NETL's Crosscutting Research Review Meeting

Award: DE-FE0011585

Project manager: Jason Hissam

Developing novel multifunctional materials for high-efficiency electrical energy storage - Optimization/durability

Feng-Yuan Zhang

Nanodynamics and High-Efficiency Lab for Propulsion and Power (NanoHELP)

Department of mechanical, aerospace and biomechanical engineering

UT Space Institute, University of Tennessee, Knoxville

U.S. DEPARTMENT OF ENERGY

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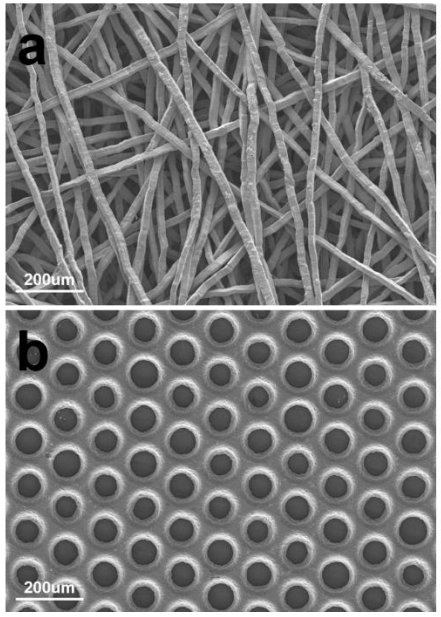
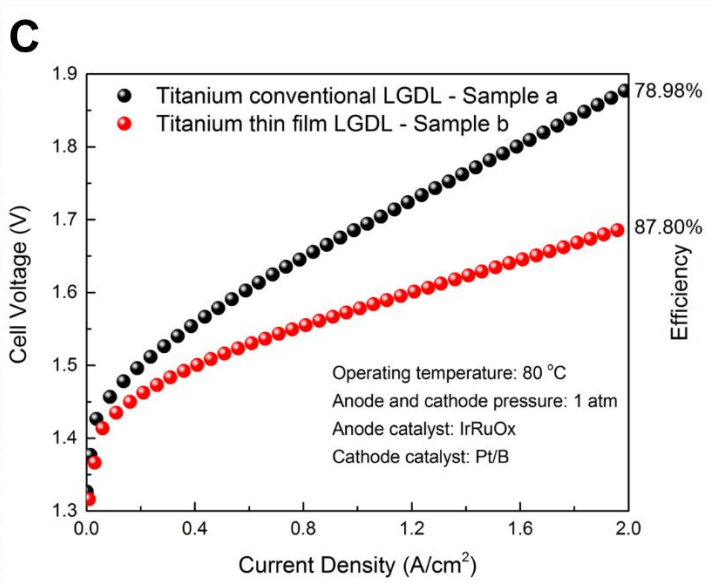
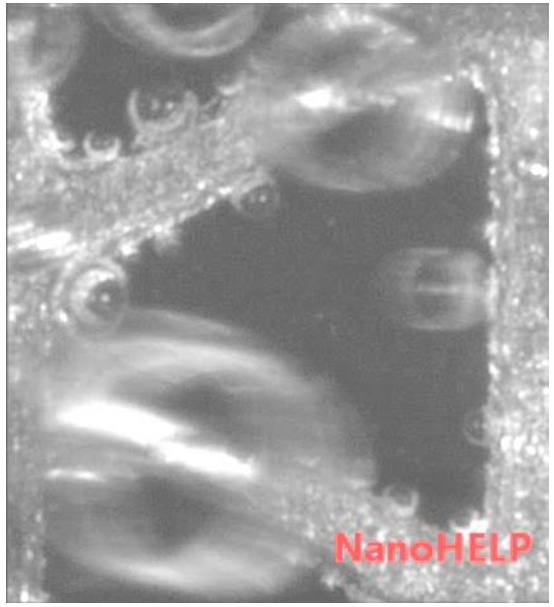
NANOHELP

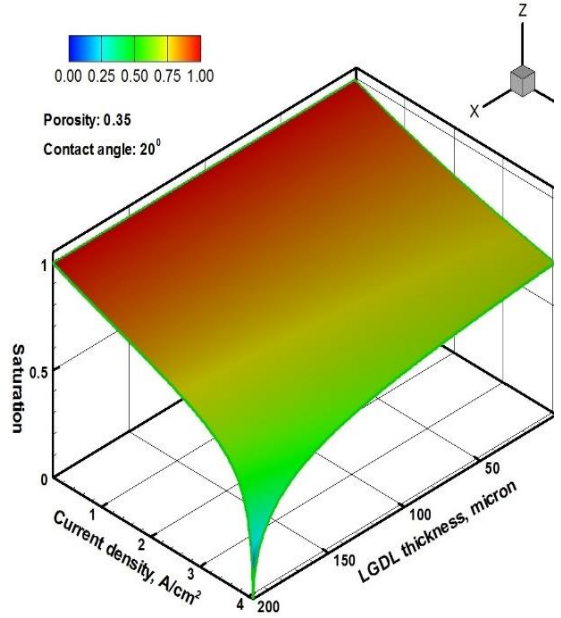
Outline

Motivation | multifunctional thin materials | In-situ reactions | Modeling | Summary

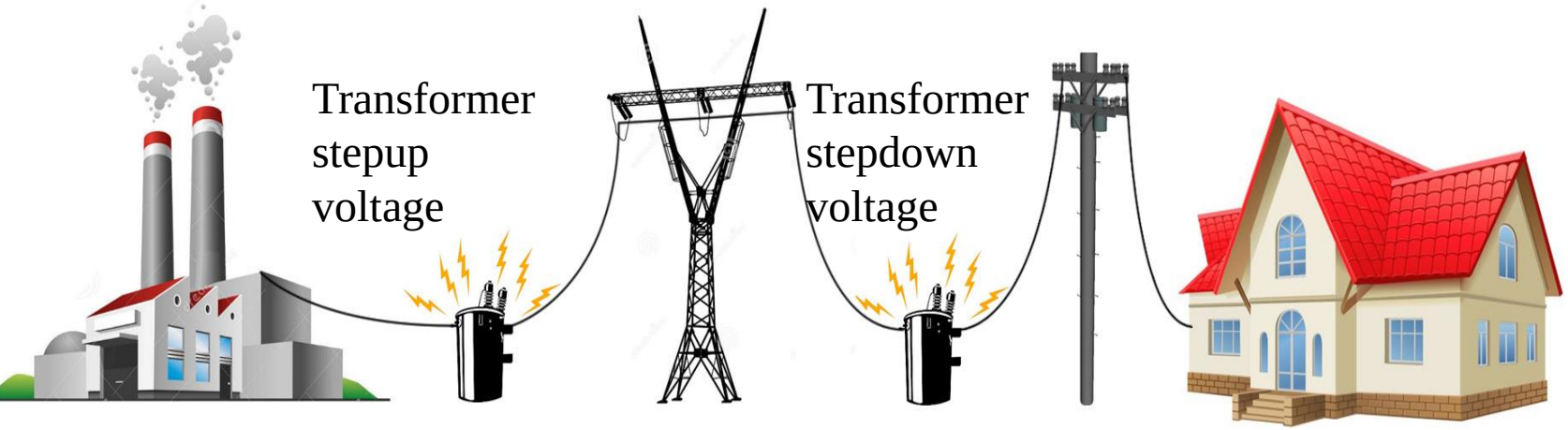








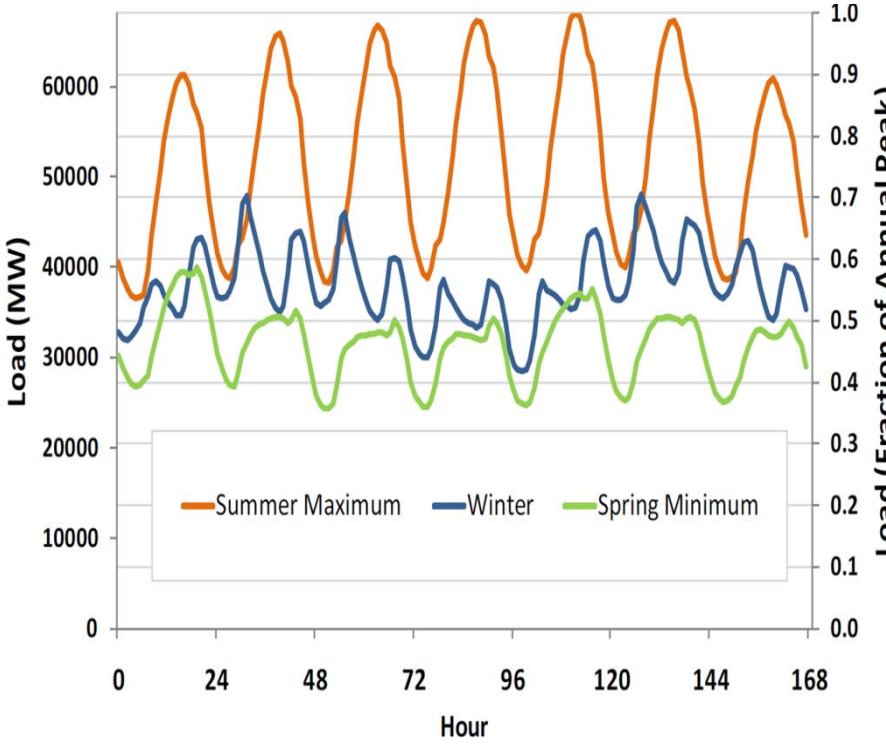
Distributed energy storage mitigates power-demand interruptions and improves greatly efficiency from coal plant to end users



Coal plant generates electricity

Long-distance transmission lines

Distribution of electricity to end users

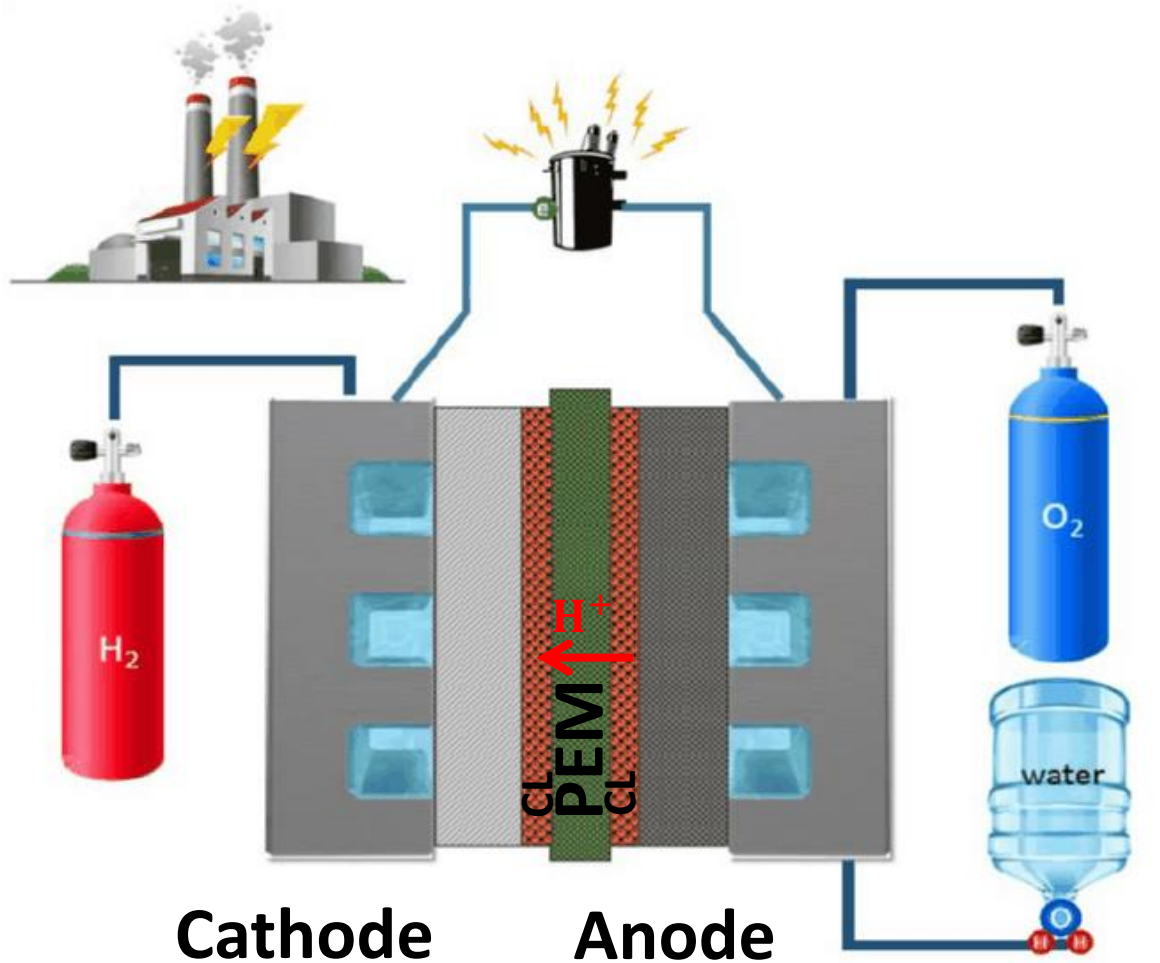


- Electricity demand changes significantly with time
- Electric grid often experiences interruptions, resulting in significant cost (> 80 Billions/year)
- Many of these interruptions may be mitigated by distributed energy storage approaches

Paul Denholm, Erik Ela, Brendan Kirby, and Michael Milligan. Technical Report NREL/TP-6A2-47187, 2010

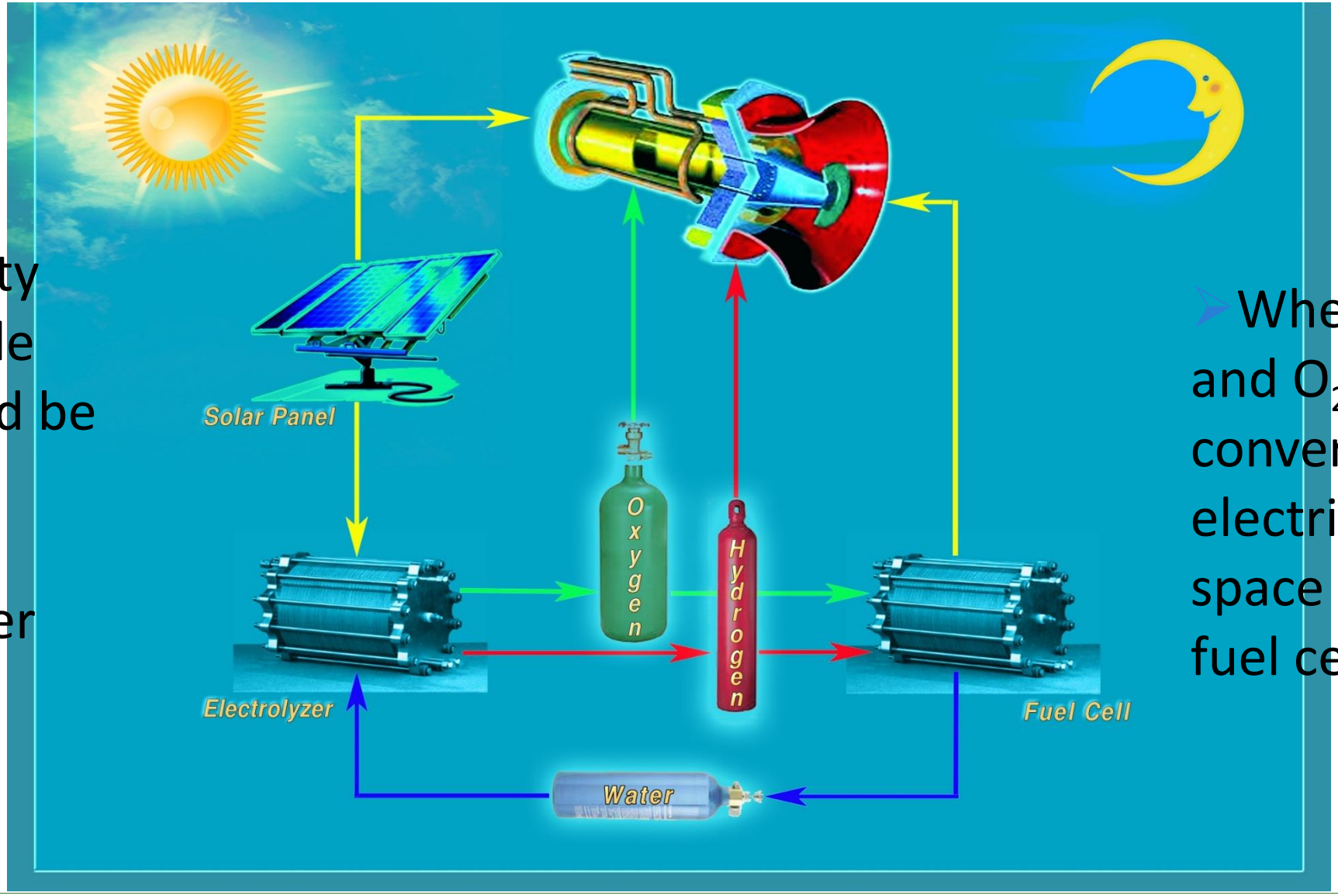
Proton exchange membrane electrolyzer cells(PEMECs) become more attractive for hydrogen production

- Advantage of PEM Electrolyzer Cells
  - High energy efficiency
  - High energy density
  - Fast charging and discharging
  - High purity of H2 and O2 productions
  - Compact system design
  - Stackable: easily scale up/down



Sustainable energy system

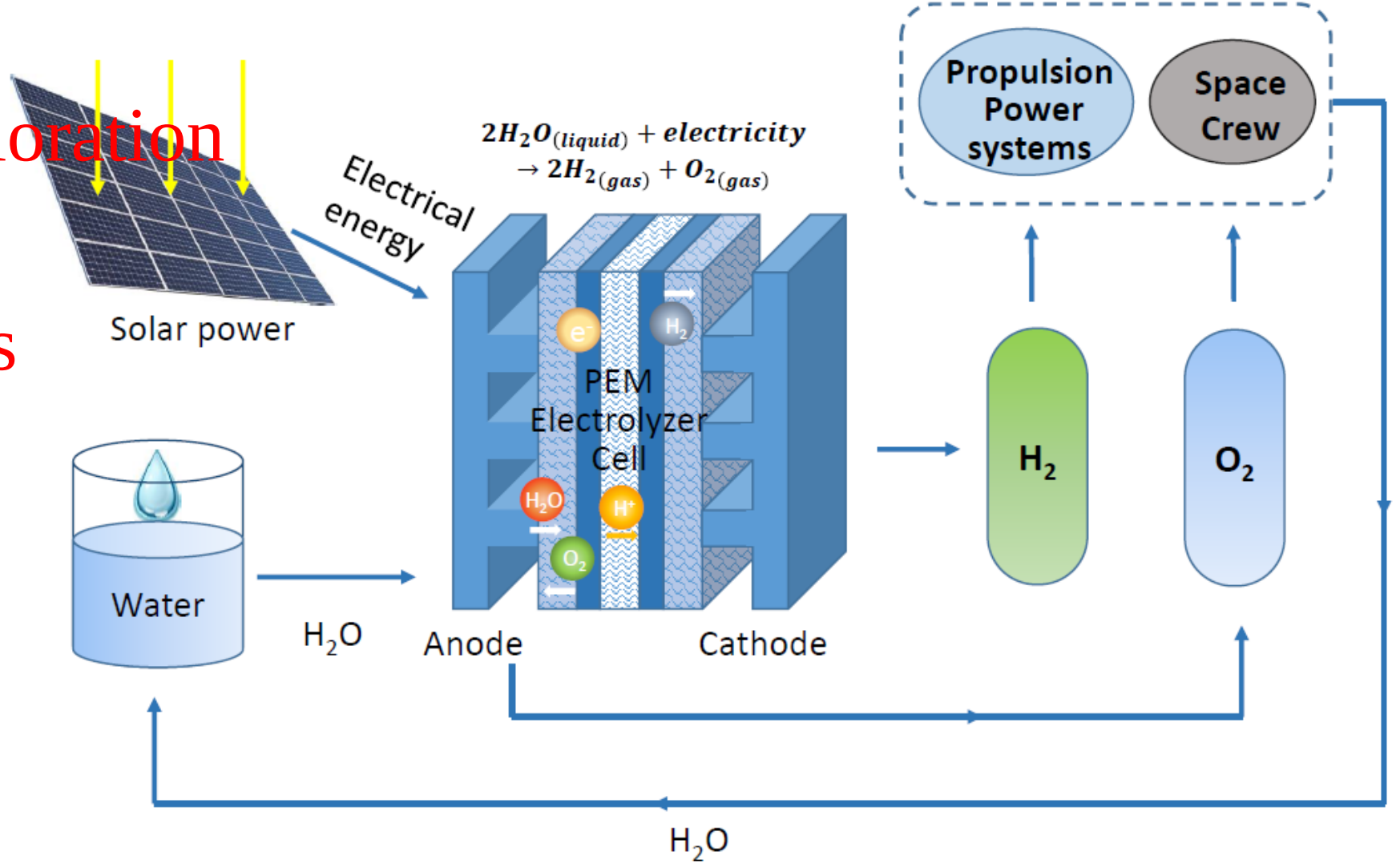
- Electricity will provide power, and be stored as H_2/O_2 via Electrolyzer cells



- When needed, H_2 and O_2 will be converted back to electricity to power space craft via micro fuel cells

High-efficiency devices for pure oxygen and hydrogen generation

- Pure H2 and O2 productions
- Human space exploration
- Submarines
- Hydrogen vehicles



