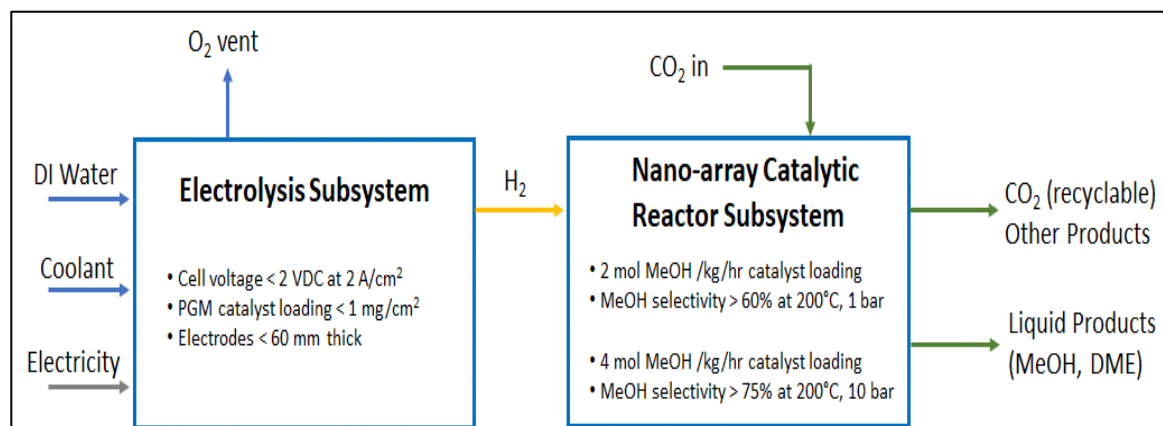


Electrolyzer Integrated Modular Nano-Array Monolithic Catalytic Reactors for Low Pressure/Temperature and High Flux Synthetic Fuel Production DOE Award DE-EE0008423

Dr. Trent Molter
SKYRE, Inc.
April 23, 2020
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Project ID # TA032



OVERVIEW

Timeline

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

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

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

Partners

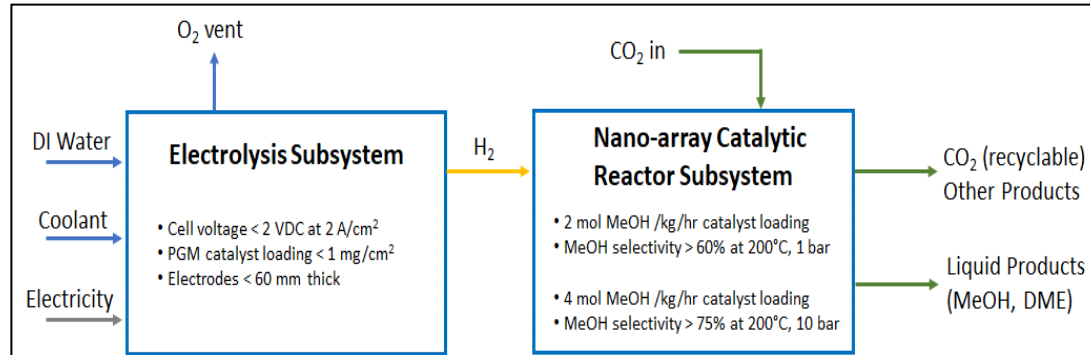
- SKYRE, Inc. - Project lead
- UCONN – Catalyst and catalytic reactor research
- CT Center for Advanced Technology – Catalytic reactor development
- Advanced Manufacturing, LLC – Catalytic reactor development and manufacture
- Stony Brook University – Brookhaven National Laboratory – Catalyst deposition/characterization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

RELEVANCE

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

APPROACH



Develop and demonstrate a pathway to low-cost fuel from waste CO₂ 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		Completion (%)	2019												2020							
			Q1			Q2			Q3			Q4			Q5			Q6				
			J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J		
1	Design and additive manufacture channeled honeycomb substrates																					
1.1	Design of channeled honeycombs	100			M1.1																	
1.2	Gasflow simulation through honeycombs	100						M1.2														
1.3	Fabrication of channeled honeycombs	100						M1.3														
1.4	Fabrication accuracy / capability study	100													M1.4							
1.5	Cost analyses and justification	33																				M1.5
2	Synthesize metal oxide nanostructure arrays onto honeycomb substrates																					
2.1	Wash-coating of metal oxide seeds on honeycombs	100			M2.1																	
2.2	Hydrothermal synthesis of nano-arrays onto seeded honeycombs	100						M2.2														
3	Decorate catalytically-active species on metal oxide nanostructure arrays																					
3.1	Wet-chemical coating of nanoparticles onto nano-arrays	100																				
3.2	Inverse micelle coating of nanoparticles onto nano-arrays	100																				
3.3	ALD of nanoparticles onto nano-arrays	100																				
4	Physicochemical structure, morphology and stability characterization																					
	Characterize as-grown nano-arrays	100																				M4.0
5	Evaluation of catalyst activity, selectivity and stability																					
5.1	CO ₂ hydrogenation testing over catalysts at 100-300°C	100																				M5.1
5.2	CO ₂ hydrogenation testing over catalysts at 1-10 atm	70																				M5.2
5.3	Catalyst stability evaluation	25																				M5.3
6	Design, fabrication, and characterization of electrolyzers, and compatibility optimization with the nano-array reactors																					
6.1	Electrolyzer fabrication and assembly	100																				M7.1
6.2	Electrolyzer characterization and performance evaluation	85																				M7.2
6.3	Compatibility of the nano-array reactor and electrolyzer	100																				M7.3
7	Design and implementation of nano-array reactors with electrolyzers																					
7.1	Fueling protocol design for electrolyzer integration with nano-array reactors	88																				M8.1
BUDGET PERIOD #1 GO/NO-GO DECISION POINT																						✱
				Actual																		Planned

APPROACH

Current Program
Status – 18-Month
Go-NoGo Criteria
Met

18-Month Go-NoGo

Demonstration of nano-array reactors with a $2 \text{ mol.kg}^{-1}.\text{hr}^{-1}$ methanol formation rate and a >60% selectivity at 200 °C and 1 bar conditions, and a $4 \text{ mol.kg}^{-1}.\text{hr}^{-1}$ 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/cm^2 , with a cell voltage < 2 Vdc at 2 A/cm^2

36-Month Go-NoGo

Demonstration of cost-effective electrolyzer integrated modular nano-array reactors with selective configurations

