2020 DOE Hydrogen and Fuel Cells Program Review Presentation

DE-EE0008426

Developing novel electrodes with ultralow catalyst loading for high-efficiency hydrogen production in proton exchange membrane electrolyzer cells

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Project ID #TA033

Overview

Timeline

- Project Start Date: 10/01/18
- Project End Date: 11/31/20

Budget

- Total Project Budget: $2,550K
  - Total Recipient Share: $550K
  - Total Federal Share: $2,000K
  - Total DOE Funds Spent*: $1,327K

* As of 02/29/2020

Barriers

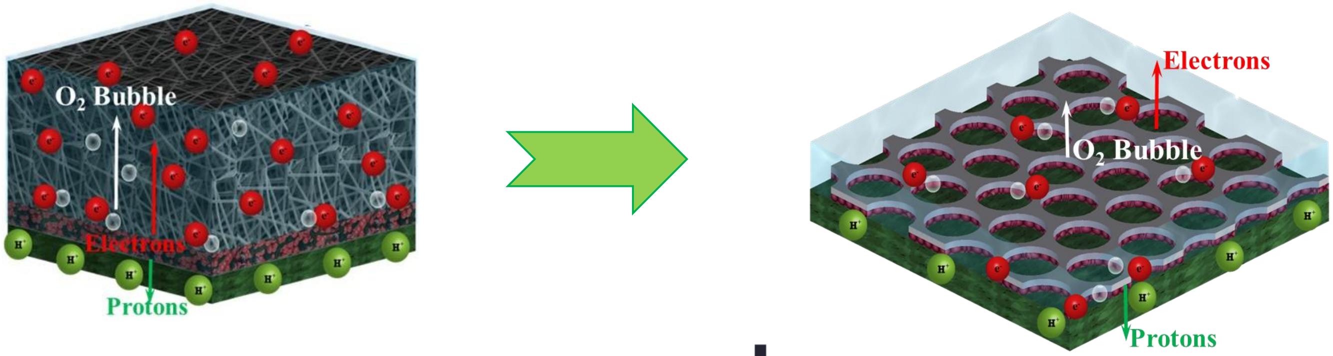
- Capital cost
- Efficiency and durability
- Target: Develop thin engineered liquid/gas diffusion layers (LGDLs) and catalyst-coated LGDLs (CCLGDLs) to support DOE Hydrogen and Fuel Cells Program goals to sustainably produce hydrogen for <$2/kg.

Project Partners

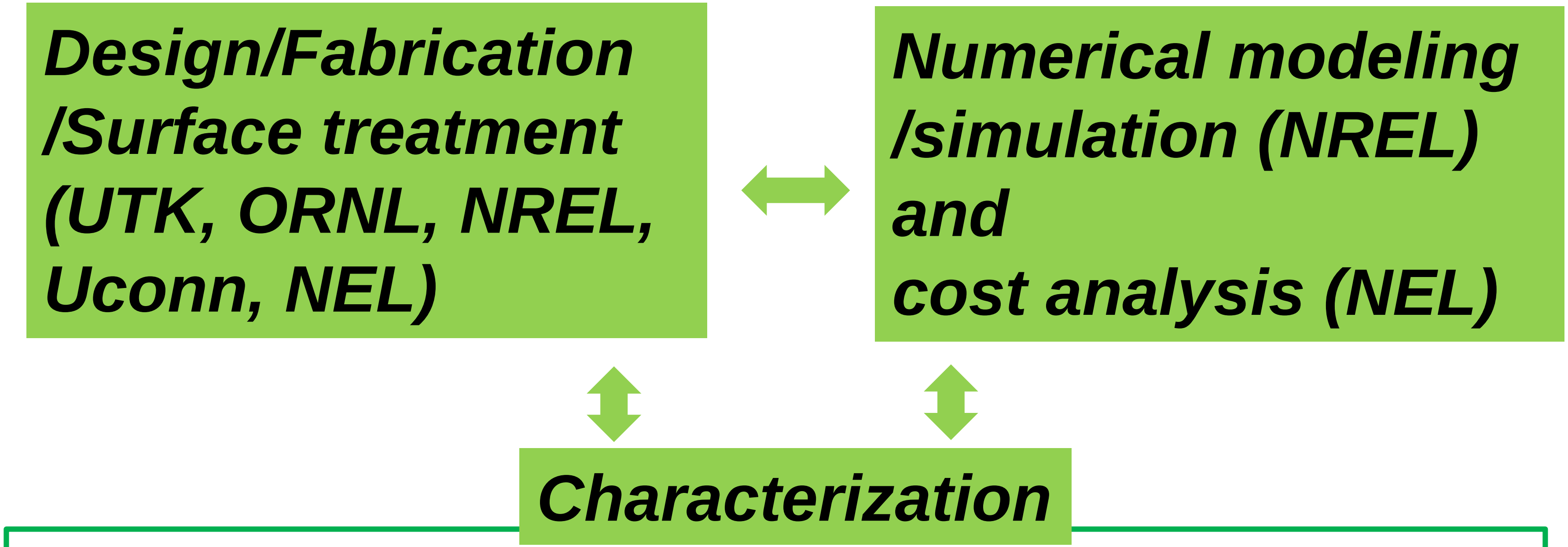
University of Tennessee Knoxville (UTK)
Oak Ridge National Laboratory (ORNL)
National Renewable Energy Laboratory (NREL)
Nel Hydrogen (Nel)
University of Connecticut (UConn)

Relevance

- Objective: Develop thin engineered liquid/gas diffusion layers (LGDLs) and catalyst-coated LGDLs (CCLGDLs) for low-cost and high-efficiency hydrogen production with proton exchange membrane electrolysis cells (PEMECs).
- Goals:
  - Reduce Ti PTL thickness from hundreds of μm to less than 100 μm;
  - Reduce the CL thickness from tens of μm to less than 0.3 μm;
  - Control the pore morphologies;
  - Improve efficiency with developed thin LGDLs vs felt baseline;
  - Increase catalytic mass activities with CCLGDLs vs CCM baseline;
  - Demonstrate excellent durability and mechanical properties of developed LGDL/CCLGDLs.



Approach



Design/Fabrication /Surface treatment (UTK, ORNL, NREL, Uconn, NEL)

Numerical modeling /simulation (NREL) and cost analysis (NEL)

Characterization

- Labscale, benchscale and systemscale in-situ tests (UTK, NREL, NEL)
- Physical ex-situ characterizations (ORNL, UCONN)
- Durability test (NREL)
- Mechanical strength test (NEL)
- Visualizations on reactions/multiphase transport (UTK)
- Current mappings (UTK)

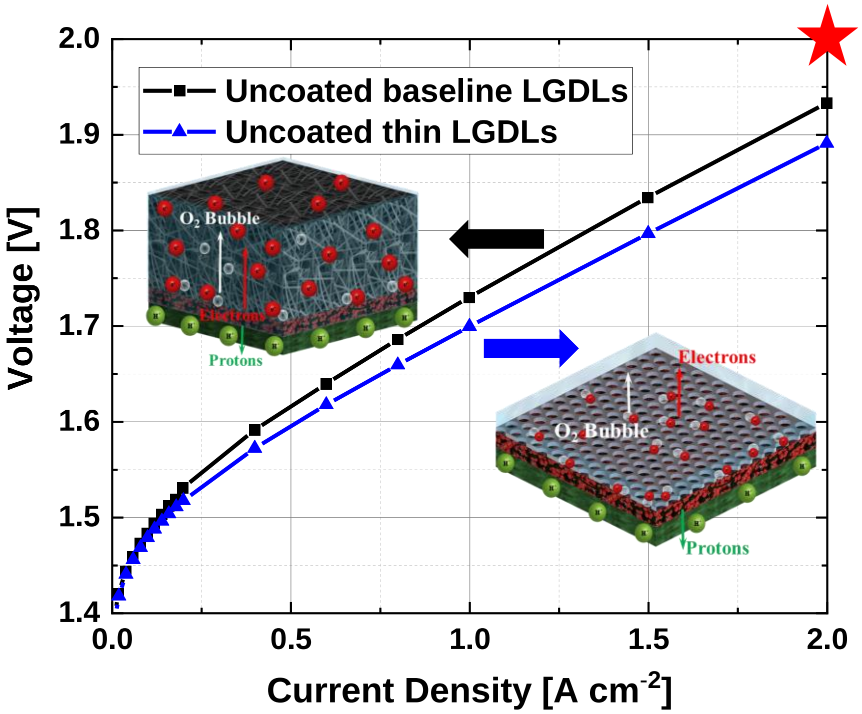
All baseline double-side/single-side CCMs for *in-situ* tests are provided from NEL

Accomplishment highlights: Demonstrate thin LGDL performance of <1.85 V at 2 A/cm^2 with Nafion 117 in labscale, benchscale and systemscale electrolyzer tests

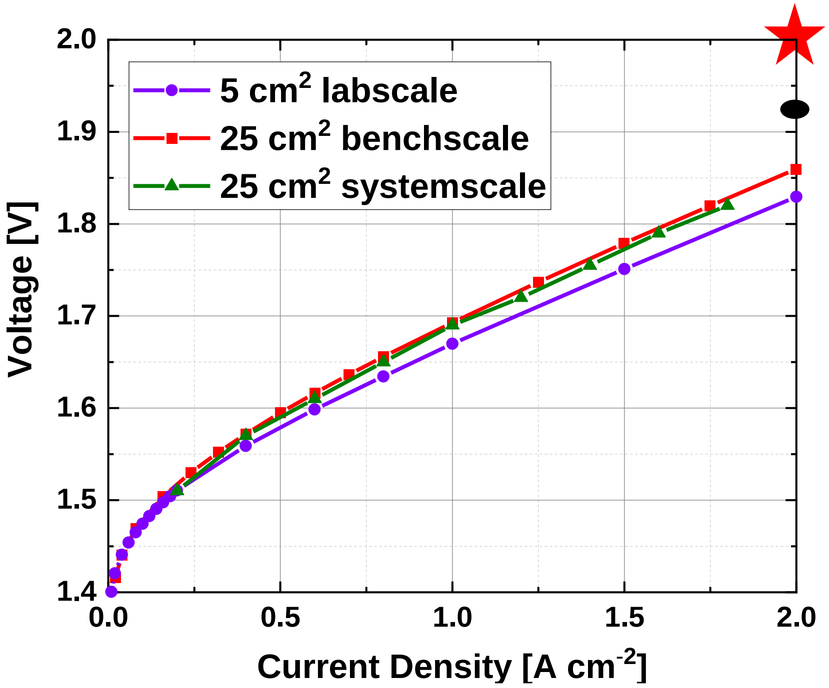
- **LGDLs with different pore morphologies gained 40 mV for uncoated and 80 mV for coated novel LGDL material**
- **Improved performance confirmed for labscale, benchscale and systemscale tests with NEL provided CCMs**

