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Title:	Materials and Interfaces for Electrocatalytic Hydrogen Production and Utilization
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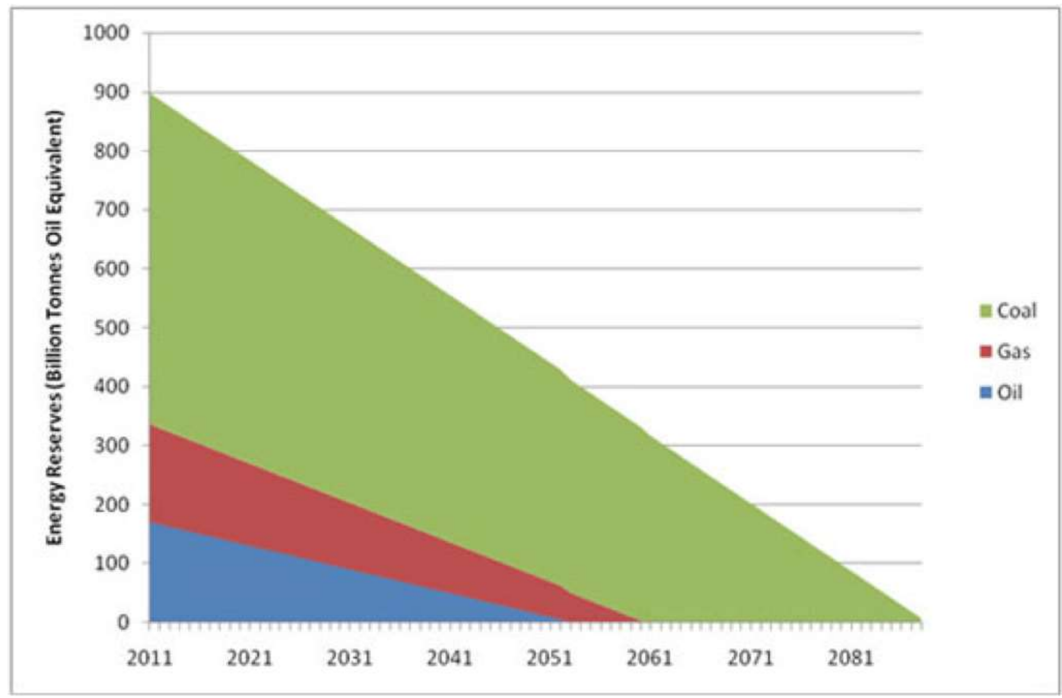
Materials and Interfaces for Electrocatalytic Hydrogen Production and Utilization

Alexander J. Gupta

Proposed Work Pertaining to Chemical Engineering Doctoral Program

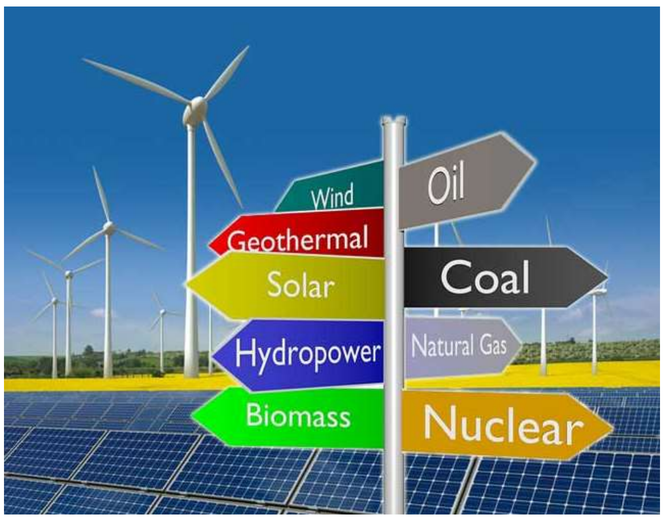
University of Louisville

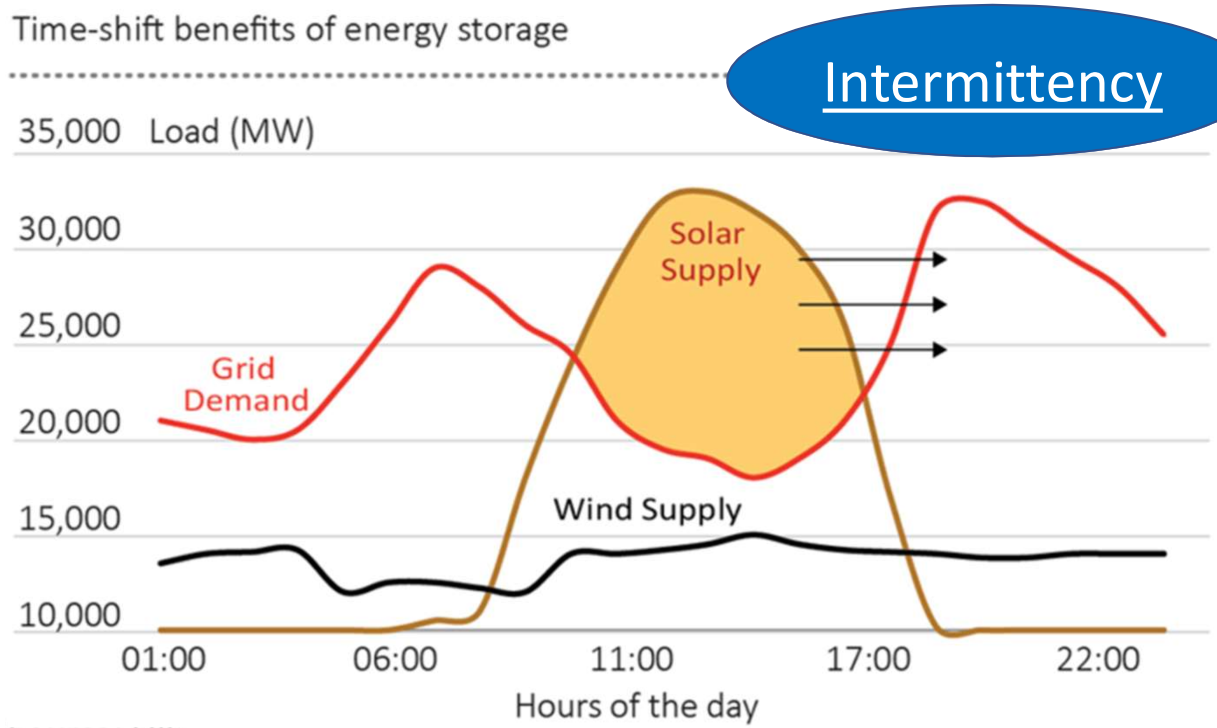
The Global Energy Outlook



MAHB Administration. *Mahb* (2019)
NASA's Jet propulsion Laboratory. *NASA* (2019)

Renewable Energy Sources





Intermittency

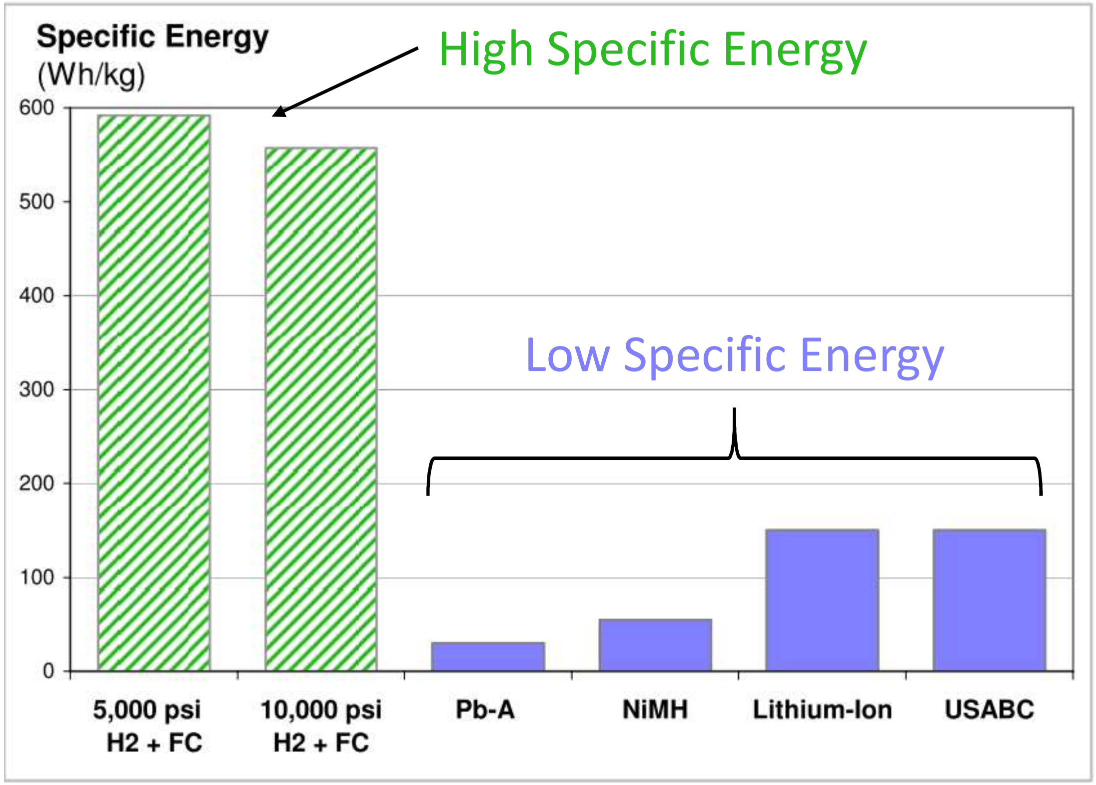
Vector needed to concentrate and store renewable energy for later use

Solarquotes Blog (2014)
Simionauc. *Energy, Climate & Sustainability (Wordpress)* (2018)

Energy Vectors

Hydrogen

Fast Refueling
Stable Storage

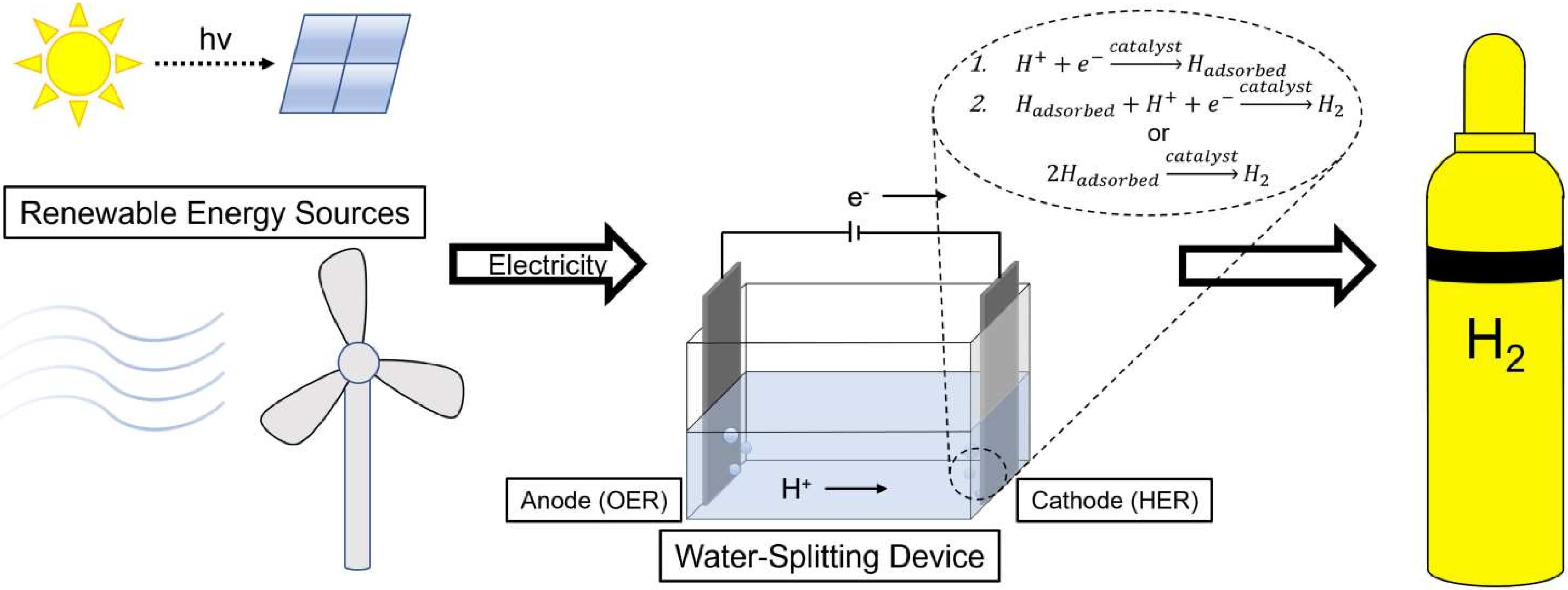


Batteries

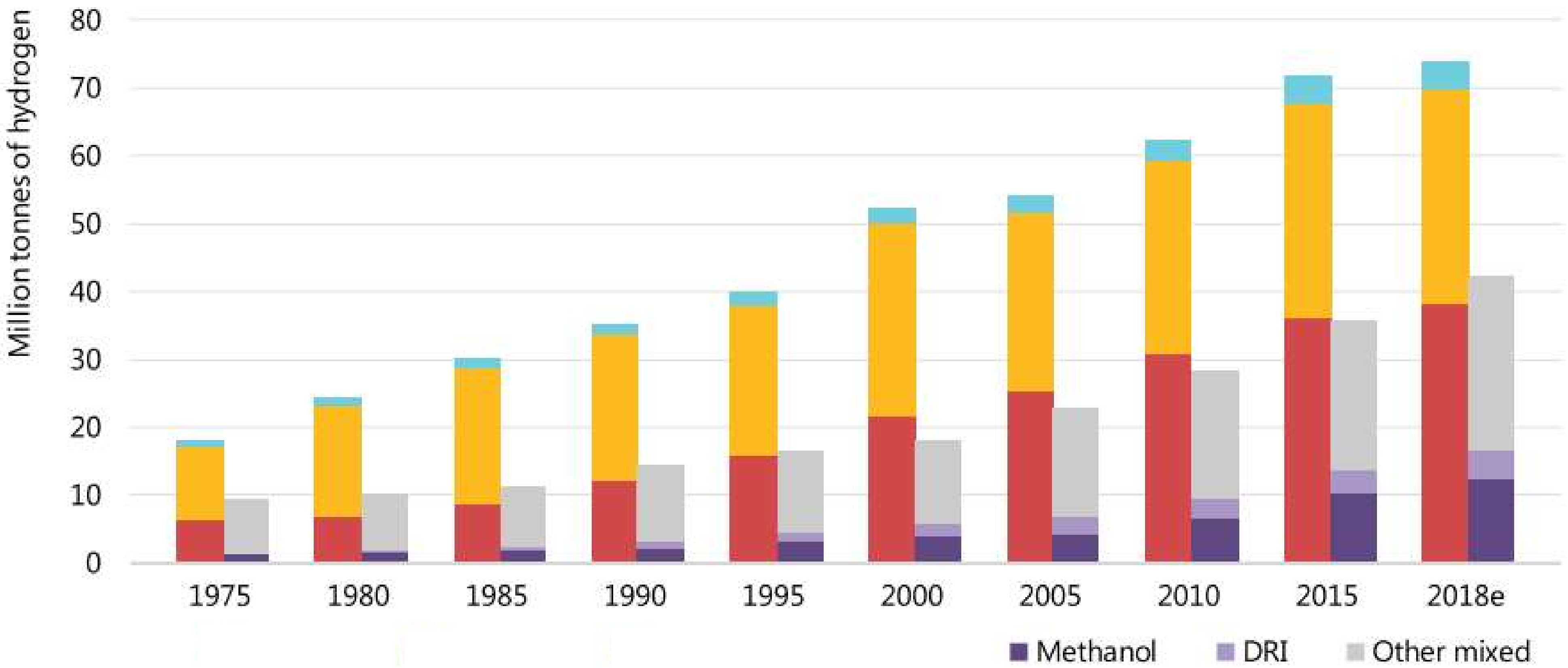
Long Charging Time
Self-Discharging

File:Toyota Mirai – Frontansicht, 11. November 2018, Düsseldorf.jpg - Wikimedia Commons
https://s3-prod.autonews.com/s3fs-public/styles/width_792/public/4MODELS-MAIN_i.jpg
Thomas, C. E. Int. J. Hydrogen Energy 34, 6005–6020 (2009)
https://download.cnet.com/Charging-Time/3000-20432_4-78273325.html
FuelCellsWorks (2019)

Water Electrolysis

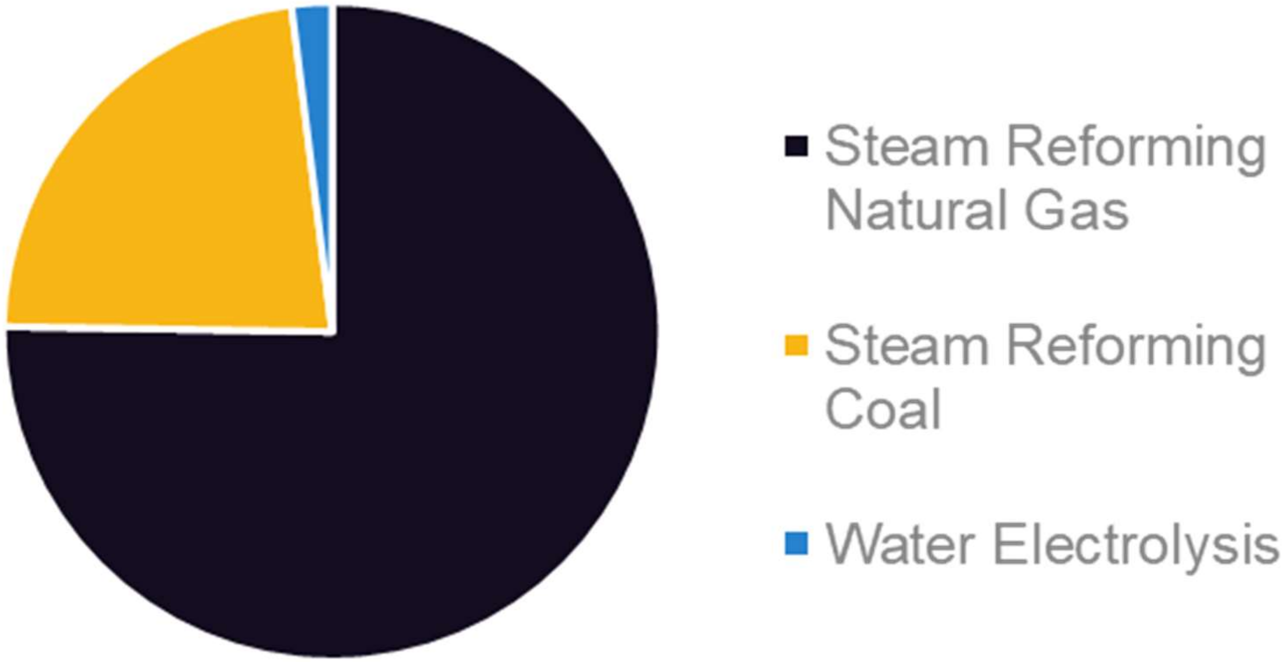


Hydrogen Demand & Other Applications



IEA. (2019)

