NETL's Crosscutting Research Review Meeting

Award: DE-FE0011585

Project manager: Jason Hissam

Developing novel multifunctional materials for high-efficiency electrical energy storage - Optimizations

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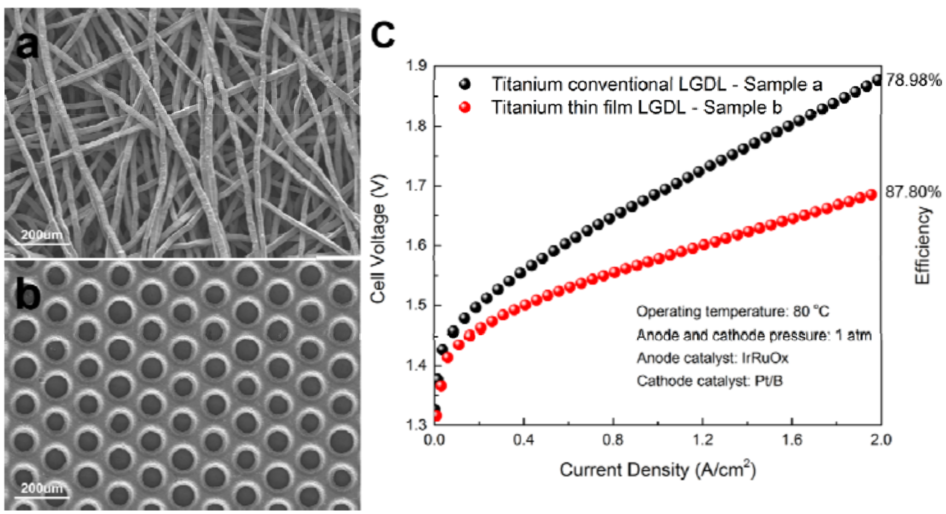
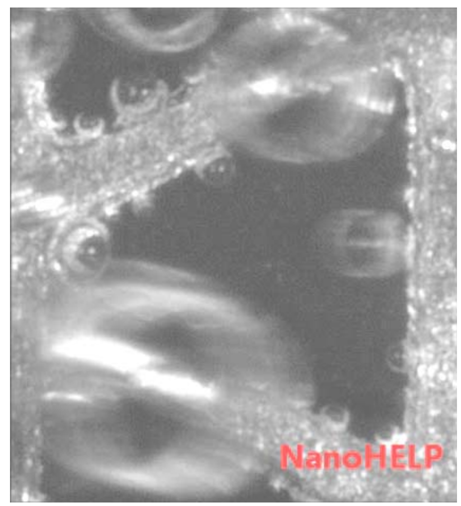
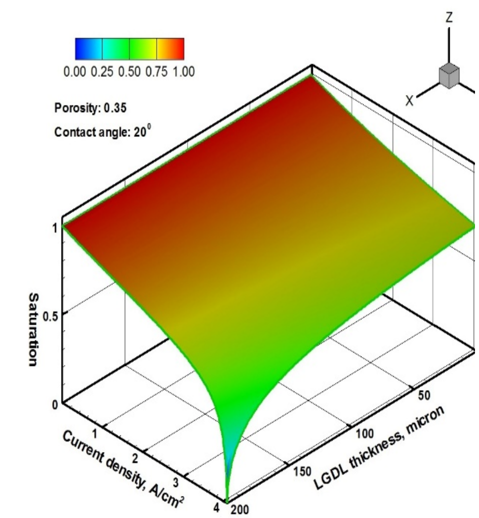
Outline

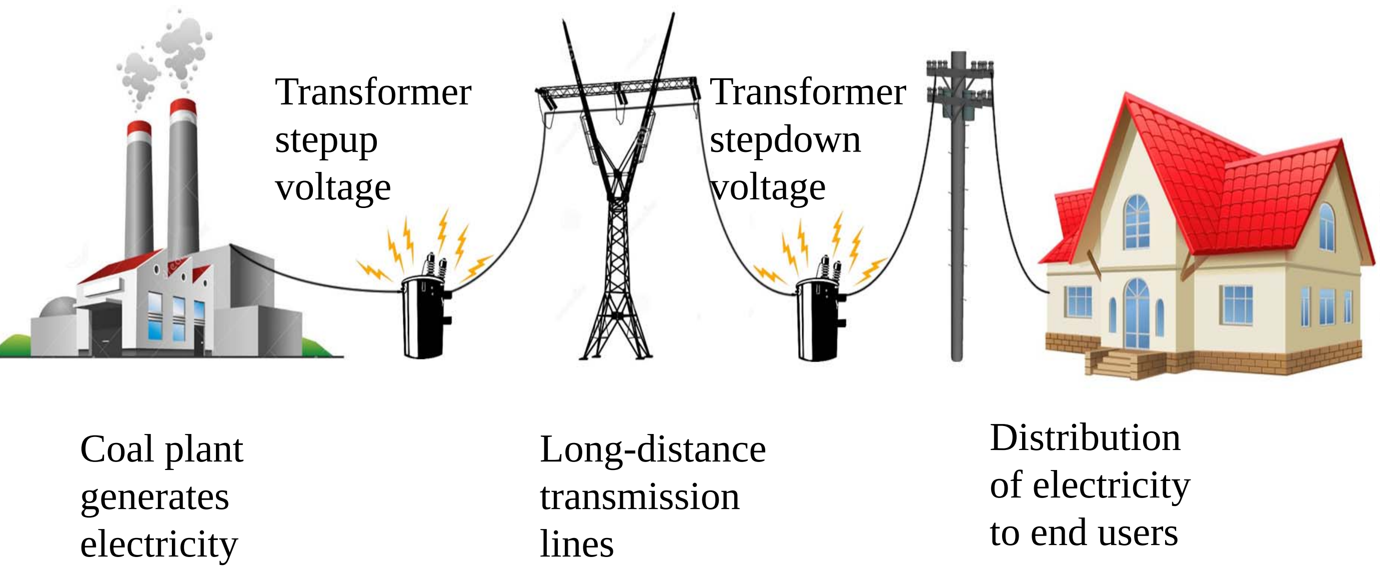
Motivation | **multifunctional thin materials** | **In-situ reactions** | **Modeling** | **Summary**

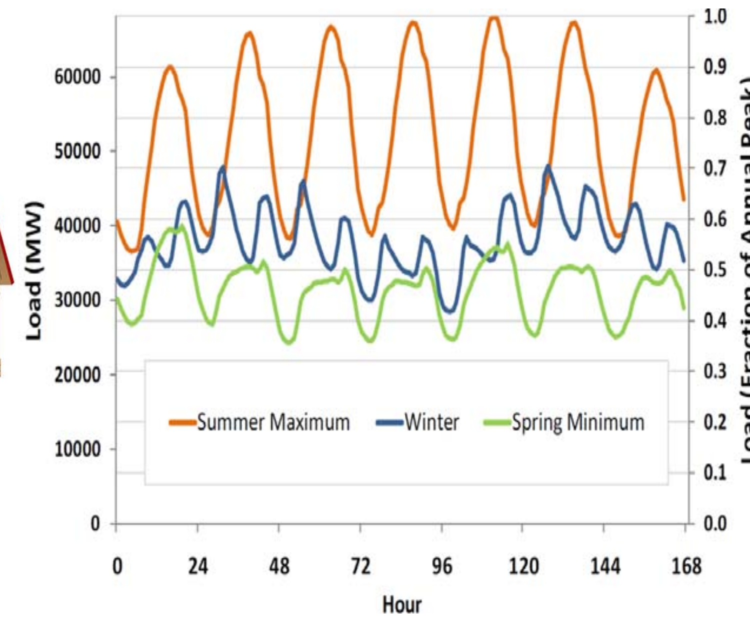






Distributed energy storage mitigates power-demand interruptions and improves greatly efficiency from coal plant to end users





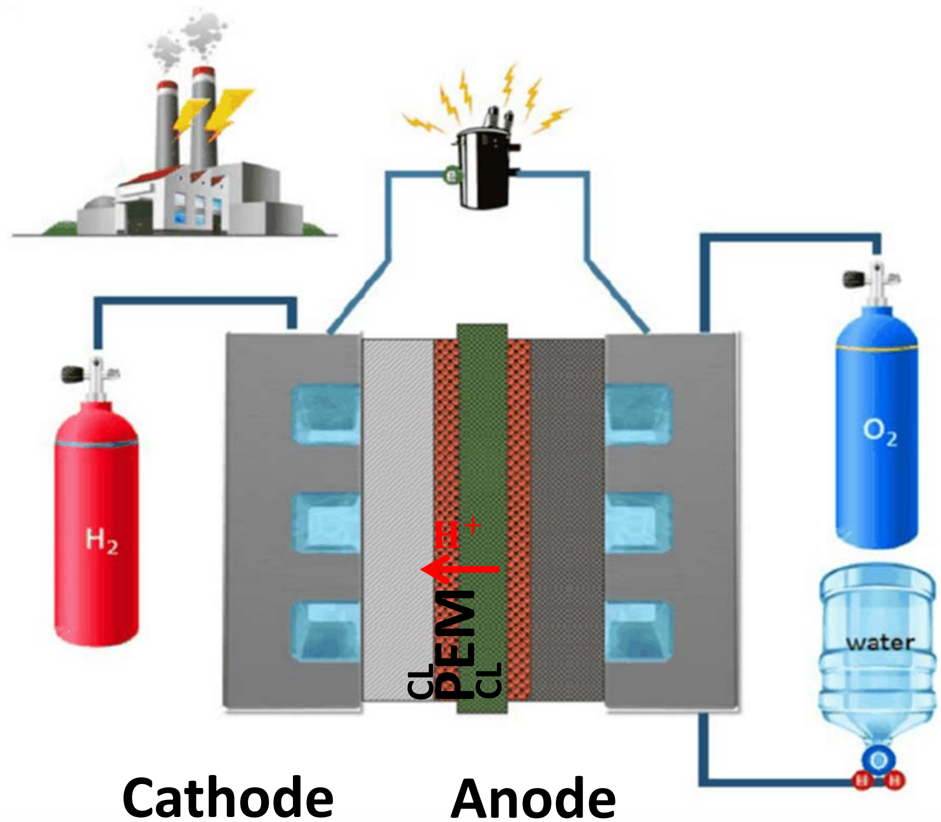
- Electricity demand changes significantly with time
- Electric grid often experiences interruptions, resulting in significant cost (> 80 Billions/year)
- Many of these interruptions may be mitigated by distributed energy storage approaches

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

Proton exchange membrane electrolyzer cells(PEMFCs) become more attractive for energy storage to promote grid modernization

- 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

- Challenges for widely application
  - Performance
  - Durability
  - High cost of materials/manufacturing

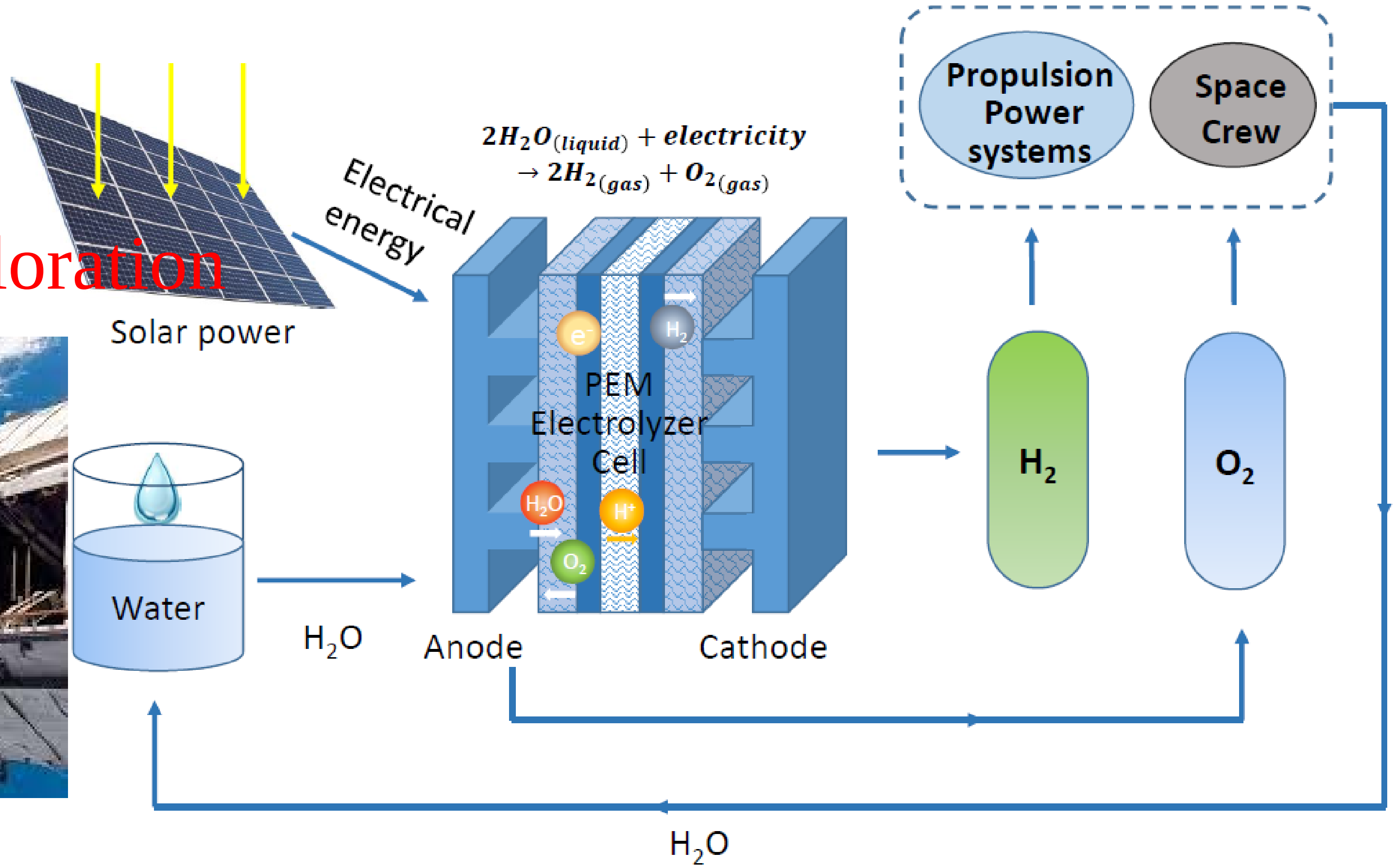


$4H^+ + 4e^- \xrightarrow{catalyst} 2H_2$

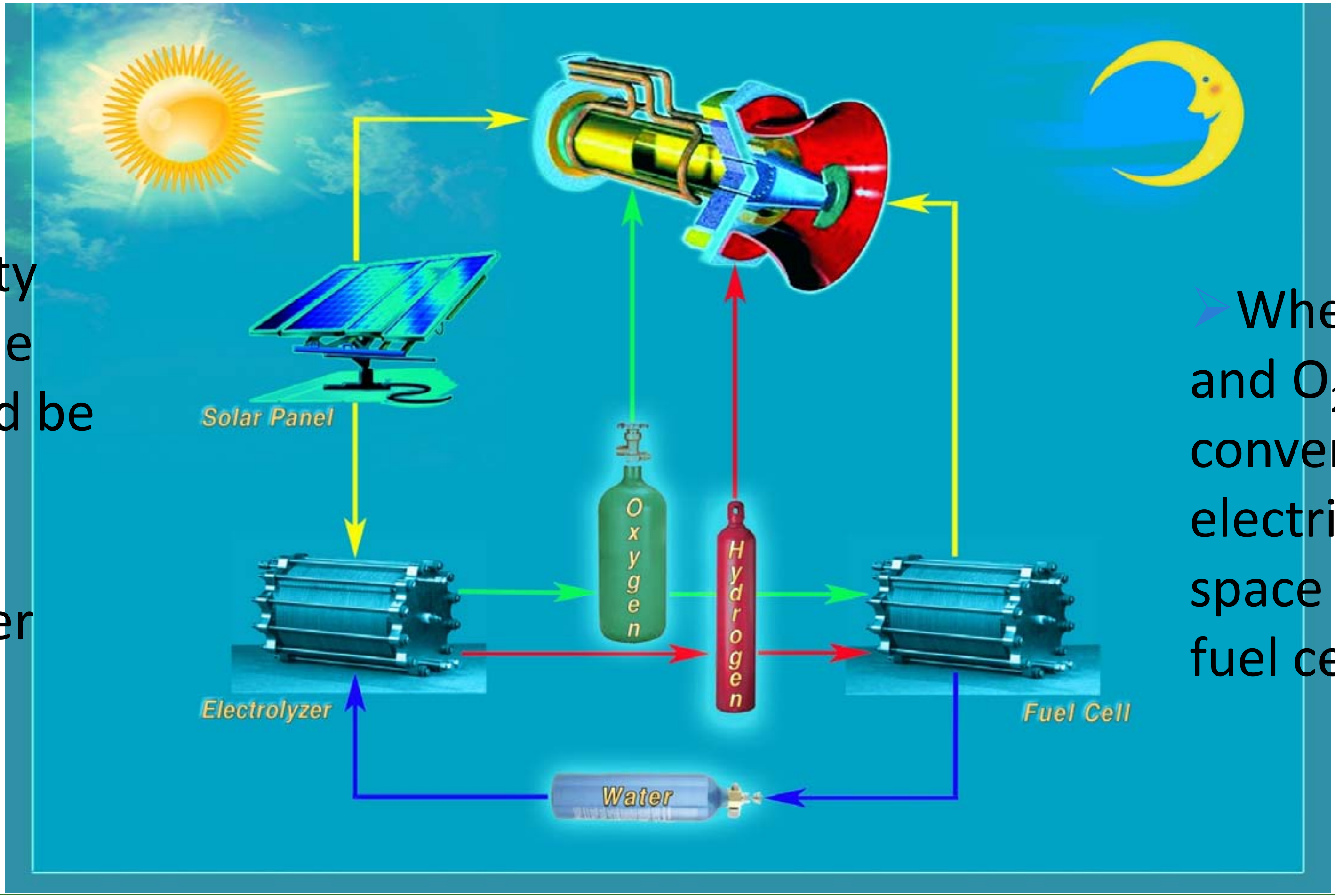
$2H_2O \xrightarrow{catalyst} O_2 + 4H^+ + 4e^-$