Baseline Ti felt: 1.93 V

Labscale tests with thin LGDL: 1.89 V



Benchscale and systemscale test with *Pt coated* thin LGDL : 1.85 V



OAK RIDGE National Laboratory

NREL NATIONAL RENEWABLE ENERGY LABORATORY

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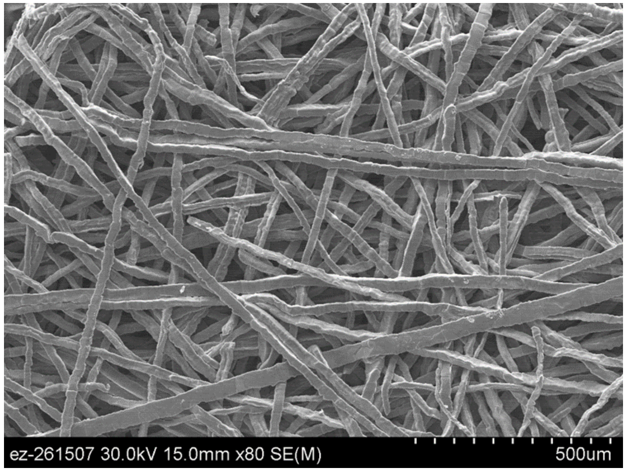
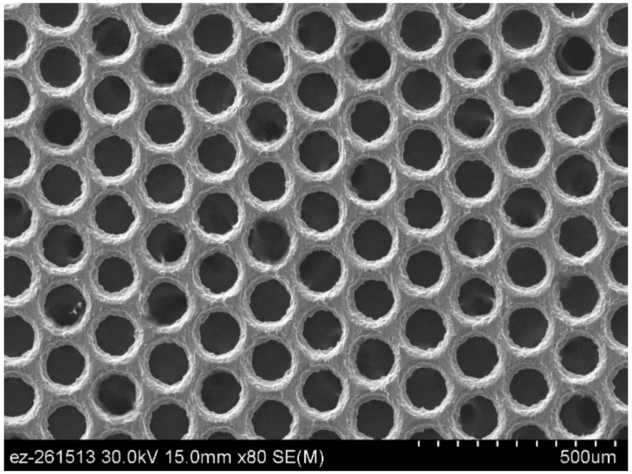
UCONN

Comparison of baseline Ti felt morphology and fully controllable novel thin LGDL properties

Baseline Ti felt



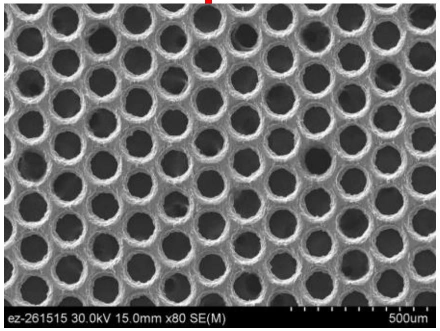
Novel thin LGDL



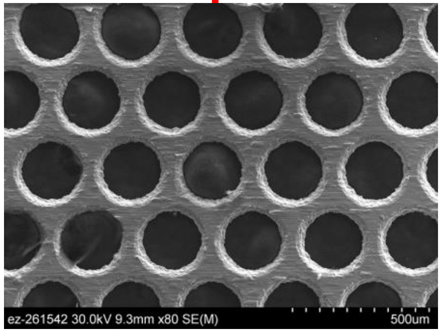
- **Baseline Ti felt:**
  - 350 μm thickness
  - 0.55 porosity
  - Noncoated
  - Uncontrolled pore morphology
- **Thin LGDL:**
  - 50 and 75 μm thickness
  - Porosity well controlled to various values between 0.2 - 0.65
  - Pore size well controlled to various values between 100 – 425 μm
  - Passed mechanical testing based on industrial procedures

Successfully fabricated more than 10 thin LGDLs with systematically varied properties

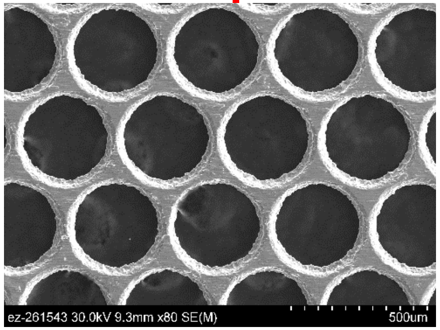
4c2 – 50 µm thick



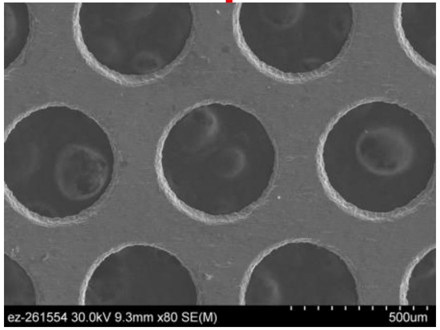
8c4 – 50 µm thick



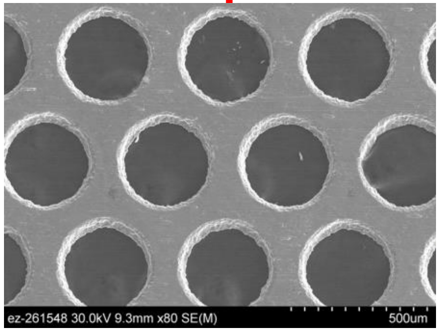
12c3 – 50 µm thick



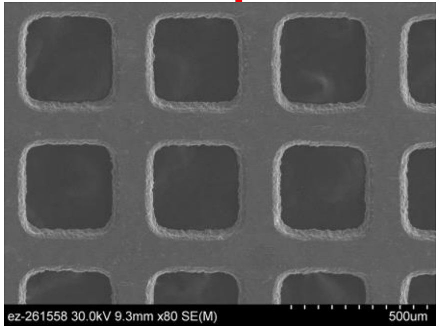
16c8 – 50 µm thick



12c6 – 50 µm thick

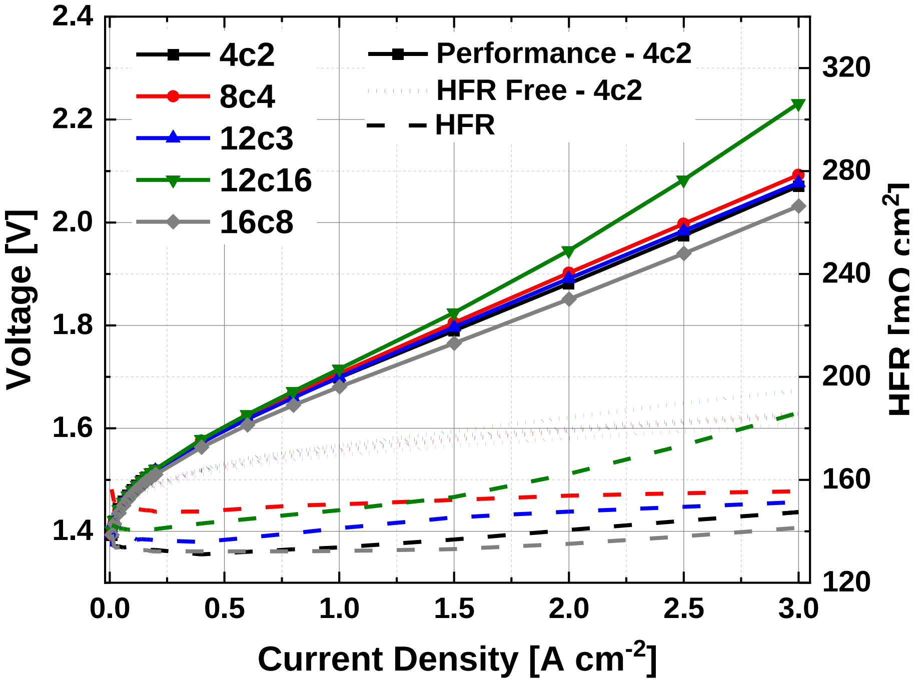


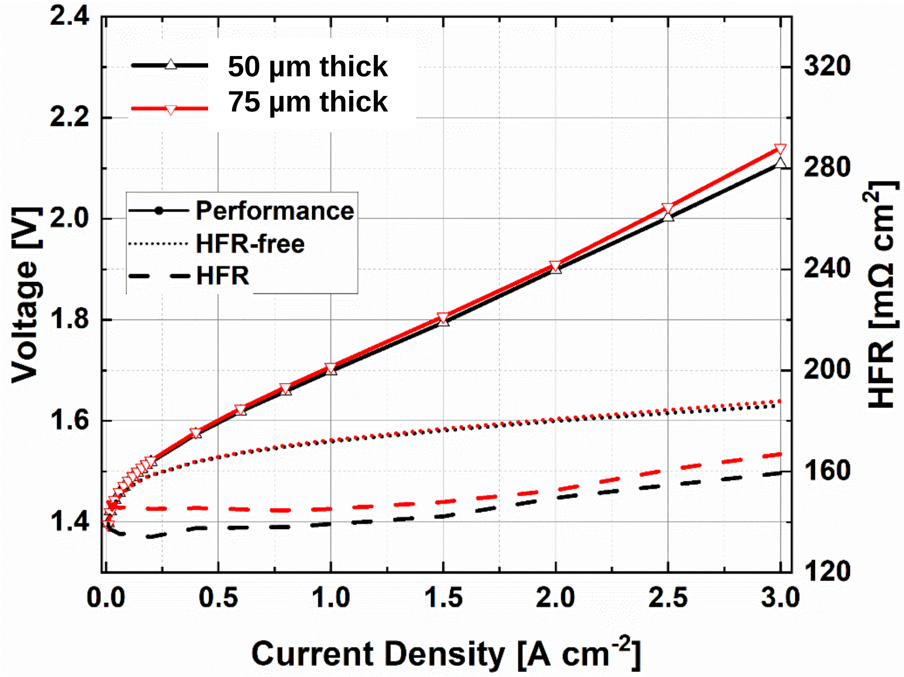
12s7 – 50 µm thick



Sample	Thickness [µm]	Pore shape	Pore size [µm]	Porosity (%)
4c2	50	Circular	105	0.427
8c4		Circular	219	0.467
12c3		Circular	323	0.648
12c6		Circular	313	0.425
12c14		Circular	317	0.21
16c8		Circular	423	0.436
4s2		Square	109	0.528
12s7		Square	326	0.444
12s7	75	Square	322	0.435
12c6		Circular	293	0.327

