NETL's Crosscutting Research Review Meeting

**Award: DE-FE0011585**

**Project manager: Jason Hissam**

# Developing novel multifunctional materials for high-efficiency electrical energy storage - Surface enhancement


**Presented by Zhenye Allen Kang**

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

*Department of mechanical, aerospace and biomechanical engineering*

*UT Space Institute, University of Tennessee, Knoxville*

# Project Started from 09/01/2013

➢ Graduate Students supported fully and partially:

* Stuart Steen (MS, 2015, current position: research engineer at Air Force)

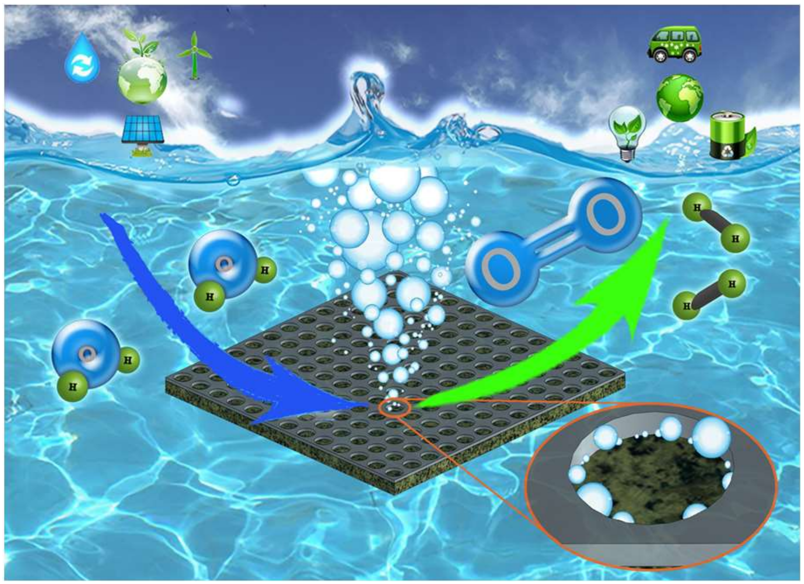
*William Barnhill (MS, 2016, current position: research engineer at GM research center)

* Joel Mo, (PhD, 2016, current position: faculty at Fudan University)

*Allen Kang (PhD, 2018(completed defense, will graduate in May)

- Publications (over 35,including 10 in journal and 1 patent

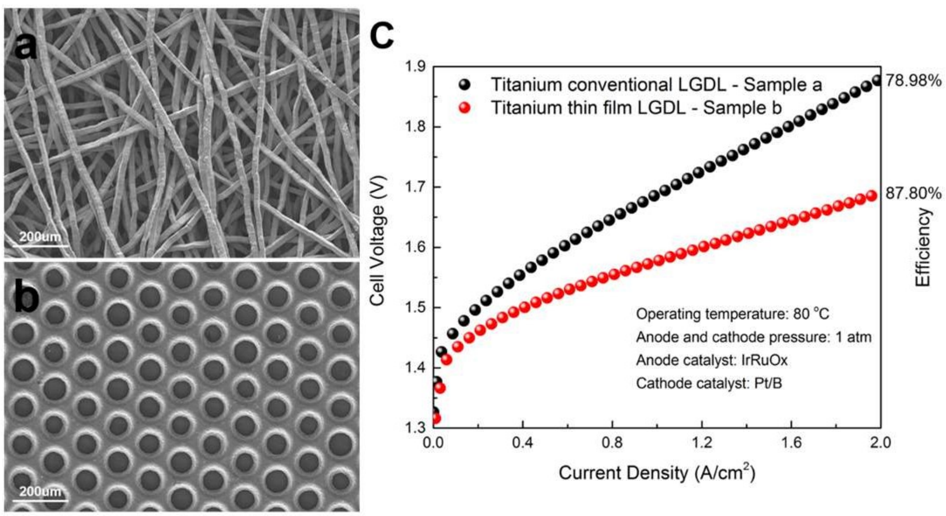
*One publication has been published and featured in the Journal of *Energy & Environmental Science* *( Impact Factor 29.5)*

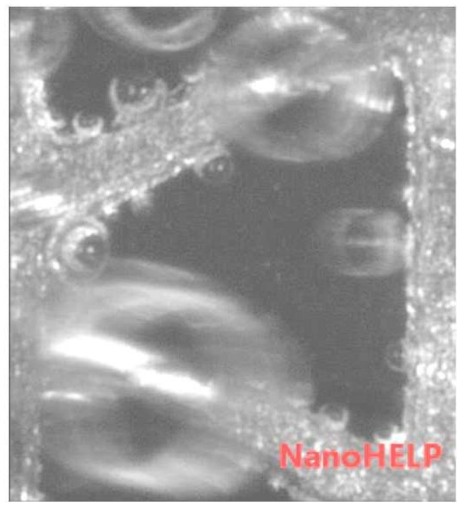


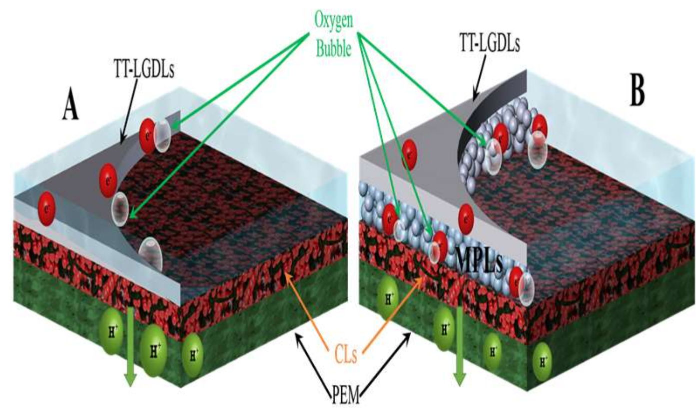
*One publication in *Science Advances* was reported by Tennessee Today and was highlighted by DOE Office of Science

# Outline

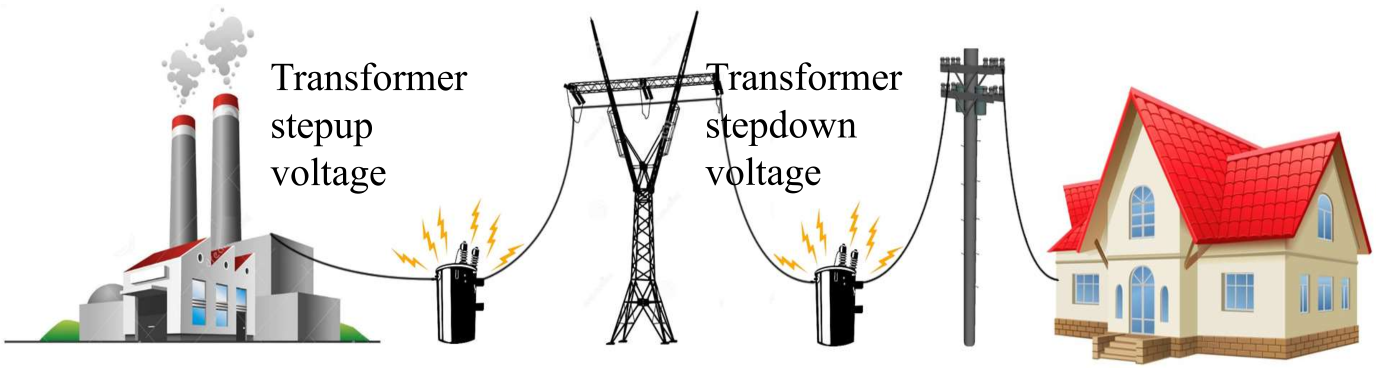
**Motivation** | **Multifunctional thin materials** | **Thin film surface modification** | **Microporous layer** | **Summary**



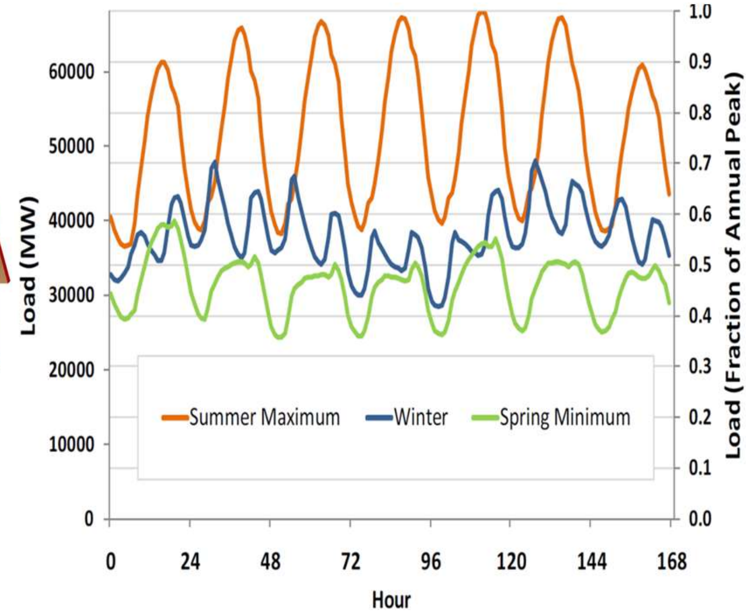
# Distributed energy storage mitigates power-demand interruptions and improves greatly efficiency from coal plant to end users




Coal plant generates electricity

Long-distance transmission lines

Distribution of electricity to end users

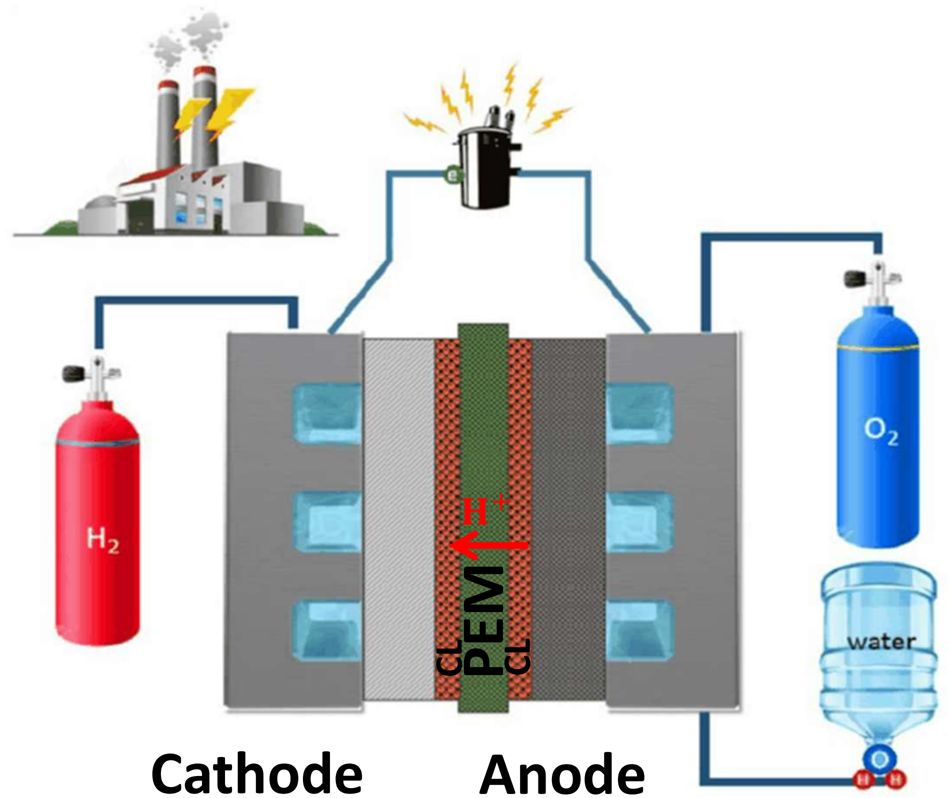



- Electricity demand changes significantly with time
- Electric grid often experiences interruptions, resulting in significant cost (> 80 Billions/year)
- Many of these interruptions may be mitigated by distributed energy storage approaches