OGS: oxygen generator system in the space station

Barry (Butch) Wilmore, Astronaut
Captain's Speech at UT

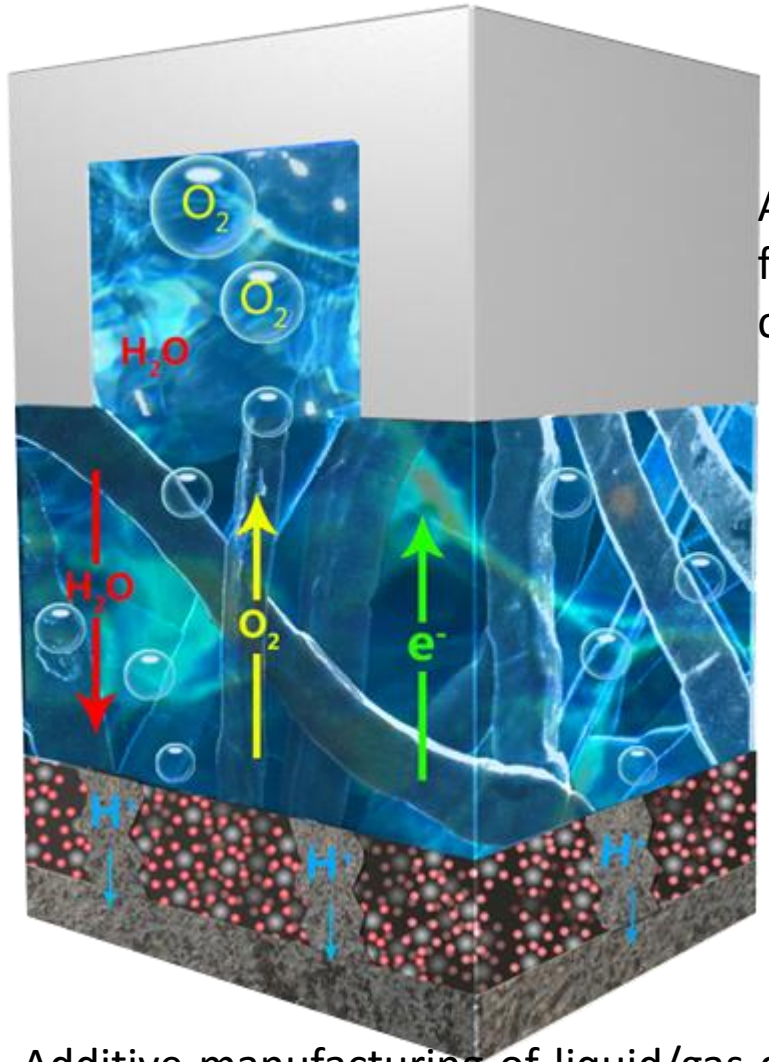
Joel from NanoHELP with Captain Barry Wilmore

Liquid/Gas Diffusion Layers (LGDLs): Multiple Functions needed for liquid water, oxygen, electrical/thermal conductivities

- LGDL: Located between flow channel and catalyst-coated membrane (catalyst layer +PEM)

- Main functions:
  - Transport reactant (liquid H_2O) in and products (H_2/O_2) out
  - Conduct electrons and heat to flow channels
  - Maintain excellent interfacial contact and conductivity

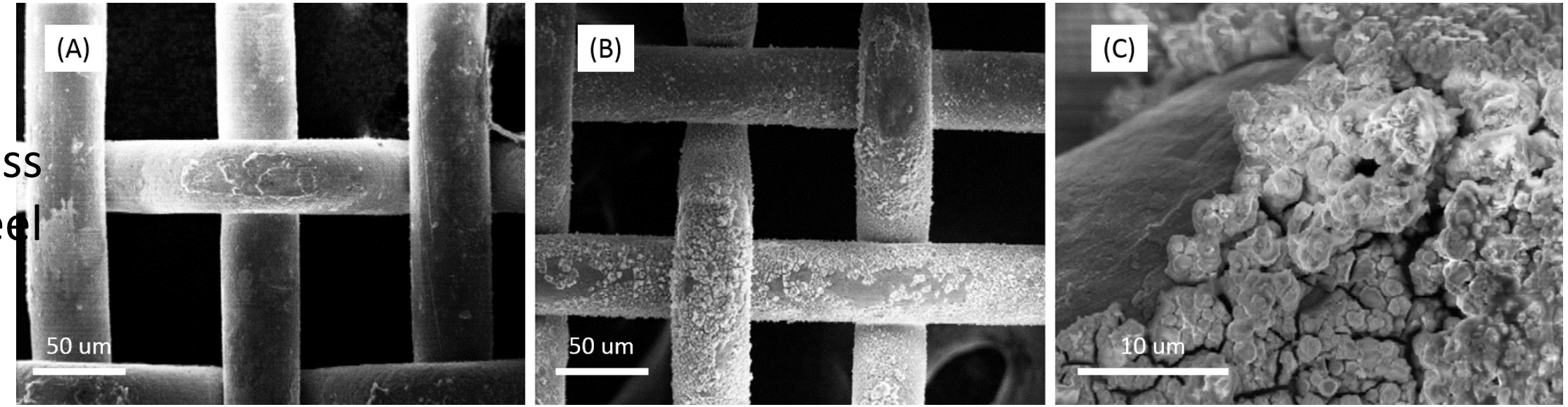
- Enhancing capillary flow, conductivities and interfacial effects with controllable pore morphology are strongly desired



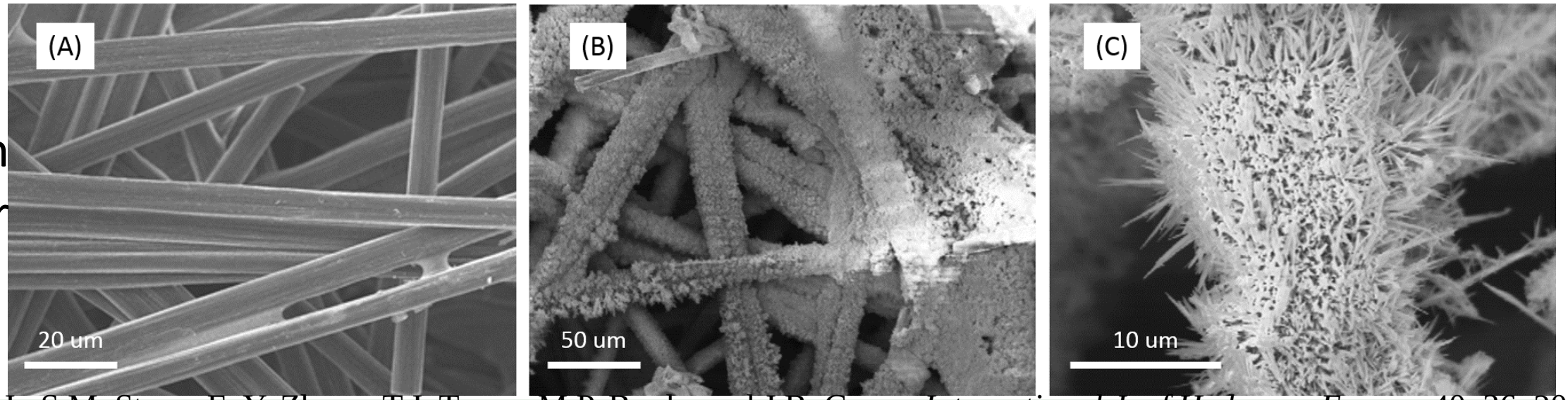
J. Mo, R.R. Dehoff, W.H. Peter, T.J. Toops, J.B. Green, F.-Y. Zhang, Additive manufacturing of liquid/gas diffusion layers for low-cost and high-efficiency hydrogen production. *International Journal of Hydrogen Energy* **41**, 3128-3135 (2016).

Conventional materials, including SS, graphite, corroded at high-potential and high-oxidative environments in PEMFCs

Stainless steel

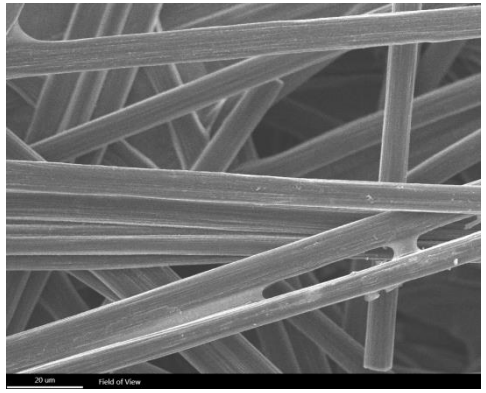


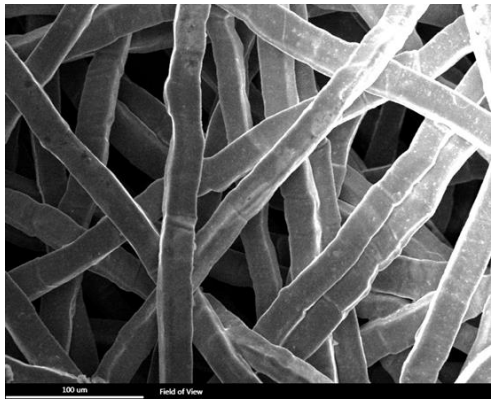
Carbon paper

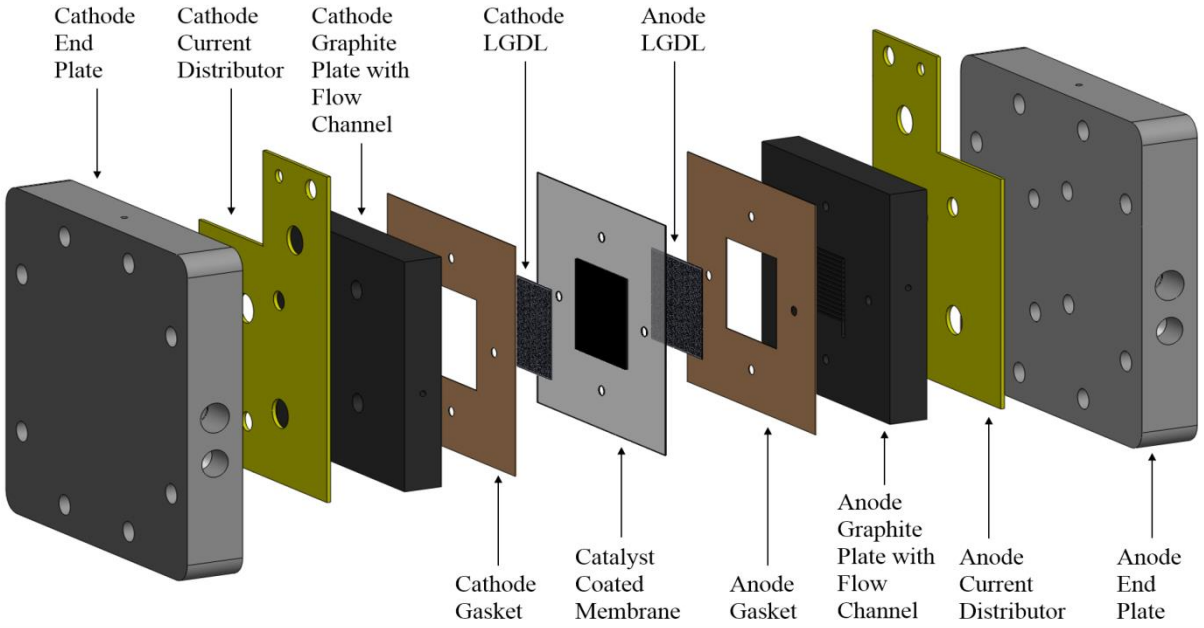


Mo, J., S.M. Steen, F.-Y. Zhang, T.J. Toops, M.P. Brady, and J.B. Green, *International J. of Hydrogen Energy*, 40, 36, 2015.

Most conventional LGDLs are made of fibers: Titanium felts for anode and carbon fibers for cathode





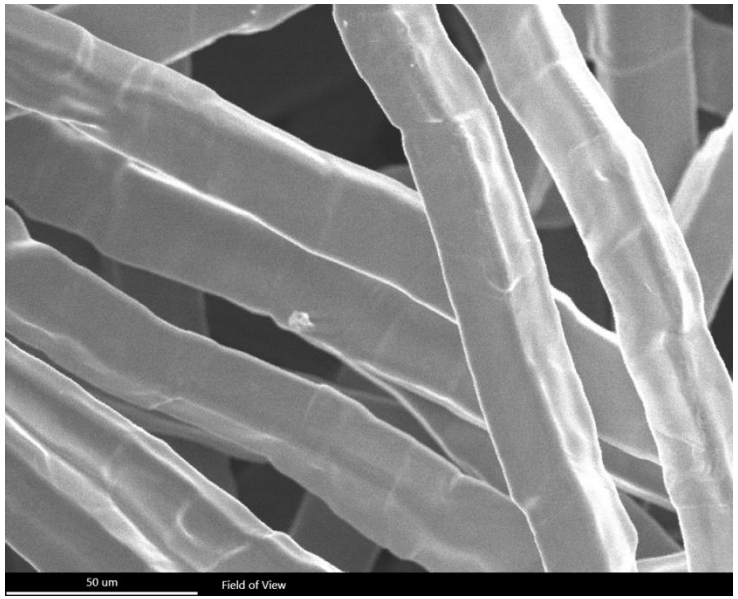


- Advantages
  - Good performance
  - "Industry Standard"
- Disadvantages
  - Thicker
  - Random pore morphology /Pore control difficulties
  - High Cost
  - Fiber penetration into membrane
  - Degradation of porosity and permeability
  - Difficult to integrate with other parts

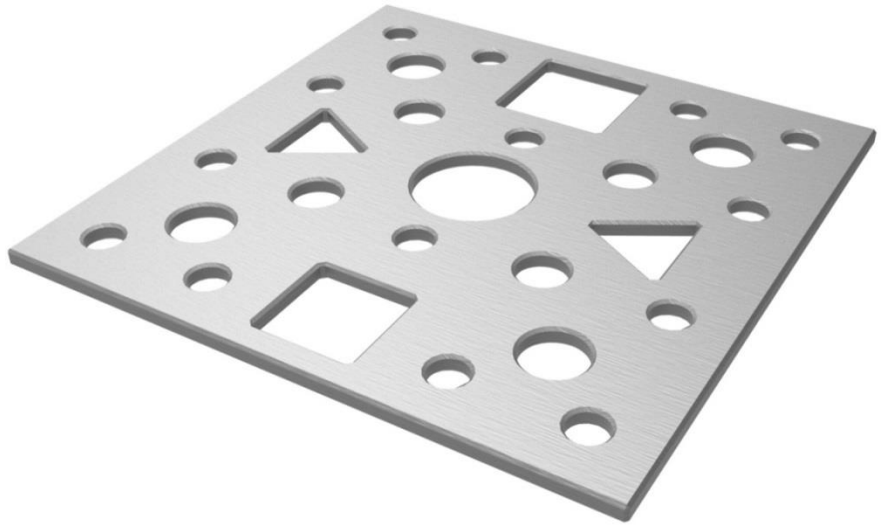
Stuart M. Steen III, Jingke Mo, Zhenye Kang, Gaoqiang Yang, and Feng-Yuan Zhang. *International Journal of Green Energy*, 2016 (in press)

Solutions: titanium and thin LGDLs with well-tuned pore parameters, smaller interfacial resistance and uniform distribution

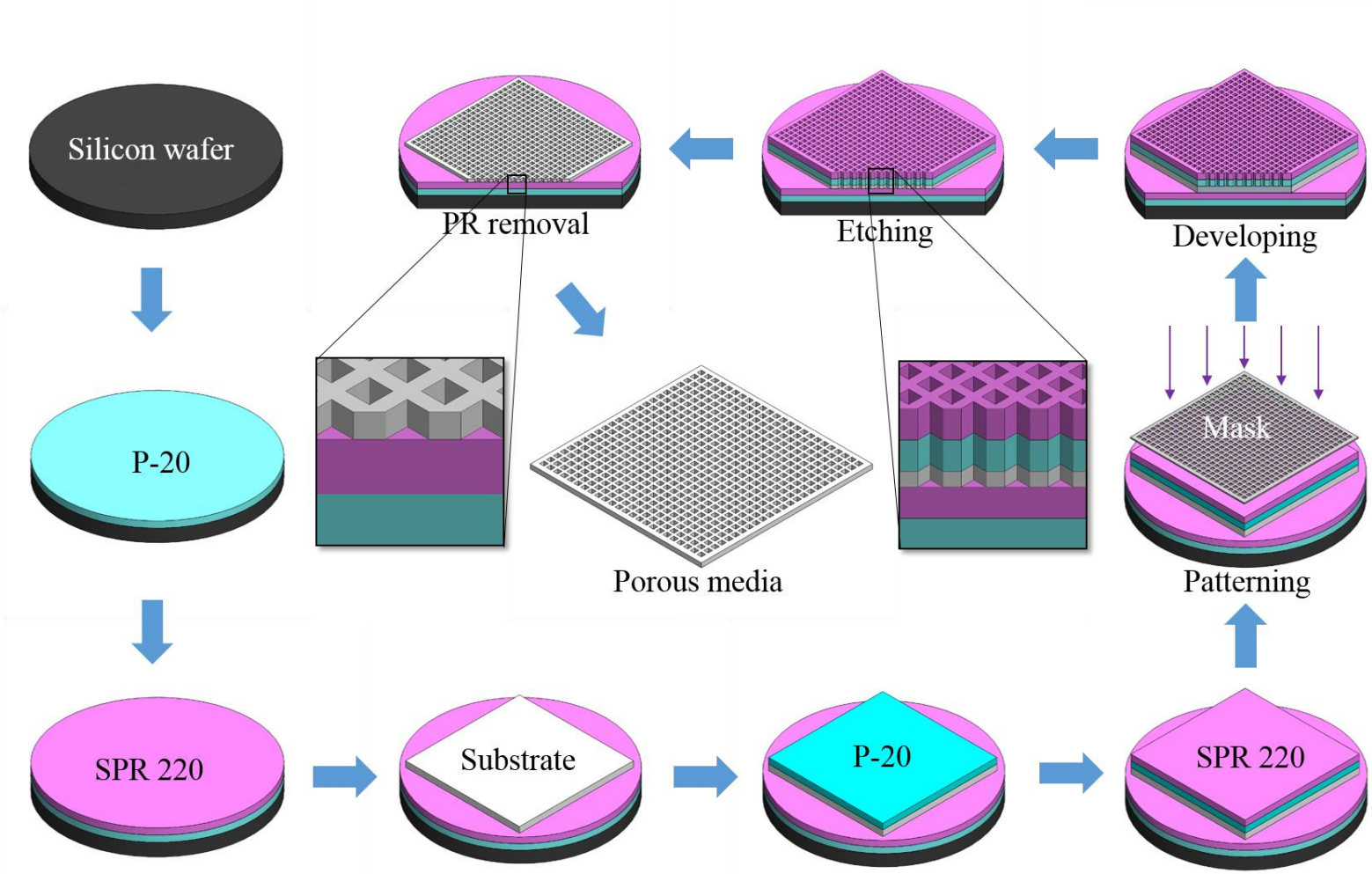
- Challenges: need multifunctional LGDLs with minimum losses of transport, electrical and thermal properties combined with high durability in oxidizing and reducing environments.



- Thinner (<0.05 mm)
- Controllable pore parameters, including pore size, shapes, porosity
- Smaller resistances
- Better thermal/electric distribution
- More catalyst utilizations
- Easy surface modification/component integration



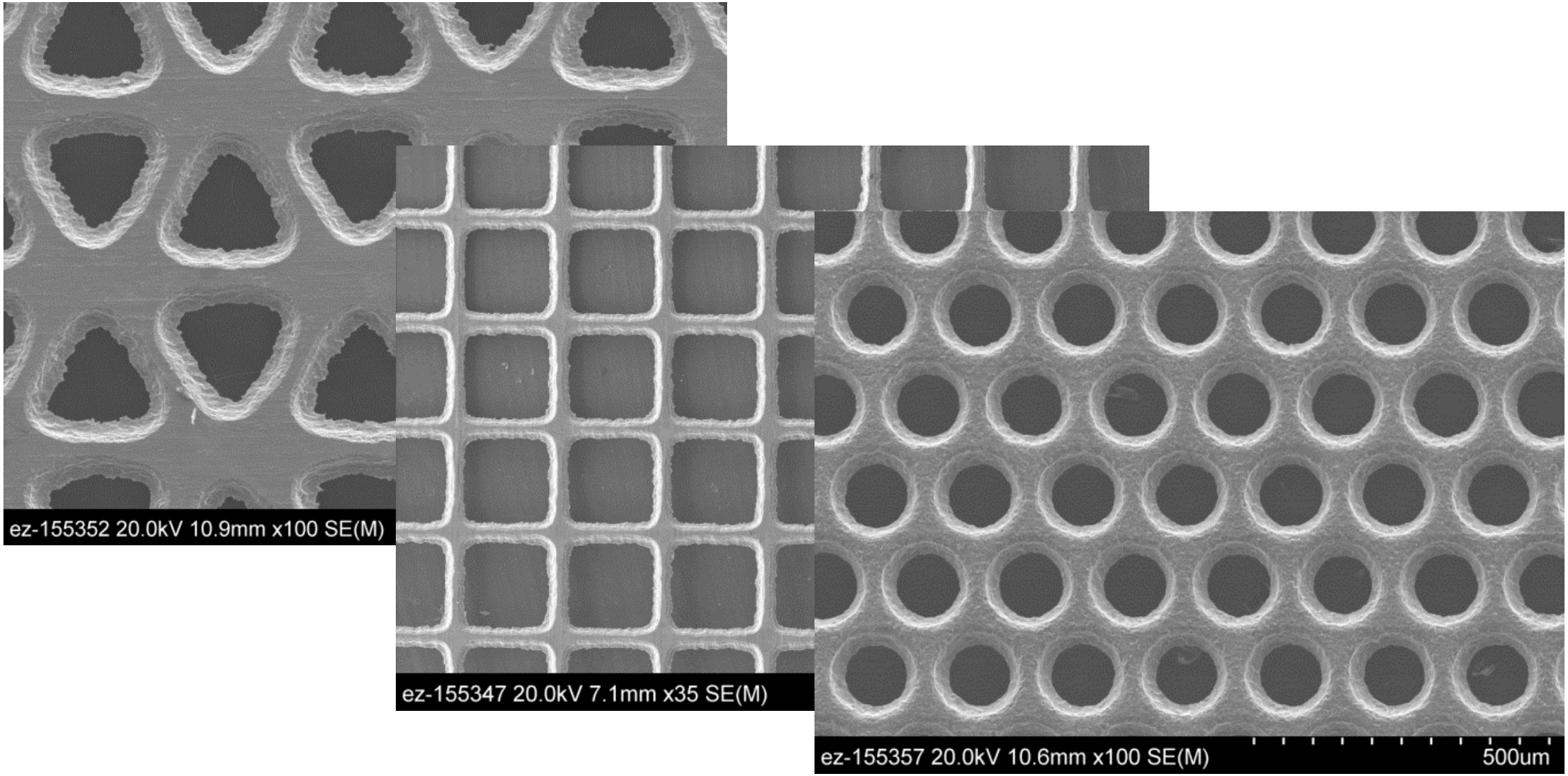
Mask Patterned Wet Etching: Low-cost and Well-controllable Fabrication Process for Thin LGDL and Current Distributor



OAK RIDGE National Laboratory
CENTER FOR NANOPHASE MATERIALS SCIENCES

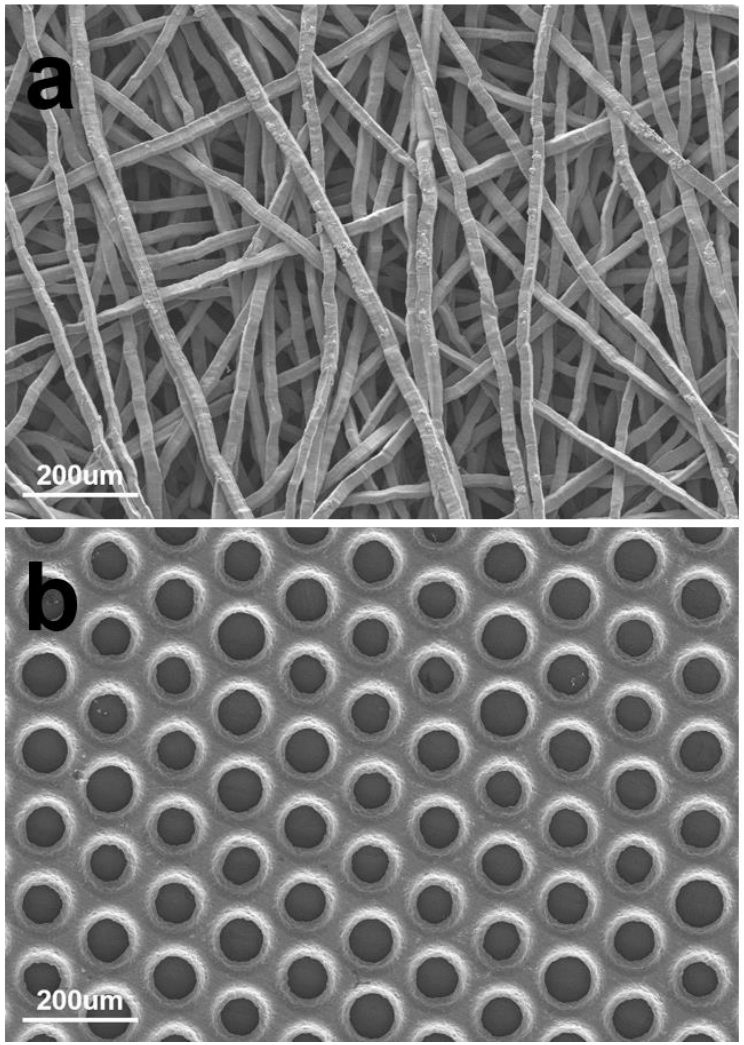
Jingke Mo, Stuart M. Steen III, S. Retterer, David A. Cullen, Alexander Terekhov, and Feng-Yuan Zhang, *ECS Transactions* 66, 3-10, 2015.