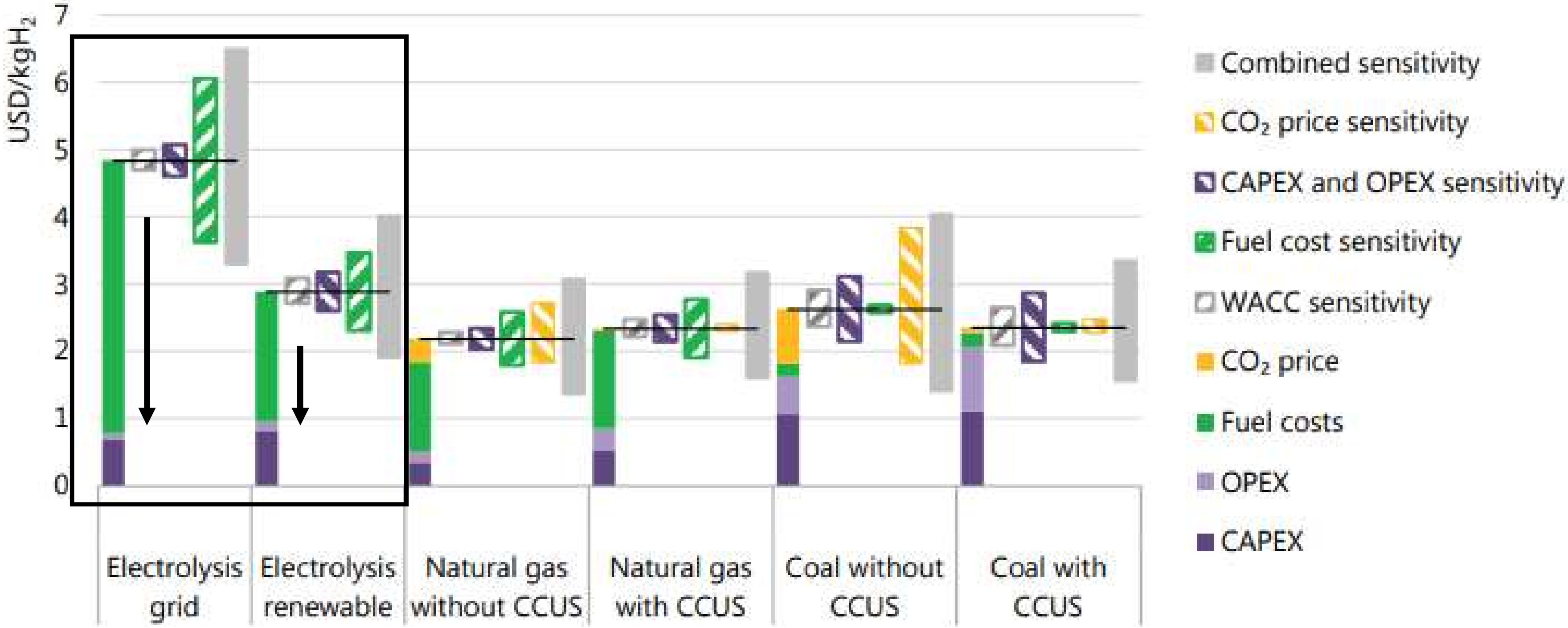
Hydrogen Production



Only ~2% of H_2 is produced via water electrolysis!

IEA. (2019)

Hydrogen Cost

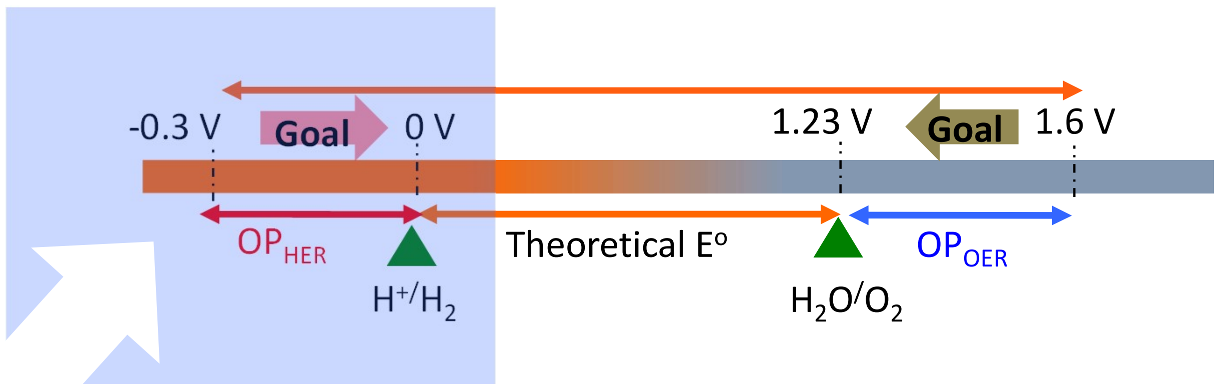


Cheaper electrolysis is a pathway toward a green energy economy based on H_2

IEA. (2019)

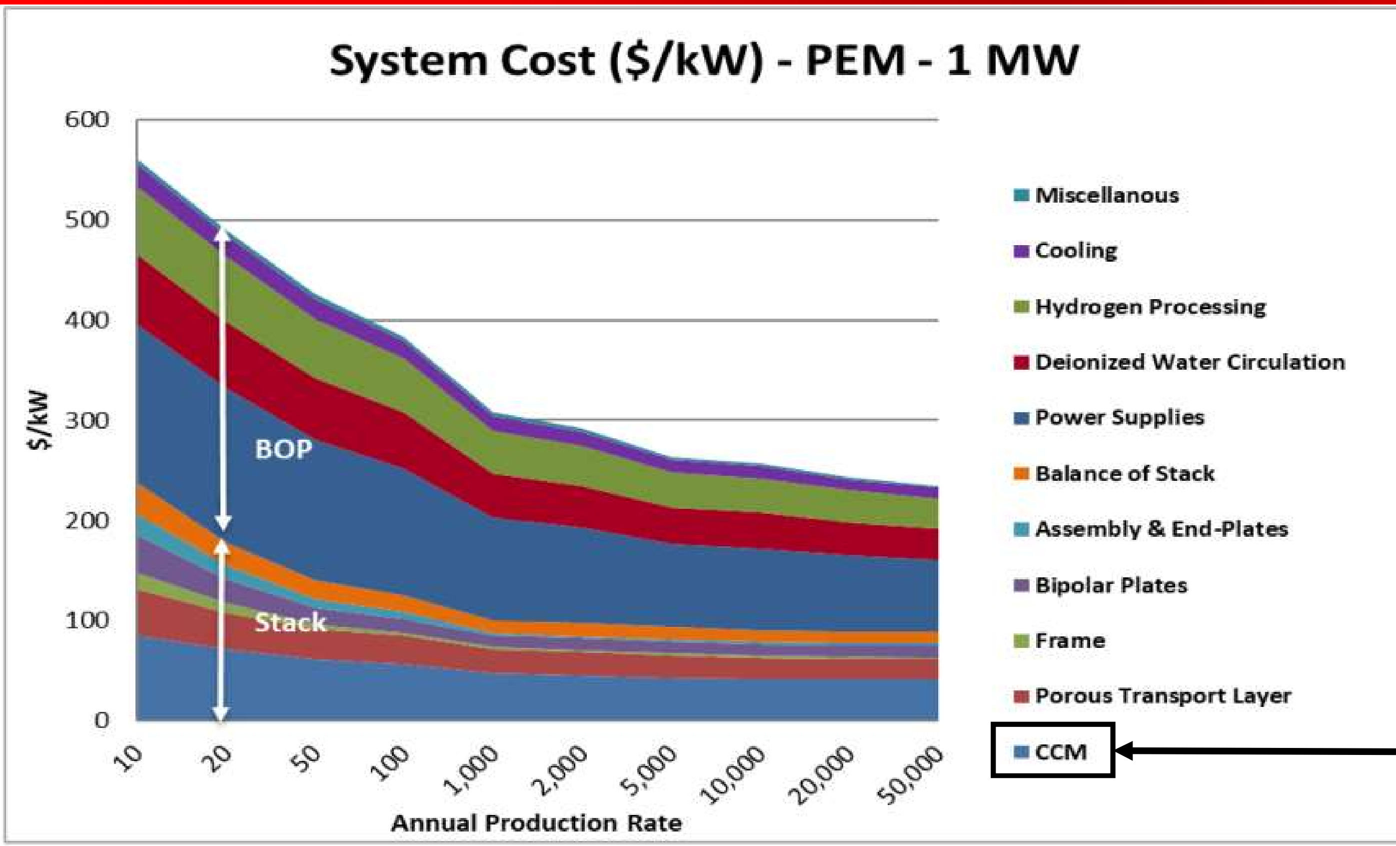
Water Electrolysis Cost: Efficiency

Problem: Energy Input for Water Splitting = 2V



Goal: : Energy Input for Water Splitting = 1.4V

Water Electrolysis Cost: Materials



Non-Precious Catalysts:

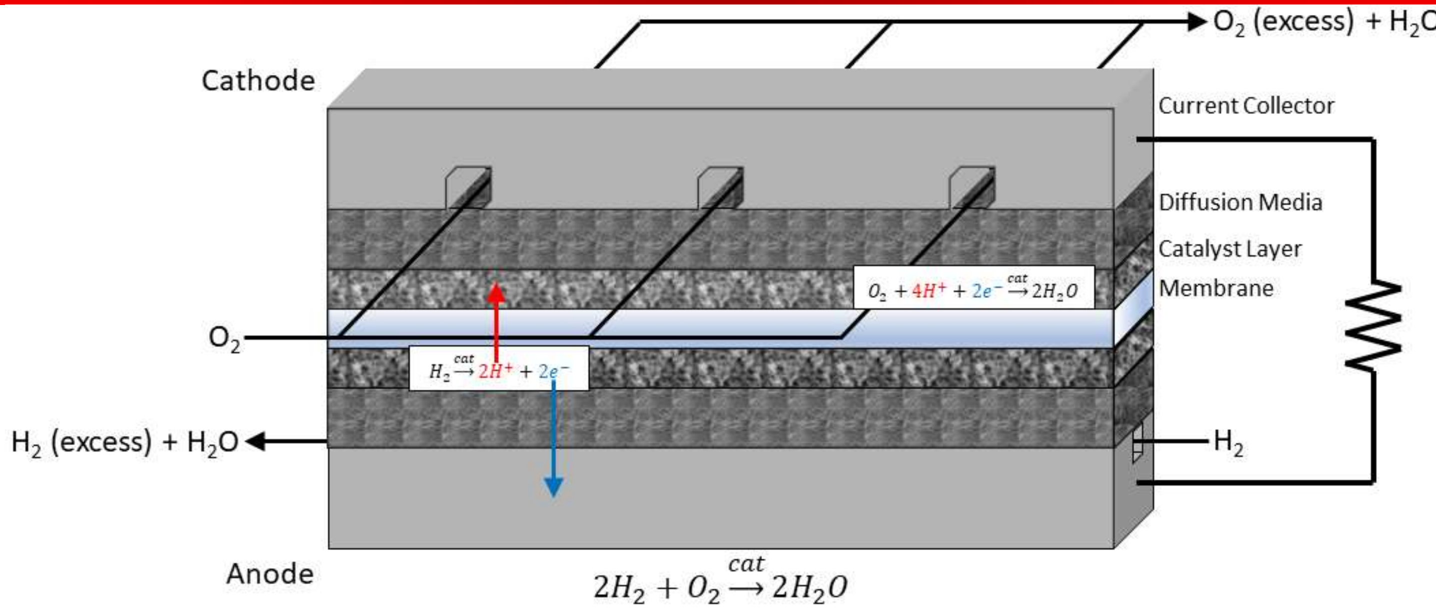
Means to decrease device cost

Pt-group metals

Greatest contributor

Mayyas, A. *et al. National Renewable Energy Laboratory* (2019)

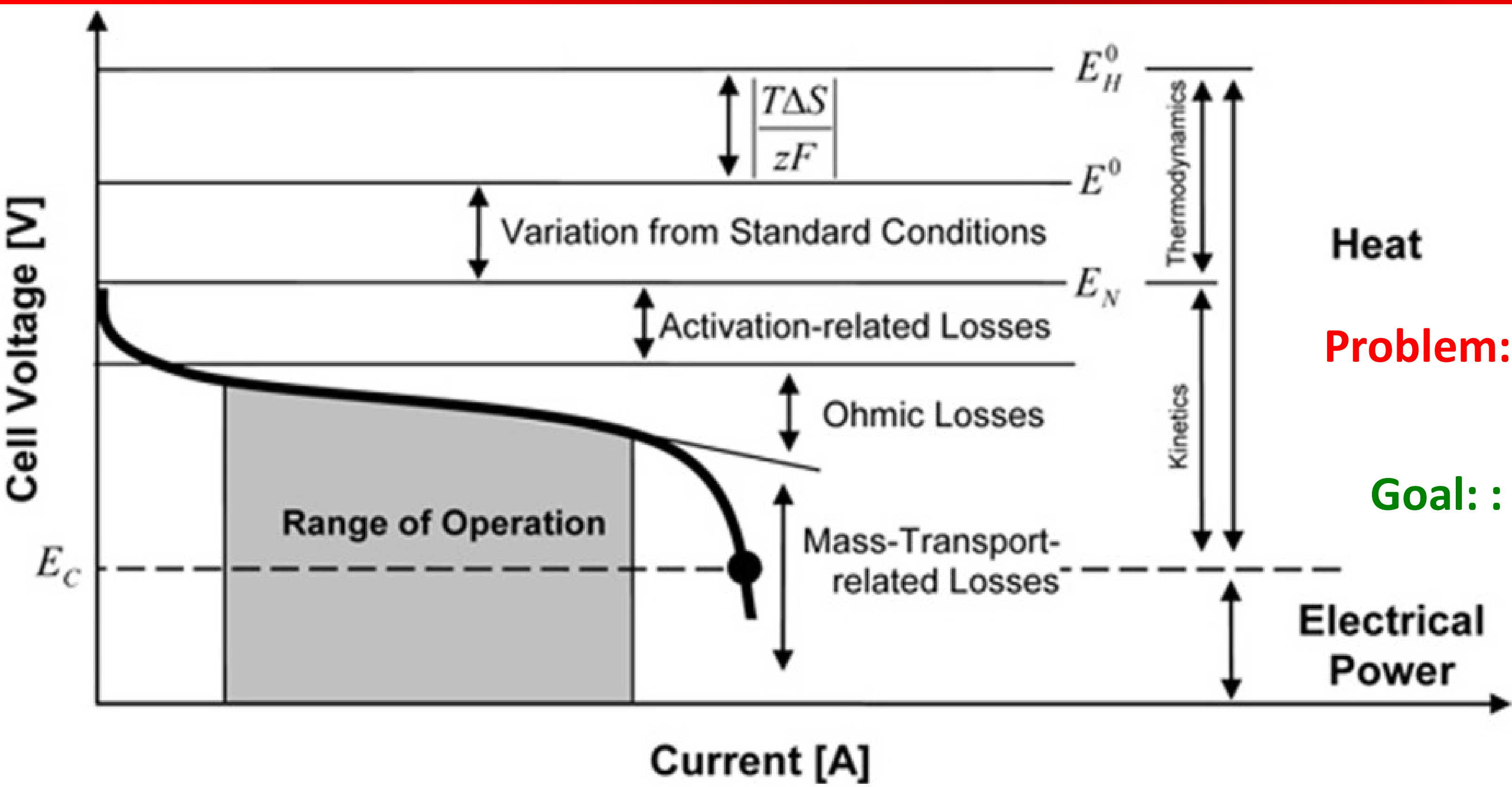
The Proton Exchange Membrane Fuel Cell



Limitations: Slow ORR | Durability | **Operability in Extreme Environments**

Water Management

PEMFC Losses



Problem: Energy Output = 0.6V

Goal: : Energy Output = 1V

Wilberforce, T. *et al. Int. J. Hydrogen Energy* 42, 25639–25662 (2017)

Progress

H_2 Fueling Stations Across North America

Fuel Cell Cars are on the Road!

