NETL's Crosscutting Research Review Meeting

Award: DE-FE0011585

Project manager: Dr. Jason Hissam

Developing novel multifunctional materials for high-efficiency electrical energy storage

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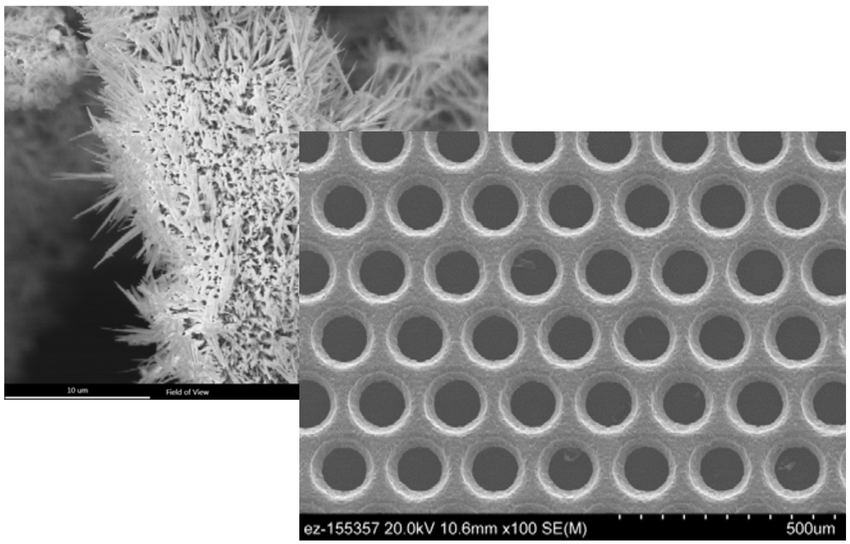
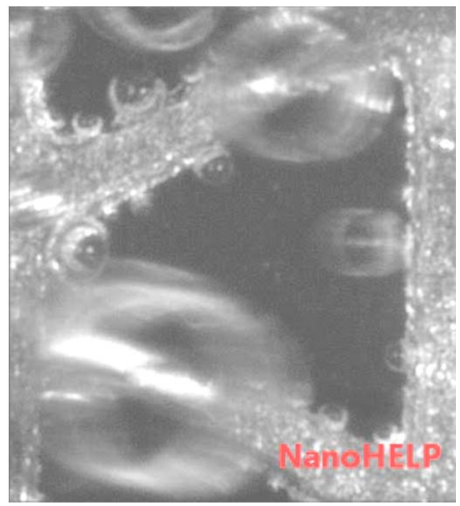
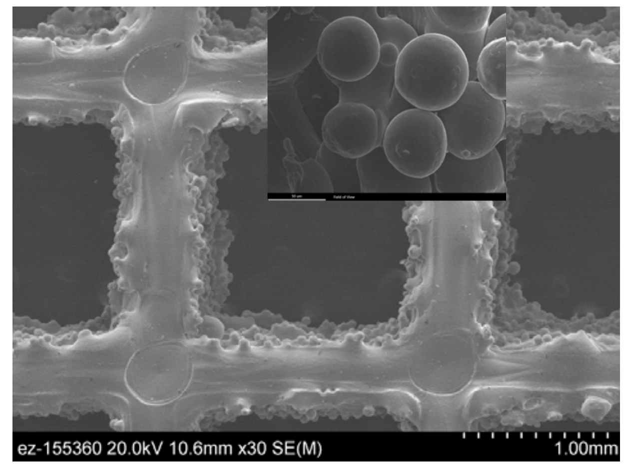
Outline

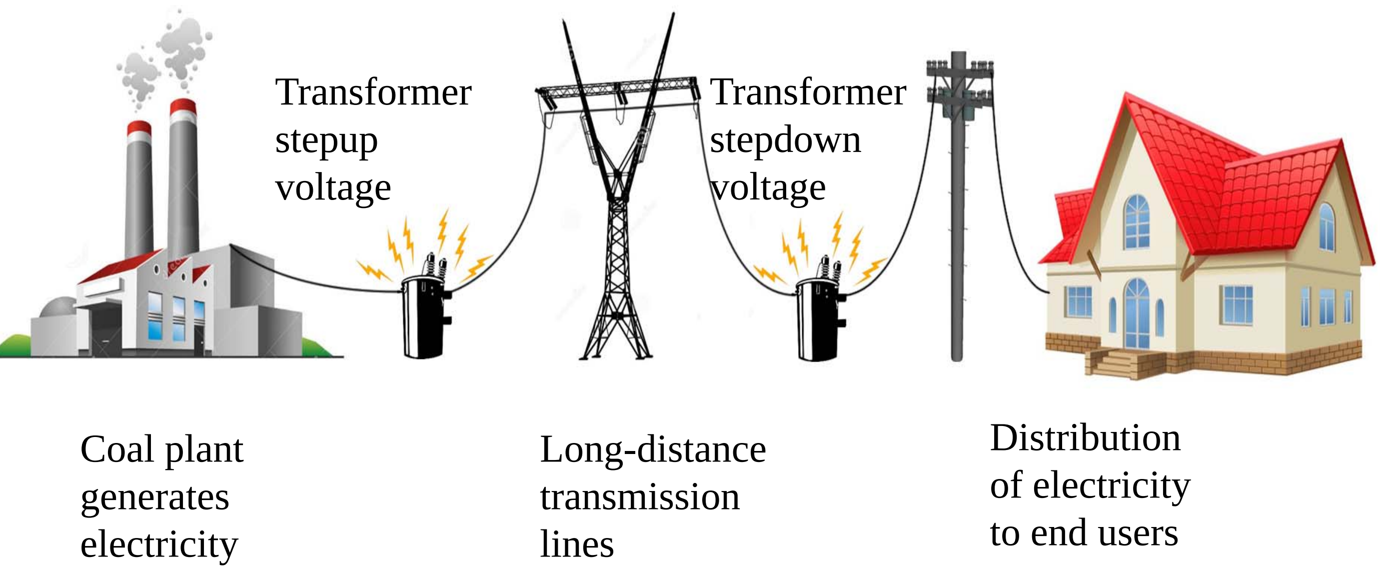
- Motivation
- multifunctional thin materials
- In-situ reactions
- Modeling
- Future work

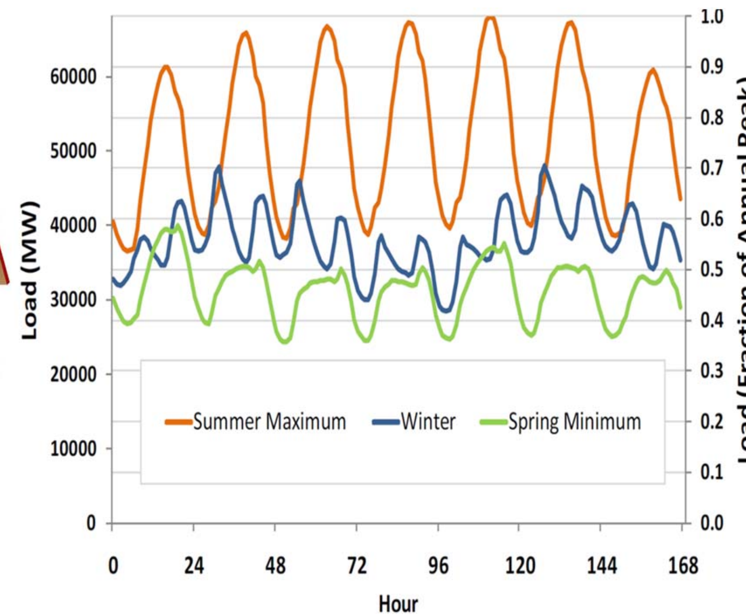






Distributed energy storage mitigates power-demand interruptions and improves greatly efficiency from coal plant to end users





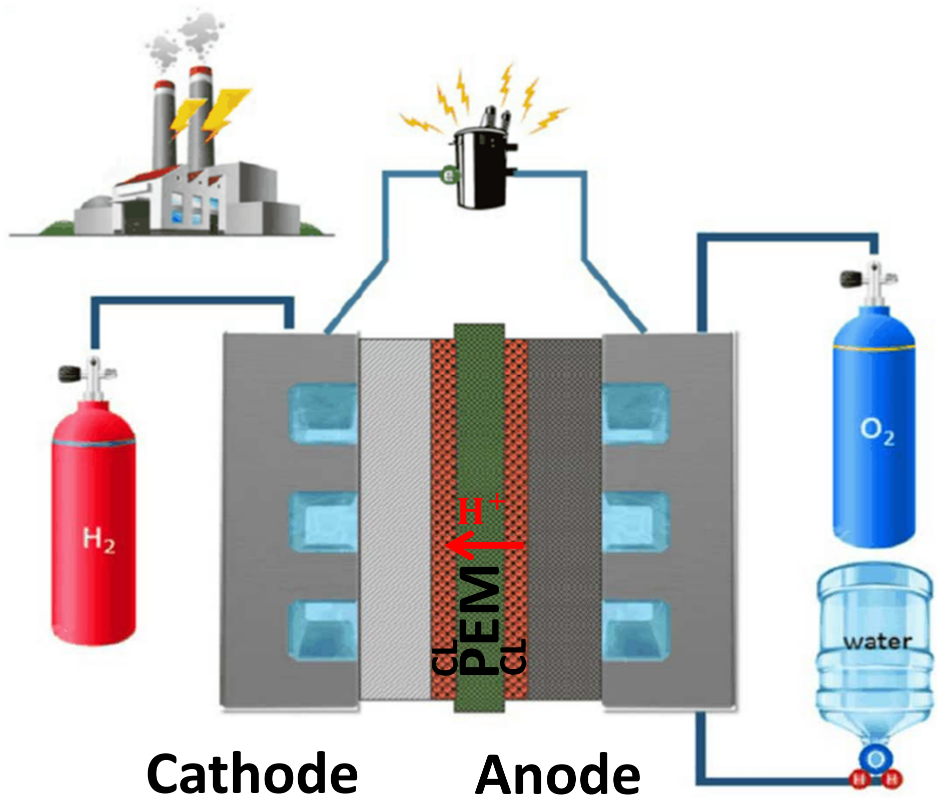
- Electricity demand changes significantly with time
- Electric grid often experiences interruptions, resulting in significant cost (> 80 Billions/year)
- Many of these interruptions may be mitigated by distributed energy storage approaches