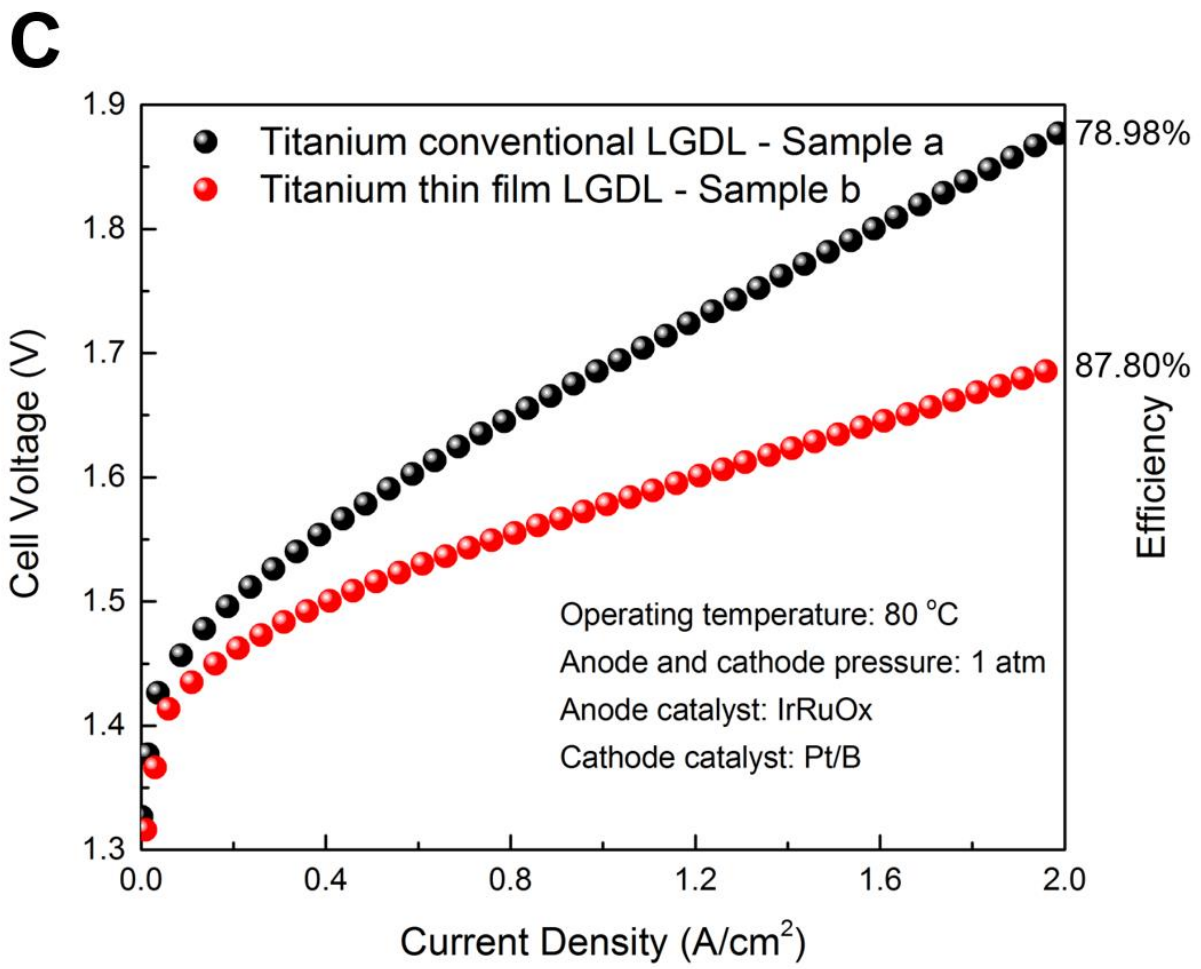
Thin LGDLs have been successfully fabricated with different design parameters



Jingke Mo, Stuart M. Steen III, S. Retterer, David A. Cullen, Alexander Terekhov, and Feng-Yuan Zhang, *ECS Transactions* 66, 3-10, 2015.

Excellent performance is obtained with developed thin LGDLs: about 10 % of efficiency improvement





Efficiency improved from 78% to 87% at a current density of 2.0 A/cm^2

Thickness is reduced from 350 µm to 25 µm

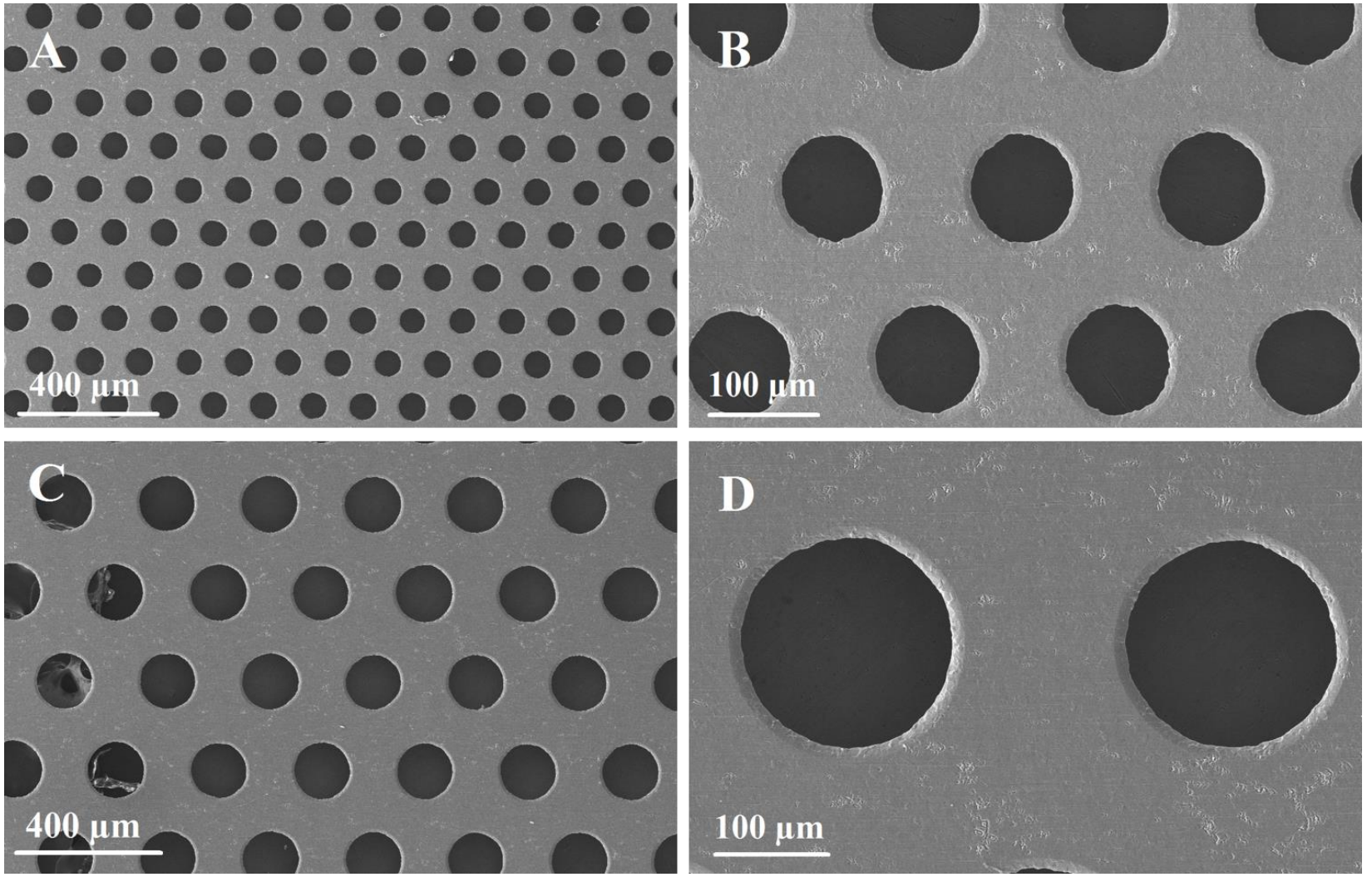
Jingke Mo, Zhenye Kang, Gaoqiang Yang, Scott T. Retterer, David A. Cullen, Todd J. Toops, Johney B. Green, and Feng-Yuan Zhang. *Applied Energy* **177**, 817-822, 2016.

Thin LGDLs with different pore morphologies

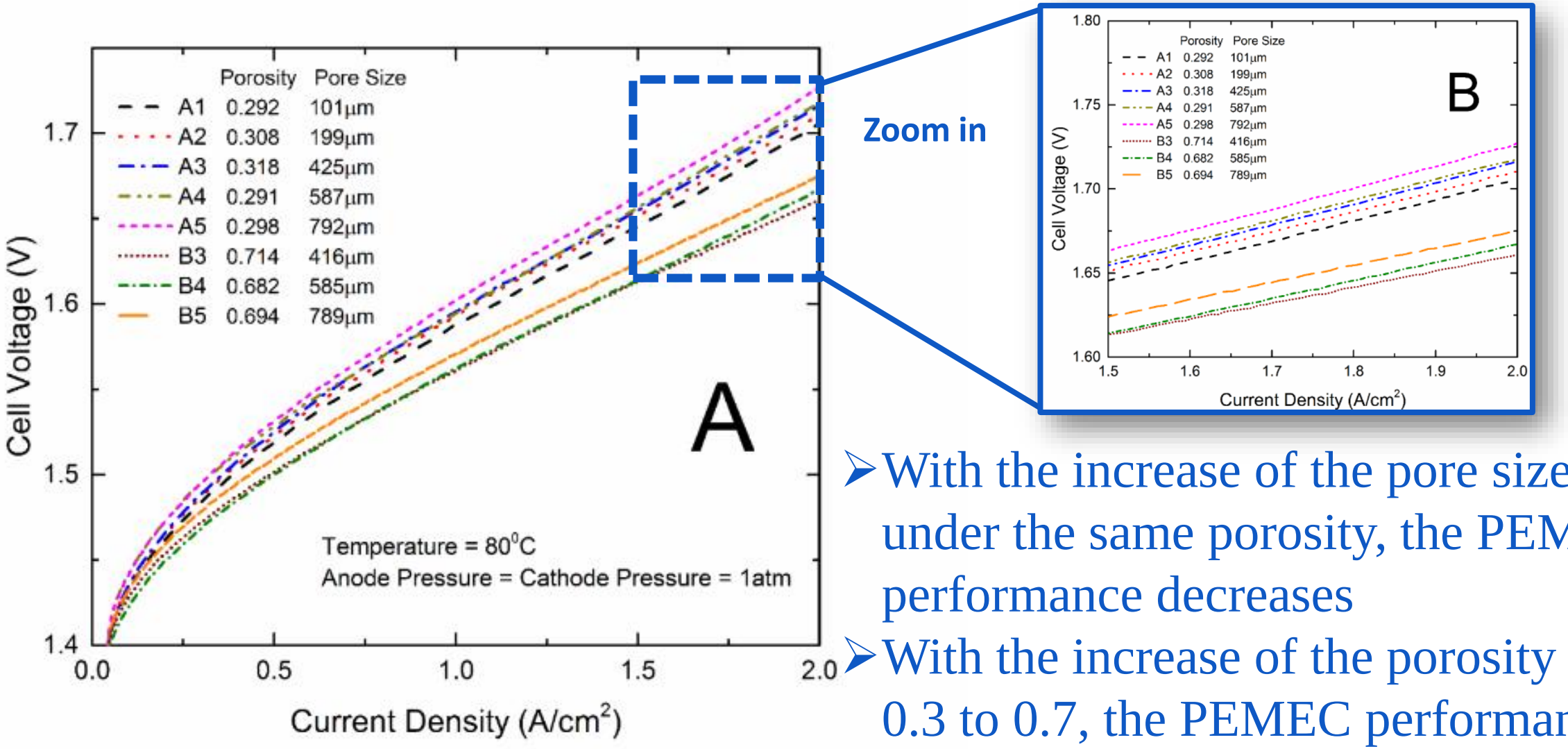
Index of the LGDL	Pore Size (D)[μm]	Land Length (L)[μm]	Calculated Porosity (ε)
A1	101.06	77.07	0.29
A2	199.11	142.41	0.31
A3	424.64	292.91	0.32
A4	586.96	448.51	0.29
A5	791.61	589.51	0.30
B3	415.51	52.74	0.71
B4	585.46	89.91	0.68
B5	789.16	113.21	0.69

Optimizations of thin and well-tunable titanium LGDLs

- Case I
  - Pore Size: 100 microns
  - Thickness: 25 microns
  - Porosity: 30%
- Case II
  - Pore Size: 200 microns
  - Thickness: 25 microns
  - Porosity: 30%



The impact of the pore size and porosity

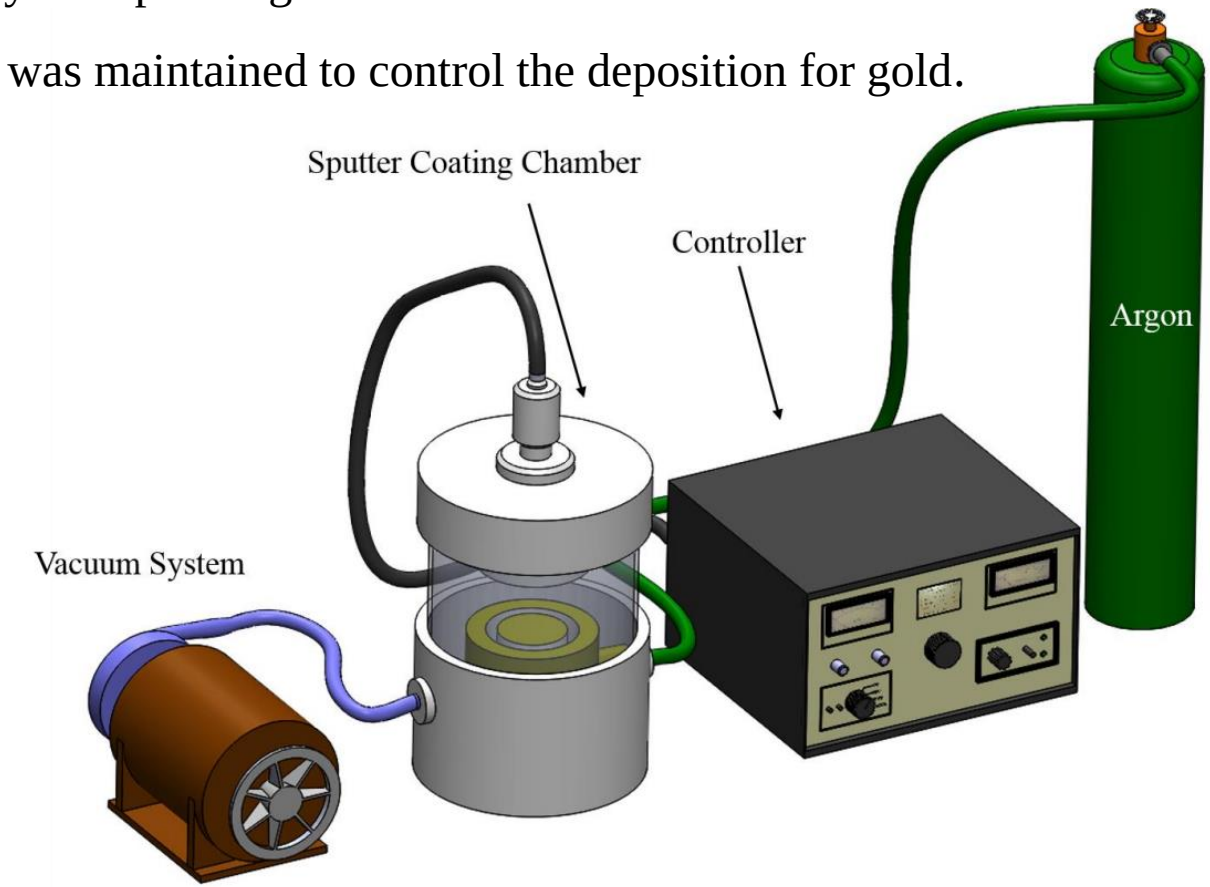


- With the increase of the pore size under the same porosity, the PEMEC performance decreases
- With the increase of the porosity from 0.3 to 0.7, the PEMEC performance is improved

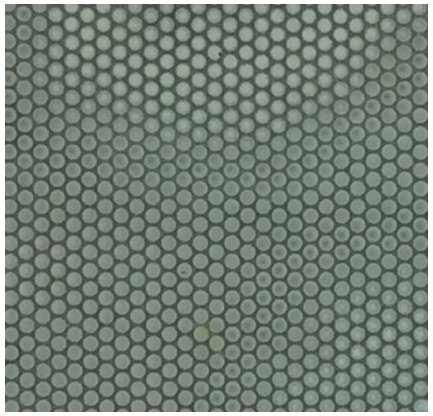
Kang, Z., J. Mo, G. Yang, S.T. Retterer, D.A. Cullen, T.J. Toops, J.B. Green, M.M. Mench, and F.-Y. Zhang, *Energy & Environmental Science* 2016. DOI: 10.1039/C6EE02368A

Surface Modification of Thin LGDLs with Advanced Micro/Nano Manufacturing Method

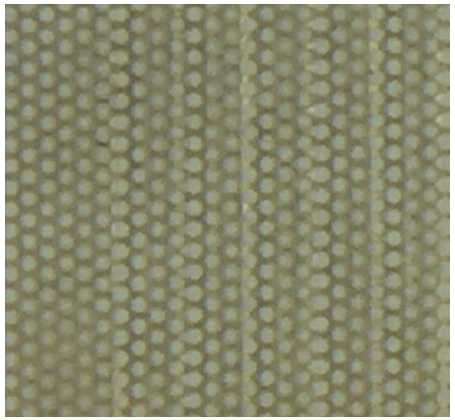
- Sputter coating
  - The thin/well tunable titanium LGDLs were used as a substrate for gold sputter deposition.
  - The thickness of the coating was controlled by the operating time.
  - A potential of 2.4 kV and a current of 20 mA was maintained to control the deposition for gold.
- Electroplating
  - electro-cleaning
  - electro-striking
  - electro-plating



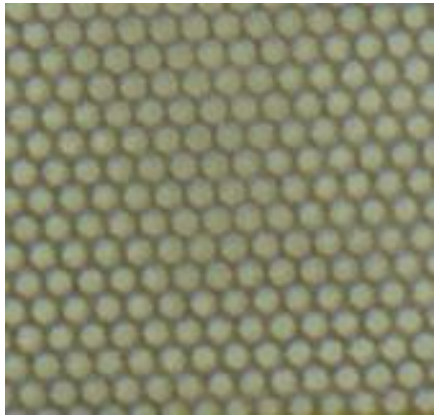
Photos and SEM Images of fresh and Surface Modified Thin LGDLs



Fresh Thin LGDL



Au Sputter Deposited



Au Electroplated

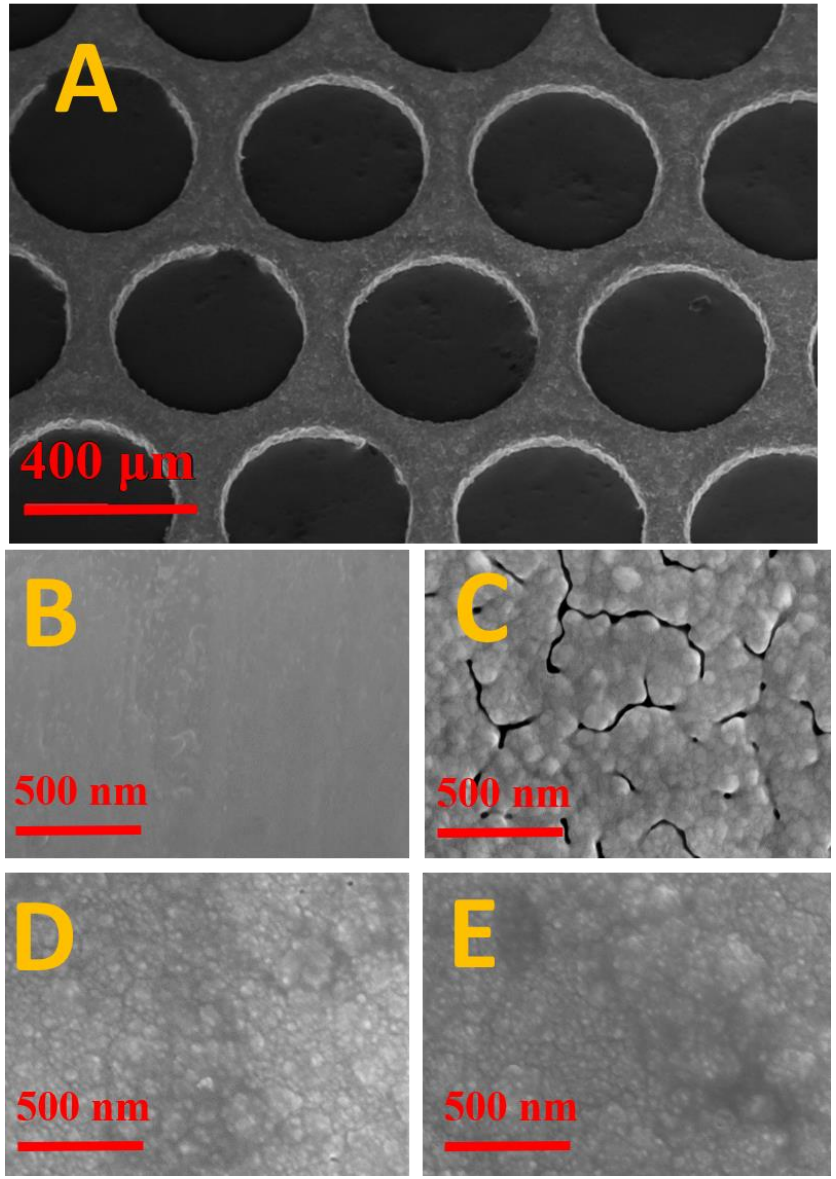
(A) Low magnification for fresh titanium thin LGDL with a pore diameter about 414 µm and porosity about 0.62

