

Electrocatalytically Upgrading Methane to Benzene in a Highly Compacted Microchannel Protonic Ceramic Membrane Reactor

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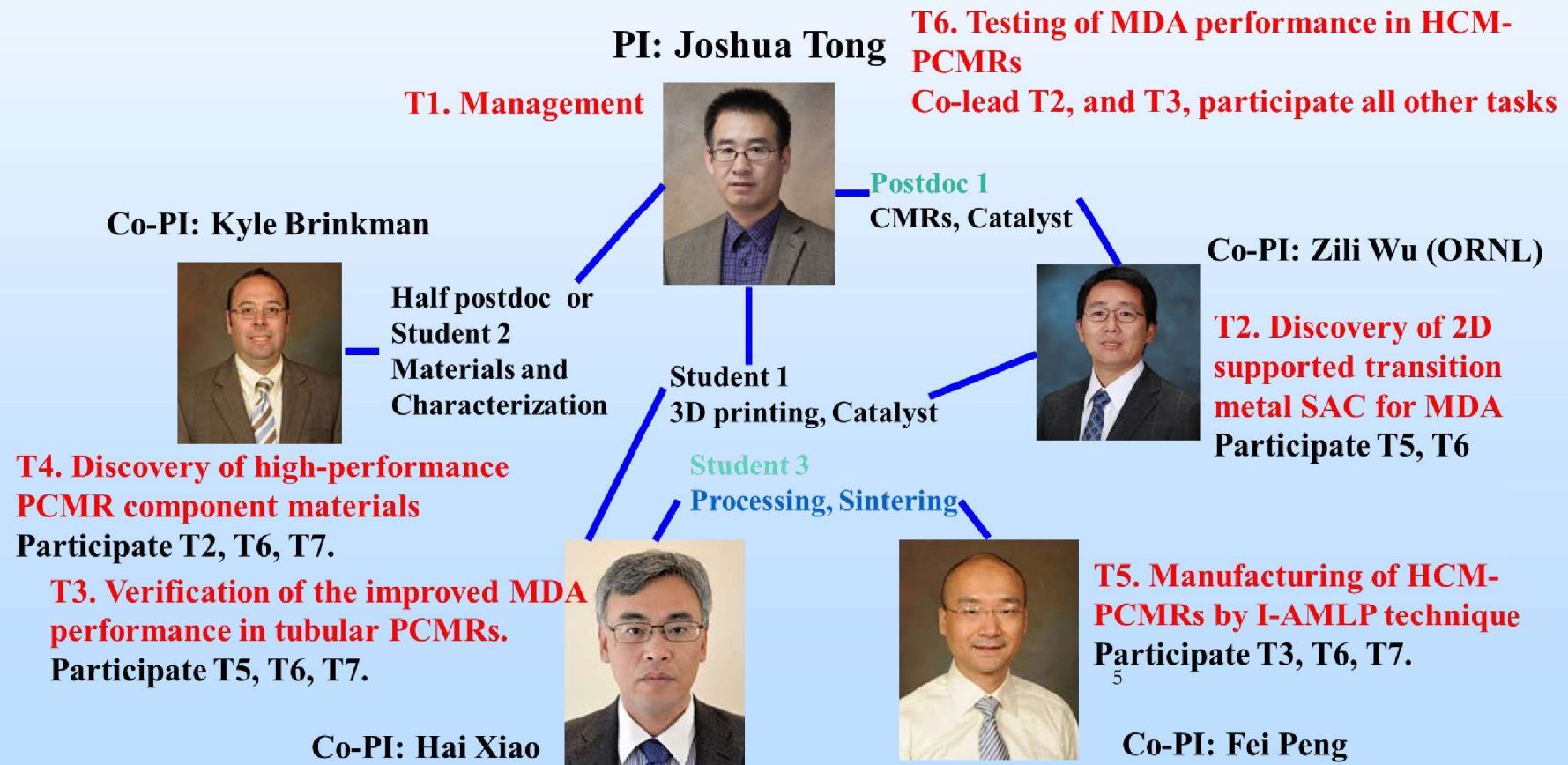
Project Overview

Funding and Participants

Project/Grant Period

06/01/2020 – 05/31/2024

Federal fund: \$1M, cost-share: \$250K, and total fund: \$1.25M



Project Overview

Goals and Objectives

The overarching goal is to develop highly compacted microchannel protonic ceramic membrane reactors (HCM-PCMRs) for efficient and cost-effective methane dehydrogenation to aromatics (MDA, e.g., benzene).