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



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

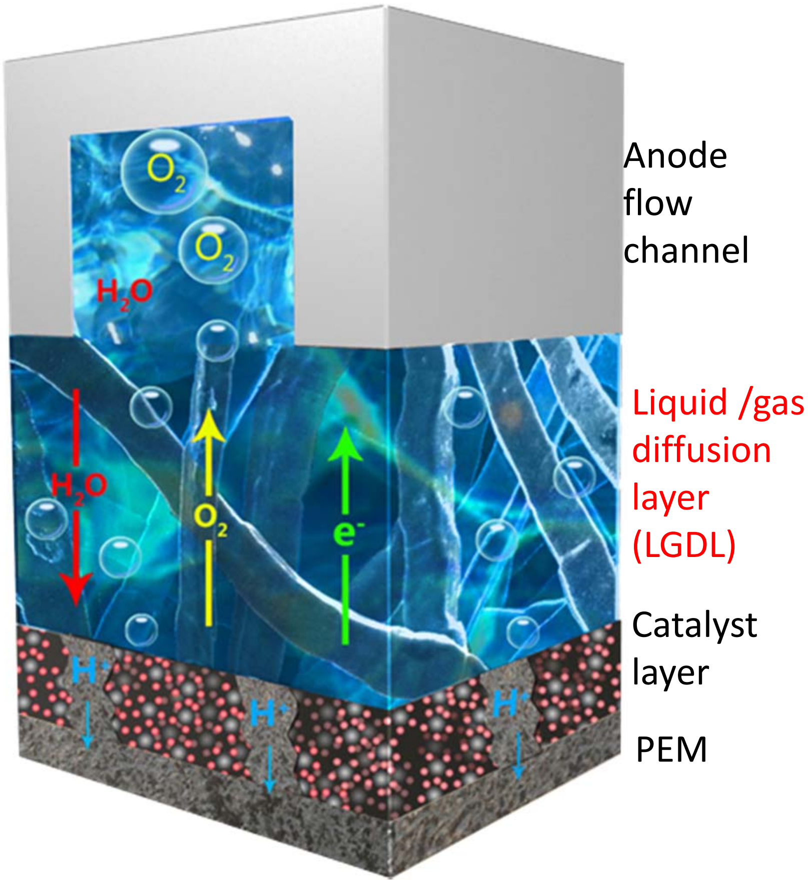
$2H_2O \xrightarrow{catalyst} O_2 + 4H^+ + 4e^-$

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

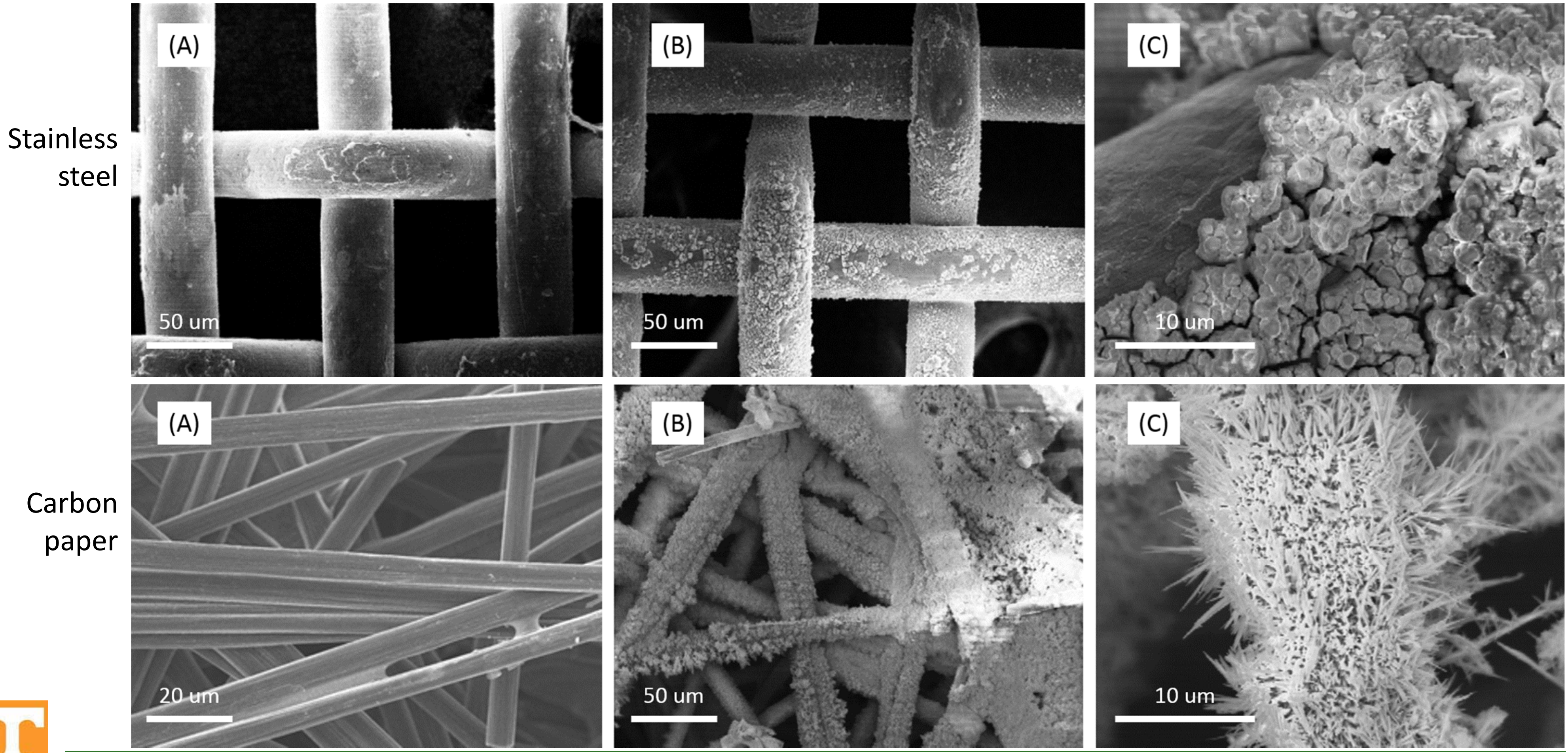
- LGDL: Located between flow channel and catalyst-coated membrane (catalyst layer +PEM)

- 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



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



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

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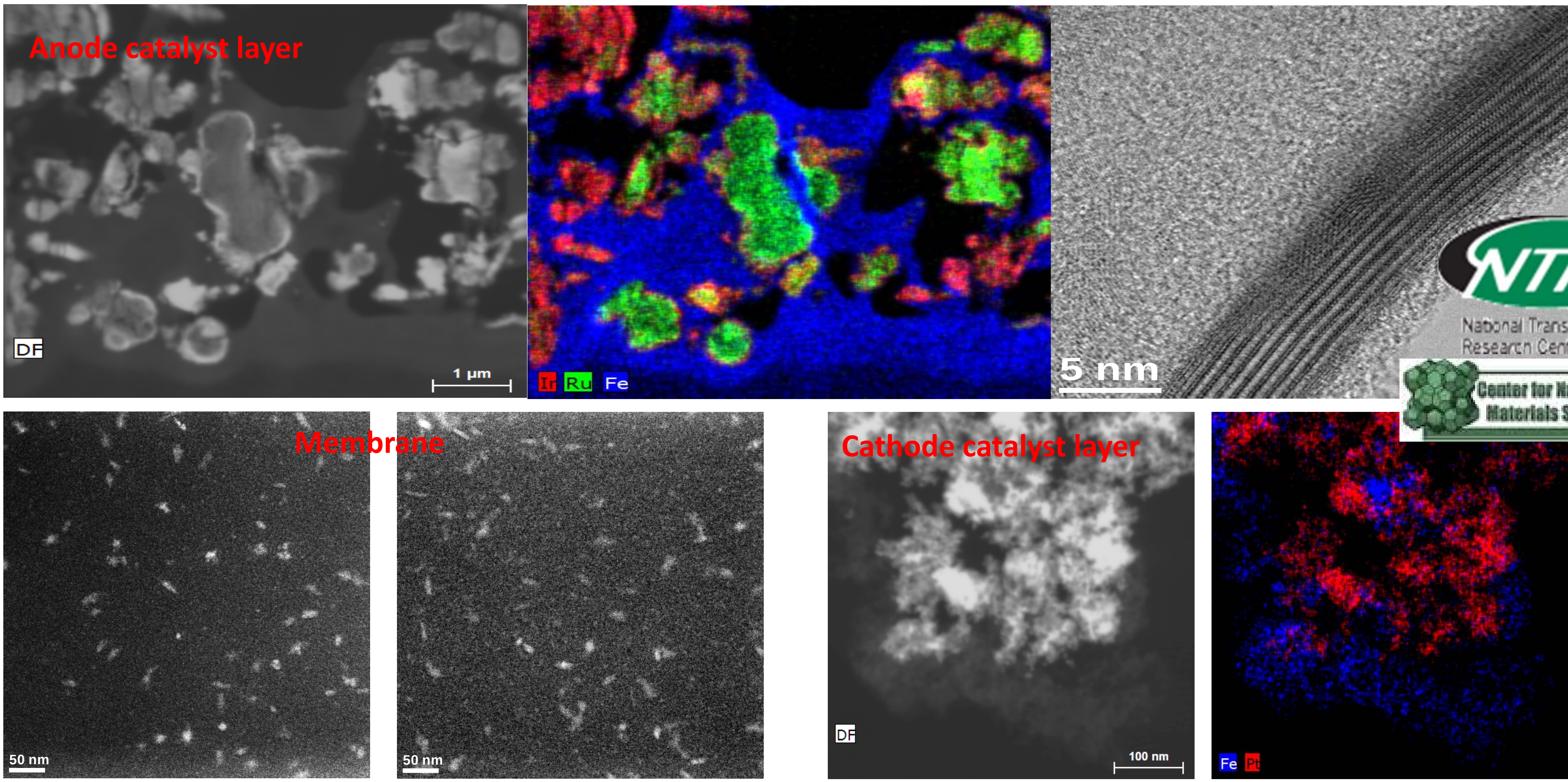