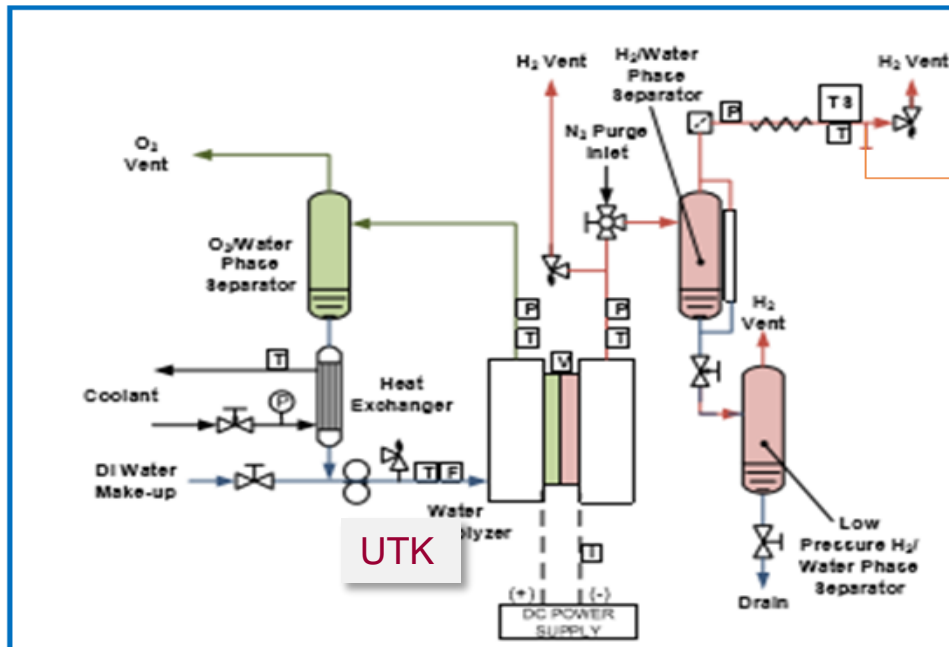
Task descriptions	Year 1 (Q1-4)				Year 2 (Q5-8)				Year 3 (Q9-12)			
1: Design/additive manufacture of honeycomb substrates												
1.1 Design of channeled honeycombs	M1.1											
1.2 Comparison reactor flow simulation		M1.2										
1.3 Fabrication of various complex channeled honeycombs		M1.3										
1.4 Fabrication accuracy/capability study				M1.4								
2: Nano-array synthesis on monolith substrates												
2.1 Seeds deposition on honeycombs		M2.1										
2.2 Nano-array deposition onto honeycombs		M2.2										
3: Metal/oxide nanoparticle decoration												
3.1 Wet-chemical processing			M3.1									
3.2 Inverse micelle template synthesis			M3.2									
3.3 Atomic layer deposition			M3.3									
4: Physico-chemical structure and stability			M4.0									
5: Evaluation of nano-array reactors												
5.1 Temperature dependent reaction kinetics					M5.1							
5.2 Pressure dependent reaction kinetics						M5.2						
5.3 Cyclic performance and deactivation						M5.3						
6: Optimization and scale up of the reactors												
6.1 Scaled reactor substrate design and scale up						M6.1						
6.2 Scaled nano-array reactor processing and testing						M6.2						
7: Design and assembly of electrolyzers												
7.1 Electrolyzer fabrication and assembly						M7.1						
7.2 Electrolyzer component performance evaluation						M7.2						
7.3 Compatibility of nano-array reactor and electrolyzer						M7.3						
Budget Period 1 Project Go/No-Go						G/N G1						
8: Design and implementation of H ₂ fueling												
8.1 H ₂ fueling protocol design.						M8.1						
8.2 H ₂ fueling protocol implementation						M8.2						
8.3 Demonstrate electrolyzer integrated nano-array reactors							M8.3					
9: Cost and life cycle analyses, and infrastructure compatibility												
9.1 Materials, energy and cost analyses								M9.1				
9.2 Fueling/Infrastructure compatibility analysis									M9.2			
9.3 End of Project Goal: Demonstration of cost-effective modular reactors										M9.3		
Project Success Metrics												

APPROACH

Detailed System Schematic

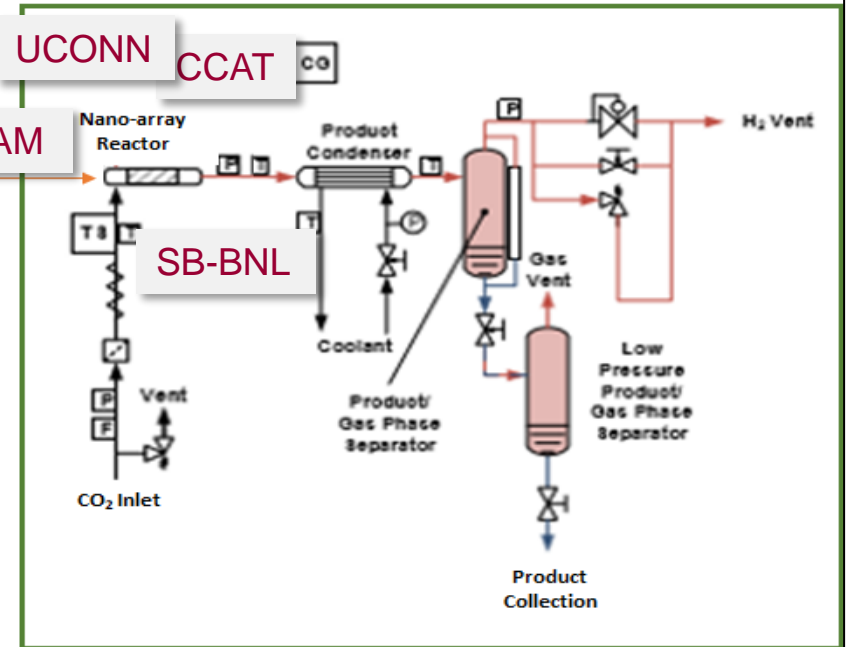
SKYRE

Electrolysis Subsystem



UTK

Nano-array Catalytic Reactor Subsystem



UCONN

CCAT

CO

AM

SB-BNL

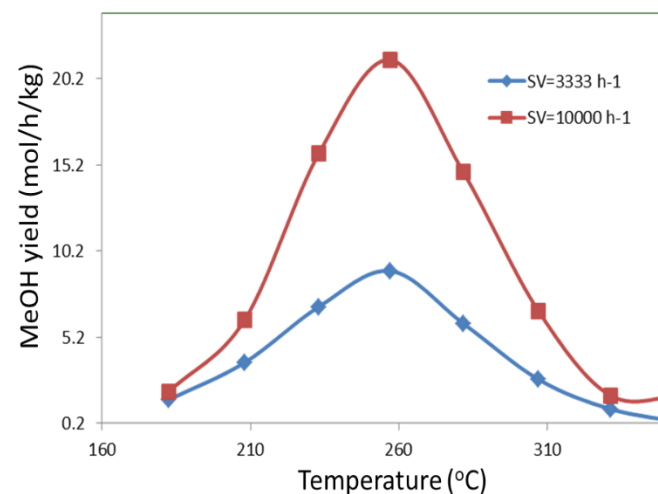
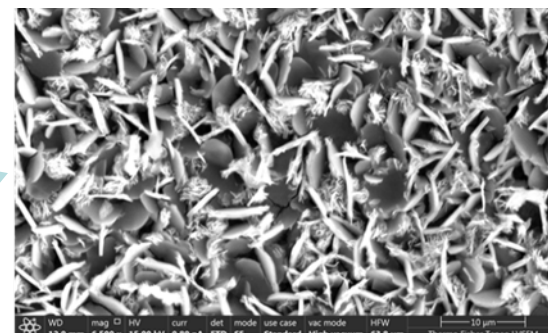
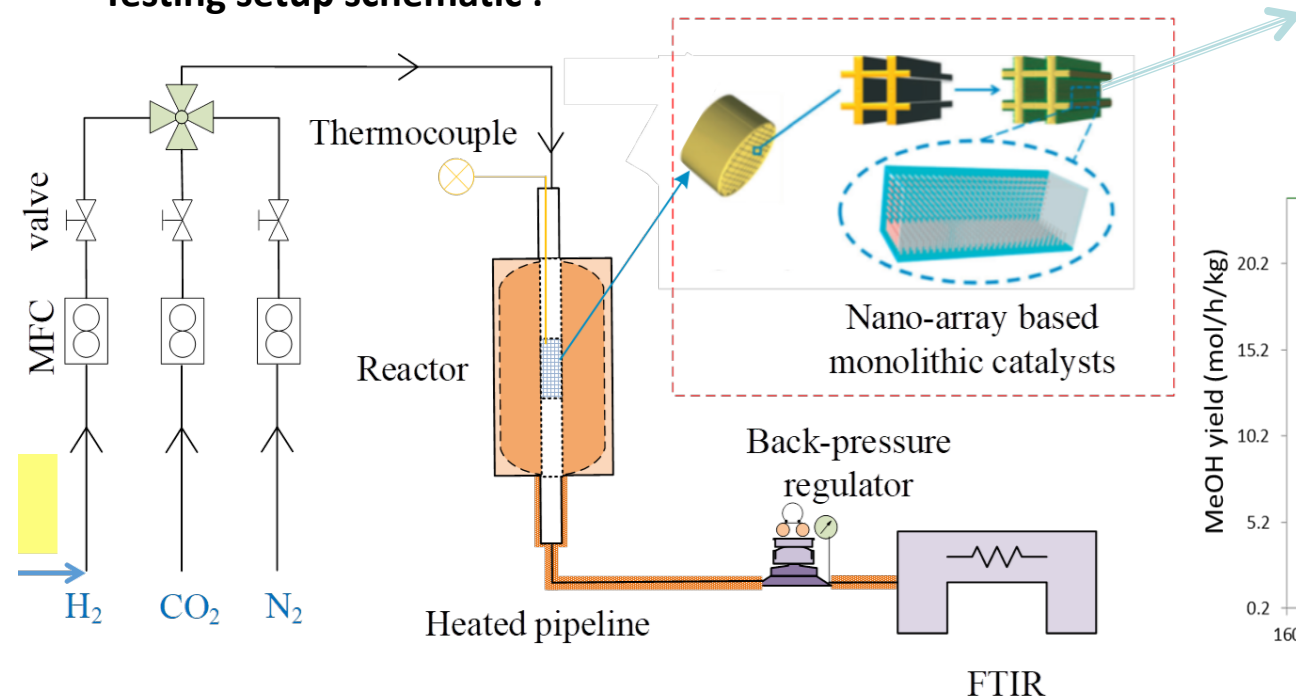
LEGEND			
	SHUT-OFF VALVE		REGULATING VALVE
	NEEDLE VALVE		FLOW SENSOR
	THREE-WAY VALVE		CURRENT SENSOR
	COALESCING FILTER		PRESSURE SENSOR
	PUMP		PRESSURE GAUGE
	RELIEF VALVE		TEMPERATURE SENSOR
	THERMOSTAT		HEATER