Space applications: high-efficiency devices for oxygen generation and energy storage

- Pure H2 and O2 productions
- Human space exploration



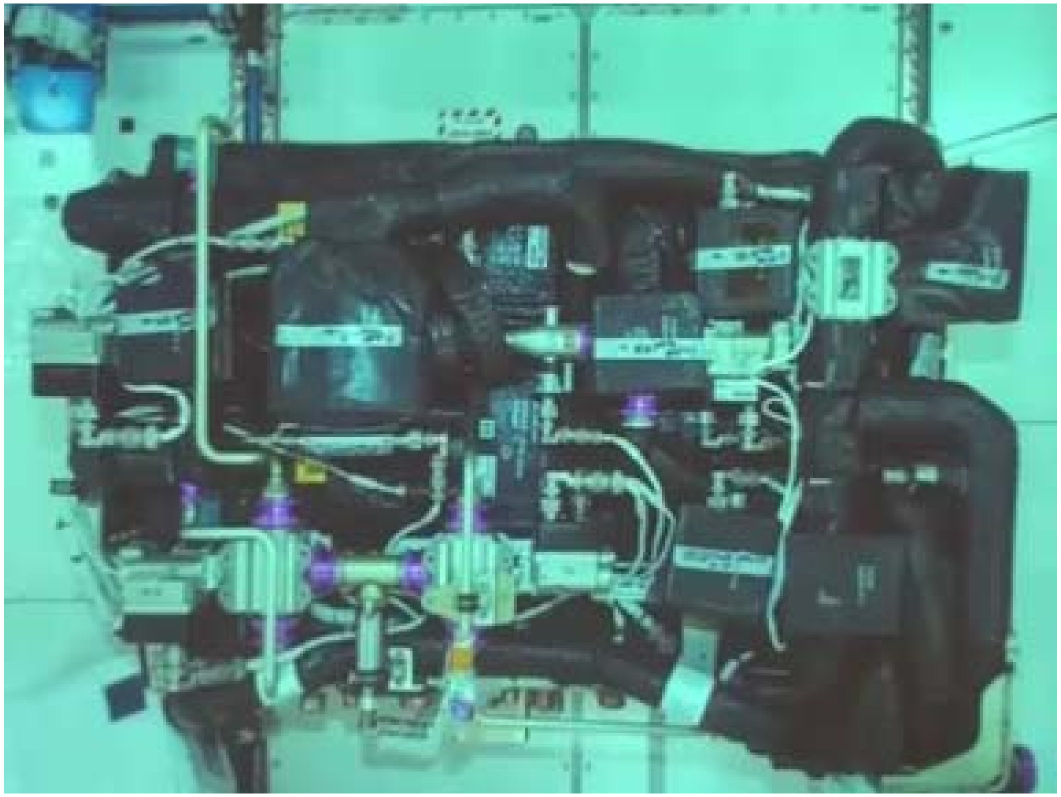
Sustainable energy system



- 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

OGS: oxygen generator system in the space station



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

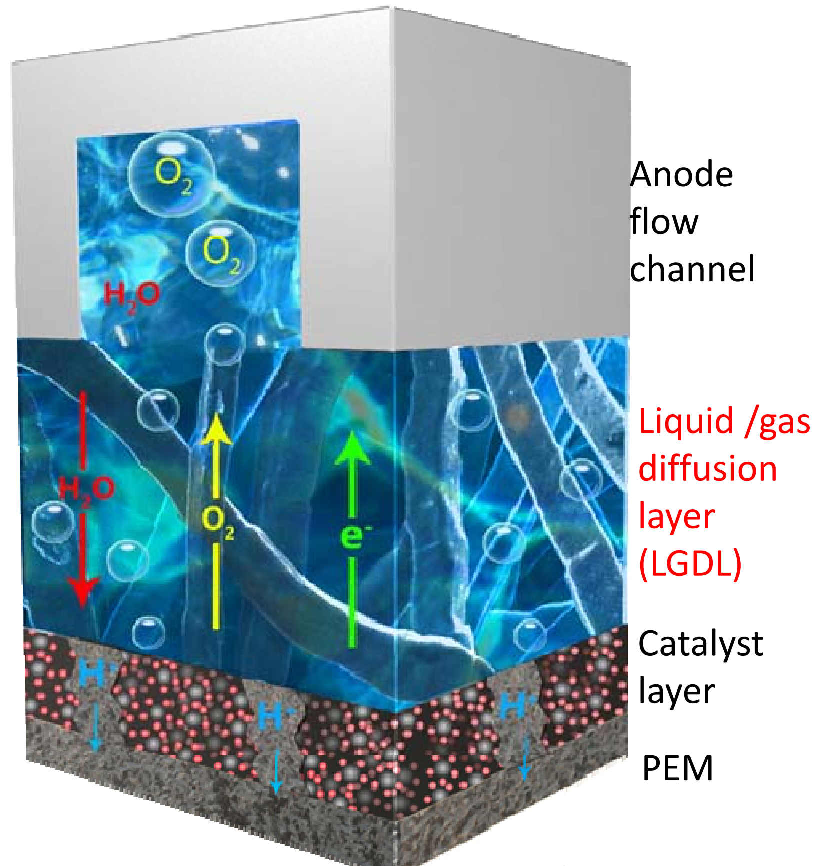
Joel from NanoHELP with Captain Barry Wilmore

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

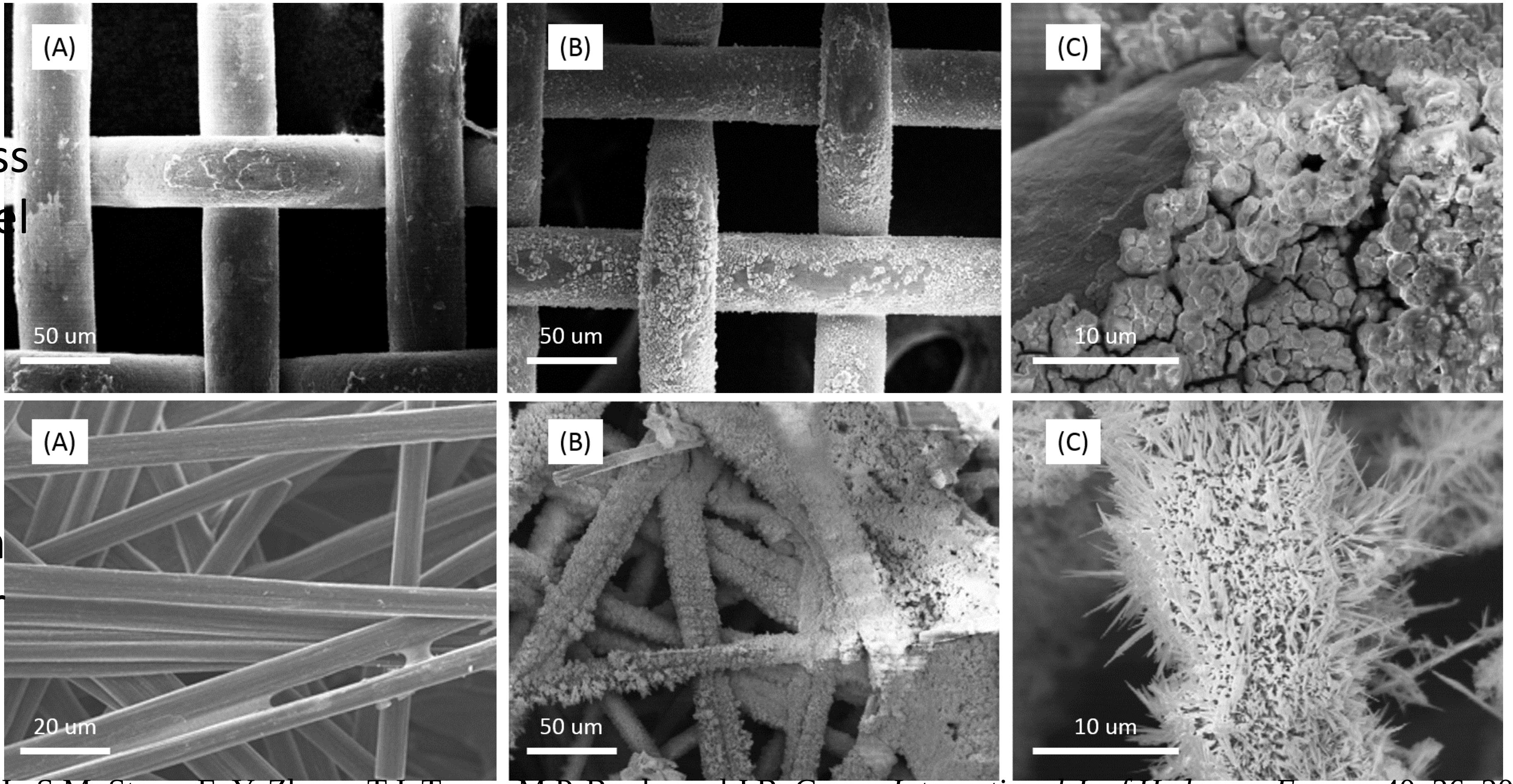


J. Mo, R.R. Dehoff, W.H. Peter, T.J. Toops, J.B. Green, F.-Y. Zhang, Additive manufacturing of liquid/gas diffusion layers for low-cost and high-efficiency hydrogen production. *International Journal of Hydrogen Energy* **41**, 3128-3135 (2016).

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

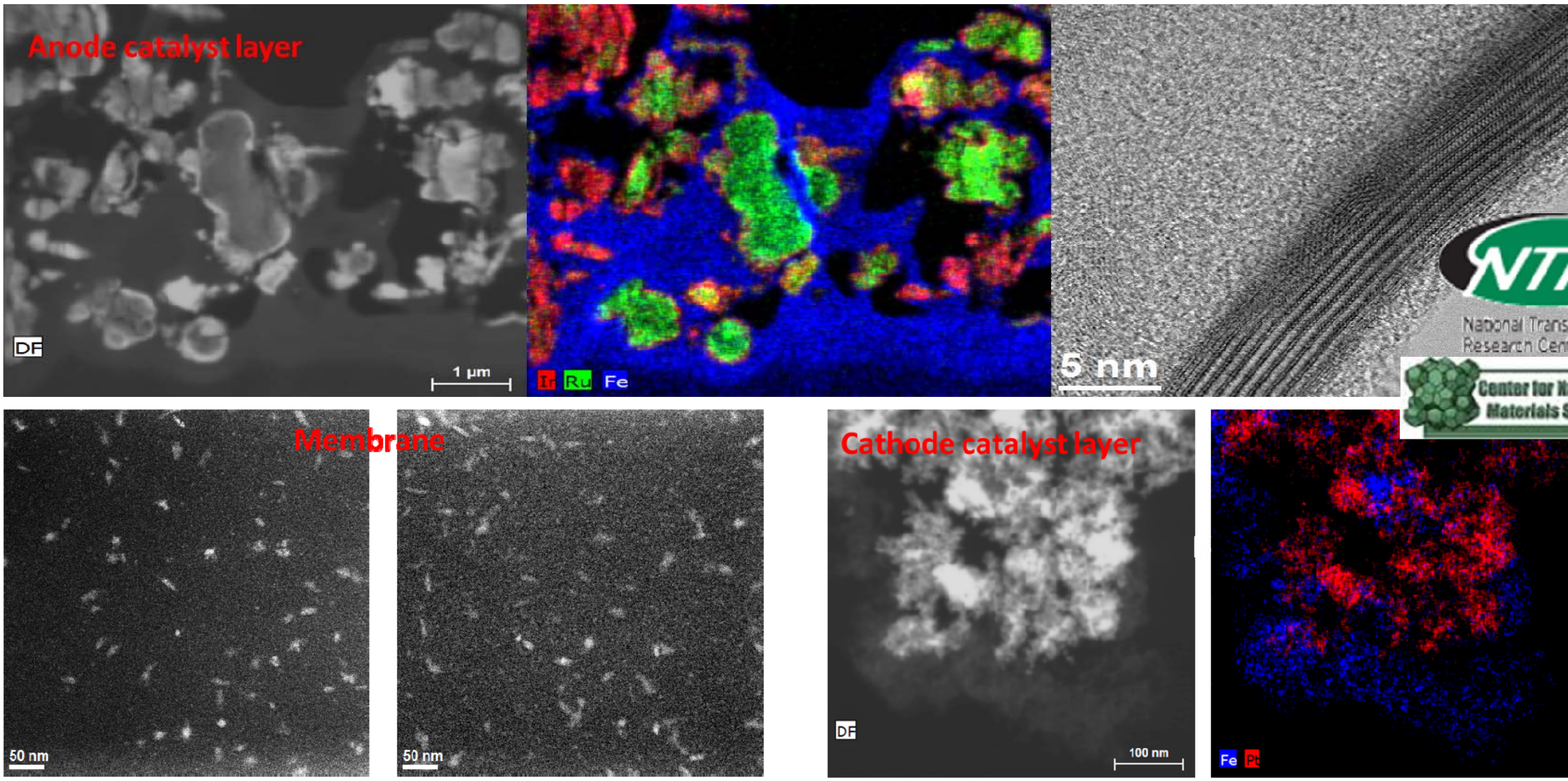
Stainless steel

Carbon paper

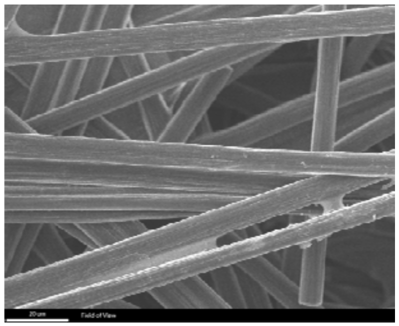


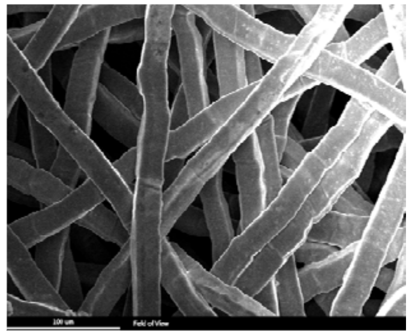
Mo, J., S.M. Steen, F.-Y. Zhang, T.J. Toops, M.P. Brady, and J.B. Green, *International J. of Hydrogen Energy*, 40, 36, 2015.