NTRC
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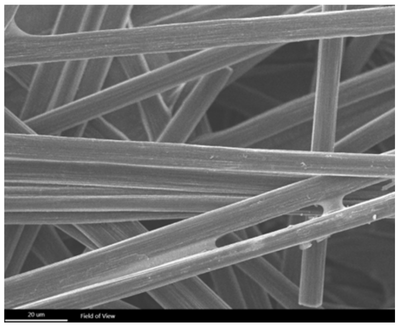
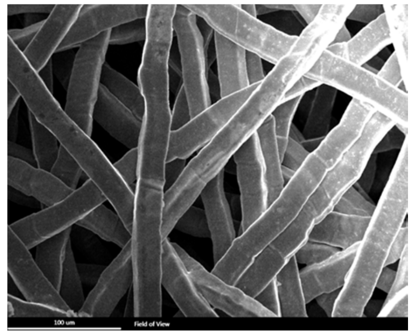
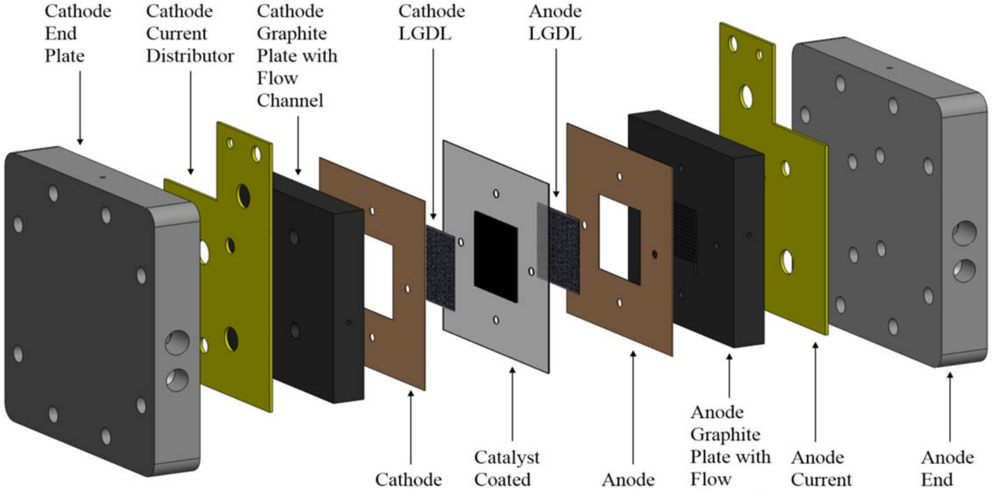
Most conventional LGDLs are made of fibers: Titanium felts for anode and carbon fibers for cathode







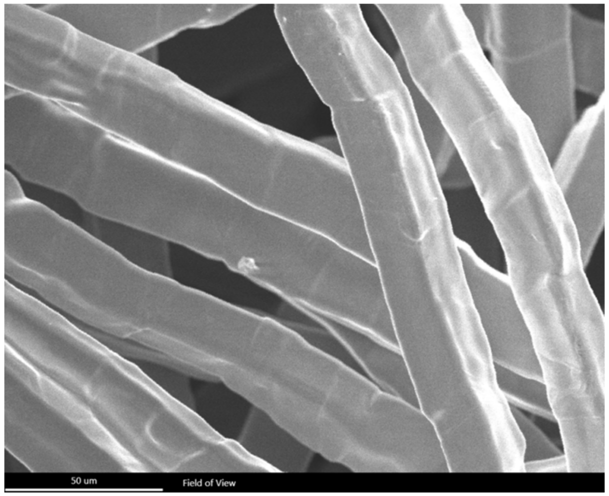
- Advantages
  - Good performance
  - “Industry Standard”

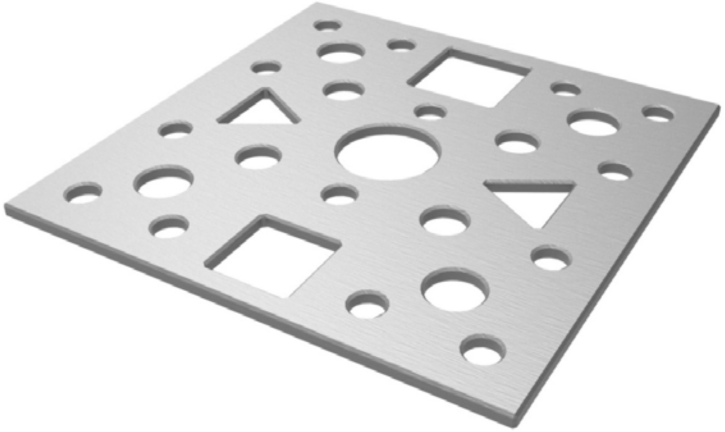
- Disadvantages
  - Thicker
  - Random pore morphology /Pore control difficulties
  - High Cost
  - Fiber penetration into membrane
  - Degradation of porosity and permeability
  - Difficult to integrate with other parts