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 :



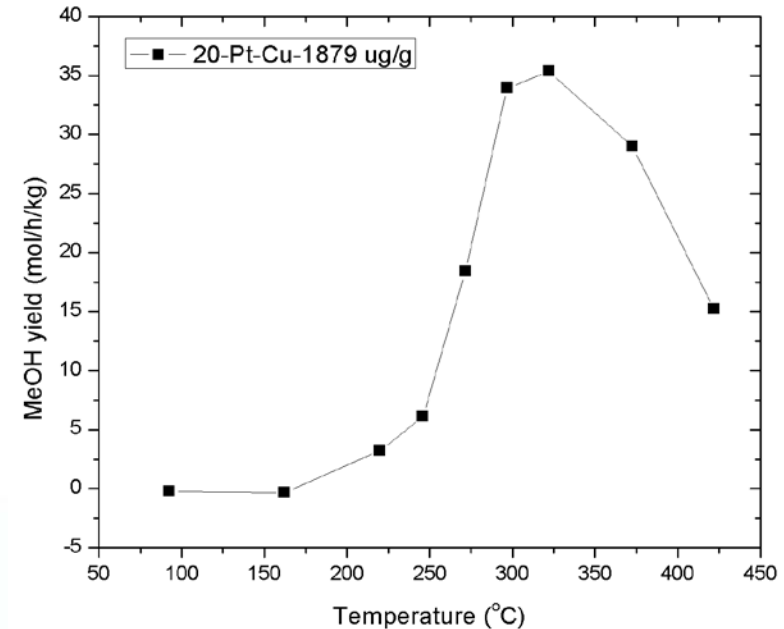
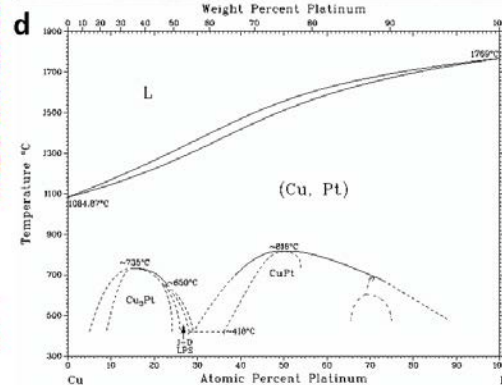
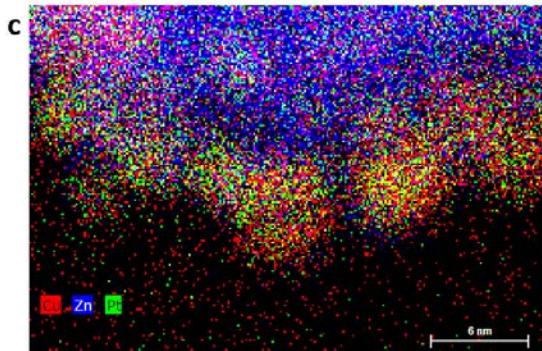
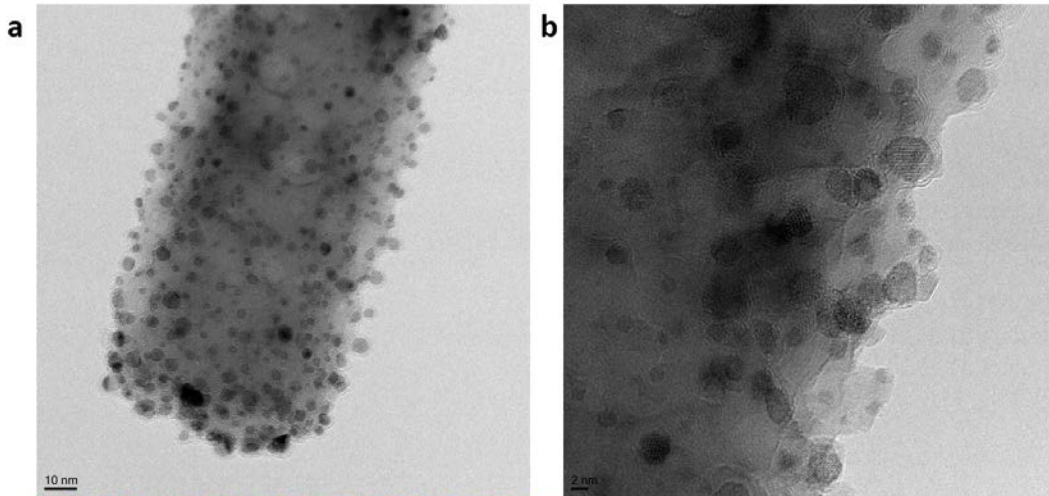
- Methanol yield: ~6.2 mol/h/kg, selectivity: 100%, at 207 °C, 10,000 h⁻¹, met go/no-go target.
- Peak methanol yield: ~21.3 mol/h/kg at ~256 °C, 10,000 h⁻¹.