*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



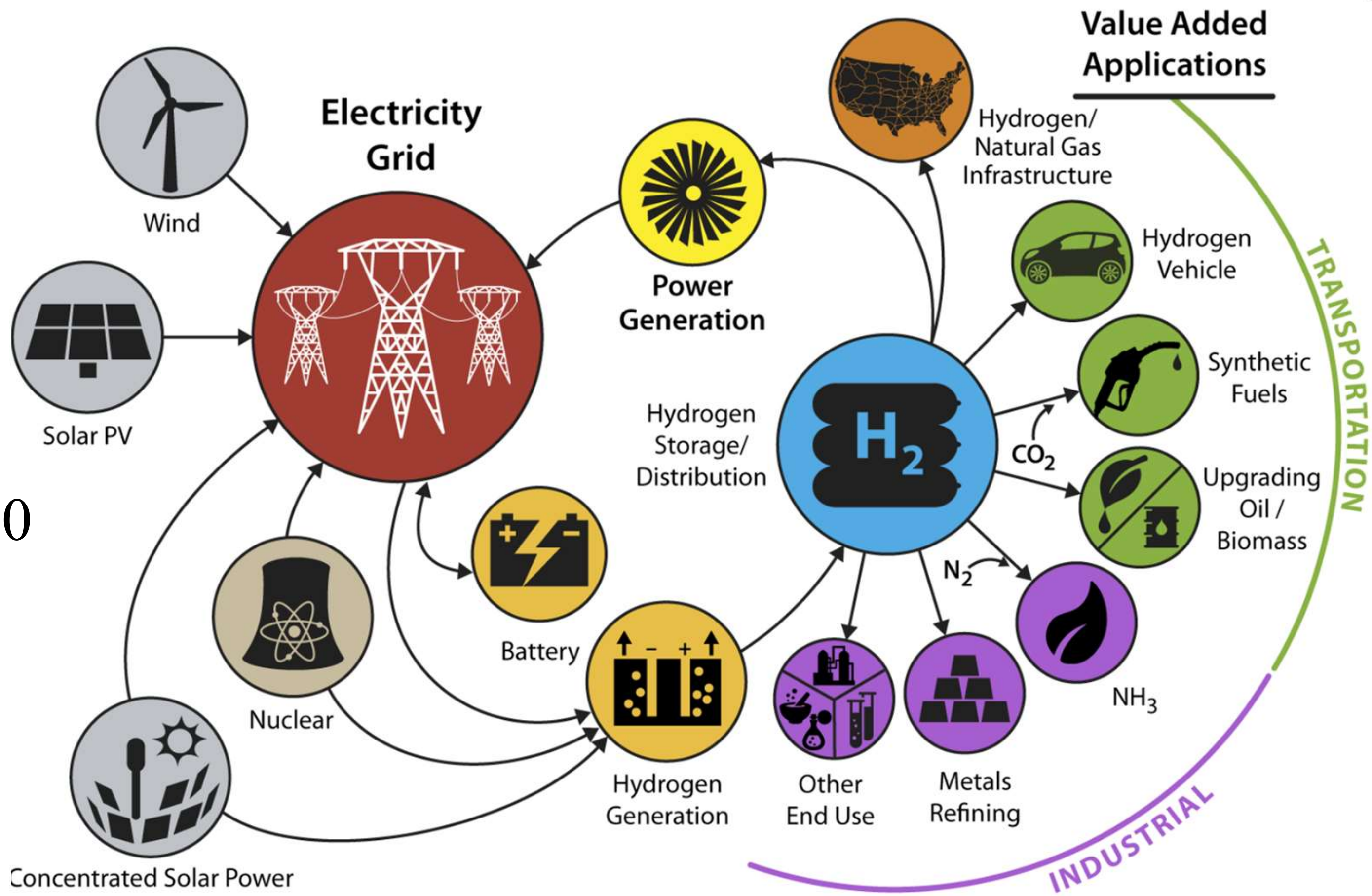

$4H^+ + 4e^- \xrightarrow{catalyst} 2H_2$

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

# Technology innovation on hydrogen -- national economic and sustainable energy system

***Potential Impacts By 2050:***

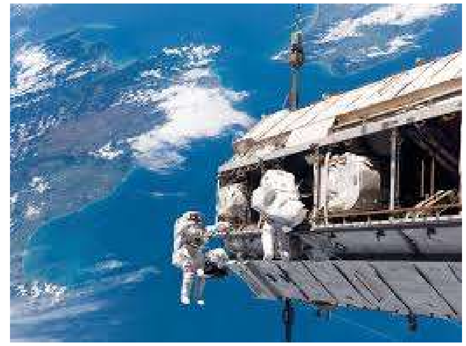
- $2.5 trillion in revenues
- 30 million jobs
- 400 million cars, 15-20 million trucks
- 18% of total global energy demand

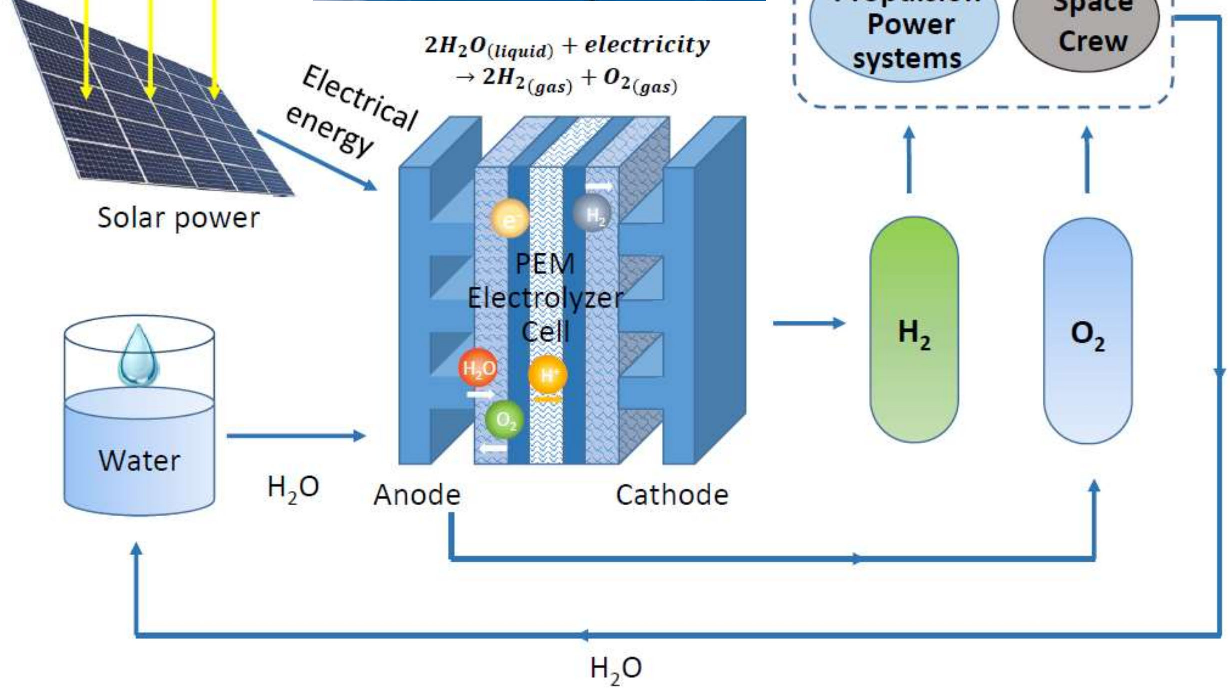



Pivovar B, Rustagi N, Satyapal S. Hydrogen at Scale (H2@Scale) Key to a Clean, Economic, and Sustainable Energy System. The Electrochemical Society Interface. 2018;27:67-72.
U.S. Department of Energy , H2@Scale Review Meeting , Washington, DC, June 9, 2017

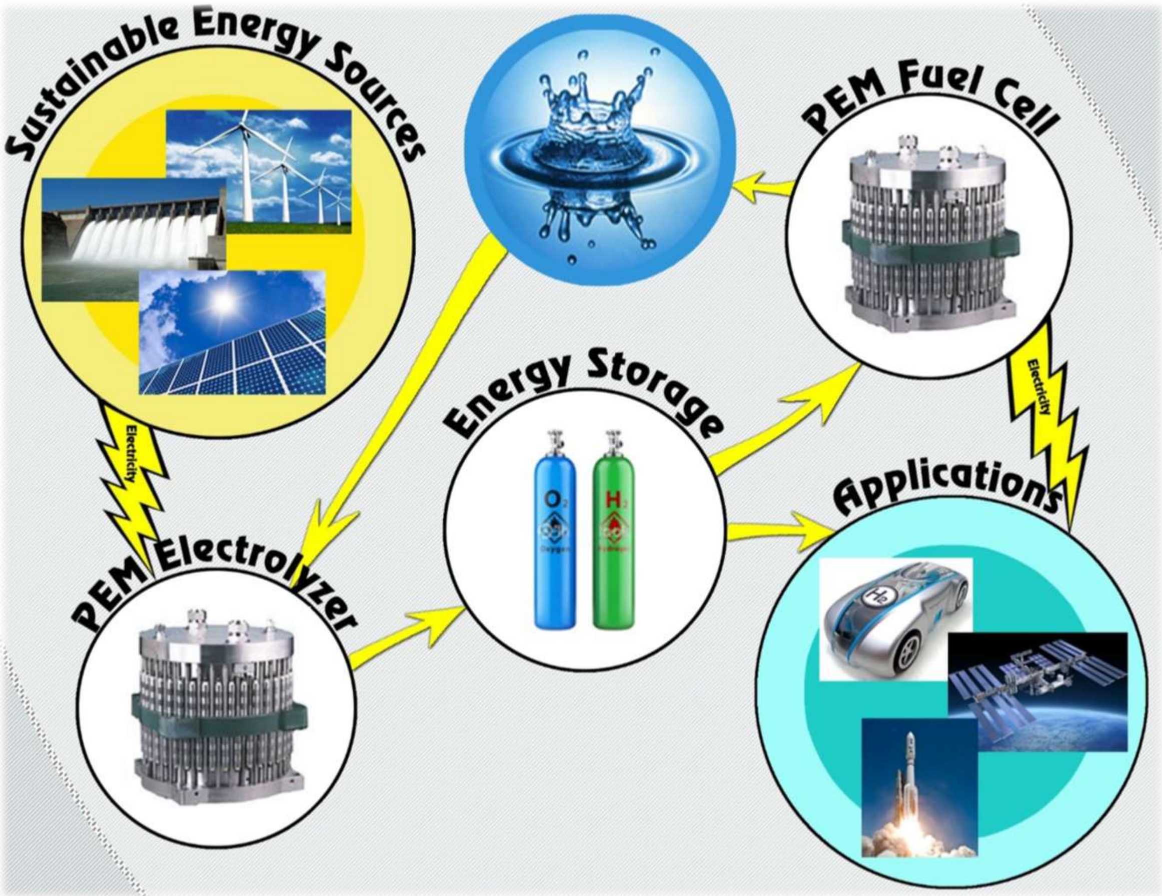
# High-efficiency devices for pure oxygen and hydrogen generation