(B) Surface characterization of fresh titanium thin LGDL

(C) Surface characterization of thin LGDL with about 179 nm thickness gold by sputter coating

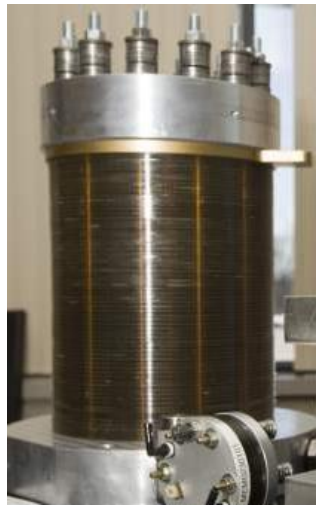
(D) Surface characterization of thin LGDL with about 186 nm thickness gold by electroplating

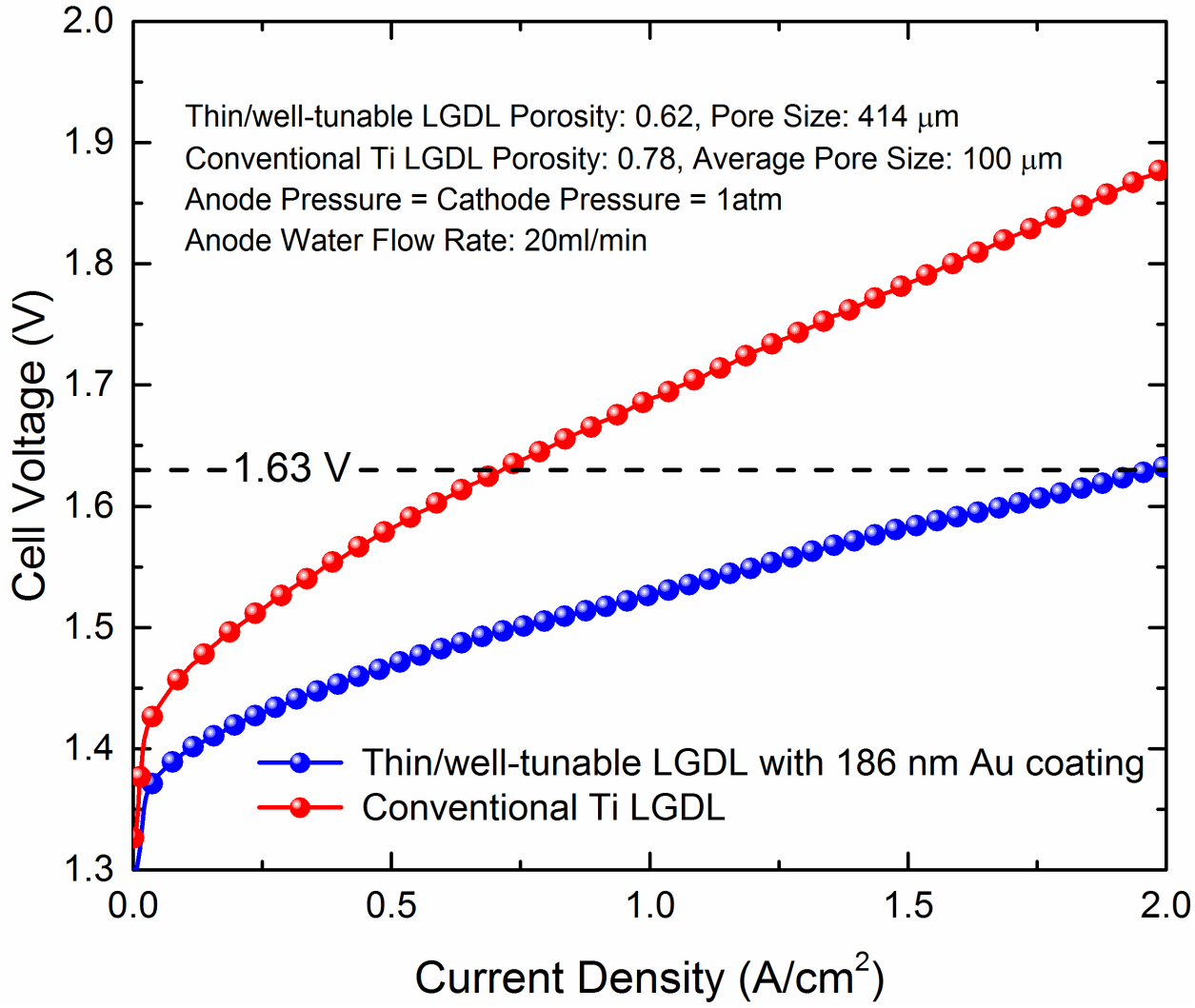
(E) Surface characterization of thin LGDL with about 826 nm thickness gold by electroplating



Volume/cost of cell stack will be reduced more than 50%

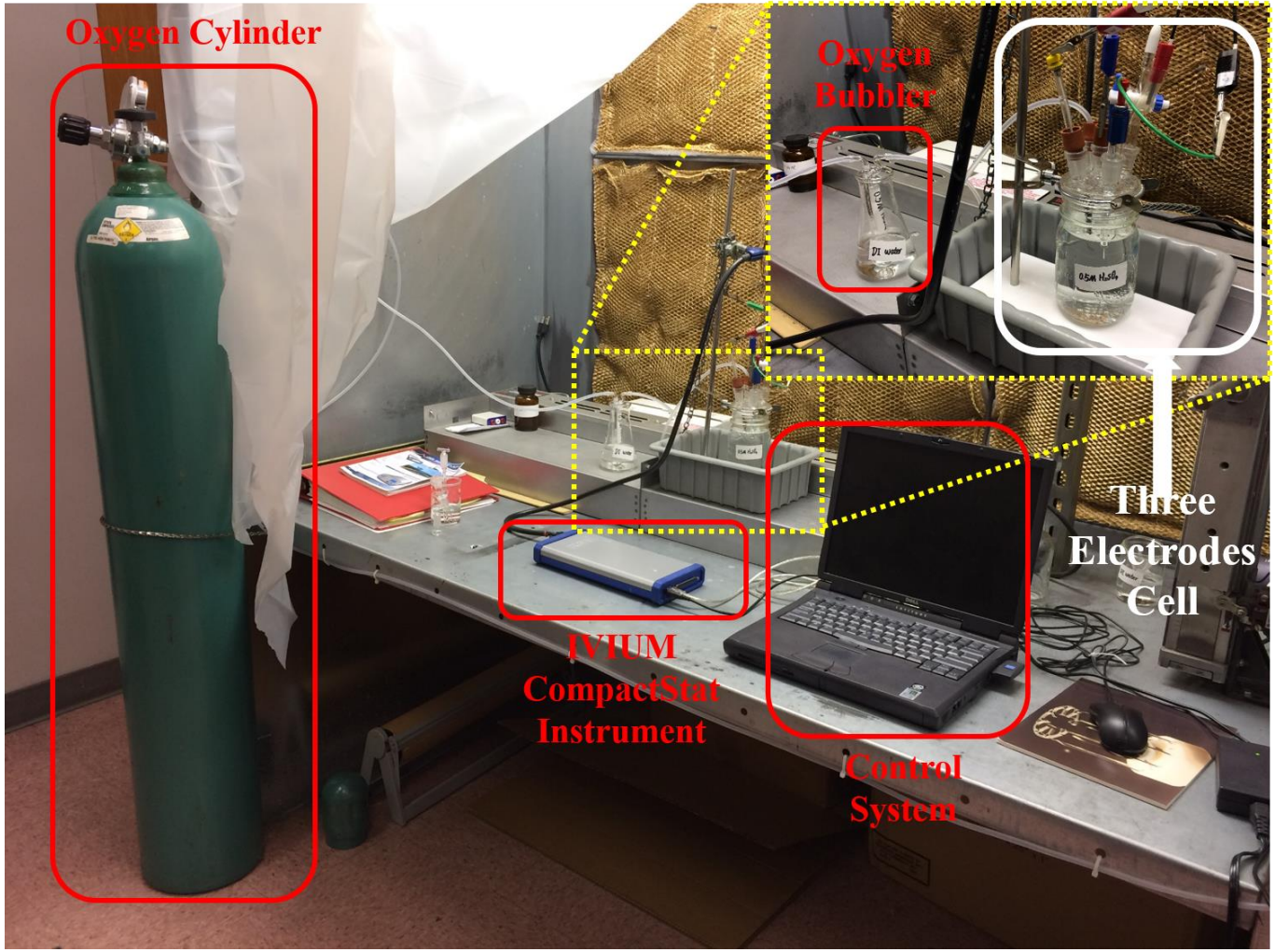
- The current density of surface modified thin LGDLs can achieve 2.0 A/cm^2 at 1.63 V. The conventional Ti Felt can only have 0.717 A/cm^2 at 1.63 V.
- The hydrogen generation rate can be improved almost **2.79 times** than conventional Ti felt.
- The stack size can be significantly reduced by the surface modified thin LGDLs.



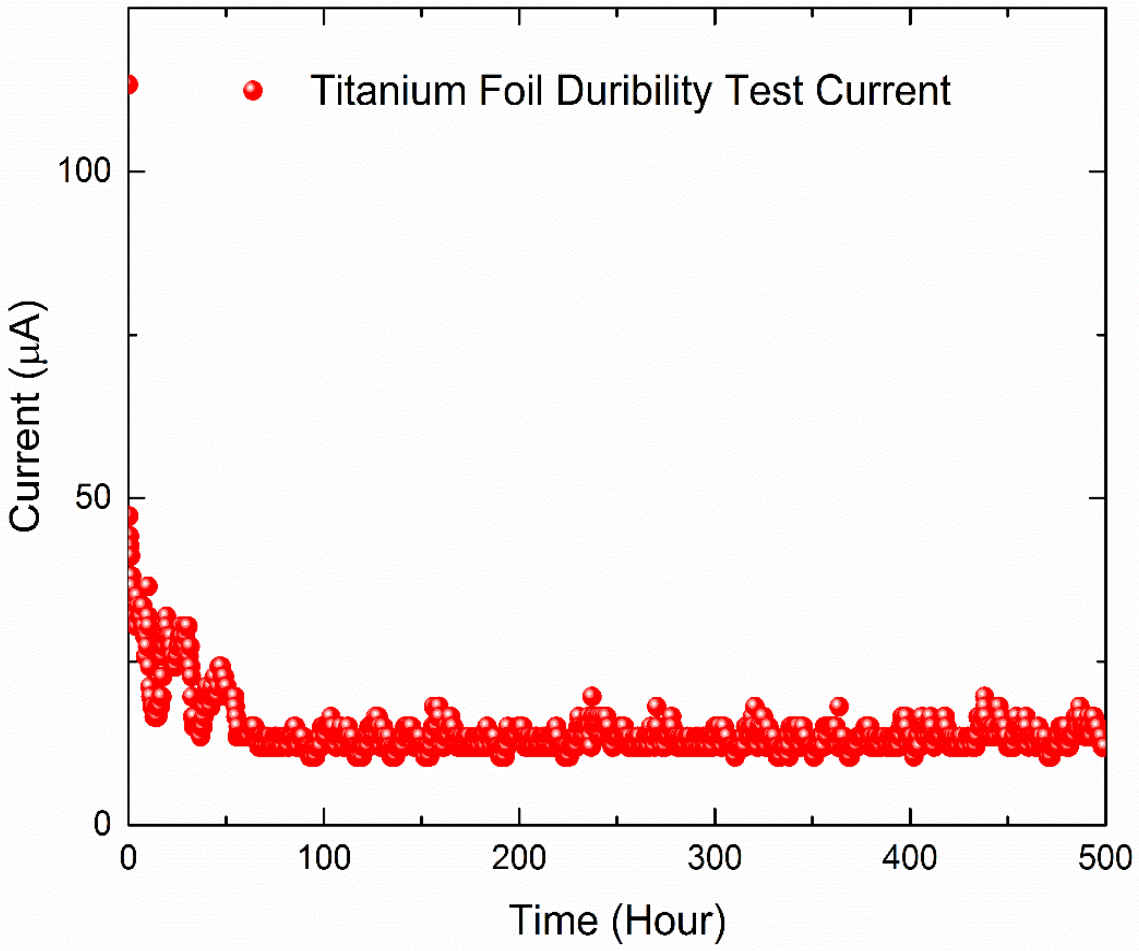


In-house *Ex-situ* Durability Test Set-up

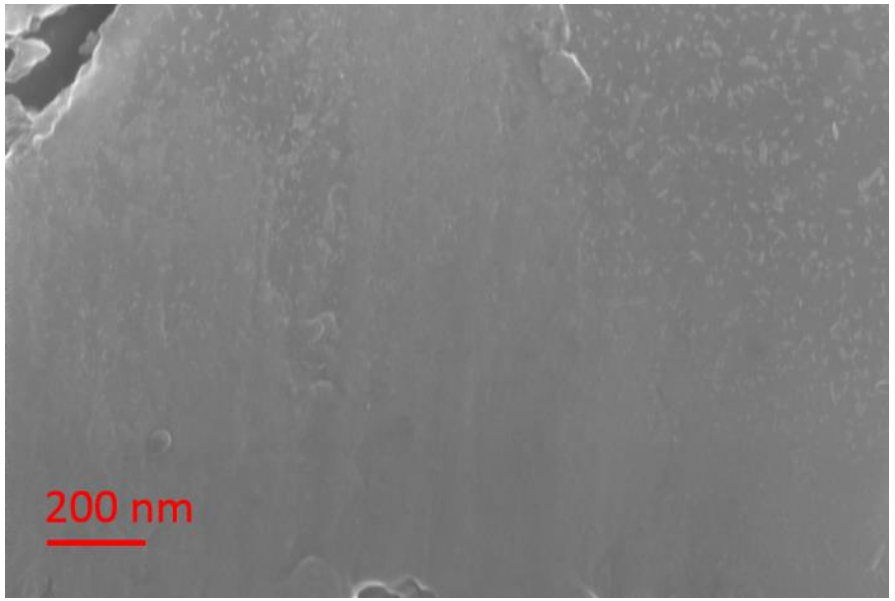
- The electrochemical durability tests are carried out in a three-electrode cell:
  - Working electrode
  - Counter electrode
  - Reference electrode
- The other components of the test system include:
  - Oxygen supply system
  - Testing instrument-pototentiastat
  - Computer with control terminal and software

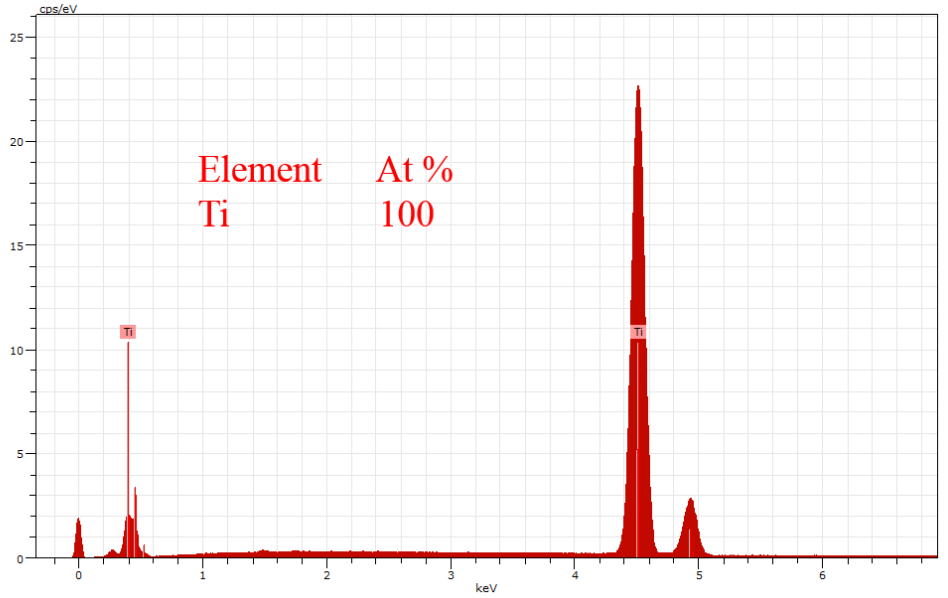


Ex-situ Durability Test Results



Chronoamperometric characteristics at 1.9 V *vs*. Ag/AgCl of anodized titanium foil at room temperature in O_2 saturated 0.5 M H_2SO_4 solution



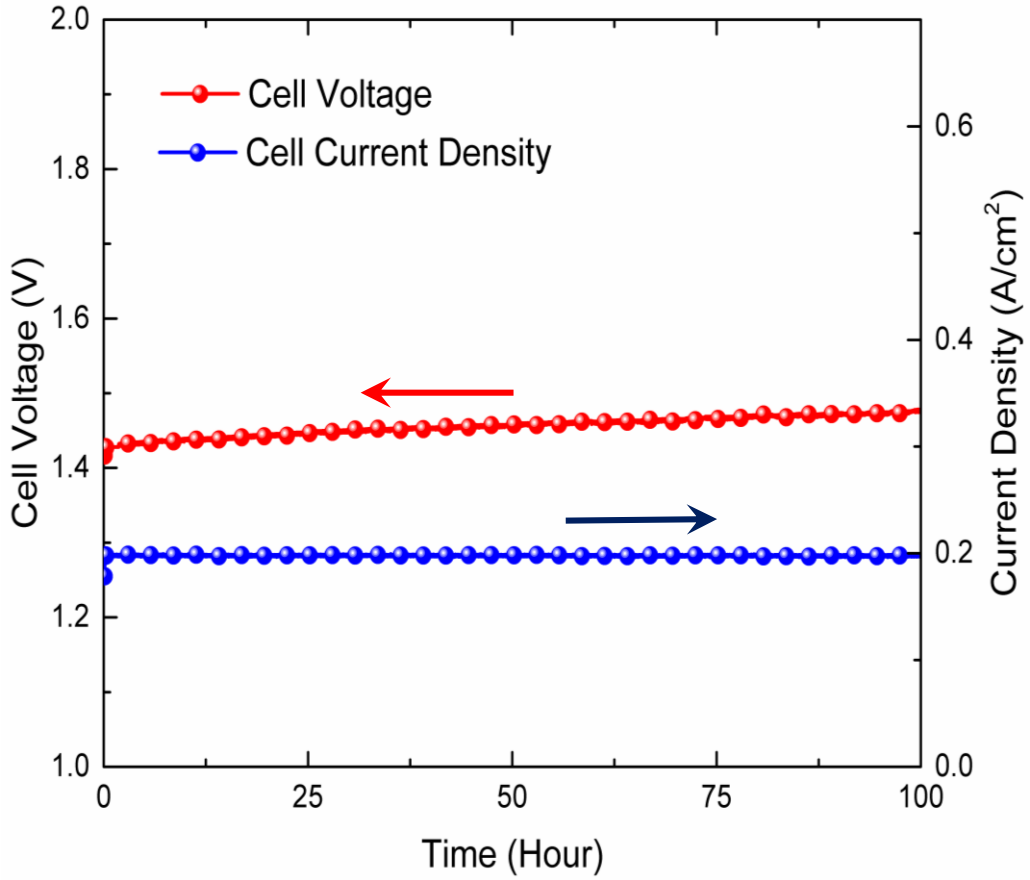


Durability of the Surface Modified Thin LGDLs

- The cell voltage of the PEMECs with electroplated thin LGDL is very stable, which remains at ~1.45 V without any obvious cell voltage decay during the 100 hours test.

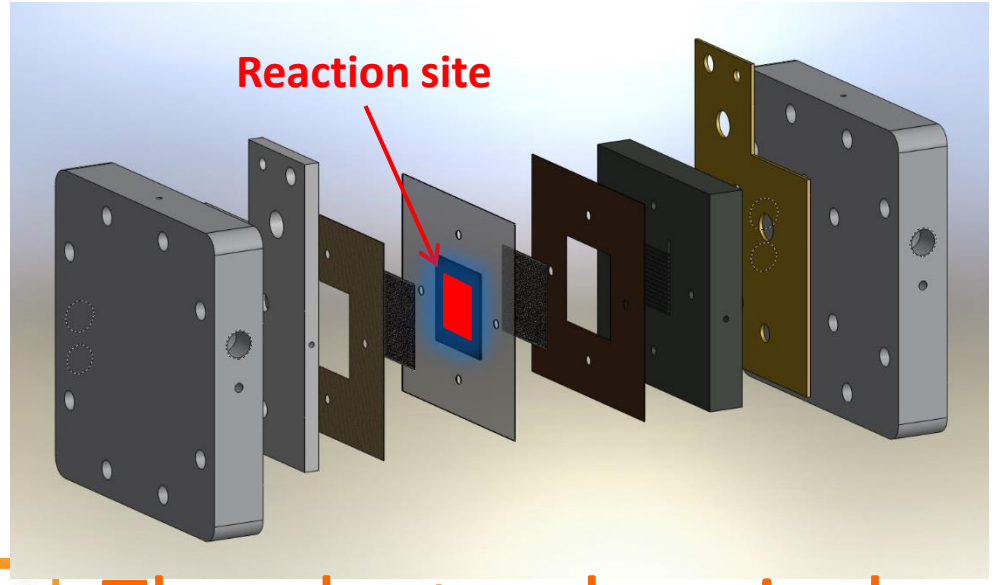
- The slightly deterioration of the performance from 1.43 V to 1.47 V may due to the degradation of membrane electrode assembly (MEA) during the test.

