Electrolyzer Integrated Modular Nano-Array Monolithic Catalytic Reactors for Low Pressure/Temperature and High Flux Synthetic Fuel Production
DOE Award DE-EE0008423

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Project ID # TA032

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**OVERVIEW**

**Timeline**
- Project Start Date: 11/01/2018
- Project End Date: 10/31/2021

**Barriers**
- High cost of hydrogen and fuels due to reactor expense/efficiency – particularly relevant when integrated with renewables.
- High cost and low reliability of gaseous and liquid hydrogen fueling infrastructure
- High cost to convert CO₂ to chemicals and fuels using intermittent renewable power
- Hydrogen fueling safety

**Budget**
- Total Project Budget: $2,540,531
- Total Recipient Share: $2,000,000
- Total Federal Share: $540,531
- Total DOE Funds Spent*: $922,112
- Total Cost-Share Spent*: $350,571

* As of 05/31/2020

**Partners**
- SKYRE, Inc. - Project lead
- UCONN – Catalyst and catalytic reactor research
- CT Center for Advanced Technology – Catalytic reactor development
- Advanced Manufacturing, LLC – Catalytic reactor development and manufacture
- Stony Brook University – Brookhaven National Laboratory – Catalyst deposition/characterization
- University of Tennessee – Knoxville – Pt nanowires and PEM electrolyzer
Objectives

- New class of electrolyzer integrated modular nanostructure array monolithic catalytic reactors for high-flux, robust, selective methanol synthesis
- Low-temperature electrolyzer for hydrogen fueling of the reactor
- Cost-effective hydrogenation reactions under low temperature (< 200 °C) and low pressure (<10 atm) conditions, significantly reducing the energy demand
- Development and implementation of nanostructured catalyst materials in catalytic and electrocatalytic reactors to achieve higher operational efficiencies
- Renewable energy integration and CO₂ mitigation to produce a widely used chemical and fuel
Develop and demonstrate a pathway to low-cost fuel from waste CO$_2$ and renewables through implementation of advanced materials and process technology.

- Electrolysis nanowire electrodes offering efficient high current density operation
- Efficient catalyst systems with known properties that offer enhanced performance and selectivity toward methanol production and hydrogen utilization
- Advanced catalytic reactor systems that leverage additive manufacturing technology to incorporate key fluid dynamics features that boost reactor efficiency
- Close integration of materials and devices to effectively and harmoniously operate the combined reactor approach
# Approach

## Electrolyzer Integrated Modular Nano-Array Monolithic Catalytic Reactors for Low Pressure/Temperature and High Flux Synthetic Fuel Production

<table>
<thead>
<tr>
<th>Task</th>
<th>Completion (%)</th>
<th>2019</th>
<th>2020</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Design and additive manufacture channeled honeycomb substrates</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1 Design of channeled honeycombs</td>
<td>100</td>
<td>M1.1</td>
<td></td>
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<tr>
<td>1.2 Gas flow simulation through honeycombs</td>
<td>100</td>
<td>M1.2</td>
<td></td>
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<tr>
<td>1.3 Fabrication of channeled honeycombs</td>
<td>100</td>
<td>M1.3</td>
<td></td>
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<tr>
<td>1.4 Fabrication accuracy / capability study</td>
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<td></td>
<td>M1.4</td>
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<tr>
<td>1.5 Cost analyses and justification</td>
<td>33</td>
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<td>M1.5</td>
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<tr>
<td>2. Synthesize metal oxide nanostructure arrays onto honeycomb substrates</td>
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<tr>
<td>2.1 Wash-coating of metal oxide seeds on honeycombs</td>
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<td>M2.1</td>
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<tr>
<td>2.2 Hydrothermal synthesis of nano-arrays onto seeded honeycombs</td>
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<td>M2.2</td>
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<td>3. Decorate catalytically-active species on metal oxide nanostructure arrays</td>
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<td></td>
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<tr>
<td>3.1 Wet-chemical coating of nanoparticles onto nano-arrays</td>
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<td>M3.1</td>
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<tr>
<td>3.2 Inverse micelle coating of nanoparticles onto nano-arrays</td>
<td>100</td>
<td></td>
<td>M3.2</td>
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<tr>
<td>3.3 ALD of nanoparticles onto nano-arrays</td>
<td>100</td>
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<td>M3.3</td>
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<tr>
<td>4. Physicochemical structure, morphology and stability characterization</td>
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<tr>
<td>Characterize as-grown nano-arrays</td>
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<tr>
<td>5. Evaluation of catalyst activity, selectivity and stability</td>
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<tr>
<td>5.1 CO₂ hydrogenation testing over catalysts at 100-300°C</td>
<td>100</td>
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<td>M5.1</td>
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<tr>
<td>5.2 CO₂ hydrogenation testing over catalysts at 1-10 atm</td>
<td>70</td>
<td></td>
<td>M5.2</td>
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<tr>
<td>5.3 Catalyst stability evaluation</td>
<td>25</td>
<td></td>
<td>M5.3</td>
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<tr>
<td>6. Design, fabrication, and characterization of electrolyzers, and compatibility optimization with the nano-array reactors</td>
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<tr>
<td>6.1 Electrolyzer fabrication and assembly</td>
<td>100</td>
<td></td>
<td>M7.1</td>
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<tr>
<td>6.2 Electrolyzer characterization and performance evaluation</td>
<td>85</td>
<td></td>
<td>M7.2</td>
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<tr>
<td>6.3 Compatibility of the nano-array reactor and electrolyzer</td>
<td>100</td>
<td></td>
<td>M7.3</td>
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<tr>
<td>7. Design and implementation of nano-array reactors with electrolyzers</td>
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<td></td>
<td></td>
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<tr>
<td>7.1 Fueling protocol design for electrolyzer integration with nano-array reactors</td>
<td>88</td>
<td></td>
<td>M8.1</td>
</tr>
</tbody>
</table>