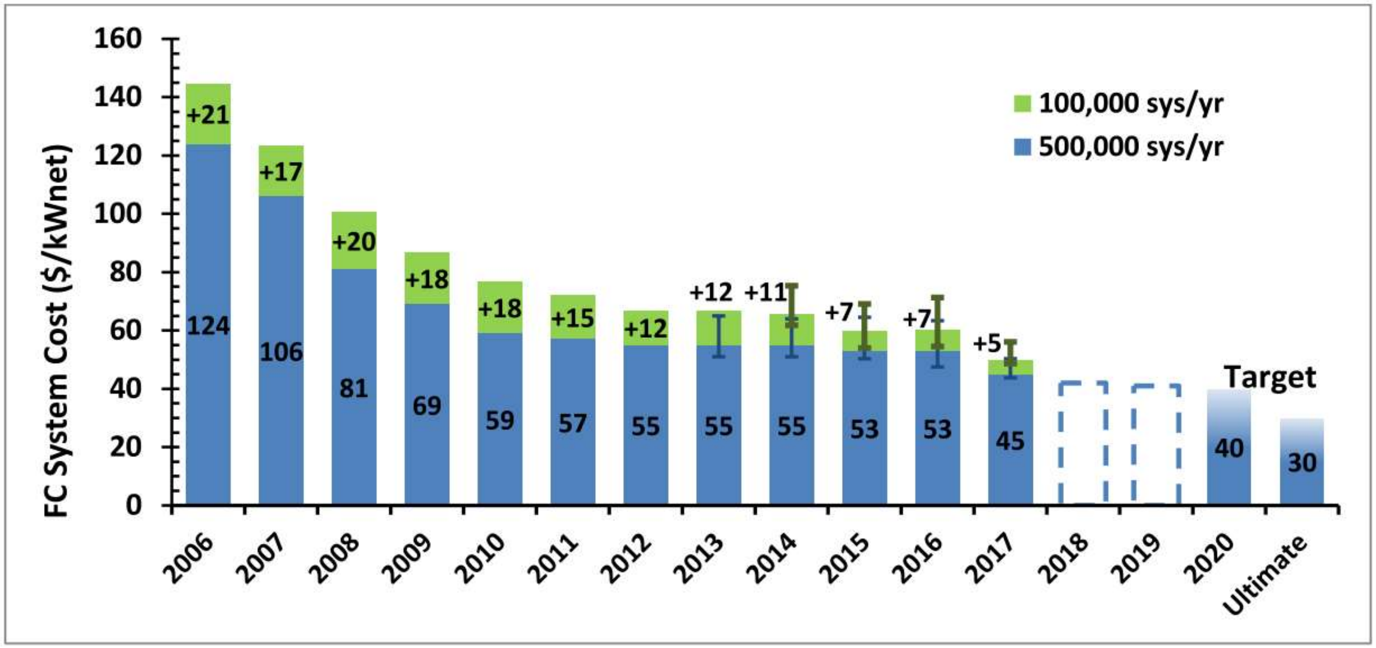
Toyota Mirai

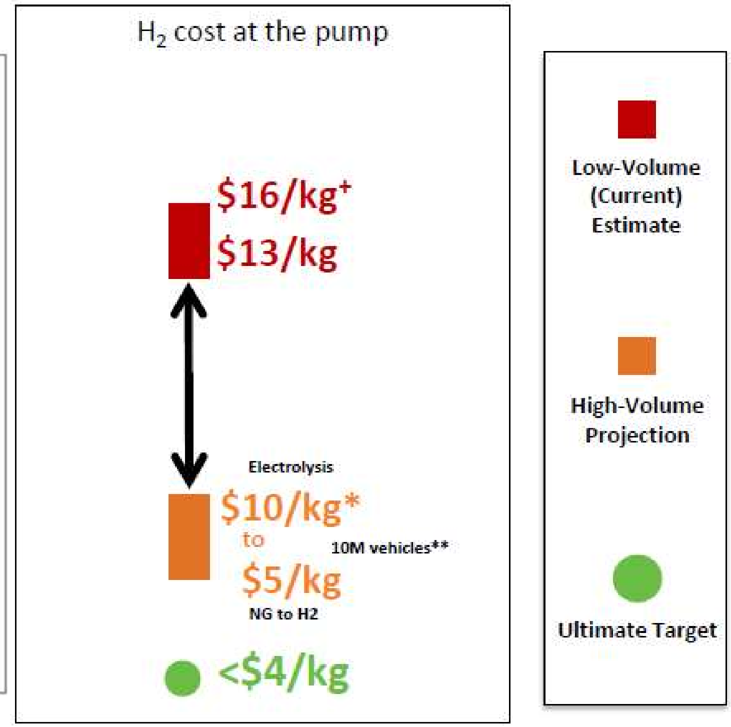
Hyundai Nexo

Honda Clarity

https://afdc.energy.gov/fuels/hydrogen_locations.html#/find/nearest?fuel=HY
https://www.caranddriver.com/news/a34788743/2021-toyota-mirai-400-mile-range/
https://h2.live/en/wasserstoffautos/hyundai-nexo
https://www.caranddriver.com/honda/clarity

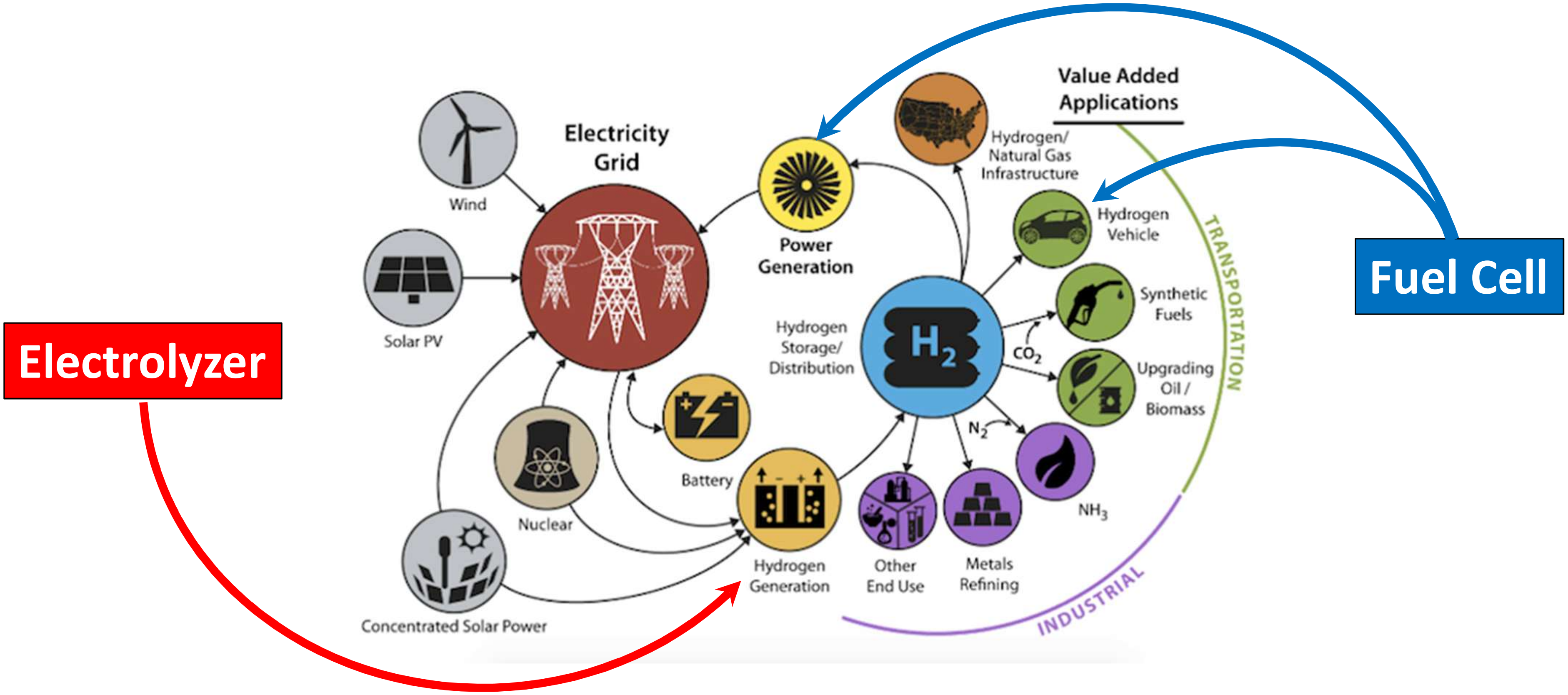
Progress Cont'd





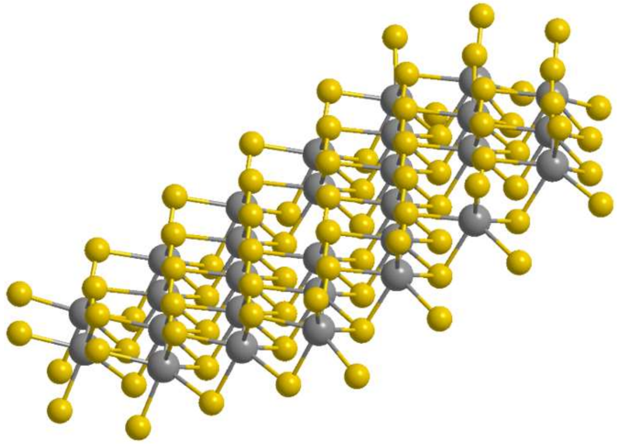
Wilson, A. *et al.* (2017)

The Hydrogen Economy



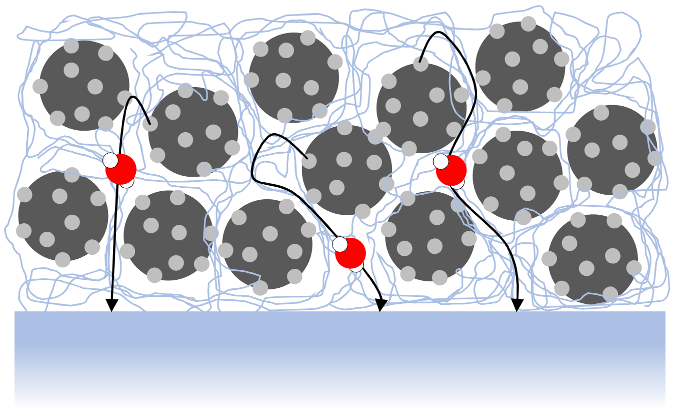
Scope of Proposed Work

<u>Aim 1</u>: Rational Design, Testing, and Characterization of Non-Precious Electrocatalysts for Hydrogen Evolution

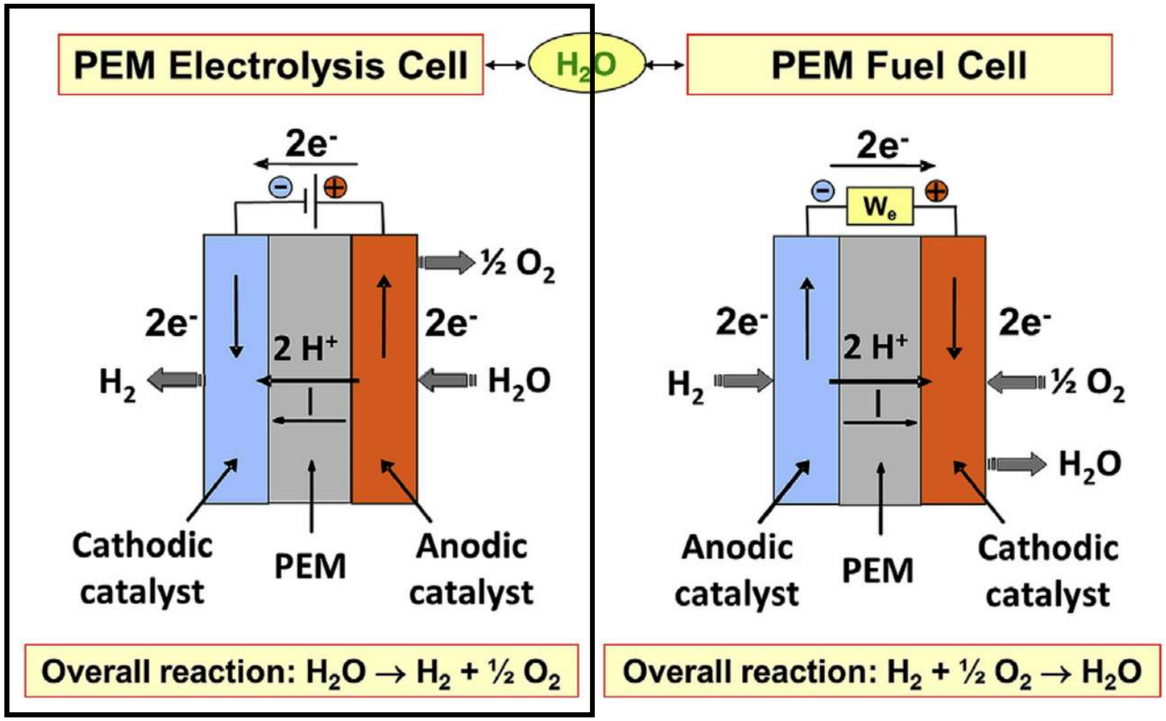


Non-Precious Molybdenum Disulfide HER Catalyst

<u>Aim 2</u>: Design of Materials and Interfaces for Enhanced Water Transport in Fuel Cells at Subzero Temperature



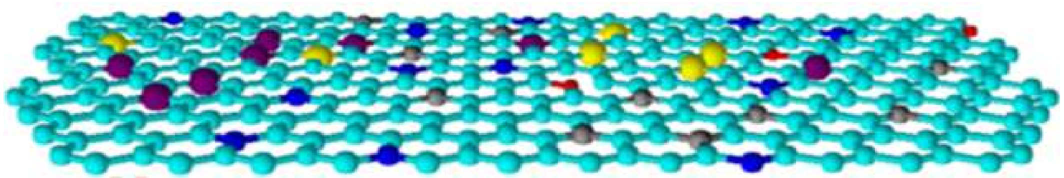
PEMFC Catalyst Layer



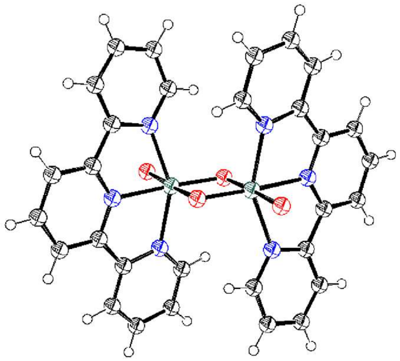
Lamy, C. *Int. J. Hydrogen Energy* 41, 15415–15425 (2016)

Non-Precious Catalysts for Hydrogen Evolution

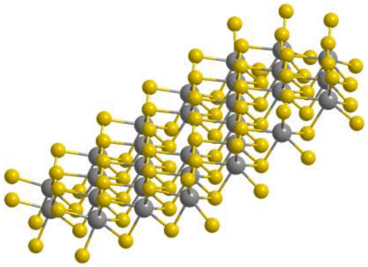
Heteroatom-Doped Nanocarbons



Molecular Catalysts



Metal Sulfides/Selenides/Carbides/Nitrides/Phosphides

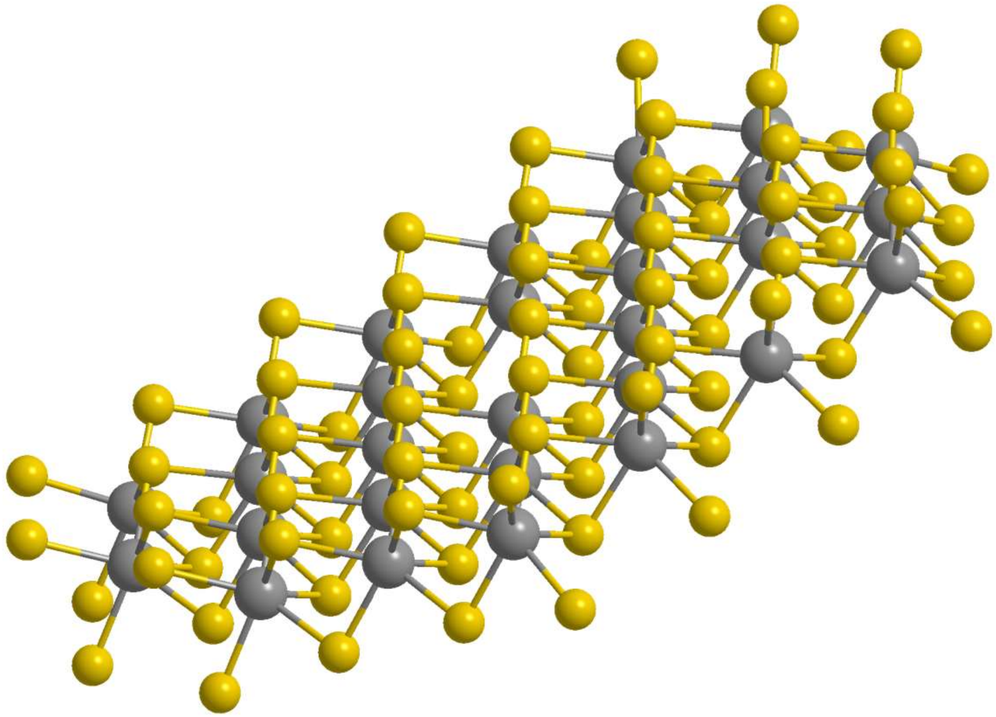


Issues

- Complicated/expensive processing
- Low efficiency

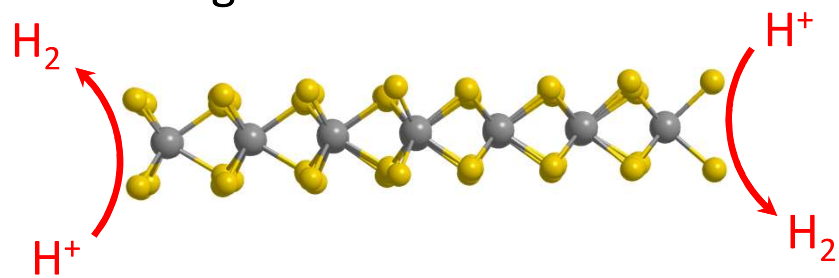
Zhang, J. *et al. ACS Catal.* 5, 7244–7253 (2015)
Blakemore, J. D. *et al. Chemical Reviews* 115, 12974–13005 (2015)

Molybdenum Disulfide (MoS_2)



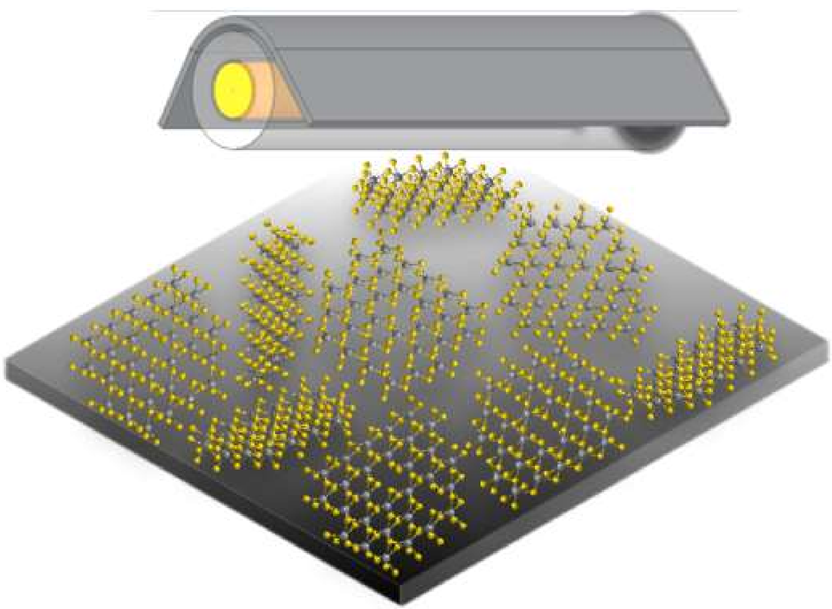
- Promising non-precious hydrogen evolution catalyst
- Transition metal dichalcogenide (metal sulfide)
- Good activity & stability