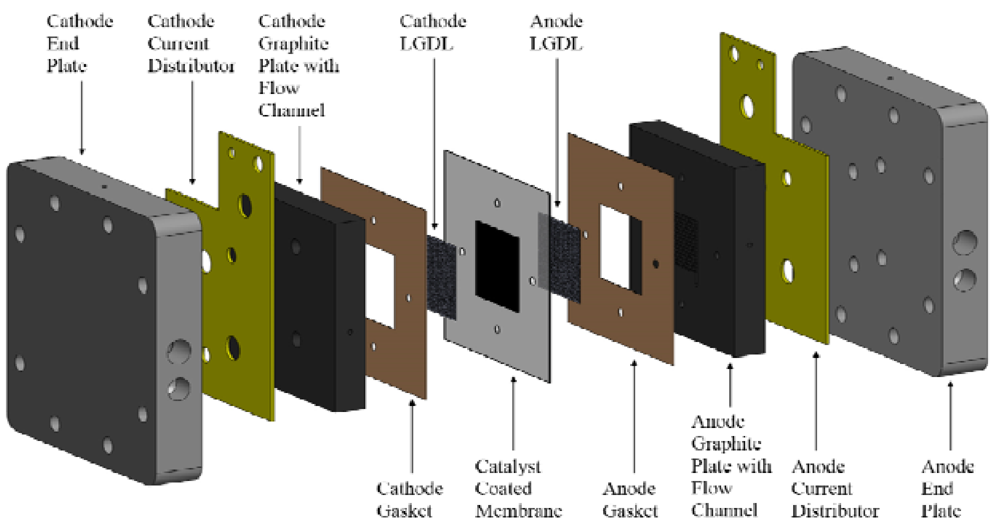
Corrosion elements (Iron) attacked both catalyst layers and membrane, degraded the performance quickly



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

J. Mo, S.M. Steen, B. Han, Z. Kang, A. Terekhov, F.-Y. Zhang, S.T. Retterer, D.A. Cullen. Investigation of titanium felt transport parameters for energy storage and hydrogen/oxygen production. AIAA **2015-3914** (2015).

Different Structures of Metallic LGDL

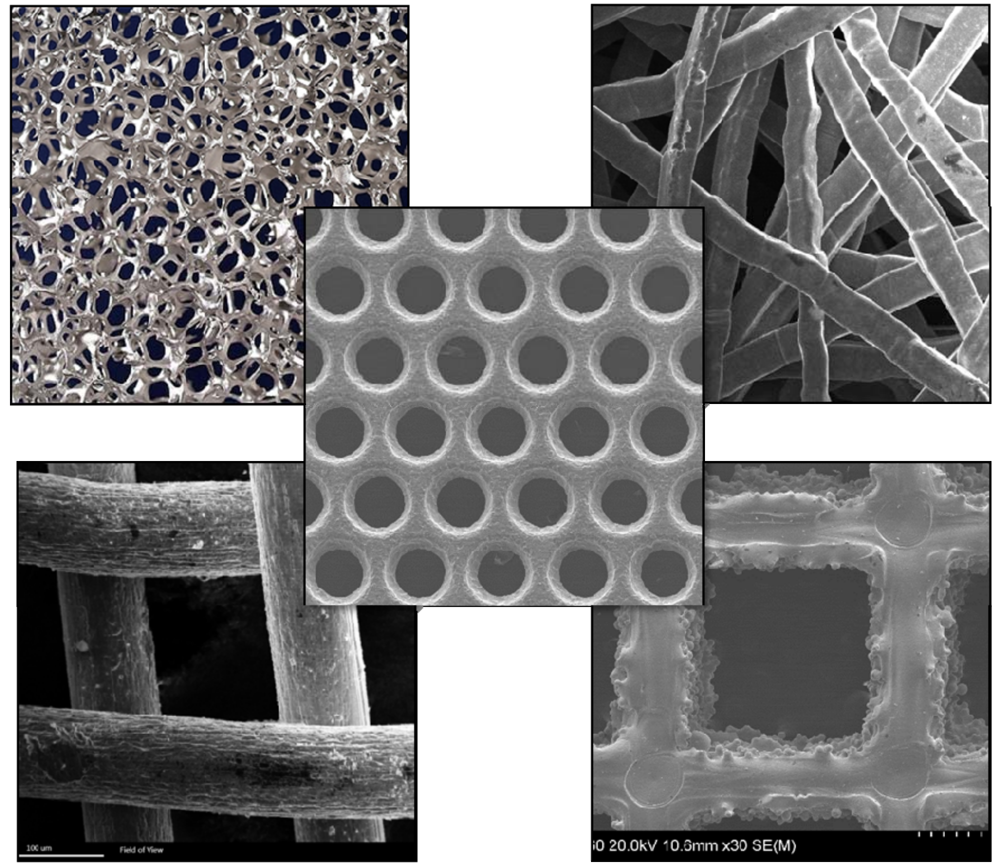
(1) **Metallic foam** (difficult to fabricate, expensive, larger pore size, random pore size, thickness difficult to control, difficult to scale)

(2) **Sintered fiber felt** (non-ordered porous structure, impossible to control individual pore size, thickness can be a problem)

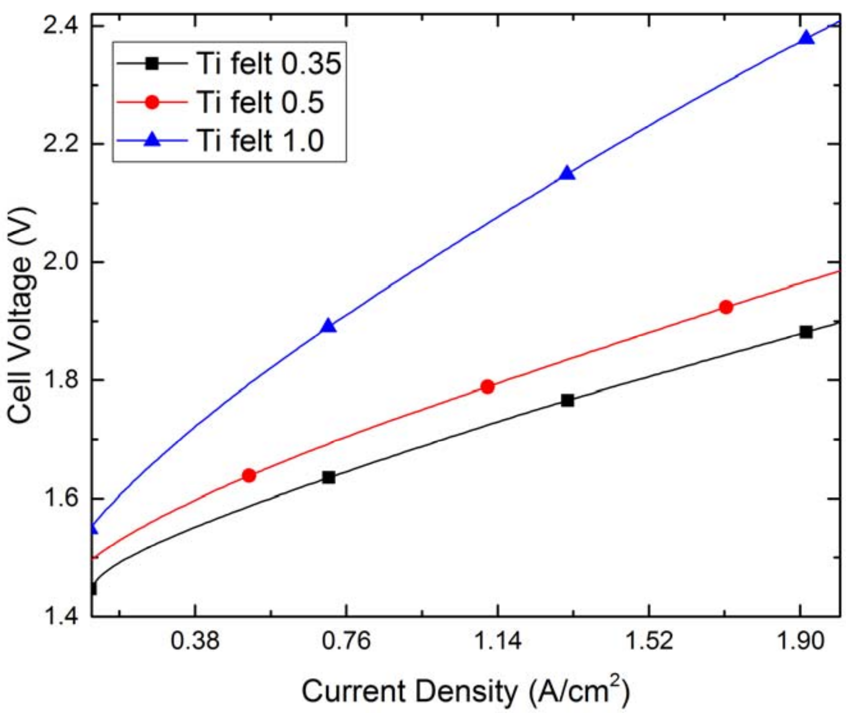
(3) **Woven & sintered mesh** (complicated to machine, low interfacial contacts, large thickness)

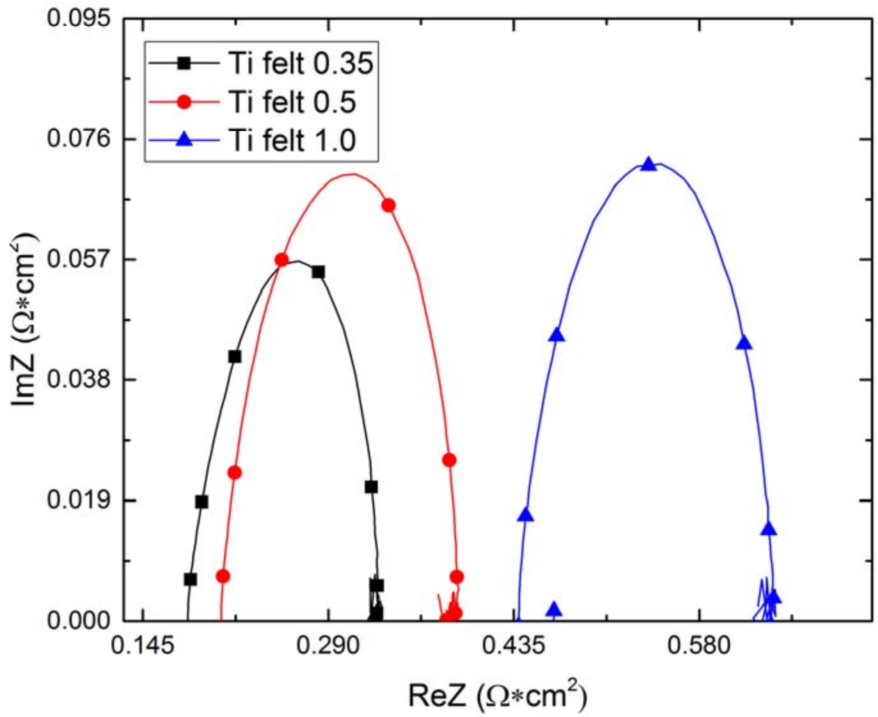
(4) **3D Printing mesh** (wettability, thickness, size of pores, shape of pores, pore distributions are all controllable)

(5) **Thin-film with straight throughout microspores** (wettability, thickness, size of pores, shape of pores, pore distributions are all controllable)



Performance of PEMEC with Different Thickness Ti Felt LGDLs

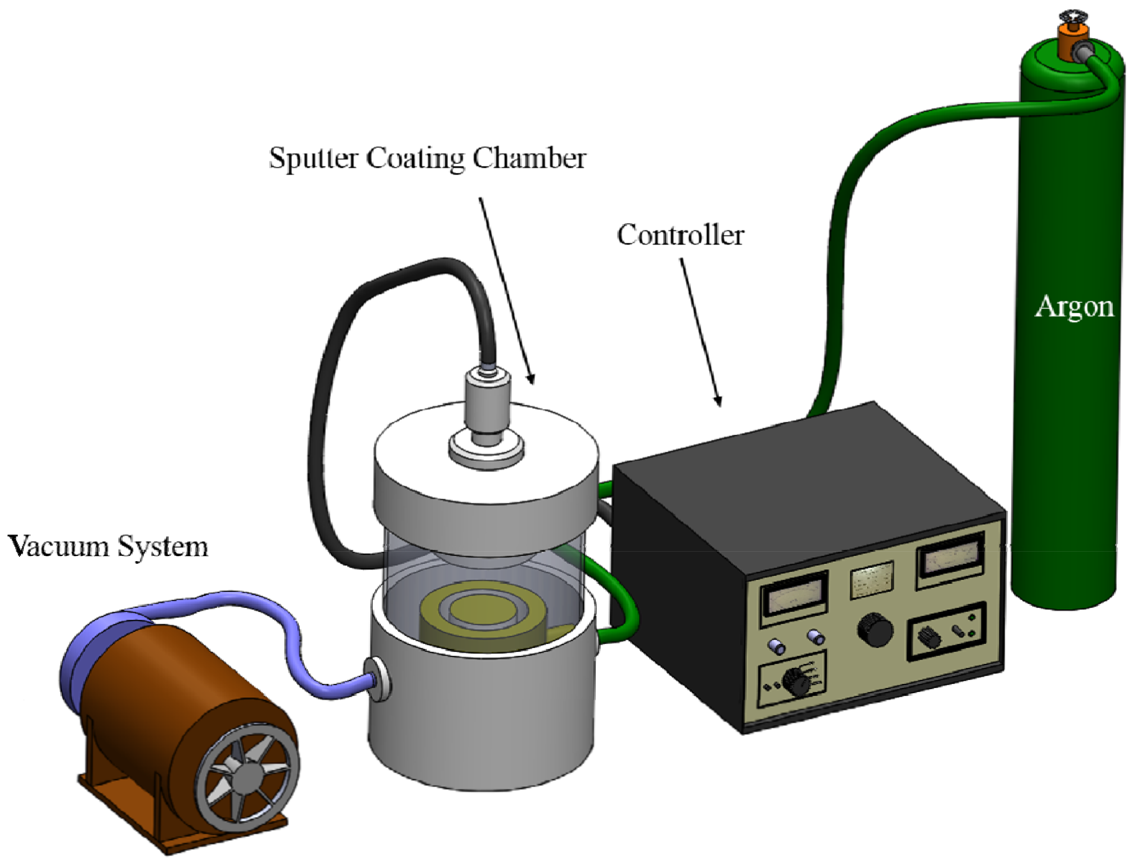




Steen, S.M. and F.-Y. Zhang: "*In-situ* and *Ex-situ* Characterizations of Electrode Interfaces in Energy Storage Electrolyzers", *ECS Trans. 2014 59(1): 95-102*

Sputter Coating Surface Treatment – Promote Interfacial Contact

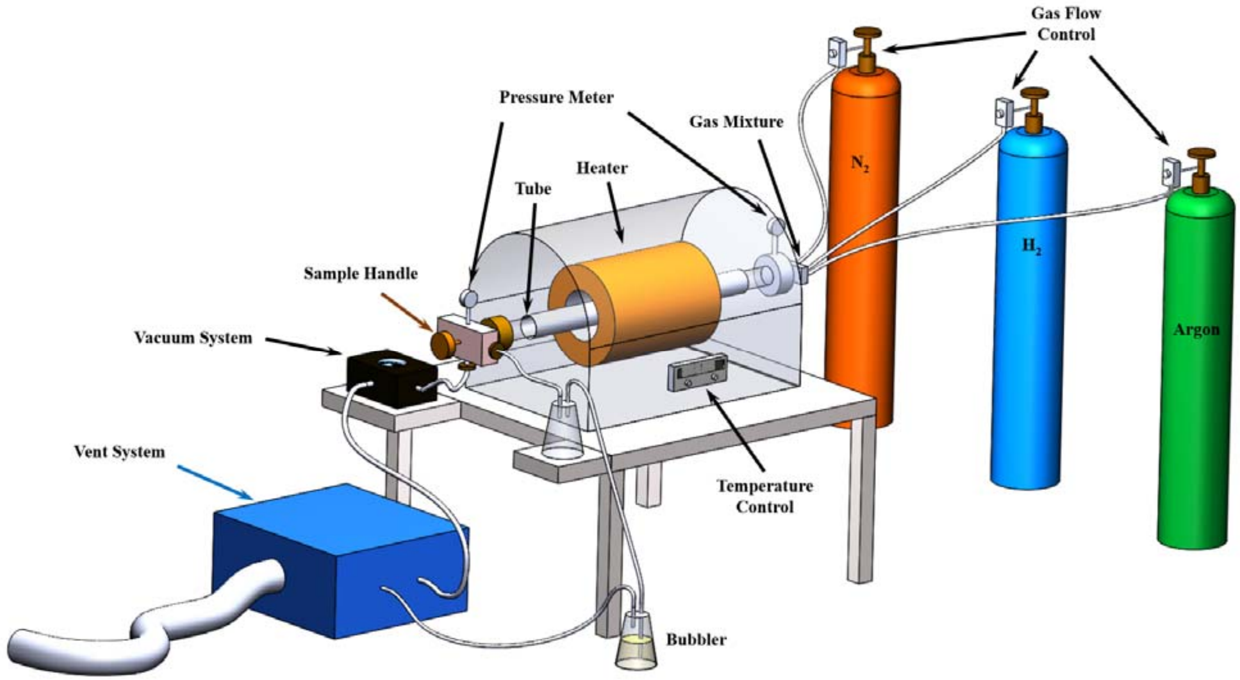
- Physical Vapor Deposition (PVD)
  - Argon Gas Tank
  - Voltage control system
  - Vacuum system
  - Sputter coating Chamber
- 2.4 kV voltage
- Twice one minutes process
- 200 nm film on the surface of fibers of titanium felt LGDL.