**Budget Period #1 Go/No-Go Decision Point**

- Actual
- Planned
## APPROACH

### 18-Month Go-NoGo

Demonstration of nano-array reactors with a 2 mol.kg⁻¹.hr⁻¹ methanol formation rate and a ˃60% selectivity at 200 °C and 1 bar conditions, and a 4 mol.kg⁻¹.hr⁻¹ methanol formation rate and a ˃75% selectivity at 200 °C and 10 bar conditions.

Demonstration of a low-temperature electrolyzer having < 60 mm thick liquid/gas diffusion electrodes and a low PGM catalyst loading of < 1 mg/cm², with a cell voltage < 2 Vdc at 2 A/cm².

### 36-Month Go-NoGo

Demonstration of cost-effective electrolyzer integrated modular nano-array reactors with selective configurations.
APPROACH
Detailed System Schematic
ACCOMPLISHMENTS
Catalytic Performance of Nanoarray Reactors at 1 Bar

Sample: Cu/Zn/Al (Zn:Al=10) nanoarray;  Testing Pressure: 1 bar
Process: Hydrothermal Cu/Zn/Al nanoarray on Al + 500 °C annealing

Testing setup schematic:

- Methanol yield: ~6.2 mol/h/kg, selectivity: 100%, at 207 °C, 10,000 h⁻¹, met go/no-go target.
- Peak methanol yield: ~21.3 mol/h/kg at ~256 °C, 10,000 h⁻¹.
ACCOMPLISHMENTS

Catalytic Performance of Nanoarray Reactors at 1 Bar

**Sample:** 20-Pt-Cu-ZnO nanoarray;  **Testing pressure:** 1 bar
**Process:** Hydrothermal ZnO nanoarray on cordierite+20 cycle ALD Pt nanofilm + block-copolymer (BCP) Cu dip-coating + RTP at 600 °C, 5 min, 4% H₂/Ar

- Methanol yield: 3.2 mol/h/kg, selectivity: 100%, at 220 °C, 17,000 h⁻¹.
- Peak methanol yield: ~35 mol/h/kg at 300 °C, 17,000 h⁻¹.
**ACCOMPLISHMENTS**

**Catalytic Performance of Nanoarray Reactors at 10 Bar**

- **Nanoarray support effect on Cu/Zn/Al catalysts:**

  - Methanol yield of 4Cu/Zn/Al-ZnO nanoarray sample: 5.6 mol/kg/h, 200 °C, met the go/no-go target (4 mol/kg/h).