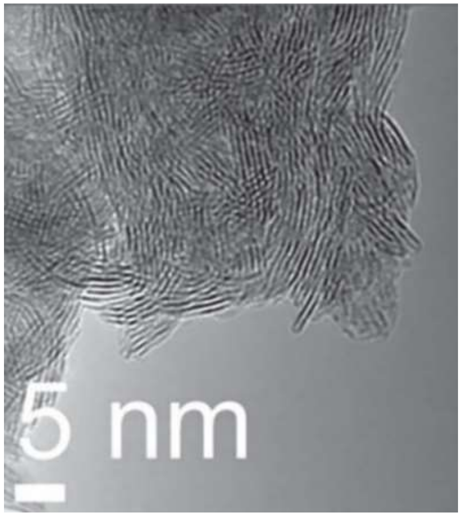
Edge Sites Active for HER

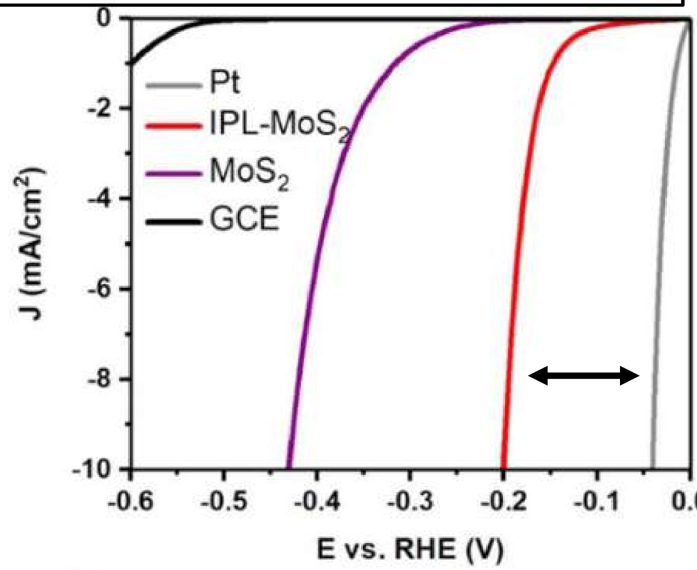


MoS_2 via Intense Pulsed Light Treatment

Gupta, A. *et al. Nanotechnology* 30, (2019)





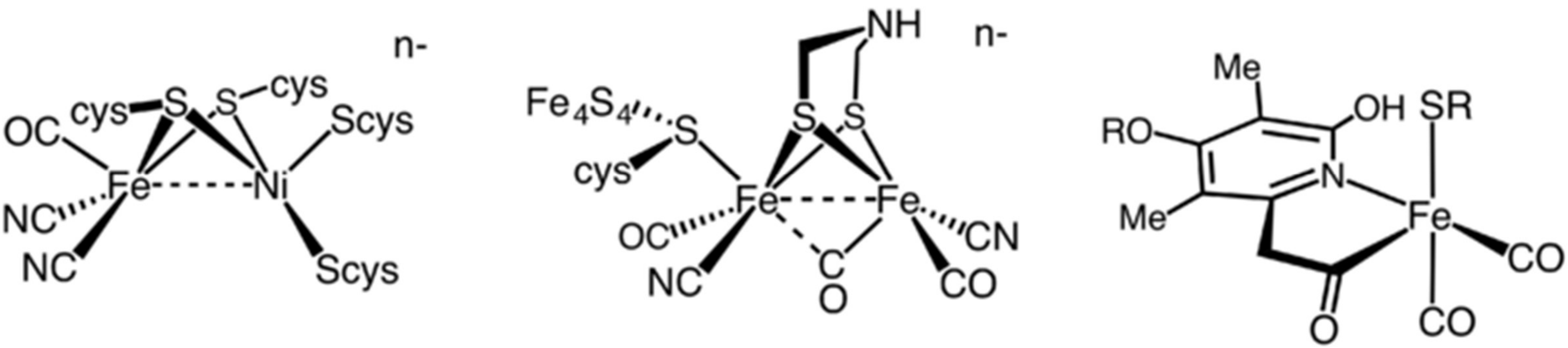


$$Q = A \iint I_0(\lambda) e^{-\alpha y} d\lambda dy$$

Decent Activity, Facile Synthesis, but <u>not as Efficient as Pt!</u>

The Hydrogenase Enzyme

Three Types of Hydrogenase Active Sites Found in Nature

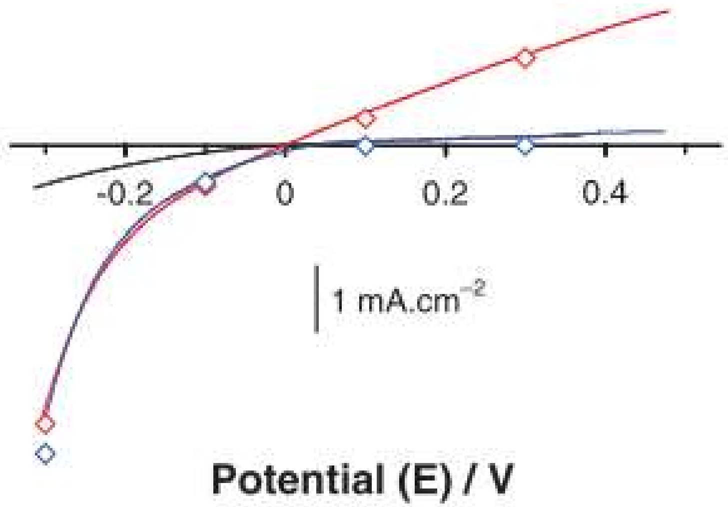


Pros:
- ≥2x More Active than Pt
- Non-Precious Metal Center

Cons
- O_2-Sensitive
- Expensive to Produce

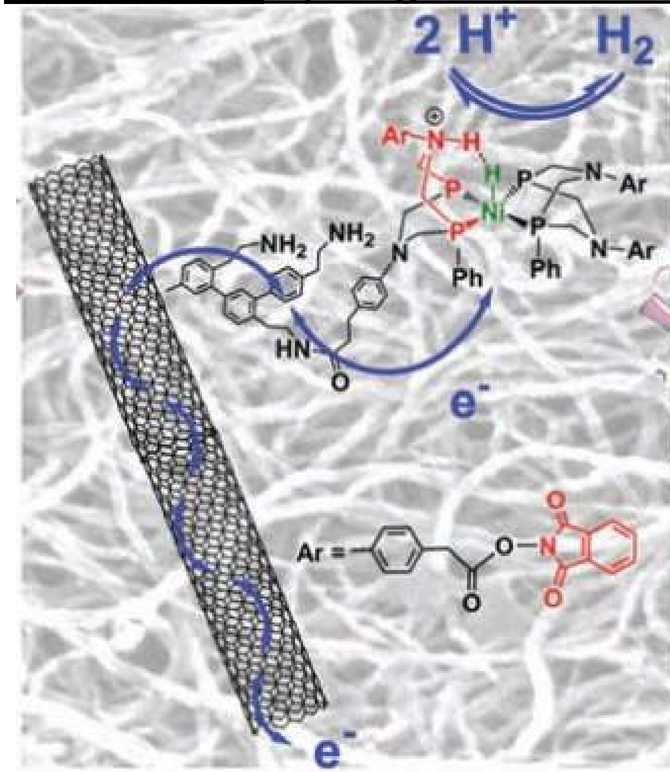
File:ActiveSitesCorrected.png – Wikimedia Commons
Artero, V. *et al. Coordination Chemistry Reviews* 249, 1518–1535 (2005)

Biomimetic Hydrogenase-Inspired Catalysts



- Reversible HER/HOR
- Less Efficient than Pt
- Expensive Fabrication

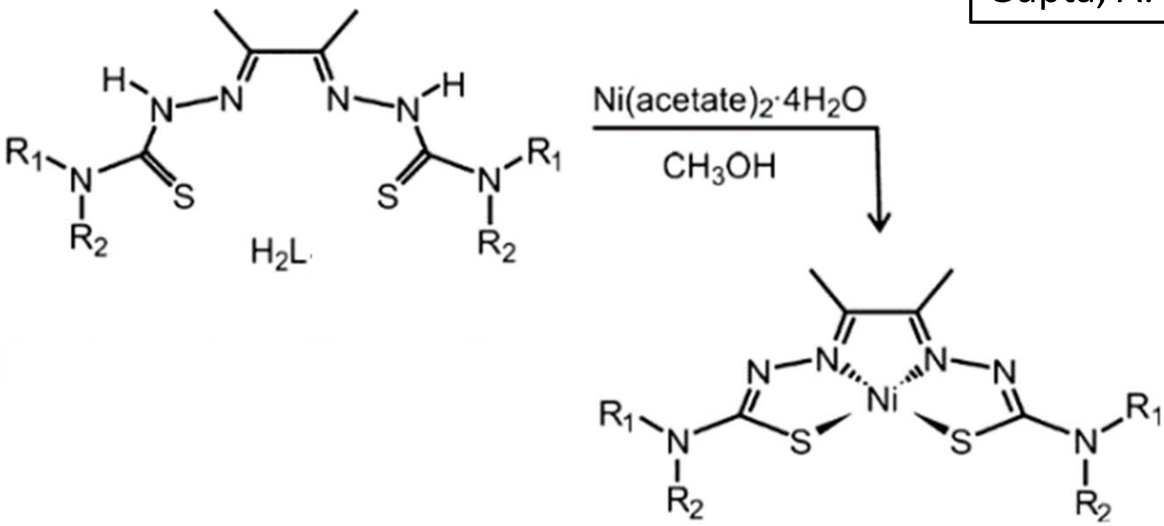
Fontecave's Hydrogenase Mimic

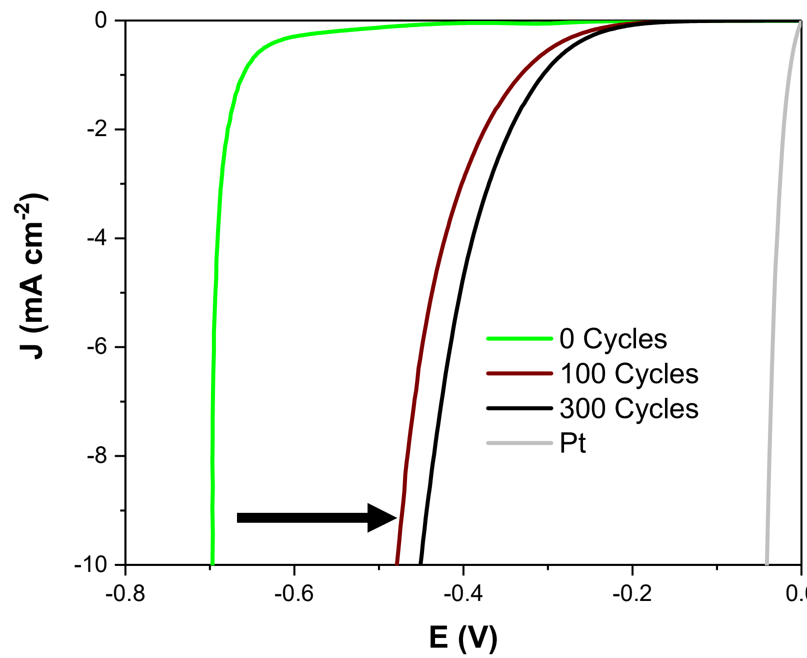


Goff, A. Le *et al. Science (80-.).* 326, 1384–1387 (2009)

Thiosemicarbazones

Gupta, A. J. *et al. Inorg. Chem.* 58, 12025–12039 (2019)





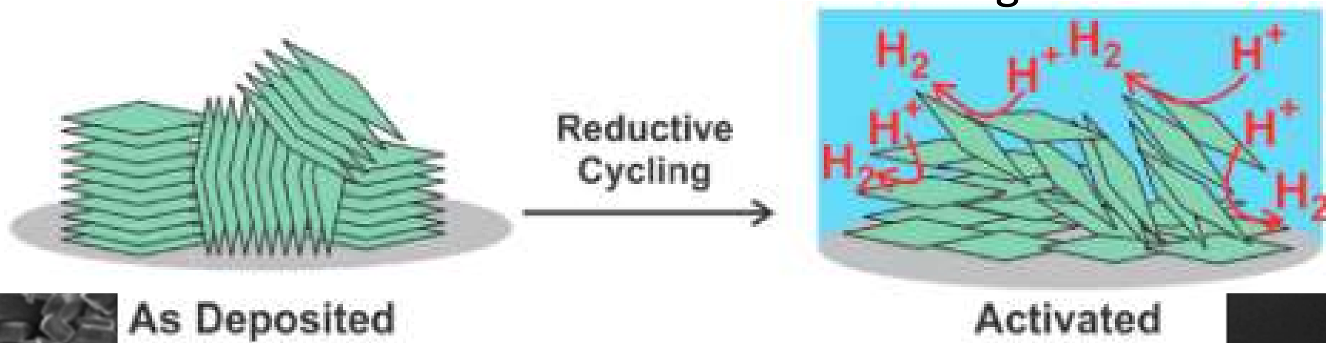
Poor Initial Activity

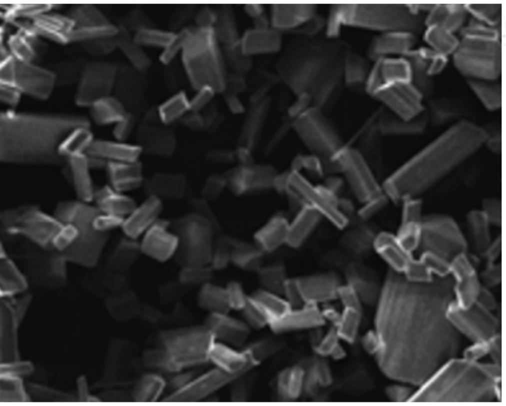
Improved Performance After Reductive Cycling

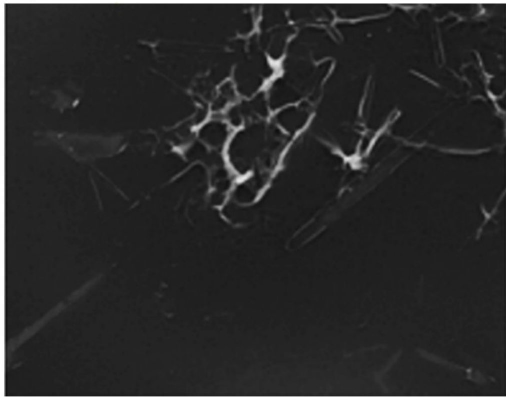
Thiosemicarbazones Cont'd

Stacking Interactions Conceal Active Sites

Break-In Disrupts Stacking Interactions





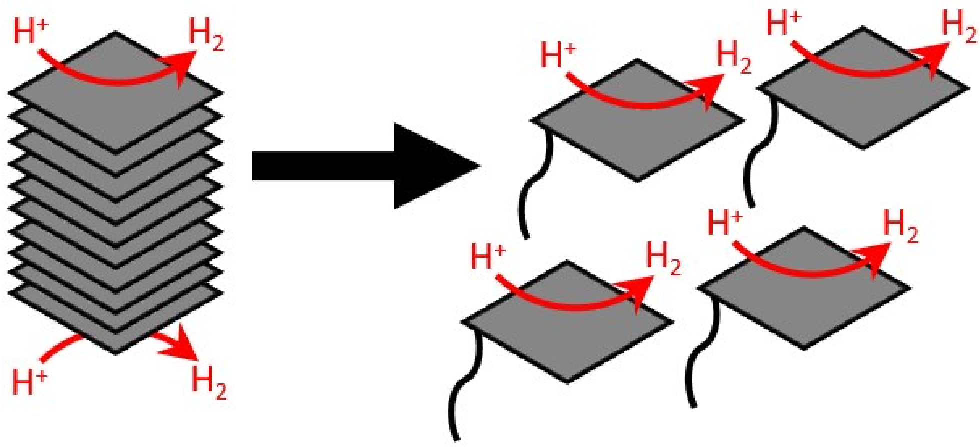


Big Improvement, but Still not a Great Catalyst…
- Remaining Stacking Interactions
- Poor Electron Transfer

Gupta, A. J. *et al. Inorg. Chem.* 58, 12025–12039 (2019)

Improved TSCs for HER Part 1

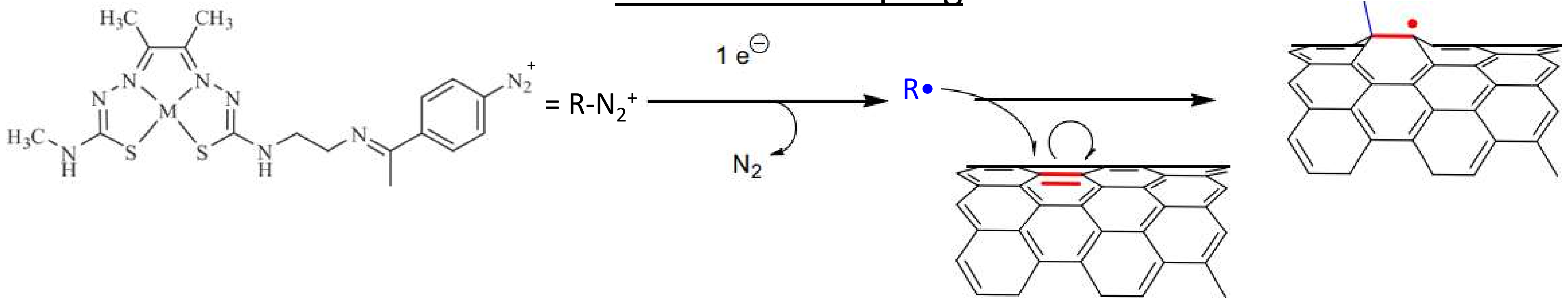
<u>Aim 1a: Facilitate Charge Transfer by Linking Molecule to Electrode Surface</u>