LGDL properties enable tuning performance

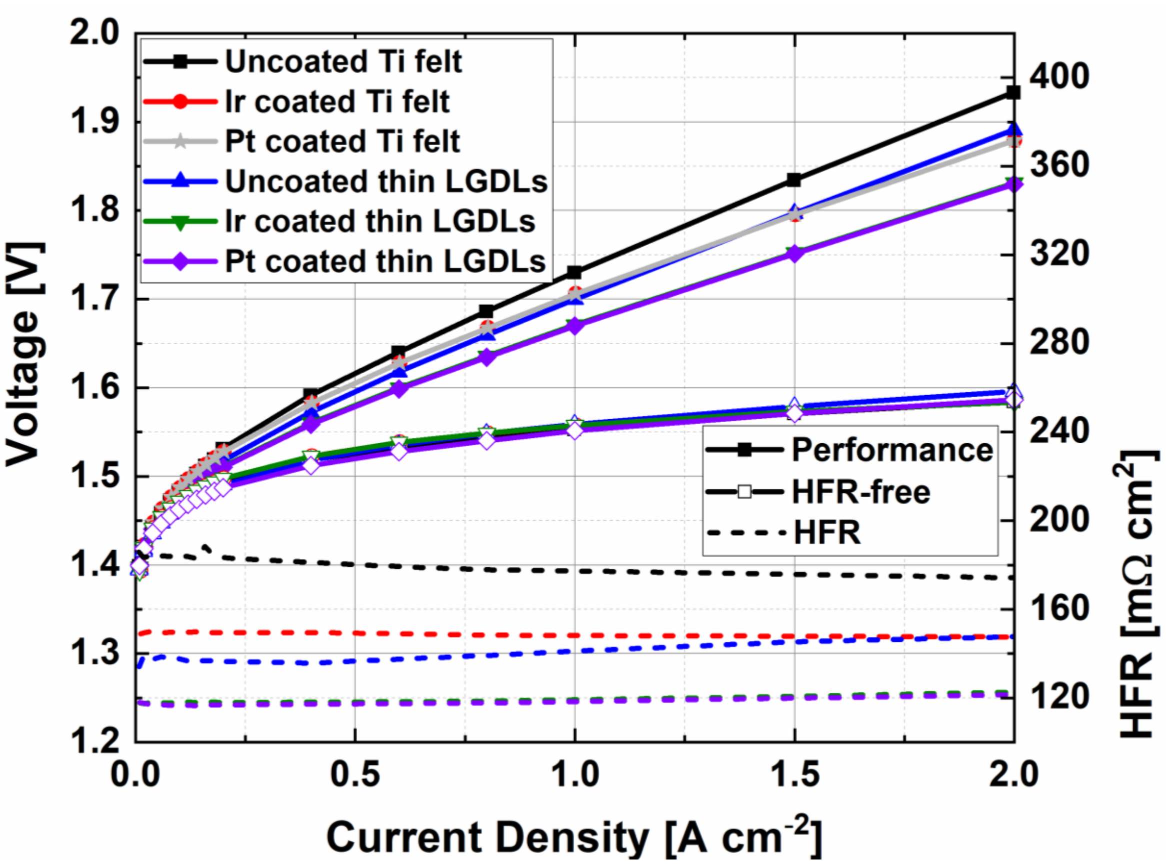


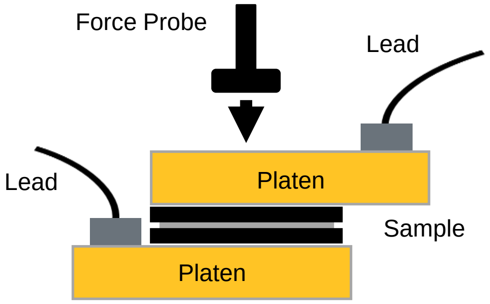


- All thin LGDL materials improve performance and pass Go/No Go decision
- Different LGDL properties result in different performance
  - Large land area increases mass transport above 1.0 A/cm^2
  - Thicker LGDLs show reduced performance

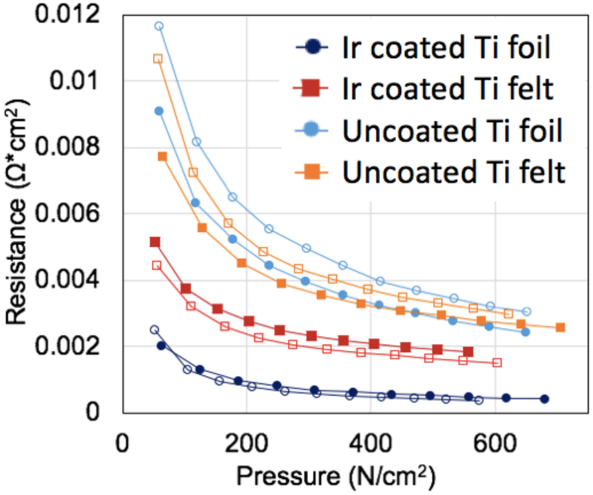
Protective coatings further improve performance

Best *in-situ* performance to date: **1.84 V at 2 A/cm^2**





Interfacial contact resistance

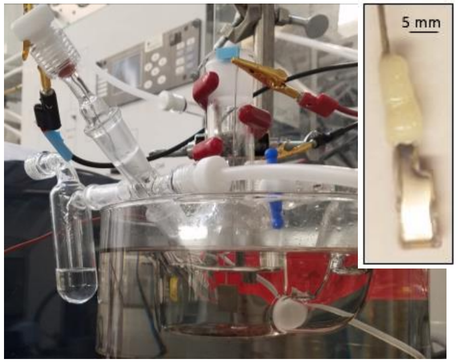


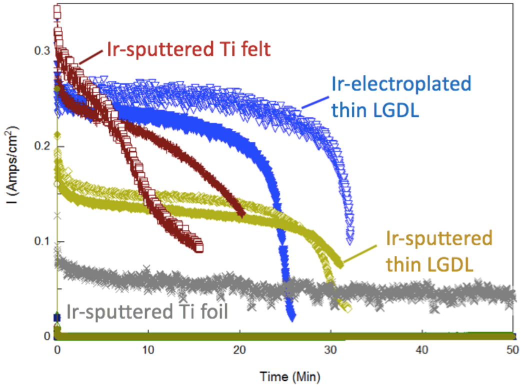
- Ir and Pt coatings improve interface resistance
- Identical improvement observed for Ir and Pt coatings => 60 mV at 2 A/cm^2
- Best performing thin coated LGDLs is 50 mV better than coated baseline LGDL at 2 A/cm^2

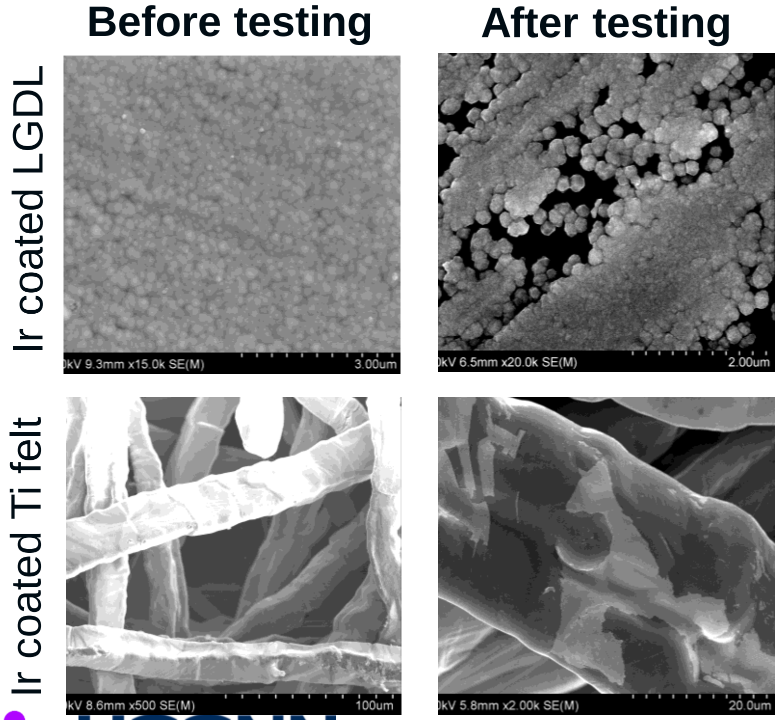
Better durability of thin LGDLs than baseline materials

- Coating morphologies varied for electrodeposited and sputtered Ir
- Corrosion modes were linked to initial coating morphology which varied by deposition & substrate
  - Particles => particle thinning
  - Film => film peeling
- Thin Ir coated Ti has lower interfacial contact resistance and greater stability than Ir coated baseline Ti felt

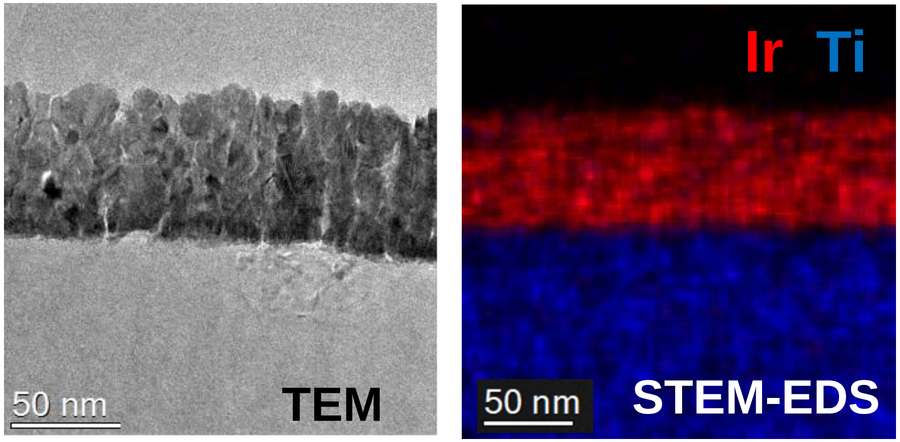
Electrochemical characterization and testing