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 a thin LGDL

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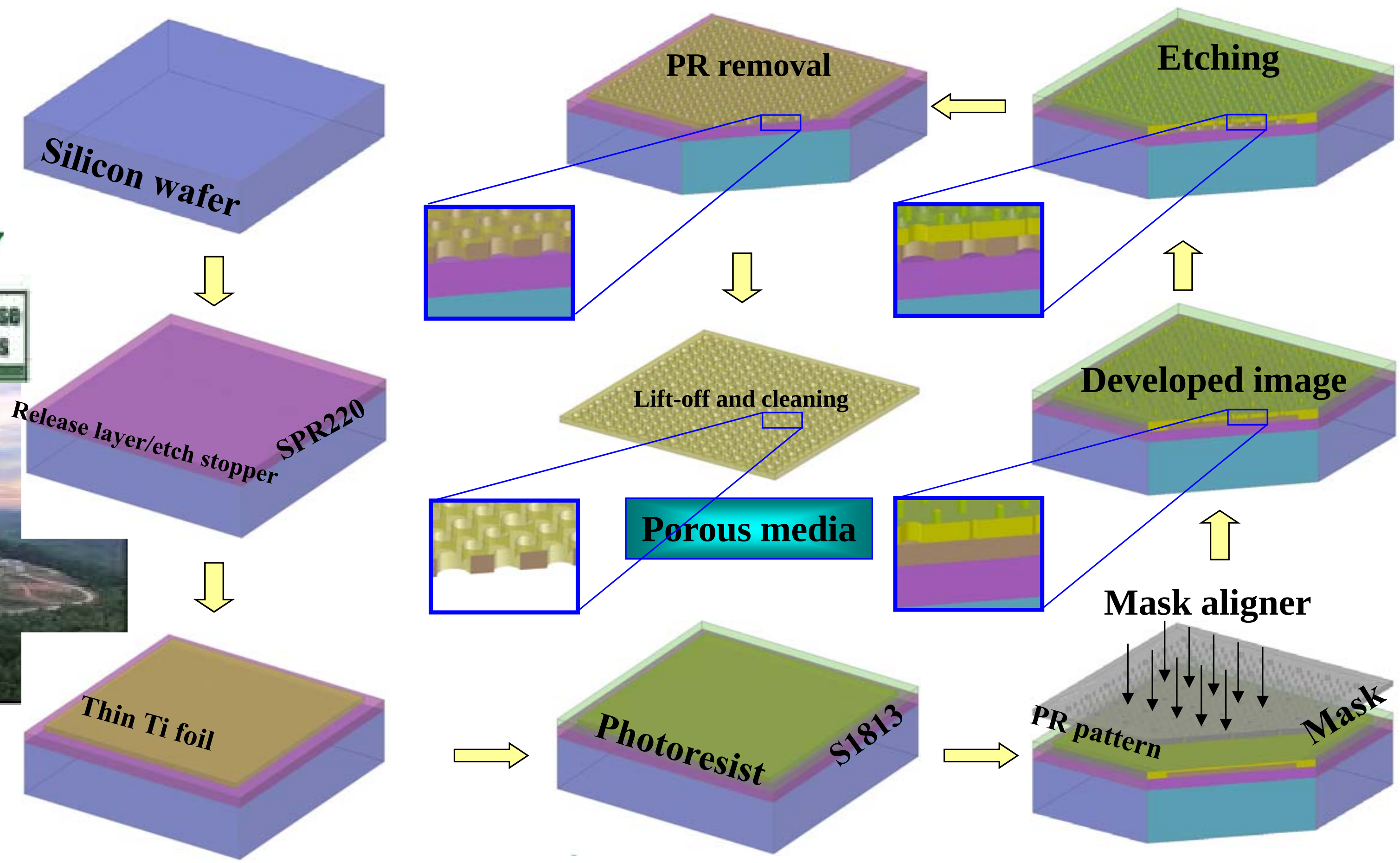
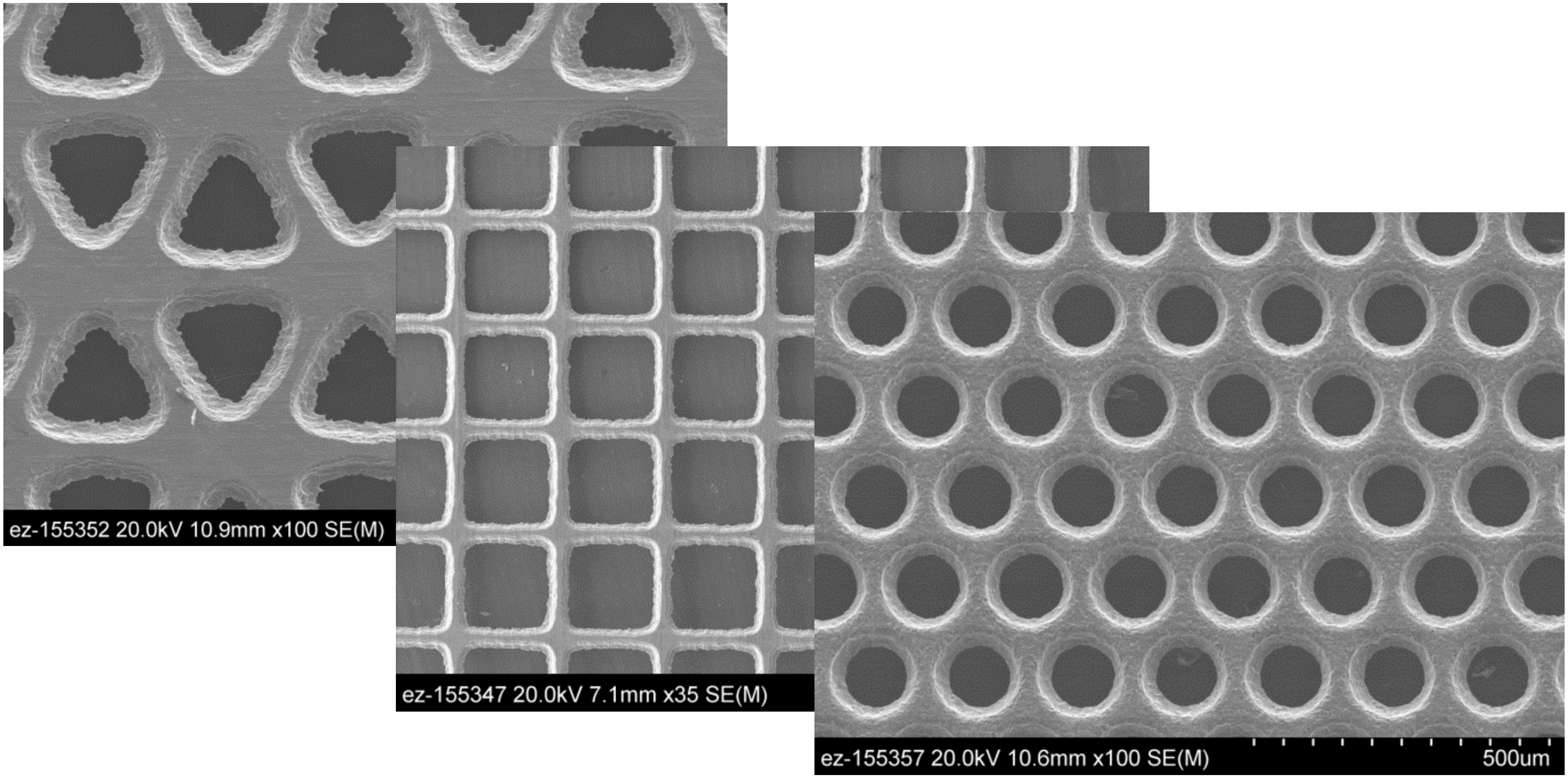
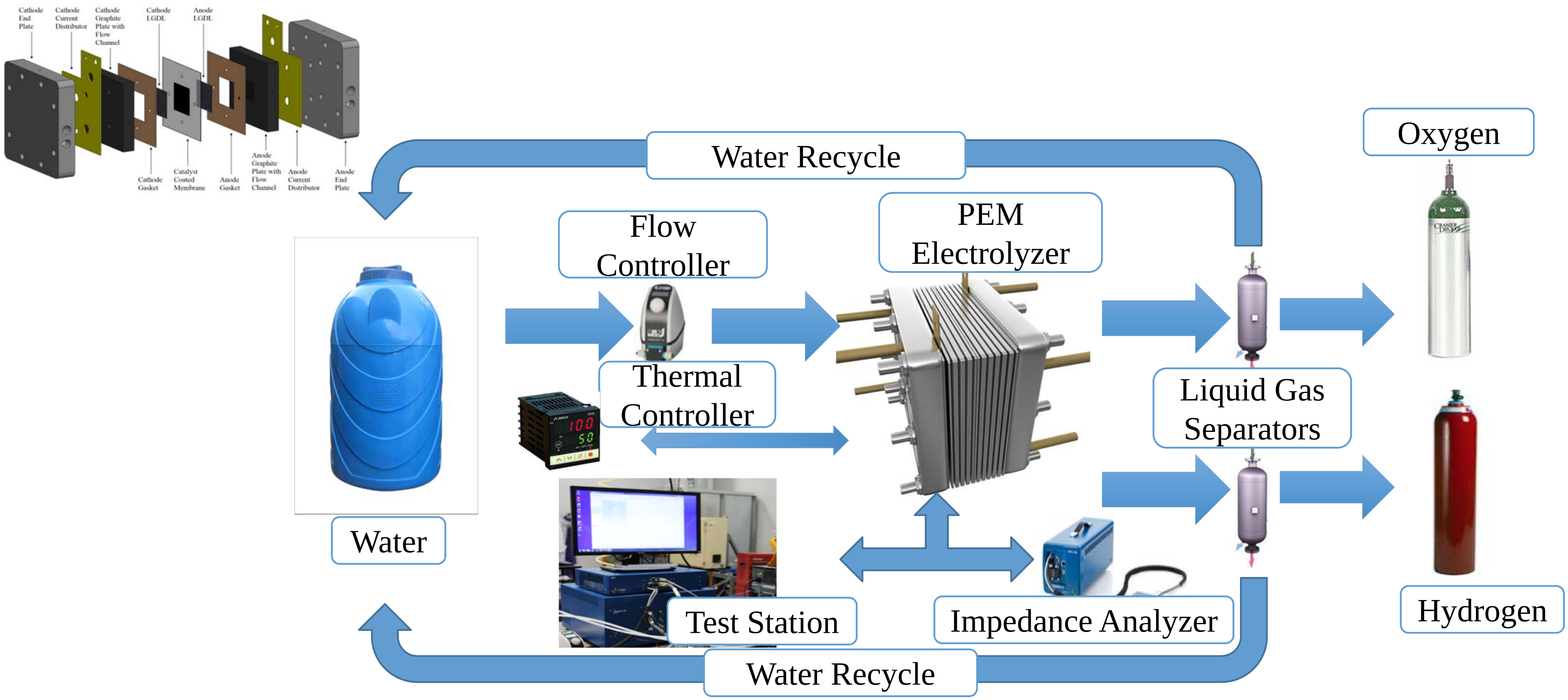


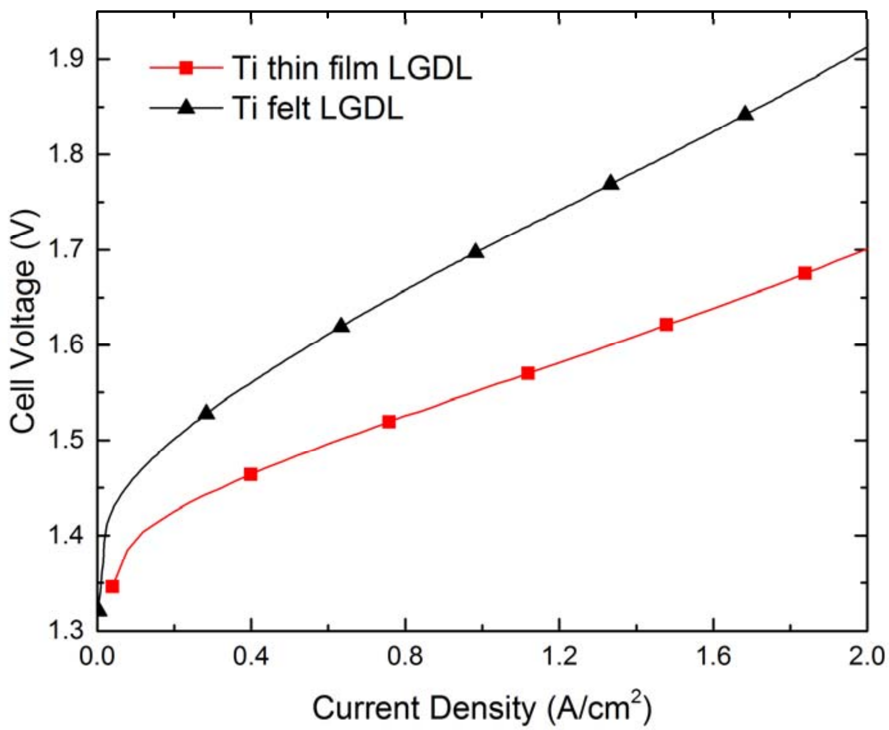
Thin LGDLs have been successfully fabricated with different design parameters

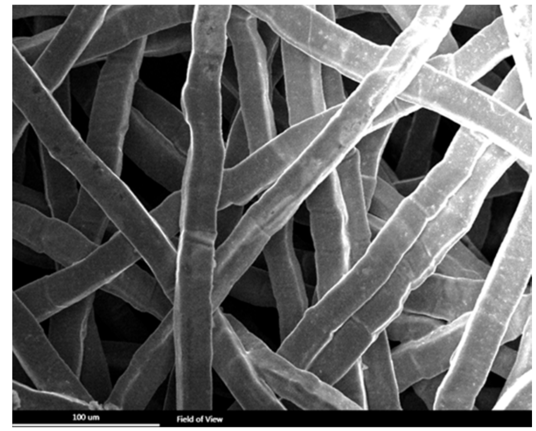


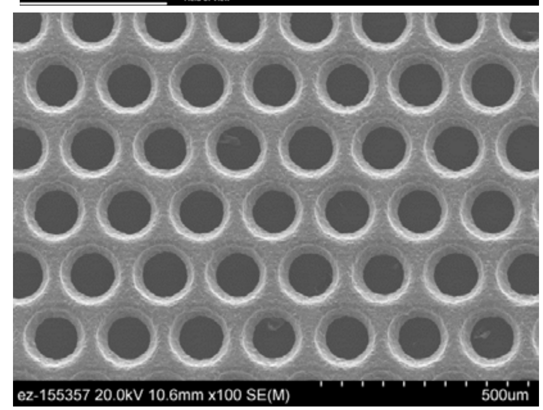
Thin LGDLs were tested in a standard electrolyzer cell with test station and control system