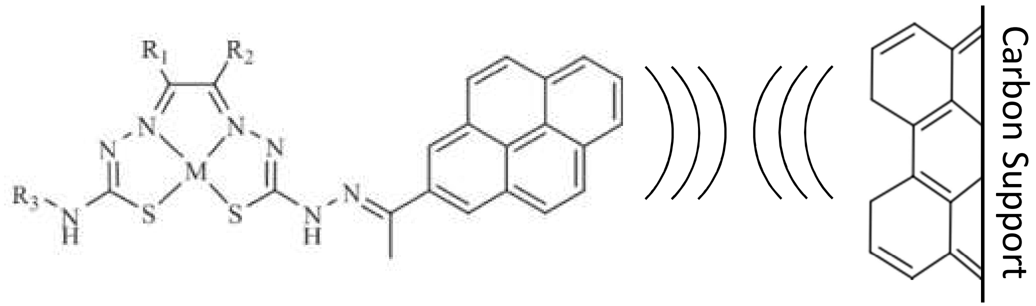
- Monolayer with Each Metal Center Exposed to Reaction Medium
- Improved Charge Transfer
- Improved Film Stability

Improved TSCs for HER Part 1 Cont'd

Diazonium Coupling

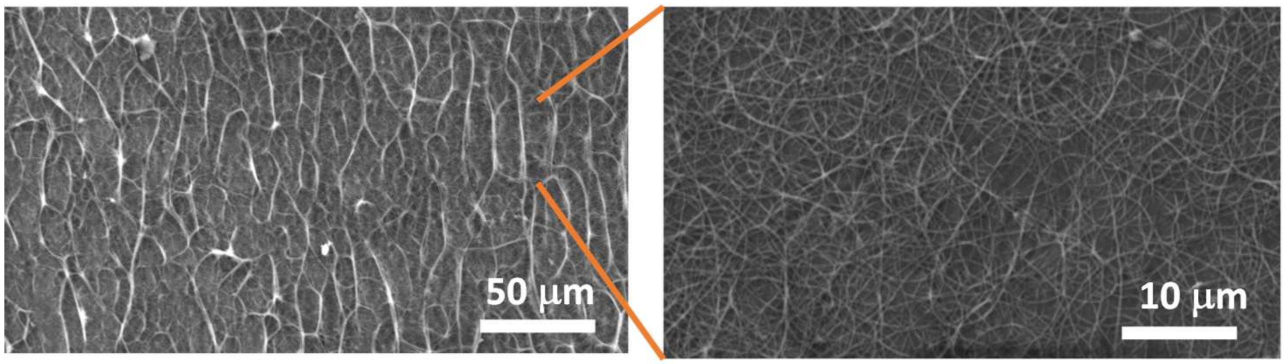


Pyrene π- π Anchoring



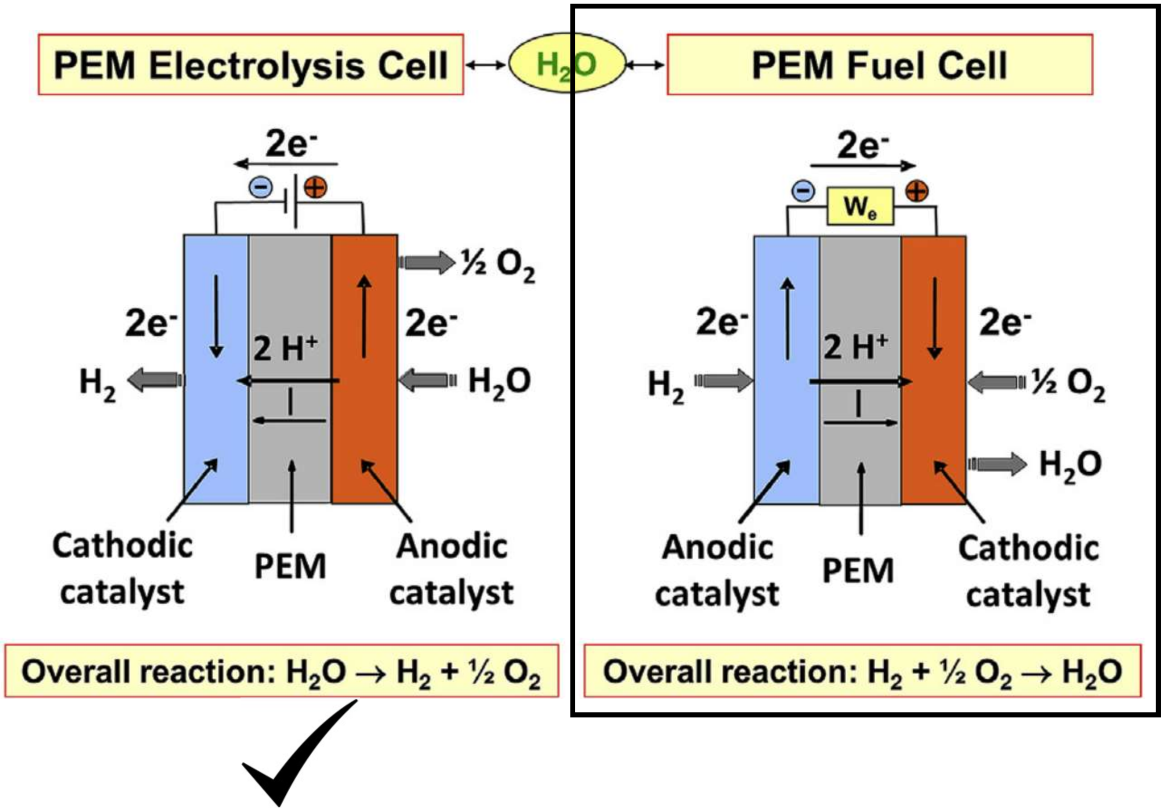
Improved TSCs for HER Part 2

Aim 1b: Incorporate High-Surface-Area Carbon Supports



Graphitic Carbon Nanofibers Prepared via Pyrolysis of Polymer Mixture

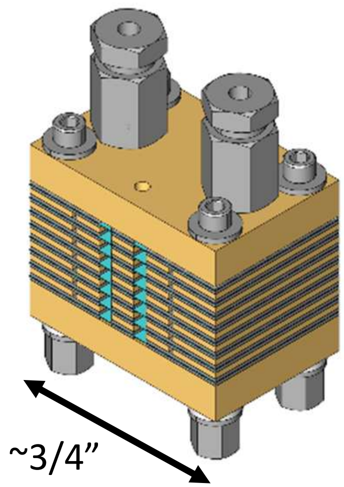
- Enhanced Percolation Volume
- Increased Specific Surface Area
- Higher Catalyst Concentration

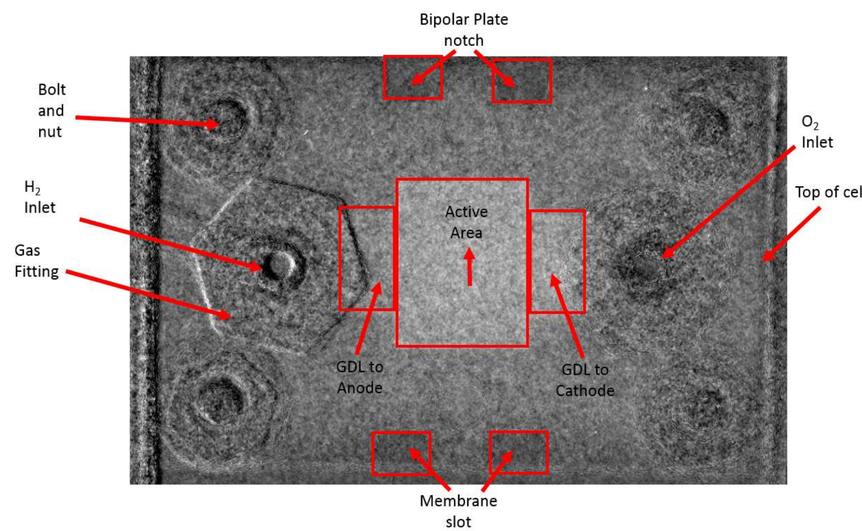


Lamy, C. *Int. J. Hydrogen Energy* 41, 15415–15425 (2016)

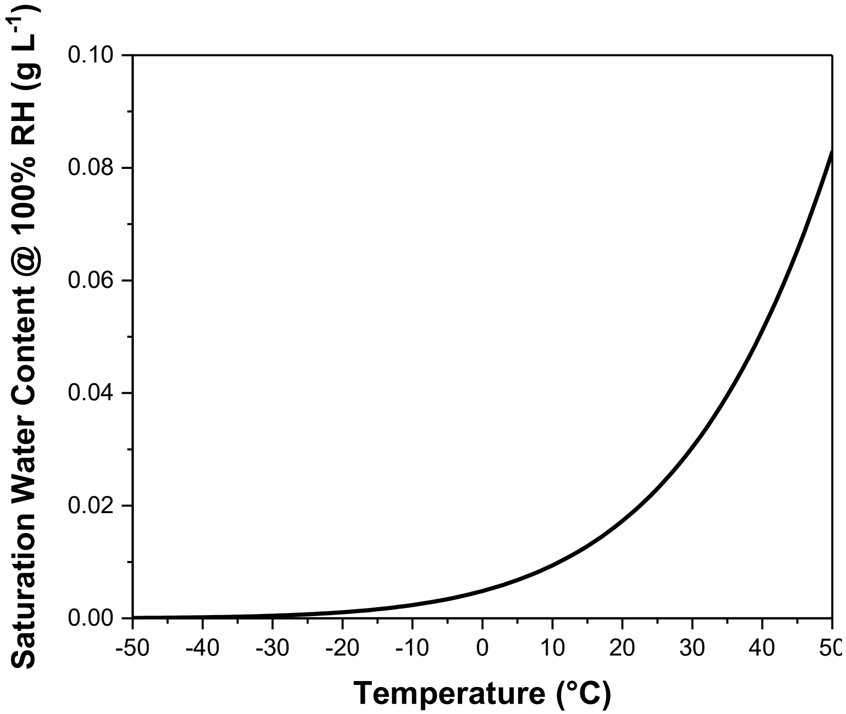
Motivation

2b stack:
Passive water
management



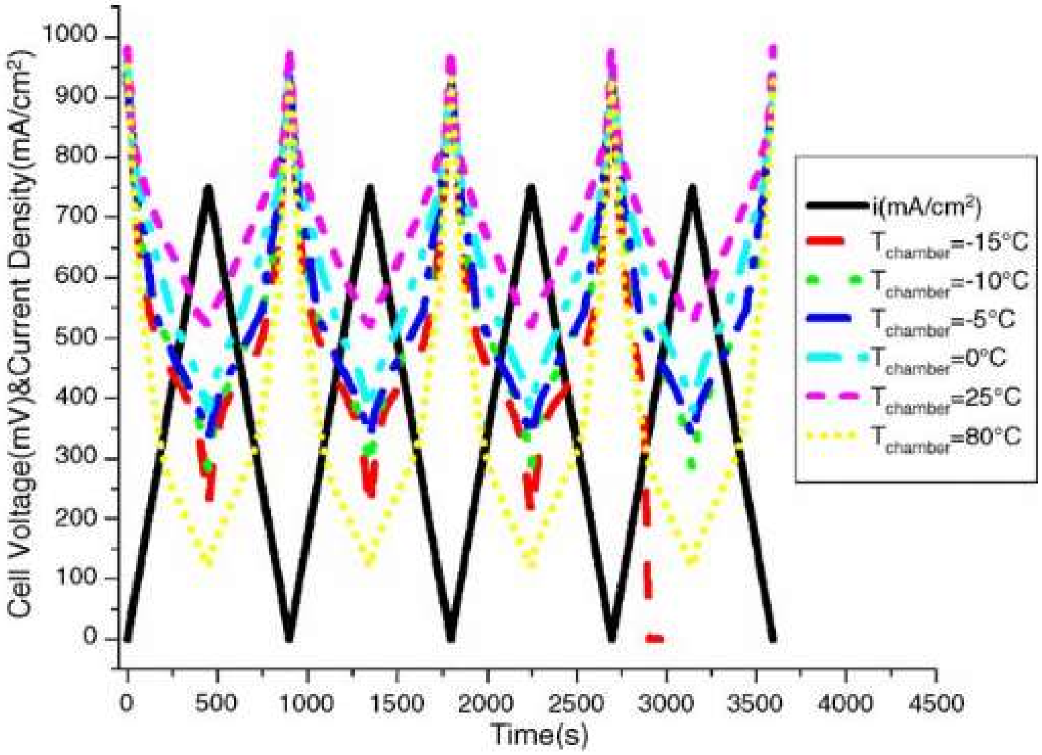


Fuel Cells for Subzero Temperature Operation



Saturation Pressure too Low for Removal of Product Water via Gas Stream

Fuel Cells for Subzero Temperature Operation



<u>Cell Failure from Active Site Blockage</u>

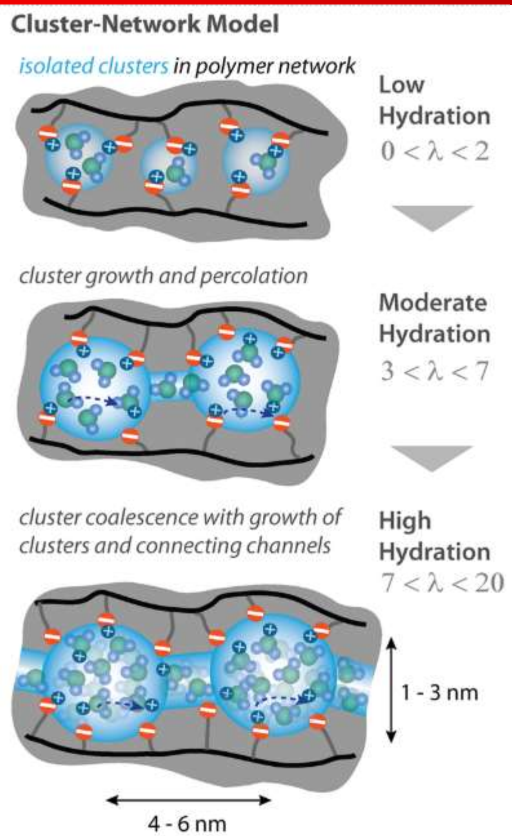
Irreversible Damage:

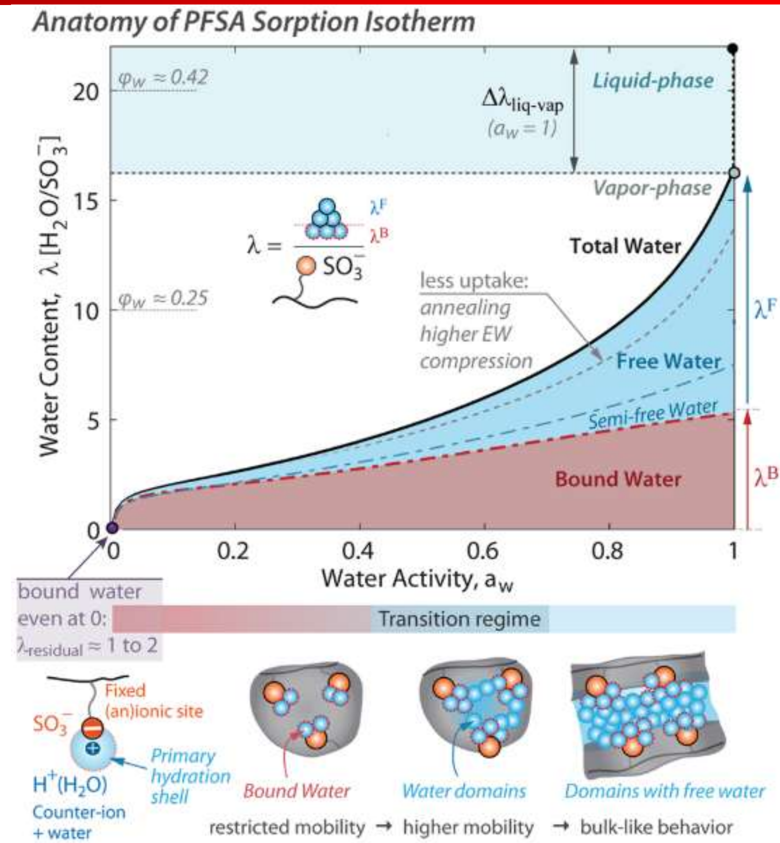
- Ice Expansion at Interfaces
- Catalyst Pore or Diffusion Media Fiber Coarsening
- Cracking/Pinholes in Membrane

Los Alamos NATIONAL LABORATORY EST. 1943

Yan, Q. *et al. J. Power Sources* 160, 1242–1250 (2006)