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





# Sustainable energy system




- Electricity will provide power, and be stored as $H_2/O_2$ via Electrolyzer cells from water
- When needed, $H_2$ and $O_2$ will be converted back to electricity via fuel cells, and produce water
- Electrolyzers/fuel cells share same stack, thus high energy density, lower volume/cost

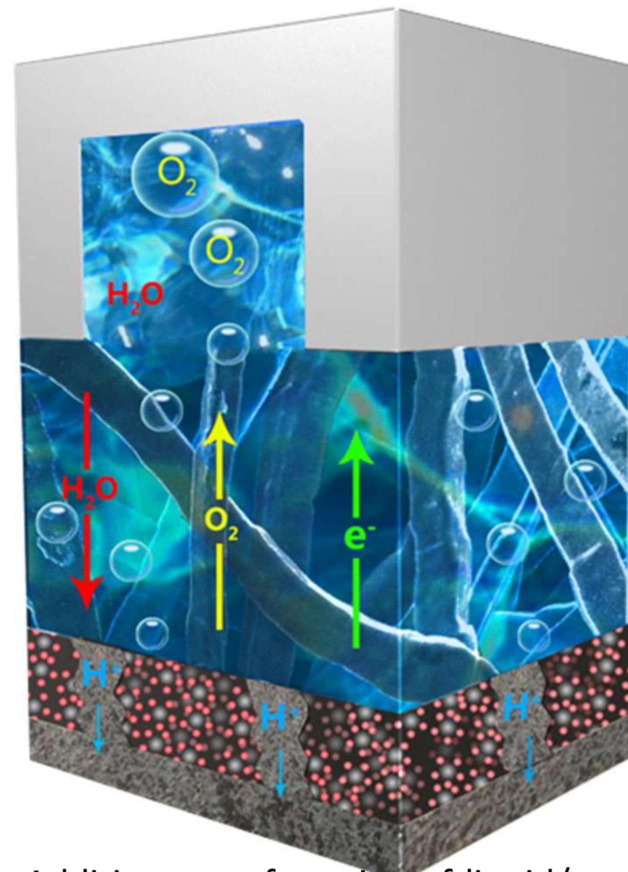
Jingke Mo, Zhenye Kang, Scott T. Retterer, David A. Cullen, Todd J. Toops, Johney B. Green Jr, Matthew M. Mench, and Feng-Yuan Zhang. Science Advances **2**(11), e1600690, 2016.

# 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




Anode flow channel

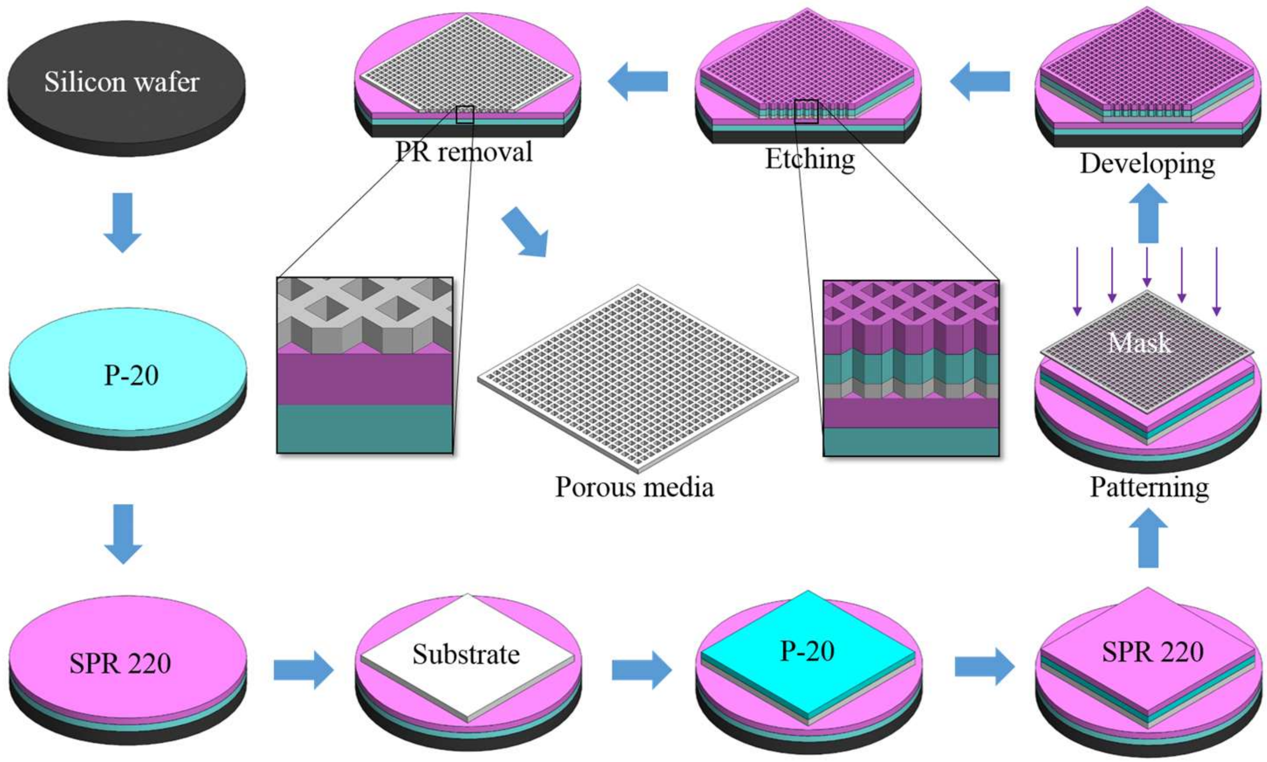
Liquid /gas diffusion layer (LGDL)

Catalyst layer

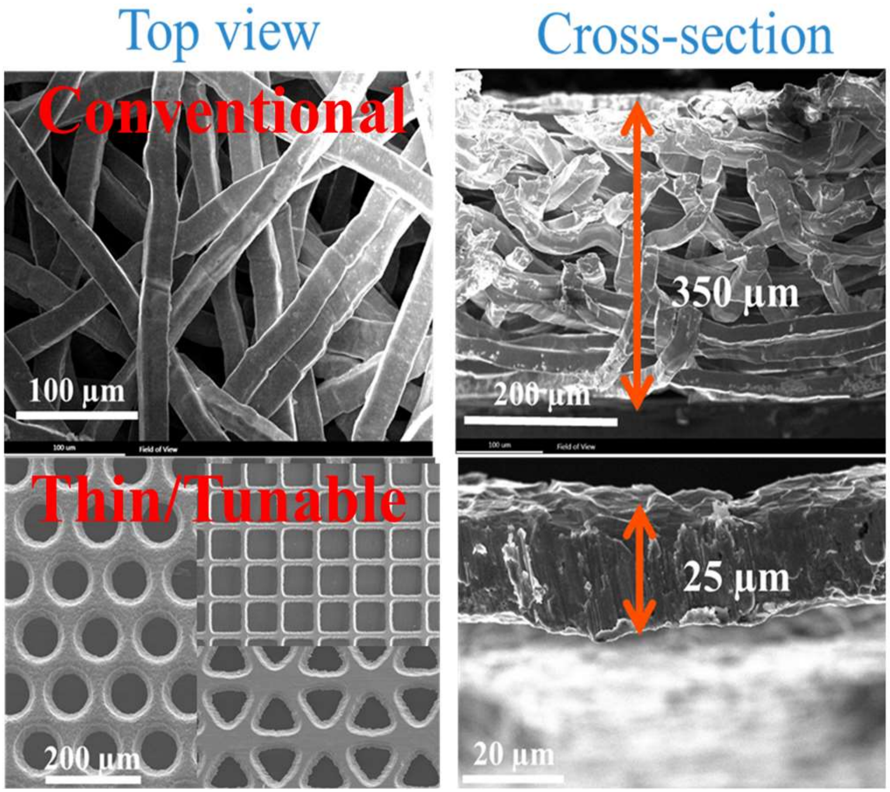
PEM

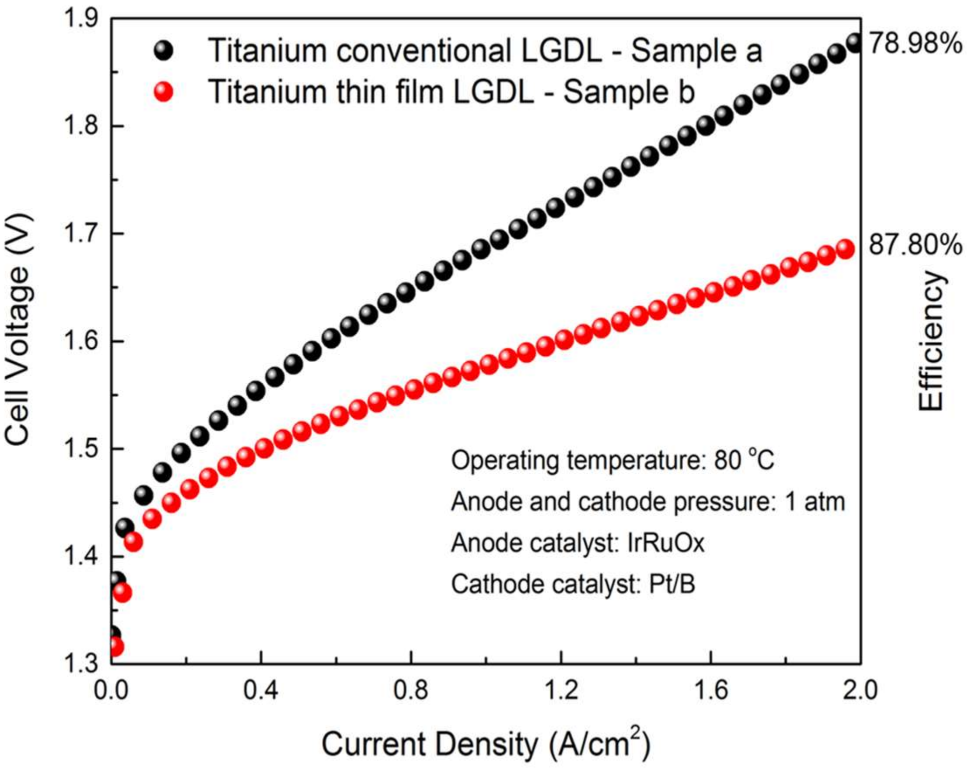
J. Mo, R.R. Dehoff, W.H. Peter, T.J. Toops, J.B. Green, F.-Y. Zhang, Additive manufacturing of liquid/gas diffusion layers for low-cost and high-efficiency hydrogen production. *International Journal of Hydrogen Energy* **41**, 3128-3135 (2016).