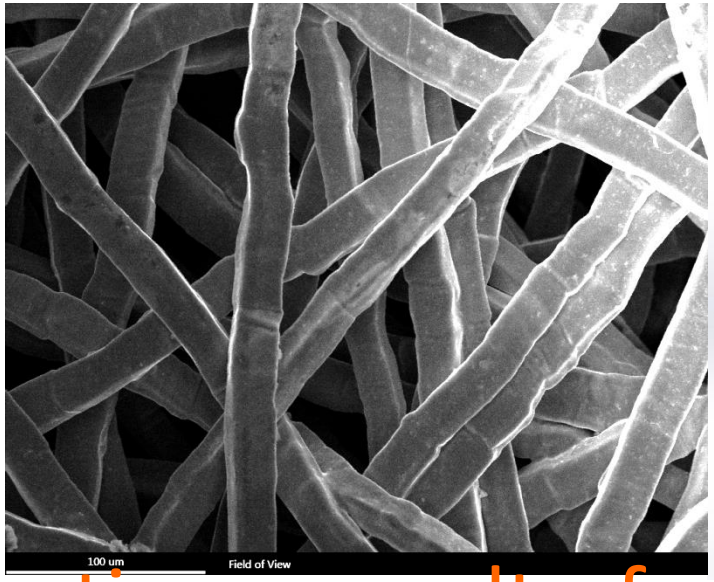
- An ultra-thin Au layer that is electroplated on the thin/well-tunable LGDLs will significantly improve the performance and efficiency of the PEMECs, which is also very stable.

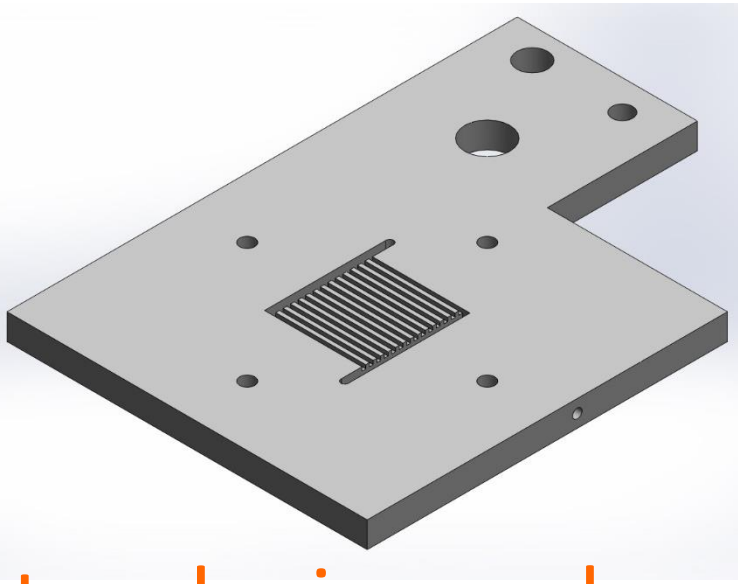


Thin and well-tunable LGDLs with straight pores make it possible to *in-situ* investigate electrochemical reactions

- The electrochemical reaction sites on CLs are next to the center part of PEM and located behind LGDLs, current distributor with flow channel and end plate
- LGDLs are typically made of titanium fibers in random pore morphology interconnected and complicated structures in the current LGDLs
- Current distributors are made from titanium to resist the high potential and oxidative environment



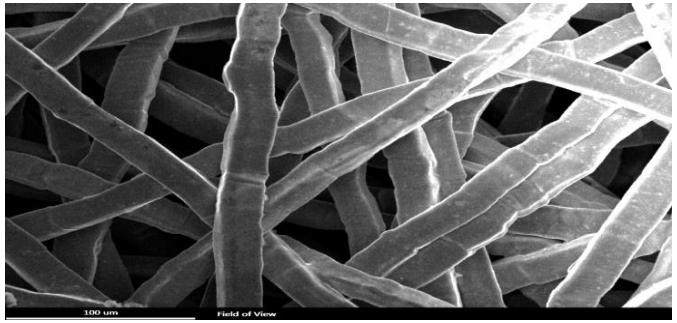


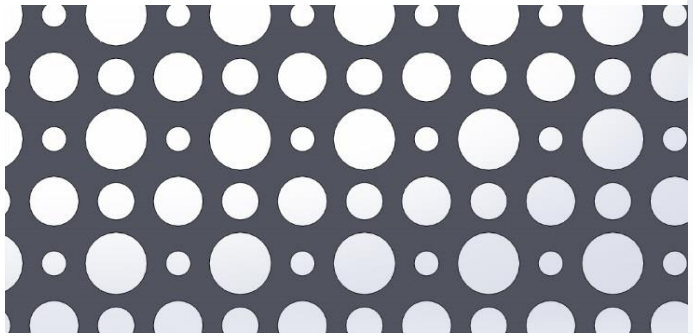


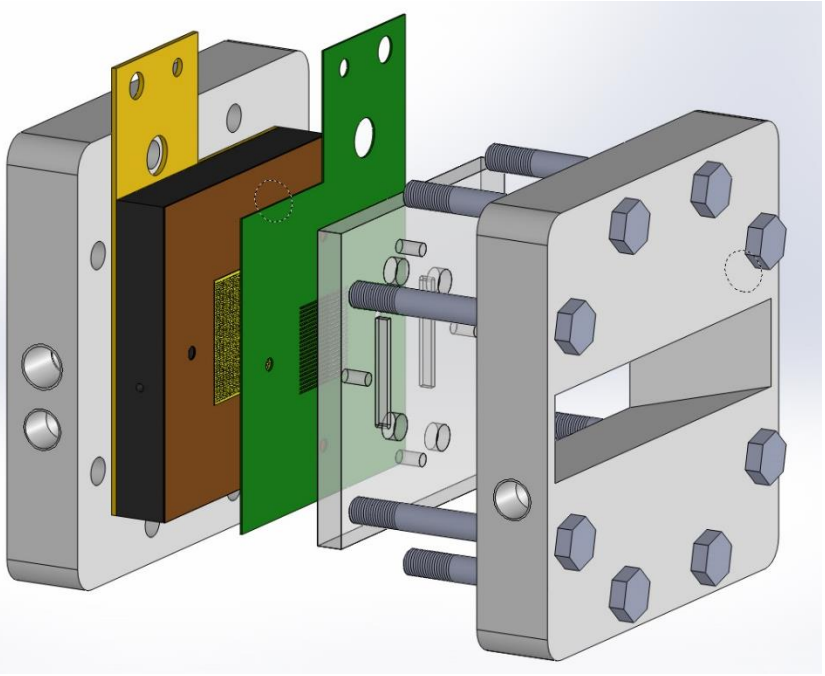
The electrochemical reactions are ultrafast and microscale

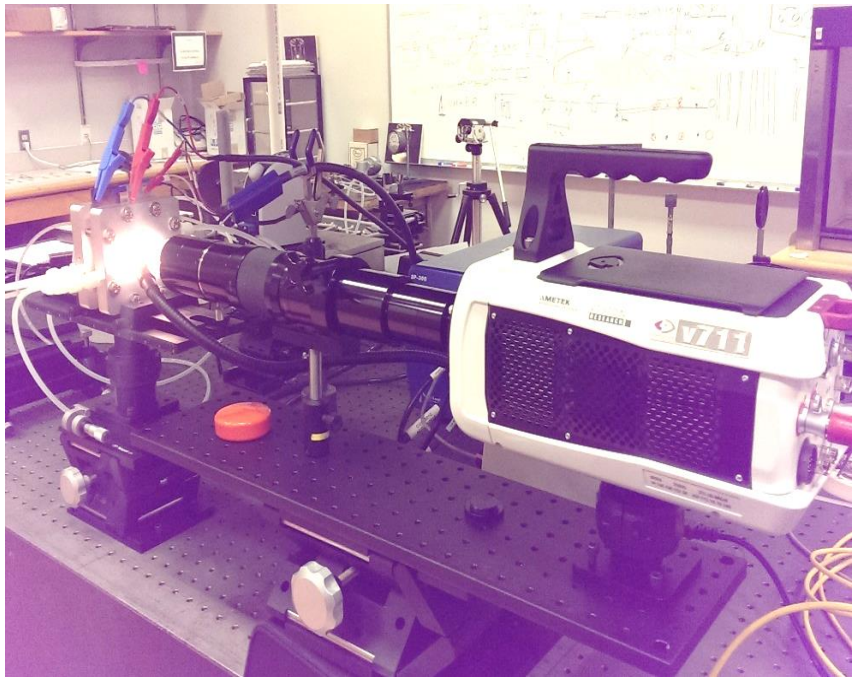
In-situ visualization with developments of novel LGDLs, transparent PEMFCs and high-speed/microscale system

- Fabricate well-tunable transport LGDLs with straight pores
- Design a transparent PEM Electrolyzer Cell
- Develop a high-speed and micro-scale visualization system with large working distance



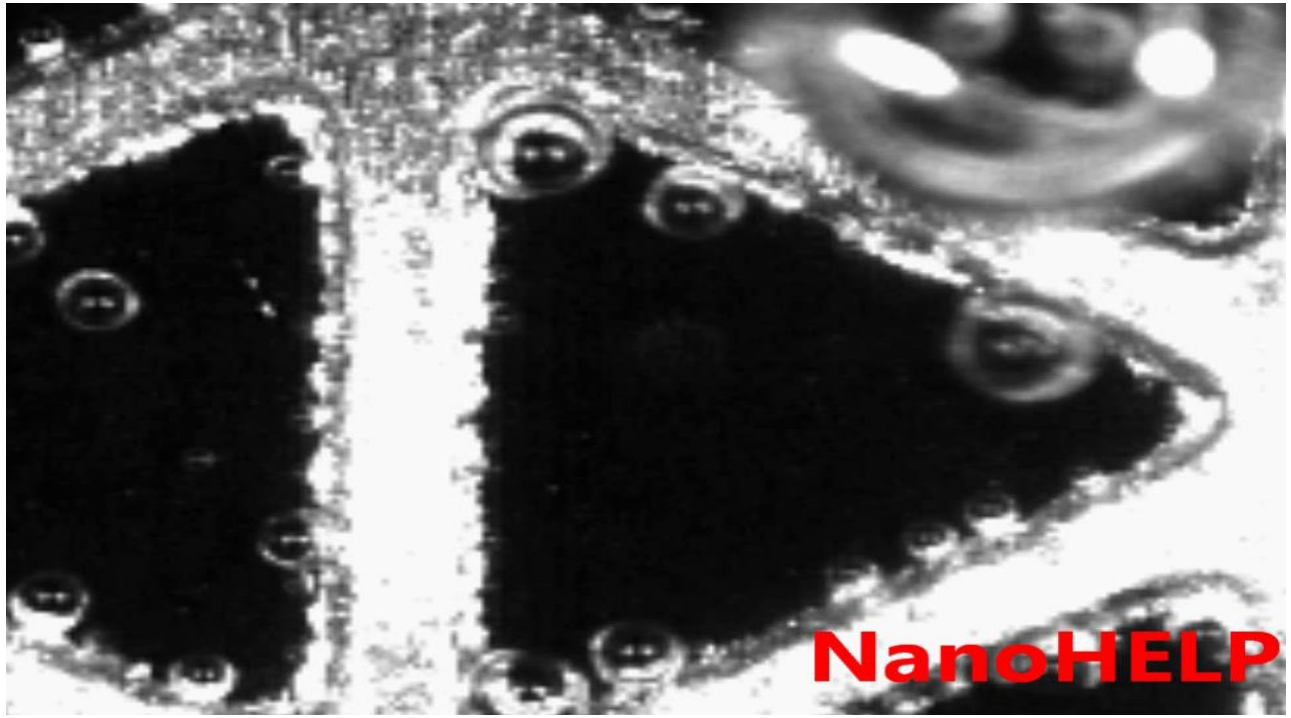


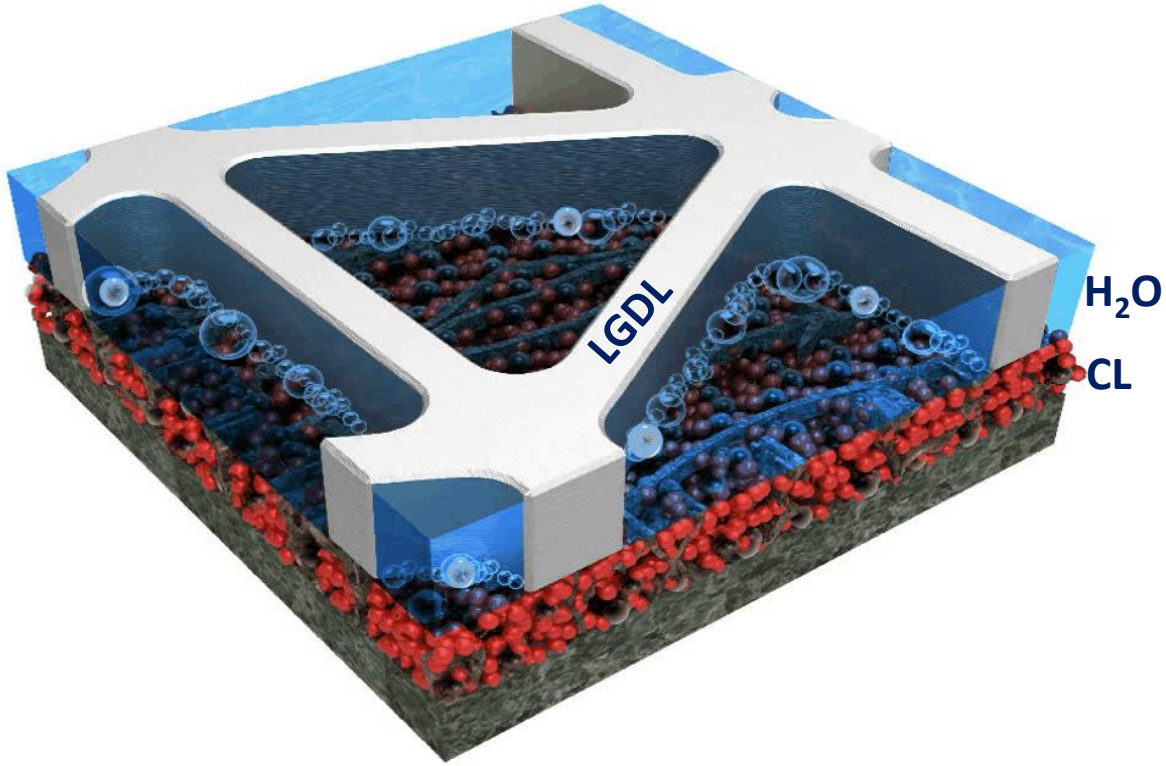




First-ever revealing the true nature of multiphase interfacial electrochemical reactions in micro porescale with microsecond time resolution

- Speed: up to 1,400, 000 fps (better than 0.8 µs time resolution)

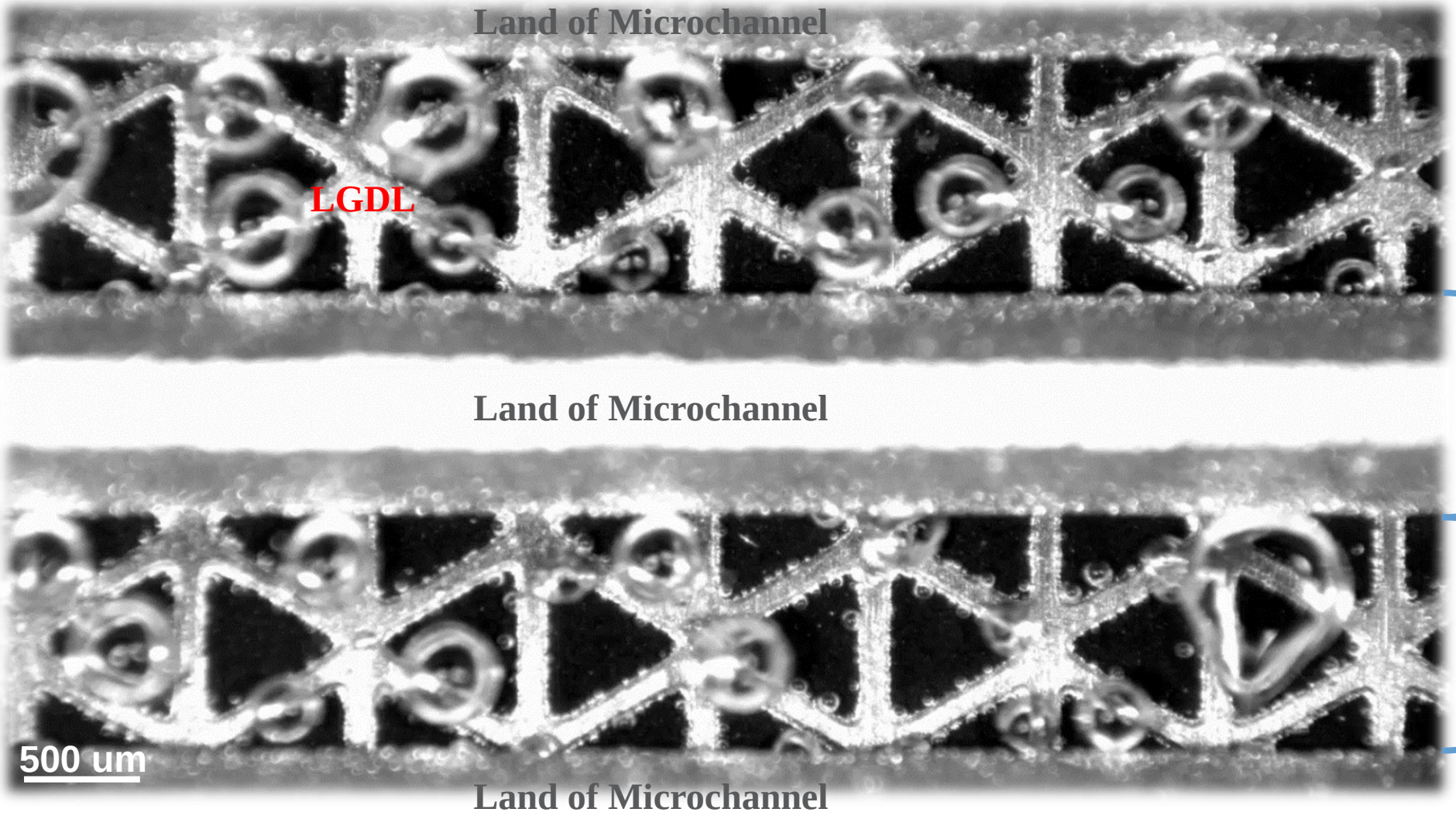




***In-situ* micro reaction - oxygen bubble generation from water(7,500 fps)**

small portion of catalyst function as designed and great opportunity for cost reduction

- Reactions at anode side: $2H_2O \xrightarrow{catalyst} O_2 + 4H^+ + 4e^-$



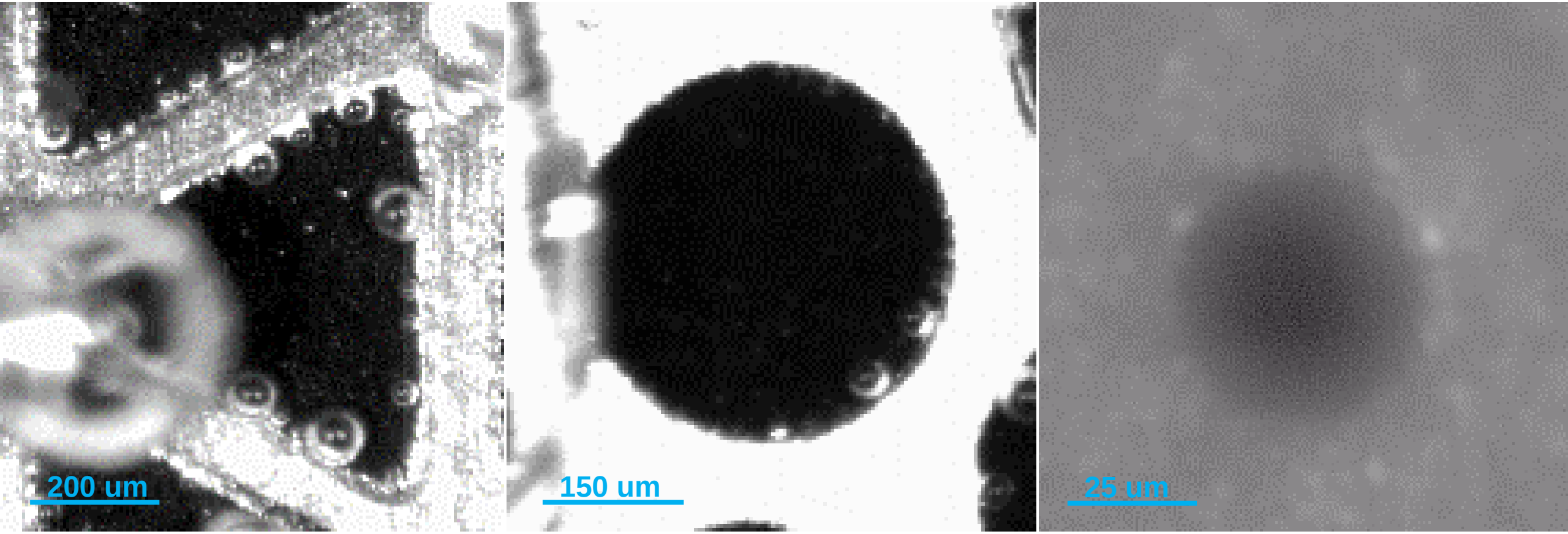
Deionized water full filled the microchannel and flow from right to left

Land of Microchannel 1 mm height

Microchannel 1 mm height 500 um depth

Jingke Mo, Zhenye Kang, Scott T. Retterer, David A. Cullen, Todd J. Toops, Johney B. Green Jr, Matthew M. Mench, and Feng-Yuan Zhang. Science Advances **2**(11), e1600690, 2016.