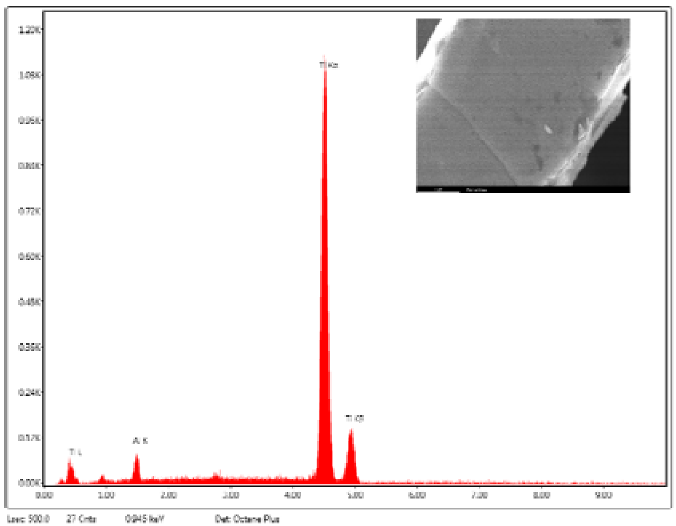
J. Mo, S.M. Steen, B. Han, Z. Kang, A. Terekhov, F.-Y. Zhang, S.T. Retterer, D.A. Cullen. Investigation of titanium felt transport parameters for energy storage and hydrogen/oxygen production. AIAA **2015-3914** (2015).

Thermal Nitridation – A Cheaper Method for Surface Treatment

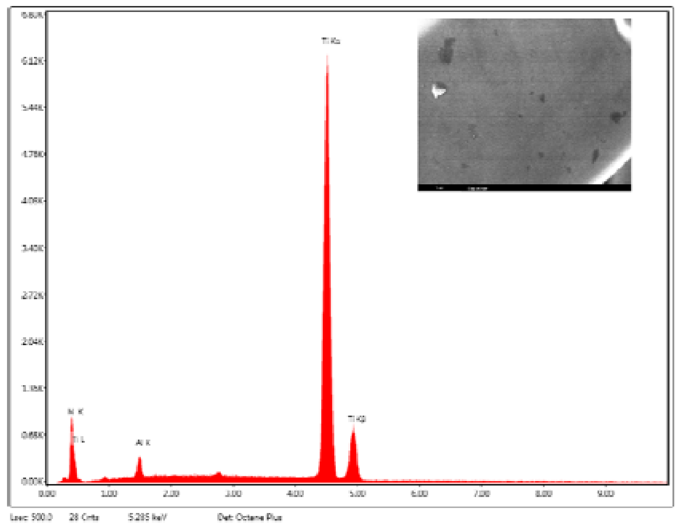
- Chemical Vapor Deposition (CVD)
  - High-temperature furnace
  - Vacuum system
  - Gas supply system
- 900 °C for 10 mins
- 1 um thickness titanium nitride thin film on the surface of fiber of titanium felt LGDL



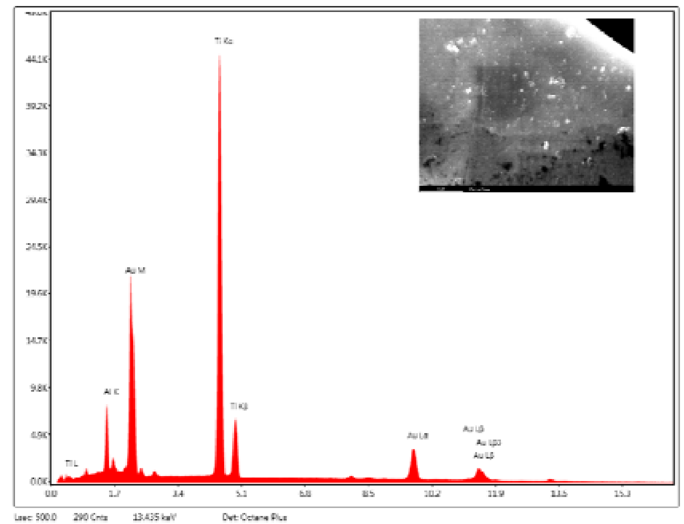
SEM and EDS Results of Origin Titanium Felt LGDL



Original Titanium Felt

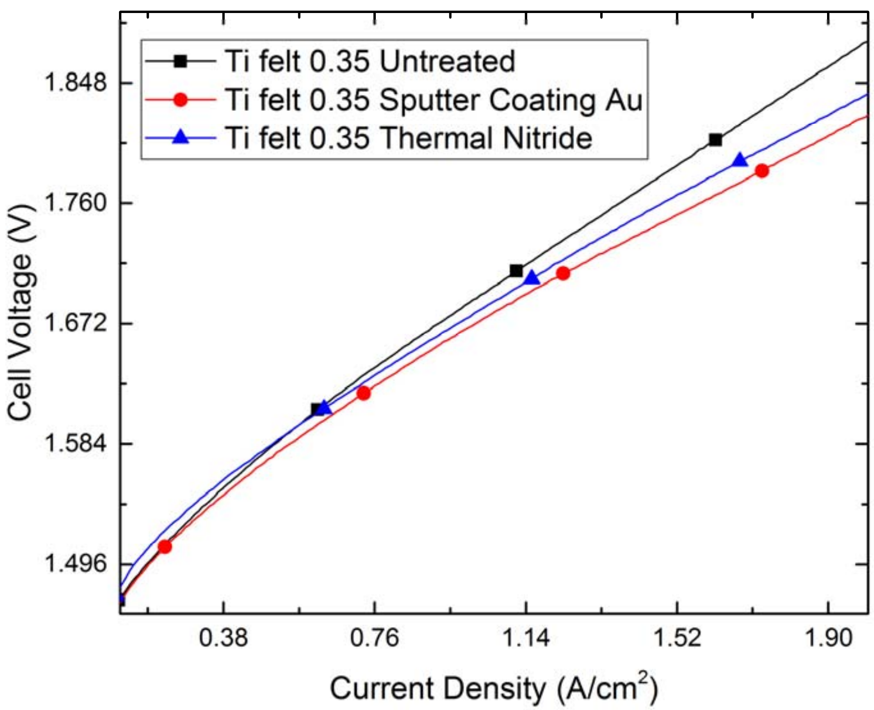


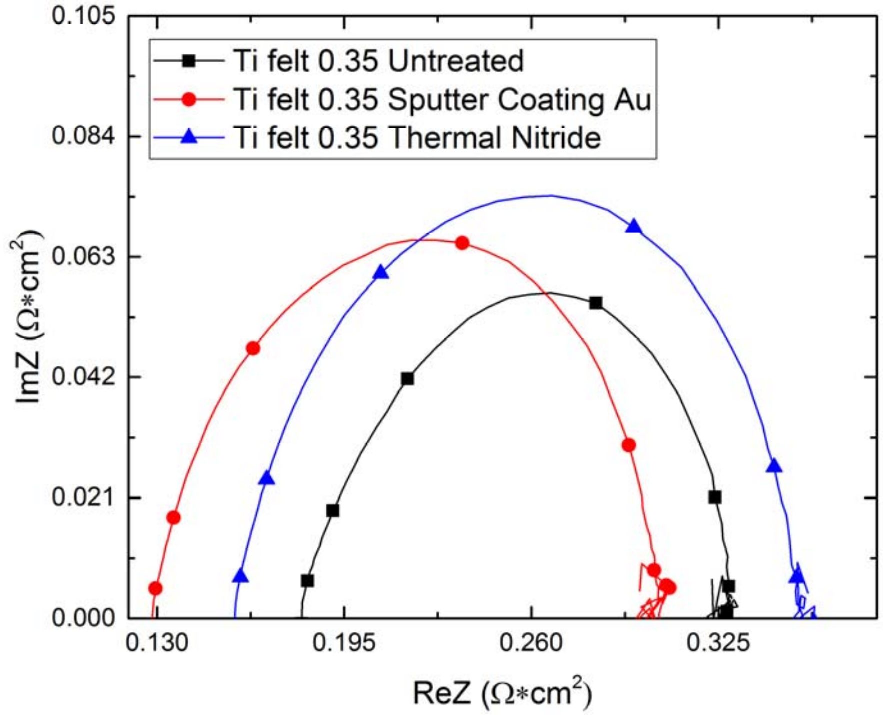
Thermal Nitride



Sputter Coating (Au)

Performance and Impedance Comparisonof PEMEC with LGDL Under Different Surface Treatments

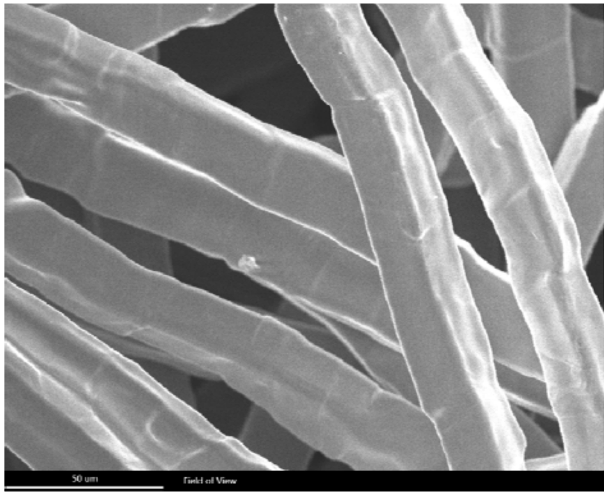


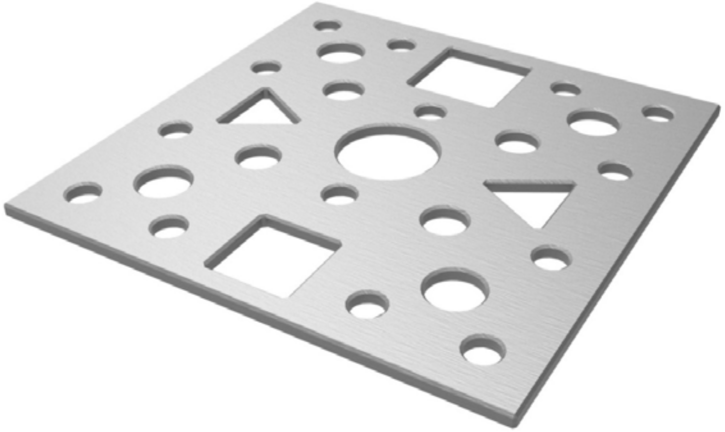


J. Mo, S.M. Steen, B. Han, Z. Kang, A. Terekhov, F.-Y. Zhang, S.T. Retterer, D.A. Cullen. Investigation of titanium felt transport parameters for energy storage and hydrogen/oxygen production. AIAA **2015-3914** (2015).

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

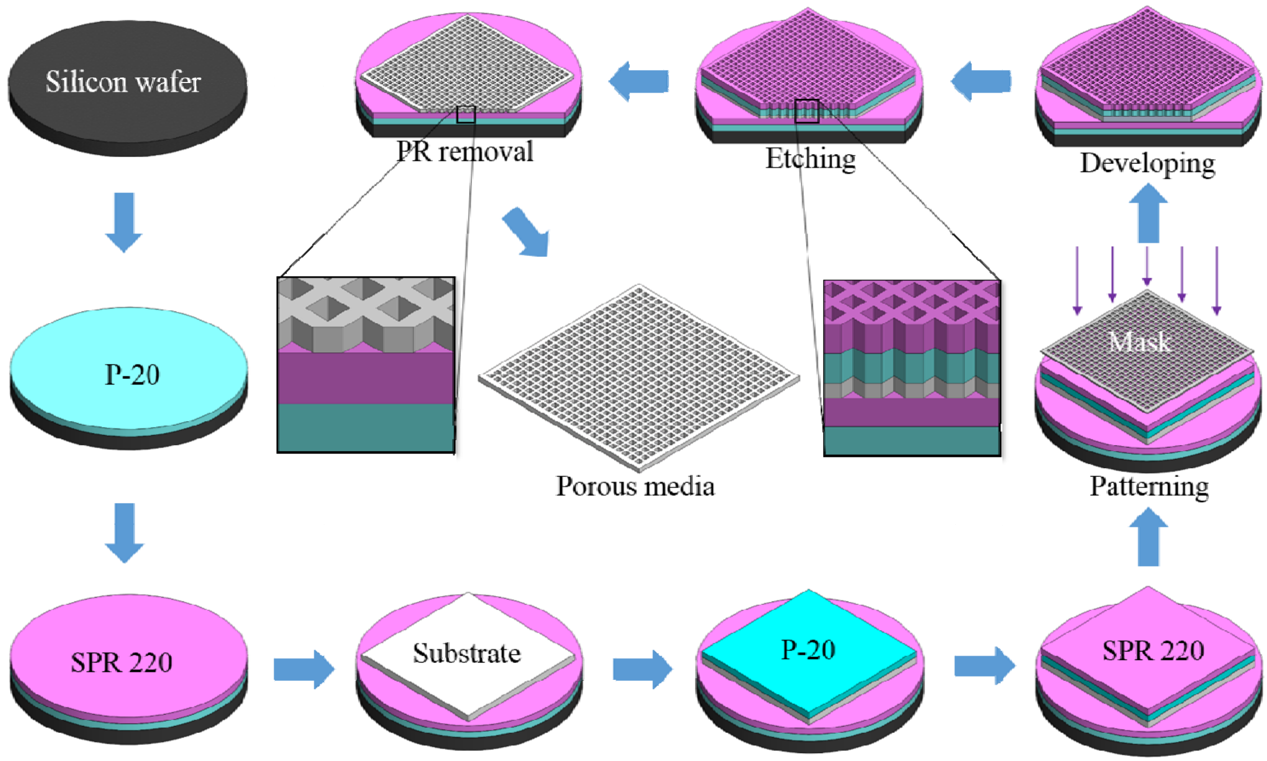
- Challenges: need multifunctional LGDLs with minimum losses of transport, electrical and thermal properties combined with high durability in oxidizing and reducing environments.