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




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



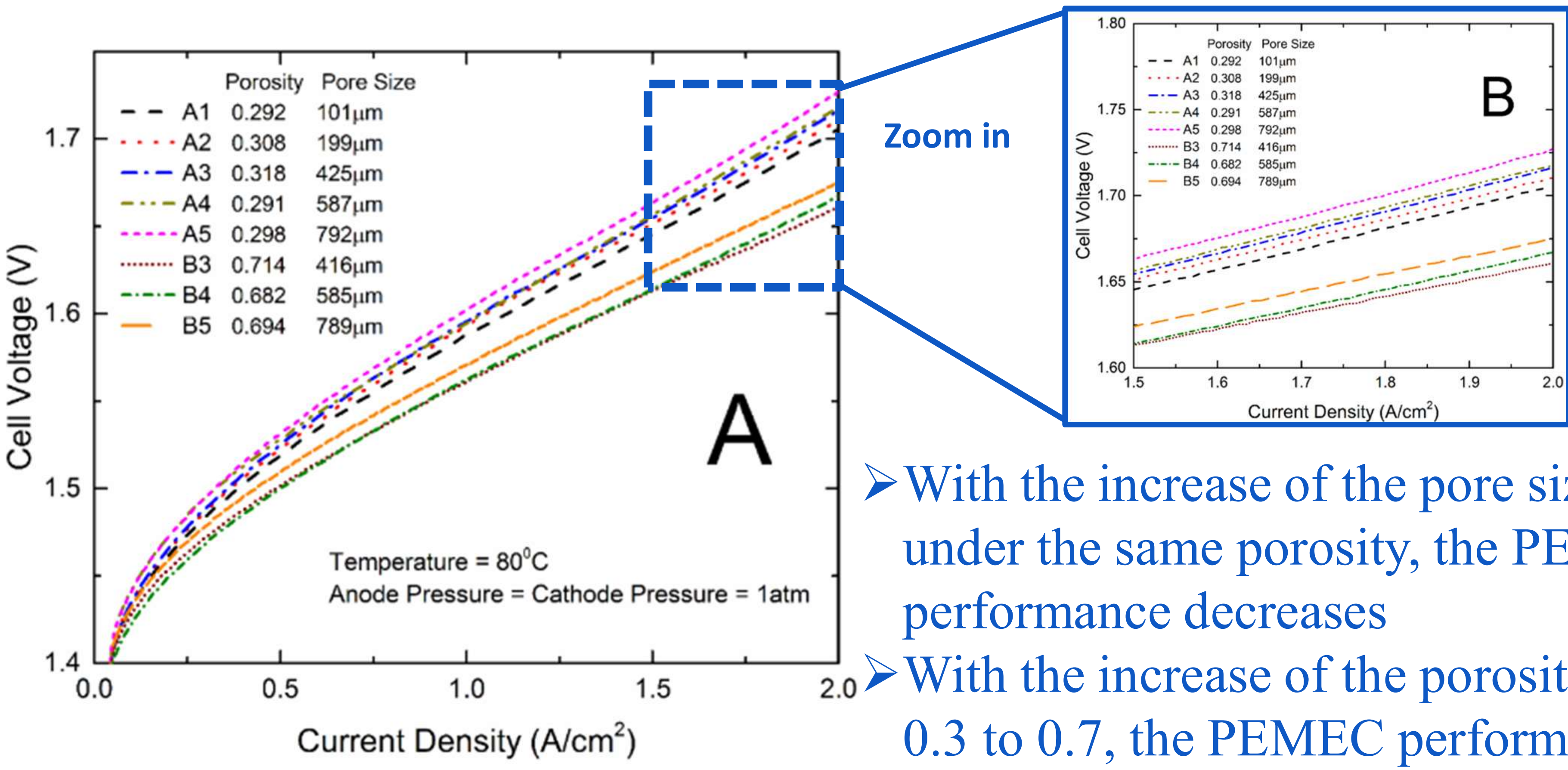




Efficiency improved from 78% to 87% at a current density of 2.0 A/$cm^2$

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.

# The impact of the pore size and porosity

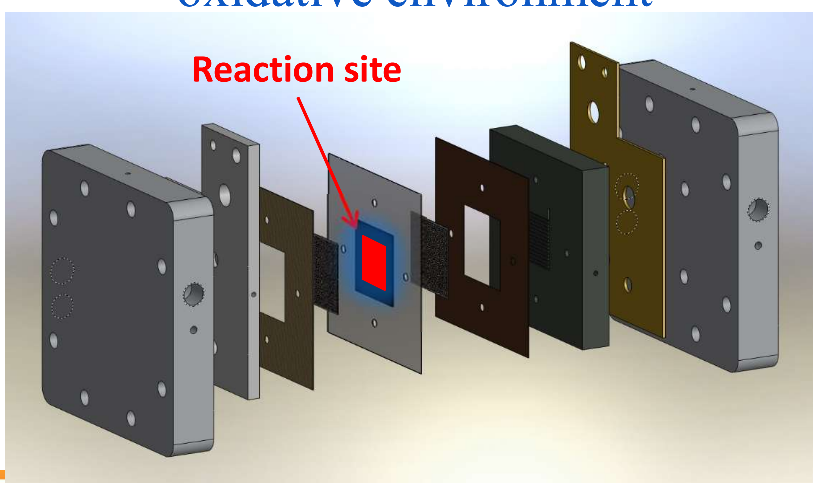


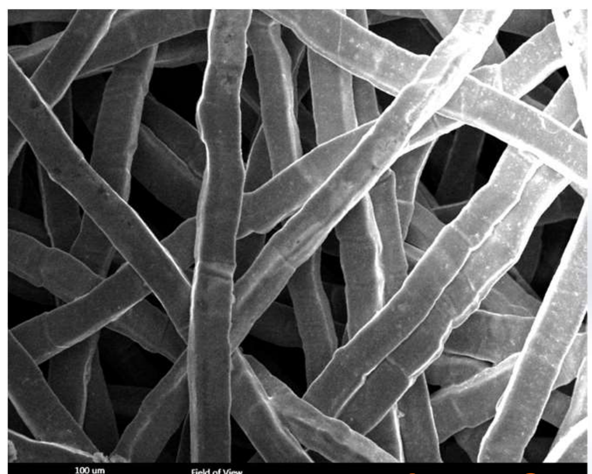

- ➢With the increase of the pore size under the same porosity, the PEMEC performance decreases
- ➢With the increase of the porosity from 0.3 to 0.7, the PEMEC performance is improved

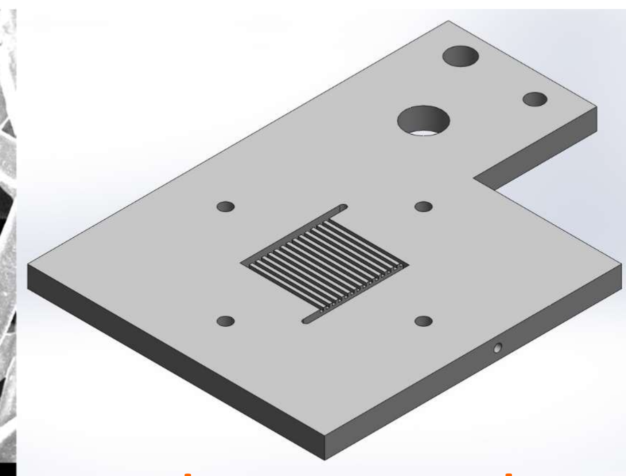
Kang, Z., J. Mo, G. Yang, S.T. Retterer, D.A. Cullen, T.J. Toops, J.B. Green, M.M. Mench, and F.-Y. Zhang, *Energy & Environmental Science* 2016. DOI: 10.1039/C6EE02368A

## 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



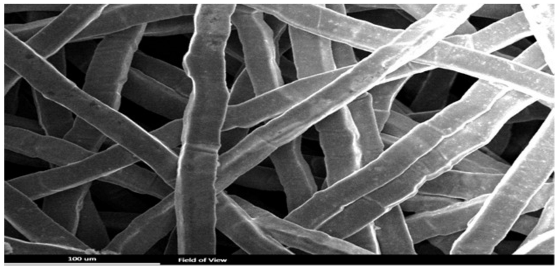



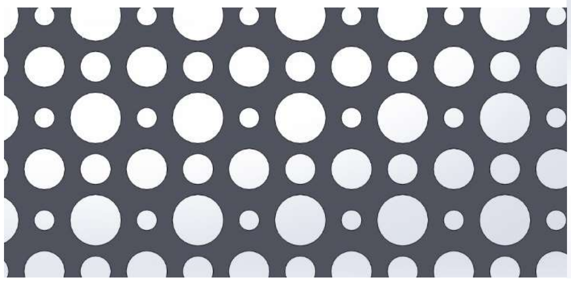



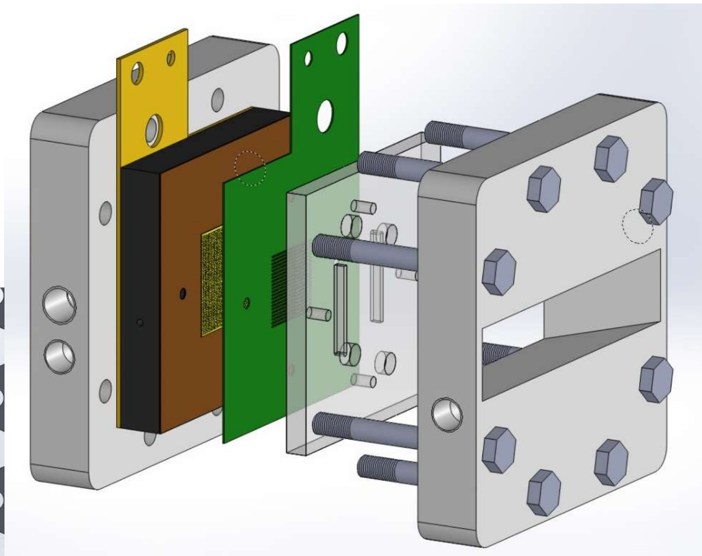
The electrochemical reactions are ultrafast and microscale

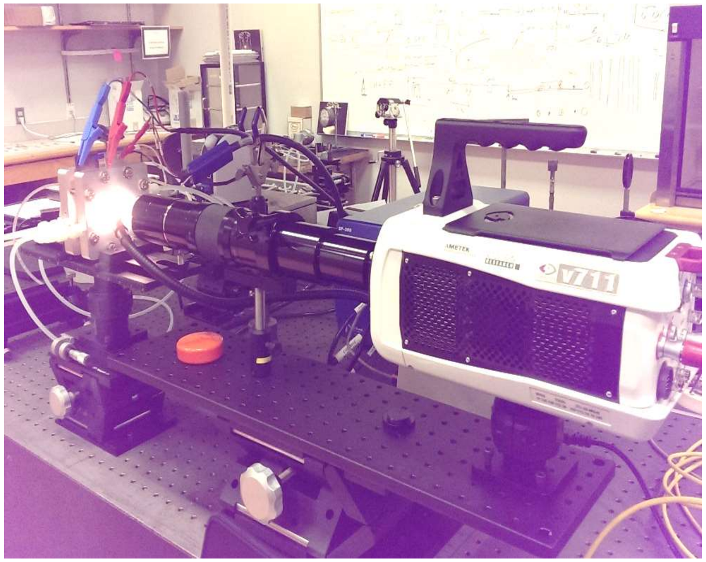
# *In-situ* visualization with developments of novel LGDLs, transparent PEMFCs and high-speed/microscale system