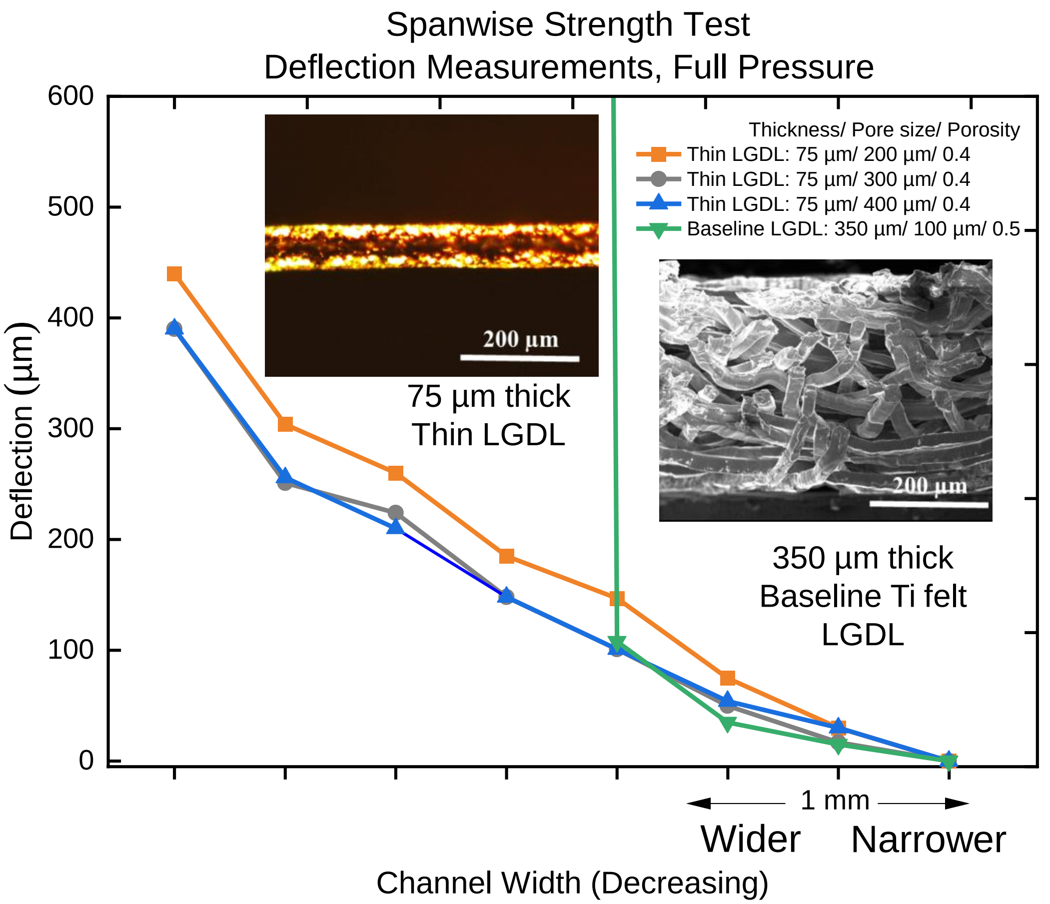


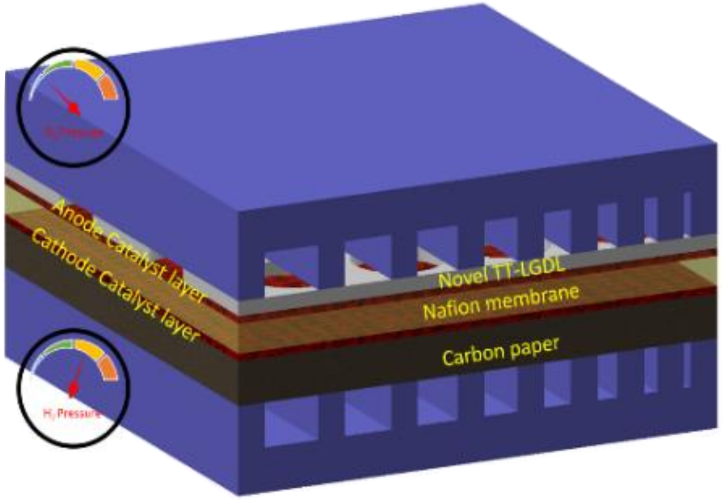


Ir/LGDL TEM & STEM-EDS cross sections



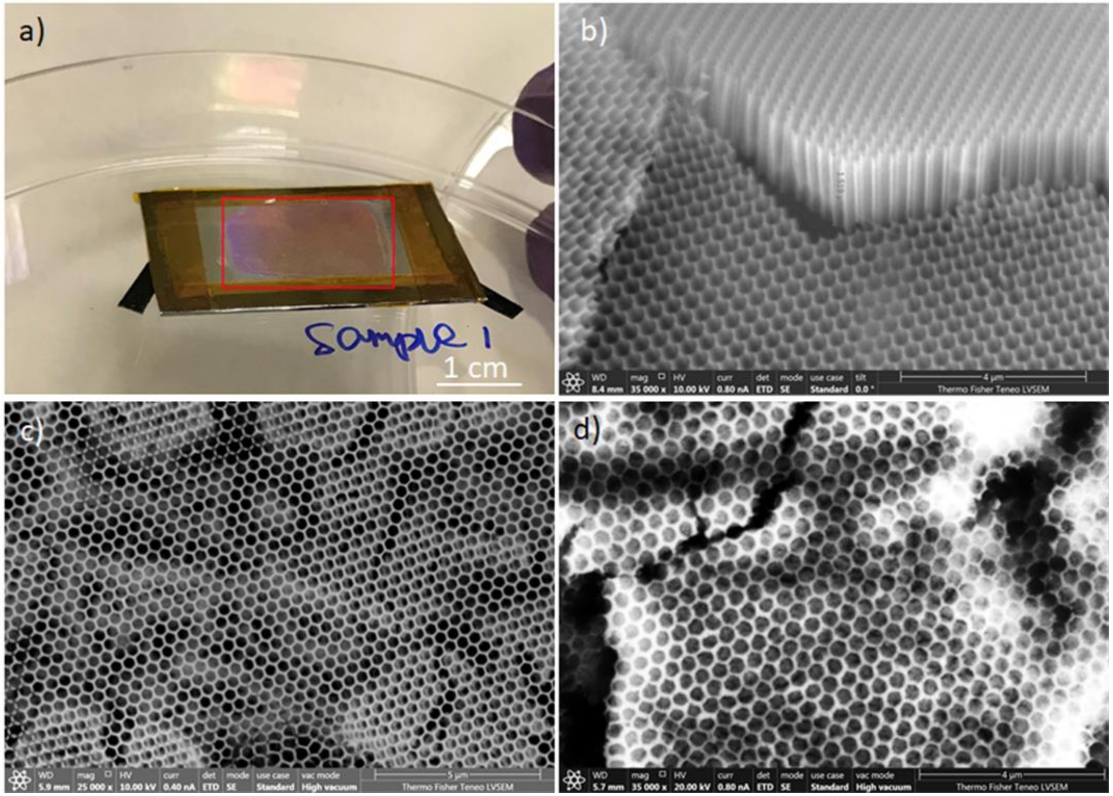
Better mechanical strength was obtained with developed thin LGDLs





- TT-LGDL samples were comparable in strength and stiffness to the conventional Ti felt sample while TT-LGDLs are much thinner
- Optimization of thickness, channel width, and operating differential pressure are required to determine the best use of the LGDL design and space saving

Nanoporous Ti LGDL fabrication

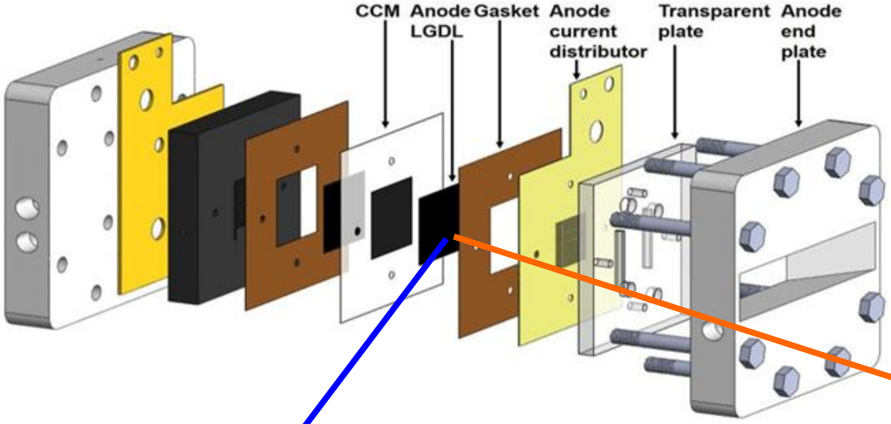


Method:

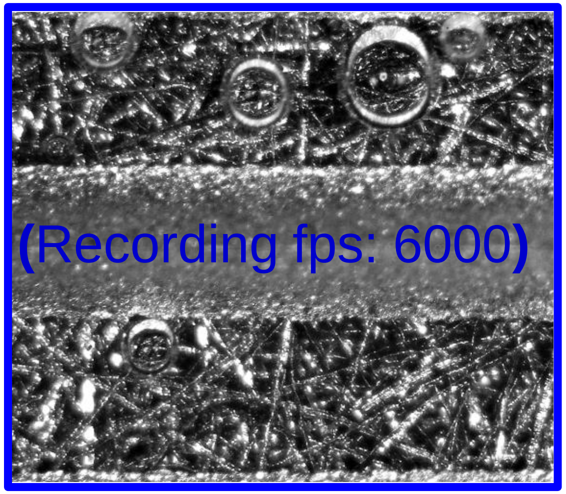
Anodized Alumina Templating
+ Reactive Ion Etching (RIE)

- Ti foil etched through using reactive ion etching (RIE), with the anodized alumina film pore structure retained in the process
- > 5 cm^2 size anodized alumina film pore template on Ti foil
- Ordered nanopore arrays templated on Ti foil through RIE
- RIE control for retaining nanopore distribution on Ti LGDL with high aspect ratio

In-situ Investigated two-phase flow/bubble dynamics and catalyst utilization with transparent PEMECs and high-speed/microscale system



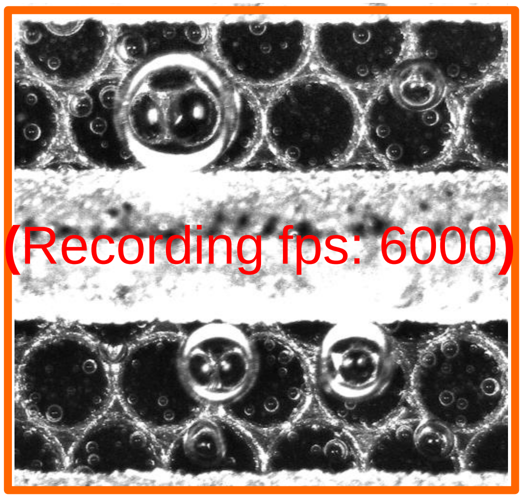
- ☐ Speed: up to 1,400, 000 fps



(Recording fps: 6000)