- 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

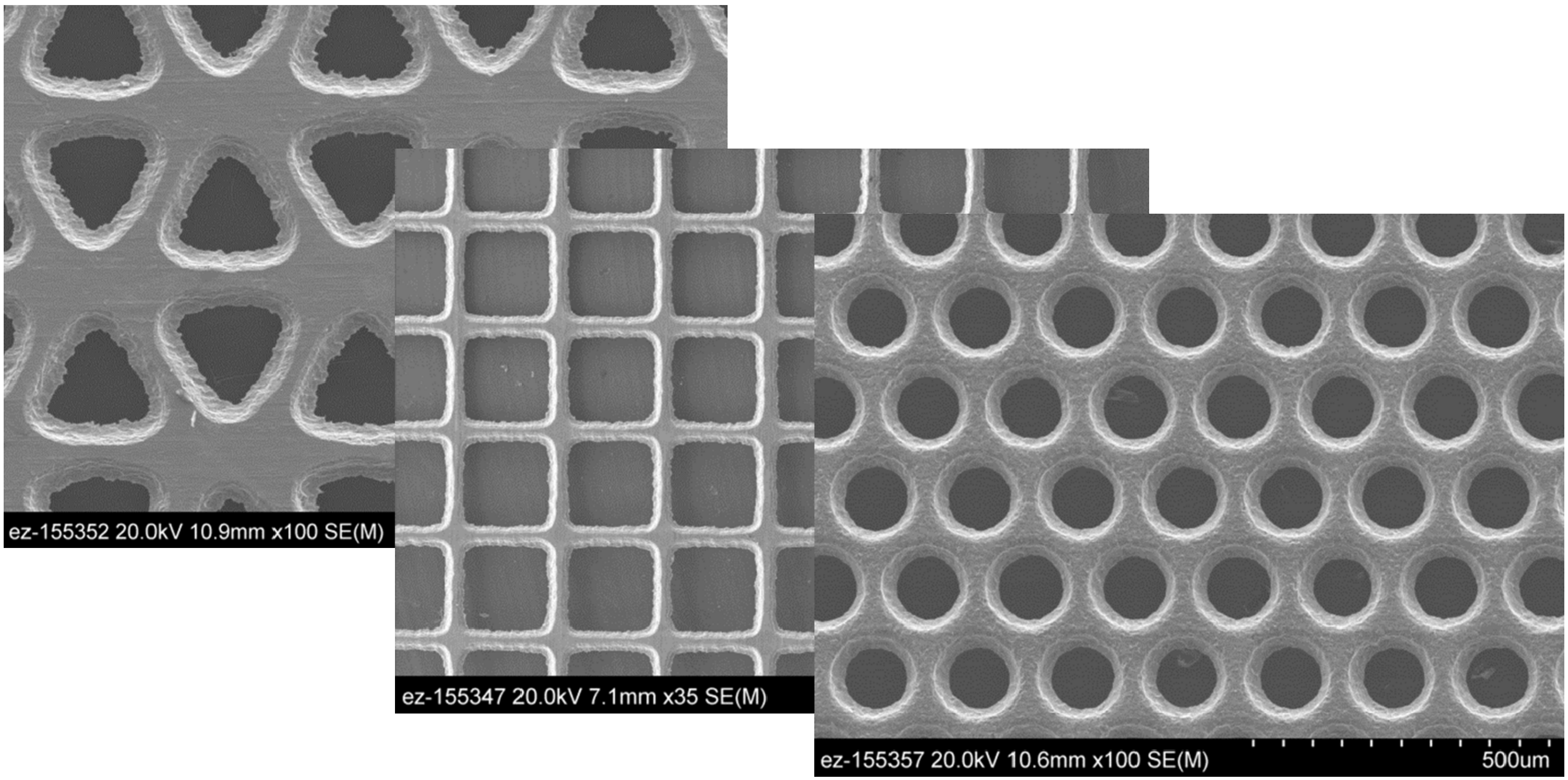


OAK RIDGE National Laboratory

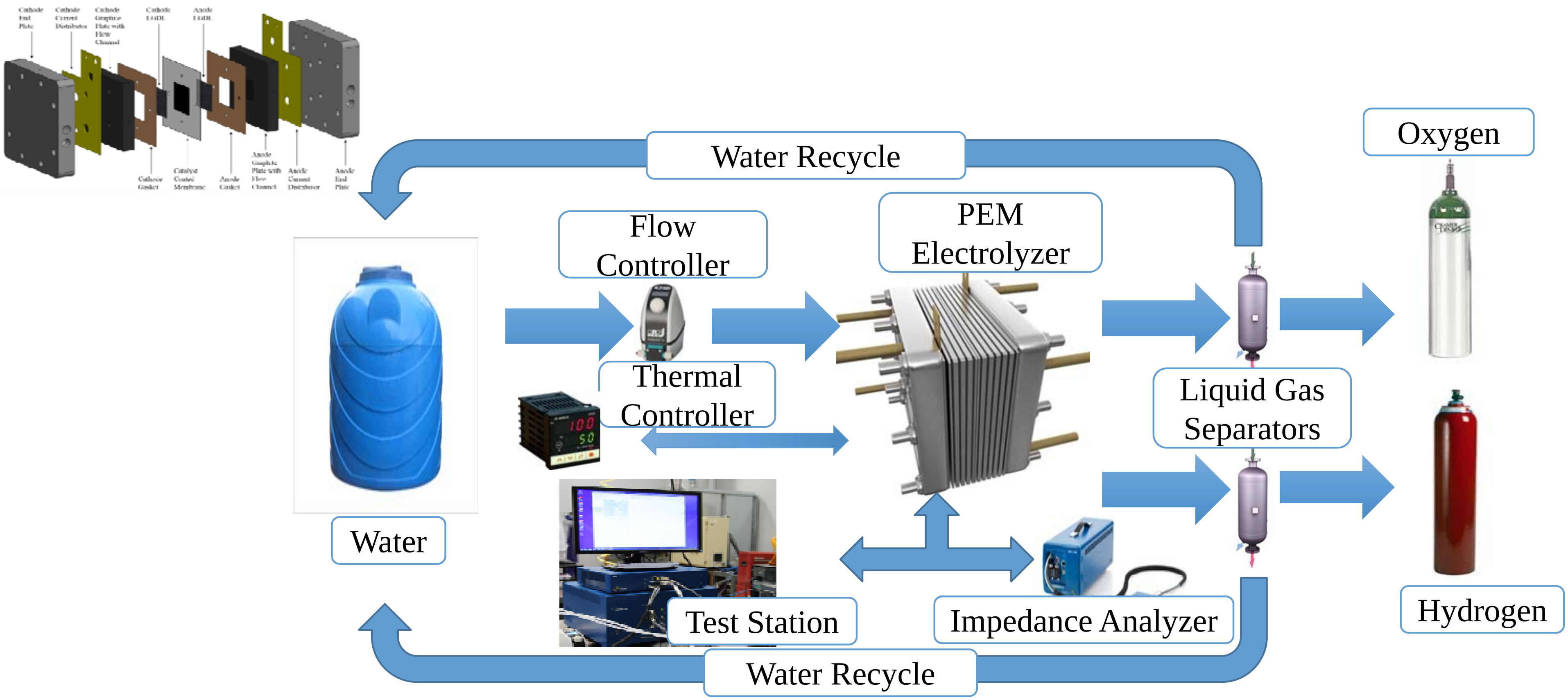
CENTER FOR NANOPHASE MATERIALS SCIENCES

J. K. Mo, S. M. Steen, A. Terekhov, S. T. Retterer, D. A. Cullen, and F. Y. Zhang: "Mask-Patterned Wet Etching of Thin Titanium Liquid/Gas Diffusion Layers for a PEMEC", *ECS Transaction, Vol 66, No 24, 2015, pp. 3-10.*

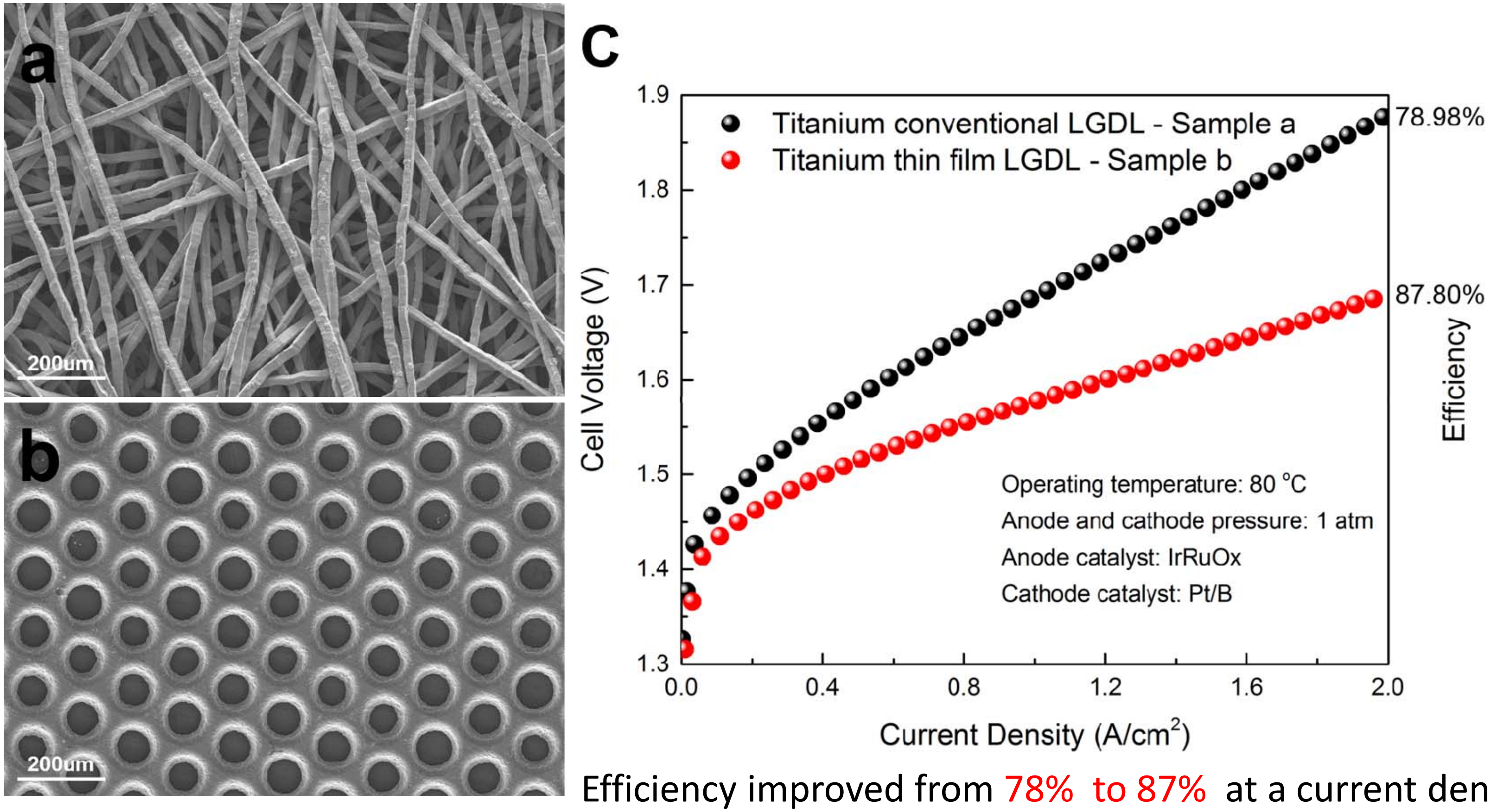
Thin LGDLs have been successfully fabricated with different design parameters



Thin LGDLs were tested in a standard electrolyzer cell with test station and control system



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

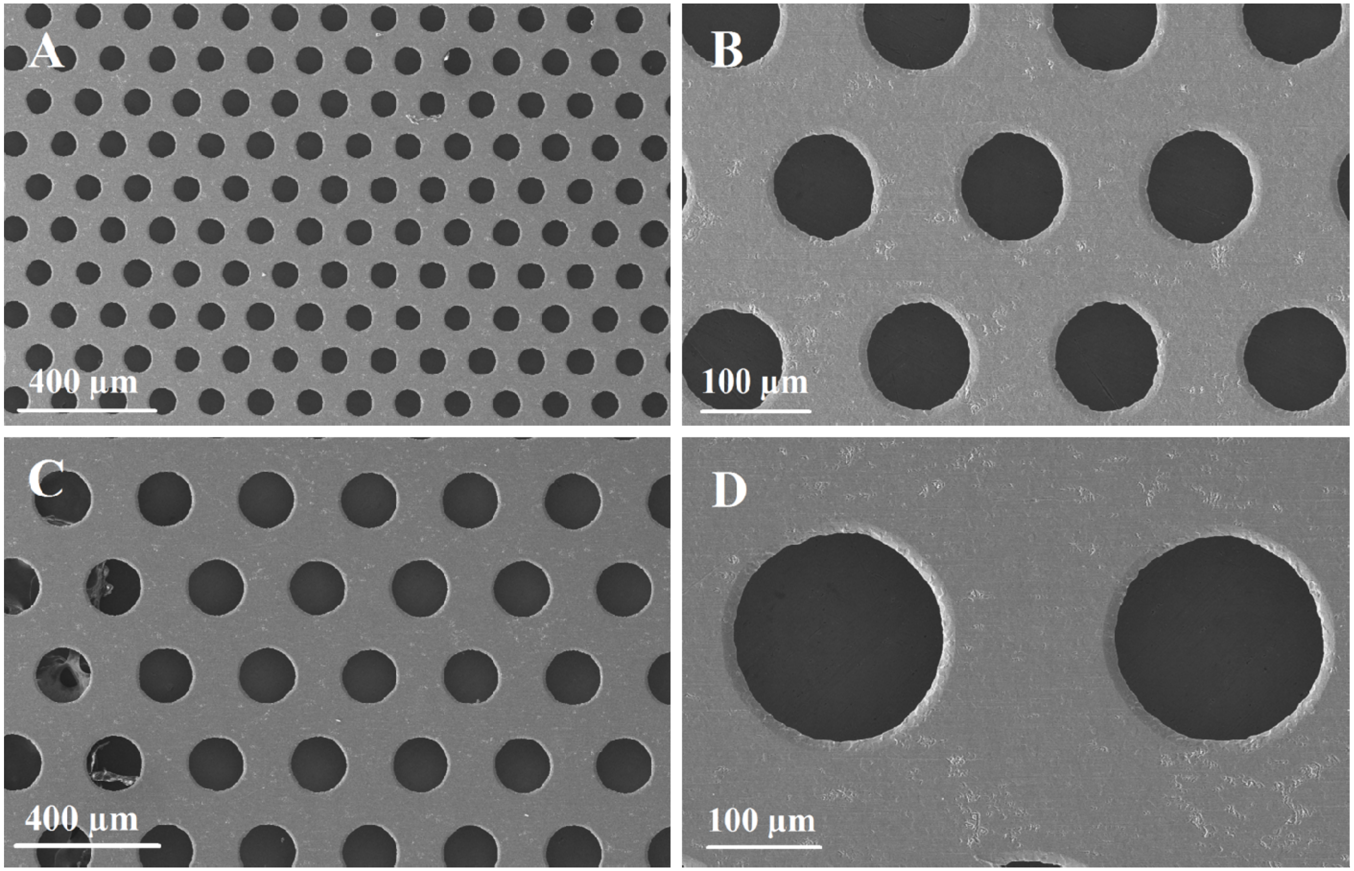
Thin LGDLs with different pore morphologies

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

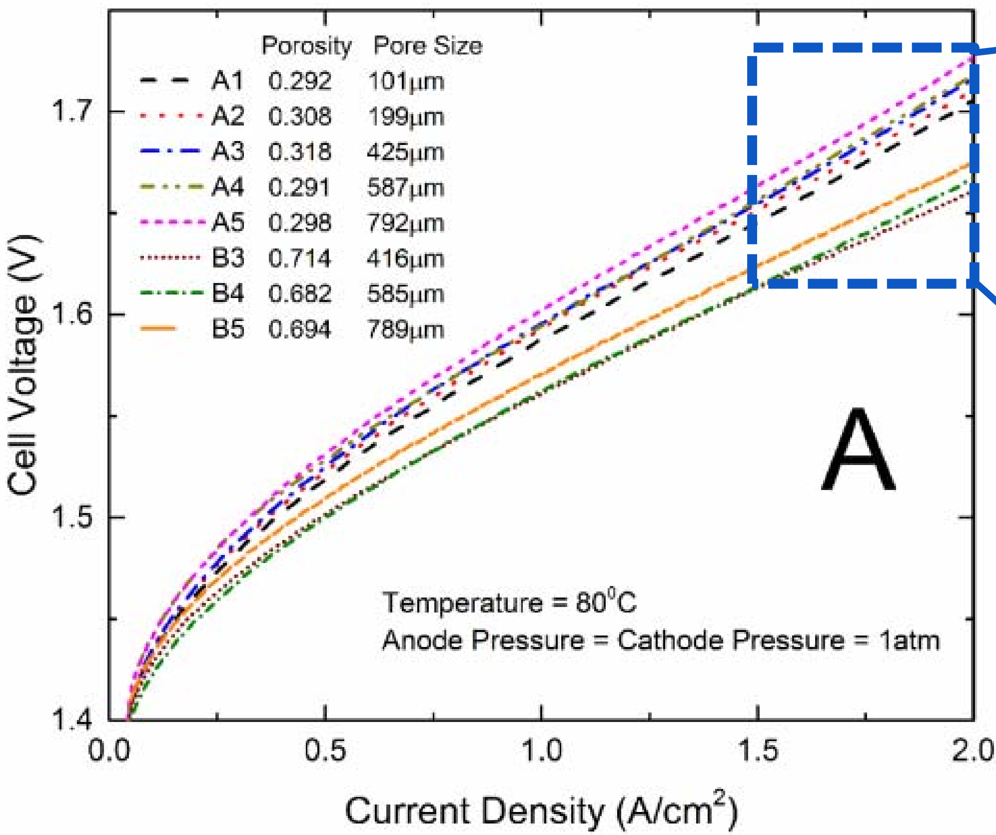
Characteristics of thin and well-tunable titanium LGDLs

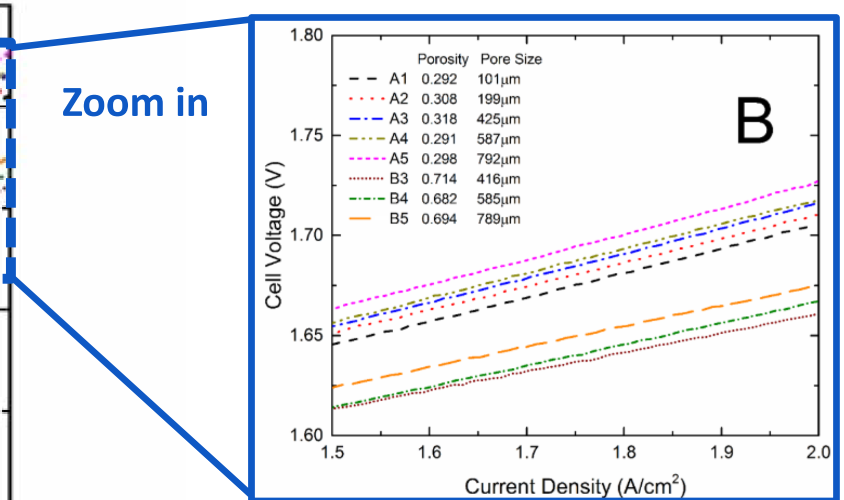
- Case I
  - Pore Size: 100 microns
  - Thickness: 25 microns
  - Porosity: 30%