- 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



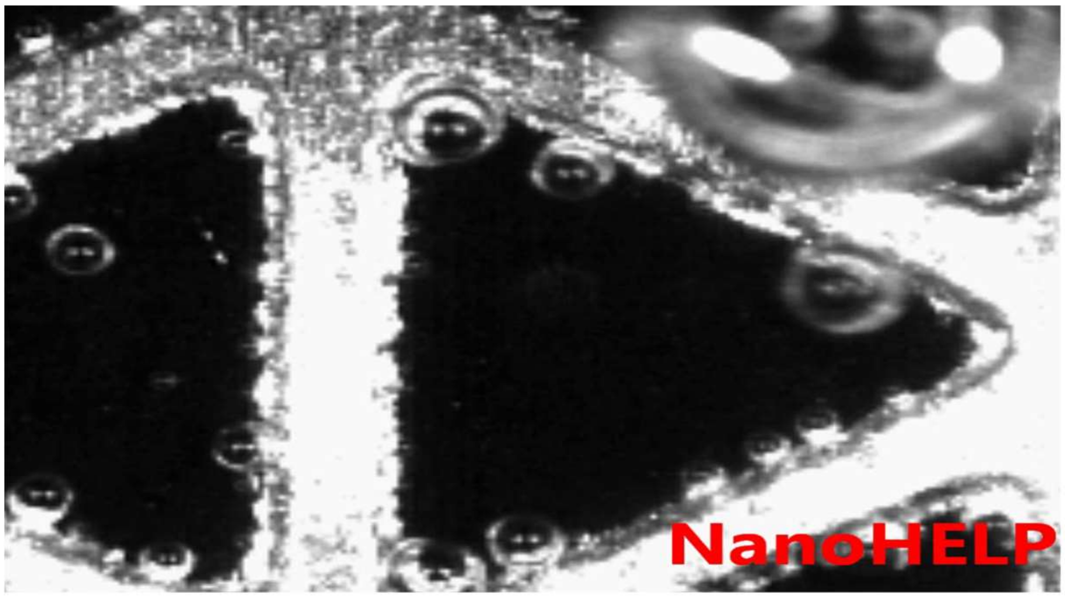


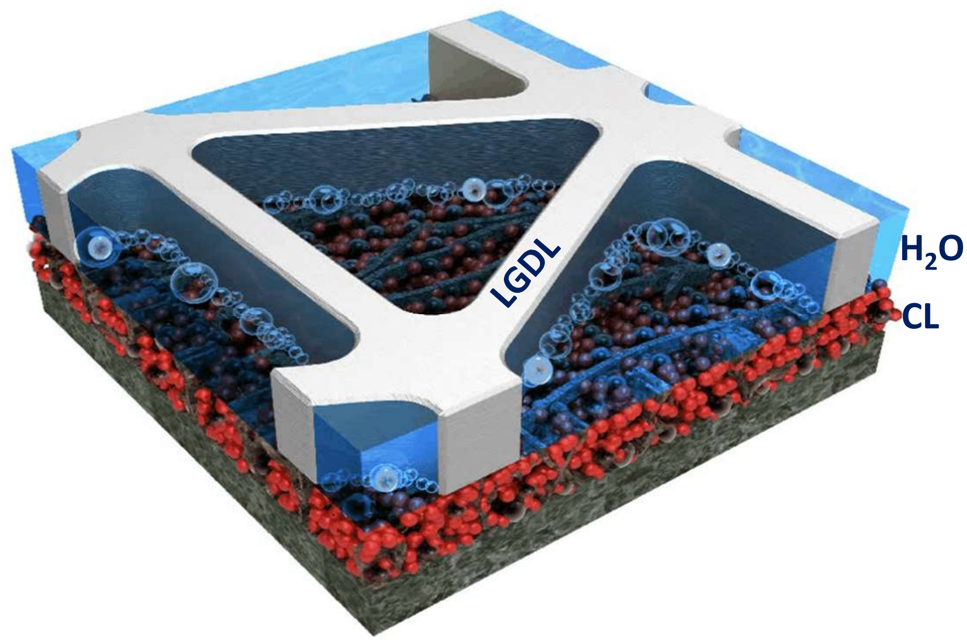




## First-ever revealing the true nature of multiphase interfacial electrochemical reactions in micro porescale with microsecond time resolution

- 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)**

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.

# New Catalyst Design and Fabrication--Significant Increase in Catalyst Mass Activity, and Reduce Cost

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UT Research Reveals Potential for 50-fold Increase in Catalyst Mass Activity

University of Tennessee and national lab research has led to a new understanding of how and where electrochemical reactions occur, by moving from traditional electrolysis technology to what is known as proton exchange membrane electrolyzer cells or PEMECs.

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the process, conduct electricity.

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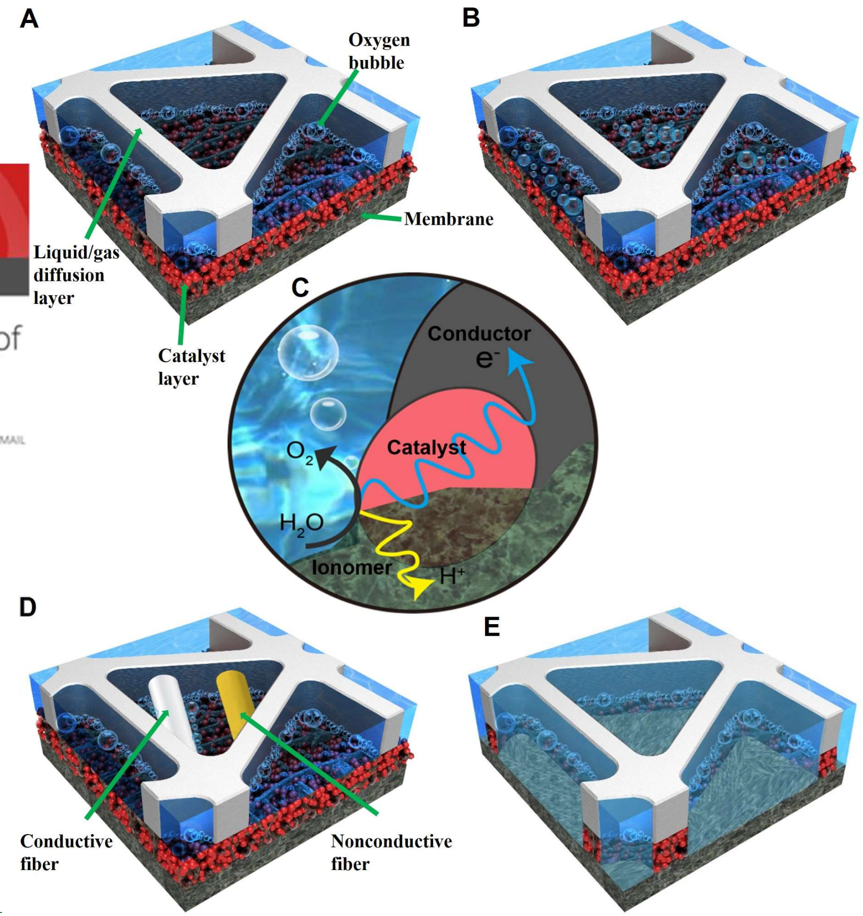
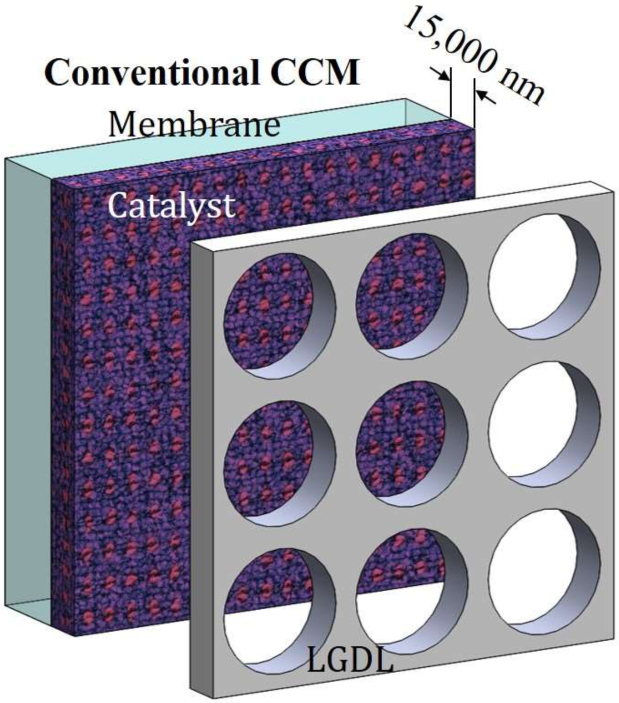


# Schematics of Comparison Fabrication Method Between Conventional CCM and Deposit Catalyst on LGDL

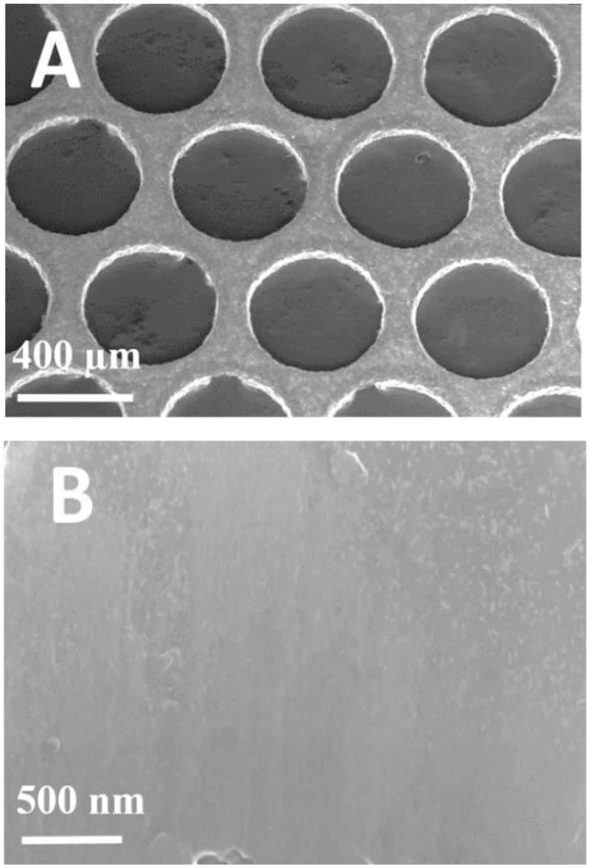



- For conventional CCM, the catalyst was fabricated on the membrane
- Novel catalyst fabrication method is depositing the catalyst only on the titanium thin well/tunable LGDL.

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.

# Surface Modifications of Titanium TT-LGDLs

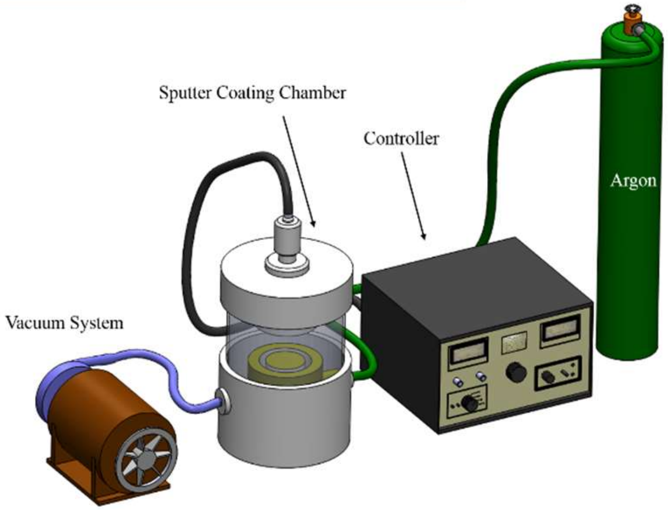
- The TT-LGDLs achieve superior performance by planar surface and thin thickness.
- However, resistance to corrosion in such systems is achieved by surface oxide formation, which can increase surface electrical resistivity and detrimentally impact cell performance.
- By protecting the surface of the TT-LGDLs using thin film surface treatment by mature and low cost micro/nano technologies, it is anticipated that the performance can be further improved.
- Two different methods were adopted:
  - Sputter coating
  - Gold electroplating




Zhenye Kang, Jingke Mo, Gaoqiang Yang, Yifan Li, Derrick A. Talley, Scott T. Retterer, David A. Cullen, Todd J. Toops, Michael P. Brady, Guido Bender, Bryan S. Pivovar, Johney B. Green Jr, and Feng-Yuan Zhang. Thin film surface modifications of thin/tunable liquid/gas diffusion layers for high-efficiency proton exchange membrane electrolyzer cells. *Applied Energy*, 2017. 206C: 983-990.