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

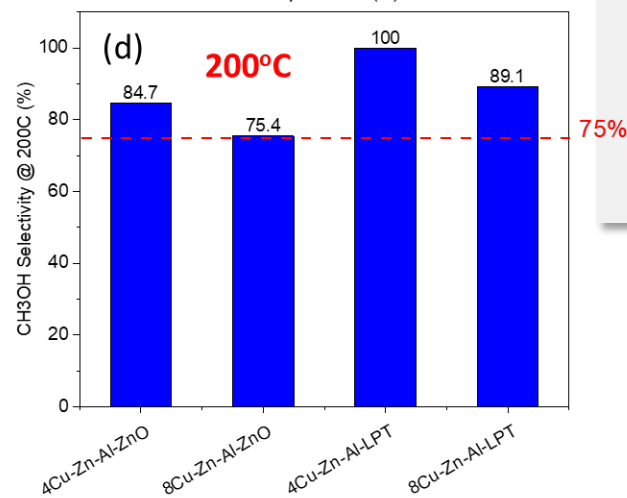
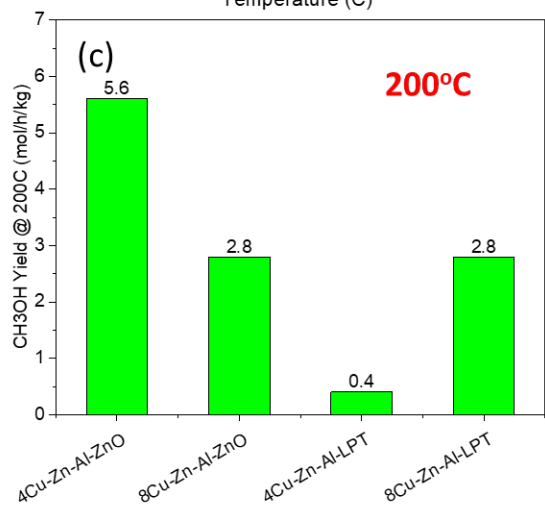
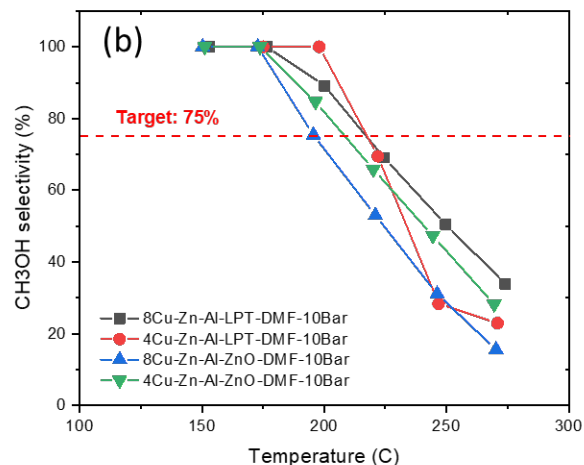
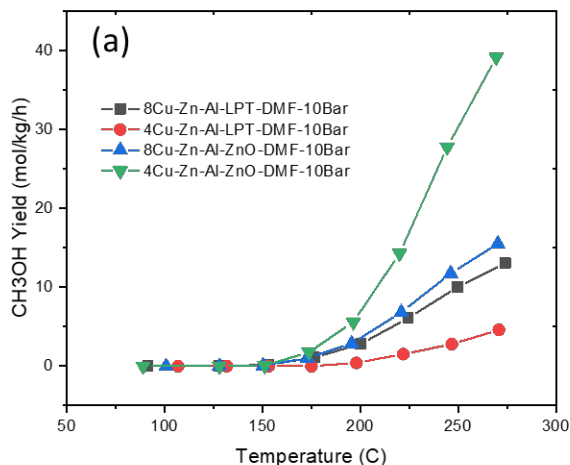


- Methanol yield: 3.2 mol/h/kg, selectivity: 100%, at 220 °C, 17,000 h⁻¹.
- Peak methanol yield: ~35 mol/h/kg at 300 °C, 17,000 h⁻¹.

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%).

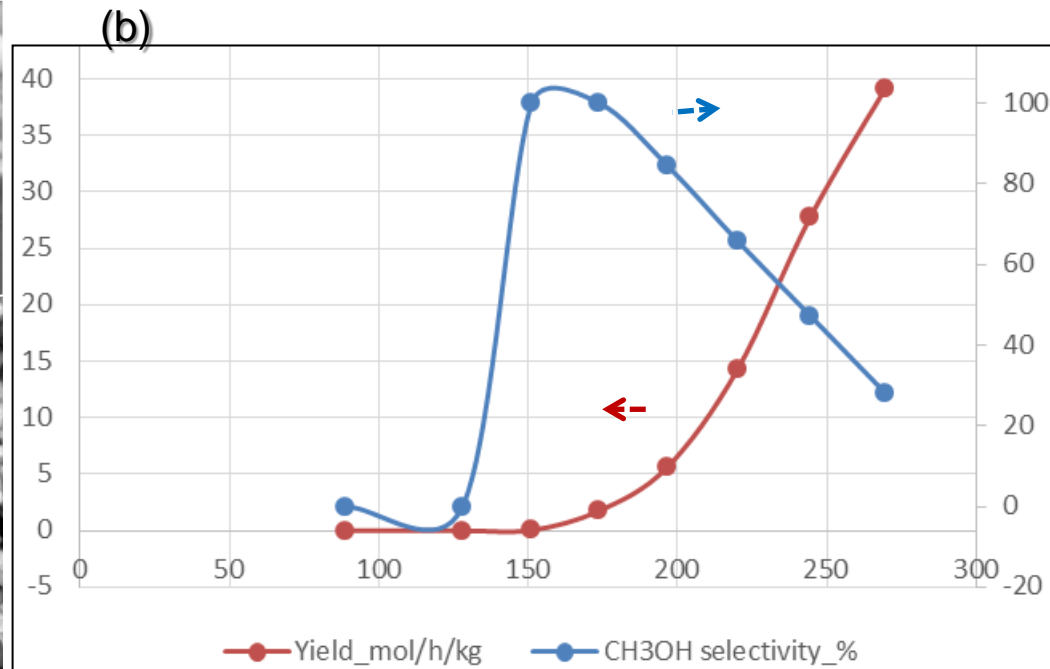
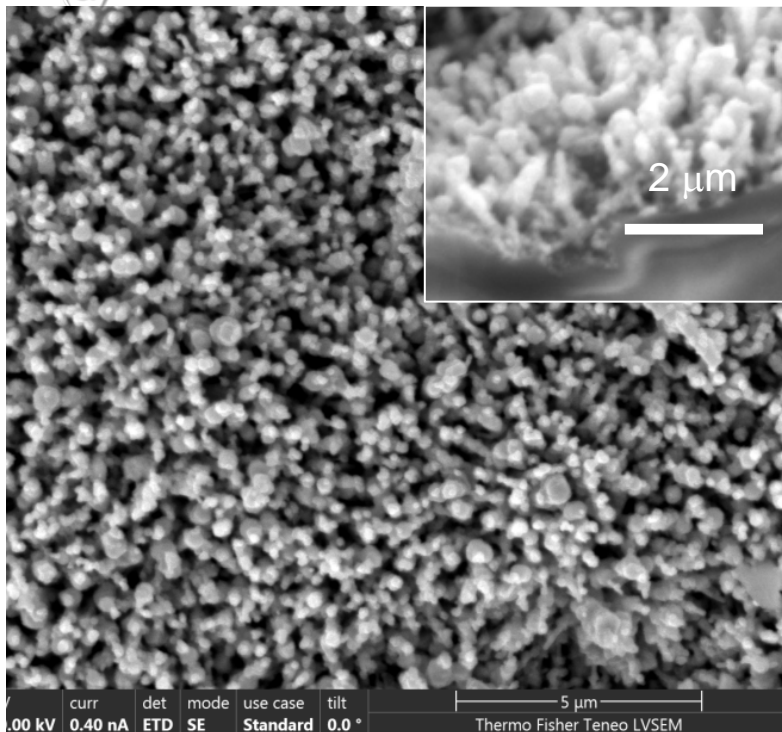
ACCOMPLISHMENTS