Demonstrate methane conversion $> 50\%$ with $>90\%$ selectivity for aromatics and light olefins at reaction temperatures $\leq 700^\circ\text{C}$.

Technology Background

1. Challenge of state-of-the-art MDA technologies

1) MDA on metal zeolite catalyst (Mo/HZSM-5 and Mo/HMCM-22)

Rapid catalyst deactivation because of coking, highest methane conversion and aromatic yield.

2) MDA on the single-atom catalyst (Fe@SiO₂)

- Low surface area ($< 1 \text{ m}^2/\text{g}$), which limits the activity.
- The reaction mechanism is unclear, and why Fe@SiO₂ catalyst.
- The reaction still requires very high temperatures ($> 1000^\circ\text{C}$), thus high energy consumption.
- The methane conversion (32%) and liquid yield (**benzene yield is 6.7%**) are still relatively low, which is still difficult to be used for dealing with flare/venting gas.

2. Challenges of protonic ceramic membrane reactors

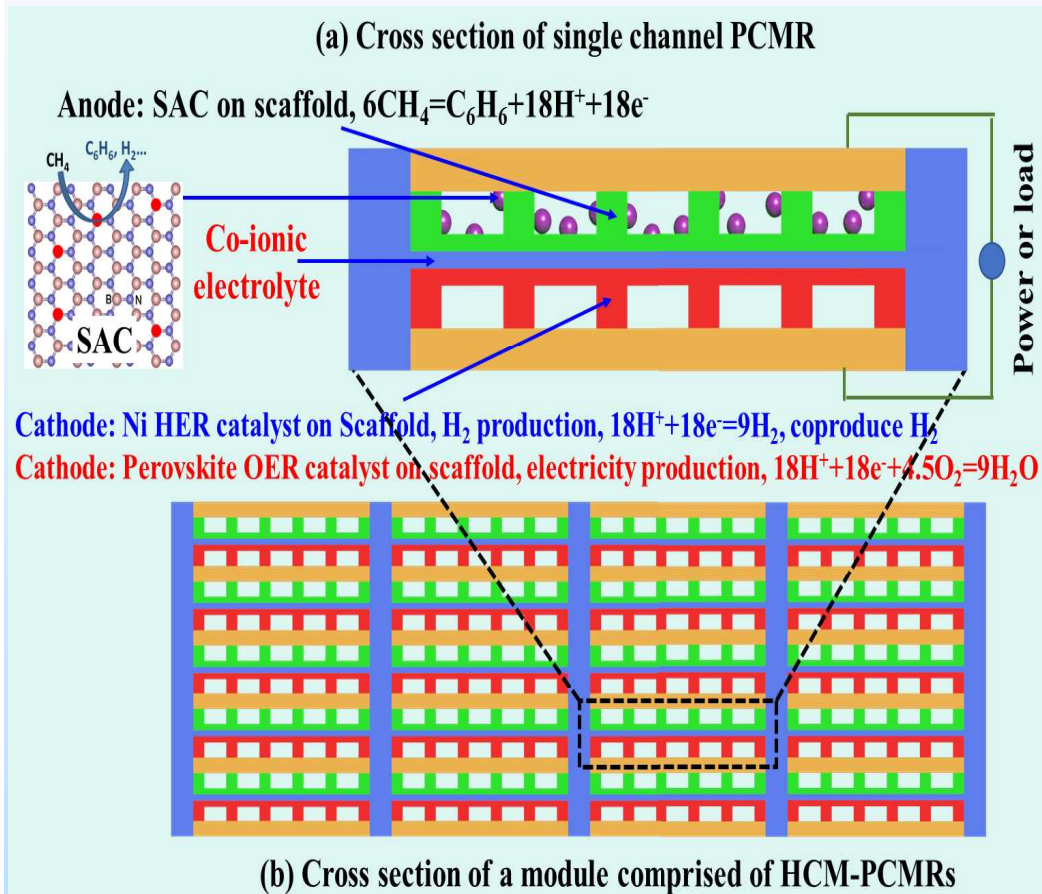
1) Low proton conductivity, 2) difficulty in adjusting co-ionic conductivity, 3) lack of electrode scaffold for MDA reaction, 4) difficulty in manufacturing into desired geometry and microstructure, and 5) small surface-to-volume ratio.

3. Challenges of additive manufacturing of ceramic energy devices

1) The cracks during ceramic consolidation (sintering), 2) the difficulty in handling precursors (pastes), 3) the difficulty in bonding, and 4) the difficulty in making heterogeneous layers.