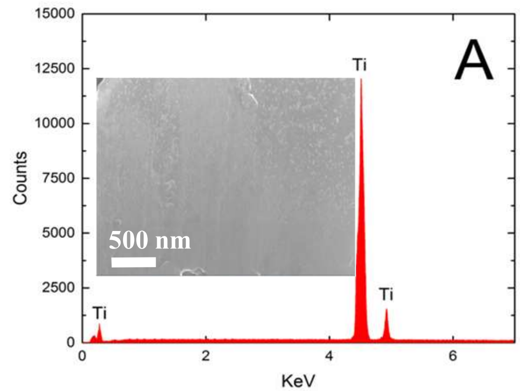
# Surface Modifications of Titanium TT-LGDLs

- Sputter deposition:
  - A potential of 2.4 kV and a current of 20 mA was maintained to control the deposition for gold.
  - The thickness of the coating was controlled by adjusting the operating time.
- Au electroplating:
  - Electro-cleaning: the TT-LGDLs acted as cathode and was put into the 4% solution of sodium hydroxide. A negative potential of 6 V was applied for 45 s at 60 $^{o}$C.
  - Electro-striking: the TT-LGDLs were immersed in 24K acid gold strike solution at room temperature, and a negative voltage of 7 V was applied for 25 s.
  - the TT-LGDLs were moved to the 24K bright gold plating solution at 38 $^{o}$C and the time for electro-plating was controlled based on the desired gold thickness.

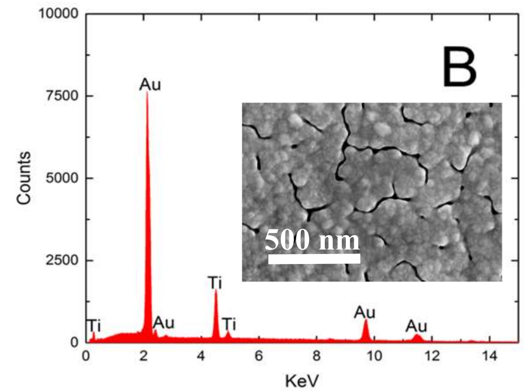



# *Ex-situ* Characterizations of Titanium TT-LGDLs

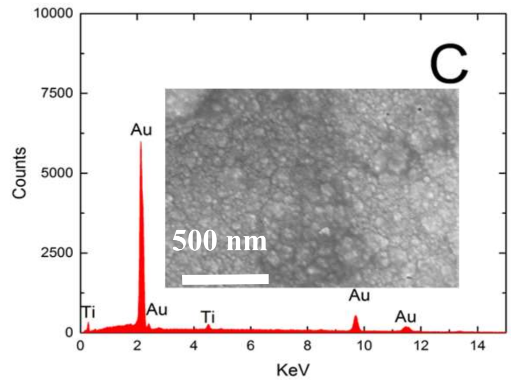
- The sputter deposited Au thin film layer is uniformly distributed on the surface, but there are some cracks formed throughout the surface.
- The gold is distributed uniformly around the surface and there are no cracks observed.
- The higher peak of Ti in (B) is attributed to the cracks with sputter coated LGDL.
- The Ti peak is very small in (C) and (D) due to uniformly distributed Au.



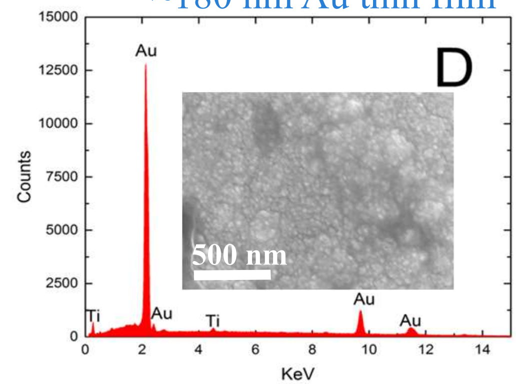

Fresh Ti TT-LGDLs




Sputter deposited ~180 nm Au thin film

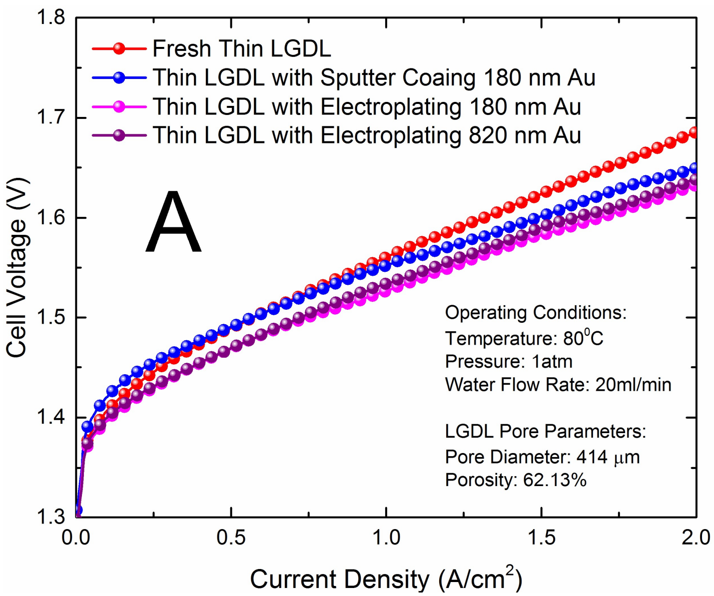


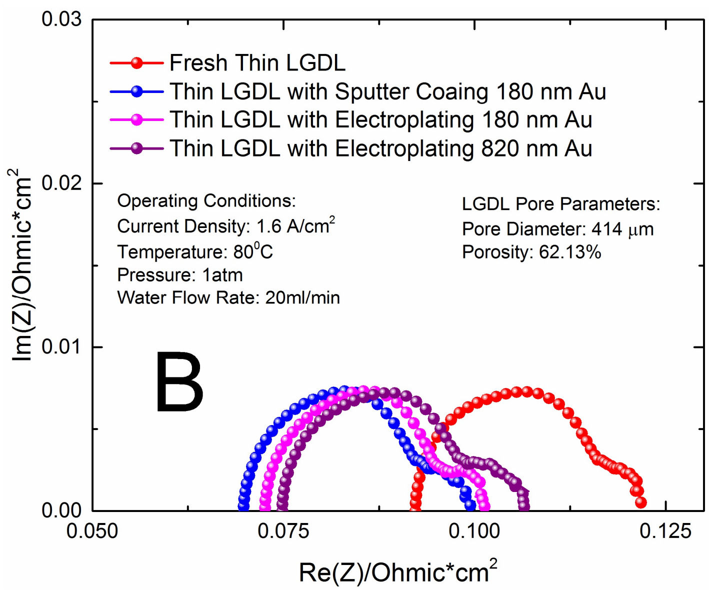

Electroplated ~180 nm Au thin film




Electroplated ~820 nm Au thin film

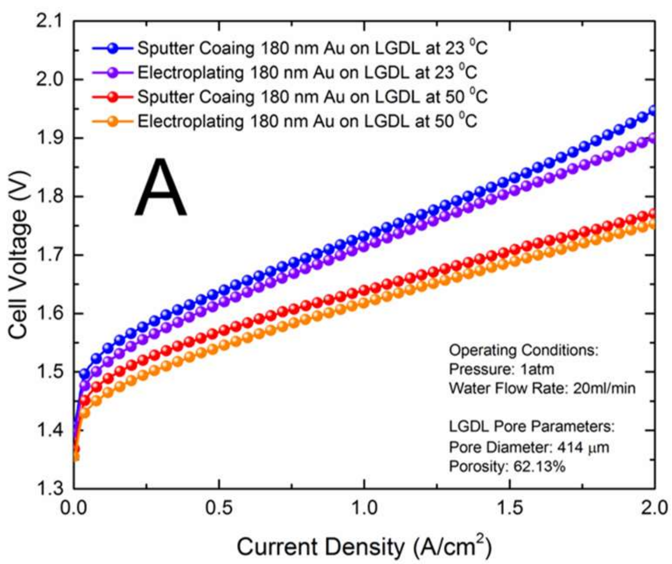
## *In-situ* Tests of Novel TT-LGDLs with Surface Modification

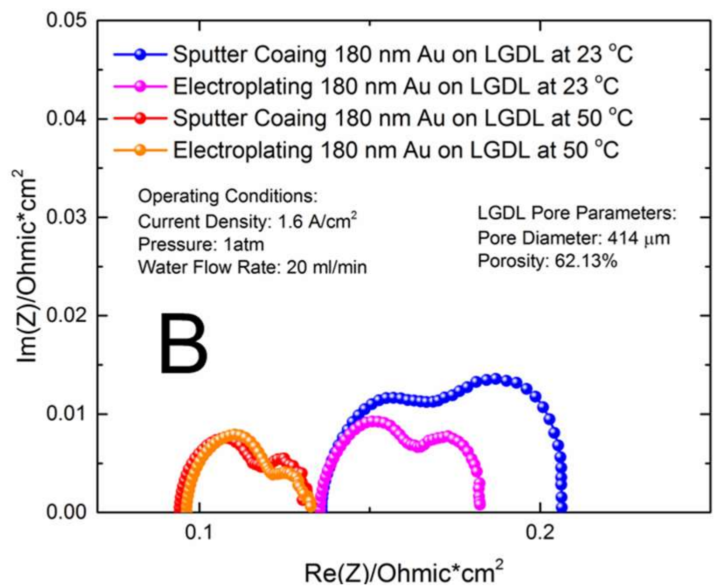



- The performance of the PEMECs was improved to 1.6492 V with 180 nm Au sputter deposited TT-LGDL
- It can be further improved to **1.6328 V** and 1.6382 V with the 180 nm and 820 nm Au electroplated thin LGDLs, respectively.
- With only a 180 nm Au film on TT-LGDLs, the hydrogen/oxygen production rate was significantly increased by about **28.2%** compared with the untreated titanium TT-LGDLs.