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



The impact of the pore size and porosity

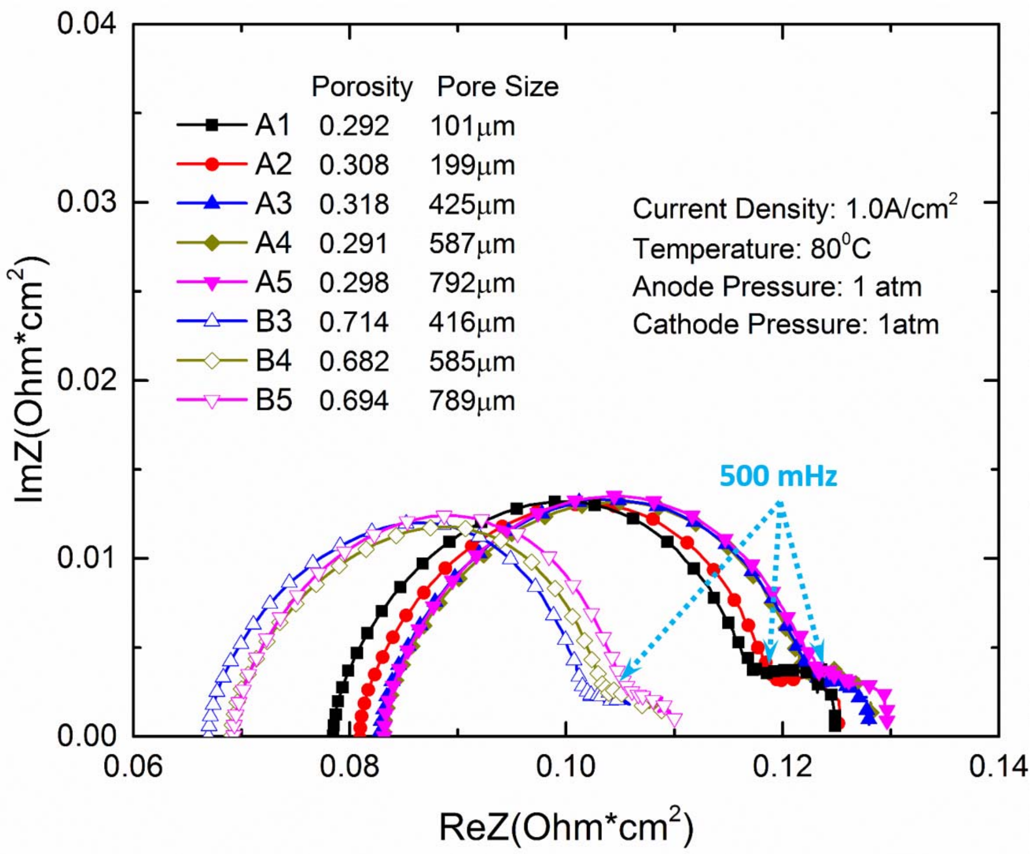




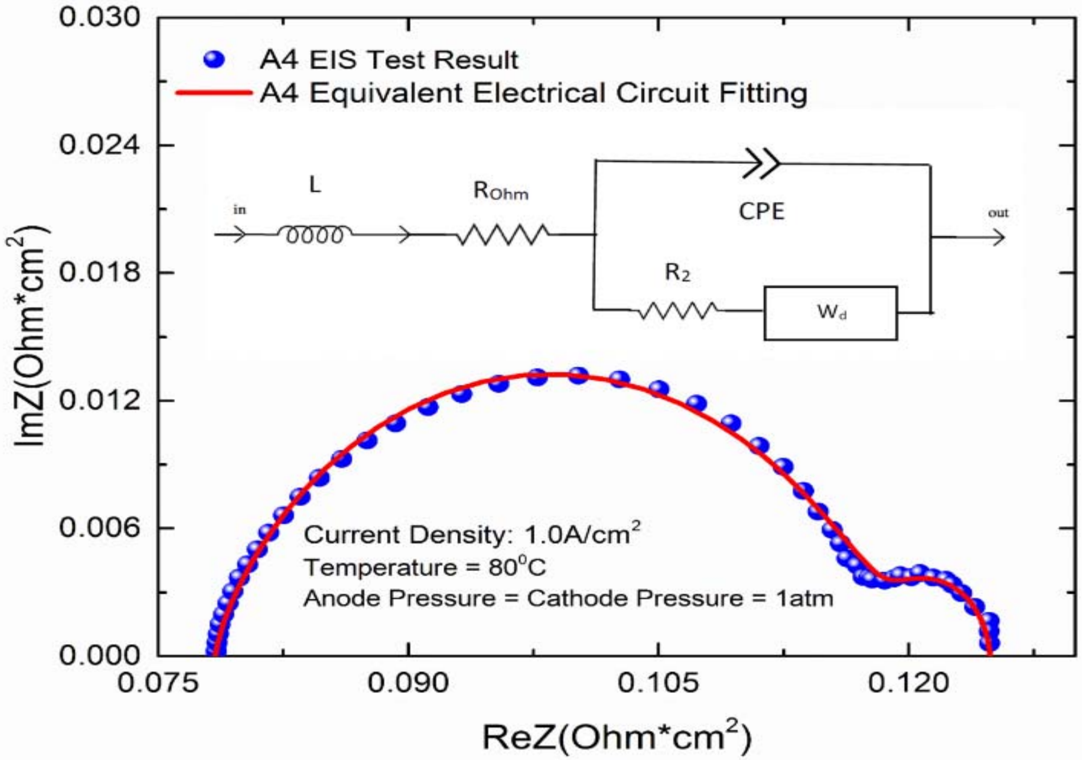
- With the increase of the pore size at the same porosity, the PEMEC performance decreases
- With the increase of the porosity from 0.3 to 0.7, the performance of the PEMEC was significantly improved
- The porosity has greater impact on PEMEC performance than pore size in this range

Electrochemical Impedance Spectrocopy

- The left x-intercepts (at the high frequency part) indicates the ohmic loss of the whole PEMEC, while the right one (at the low frequency part) is the sum of the resistance
- The distance between the two intercepts indicates the sum of activation and mass transport losses
- LGDLs with a porosity of 0.3 have larger ohmic resistance, and the value decreases with the increase of porosity
- The ohmic loss decreases significantly from around 0.08 ohm*cm2 for the LGDL with a porosity of 0.7 to less than 0.07 ohm*cm2 for one with a porosity of 0.3
- LGDLs having a porosity of 0.7 show smaller first and second arcs, which indicates that the activation and mass transfer losses decrease with the increase of porosity from 0.3 to 0.7, and the sum of activation and mass transfer losses are reduced from about 0.046 ohm*cm2 for 0.3 porosity LGDLs to 0.039 ohm*cm2 for 0.7 porosity LGDLs



EIS model

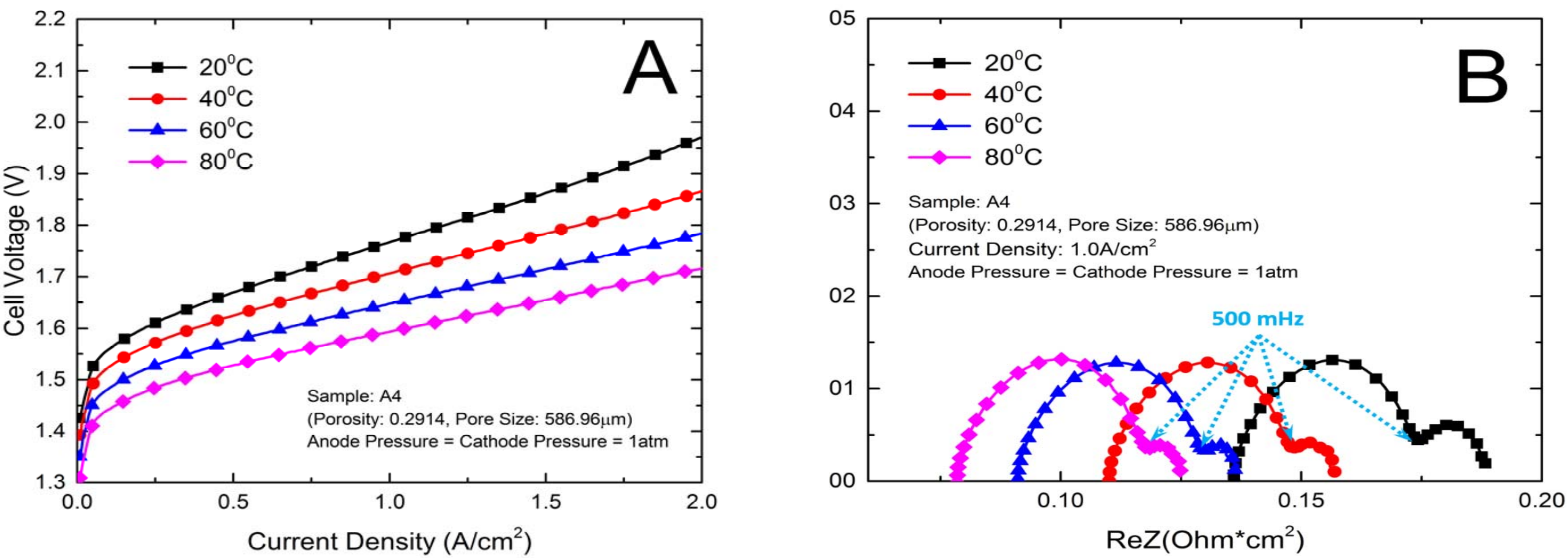


0.030
0.024
0.018
0.012
0.006
0.000
0.075
0.090
0.105
0.120
ImZ(Ohm*cm²)
ReZ(Ohm*cm²)
A4 EIS Test Result
A4 Equivalent Electrical Circuit Fitting
L
ROhm
CPE
R2
Wd
in
out
Current Density: 1.0A/cm²
Temperature = 80°C
Anode Pressure = Cathode Pressure = 1atm

EIS model results

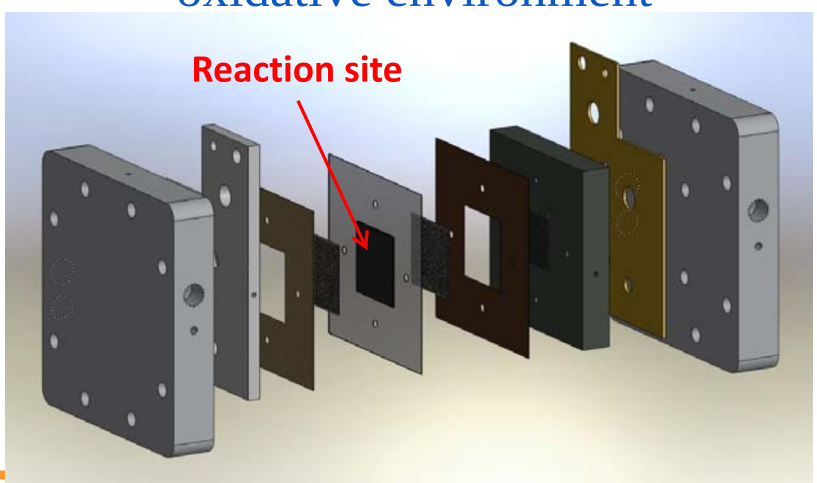
Sample	L_{Ind} [H]	R_{Ohm} [Ω*cm^2]	R_2 [Ω*cm^2]	R_d [Ω*cm^2]	ERROR [%]
A1	1.23E-08	0.0779	0.0406	0.006	0.31
A2	1.19E-08	0.0804	0.0410	0.005	0.29
A3	1.28E-08	0.0822	0.0411	0.004	0.23
A4	1.24E-08	0.0825	0.0418	0.004	0.31
A5	1.21E-08	0.0824	0.0420	0.004	0.20
B3	1.24E-08	0.0665	0.0363	0.003	0.45
B4	1.20E-08	0.0688	0.0365	0.003	0.48
B5	1.28E-08	0.0696	0.0381	0.002	0.33

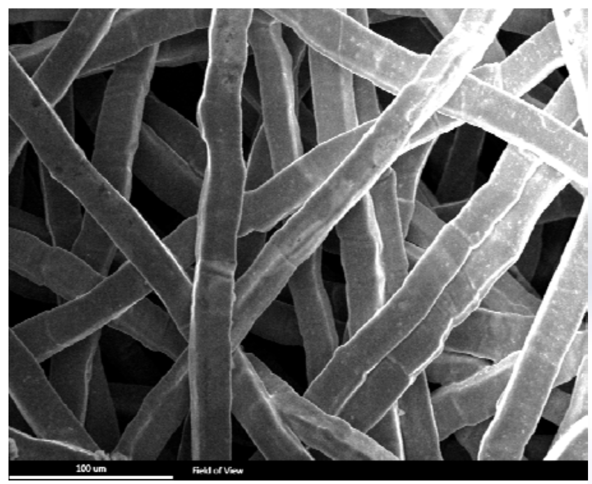
Better performance will be obtained with temperature increase

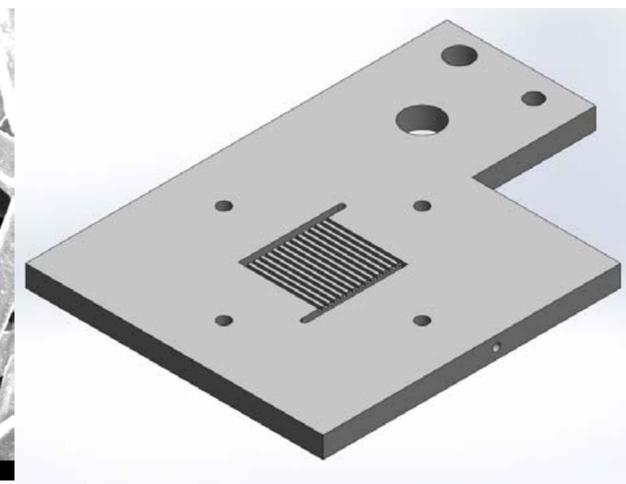


Thin and well-tunable LGDLs with straight pores make it possible to *in-situ* investigate electrochemical reactions