Baseline Ti felt: 350 µm in thickness, 100 µm in diameter and 0.55 in porosity

Novel TT-LGDLs: 50 µm in thickness, 300 µm in diameter and 0.60 in porosity



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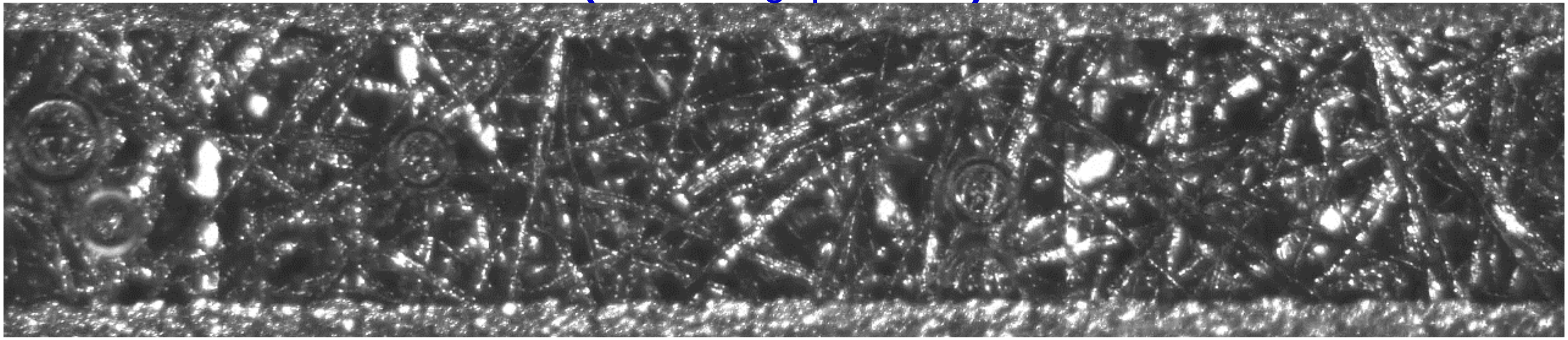
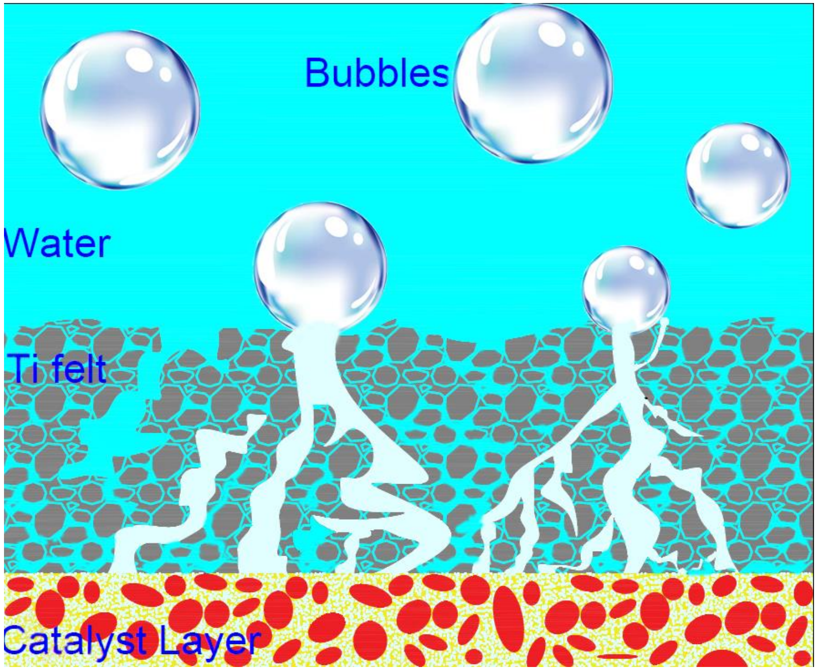
Results and discoveries with baseline Ti felt material

(Recording fps: 6000)

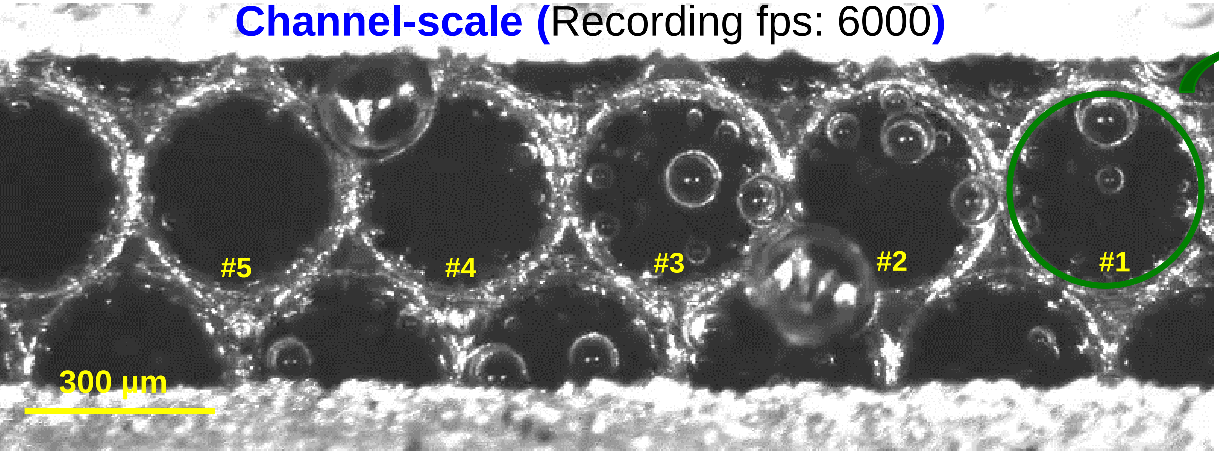


Oxygen bubble pathways in baseline material

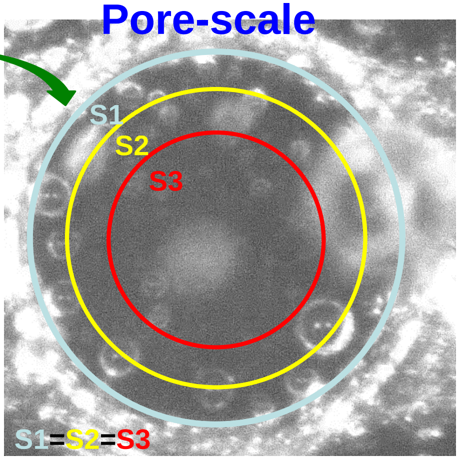


- Bubbles are generated from catalyst layer surface and merged into larger ones through pore pathways, and finally detached from the baseline Ti felt surface
- The bubble formation is not uniform at the baseline Ti felt surface, and most of bubbles are detached from a small number of preferred pores, with main detachment diameters from 100 µm to 200 µm
- The detachment diameters and bubble formation sites are increased with current densities

Novel LGDL enables direct visualizations of reaction sites and bubble evolutions



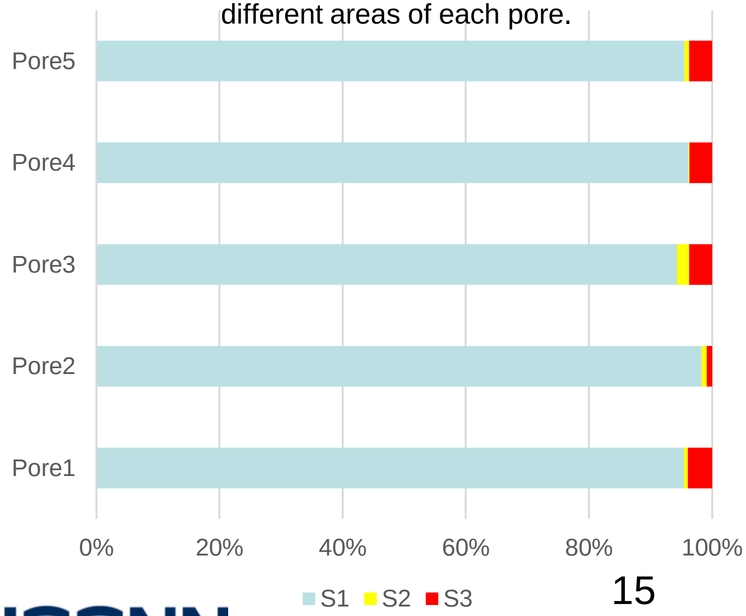
Channel-scale (Recording fps: 6000**)**



Pore-scale

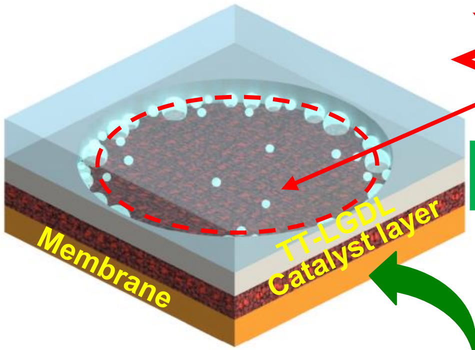
- Reaction sites are increased with current densities. The reactions mainly occurs in LGDL pore edge areas
- At high current density, reactions are also observed in the middle area of pores, while over 95% of oxygen volume is from the pore edge area
- The bubble detachment diameters are <50 µm with higher detachment frequency, which shows much better mass transport than baseline materials

Volume of bubbles produced from different areas of each pore.



Catalyst-coated LGDLs (CCLGDLs) facilitated with thin LGDLs / *in-situ* visualization discoveries

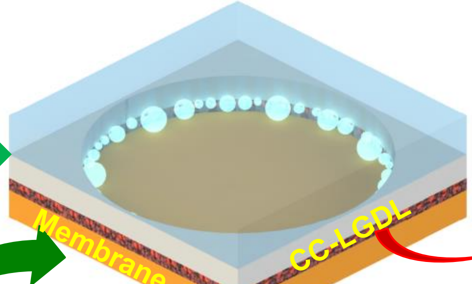
TT-LGDLs Electrode:
Catalyst layers (~20 µm in thickness)
TT-LGDL (50 µm in thickness)

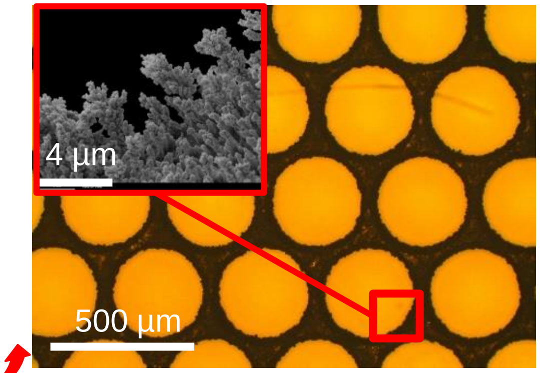


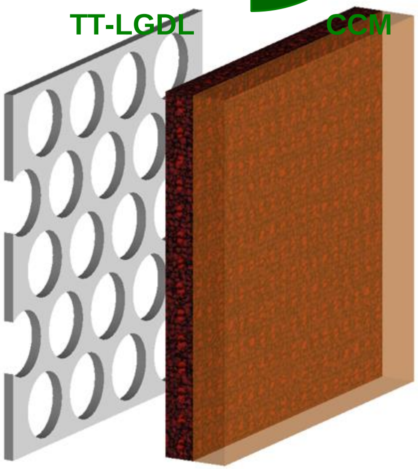
Catalysts are underutilized.