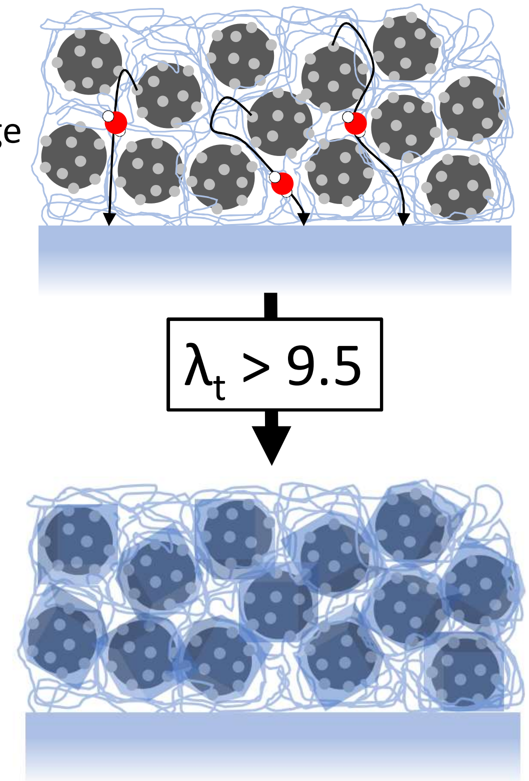
Understanding of Nafion

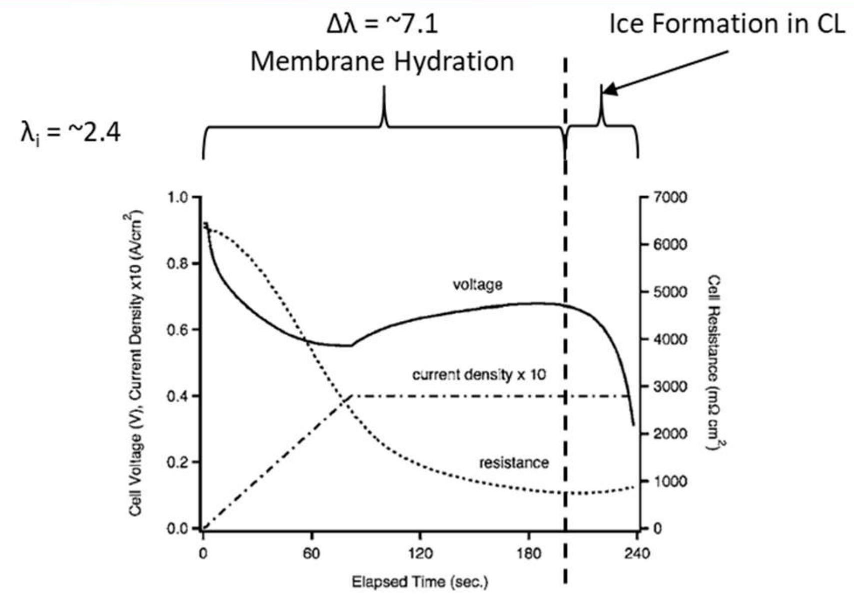




Kusoglu, A. *et al. Chem. Rev.* 117, 987–1104 (2017)

Operating Mechanism at Subzero Temperature

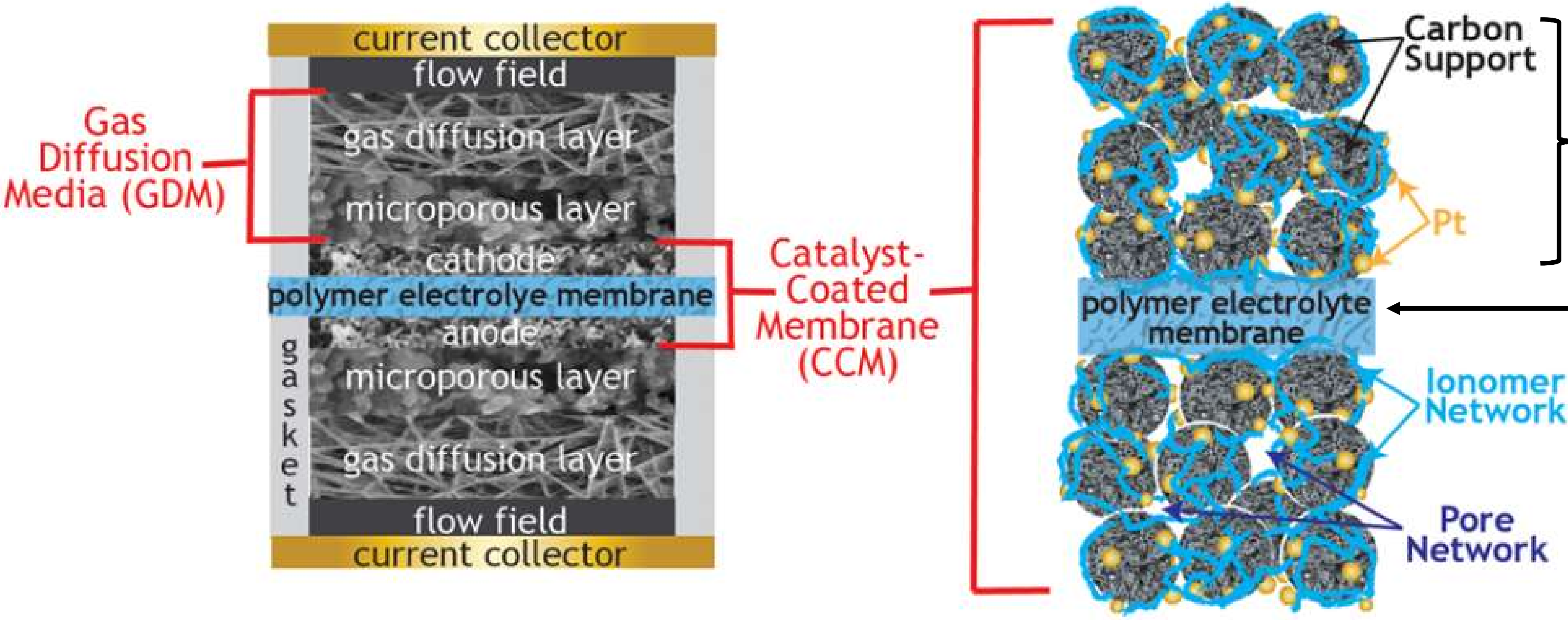




$\lambda_{non\text{-}freezing} = 4.8$

Tajiri, K. *et al. J. Electrochem. Soc.* 154, B147–B152 (2007)

Mitigating Strategies



Higher Ionomer-to-Carbon Ratio and/or Thicker Catalyst Layer

Thicker Membrane

Low λ_i

Sassin, M. B. *et al. Anal. Chem.* 89, 511–518 (2017)

Model for Cell Water/Ice Capacity

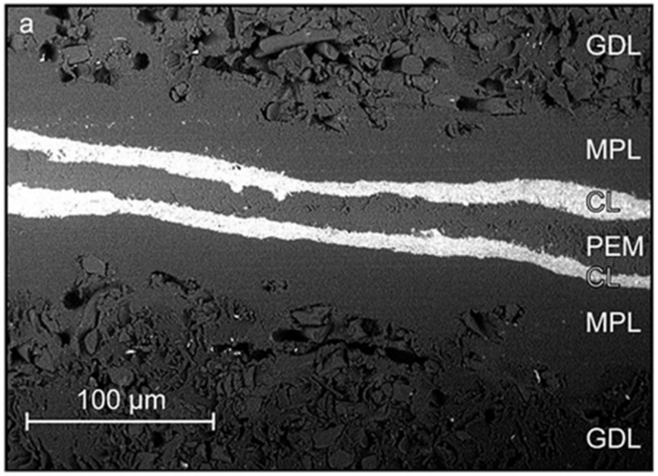
Interpolate diffusion media pore volume from data by Atkinson *et al*

Catalyst layer porosity & thickness:

- $\varepsilon = -0.017w_{Nafion} + 0.758 = \frac{t_{CL} - \left(\frac{l_C}{\rho_C} + \frac{l_{Pt}}{\rho_{Pt}} + \frac{l_{Nafion}}{\rho_{Nafion}}\right)}{t_{CL}}$

Mass of water in ionomer:

- $m_{H_2O} = (\lambda_{sat} - \lambda_i)\frac{M_{H_2O}m_{Nafion}}{EW}$



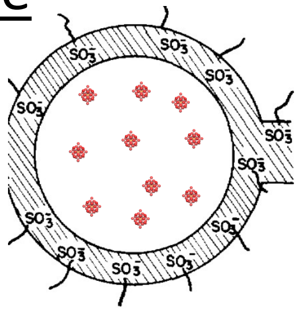
PEMFC Cross Section

Goal: Utilize as much Water Storage Capacity as Possible!

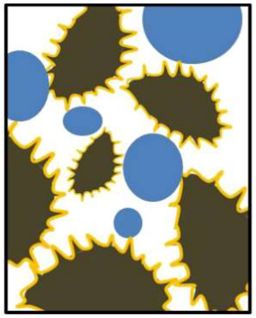
Atkinson, R. W. *et al. ACS Appl. Energy Mater.* 1, 191–201 (2018)
Taghiabadi, M. M. *et al. Fuel Cells* 18, 731–741 (2018)
Klingele, M. *et al. J. Mater. Chem. A* 3, 11239–11245 (2015)

Approach

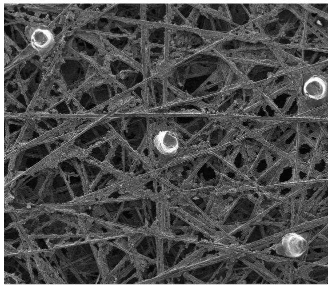
<u>Tailor Materials and Interfaces for Enhanced Freeze Tolerance</u>



Aim 2a: Dope Membrane with Hydrophilic Compounds to Increase Water Sorption and Confer Antifreeze Properties

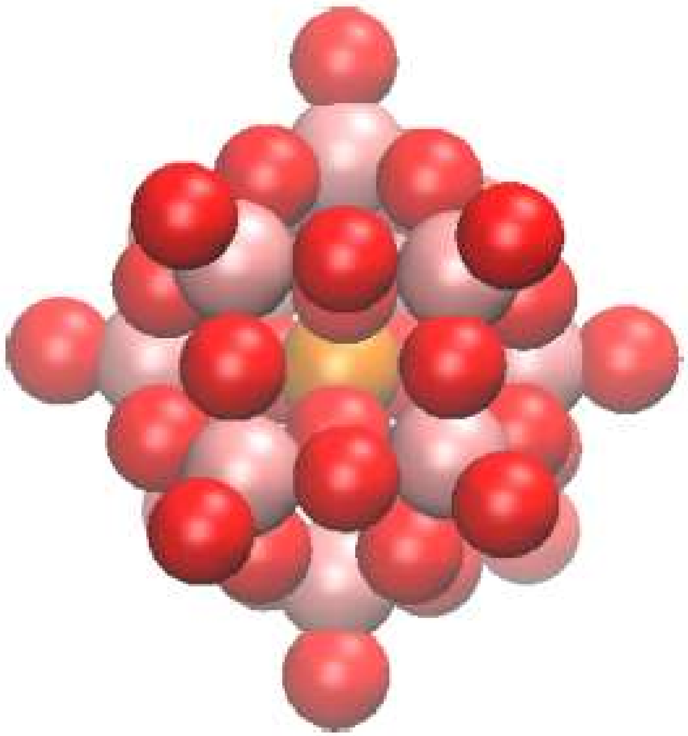


Aim 2b: Passively Expel Supercooled Water from Active Sites Using a Superhydrophobic Catalyst Layer



Aim 2c: Create an Additional Water Storage Reservoir by Impregnating Diffusion Media with Polyelectrolyte Channels

Aim 2a: Doped Membrane



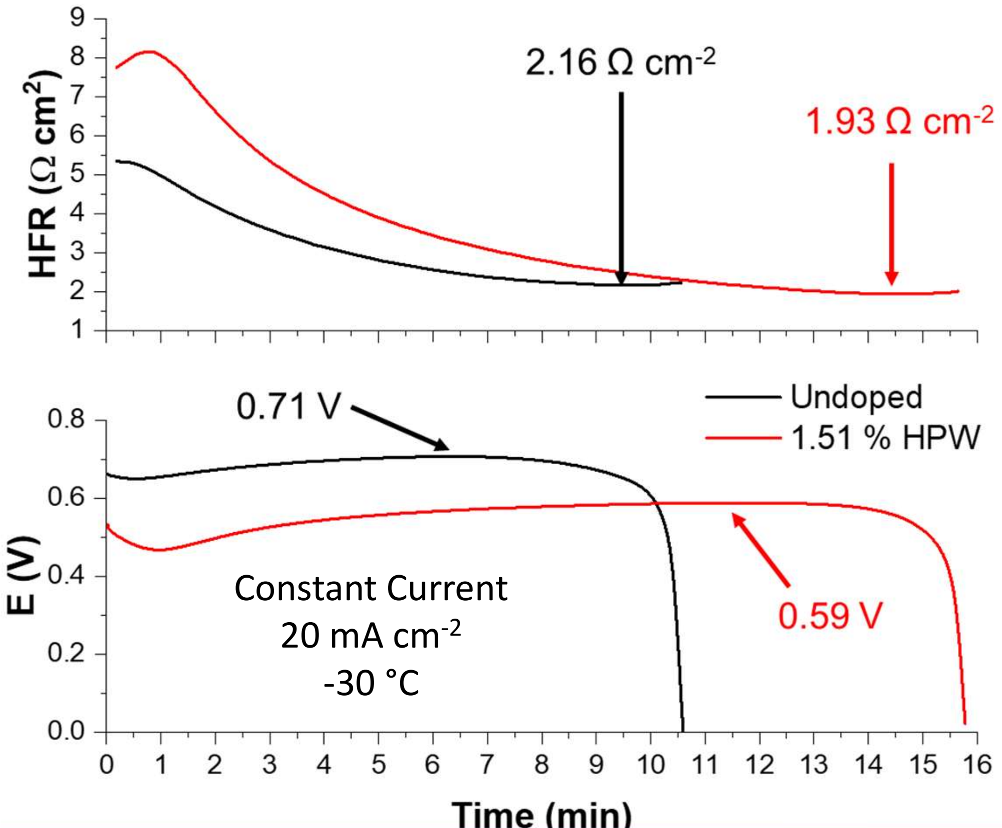
“Keggin” Heteropoly acid Structure

Hypothesis:

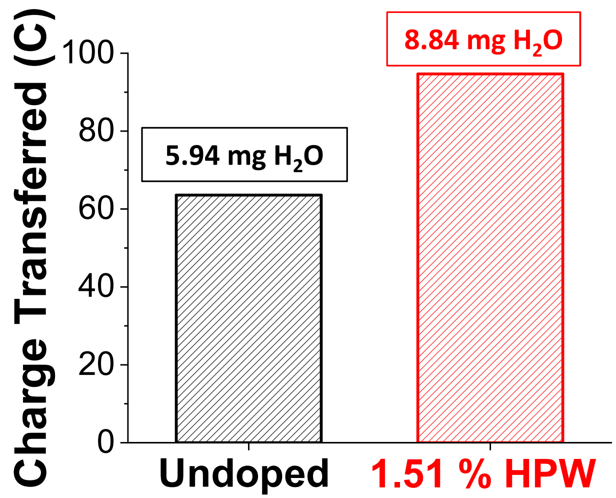
1. Mitigate ice crystal formation in membrane via internal antifreeze action
2. Increase driving force for water sequestration in membrane
3. Increase water absorbed by membrane before it accumulates elsewhere (λ_t)

Liu, Y. *et al. J. Phys. Chem. C* 118, 854–863 (2014)

Aim 2a: Preliminary Results



HPW Conc. (wt%)	λ_{sat} (H_2O/SO_3^-)	$\lambda_{non\text{-}freezing}$ (H_2O/SO_3^-)
0.0	20.8	5.1
0.5	16.5	9.7
1.0	16.4	8.9
1.5	14.6	9.3



50 % Greater Freeze Tolerance

Los Alamos NATIONAL LABORATORY EST. 1943

Future Work: Aim 2a

Investigate Origin of Improved Freeze Tolerance

Explore Catalyst Poisoning Effect over Temperature, Current, and Concentration

	HPW Concentration (wt%)			
Current Density (mA cm^{-2})	0	0.5	1	1.5
20	T = -10 °C			
1	OR			
0.05	T = -30 °C			

Aim 2b: Superhydrophobic Catalyst Layer

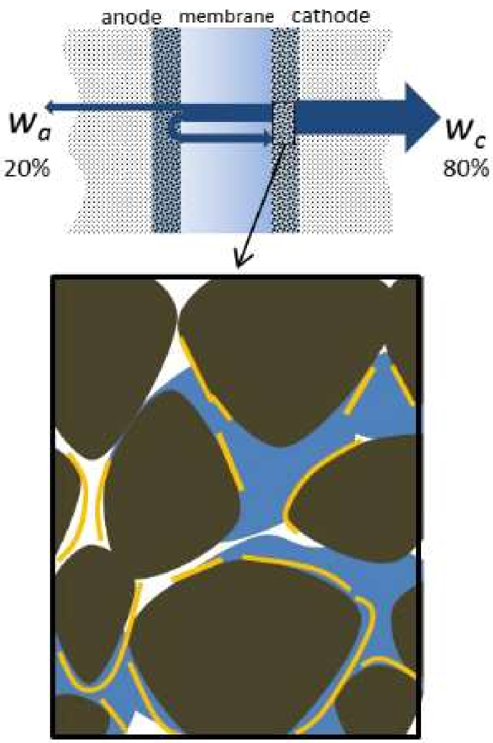
Goal: Clear Active Sites via Passive Expulsion of Water

- Superhydrophobic: θ > 150 °
- Activation Energy for Wetting:
  - $\Delta G_C = \frac{4\pi}{3}\left[\frac{2\sigma}{\rho_w R_w T ln\left(\frac{p}{p_{sl}}\right)}\right]^2 \sigma f(\theta)$
    - $f(\theta) = \frac{1}{4}(2 + cos\theta)(1 - cos\theta)^2$
- Time to Freeze 55x Longer on Superhydrophobic Surface
- Additives (PTFE, DSO, FEP, etc.)
  - Adversely Impact Efficiency & θ < 150 °

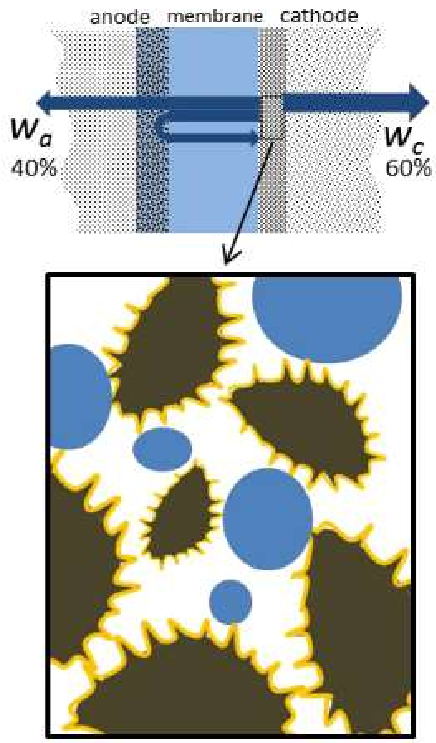
Liu, Z. *et al. Int. J. Heat Mass Transf.* 51, 5975–5982 (2008)