# Effects of Temperature

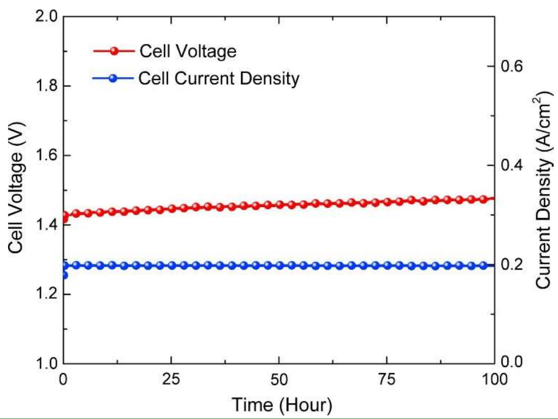


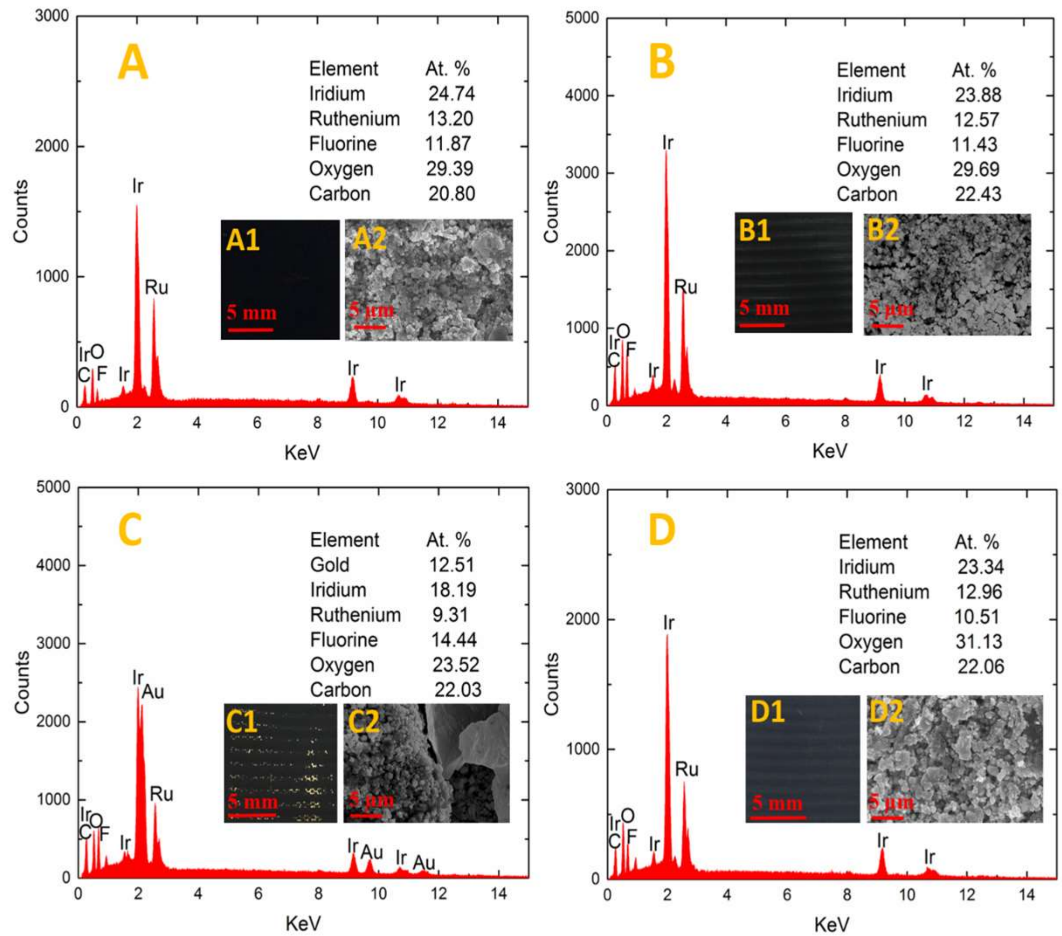




- The cell voltages of the PEMECs with Au sputter coated TT-LGDLs are1.947 V, 1.770 V and 1.649 V at 23 °C, 50 °C and 80 °C, respectively.
- The voltages of the PEMECs with electroplating Au TT-LGDLs are 1.900 V, 1.753 V and 1.6328 V at 23 °C, 50 °C and 80 °C, respectively.
- The performance of the TT-LGDLs with electroplated Au is better than sputter coating at different temperatures.

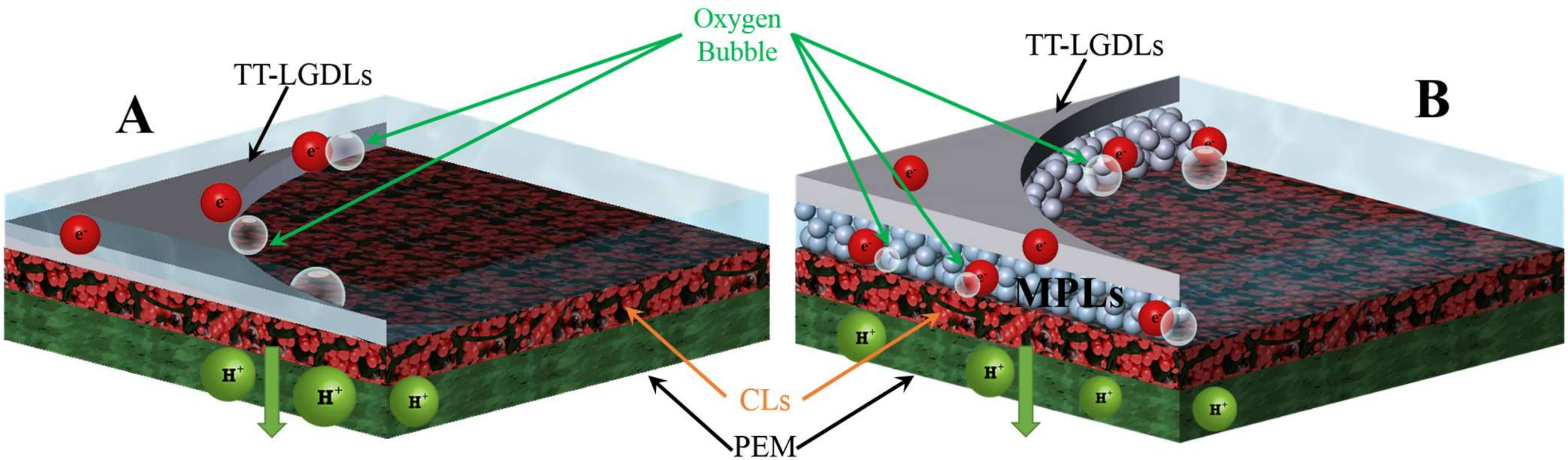
# Stability of the Surface Treated TT-LGDLs

- Fresh CCM has a flat surface and shows a uniformly distributed dark color, as shown in Figure (A1)
- After the test with untreated titanium TT-LGDLs, the shape of the channel and LGDL is indented on the CCM, as shown in Figure (B1).
- After the tests with the sputter coated TT-LGDLs, Au is clearly observed on the CCM surface, as shown in Figure (C1), which means the Au is partially peeled off from the TT-LGDL
- While the CCM, examined after testing with the 180 nm Au electroplated LGDL, shows no peeled off Au.



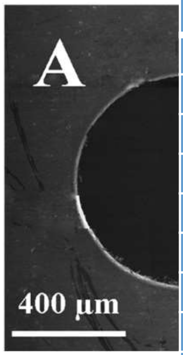



# The Concept of the MPLs on TT-LGDLs

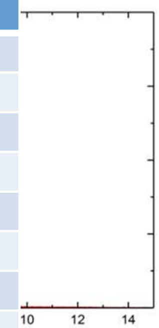



- Based on our previous discoveries, the oxygen evolution reaction sites only occurs at the rim of the TT-LGDL pores due to the large in-plane electrical resistance of the CL and the difficult two-phase transport under the TT-LGDL land area.
- By introducing the MPLs between the CLs and TT-LGDLs, as shown in Fig. 1(B), it is anticipated that more OER sites will be formed and the PEMEC performance can be improved compared with the fresh TT-LGDLs

# The Concept of the MPLs on TT-LGDLs

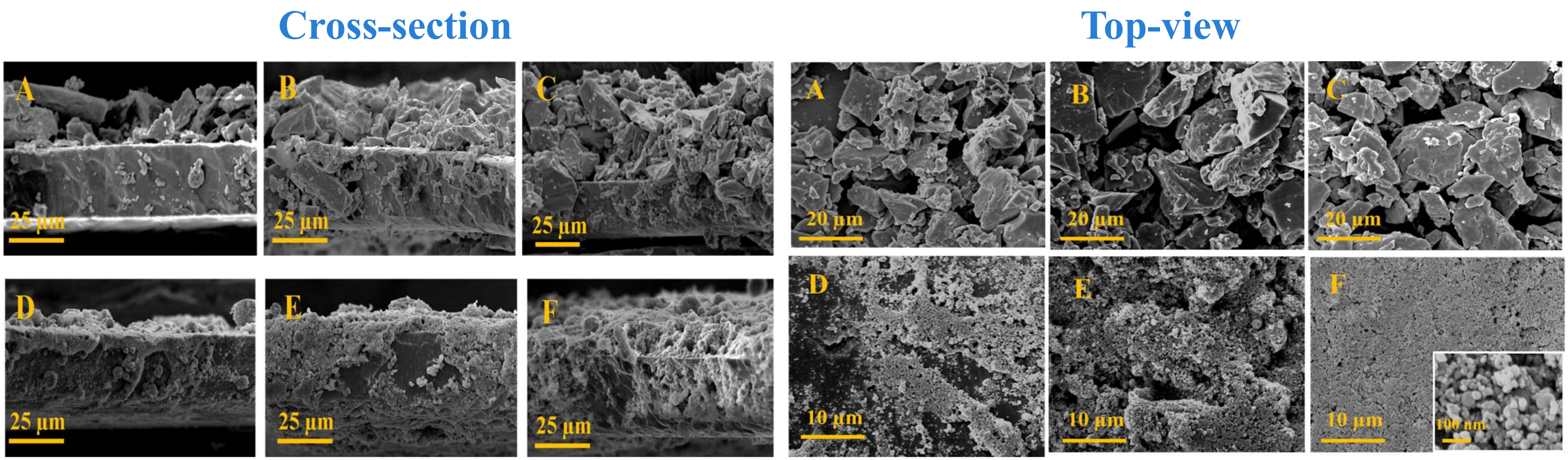



| Sample | TT-LGDLs | Ti Particles | Particle Shape | MPL Thickness (µm) |
|---|---|---|---|---|
| A | ~800 µm pore diameter; ~30% porosity | Null | Null | 0 |
| A1 | A | 5 µm microparticles | Irregular | ~15 |
| A2 | A | 5 µm microparticles | Irregular | ~20 |
| A3 | A | 5 µm microparticles | Irregular | ~40 |
| A4 | A | 30-50 nm nanoparticles | Sphere | ~5 |
| A5 | A | 30-50 nm nanoparticles | Sphere | ~8 |
| A6 | A | 30-50 nm nanoparticles | Sphere | ~12 |
| B | ~100 µm pore diameter; ~30% porosity | Null | Null | 0 |
| B1 | B | 5 µm microparticles | Irregular | ~20 |



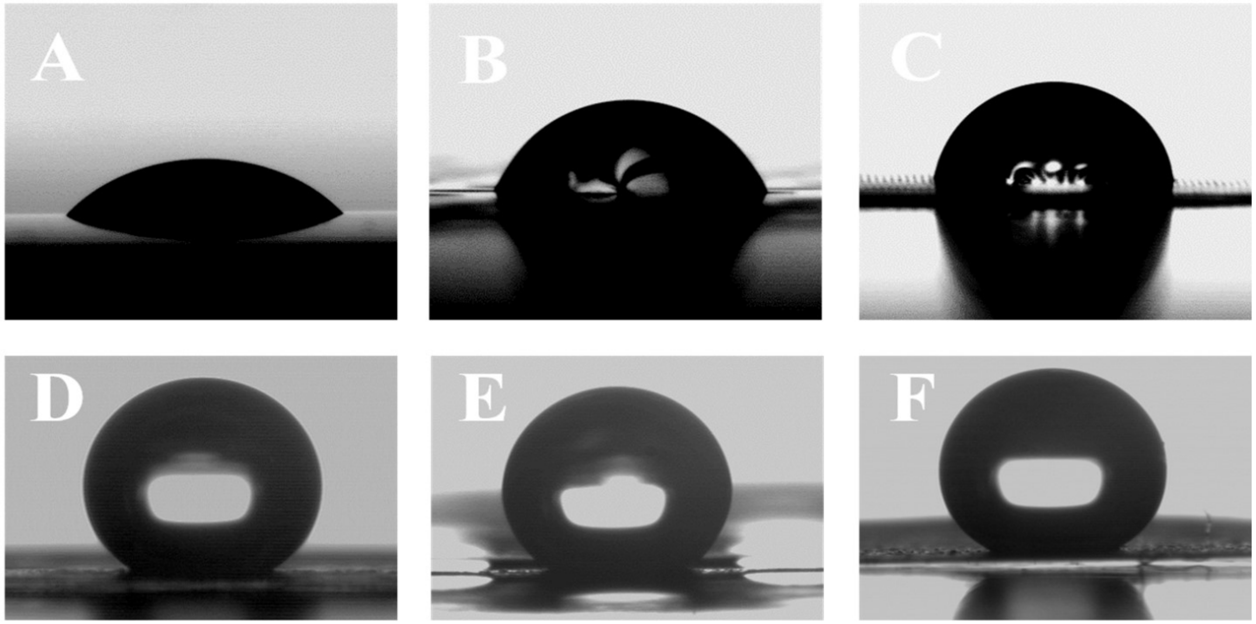

- The MPLs were fabricated by low temperature air spraying method. MPL ink was prepared with micro or nano Ti particles, Nafion dispersion, ethylene glycol, and isopropyl alcohol (IPA).
- Two TT-LGDLs were used as the substrate for MPLs. The TT-LGDLs had the same porosity about 30%, and one of them had a large pore diameter about 800 µm and the other had a small pore diameter about 100 µm.
- The medium head airbrush Model 150-1 was used for air spraying.
- The MPL thickness was controlled by the spray number of times, and three MPLs with different thickness were prepared with both micro and nano Ti particles.