  - Methanol selectivity of LPT derived TiO₂ and ZnO nanoarray samples at 200 °C > 75%, met the go/no-go target (75%).
ACCOMPLISHMENTS
Catalytic Performance of Nanoarray Reactors

Sample: 4-Cu/Zn/Al on ZnO nanoarray  
Testing pressure: 10 bar

Process: Hydrothermal Cu/Zn/Al on ZnO nanoarray cordierite substrate + 500 °C annealing
Pressure: 10 bar; Temperature ramp: RT-300 °C

- Methanol yield: \(~5.6\) mol/h/kg, selectivity: 84.7%, at 196 °C/10 bar, 10,000 h\(^{-1}\),
- Met go/no-go performance metrics at 200°C/10 bar, 4 mol/h/kg and 75%.
ACCOMPLISHMENTS

Catalytic Performance of Nanoarray Reactors at 10 Bar

- Better methanol yield on 8Cu/Zn/Al-LPT than 4Cu/Zn/Al-LPT.
- Methanol selectivity of LPT derived TiO$_2$: 4Cu/Zn/Al, ~100%; while 8Cu/Zn/Al, 90%.
- Pd doping improves the methanol yield, however decrease selectivity, which is still above 75%.
New synthesis route: metal dissolution method.
CuO and ZnO are crystalline, while ZrO2 seems to be in the amorphous phase or less crystalline.
CCZ-2 and CCZ-3 of Cu:Zr:Zn ratios 5/4/1 and 4.5/4.5/1 showed the higher surface area than other samples.

**ACCOMPLISHMENTS**

**Catalytic Performance of Cu-Zr-Zn Based Nanopowders**

- Cu-Zn-Zr based mesoporous nanoparticles using metal dissolution method:

<table>
<thead>
<tr>
<th>Name</th>
<th>Material (nominal ratio)</th>
<th>Actual ratio (calculated from XRF)</th>
<th>Surface Area (m²/g)</th>
<th>Pore volume (cc/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial</td>
<td>Commercial catalyst (Cu/Zn/Al)</td>
<td>6.9/2.4/0.7</td>
<td>105</td>
<td>0.239</td>
<td>5.61</td>
</tr>
<tr>
<td>CZZ-1</td>
<td>Cu:Zr:Zn=6/3/1</td>
<td>5.4/3.8/0.8</td>
<td>93</td>
<td>0.175</td>
<td>3.82</td>
</tr>
<tr>
<td>CZZ-2</td>
<td>Cu:Zr:Zn=5/4/1</td>
<td>3.7/5.4/0.8</td>
<td>131</td>
<td>0.202</td>
<td>3.82</td>
</tr>
<tr>
<td>CZZ-3</td>
<td>Cu:Zr:Zn=4.5/4.5/1</td>
<td>3.3/5.8/0.8</td>
<td>164</td>
<td>0.237</td>
<td>3.82</td>
</tr>
<tr>
<td>CZZ-4</td>
<td>Cu:Zr:Zn=5/3/2</td>
<td>4.3/4.0/1.7</td>
<td>111</td>
<td>0.203</td>
<td>3.83</td>
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<tr>
<td>CZZ-5</td>
<td>Cu:Zr:Zn=6/1/3</td>
<td>5.4/1.7/2.9</td>
<td>59</td>
<td>0.260</td>
<td>3.83</td>
</tr>
</tbody>
</table>
Without adding promoters/dopants, new catalysts showed higher methanol yield and selectivity than commercial Cu/ZnO/Al₂O₃ catalyst at 240 °C-300 °C.

CZZ-2 with Cu:Zr:Zn ~5/4/1 showed the best yield and selectivity.
ACCOMPLISHMENTS

Synthesis of uniform Pt-Cu NP loaded ZnO nanoarray catalysts on 3D cordierite honeycomb by ALD and BCP methods

Uniform Pt-Cu nanoparticle (NP) loading was achieved on ZnO nanoarray by modified Pt atomic layer deposition (ALD) and Cu nanoparticle dip-coating via block copolymer (BCP) template method.
ACCOMPLISHMENTS

Enhanced CO₂ hydrogenation performance by ALD Pt-BCP Cu NP loaded ZnO nanoarray catalysts

Pt-Cu NP loaded ZnO nanoarray achieves the methanol yield exceeding that of commercial reference via optimized Pt loading and thermal annealing temp.