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

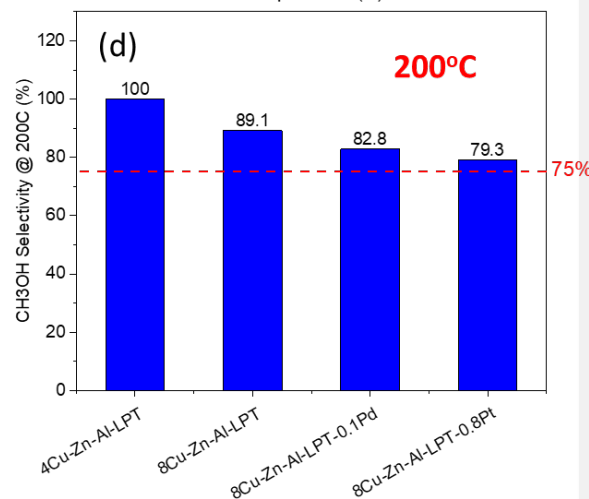
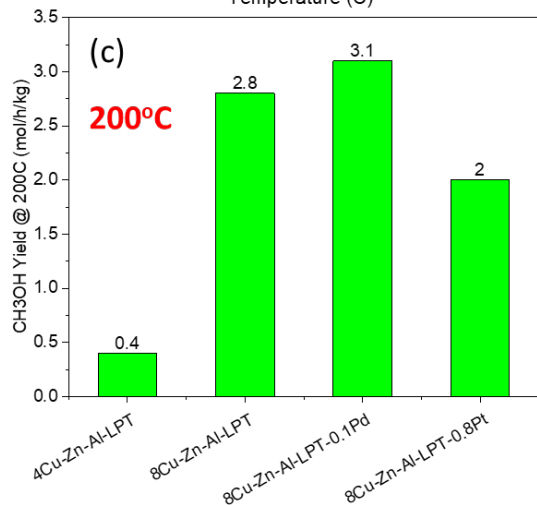
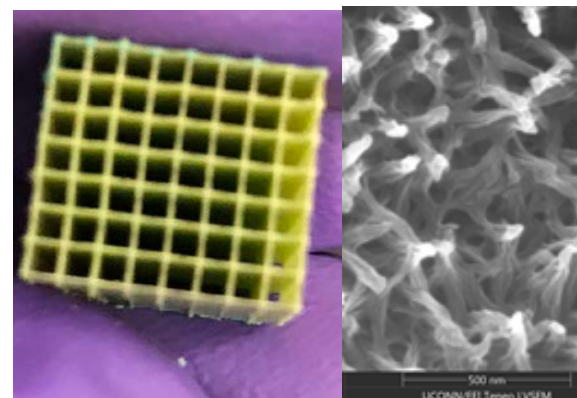
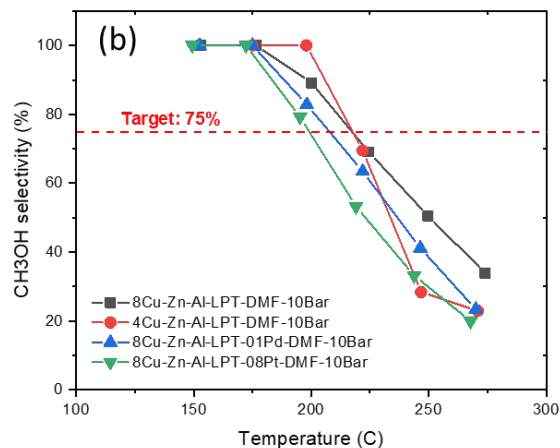
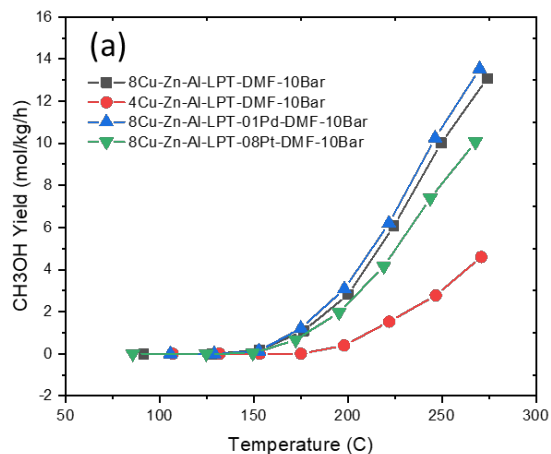


- Methanol yield: ~5.6 mol/h/kg, selectivity: 84.7%, at 196 °C/10 bar, 10,000 h⁻¹,
- Met go/no-go performance metrics at 200°C/10 bar, 4 mol/h/kg and 75%.

ACCOMPLISHMENTS

Catalytic Performance of Nanoarray Reactors at 10 Bar

❖ Pt/Pd doping effect on LPT supported Cu/Zn/Al catalysts:

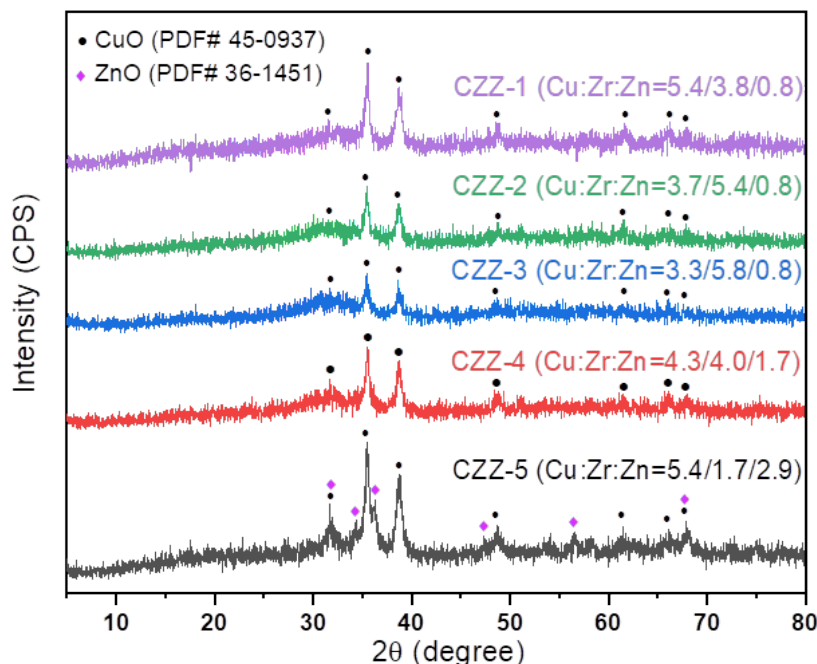


- Better methanol yield on 8Cu/Zn/Al-LPT than 4Cu/Zn/Al-LPT.
- Methanol selectivity of LPT derived TiO₂: 4Cu/Zn/Al, ~100%; while 8 Cu/Zn/Al, 90%.
- Pd doping improves the methanol yield, however decrease selectivity, which is still above 75%.