- 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

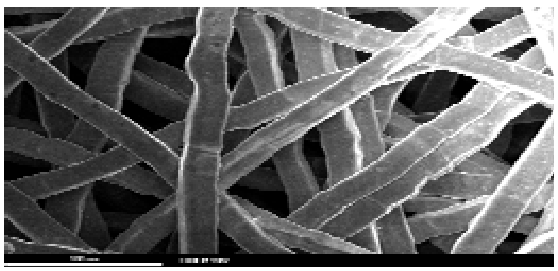


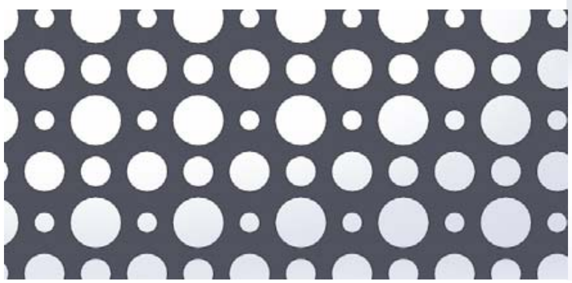


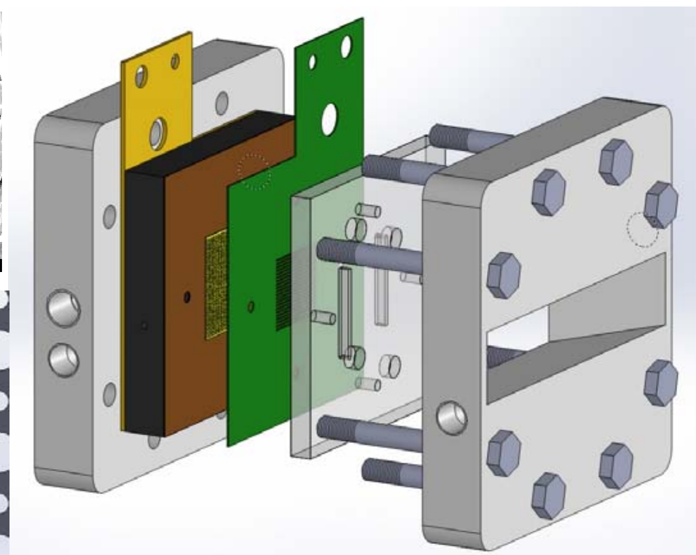


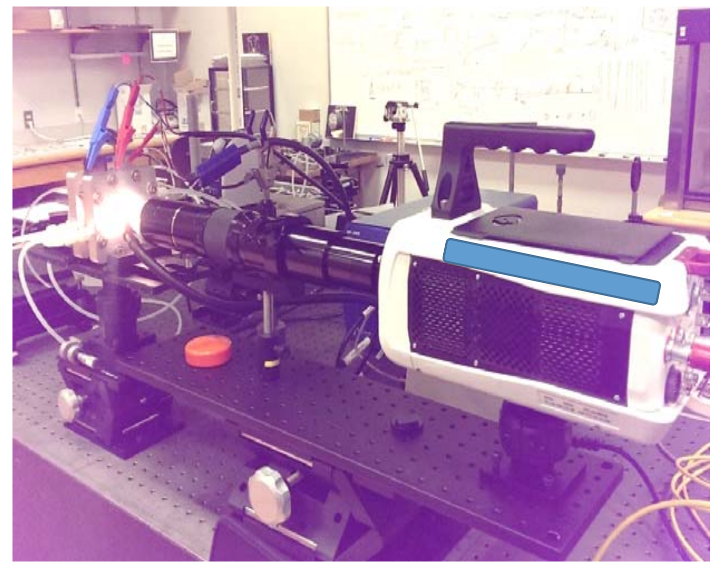
In-situ visualization with developments of novel LGDLs, transparent PEMFCs and high-speed/microscale system

- Fabricate well-tunable transport LGDLs with straight pores
- Design a transparent PEM Electrolyzer Cell
- Develop a high-speed and micro-scale visualization system (HMVS)





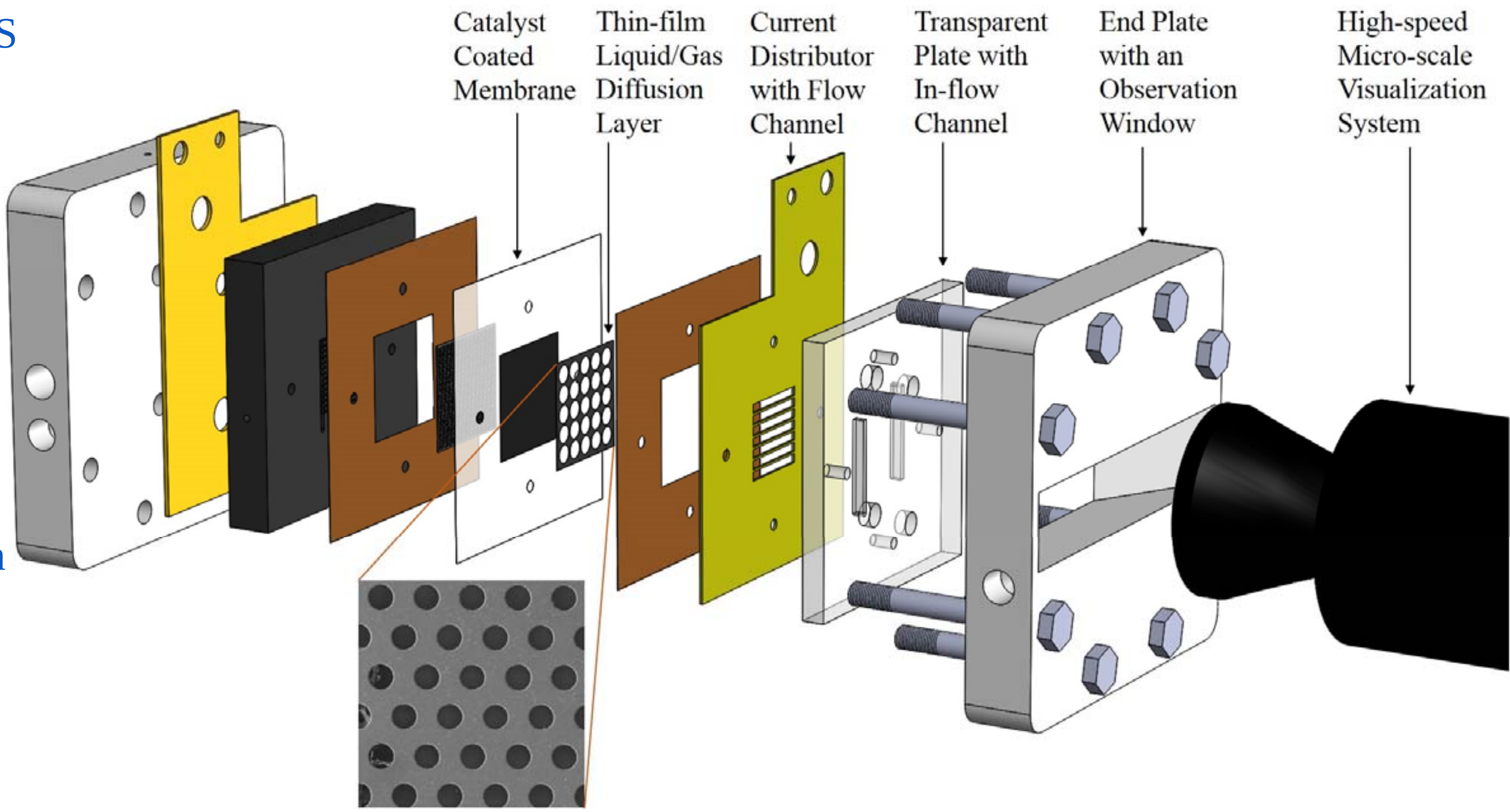




J. Mo, S.M. Steen, B. Han, F.-Y. Zhang. High-speed and micro-scale measurements of flow and reaction dynamics for sustainable energy storage. AIAA **2015-3913** (2015).

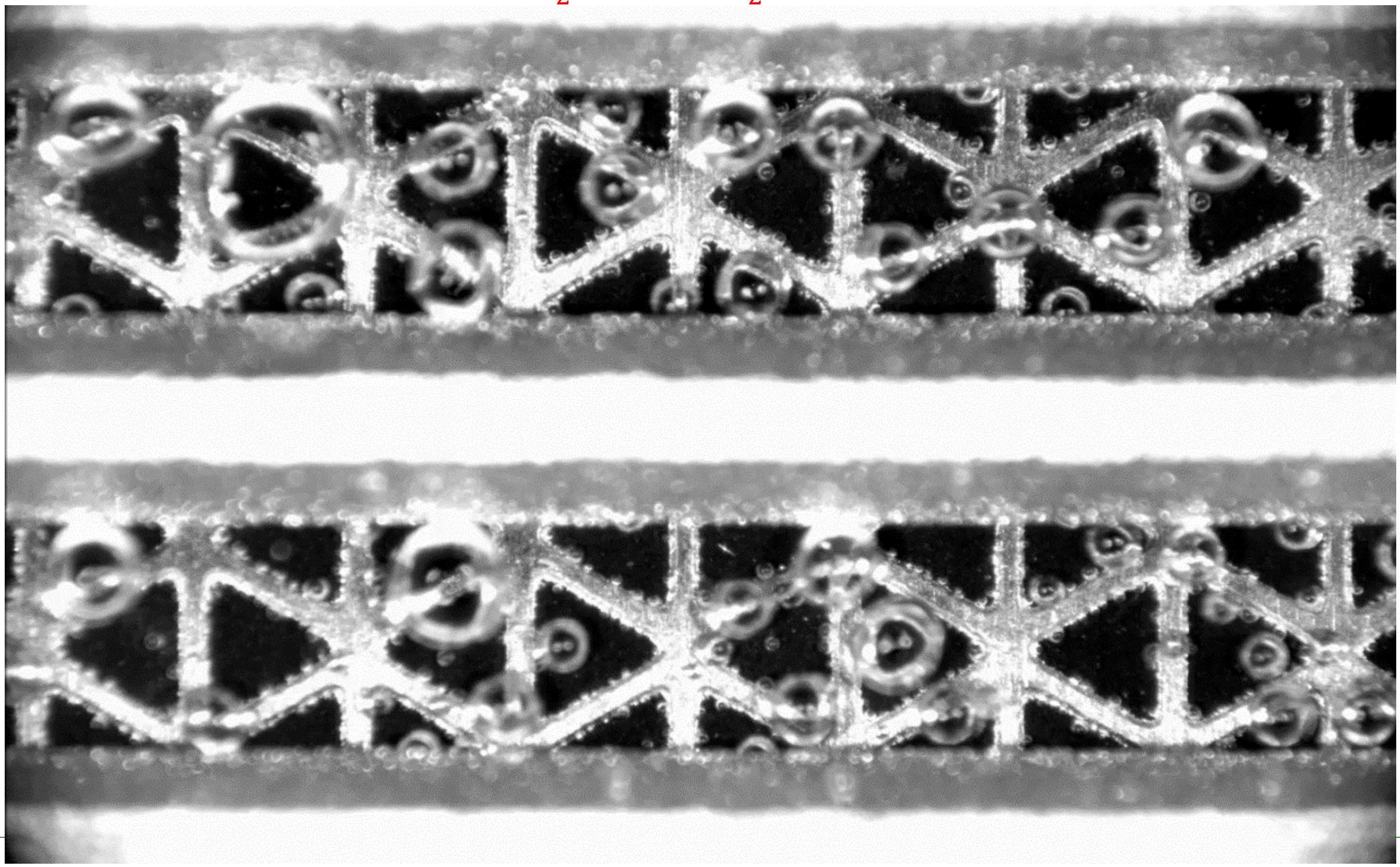
High-speed and Micro-scale Visualization System (HMVS)

- Transparent PEM water electrolyzer cell with HMVS
- Observation window on the end plate
- Conventional bipolar plate (BP) was split into two components:
  - Thin titanium current distributor with throughout flow pattern
  - Transparent block with inflow channels
- Thin/well-tunable LGDLs with straight-through pore

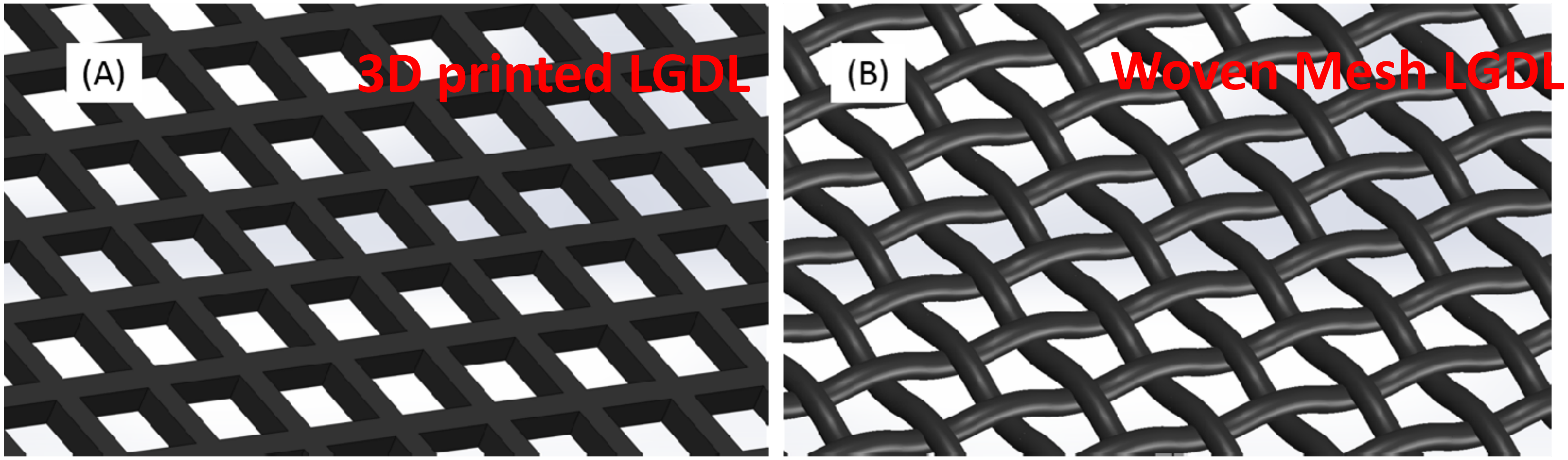


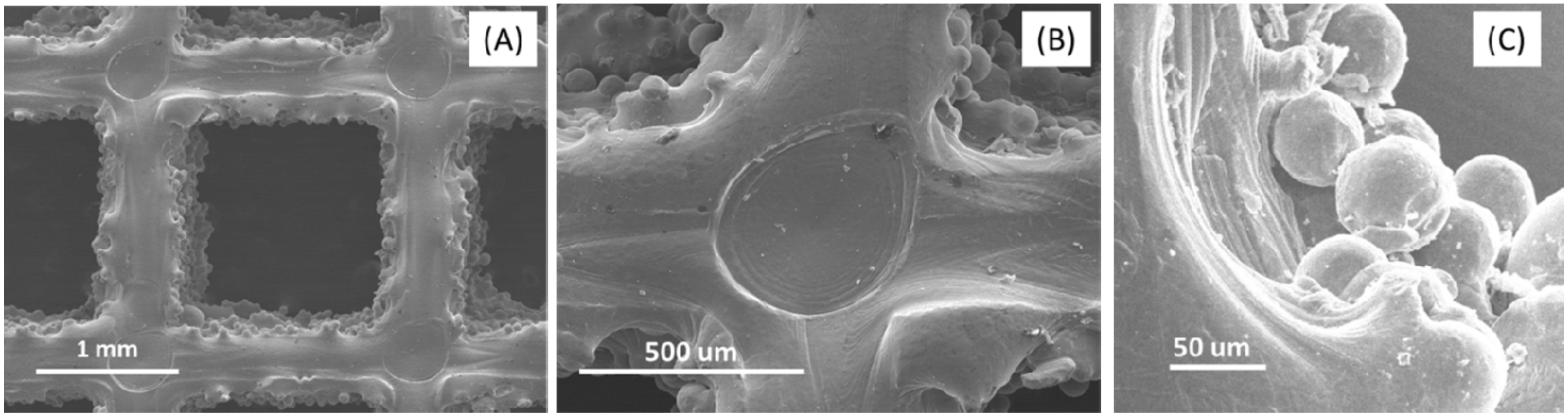
Only small portion of catalyst function as designed and great opportunity for cost reduction

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

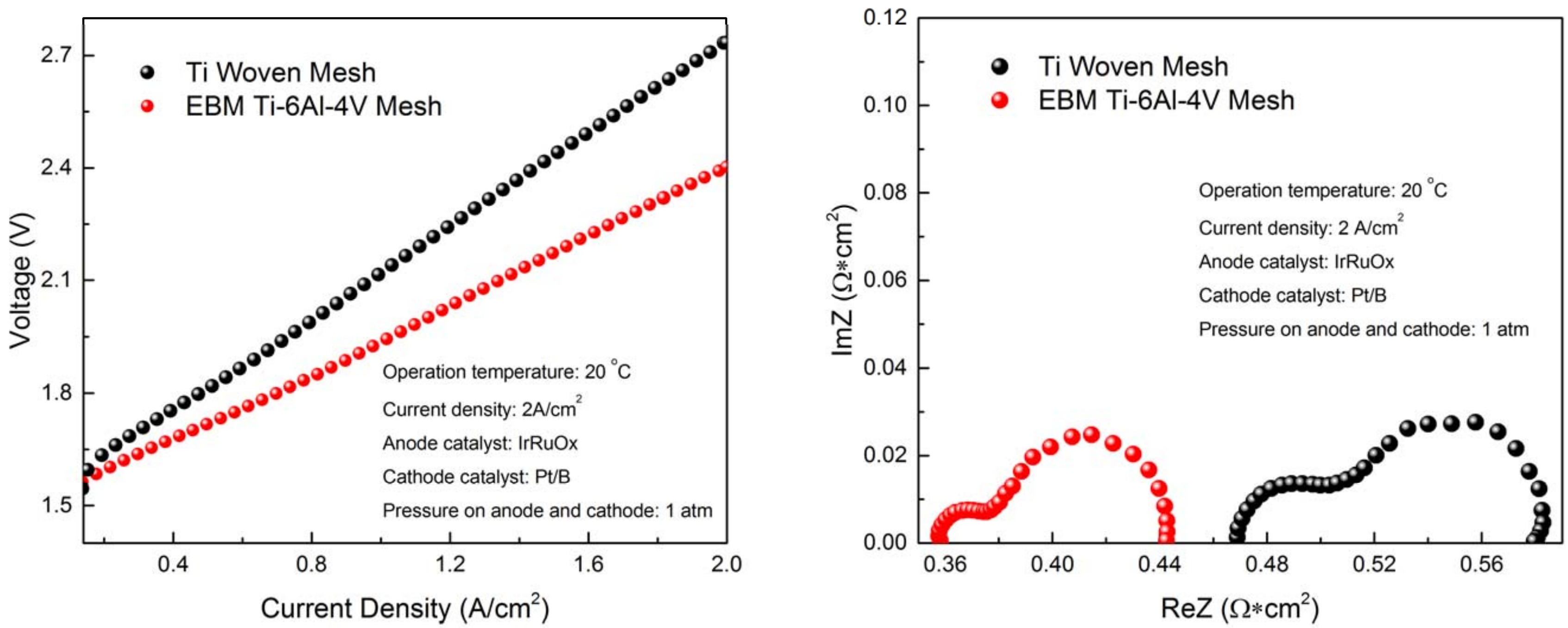


Additive manufacturing of LGDL to enhance interfacial effects with low cost





Performance and Impedance Comparison Between Woven Mesh and 3D Printing LGDL



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).