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



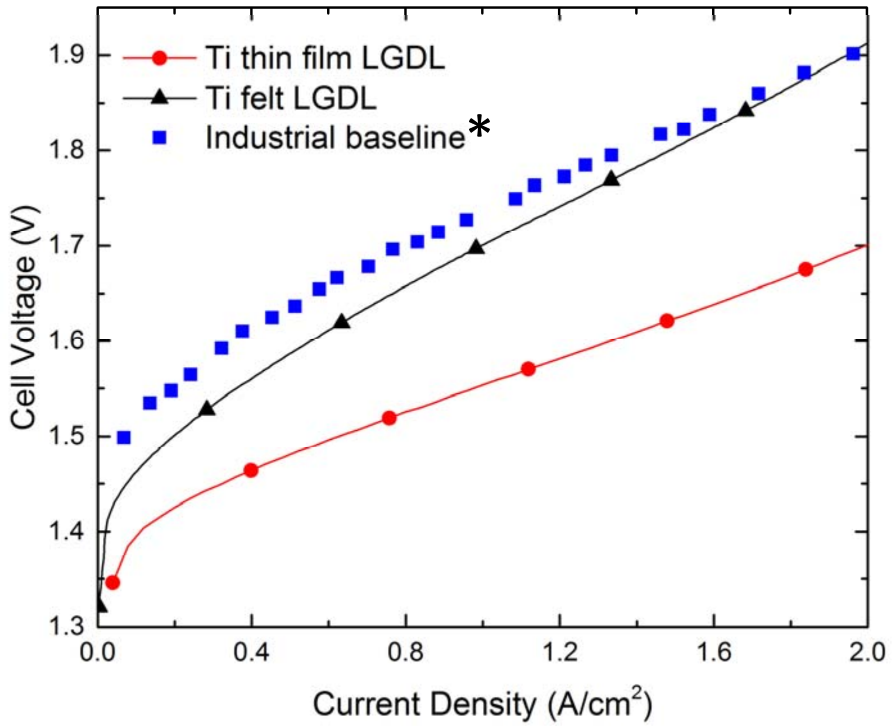


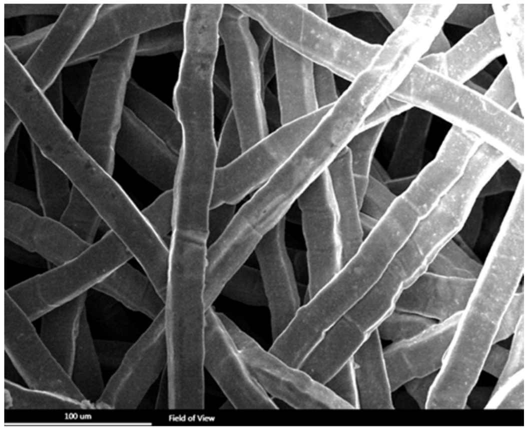


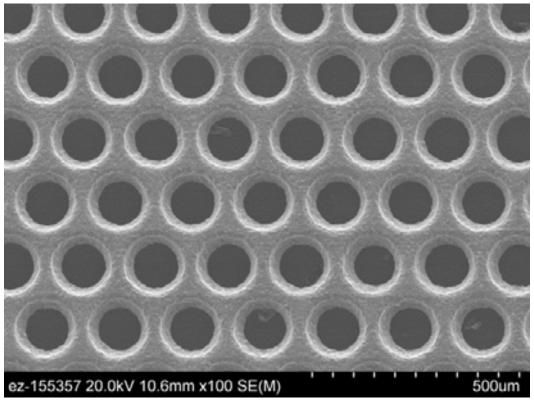
Efficiency is improved from 77% to 87% at a current density of 2.0 A/cm^2

Thickness is reduced from 350 µm to 25 µm

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



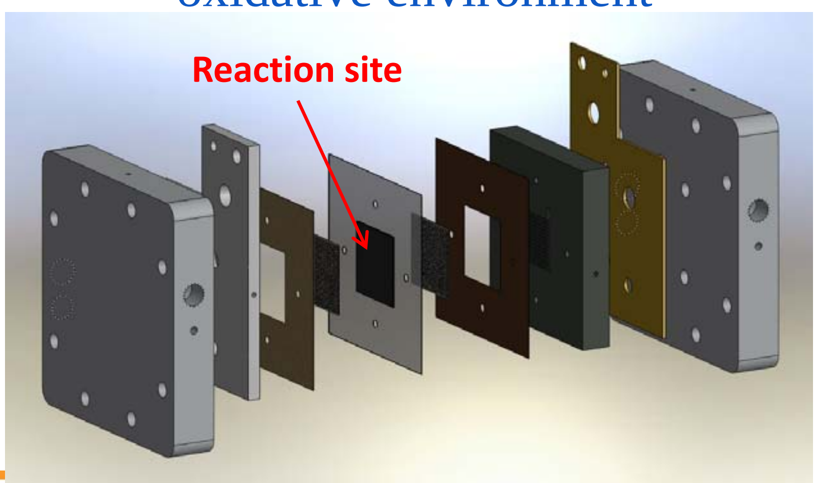


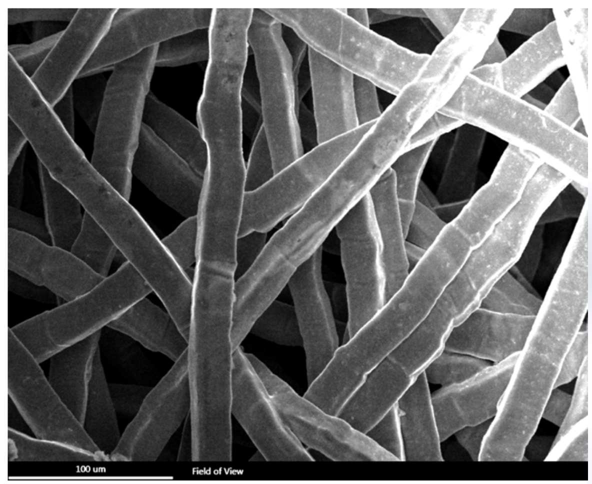


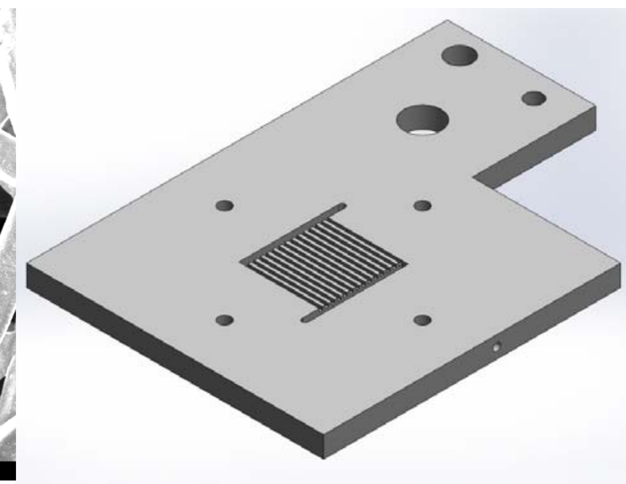
*E. B. Anderson, "Latest Advancements in PEM Electrolysis," Technical Forum of *Hydrogen-Fuel Cells-Batteries,* April, 2014

Thin and well-tunable LGDLs with straight pores make it possible to *in-situ* investigate 3-phase reactions and interfaces

- 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

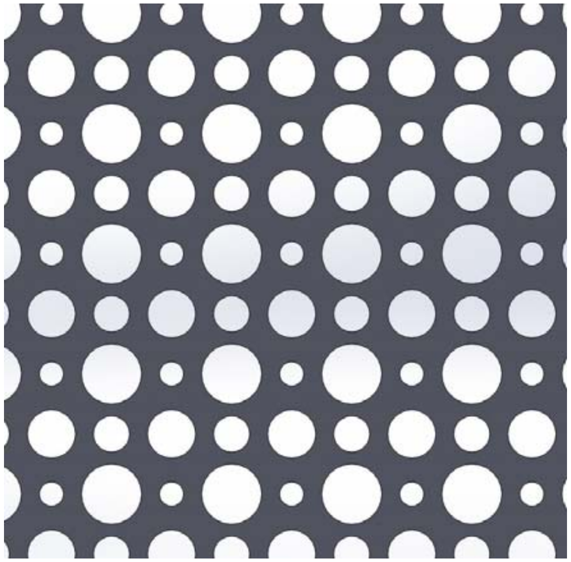


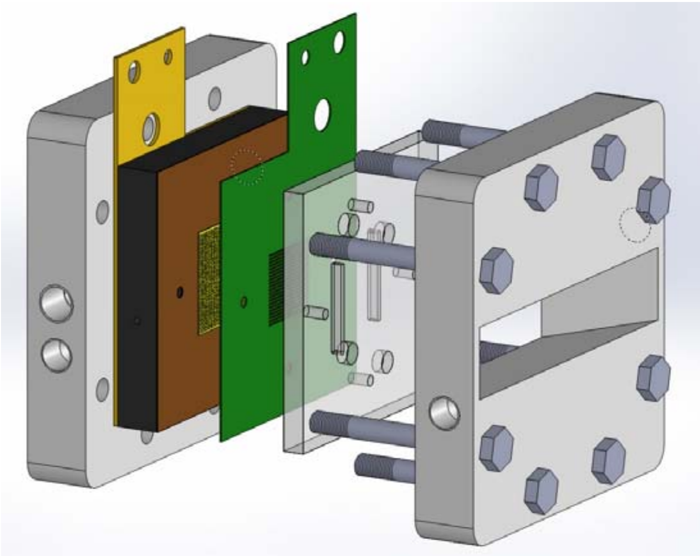


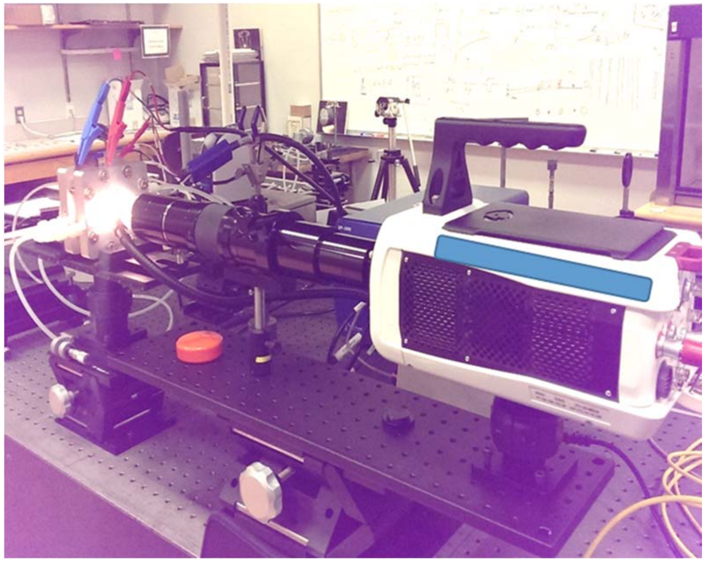


In-situ visualization with developments of novel LGDLs, transparent PEMFCs and high-speed/microscale system