Optimizing Pt loading by ALD cycles

Optimal Pt-Cu NP loaded ZnO nanoarray achieving the maximum methanol yield of 35 mol h⁻¹ kg⁻¹

Optimizing post-synthesis thermal annealing

Methanol yield exceeding commercial reference

<table>
<thead>
<tr>
<th>Catalyst type</th>
<th>Temp. (C)</th>
<th>Selectivity (%)</th>
<th>Yield (mol h⁻¹ kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial (Cu-Zn-Al powder)</td>
<td>197</td>
<td>54.3</td>
<td>1.25</td>
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<tr>
<td>ALD Pt-BCP Cu NPs on ZnO nanoarray</td>
<td>220</td>
<td>100</td>
<td>3.2</td>
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ACCOMPLISHMENTS

Reactor Development

<table>
<thead>
<tr>
<th></th>
<th>1 bar pressure</th>
<th>200°C</th>
<th>300°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preliminary Data)</td>
<td>Equilibrium</td>
<td>Catalytic</td>
<td>Equilibrium</td>
</tr>
<tr>
<td>CO₂ Molar Conversion</td>
<td>59.5%</td>
<td>5.0%</td>
<td>56.9%</td>
</tr>
<tr>
<td>(single pass)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Selectivity⁽¹⁾</td>
<td>0.0%</td>
<td>96.6%</td>
<td>0.0%</td>
</tr>
</tbody>
</table>

⁽¹⁾Selectivity = [ CH₃OH+(CH₃)₂O ] / [ CH₃OH+(CH₃)₂O+CO+CH₄ ]

Catalytic reactions may enable feasibility - selectivity is zero without catalysis

Advanced Catalytic Reactor Design Concepts

- Over 50 reactor substrates fabricated using additive manufacturing with varying channel sizes, shapes (twisted/linear, and cross sectional geometry)
- Conceptual design of integrated reactor completed and fabricated using additive manufacturing
- Advance reactor design may enable optimize heat and mass transport

CAD Model

3D printed prototype (non-working)
ACCOMPLISHMENTS
Successfully Fabricated Thin Pt Nanowire (PtNW) Electrodes

LGDL parameters: 25 µm thick; ~50% porosity; ~400 µm pore opening

SEM-EDS characterization
High-resolution TEM (HRTEM)

• Catalyst layer composed of PtNW was successfully grown on titanium LGDLs via chemical synthesis route at room temperature.
• Crystalline structure and diameter (~5 nm) of PtNW were confirmed by HRTEM
• XPS analysis verified the metallic nature of as-synthesized PtNW
ACCOMPLISHMENTS
PEM Electrolyzers With Ultralow-PGM Met Go/No-GO

In-situ performance of thin PtNW GDE at 0.05 mgPt/cm²:
- 1.94 V at 2 A/cm²
- 2.069 V at 2 A/cm² (50 °C)
- 2.248 V at 2 A/cm² (80 °C)

- Thin PtNW GDE at 0.05 mgPt/cm² shows cell voltage of 1.94 V at 2 A/cm² at 80 °C.
- At lower temps 50 °C and 20 °C, cell voltages are 2.069 V and 2.248 V at 2 A/cm², respectively.
- Increasing operating temps reduce HFR values from 0.207 Ω*cm² at 20 °C to 0.173 Ω*cm² at 50 °C and 0.144 Ω*cm² at 80 °C.
- EIS indicates small mass transport loss at 50 °C and 80 °C, but much larger transport loss at 20 °C.
ACCOMPLISHMENTS AND PROGRESS
Responses to Previous Year Reviewers’ Comments

• This project was not reviewed last year.
# Collaboration and Coordination

<table>
<thead>
<tr>
<th>Name</th>
<th>Organization</th>
<th>Primary Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dr. Trent Molter</td>
<td>SKYRE, Inc. (SI)</td>
<td>Component integration, fueling protocols and program management</td>
</tr>
<tr>
<td>(Principal Investigator)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prof. Pu-Xian Gao</td>
<td>University of Connecticut (UConn)</td>
<td>Nano-array integrated reactor design, fabrication, characterization and testing</td>
</tr>
<tr>
<td>Prof. Steven Suib</td>
<td>University of Connecticut (UConn)</td>
<td>Catalytic nanoparticle decoration and testing</td>
</tr>
<tr>
<td>Dr. Tom Maloney</td>
<td>Connecticut Center for Advanced Technology (CCAT)</td>
<td>Additive manufacturing of different reactor substrates</td>
</tr>
<tr>
<td>Dr. Dongsheng Li</td>
<td>Advanced Manufacturing LLC (AMLLC)</td>
<td>Design, optimization and post-processing of additively-manufactured reactor substrates</td>
</tr>
<tr>
<td>Prof. Chang-Yong Nam</td>
<td>Stony Brook University (SBU) Brookhaven National Laboratory</td>
<td>Metal catalyst deposition; structural and chemical characterization</td>
</tr>
<tr>
<td>Prof. Feng-Yuan Zhang</td>
<td>University of Tennessee – Knoxville (UTK)</td>
<td>Electrolyzer assembly and testing</td>
</tr>
</tbody>
</table>
REMAINING CHALLENGES AND BARRIERS