ACCOMPLISHMENTS

Catalytic Performance of Cu-Zr-Zn Based Nanopowders

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



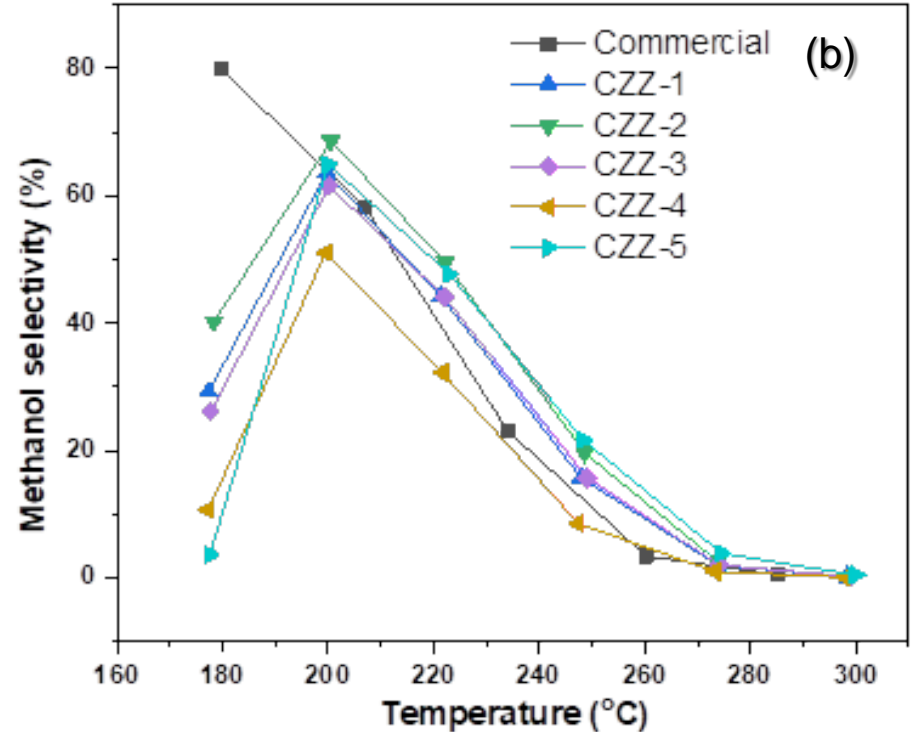
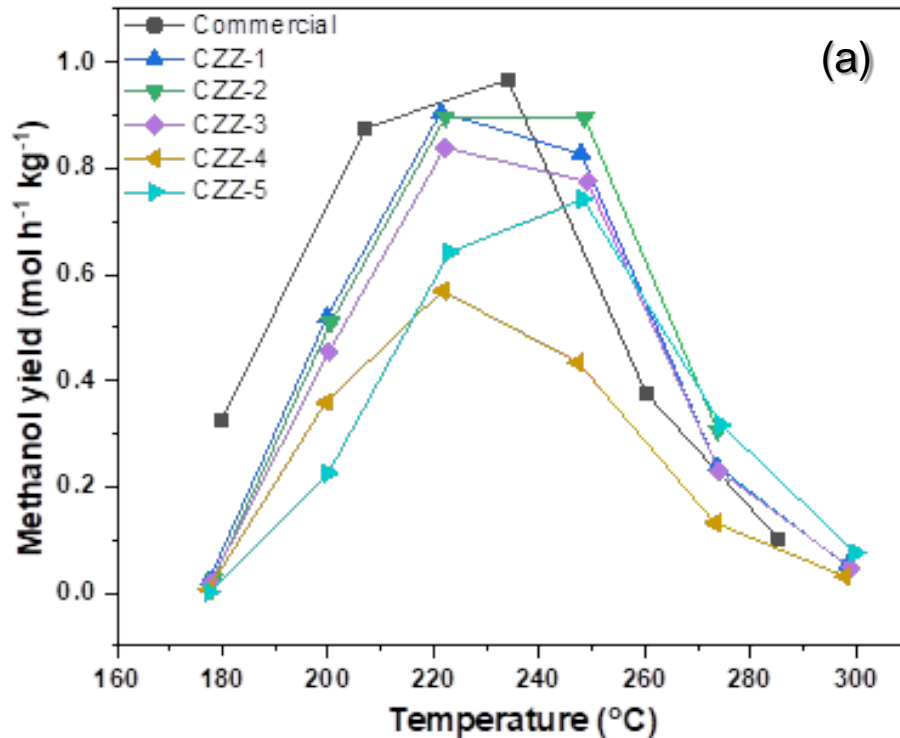
Name	Material (nominal ratio)	Actual ratio (calculated from XRF)	Surface Area (m ² /g)	BJH Pore size distribution (desorption)	
				Pore volume (cc/g)	Pore diameter (nm)
Commercial	Commercial catalyst (Cu/Zn/Al)	6.9/2.4/0.7	105	0.239	5.61
CZZ-1	Cu:Zr:Zn=6/3/1	5.4/3.8/0.8	93	0.175	3.82
CZZ-2	Cu:Zr:Zn=5/4/1	3.7/5.4/0.8	131	0.202	3.82
CZZ-3	Cu:Zr:Zn=4.5/4.5/1	3.3/5.8/0.8	164	0.237	3.82
CZZ-4	Cu:Zr:Zn=5/3/2	4.3/4.0/1.7	111	0.203	3.83
CZZ-5	Cu:Zr:Zn=6/1/3	5.4/1.7/2.9	59	0.260	3.83

- New synthesis route: metal dissolution method.
- CuO and ZnO are crystalline, while ZrO₂ seems to be in the amorphous phase or less crystalline.
- CZZ-2 and CZZ-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 Nanopowders using metal dissolution method:



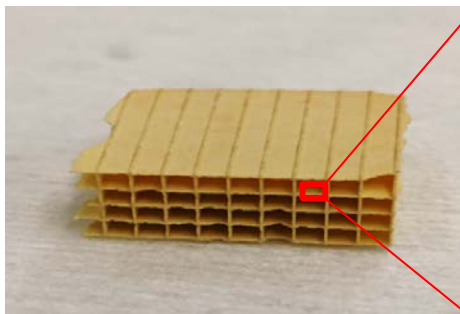
- Without adding promoters/ dopants, new catalysts showed higher methanol yield and selectivity than commercial Cu/ZnO/Al₂O₃ catalyst at 240 °C-300 °C.
- CZZ-2 with Cu:Zr:Zn ~5/4/1 showed the best yield and selectivity.

ACCOMPLISHMENTS

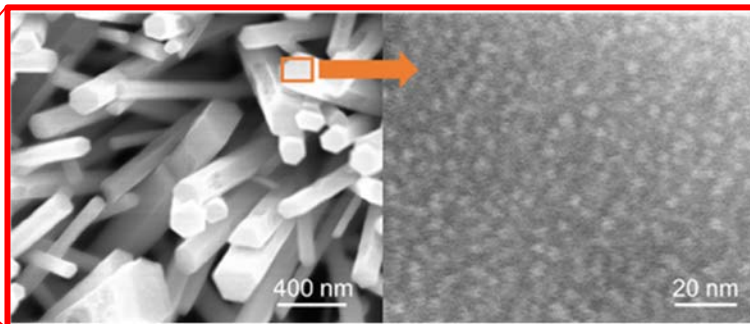
Synthesis of uniform Pt-Cu NP loaded ZnO nanoarray catalysts on 3D cordierite honeycomb by ALD and BCP methods

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

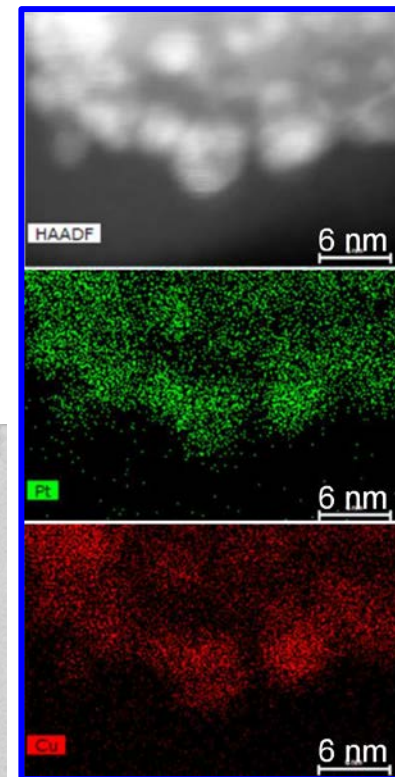
3D cordierite honeycomb



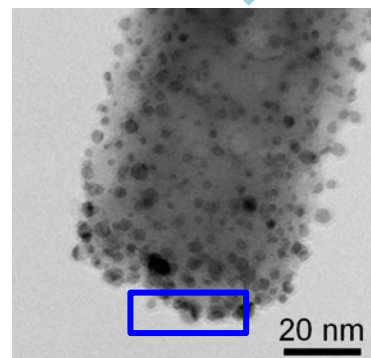
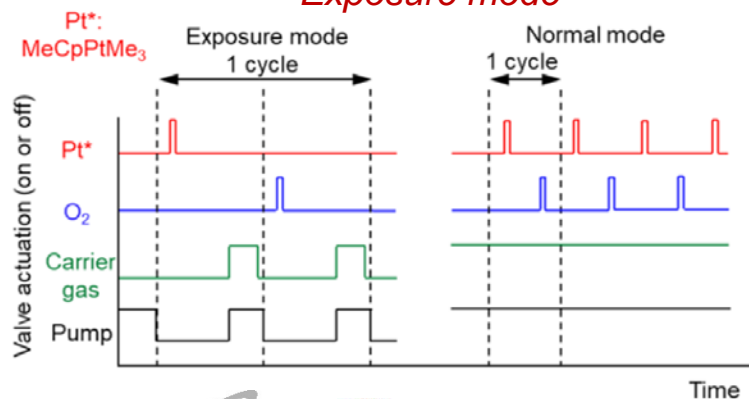
Uniform Pt NPs on ZnO nanoarray