Aim 2b: Electrosprayed Catalyst Layers

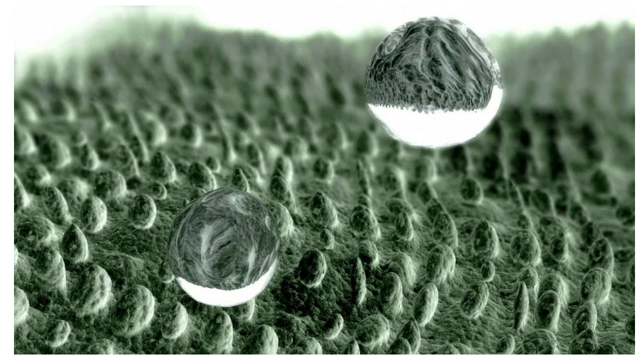
Normal



Electrosprayed



Lotus Effect

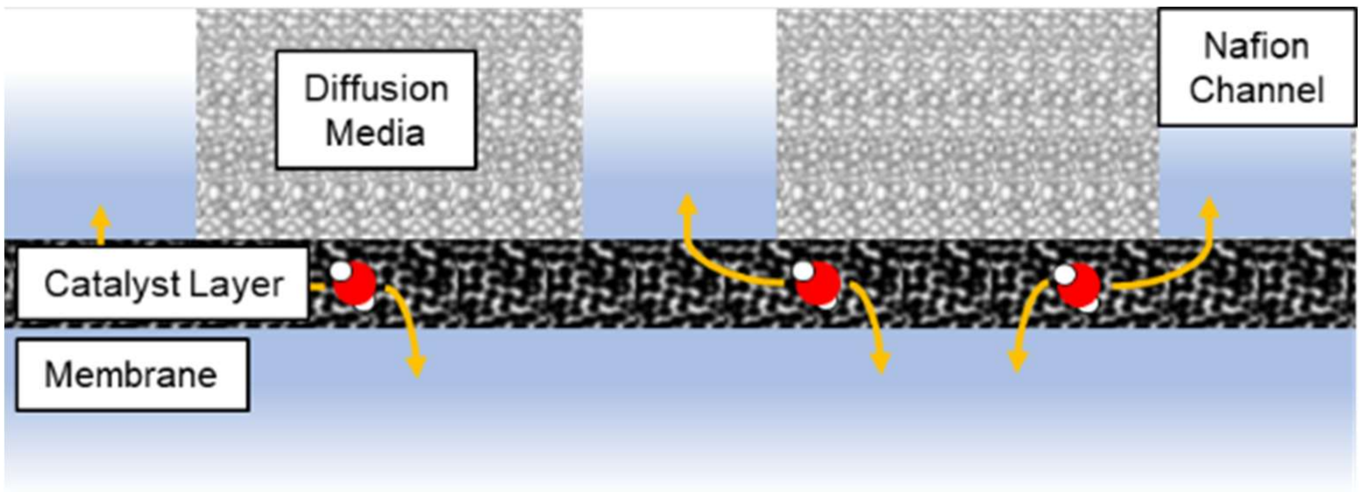


- $\theta > 150°$
- Reduced Pore Wetting

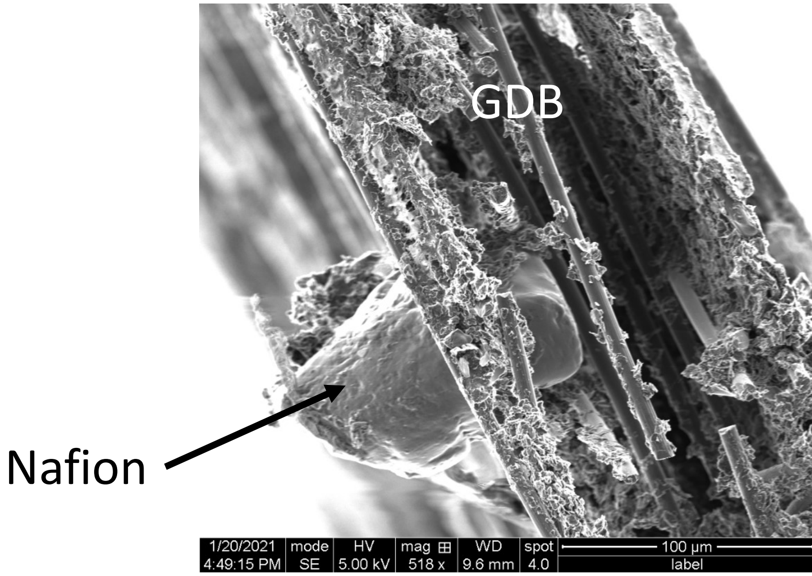
Folgado, M. A. *et al. Fuel Cells* 18, 602–612 (2018)
https://i.ytimg.com/vi/HF4blivJQ6o/maxresdefault.jpg

Aim 2c: Structured Amphiphilic Diffusion Media

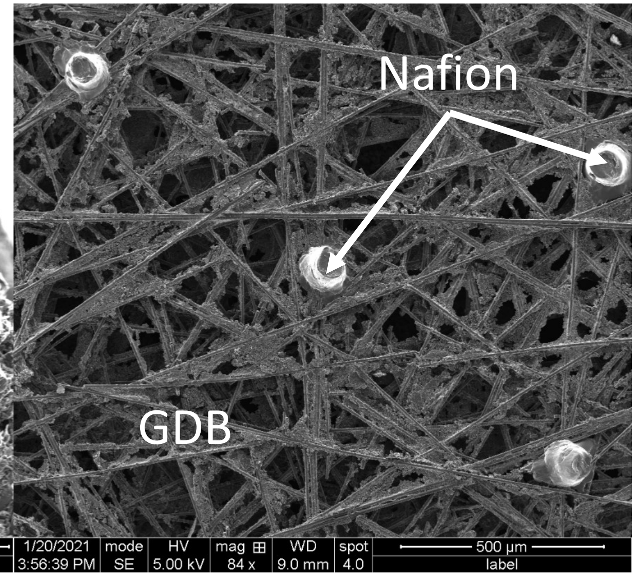
Goal: Create Additional Water Sequestration Volume while Sacrificing Minimal Gas Diffusion Space



Aim 2c: Structured Amphiphilic Diffusion Media



Cross Section

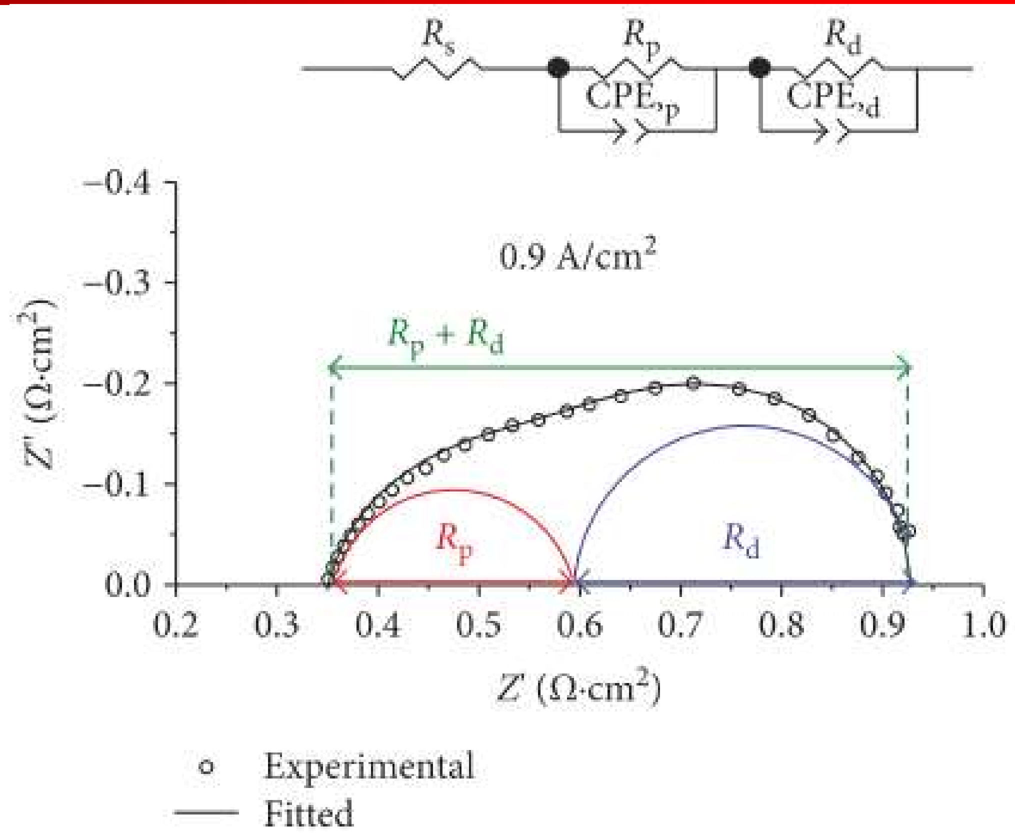


Top Down

Approach: Hot Press Nafion through a Template into Gas Diffusion Backing

Subzero Temperature Operating Mechanism

- At Constant Current:
  - R_p present initially
  - R_d appears later
- Questions:
  - Diffusion limitations or something else?
  - Diffusion limitations at anode vs. cathode?
  - Diffusion resistances dominate in catalyst layer or diffusion media?
  - Knudsen diffusion resistance becomes significant with ice buildup?
  - Oxygen diffusion resistance through ionomer behavior at low temperature?

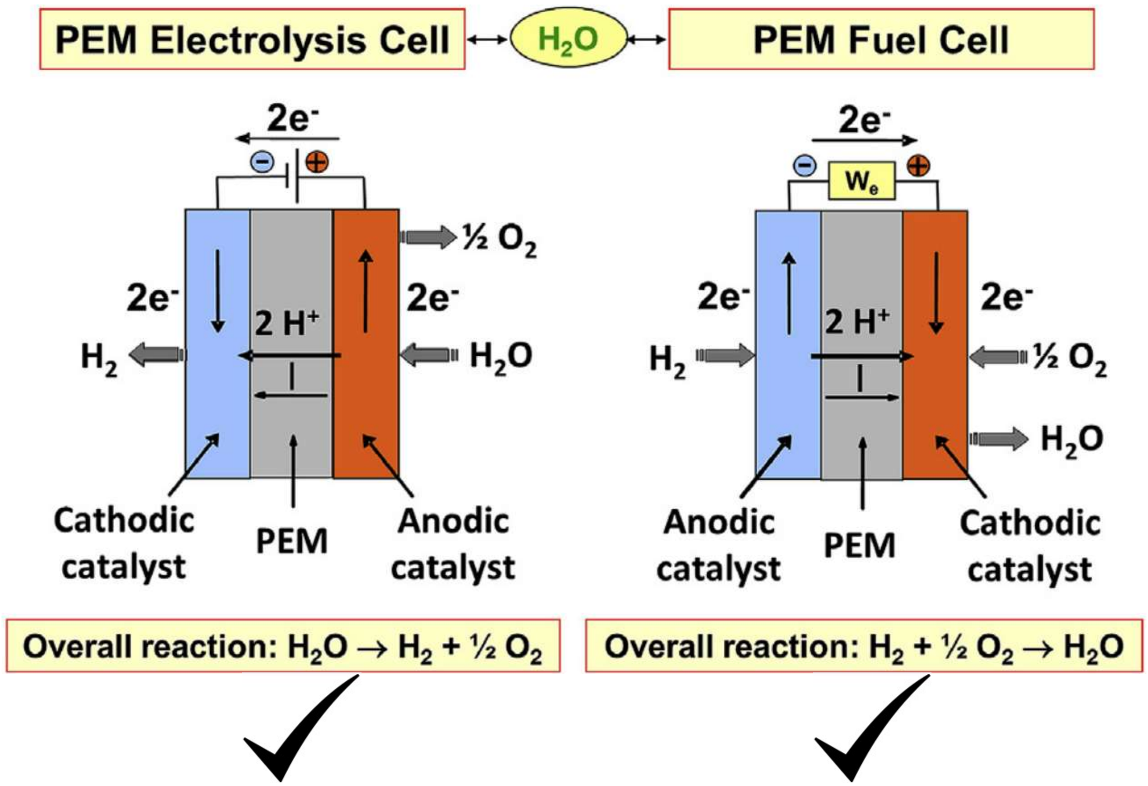


Monitoring Water/Ice Distribution *in-situ*

- Diffusion resistance from Fick's 1st law:
  - $R_d = \cancel{R_{DM}}^{0} + R_{CL,gas} + \cancel{R_{CL,ion}}^{0}$
- $R_d = R_{CL,gas} = R_{Knudsen} = \frac{h_{CL}}{D_{O_2}^{eff}}$
- $D_{O_2}^{eff} = \frac{\varepsilon_0}{\tau} D_{O_2}$
- $D_{O_2} = \left(\frac{1}{D_{Knudsen,O_2}} + \frac{1}{D_{O_2,mix}} \right)^{-1} \approx D_{Knudsen,O_2}$
  - $D_{Knudsen,O_2} = \frac{2r_{Knudsen}}{3} \sqrt{\frac{8RT}{\pi M_{O_2}}}$

Possible Result:
Real-Time Monitoring of Freeze Mechanism via EIS

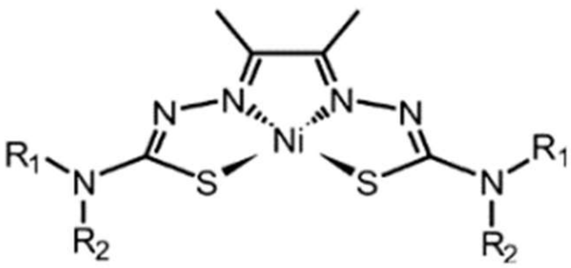
$D_{Knudsen}$ ~ Catalyst Layer Ice Coverage



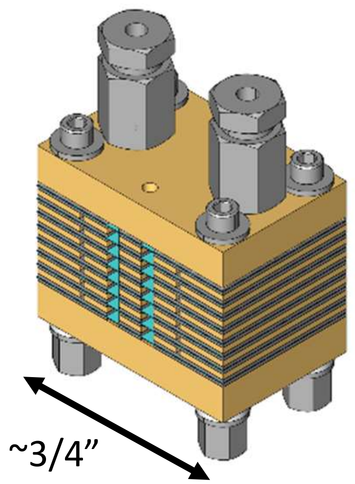
Lamy, C. *Int. J. Hydrogen Energy* 41, 15415–15425 (2016)

Impact of the Study

- <u>Efficient Non-Precious HER Catalysts:</u>
  - Translate Hydrogenase Activity to electrodes



- <u>Fuel Cells for Subzero Temperature Operations:</u>
  - Unlock New PEMFC Applications
  - Augment Transportation, Grid Storage, and Auxiliary power applications
  - Contribute to Fundamental Understanding of Temperature-Dependence in Energy Conversion Systems

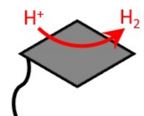


Contribute to Adoption of Green H_2 Economy

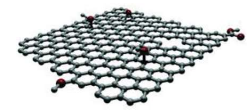
Timelines

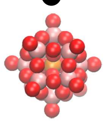
Efficient Non-Precious HER Catalysts

EOY 2021
Surface-Linked TSC

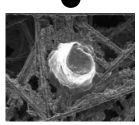


EOY 2022
HSAC

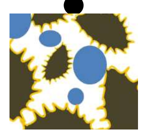




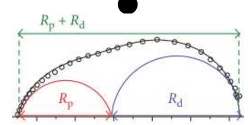
EO Q1 2021
Membrane Dopants



EO Q2 2021
Amphiphilic DM



EO Q3 2021
Superhydrophobic CL



EOY 2021
Freeze Mechanism

Fuel Cells for Subzero Temperature Operations

Acknowledgements

- Fellow Students & Postdocs of Gupta Research Group at U of L and of MPA-11 at LANL for the Camaraderie
- Drs. Komini-Babu, Spendelow, Borup, and Martinez for Guidance at LANL
- Dr. Gupta for Bringing me in to Academic Life
- Drs. Buchanan, Jaeger, and Willing for Serving on this Committee

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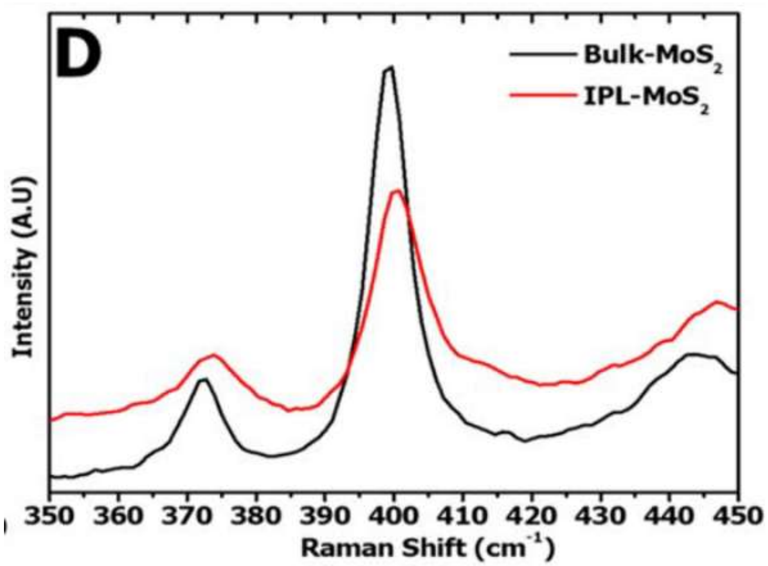
  - Los Alamos National Laboratory Directed Research & Development (LDRD)
  - Department of Energy Office of Energy Efficiency & Renewable Energy (EERE)

