model

- 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