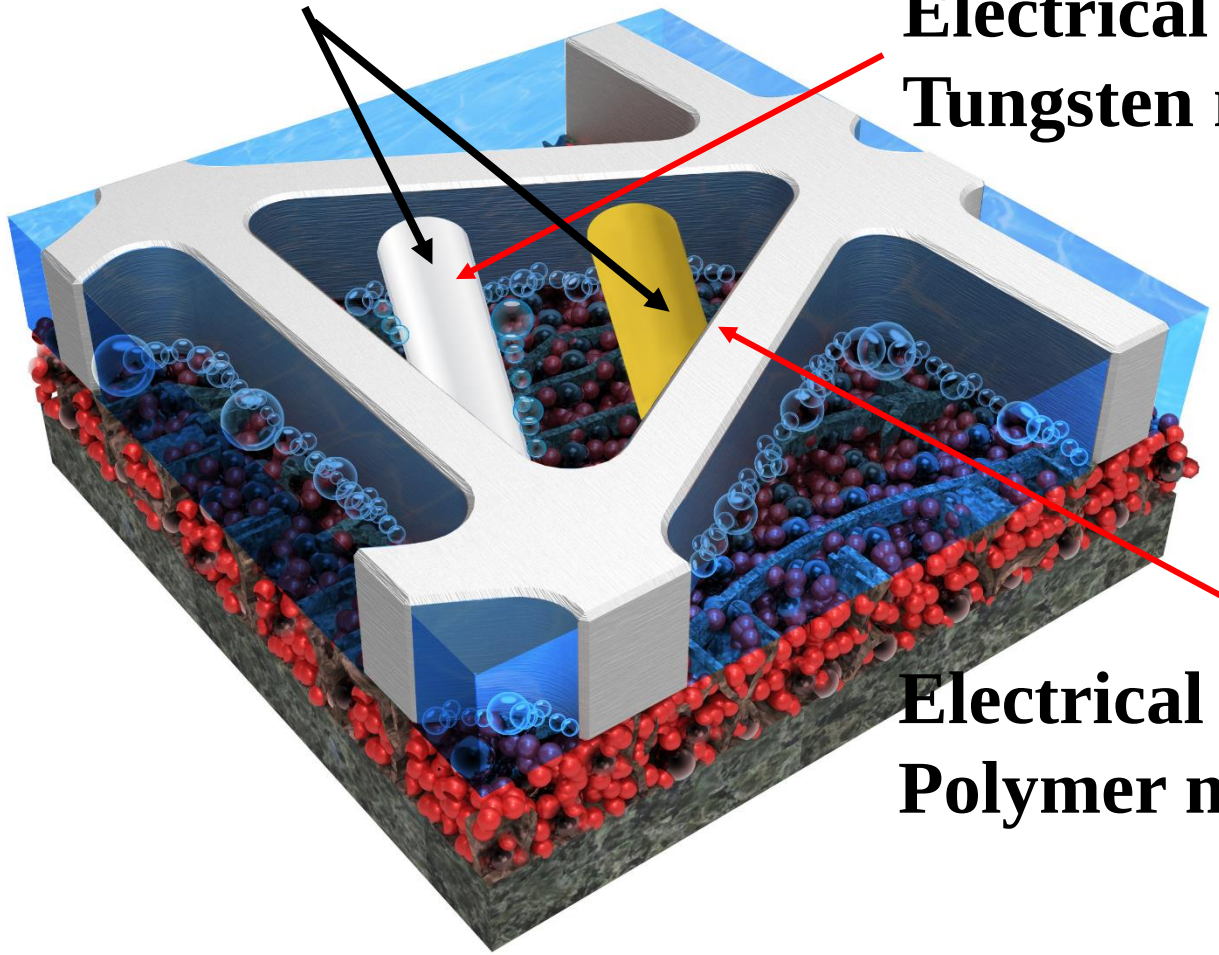
Discovery: Electrochemical Reactions Only Occur at the Interface of LGDLs and CL Instead of Entire Catalyst Layer



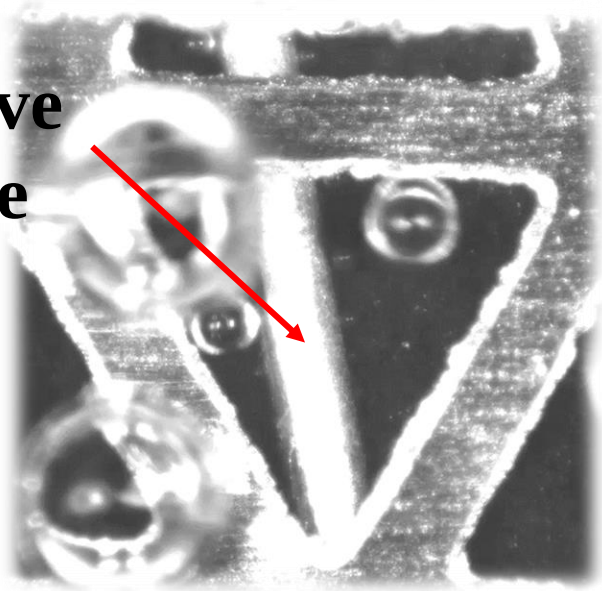
Operation conditions: current density: 2A/cm^2, pressure: 1 atm, temperature: 20 ^{o}C

Bubble nucleation sites = reaction sites ?!

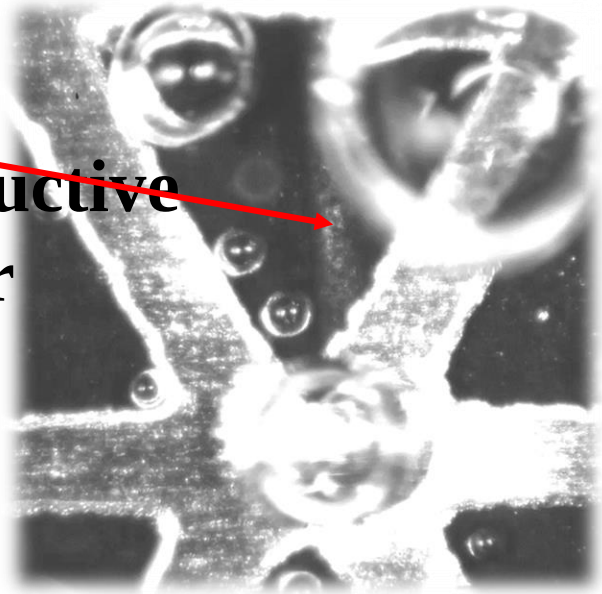
Similar nucleation conditions



Electrical conductive
Tungsten microwire

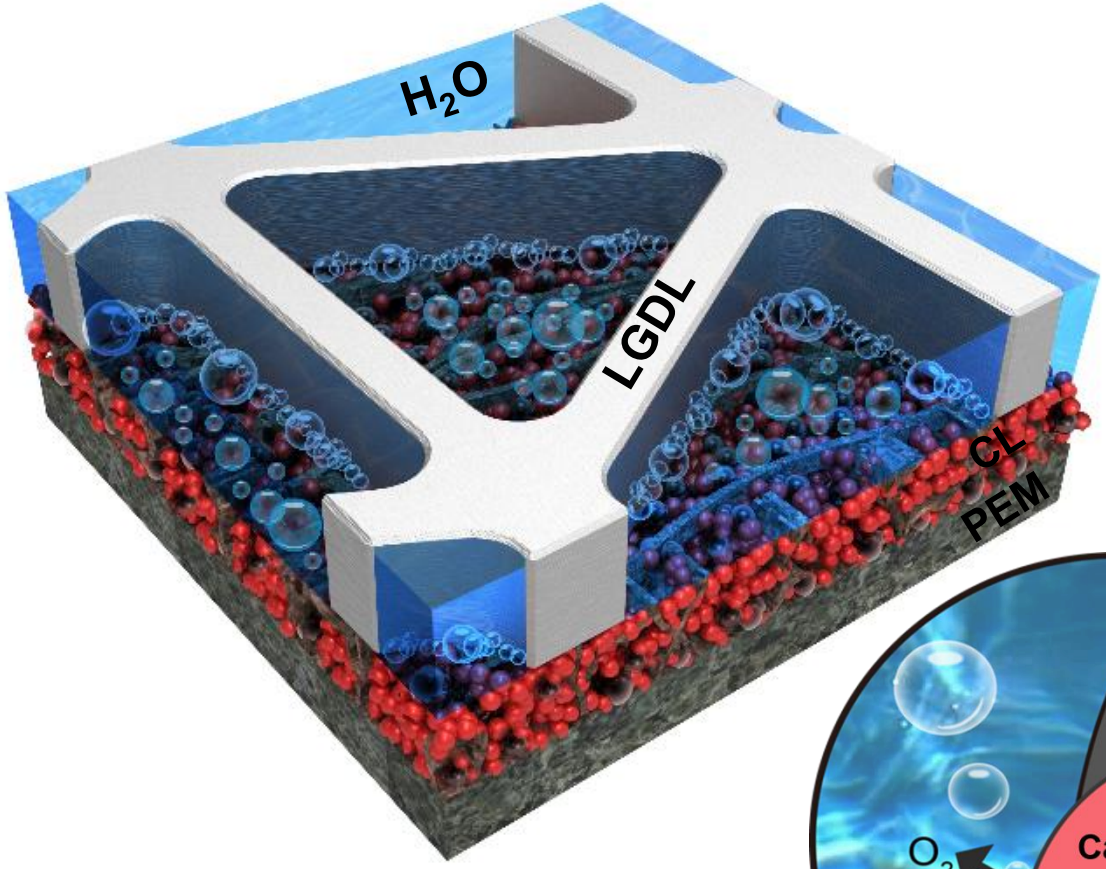


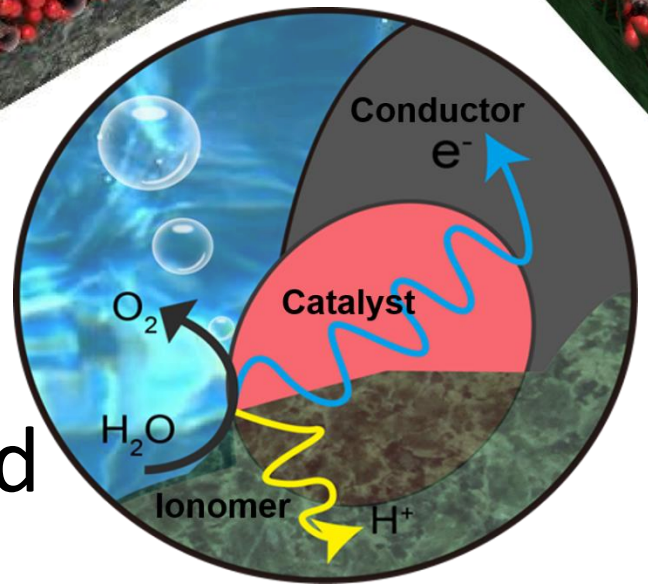
Electrical nonconductive
Polymer microfiber

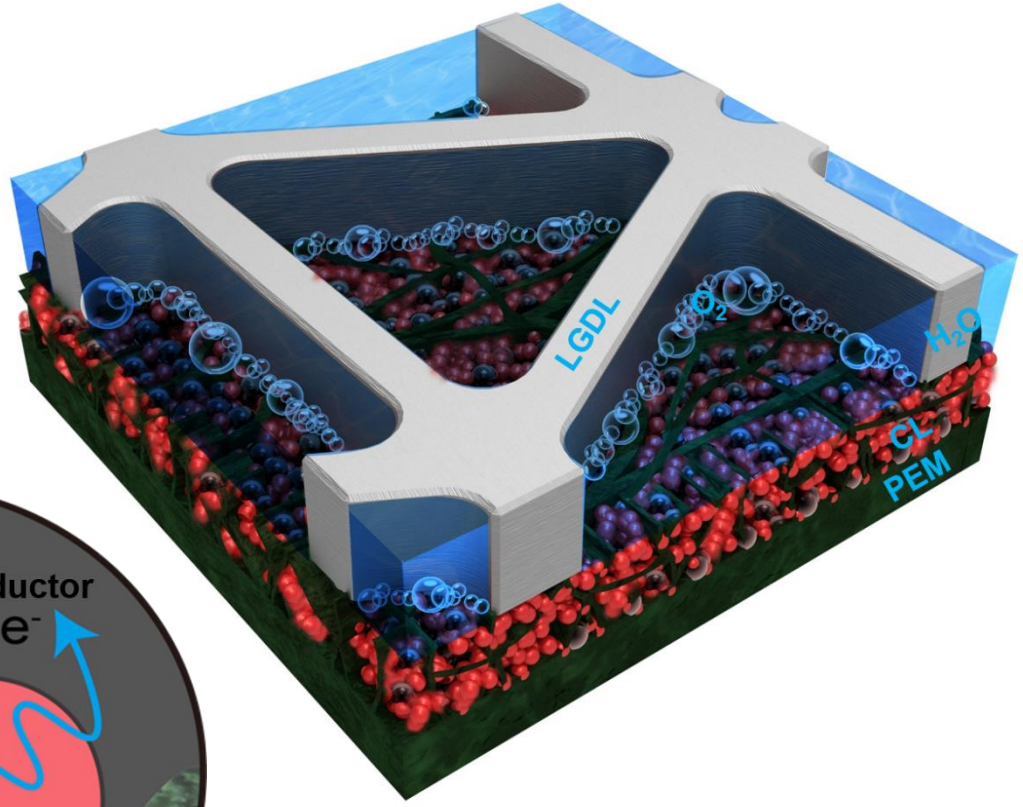


The oxygen bubble generate along with the tungsten wire (conductive), while no bubble generate along with polymer fiber (nonconductive)

Triple Phase Boundary Reactions in PEMEC—significant catalysts were not functioned as expected and designed





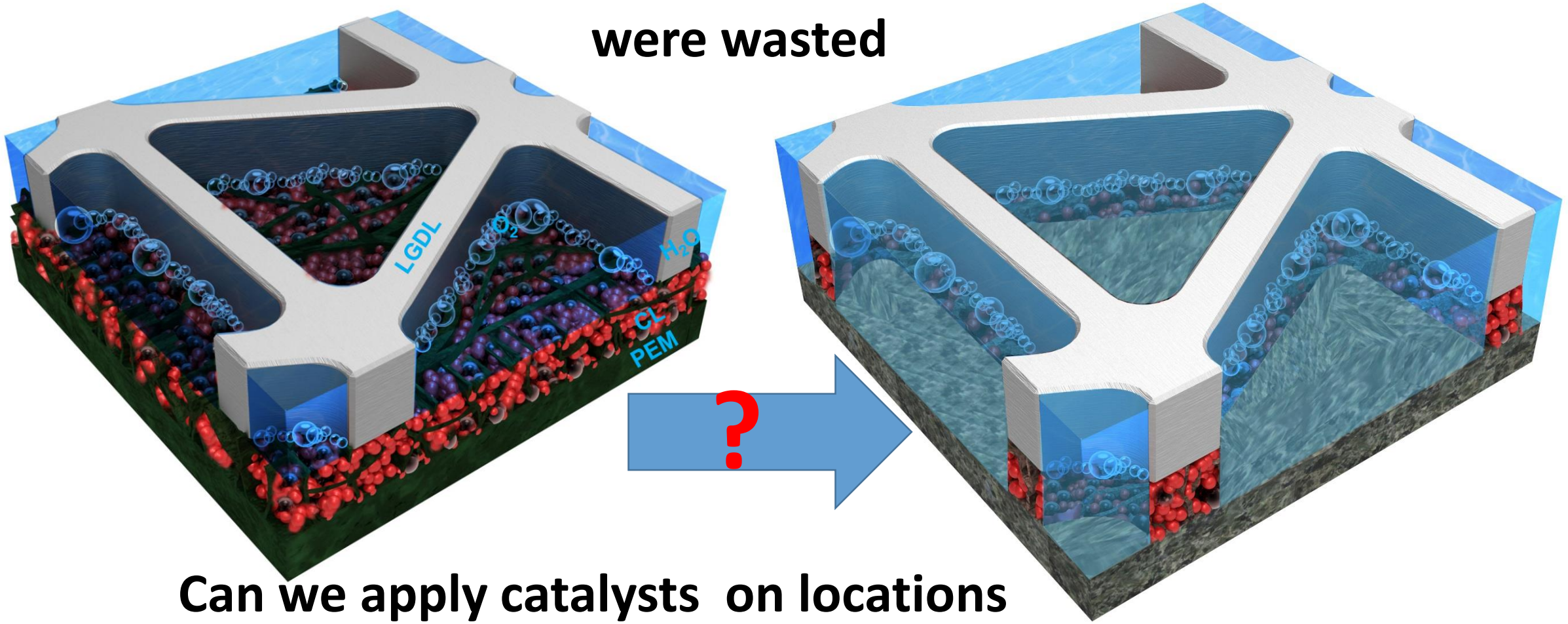


Designed and assumed

True reactions

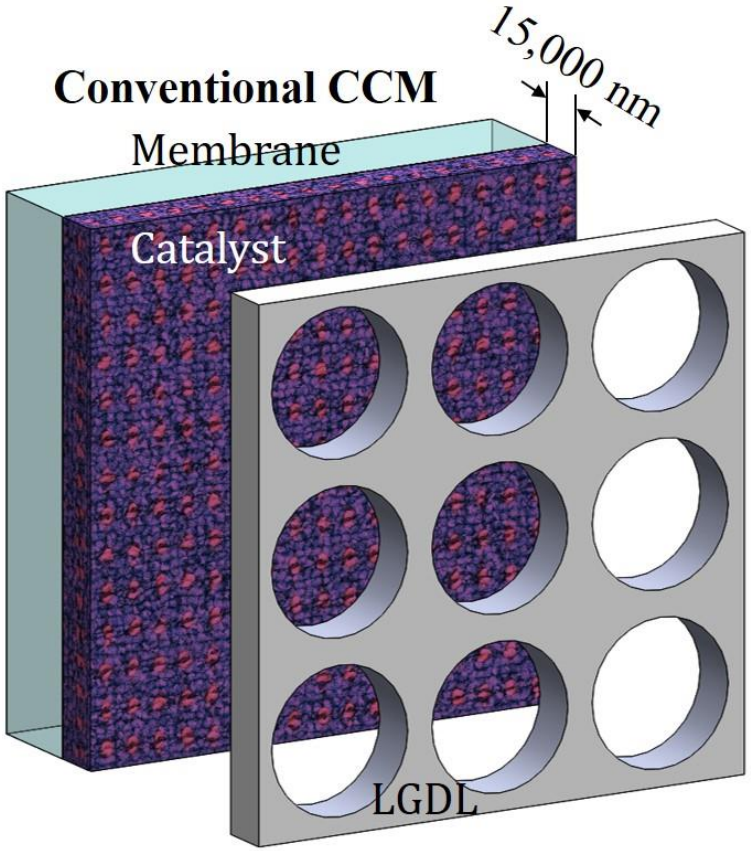
Novel Catalyst Design and Fabrication—significant cost reduction

significant catalysts were wasted



Can we apply catalysts on locations next to good electron conductors?

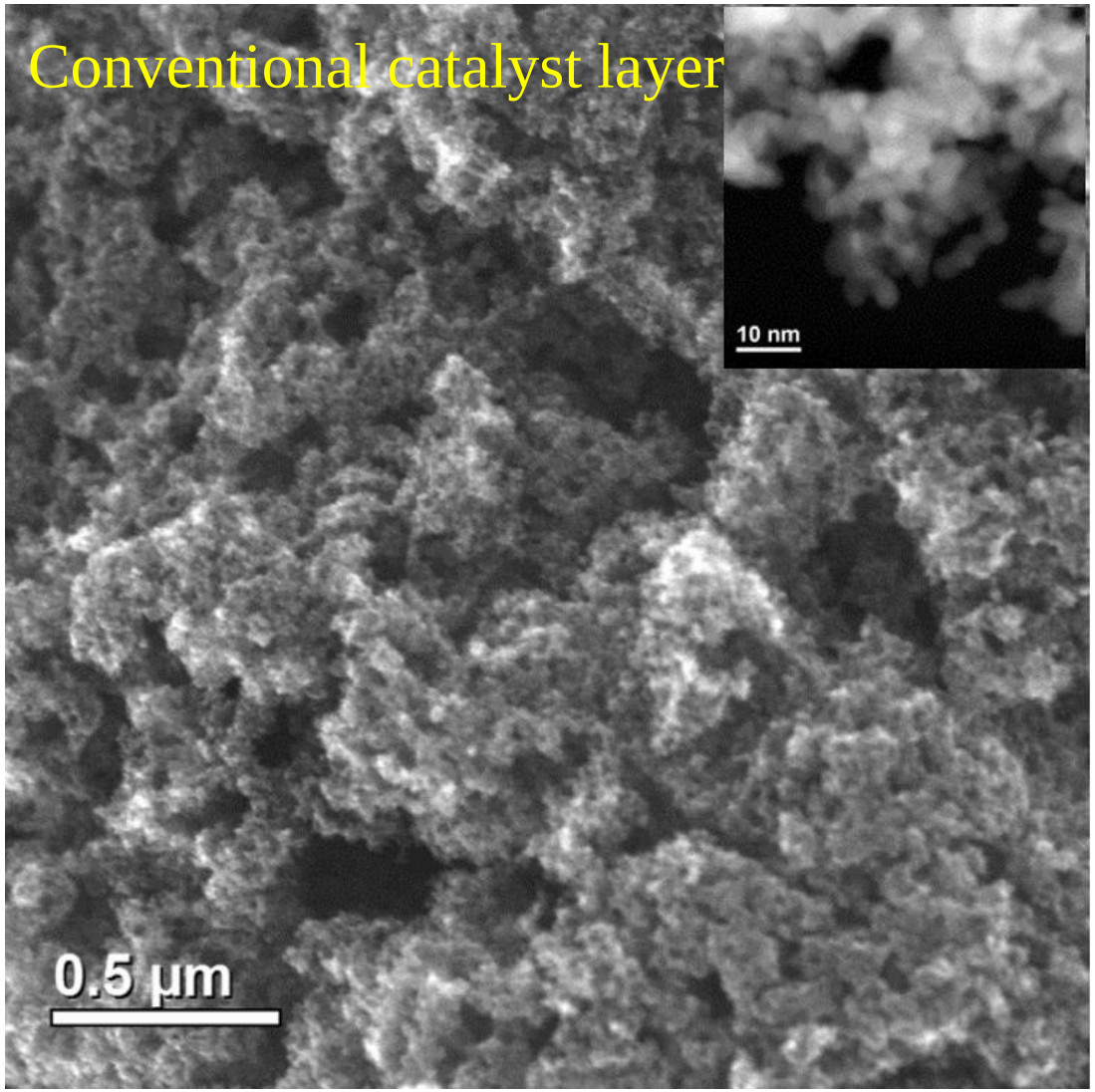
Schematics of Comparison Fabrication Method Between Conventional CCM and Deposit Catalyst on LGDL

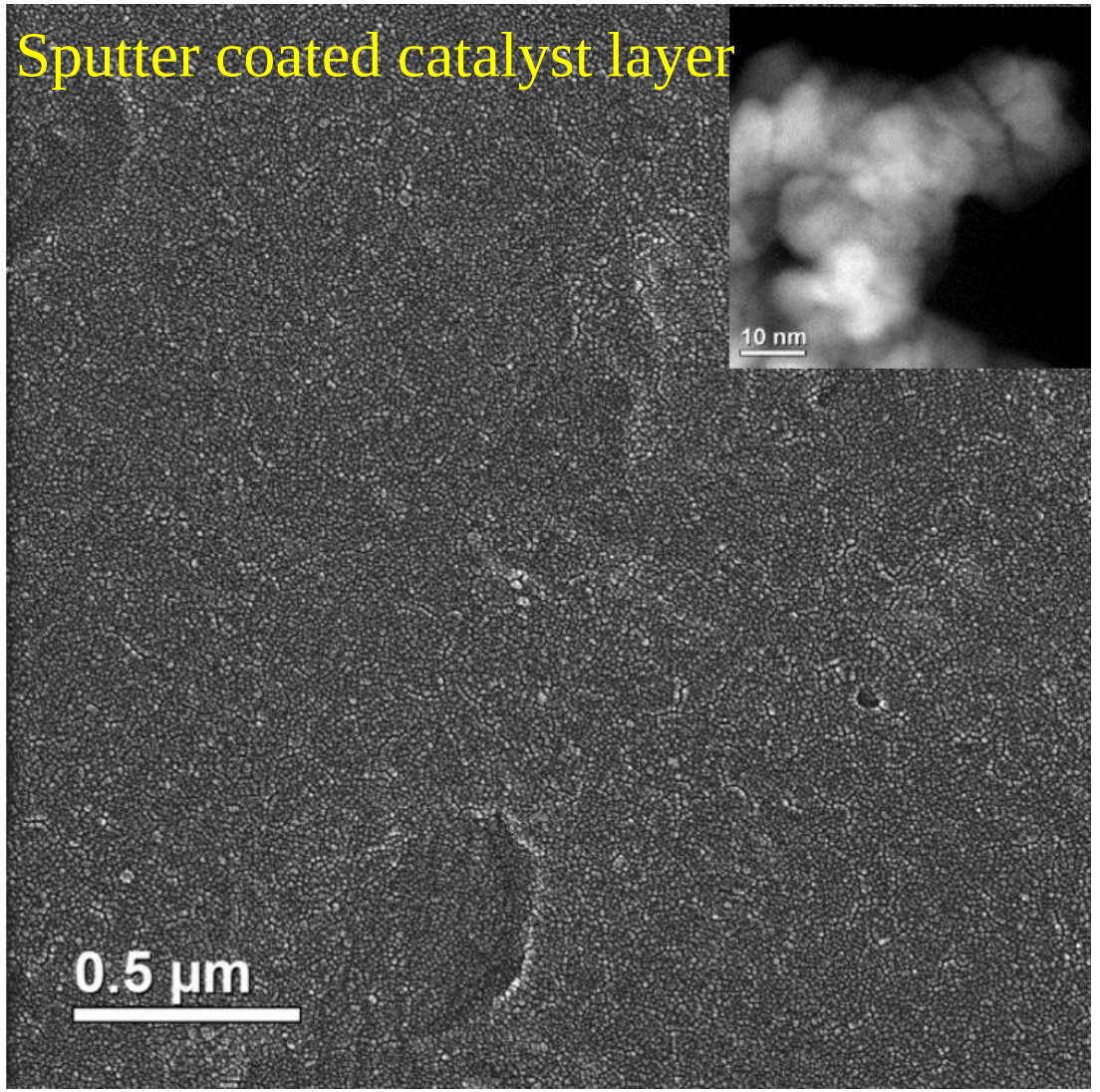


- For conventional CCM, the catalyst was fabricated on the membrane
- Novel catalyst fabrication method is depositing the catalyst only on the titanium thin well/tunable LGDL.