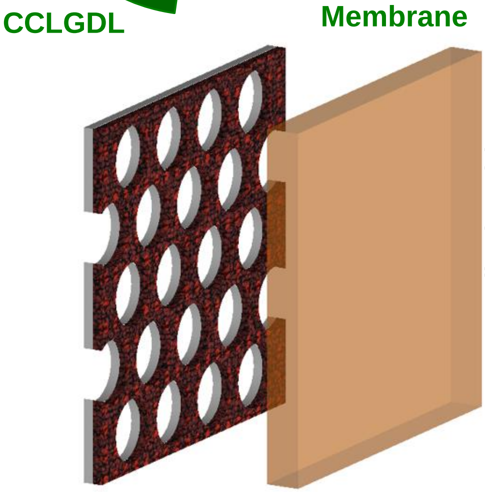
Remove the catalysts in pore area

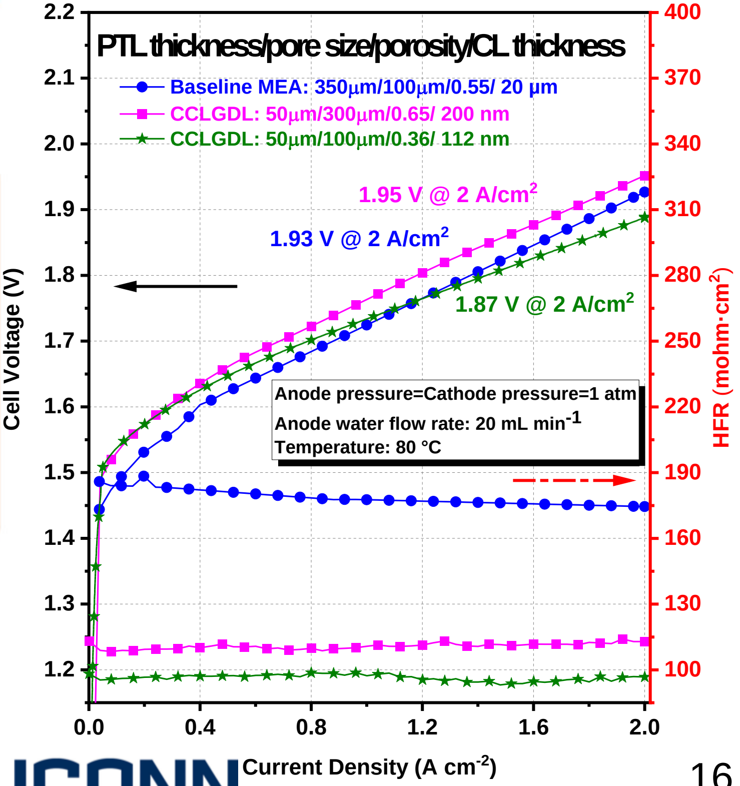
Novel CCLGDLs Electrode:
Catalyst layers (in nanometer scale ranging from 110 to 220 nm and attached to LGDL)
TT-LGDL (50 µm in thickness)





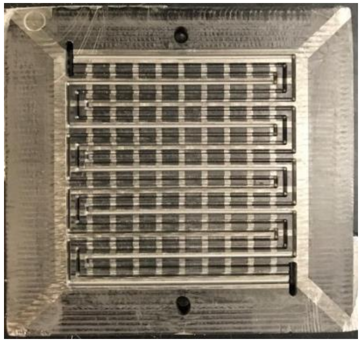


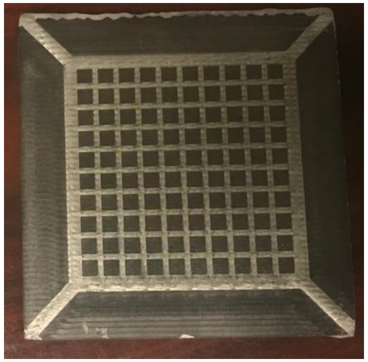


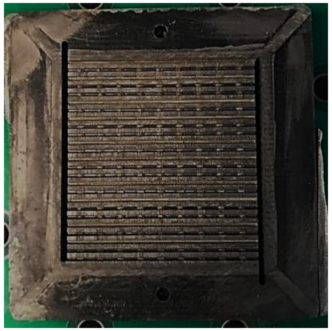


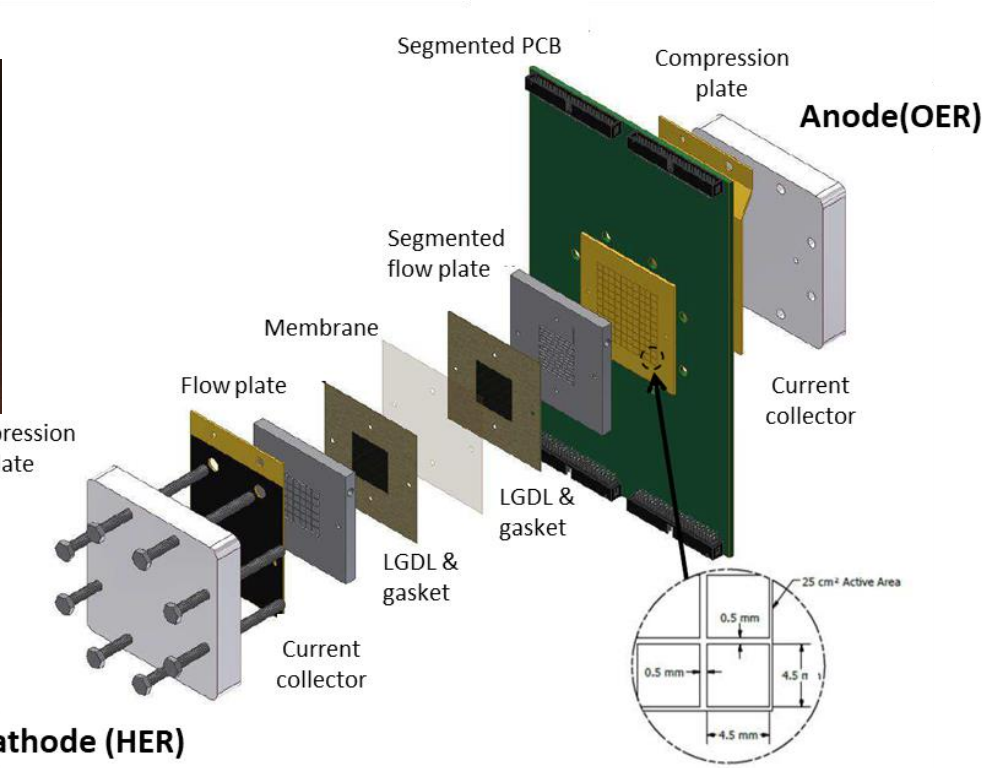
Anode pressure=Cathode pressure=1 atm
Anode water flow rate: 20 mL min^{-1}
Temperature: 80 °C

Current distribution measured *in-situ* at 5 cm^2 and 25 cm^2



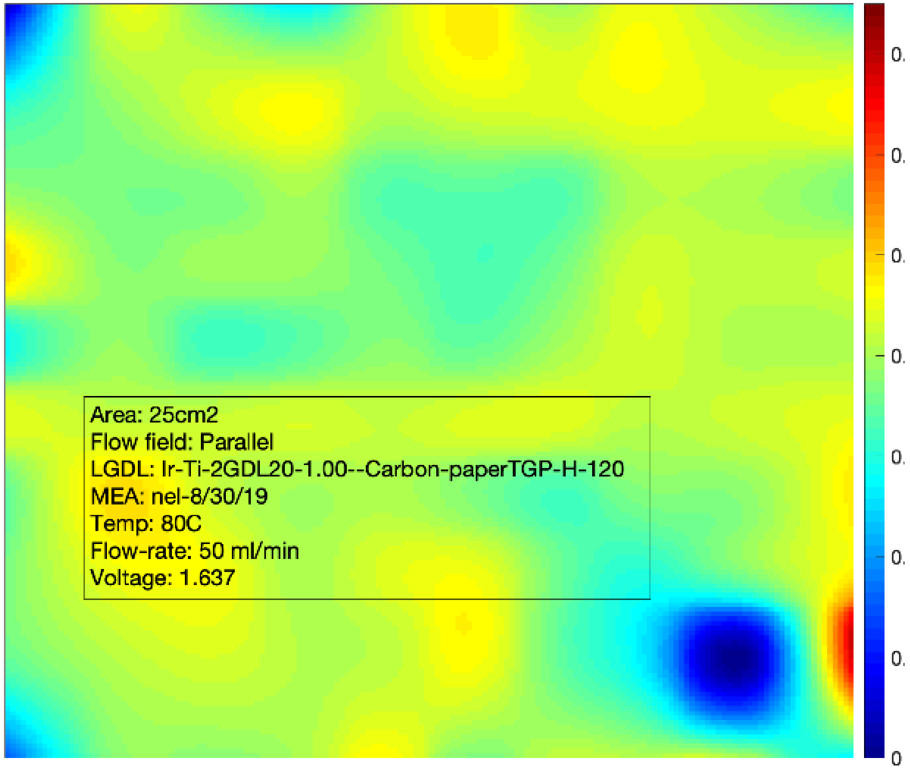




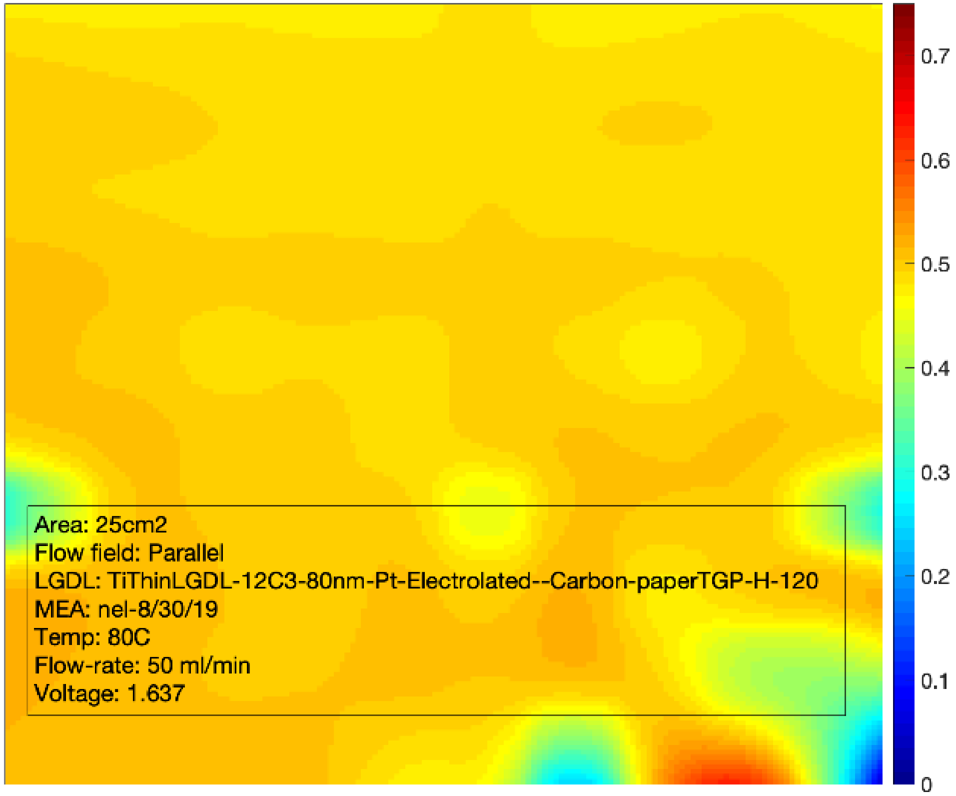


- Current distribution collected by printed circuit board (PCB) in direct contact with segmented flow fields (serpentine & parallel, 5 cm^2 & 25 cm^2 available)
- Resolution is 4.5 mm x 4.5 mm segments machined into flow fields
- Current passes through shunt resistors in PCB, voltage drop measured, and current calculated via Ohm's law