Cu NPs
by BCP
& annealing



Modified Pt NP ALD protocol ensuring deposition uniformity:
"Exposure mode"



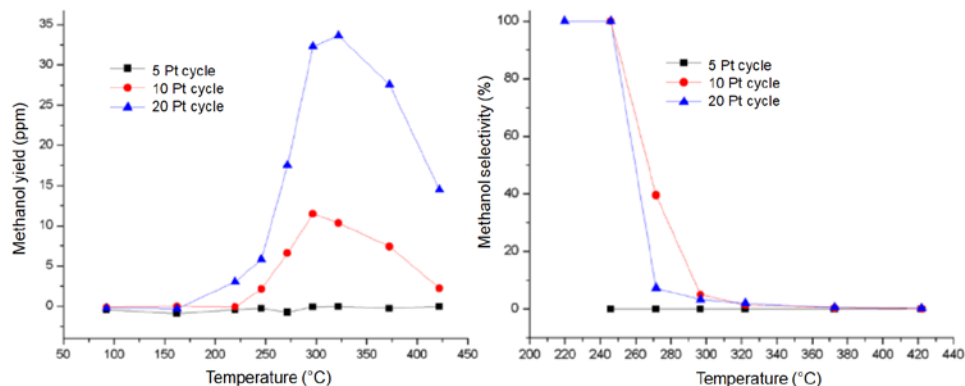
Pt-Cu alloy NP loaded ZnO nanoarray

ACCOMPLISHMENTS

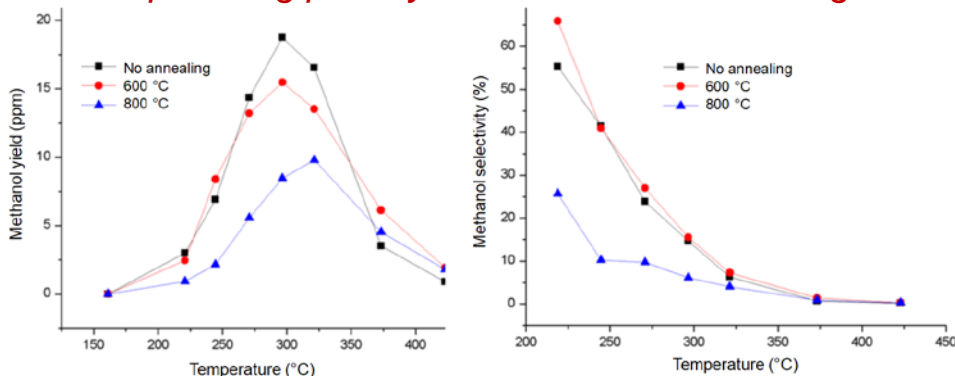
Enhanced CO₂ hydrogenation performance by ALD Pt-BCP Cu NP loaded ZnO nanoarray catalysts

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

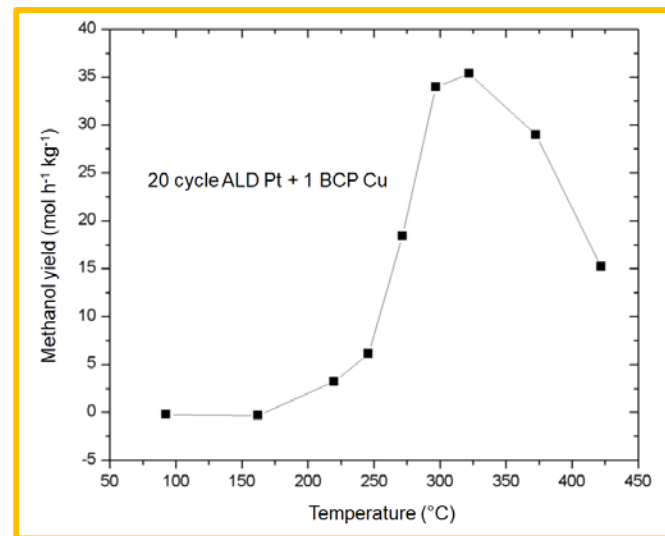
Optimizing Pt loading by ALD cycles



Optimizing post-synthesis thermal annealing



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



Methanol yield exceeding commercial reference

Catalyst type	Temp. (C)	Selectivity (%)	Yield (mol h ⁻¹ kg ⁻¹)
Commercial (Cu-Zn-Al powder)	197	54.3	1.25
ALD Pt-BCP Cu NPs on ZnO nanoarray	220	100	3.2

ACCOMPLISHMENTS

Reactor Development

1 bar pressure (Preliminary Data)	200°C		300°C	
	Equilibrium	Catalytic	Equilibrium	Catalytic
CO ₂ Molar Conversion (single pass)	59.5%	5.0%	56.9%	12.5%
Selectivity⁽¹⁾	0.0%	96.6%	0.0%	97.5%

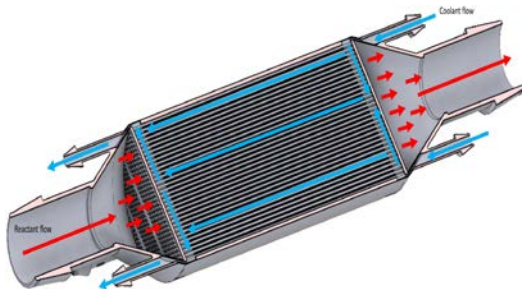
⁽¹⁾Selectivity = $[\text{CH}_3\text{OH} + (\text{CH}_3)_2\text{O}] / [\text{CH}_3\text{OH} + (\text{CH}_3)_2\text{O} + \text{CO} + \text{CH}_4]$

Catalytic reactions may enable feasibility - selectivity is zero without catalysis

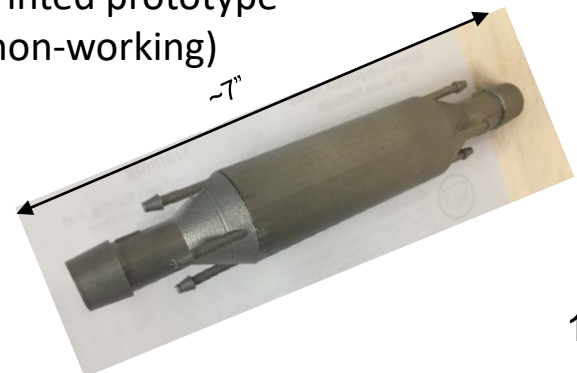
Advanced Catalytic Reactor Design Concepts

- 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)