Technical Approach/Project Scope

Technology Concept



Schematic description of highly compacted microchannel protonic ceramic membrane reactors (HCM-PCMRs)

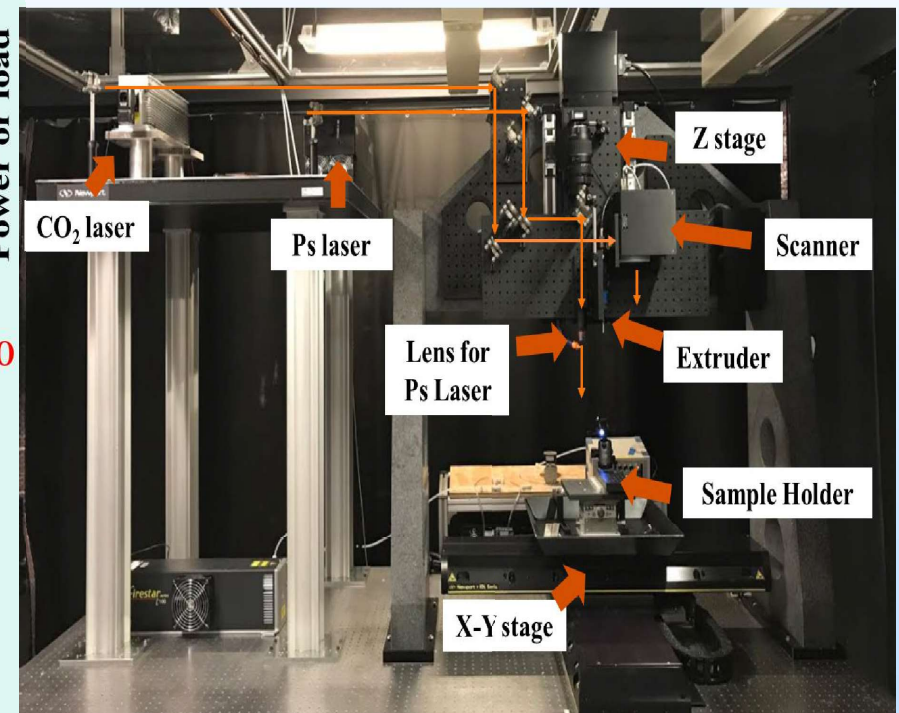
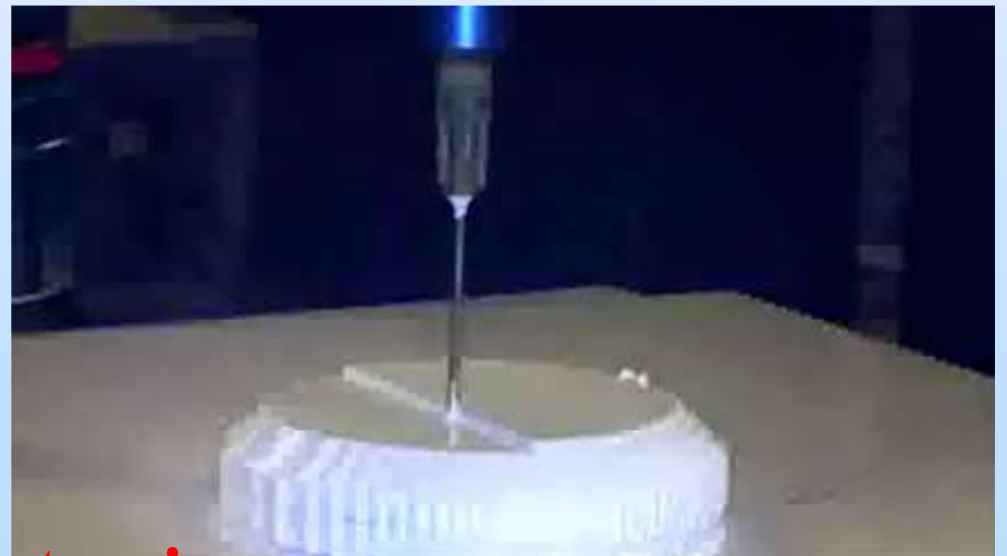
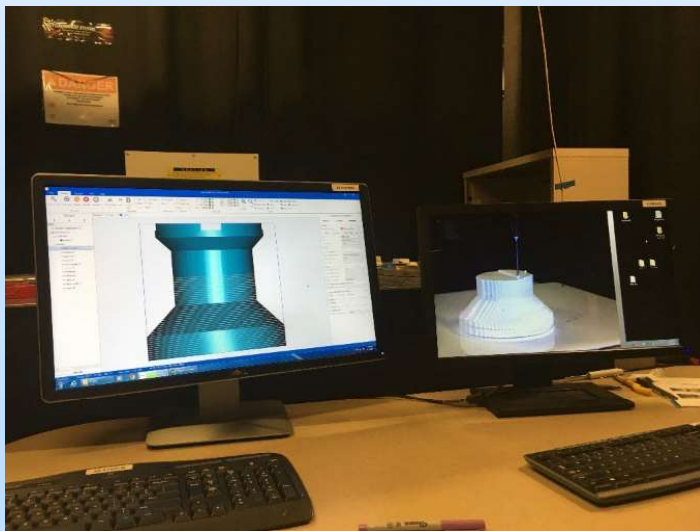
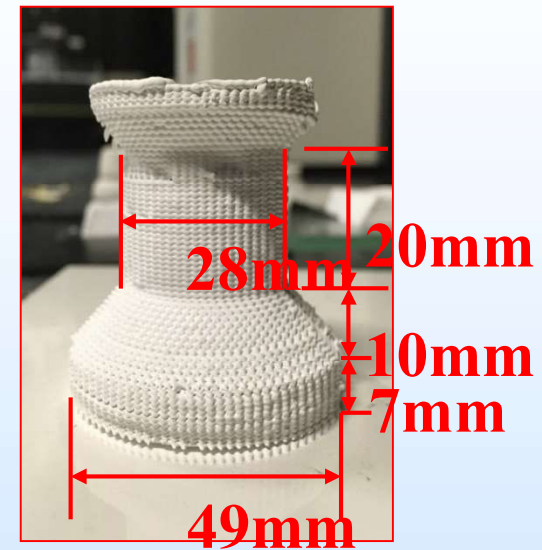
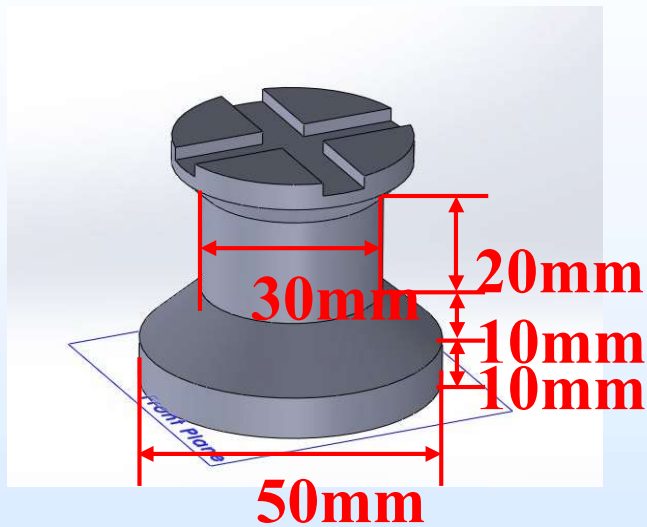