Current density distribution with parallel flow fields



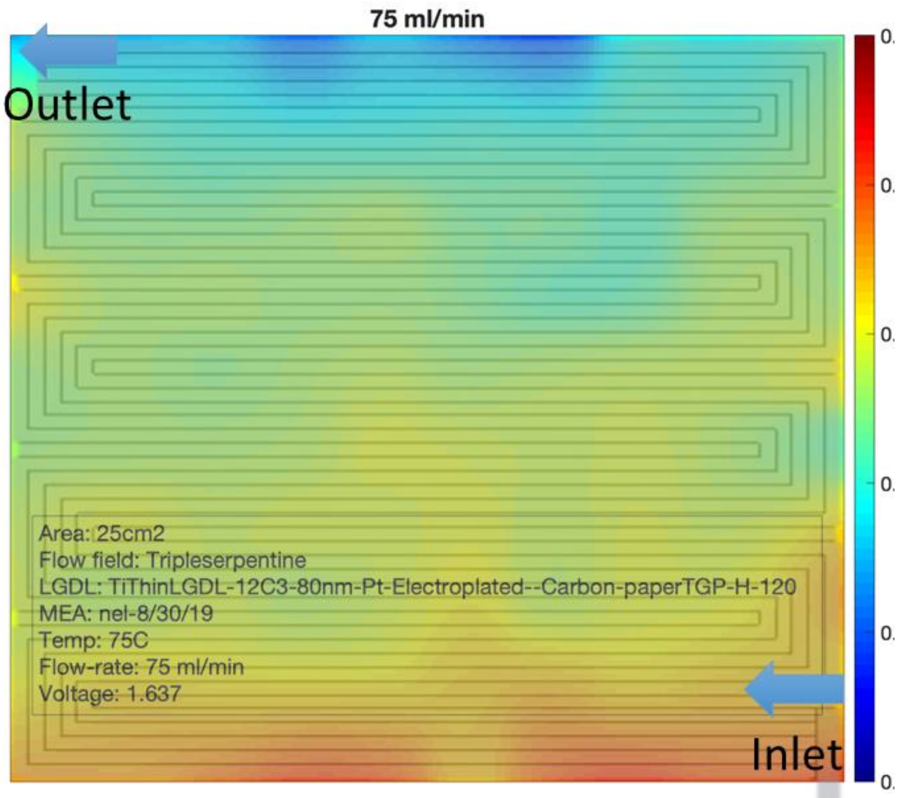
Area: 25cm2
Flow field: Parallel
LGDL: Ir-Ti-2GDL20-1.00--Carbon-paperTGP-H-120
MEA: nel-8/30/19
Temp: 80C
Flow-rate: 50 ml/min
Voltage: 1.637



Area: 25cm2
Flow field: Parallel
LGDL: TiThinLGDL-12C3-80nm-Pt-Electrolated--Carbon-paperTGP-H-120
MEA: nel-8/30/19
Temp: 80C
Flow-rate: 50 ml/min
Voltage: 1.637

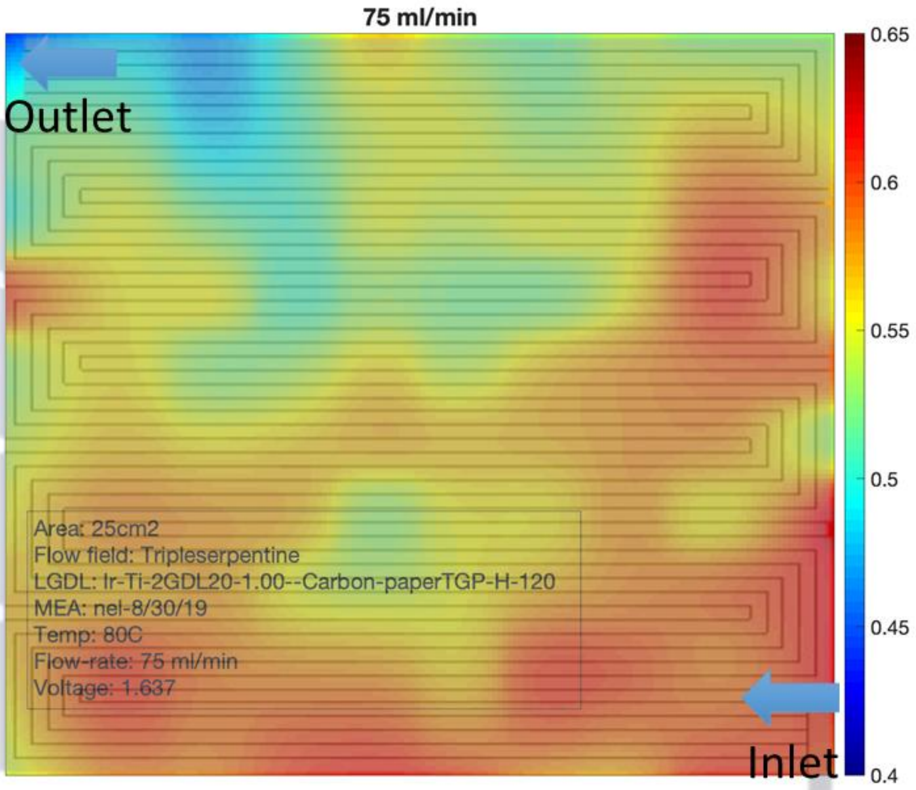
- HFR comparable to others (140 – 200 mΩ cm^2)
- Segmented plates and PCB cause 40-50 mΩ-cm^2 higher ASR
- Current density distribution is relatively uniform *for parallel flow fields*
- Experiments show lateral current spread through LGDL

Serpentine flow field induces current distribution



Area: 25cm2
Flow field: Tripleserpentine
LGDL: TiThinLGDL-12C3-80nm-Pt-Electroplated--Carbon-paperTGP-H-120
MEA: nel-8/30/19
Temp: 75C
Flow-rate: 75 ml/min
Voltage: 1.637

PEMEC with thin LGDL



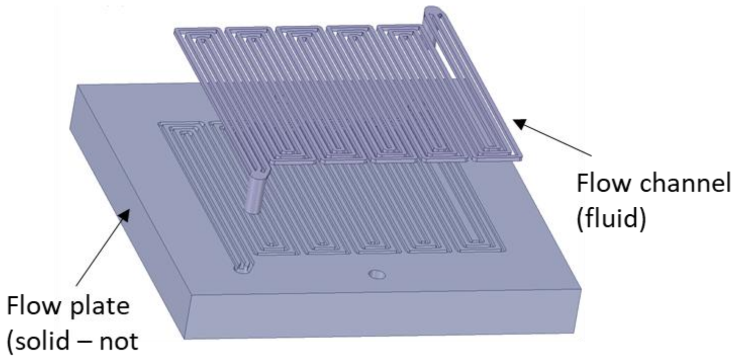
Area: 25cm2
Flow field: Tripleserpentine
LGDL: Ir-Ti-2GDL20-1.00--Carbon-paperTGP-H-120
MEA: nel-8/30/19
Temp: 80C
Flow-rate: 75 ml/min
Voltage: 1.637

PEMEC with Ti felt

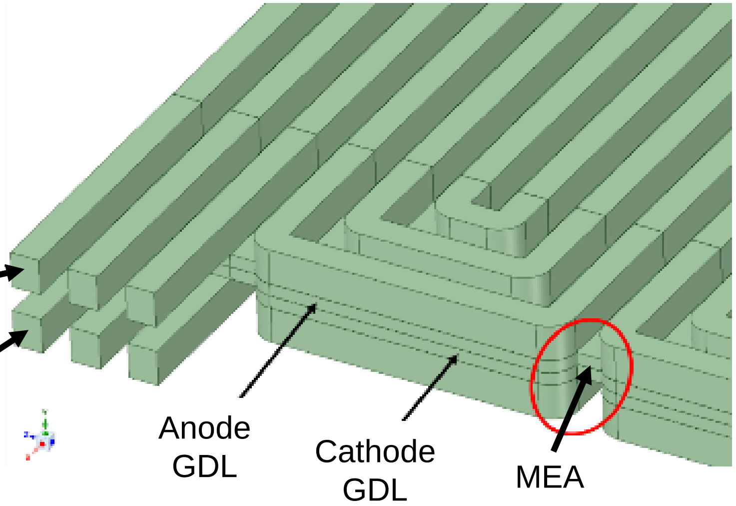
- Mass transport clearly affected by LGDL structure and flow field
- Current distribution responds to flow rate (less intense distribution at low flow rate)
- Qualitative agreement with NREL modeling of triple serpentine architecture

Novel electrode cell modeling

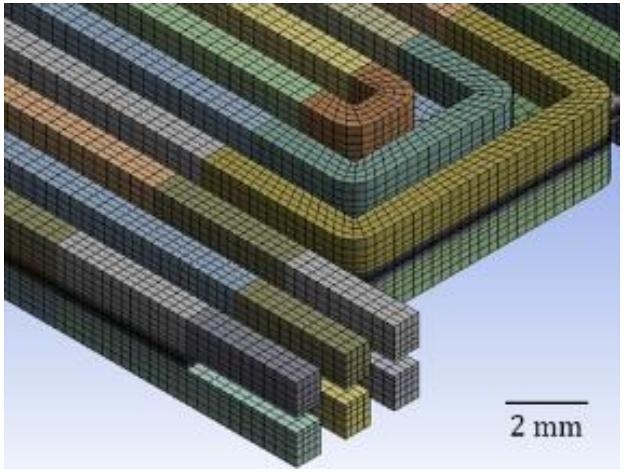
- PEMEC novel electrode cell is modeled by numerical, analytical, and empirical methods to aid in electrode development
- Conservation and transport equations were solved in 3D for species distributions in LGDLs and channels
- Electrochemical models are integrated with the CFD model to simulate the kinetic processes in the catalyst layers