# *Ex-situ* investigation of the MPLs




- The MPLs were mainly spread on the top surface of the TT-LGDLs.
- The thickness of the micro particle MPLs is in the range of 15-40 µm, while the nano particle MPLs is about 5-12 µm.
- The surface roughness of the MPLs is much worse than fresh TT-LGDL surface.
- The nano Ti particle has a sphere shape, and the particle size is mainly in the range of 30-50 nm.
- The micro particle shape is irregular and its size is in micrometers.

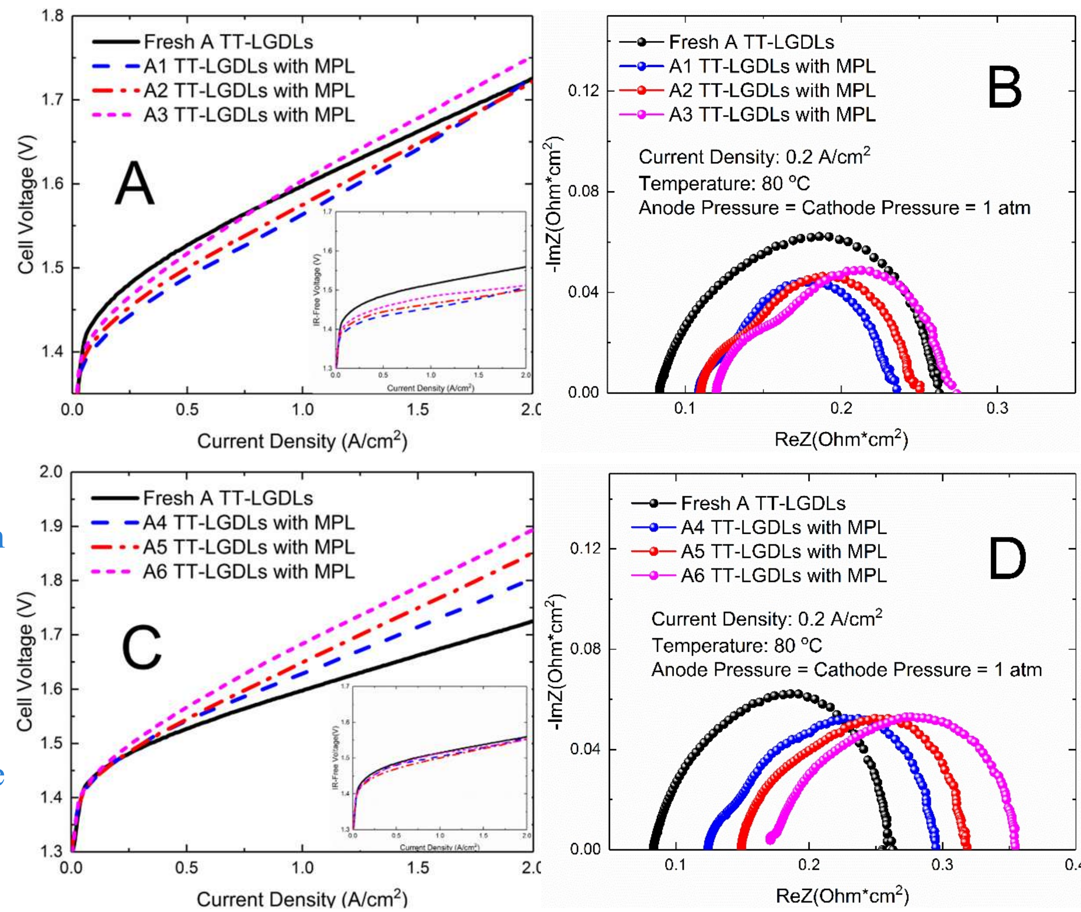
# Wettability of MPLs




- (A) Fresh Ti thin foil about 45°; (B) Fresh A about 64°; (C) Fresh B about 81°; (D) A2 about 145°; (E) A5 about 162°; (F) B1 about 150°.
- The MPLs showed super hydrophobic wettability, which is not an ideal property of the MPLs in PEMECs since it may increase the water/gas transport resistance.

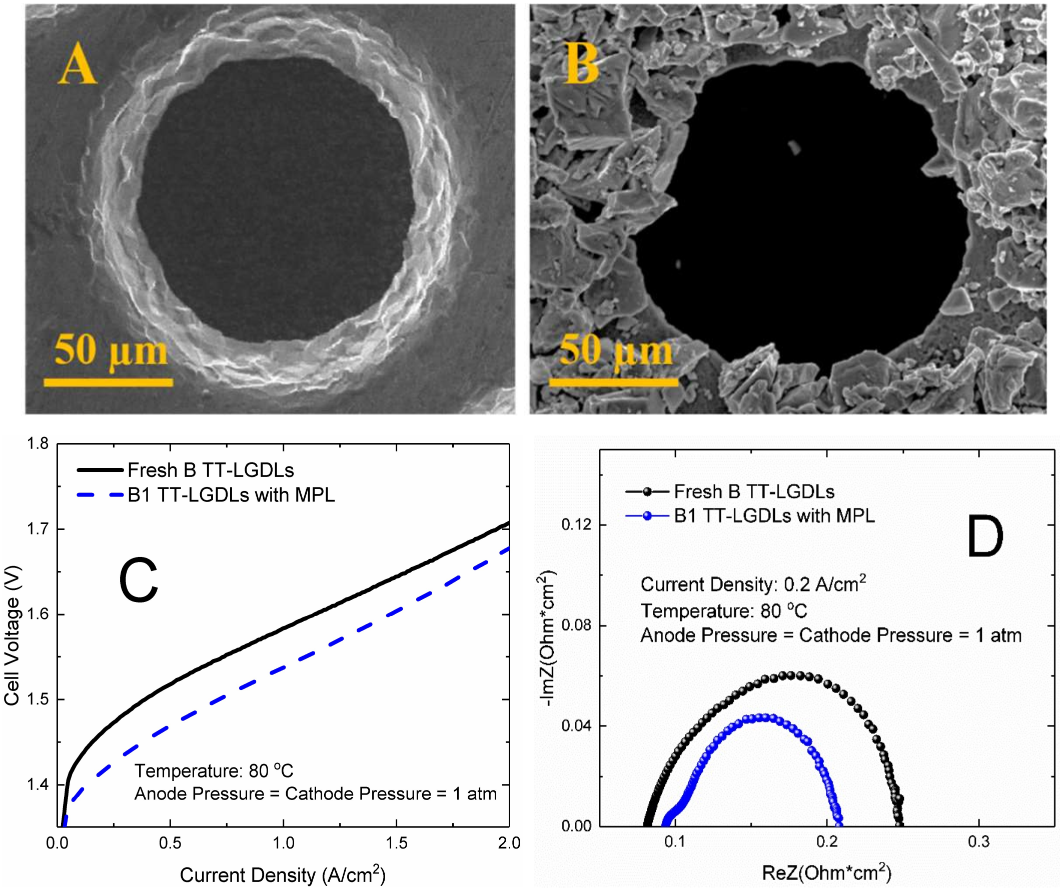
# *In-situ* Characterization of MPLs

- The performance of PEMEC can be slightly improved under the low current density range (<0.5 A/cm$^2$) where the activation overpotential is the main factor of the total cell voltage.
- The activation resistance of the fresh A TT-LGDLs, sample A1, A2, and A3 is about 179, 126, 140 and 151 mΩ*cm$^2$, respectively.
- The cell voltage will increase to 1.804, 1.852, and 1.894 V for the sample A4, A5, and A6, respectively, which is mainly due to the greatly increased ohmic resistances, while the activation resistances between each sample are nearly the same.
- The ohmic resistance of fresh A TT-LGDLs, A4, A5 and A6 is about 83, 124, 149, and 171 mΩ*cm$^2$, respectively.
- The dense structure of the nano particle MPLs will prevent the possibility of increasing OER sites under the TT-LGDL land area



# *In-situ* Characterization of MPLs

- The effects of MPLs are expected to increase the OER sites, which will enhance the PEMEC performance by reducing the activation loss.
- Some Ti particles are located not only at the surface of TT-LGDL land but also in the pore area.
- The ohmic resistance will increase from 81.9 to 93.8 $m\Omega*cm^2$ when adding the micro particle MPLs on sample B TT-LGDLs.
- The activation resistance can be significantly reduced from 165 to 114 $m\Omega*cm^2$.
- The cell voltage can be decreased from 1.707 V to 1.687 V at 2.0 $A/cm^2$.



## Summary

- A novel-designed thin titanium LGDL with 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
- Thinfilm surface modification methods were adopted to further improve the PEMEC performance (from 1.67V to **1.63 V** at 80 $^{o}$C and 2.0 A/cm$^2$).
- MPLs offer some improved performance under specific conditions but may not be required for optimum TT-LGDLs in PEMECs.
- The stack size/volume/cost can be significantly reduced by the novel thin LGDLs.

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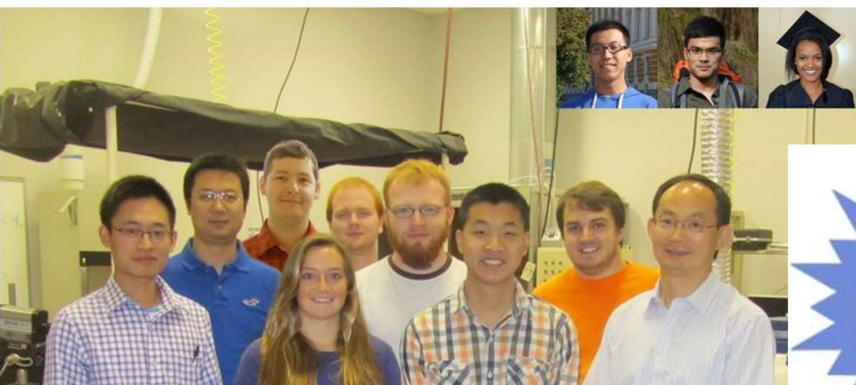

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