Jingke Mo, Zhenye Kang, Scott T. Retterer, David A. Cullen, Todd J. Toops, Johney B. Green Jr, Matthew M. Mench, and Feng-Yuan Zhang. Science Advances **2**(11), e1600690, 2016.

SEM and TEM Comparison Between Sputter Coating Catalyst on LGDL and Conventional CCM

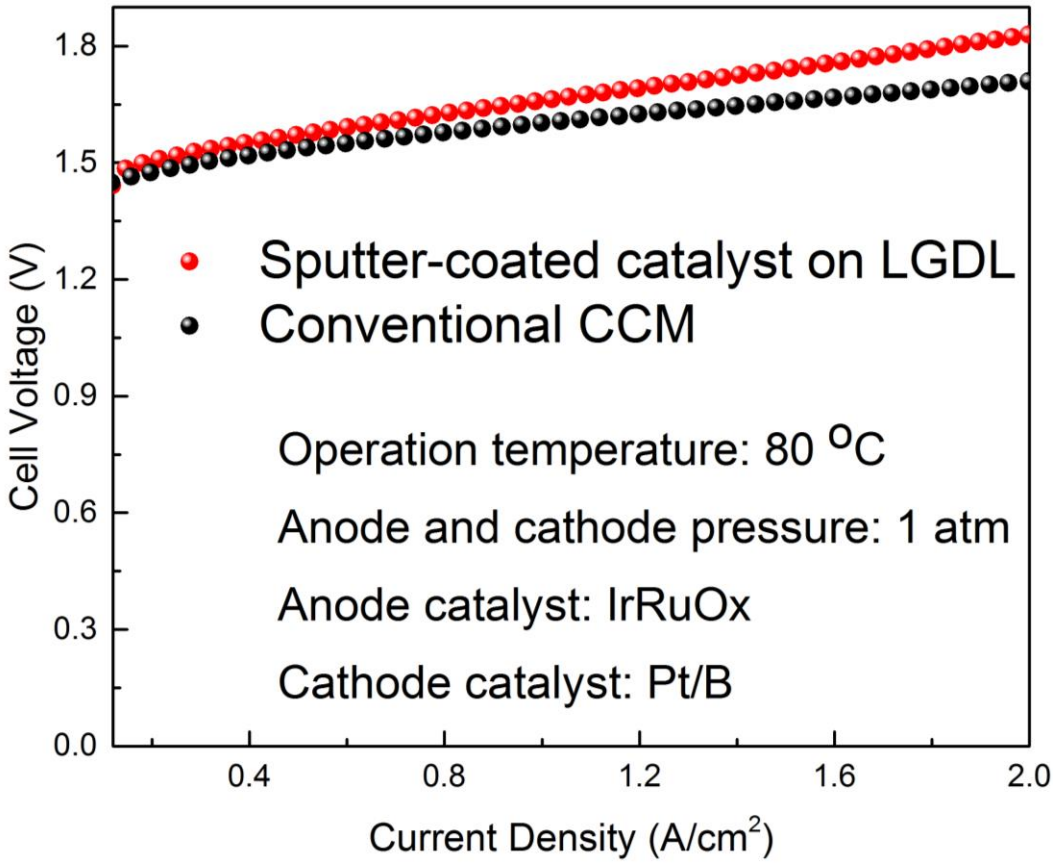


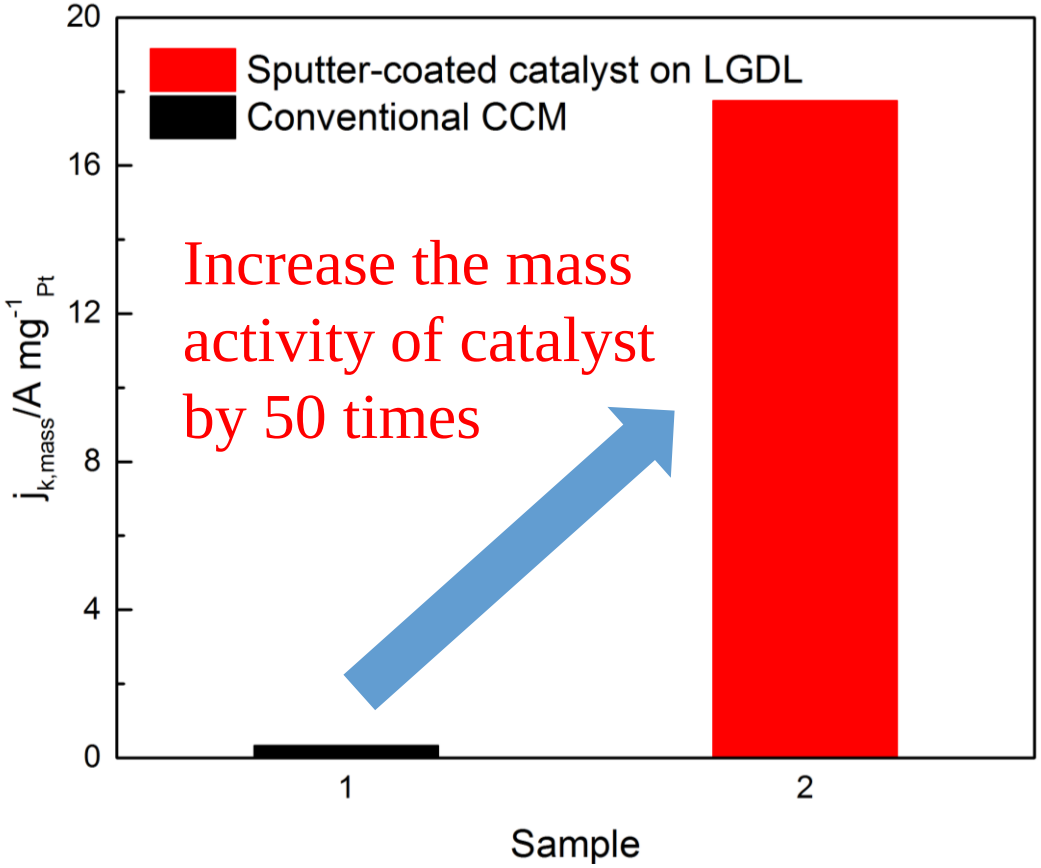


New catalyst layer have a much more smooth surface and less porous

Jingke Mo, Zhenye Kang, Scott T. Retterer, David A. Cullen, Todd J. Toops, Johney B. Green Jr, Matthew M. Mench, and Feng-Yuan Zhang. Science Advances **2**(11), e1600690, 2016.

50 times Increase in Catalyst Mass Activity, and Reduce Cost

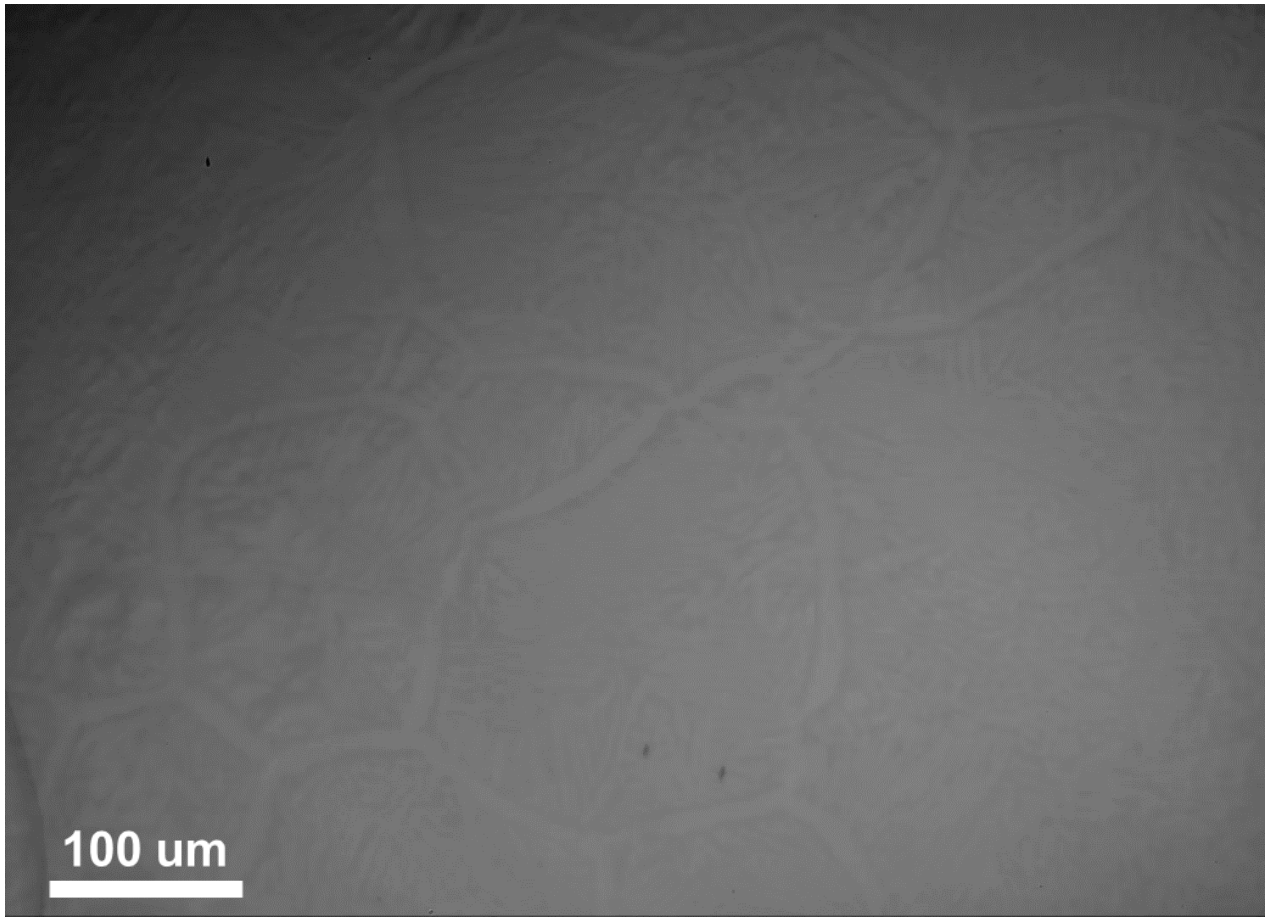




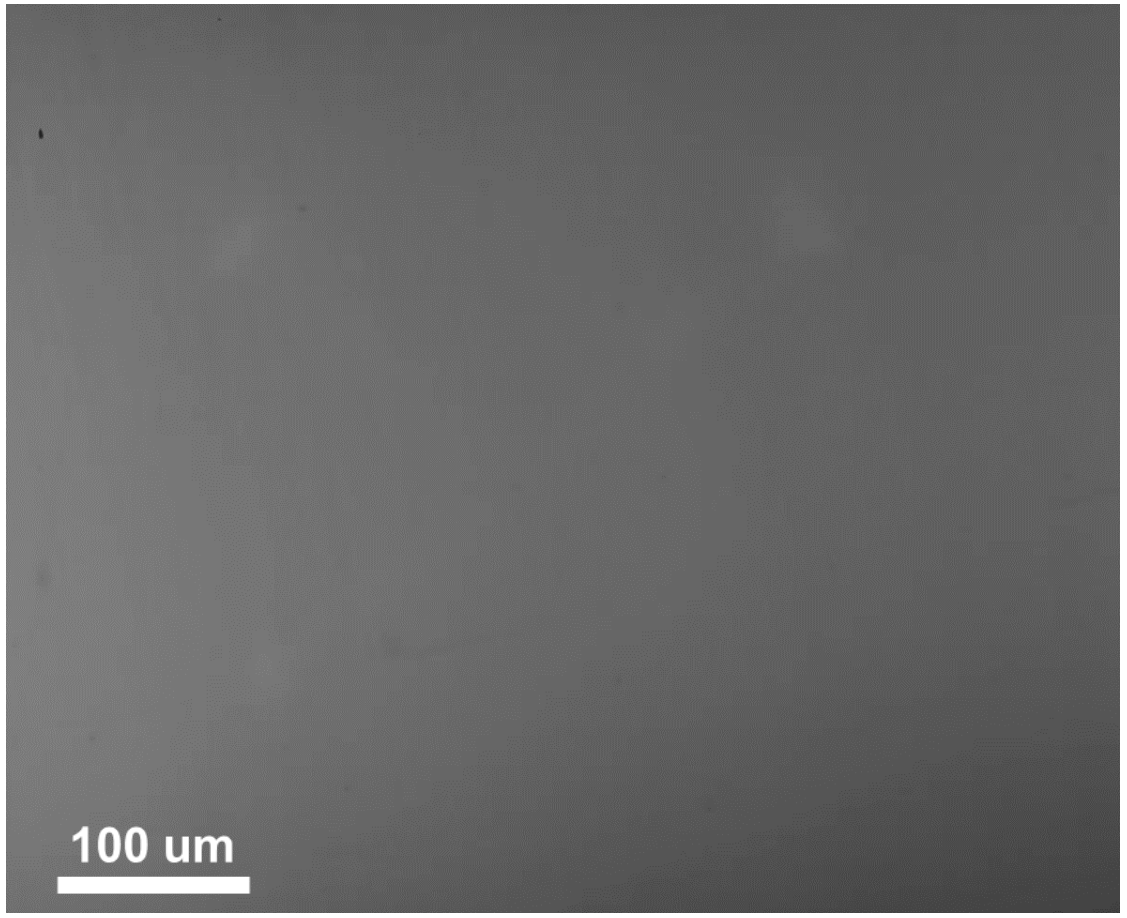
With similar performance, the novel fabricated catalyst layer increases the mass activity of catalyst by 50 times compared to conventional CCM

Jingke Mo, Zhenye Kang, Scott T. Retterer, David A. Cullen, Todd J. Toops, Johney B. Green Jr, Matthew M. Mench, and Feng-Yuan Zhang. Science Advances **2**(11), e1600690, 2016.

Direct observations of HEA in-situ corrosion behaviors with high-speed and micro-scale visualization systems



Alloy 1



Alloy 2

Collaborating with Dr. Peter Liaw's group

Two phase model coupled with comprehensive performance analysis for a PEM electrolyzer cell has been developed

➢ Gas/liquid two-phase transport equations

Oxygen transport:

$$\nabla \cdot \left(-\frac{K k_{O_2}}{\mu_{O_2}/\rho_{O_2}} \nabla p_{O_2} \right) = N_{O_2}$$

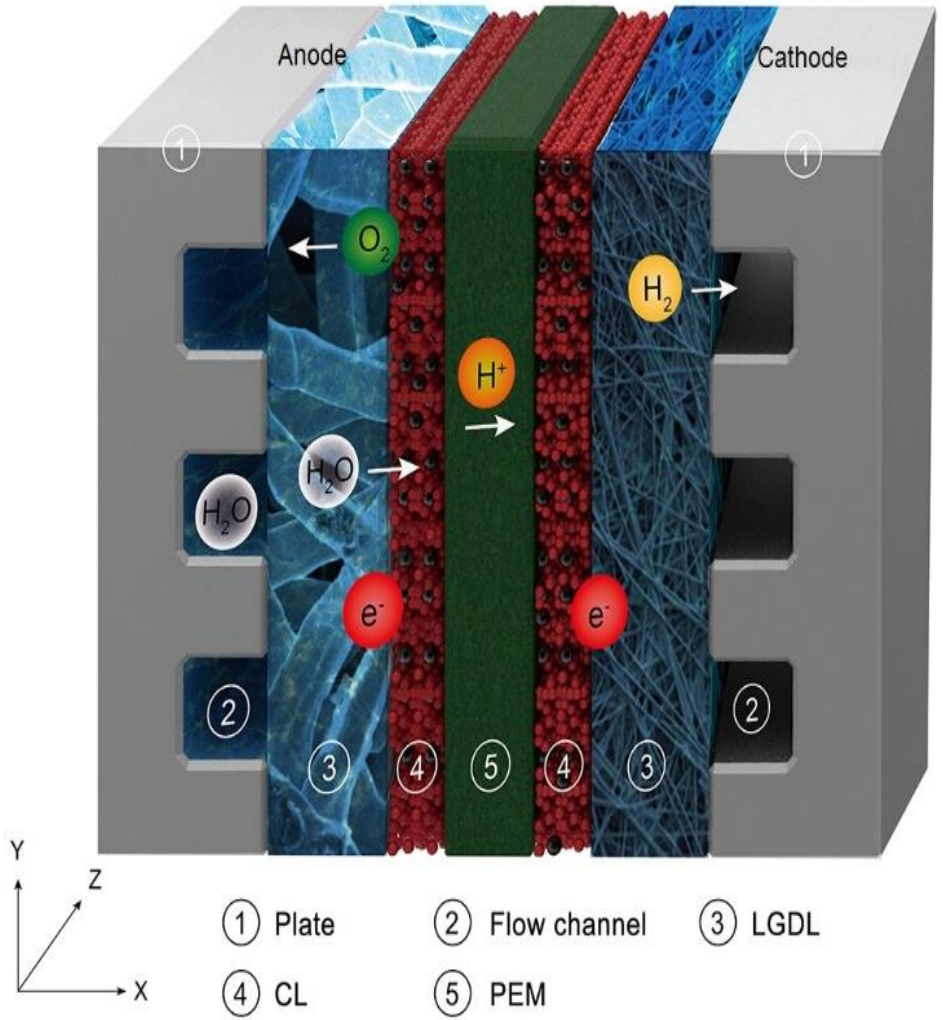
Liquid water transport:

$$\nabla \cdot \left(-\frac{K k_{H_2O}}{\mu_{H_2O}/\rho_{H_2O}} \nabla p_{H_2O} \right) = N_{H_2O}$$

Capillary pressure:

$$p_c = p_{O_2} - p_{H_2O} = J(s)\left(\frac{\varepsilon}{K}\right)^{1/2} \sigma cos\theta$$

$$J(s) = \begin{cases} 1.417(1-s) - 2.120(1-s)^2 + 1.263(1-s)^3, \\ 0 < \theta < 90^0, hydrophilic \\ 1.417s - 2.120s^2 + 1.263s^3, \\ 90^0 < \theta < 180^0, hydrophobic \end{cases}$$ **Leverett's function**



The electrochemical voltage consists of open circuit voltage, activation, diffusion overpotential and ohmic loss

Electrochemical performance

Total potential:

$$V = V_{ocv} + V_{act} + V_{diff} + V_{ohm}$$

Open circuit voltage:

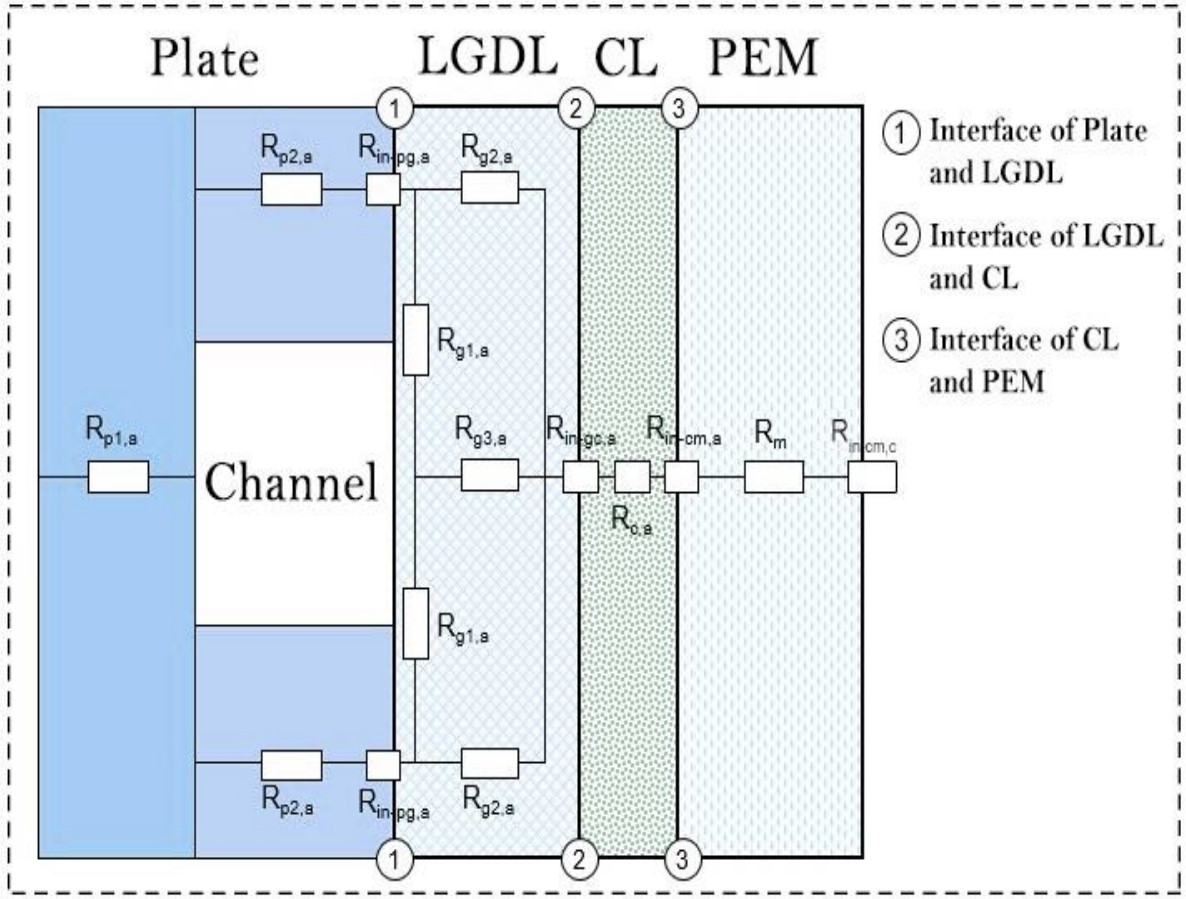
$$V_{ocv} = V_0 + \frac{RT}{zF}\ln\left(\frac{\alpha_{H_2}\alpha_{O_2}^{0.5}}{\alpha_{H_2O}}\right)$$