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

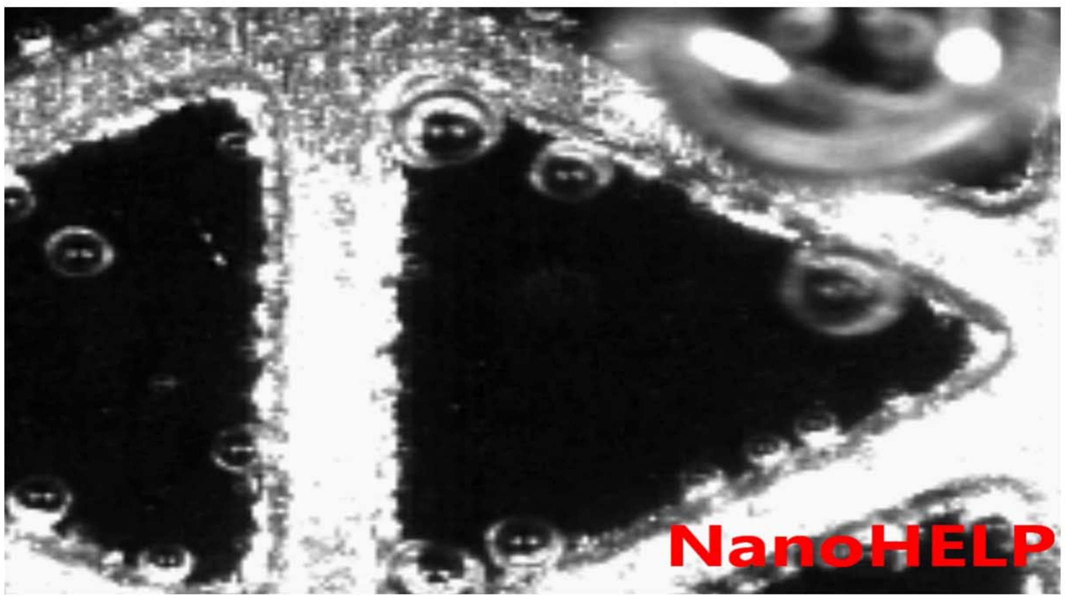


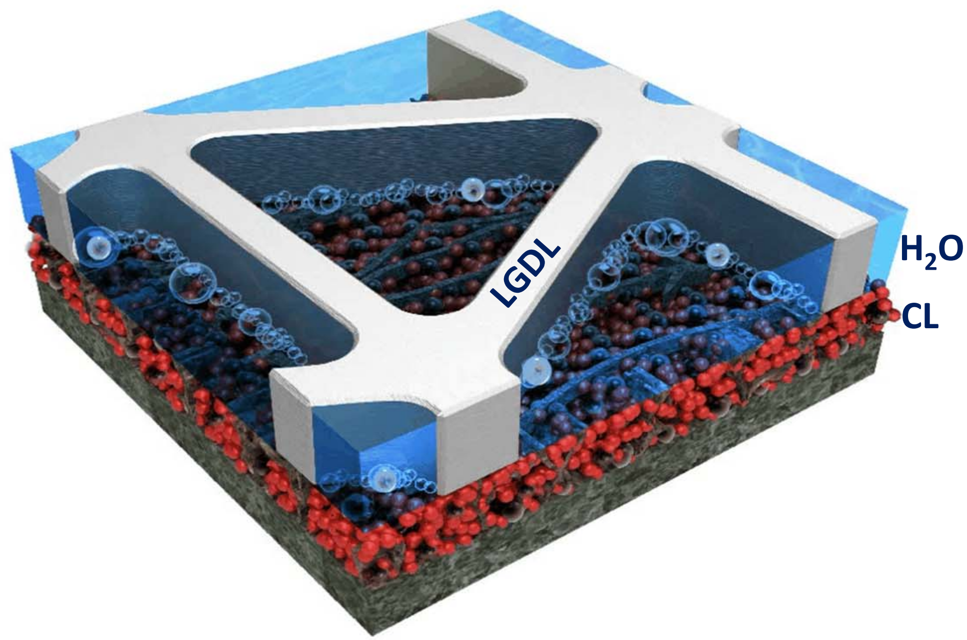




First-ever revealing the true nature of multiphase interfacial electrochemical reactions in micro porescale with microsecond time resolution

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

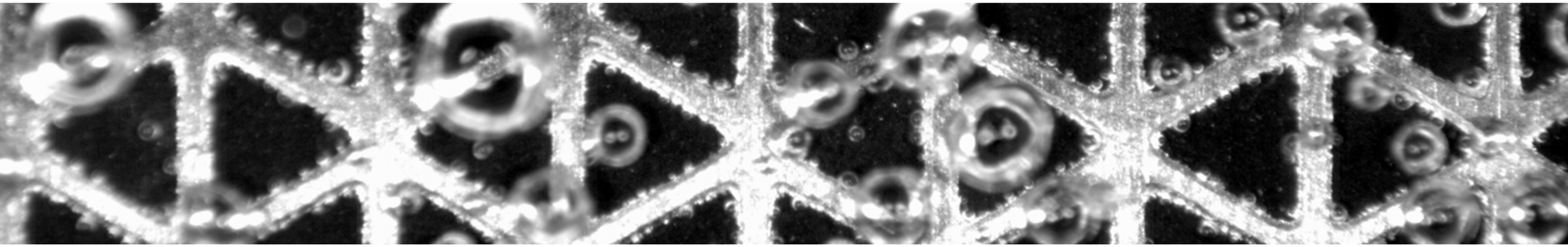




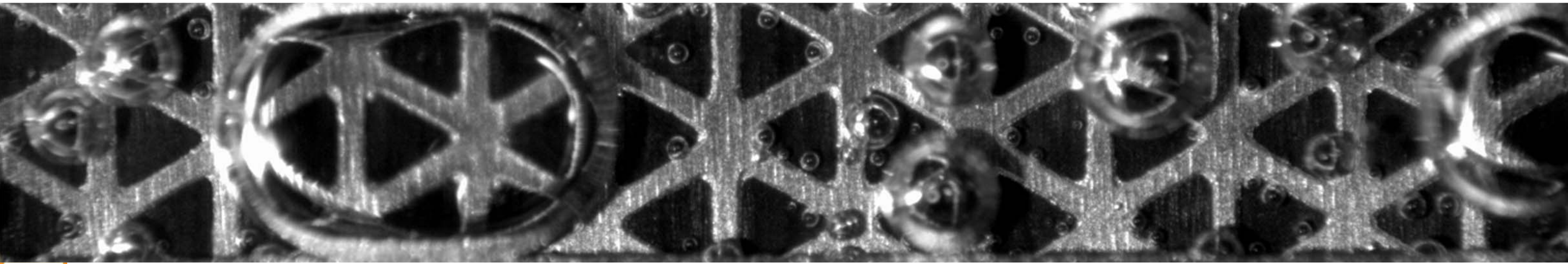
In-situ **micro reaction - oxygen bubble generation from water(10,000 fps)**

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

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



- Reactions at cathode side: $4H^+ + 4e^- \xrightarrow{catalyst} 2H_2$



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:

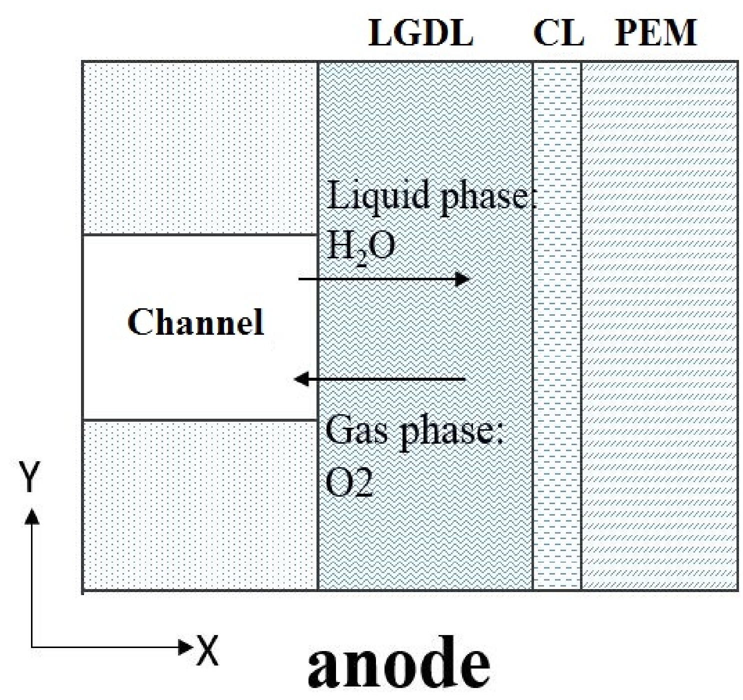
$$\nabla \cdot \left(-\frac{K k_{H_2O}}{\mu_{H_2O}/\rho_{H_2O}} \nabla p_{H_2O} \right) = N_{H_2O}$$

Capillary pressure:

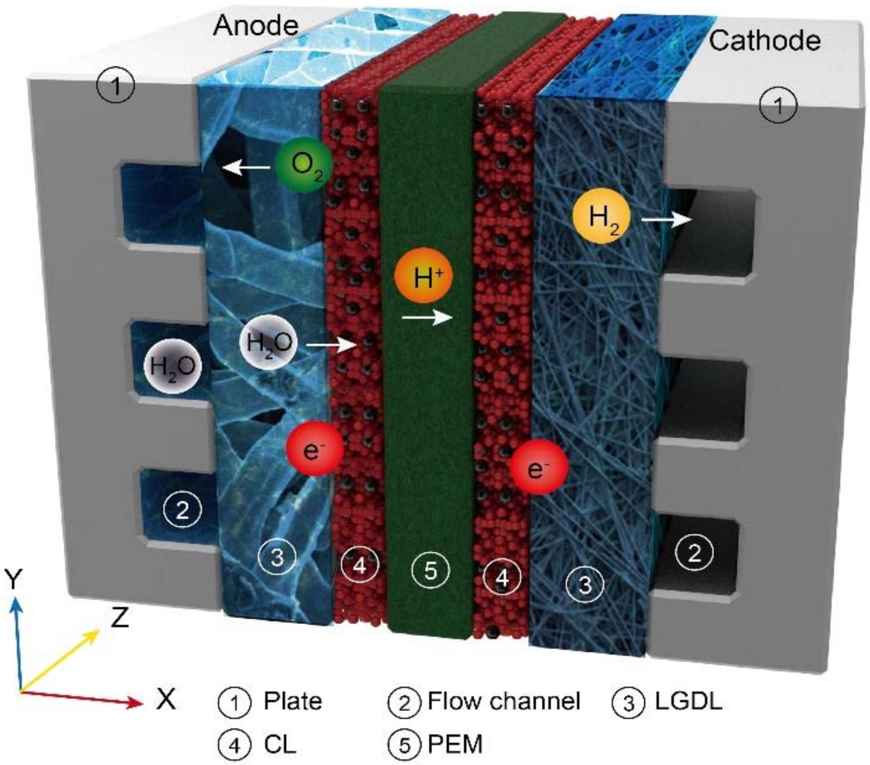
$$p_c = p_{O_2} - p_{H_2O} = J(s) \left(\frac{\varepsilon}{K} \right)^{1/2} \sigma cos\theta$$

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

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:

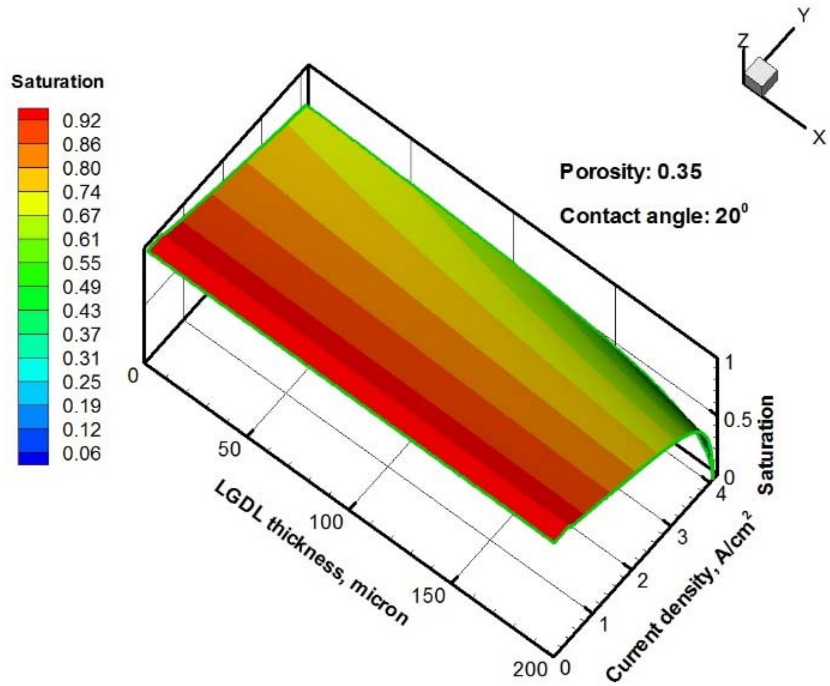
$$V_{act} + V_{diff} = \frac{RT_a}{\alpha_a F} \ln\left(\frac{j}{sj_0}\frac{C_{O_2,m}}{C_{O_2,m0}}\right) + \frac{RT_c}{\alpha_c F} \ln\left(\frac{j}{sj_0}\frac{C_{H_2,m}}{C_{H_2,m0}}\right)$$

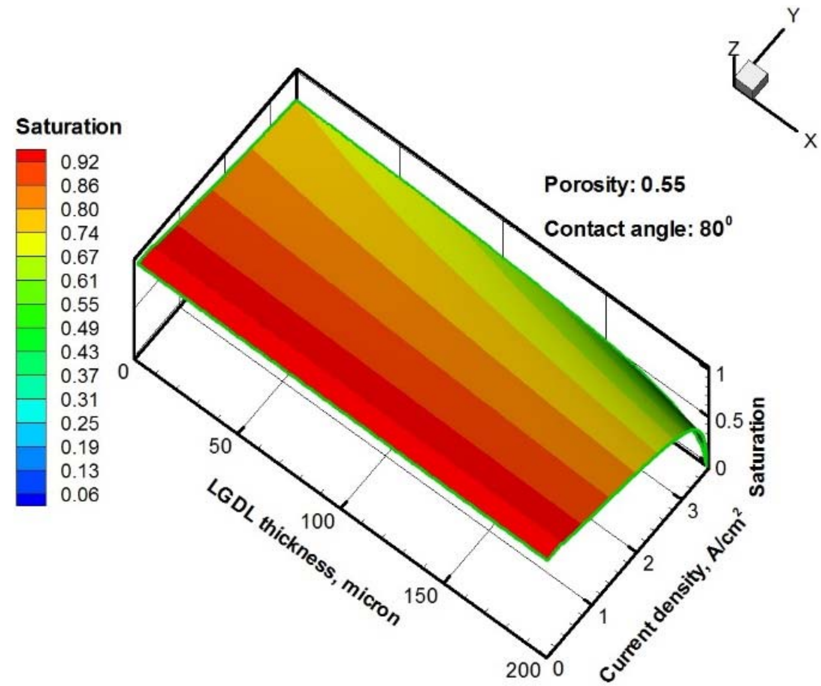
Ohmic loss:

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

Liquid saturation distribution in the LGDL

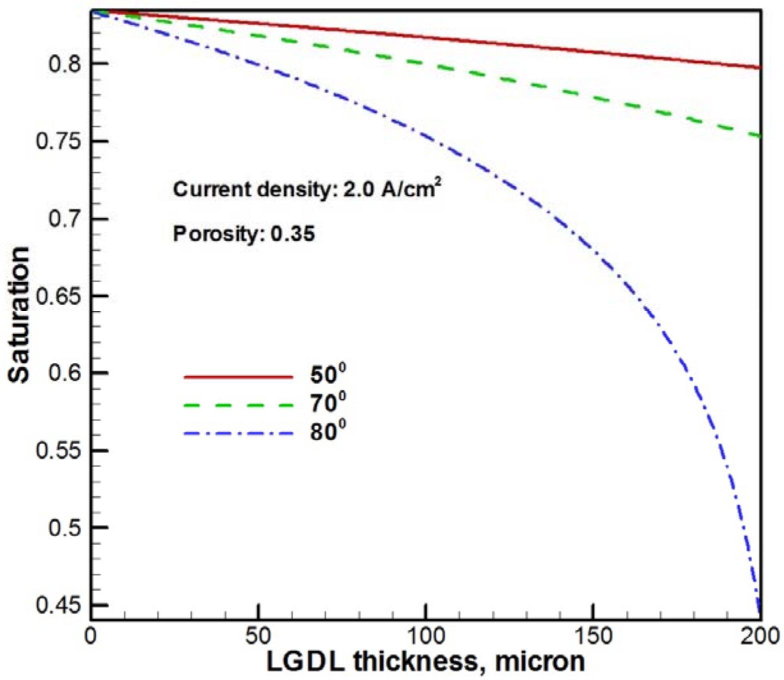
The liquid water saturation distribution along the LGDL thickness direction at different current density.

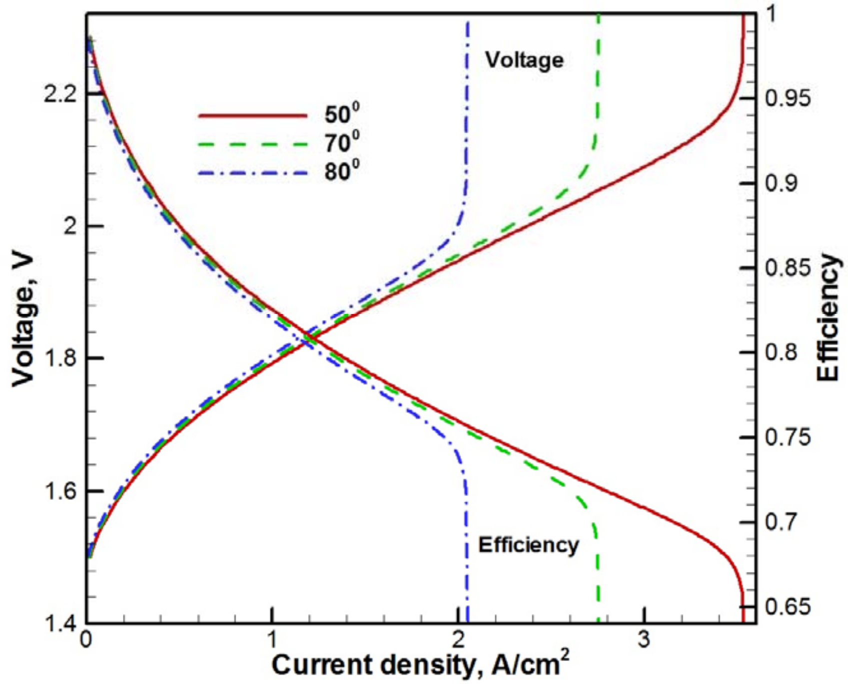




Smaller contact angles will decrease the flow resistance and result in better performance and higher efficiency