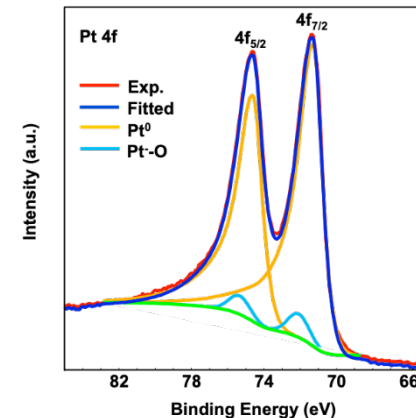
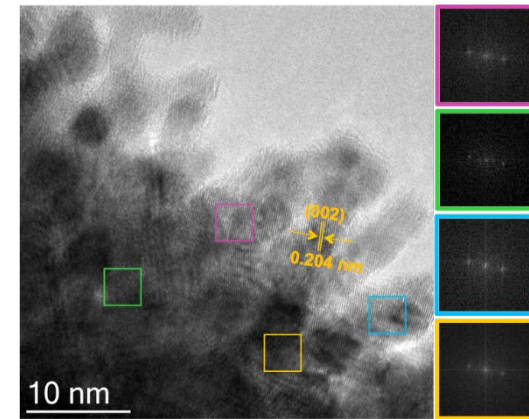
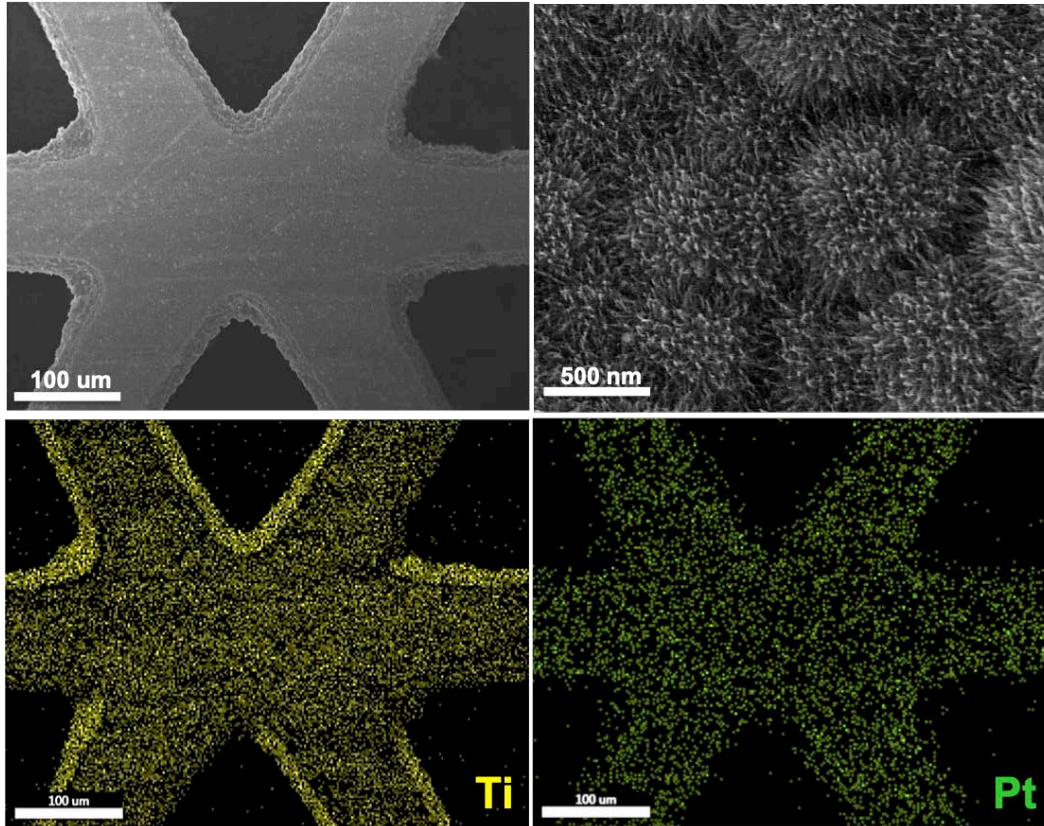
ACCOMPLISHMENTS

Successfully Fabricated Thin Pt Nanowire (PtNW) Electrodes

LGDL parameters: 25 μm thick; $\sim 50\%$ porosity; $\sim 400 \mu\text{m}$ pore opening

SEM-EDS characterization

High-resolution TEM (HRTEM)



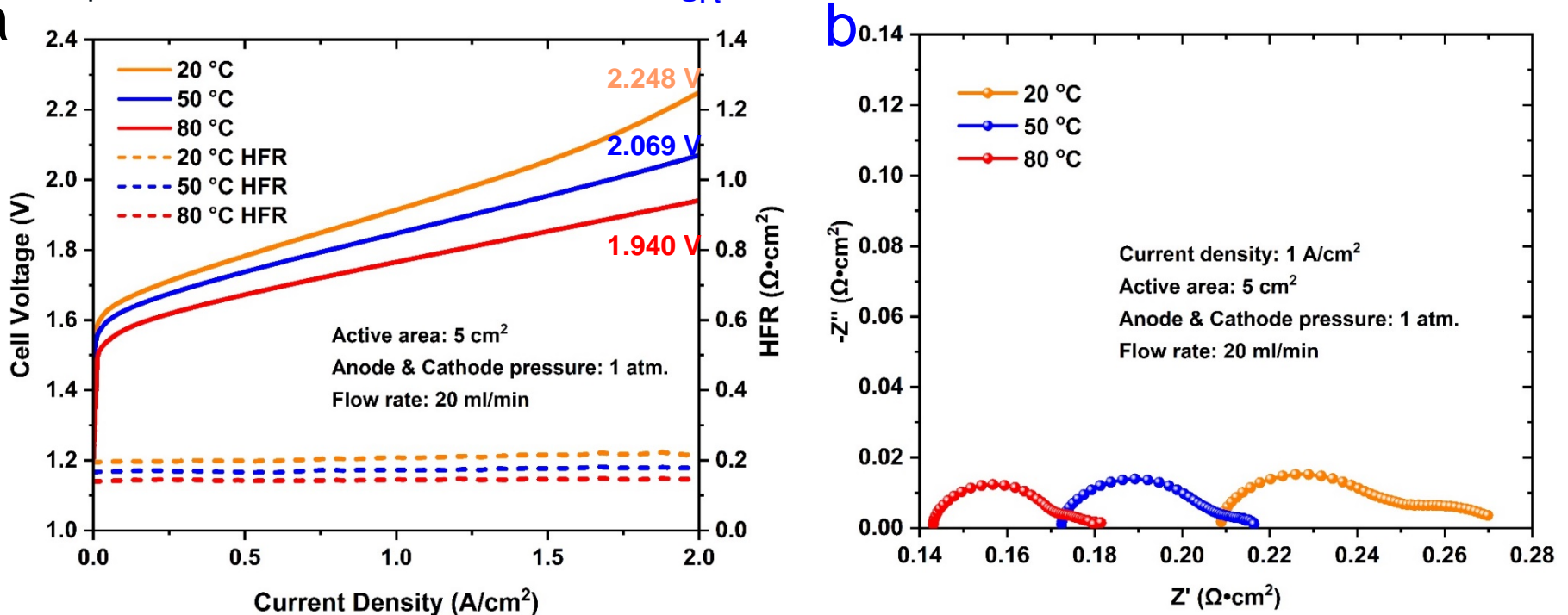
High-resolution
XPS spectrum
of Pt 4f

- Catalyst layer composed of PtNW was successfully grown on titanium LGDLs via chemical synthesis route at room temperature.
- Crystalline structure and diameter ($\sim 5 \text{ nm}$) 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 $0.05 \text{ mg}_{\text{Pt}}/\text{cm}^2$: **1.94 V** at $2 \text{ A}/\text{cm}^2$



- Thin PtNW GDE at $0.05 \text{ mg}_{\text{Pt}}/\text{cm}^2$ shows cell voltage of 1.94 V at $2 \text{ A}/\text{cm}^2$ at 80 °C.
- At lower temps 50 °C and 20 °C, cell voltages are 2.069 V and 2.248 V at $2 \text{ A}/\text{cm}^2$, respectively.
- Increasing operating temps reduce HFR values from $0.207 \Omega \cdot \text{cm}^2$ at 20 °C to $0.173 \Omega \cdot \text{cm}^2$ at 50 °C and $0.144 \Omega \cdot \text{cm}^2$ 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

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

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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂RR 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

SUMMARY

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 mg_{Pt}/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).