Triple serpentine flow channel drawing



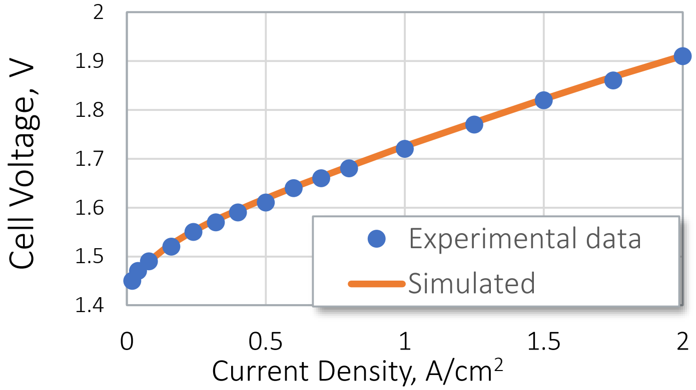
Computational domains modeled in 3D



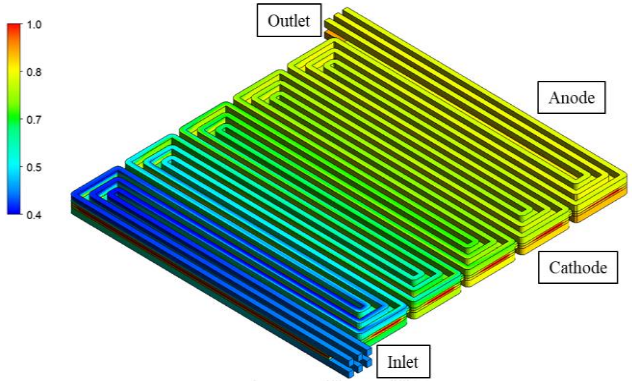
Mesh for the computational domains

PEM electrolyzer cell modeling results

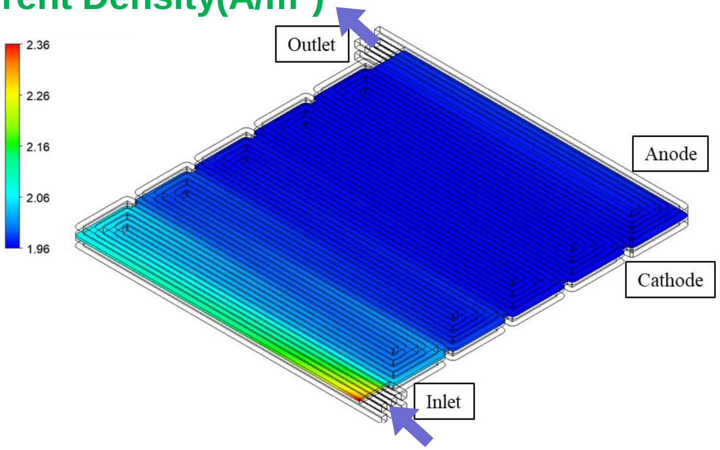
1. Modeled and Tested VI relation



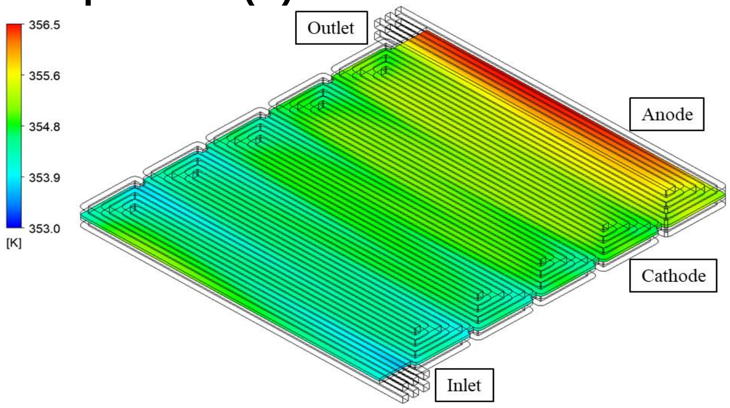
2. Gas Volume Fraction



3. Current Density(A/m^2)



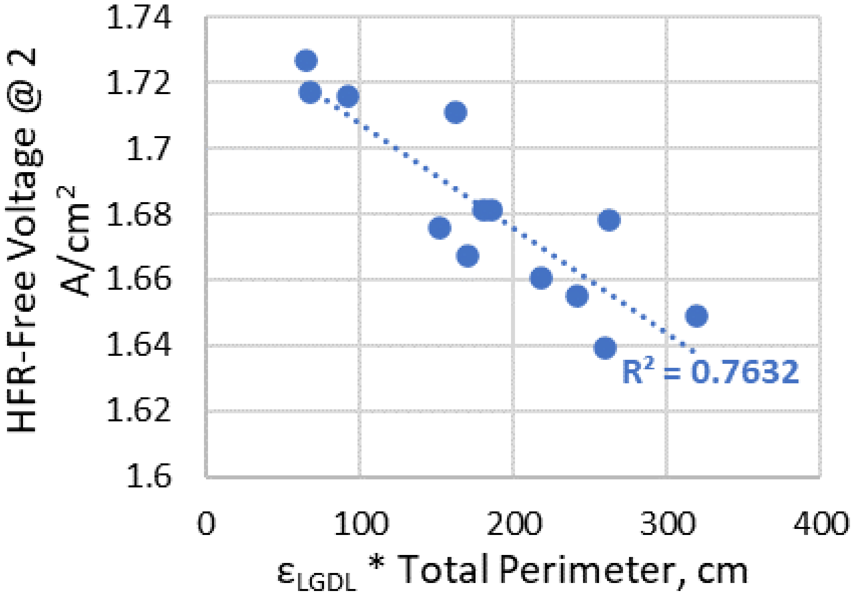
4. Temperature (K)

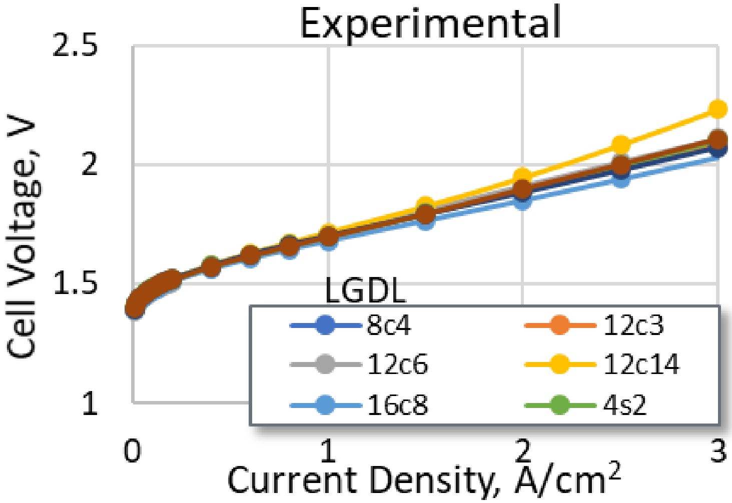


1. Model was validated to laboratory triple serpentine 25cm^2 cell
2. Gas-water two-phase modeling result and the distribution of gas volume fraction
3. Current density profiles is shown as a function of cell voltage
4. Thermal-flow modeling predicts the temperature distributions

Empirical & numerical analysis of pore parameters

- Pore size, shape, and alignment can be analyzed empirically
  - One emerging trend from the data is that voltage roughly scales with total edge length: $\varepsilon_{LGDL} = N_{pores}\,(2\pi R_{pore})$
- The alignment of the LGDL pores with the channels significantly affects the cell performance
- The results of the model can be used to pinpoint the phenomena that lead to performance degradation





- Currently the model considers transport of gaseous products and water through the channels
  - Not enough to explain trends in experimental data
  - Need to also consider water transport in the membrane, as local dry-out could be a problem

Collaboration and coordination

Strong collaboration of comprising of academia, national labs, and private industry

Name (PI/CoPI)	Organization	Primary Role
Feng-Yuan Zhang, Matthew Mench	UTK (Prime)	Design, fabrication, surface treatment, lab-scale tests, high-speed and multiscale visualization, current mapping
David Cullen, Harry Meyer	ORNL	Fabrication, surface treatment and ex-situ characterizations
Guido Bender, Zhiwen Ma	NREL	Surface treatment, benchscale and durability tests, numerical modeling and simulations
Chris Capuano, Luke Dalton, Kathy Ayers	Nel Hydrogen	Baseline CCMs, mechanical strength and system-scale tests, cost analysis
Pu-Xian Gao	UConn	Design, Nano structures and materials, ex-situ characterizations

Responses to Previous Year Reviewers' Comments

This project was not reviewed last year.

Summary

- All five milestones, smart milestones and Go/NoGo decision points were met
- Our team designed, fabricated, characterized engineered thin titanium LGDLs with different pore morphologies and thicknesses
- The developed thin LGDLs are much thinner with well-tunable pore morphologies, and provide better electrochemical performance, durability and mechanical proprieties than baseline Ti felt material
- A 3D CFD model that can be used to study electrolyzer performance and investigate the effects of LGDL porosity and pore coverage has been developed and validated
- *In-situ* high-speed/microscale visualizations and current mappings have been successfully conducted to provide the insights of the developed LGDLs
- Catalyst-coated LGDLs (CCLGDLs) have been developed and the preliminary results show better performance than conventional MEAs

Future Work

- *In-situ* and *ex-situ* CCLGDL evaluations and optimizations
- Performance tests with labscale, benchscale, and systemscale electrolyzer cells
- Modeling and simulation development with experimental validation of LGDLs and CCLGDLs
- In-situ current mapping and high-speed visualizations with LGDLs and CCLGDLs; movie clips/ images of reactions and transports, and their analyses
- Cost analyses of thin LGDLs and CCLGDLs

Acknowledgement

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- DOE program manager: Michael Hahn
- **Project team**
  - **UT**: Feng-Yuan Zhang, Matthew Mench, Douglas Aaron, Gaoqiang Yang (2019 Chancellor’s Extraordinary Professional Promise Award, now at LANL), Yifan Li (2020 Chancellor’s Extraordinary Professional Promise Award, now at UConn), Kui Li, Shule Yu, Lei Ding, Weitian Wang, Anirban Roy, Frida Roenning
  - **ORNL**: David Cullen (2019 Presidential Early Career Award), Harry Meyer, Haoran Yu, Jefferey Baxter
  - **NREL**: Guido Bender, Zhiwen Ma, Zhenye Kang, James Young, Jacob Wrubel, Liam Witteman
  - **Nel**: Christopher Capuano, Kathy Ayers, Luke Dalton, Jennifer Glenn, Alex Keane, Shaina Errico
  - **UCONN**: Pu-Xian Gao, Can Cui, Liaoyong Wen (Now at West' U.), Fangyuan Liu