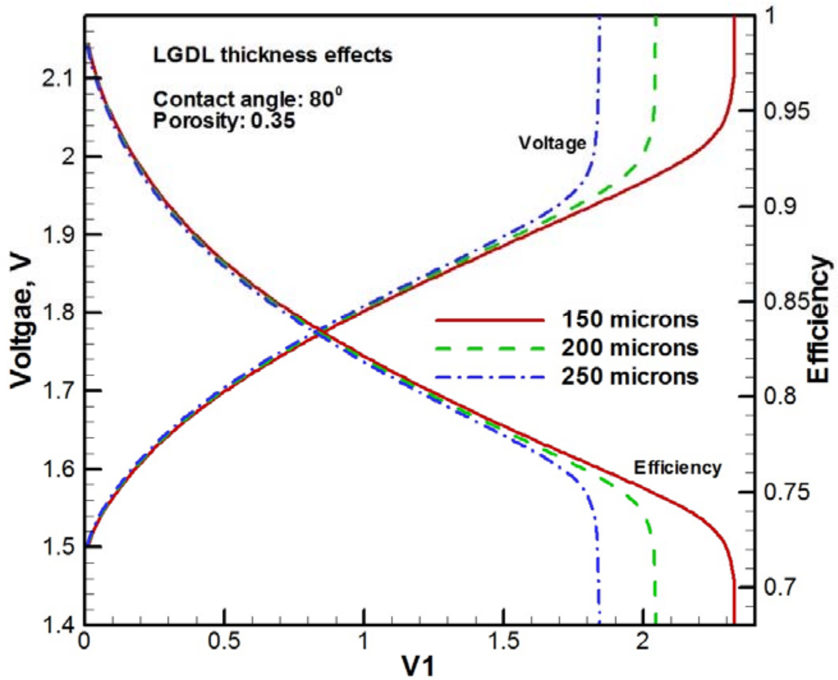
- **Effects of contact angle on the liquid saturation distribution inside LGDL**
- **Effects of contact angle on the cell performance and efficiency**



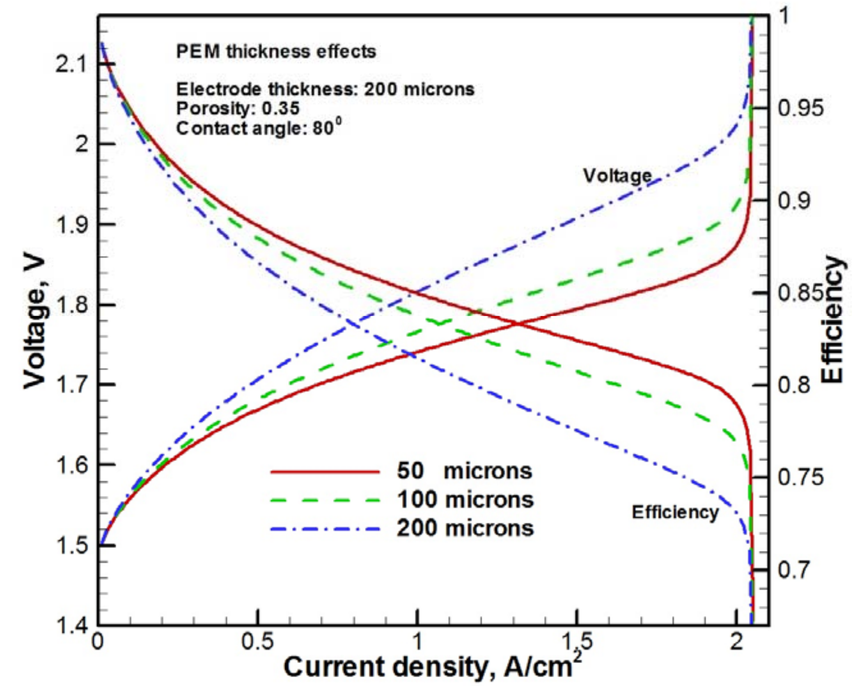


Thinner LGDLs and membranes will decrease the ohmic/transport resistances and enhance the performance

- Effects of LGDL thickness on the cell performance and efficiency



- Effects of PEM thickness on the cell performance and efficiency



Future work: Optimization of LGDLs, surface treatment and durability test of LGDLs and further modeling development

- Optimization of pore parameters
  - Porosity
  - Pore size
  - Thickness
- Surface treatments
  - Enhance two-phase transport
  - Minimize surface contact resistance
  - Improve durability and corrosion resistance

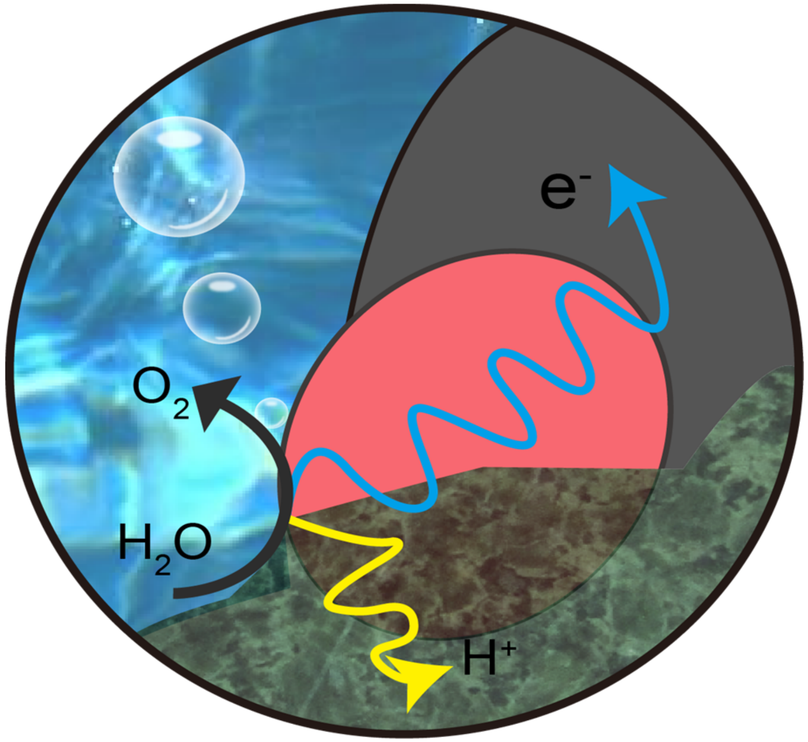
- Validating two-phase model for thin/well-tunable LGDLs
  - Validate with the new experimental data.
  - Modeling the effects of LGDL porosity and pore size

Exploring microscale and multiphase reactions with optimization of pore scale interfacial effects and two-phase flow

- Multiphase boundary interfacial effects play critical roles in electrochemical devices, such as electrolyzers, fuel cells, and flow batteries.
- For instance, anode reaction in electrolyzers only occurs at multi-interfaces:

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

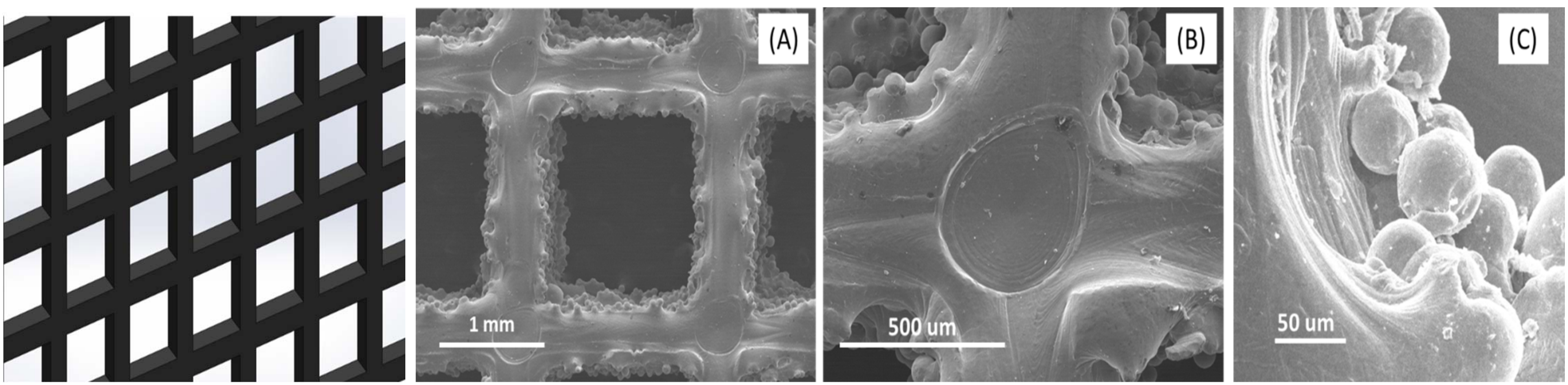
- 3-phase & multi-materials co-exist:
  - Solid phases: catalyst, conductors for electrons, and conductors for protons
  - Liquid phase: water
  - Gas phase: Oxygen at anode/ Hydrogen at cathode



Optimization of pore scale interfacial effects and two-phase flow will become critical

Additive manufacturing (3d printing) from CAD Model to physical part: Faster and cheaper

- electron beam melting technology: powder bed additive manufacturing
- titanium powder materials are spread into a 50-micrometer thin layer and melted
- Shorten manufacturing cycles from design to products
- Reducing the material scraps
- Easily integrating components



Directly from CAD model to virtually slice, layer-by-layer path, physical part

Acknowledgement

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- Students, Postdoc and Staff:

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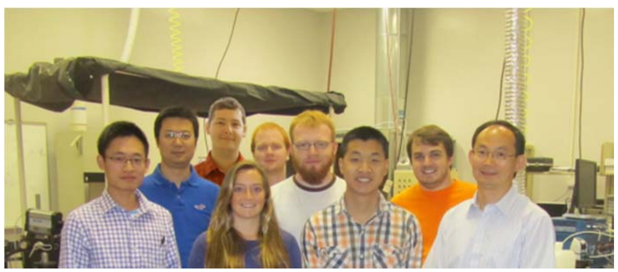
- Collaborators:

Drs.: Scott Retterer, Dave Cullen, Mike Brady, Todd Toops, Jun Qu, Johney Green, Ryan Dehoff, William Peter



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