Activation and diffusion overpotential:

$$V_{act} + V_{diff} = \frac{RT_a}{\alpha_a F}\ln\left(\frac{j}{sj_0}\frac{C_{O_2,m}}{C_{O_2,m0}}\right) + \frac{RT_c}{\alpha_c F}\ln\left(\frac{j}{sj_0}\frac{C_{H_2,m}}{C_{H_2,m0}}\right)$$

Ohmic loss:

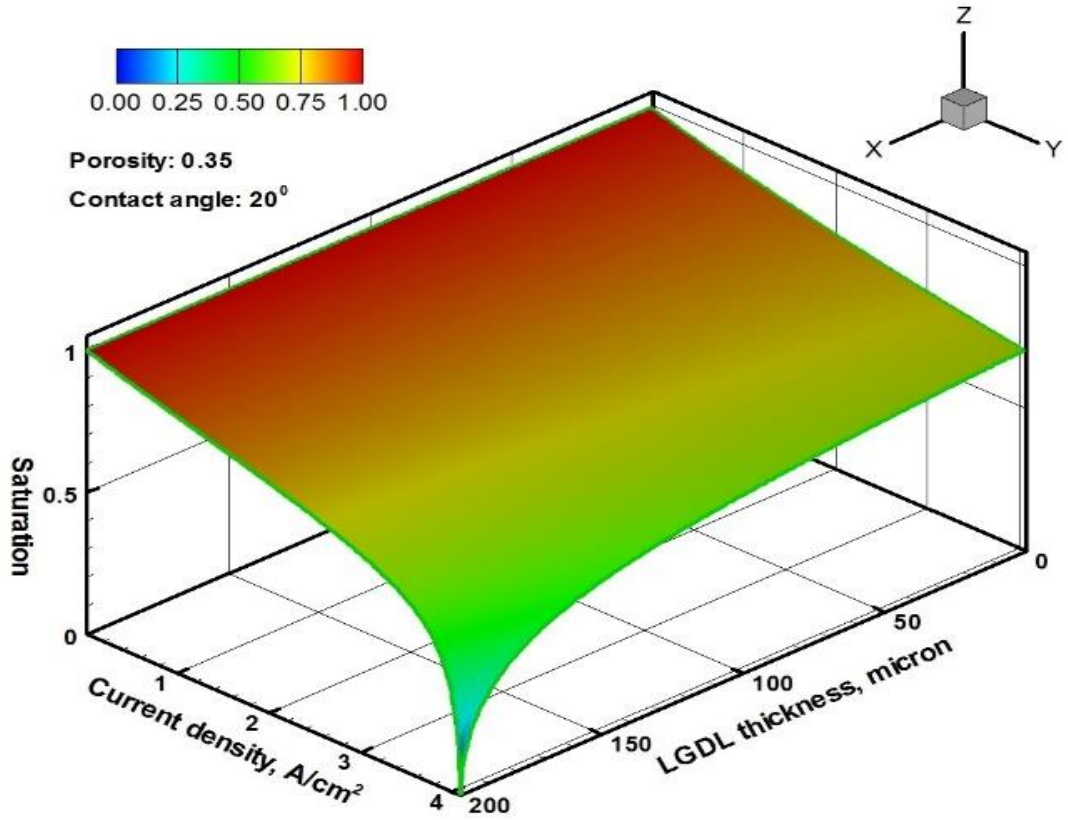
$$V_{ohm} = (R_{plate} + R_{LGDL} + R_{PEM} + R_{inerface})jA$$



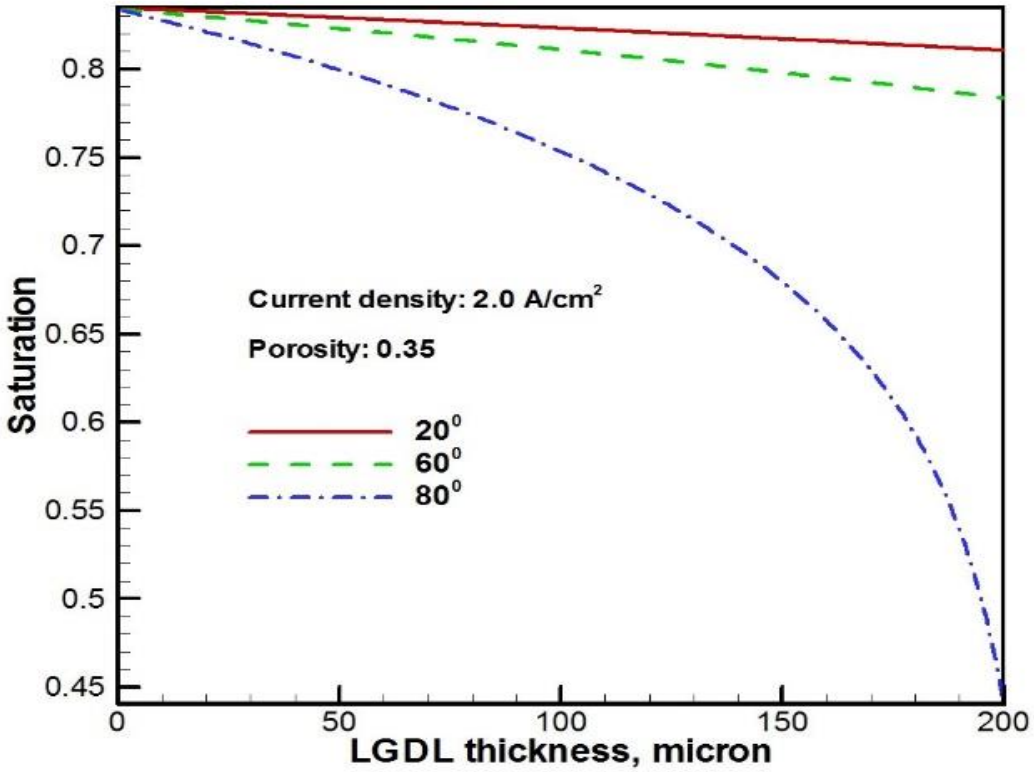
Han, B., Steen, S. M., Mo, J., and Zhang, F.-Y. "Electrochemical performance modeling of a proton exchange membrane electrolyzer cell for hydrogen energy," *International Journal of Hydrogen Energy* Vol. 40, No. 22, 2015

Liquid saturation distribution in the LGDL

The liquid water saturation distribution along the LGDL thickness direction at different contact angles and porosities.



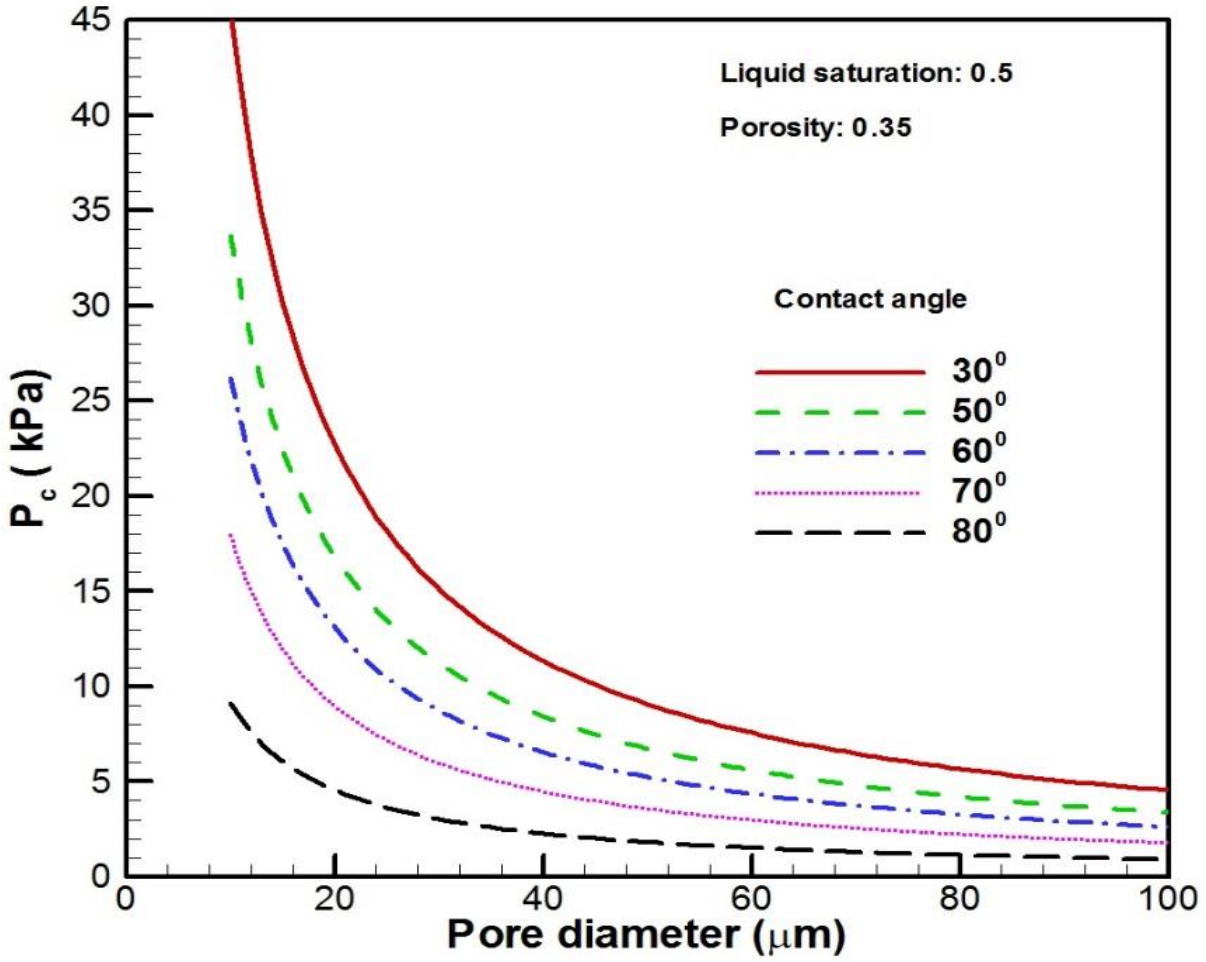
(a)

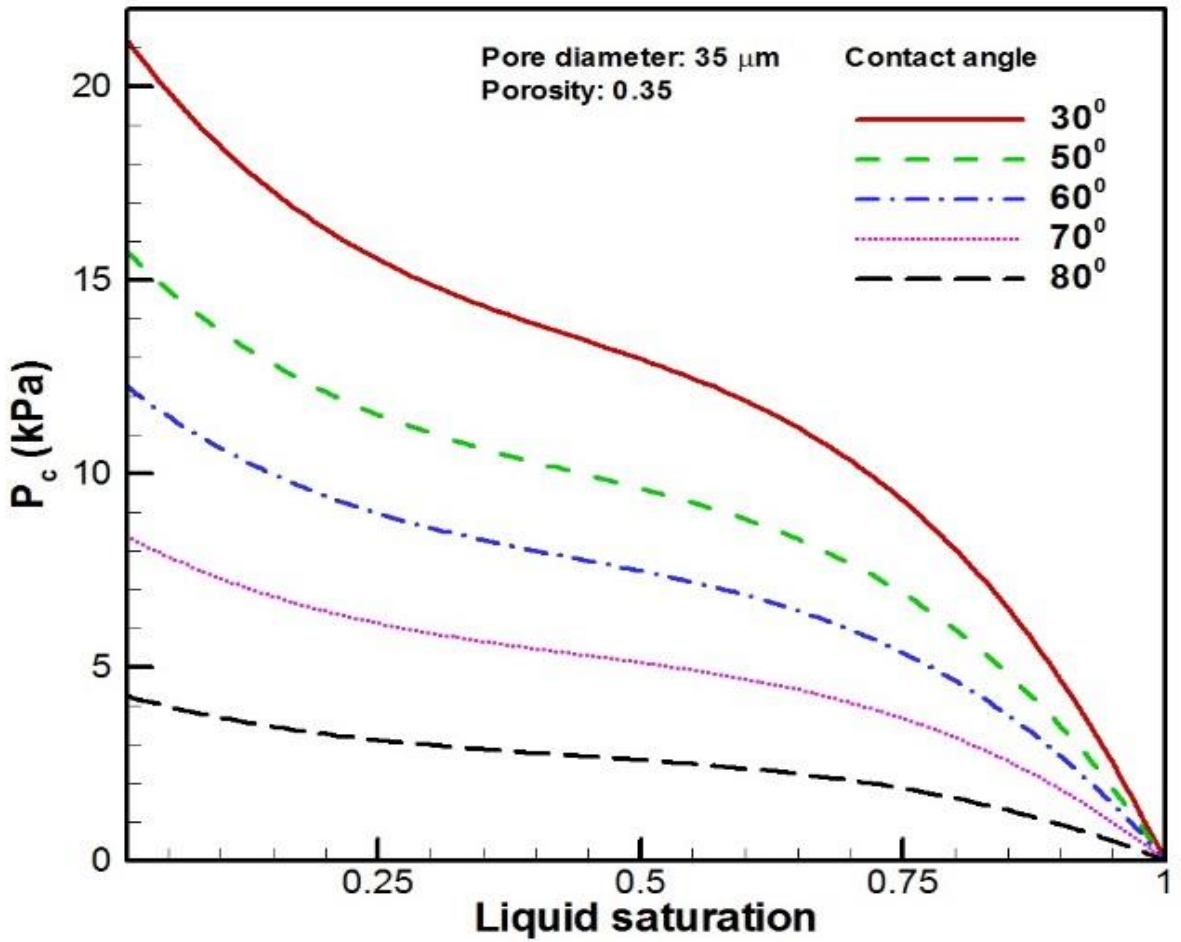


(b)

B. Han, J. Mo, Z. Kang, G. Yang, W. Barnhill and F.-Y. Zhang, Modeling of two-phase transport in proton exchange membrane electrolyzer cells for hydrogen energy. *Int J Hydrogen Energ*, 2017

Capillary pressure distribution in LGDLs

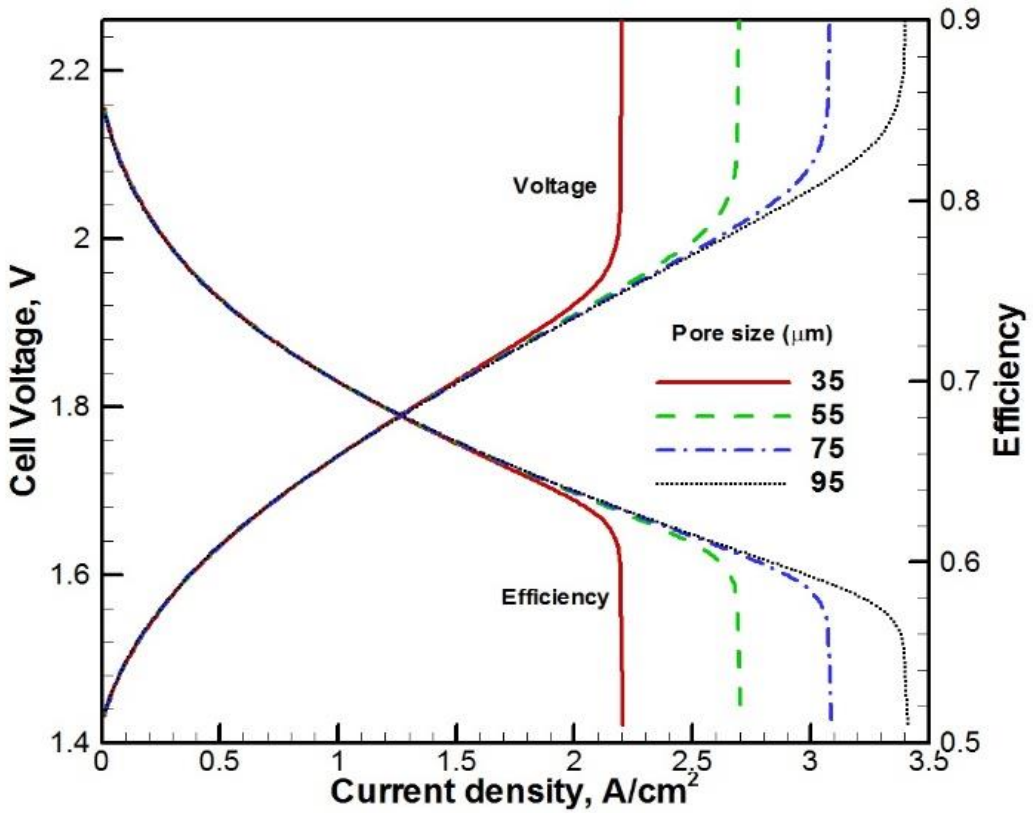




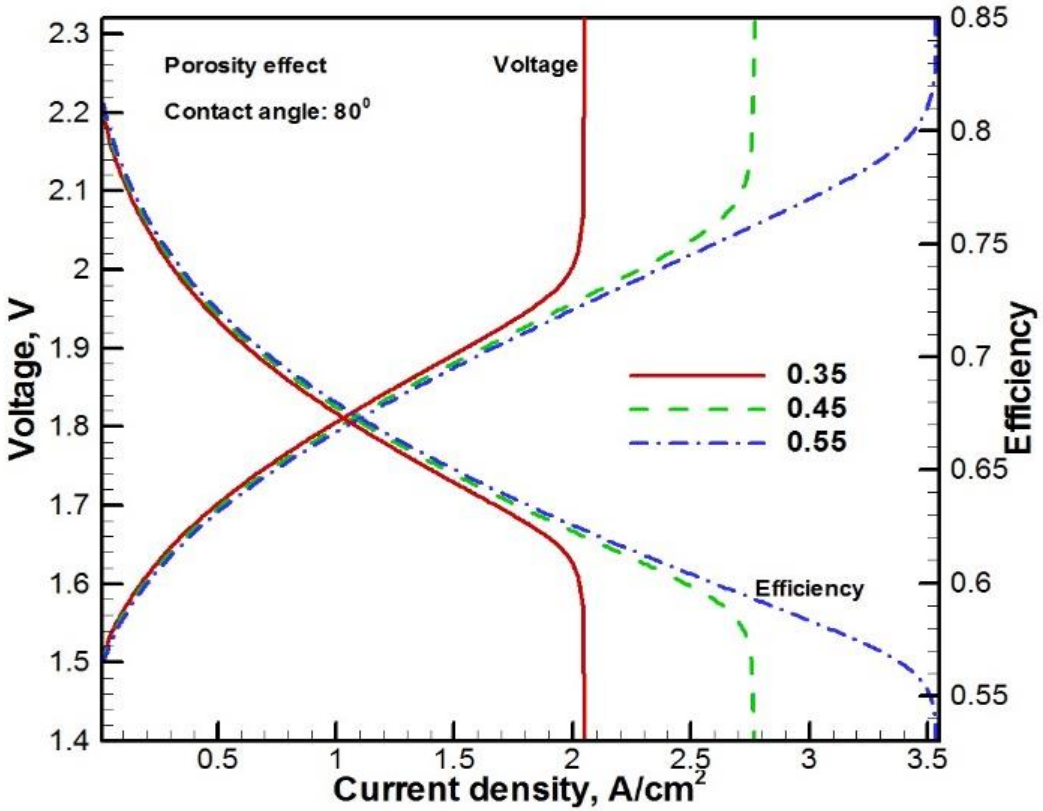
B. Han, J. Mo, Z. Kang, G. Yang, W. Barnhill and F.-Y. Zhang, Modeling of two-phase transport in proton exchange membrane electrolyzer cells for hydrogen energy. *Int J Hydrogen Energ*, 2017

Thinner LGDLs and membranes will decrease the ohmic/transport resistances and enhance the performance

Effect of LGDL pore size on the cell performance and efficiency



Effects of LGDL porosity on the cell performance and efficiency



Summary

- A novel-designed thin titanium LGDL with microscale and well-tunable pore morphologies is developed based on micro/nanomanufacturing techniques
- Superior multifunctional performance for energy storage is obtained
- New thin LGDLs exhibit excellent durability and can be easily modified with advanced surface treatment
- By developing a thin/well-tunable liquid/gas diffusion layer (LGDL), and other designs, the true mechanism of electrochemical reactions on both micro-spatial and micro-temporal scales is revealed for the first time
- Based on the discovered mechanism of electrochemical reaction, a novel catalyst layer fabrication method was introduced, which significantly increase the mass activity of catalyst by 50 times at a similar performance.
- Modeling bubble dynamics and two-phase flow and simulating the effects of material properties on device performance

Acknowledgement

- DOE/NETL: Jason Hissam, Crosscutting Technology Team
- Students, Postdoc and Staff:

Stuart Steen, William Barnhill, Dr. Joel Mo, Allen Kang, Yeshi Dohrmann, Derrick Talley, Dr. Bo Han, Gaoqiang Yang, Yifan Li, Alexander Terekhov, Douglas Warnberg, Kathleen Lansford

- Collaborators:

Suresh Babu, Fred List, Scott Retterer, Dave Cullen, Mike Brady, Peter Liaw, Dongping Li, Jun Liu, Todd Toops, Jun Qu, Johney Green, Ryan Dehoff, William Peter, Joey Kish