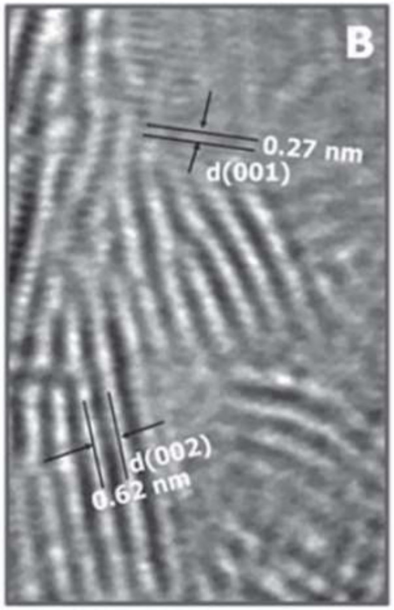
Publications

- **Gupta, A.**, *et al.* Heteropoly acids for prolonged proton exchange fuel cell operation at subzero temperature. *In Preparation*
- **Gupta, A.**, *et al.* Challenges of water transport in proton exchange fuel cells at subzero temperatures. *In Preparation*
- Saraei, N., **Gupta, A. J.**, Hietsoi, O., Frye, B. C., Hofsommer, D. T., Sumanasekera, G., Gupta, G., Mashuta, M. S., Buchanan, R. M., & Grapperhaus, C. A. (2021). Small molecule crystals with 1D water wires modulate electronic properties of surface water networks. *Applied Materials Today*, *22*, 100895. https://doi.org/10.1016/j.apmt.2020.100895
- Ghahremani, A. H., Martin, B., **Gupta, A.**, Bahadur, J., Ankireddy, K., & Druffel, T. (2020). Rapid fabrication of perovskite solar cells through intense pulse light annealing of SnO2 and triple cation perovskite thin films. *Materials and Design*, *185*. https://doi.org/10.1016/j.matdes.2019.108237
- **Gupta, A.** J., Vishnosky, N. S., Hietsoi, O., Losovyj, Y., Strain, J., Spurgeon, J., Mashuta, M. S., Jain, R., Buchanan, R. M., Gupta, G., & Grapperhaus, C. A. (2019). Effect of Stacking Interactions on the Translation of Structurally Related Bis(thiosemicarbazonato)nickel(II) HER Catalysts to Modified Electrode Surfaces. *Inorganic Chemistry*, *58*(18), 12025–12039. https://doi.org/10.1021/acs.inorgchem.9b01209
- Saraei, N., Hietsoi, O., Frye, B. C., **Gupta, A. J.**, Mashuta, M. S., Gupta, G., Buchanan, R. M., & Grapperhaus, C. A. (2019). Water wire clusters in isostructural Cu(II)and Ni(II)complexes: Synthesis, characterization, and thermal analyses. *Inorganica Chimica Acta*, *492*, 268–274. https://doi.org/10.1016/j.ica.2019.04.012
- **Gupta, A.**, Ankireddy, K., Kumar, B., Alruqi, A., Jasinski, J., Gupta, G., & Druffel, T. (2019). Intense pulsed light, a promising technique to develop molybdenum sulfide catalysts for hydrogen evolution. *Nanotechnology*, *30*(17). https://doi.org/10.1088/1361-6528/aaffac
- Saraei, N., Hietsoi, O., Mullins, C. S., **Gupta, A. J.**, Frye, B. C., Mashuta, M. S., Buchanan, R. M., & Grapperhaus, C. A. (2018). Streams, cascades, and pools: various water cluster motifs in structurally similar Ni(ii) complexes. *CrystEngComm*, *20*(44), 7071–7081. https://doi.org/10.1039/C8CE01153B
- Zhang, C., Bhoyate, S., Kahol, P. K., Siam, K., Poudel, T. P., Mishra, S. R., Perez, F., **Gupta, A.**, Gupta, G., & Gupta, R. K. (2018). Highly Efficient and Durable Electrocatalyst Based on Nanowires of Cobalt Sulfide for Overall Water Splitting. *ChemNanoMat*, *4*(12), 1240–1246. https://doi.org/10.1002/cnma.201800301

IPL-MoS_2 Structural/Chemical Validation

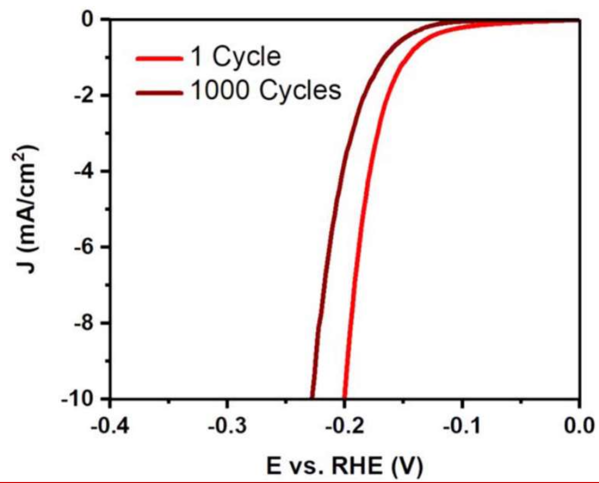
$$MoS_4^{2-} + 2NH_4{}^{+} \xrightarrow{\Delta} MoS_2 + H_2S + S + 2NH_3.$$



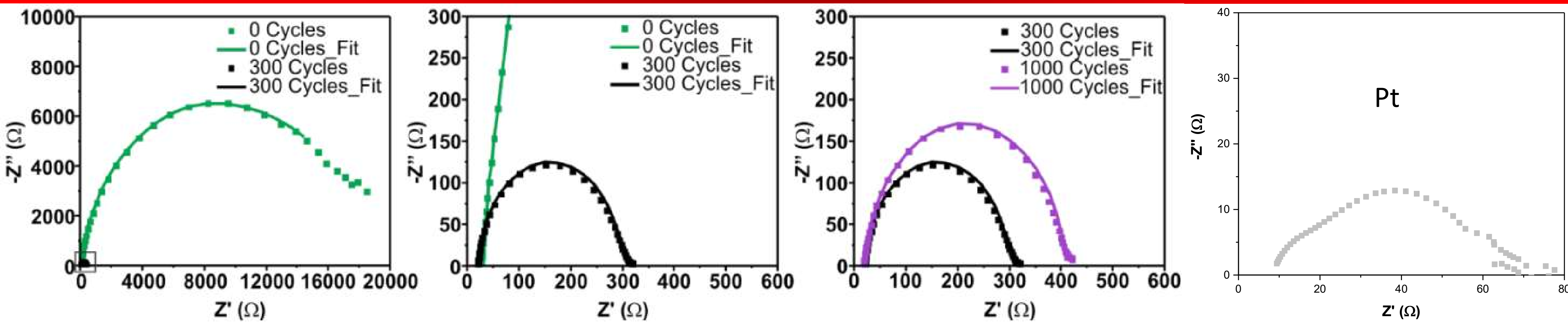


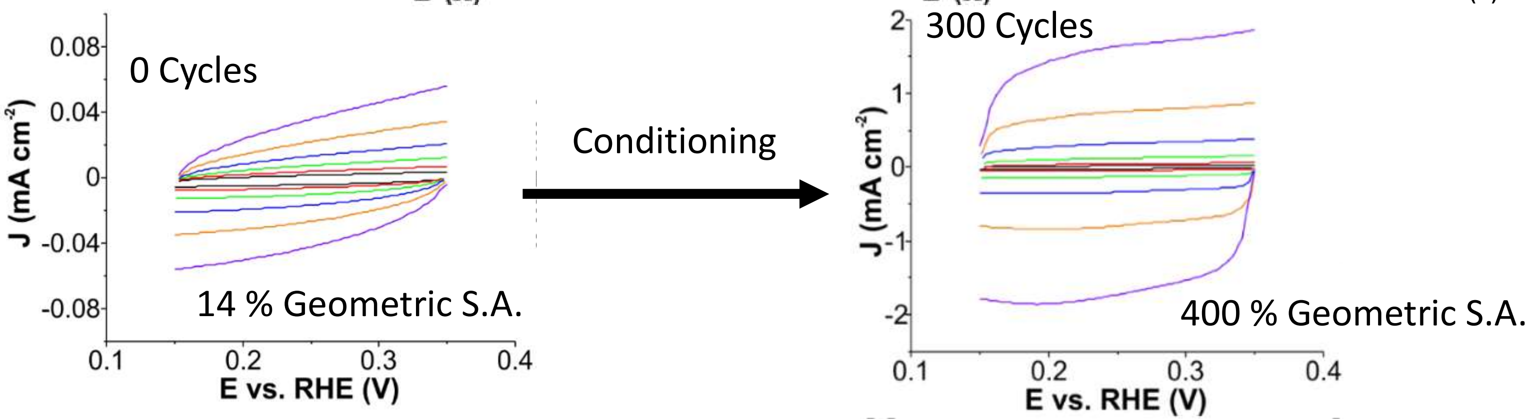
IPL-MoS_2 Activity & Stability

MoS_2 catalyst	Overpotential (mV) @ 10 mA cm^{-2}	Tafel slope (mV dec^{-1})
IPL-MoS_2 (this study)	200	62.3
Core–shell MoO_3–MoS_2 nanowires [34]	~250	50–60
MoS_2 NSs-550 [35]	~200	68
Amorphous molybdenum sulfide [36]	200	60
1T-MoS_2 [13]	187	43
Defect-rich MoS_2 nanosheets [37]	~150	50
MoS_2/RGO [38]	~150	41



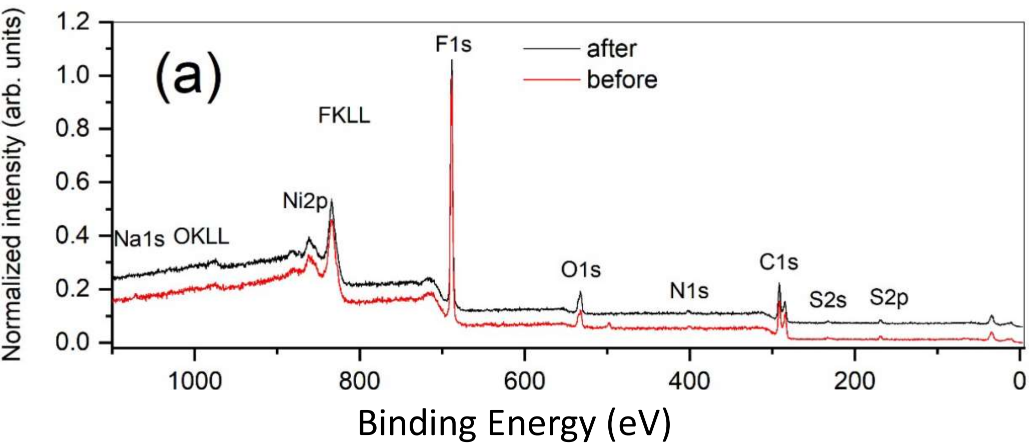
TSC Charge Transfer & ECSA Evolution

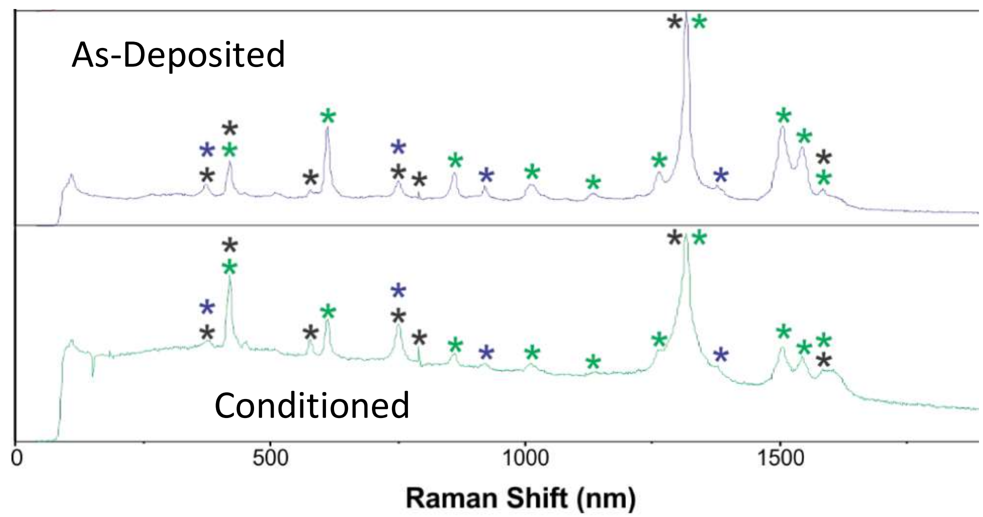


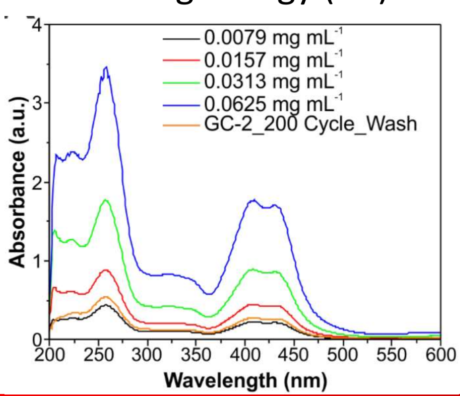


Gupta, A. J. *et al. Inorg. Chem.* 58, 12025–12039 (2019)

TSC Retention of Chemical Identity

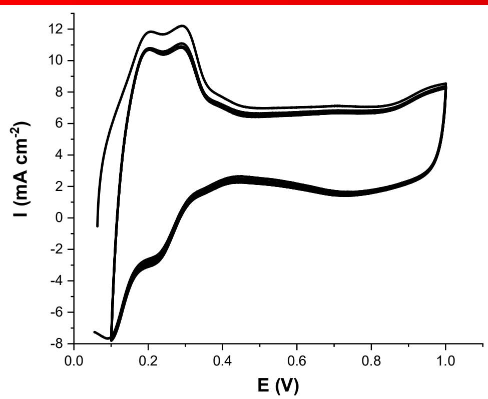


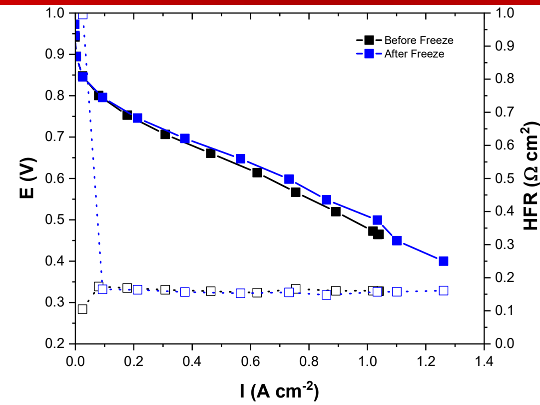




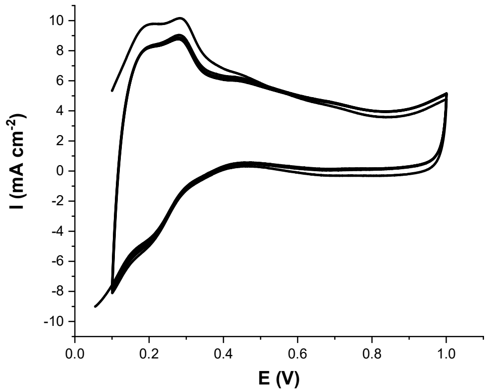
HPA-Doped Membrane Supplemental

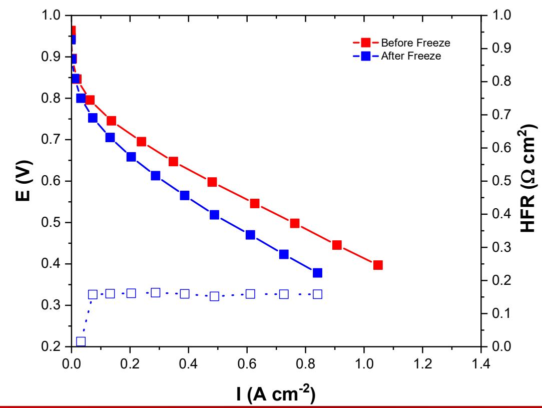
Undoped





HPW

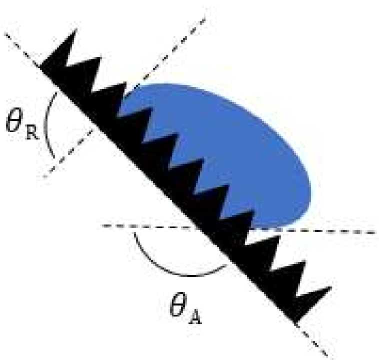




Cell Ice Capacity (mg) by Component

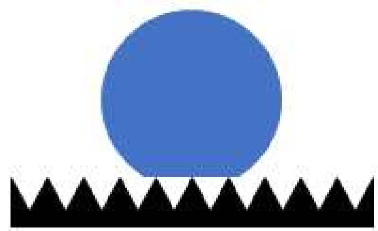
	Component	Undoped	1.32 % HPW
Theoretical Capacity	DM Pores	40.3	
	Membrane	24.3	
	CL Pores*	1.9	1.3
	CL Ionomer*	0.3	0.2
	Entire Cell	109.3	108
Observed Ice Capacity		5.9	8.8

Superhydrophobic Surface Supplemental

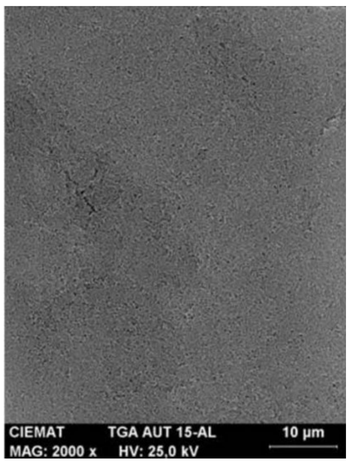


Advancing/Receding Contact Angle

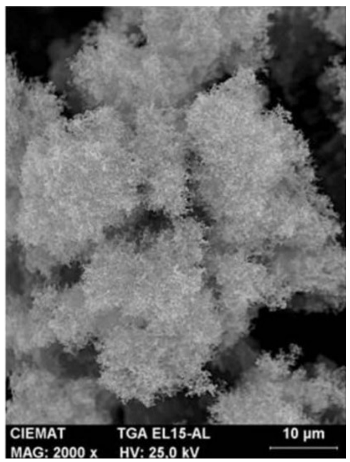
Wenzel (Homogeneous) Wetting



Cassie-Baxter (Heterogeneous) Wetting



Airbrushed



Electrosprayed

Increasing Roughness Amplifies Wetting Tendency of a Surface

Los Alamos NATIONAL LABORATORY EST. 1943

Chaparro, A. M. *et al. J. Electrochem. Soc.* 157, B993 (2010)