• Regroup after COVID-19 lab operation pause and resume hardware work.
• Successful scale-up, implementation and integration of materials and process work to produce a viable system.
  – Catalytic reactor
  – Electrolyzer
  – Integrated system
PROPOSED FUTURE WORK

Complete the following tasks (BP1):

- Pressure dependent study of CO$_2$ hydrogenation over various nanopowder and nanoarray reactors.
- Stability study of nanoarray reactors at high pressure
- Kinetics experimental-theory study over nanostructured monolithic reactors.
- Optimization study of Cu-Zr-Zn mesoporous nanopowders for CO$_2$ hydrogenation
- Preliminary economic analysis of utilizing advanced reactor
- Identify the composition and crystalline phase of ALD Pt-BCP Cu NPs on ZnO nanoarray
  - Scanning transmission electron microscopy (STEM)
  - Electron energy loss spectroscopy (EELS)
- Identify the electronic interaction among Pt, Cu, and ZnO
  - X-ray photoemission spectroscopy (XPS) on planar substrates
- Optimization of PtNW electrodes with improved uniformity and surface coverage on thin LGDLs
- Ex-situ materials and electrochemical characterizations of optimized PtNW electrodes
PROPOSED FUTURE WORK

Initiate the following work for BP2:

- Optimization and scale-up of nanoarray reactor fabrication
- Detailed process analysis and economic analysis
- Identify how CO$_2$ hydrogenation performance is influenced by the interaction among Pt, Cu, and ZnO
  - Ultraviolet photoemission spectroscopy (UPS)
  - Ambient pressure XPS (AP-XPS)
- Identify the guiding principles for designing high-performance Pt-Cu alloy CO$_2$ hydrogenation catalysts
- In-situ cell performance evaluations of PtNW electrodes with different catalyst loadings
- Fabrication of the PtNW electrodes for the electrolyzers integrated with nanoarray reactor for CO$_2$RR and their characterization
- Develop and demonstrate the integrated system which leverages individual materials and process technologies
TECHNOLOGY TRANSFER ACTIVITIES

• Conducting outreach to refine market scope and requirements

• Value can be ascribed to aggregated system and selective technologies developed as part of this project
  – Renewable liquid fuels
  – CO₂ Utilization/transformation
  – Renewable hydrogen
  – Efficient catalytic reactors
  – Efficient electrocatalytic reactors
  – Additive manufacturing technology
**Objective:** Investigate new electrolyzer integrated modular nanostructure array monolithic catalytic reactors for high-flux, robust, selective methanol synthesis

**Relevance:** Low-T, efficient electrolyzer for H₂ fueling. Cost-effective hydrogenation reactions under low T (< 200 °C) and low P (<10 atm), reducing energy. Nanostructured catalysts for high efficiency catalytic and electrocatalytic reactors. Renewables integration/CO₂ mitigation producing widely used chemical and fuel.

**Approach:** Electrolysis nanowire electrodes offering efficient high current density. Efficient catalysts offering enhanced performance and selectivity toward MeOH production and H₂ utilization. Advanced reactors that leverage additive manufacturing to incorporate fluid dynamics features that boost reactor efficiency. Integration of materials/devices to effectively and harmoniously operate reactors.

**Accomplishments:** Demonstrated catalytic performance of nanoarray reactor (1 bar - Methanol yield: ~6.2 mol/h/kg, selectivity: 100%, at 207 °C, 10,000 h⁻¹, met go/no-go target, peak methanol yield: ~35 mol/h/kg at 300 °C, 17,000 h⁻¹, 10 bar - Methanol yield: ~5.6 mol/h/kg, selectivity: 84.7%, at 196 °C/10 bar, 10,000 h⁻¹, met go/no-go performance metrics at 200°C/10 bar, 4 mol/h/kg and 75%) Demonstrated electrolyzer performance - thin PtNW GDE at 0.05 mgPt/cm² shows cell voltage of 1.94 V at 2 A/cm² at 80 °C.

**Collaborations:** Strong, diverse team comprised of industry and research. (Skyre, CCAT, Adv. Mfg., UConn, Stony Brook – BNL, University of Tennessee – Knoxville).