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:

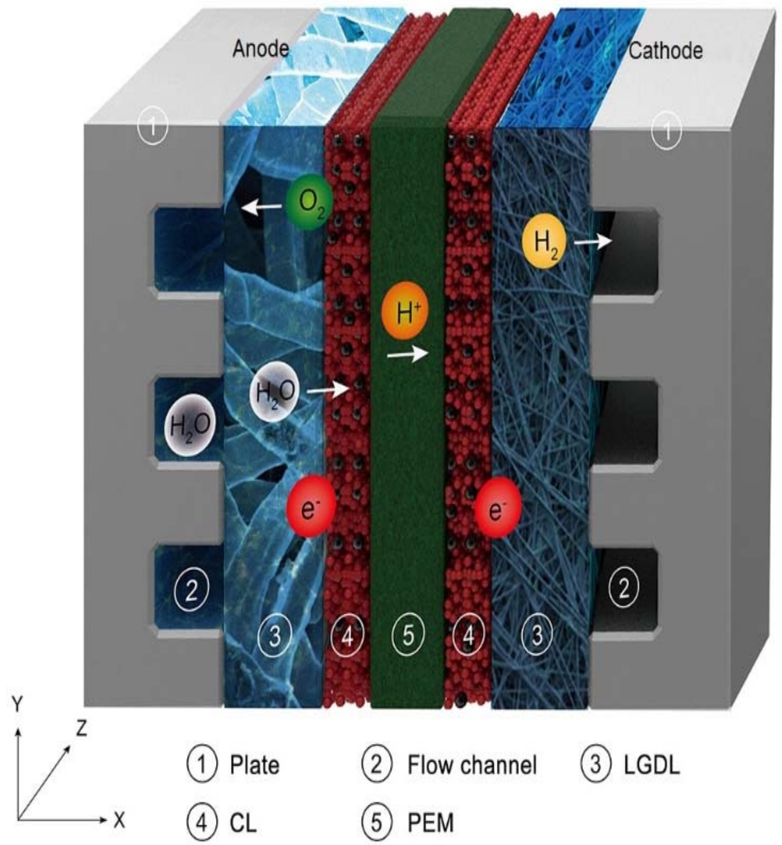
$$\nabla \cdot \left(-\frac{K k_{H_2O}}{\mu_{H_2O}/\rho_{H_2O}} \nabla p_{H_2O} \right) = N_{H_2O}$$

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



Han, B., J. Mo, Z. Kang, and F.-Y. Zhang, *Electrochimica Acta*, 2016. **188**

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:

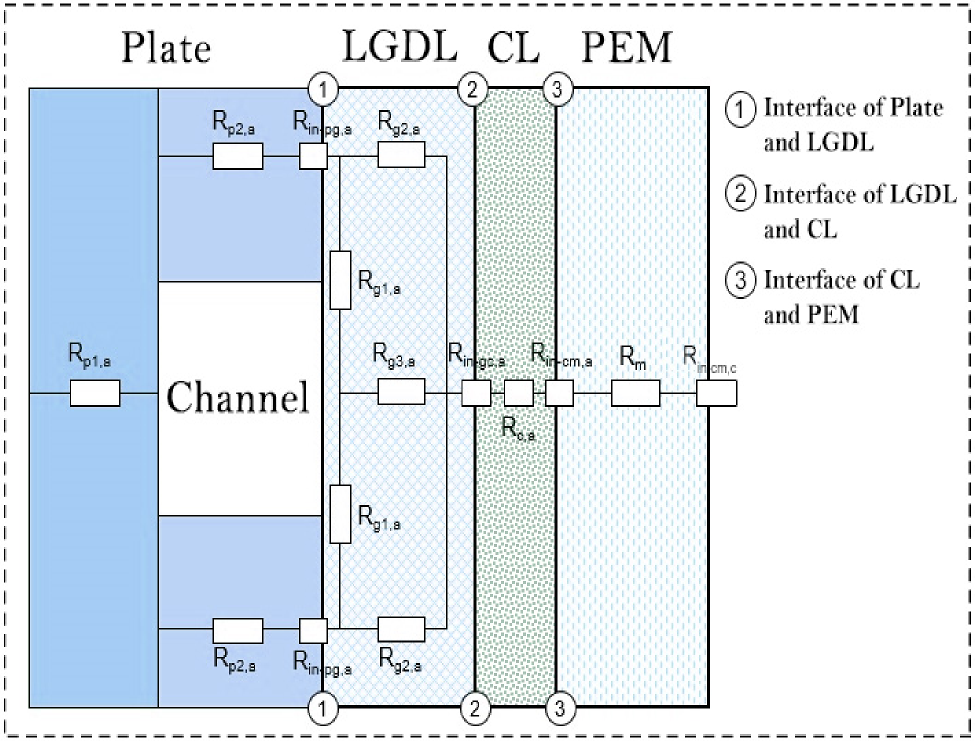
$$V_{ocv} = V_0 + \frac{RT}{zF}\ln\left(\frac{\alpha_{H_2}\alpha_{O_2}^{0.5}}{\alpha_{H_2O}}\right)$$

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:

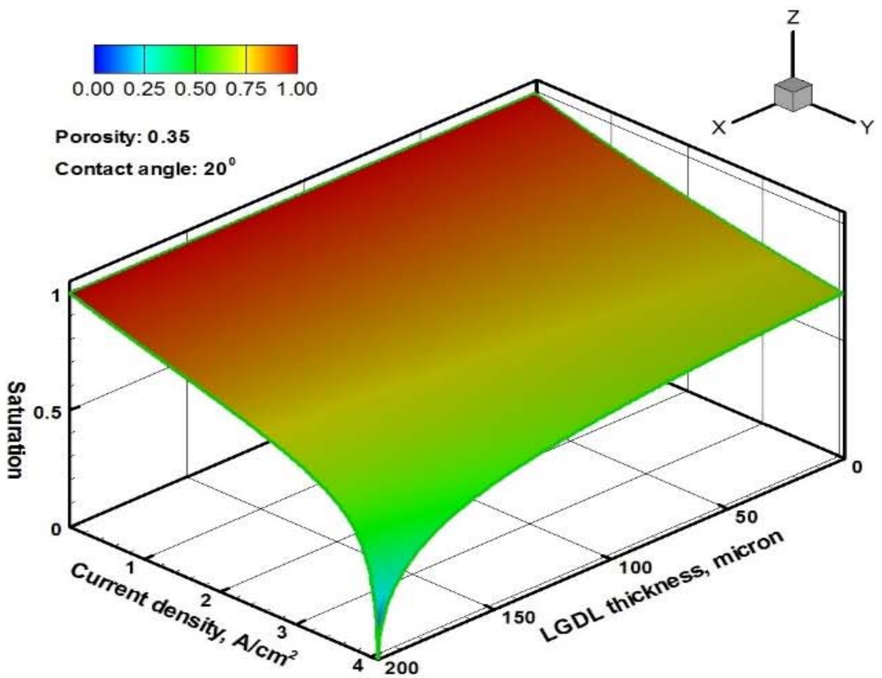
$$V_{ohm} = (R_{plate} + R_{LGDL} + R_{PEM} + R_{inerface})jA$$



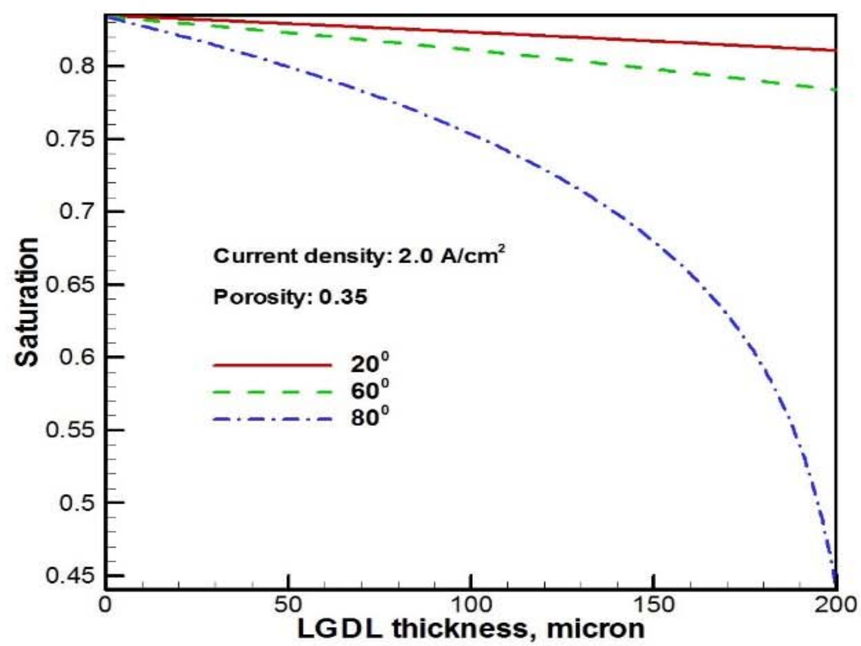
Han, B., Steen, S. M., Mo, J., and Zhang, F.-Y. "Electrochemical performance modeling of a proton exchange membrane electrolyzer cell for hydrogen energy," *International Journal of Hydrogen Energy* Vol. 40, No. 22, 2015

Liquid saturation distribution in the LGDL

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



(a)

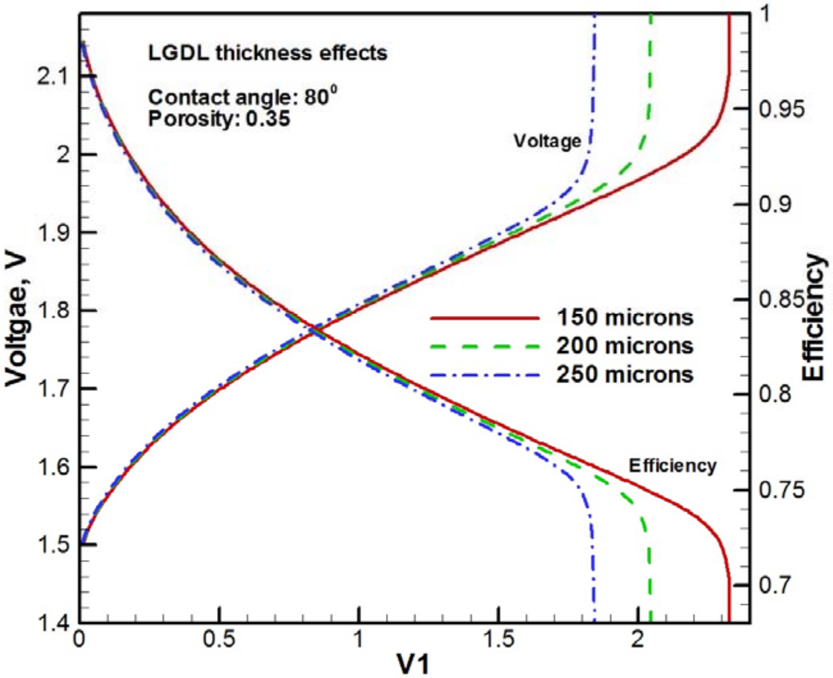


(b)

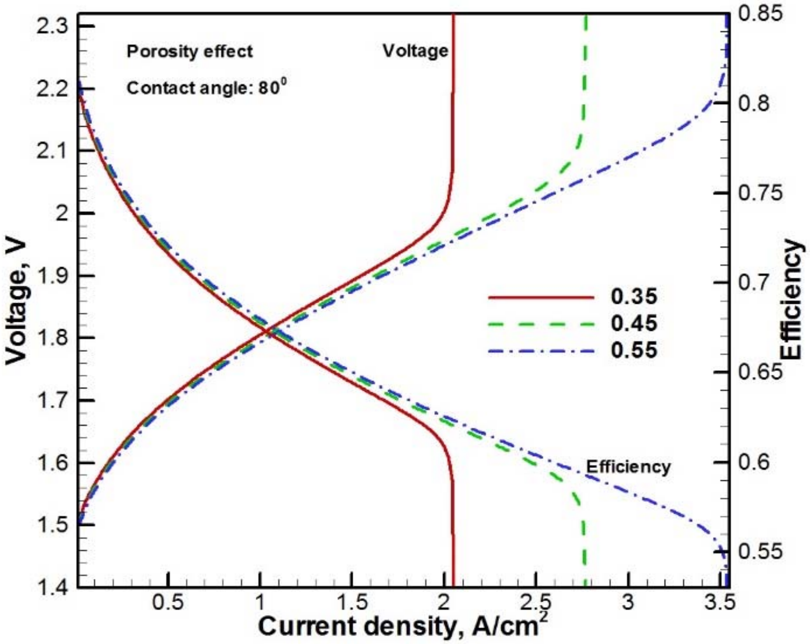
Han, B., J. Mo, Z. Kang, and F.-Y. Zhang, *Effects of membrane electrode assembly properties on two-phase transport and performance in proton exchange membrane electrolyzer cells.* Electrochimica Acta, 2016. **188**: p. 317-326

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

- **Effects of LGDL thickness on the cell performance and efficiency**



- **Effects of LGDL porosity on the cell performance and efficiency**



Han, B., J. Mo, Z. Kang, and F.-Y. Zhang, *Electrochimica Acta*, 2016. **188**

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
- Performance increase with porosity, while decreases with the increase of pore size from 100 to 800 μm
- 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
- With high-speed and microscale visualization system, the multiscale details about corrosion dynamics were exposed
- Additive manufacturing of multifunctional materials and demonstrated its potential
- Modeling two-phase flow and simulating the effects of material properties

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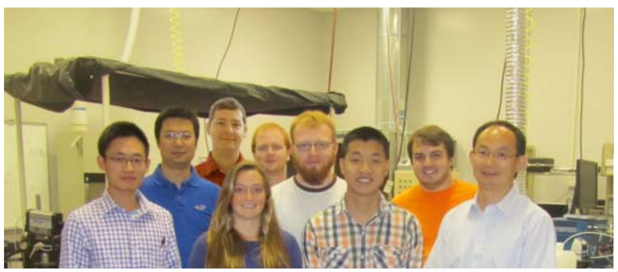
- Collaborators:

Scott Retterer, Dave Cullen, Mike Brady, Peter Liaw, Karin Dahmen, Todd Toops, Jun Qu, Johney Green, Suresh Babu, Ryan Dehoff, William Peter, Joey Kish



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