Photo of integrated additive manufacturing and laser processing (I-AML) ⁵

Technical Approach/Project Scope



Materials Extrusion

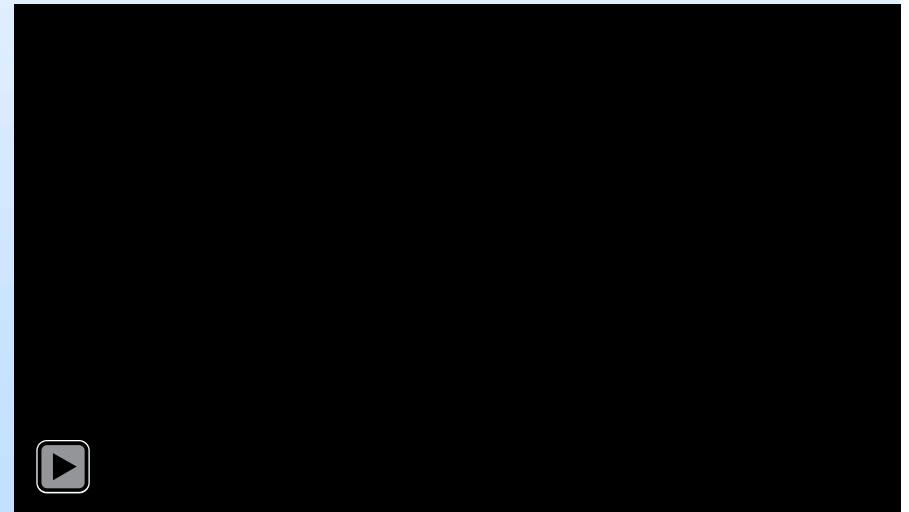
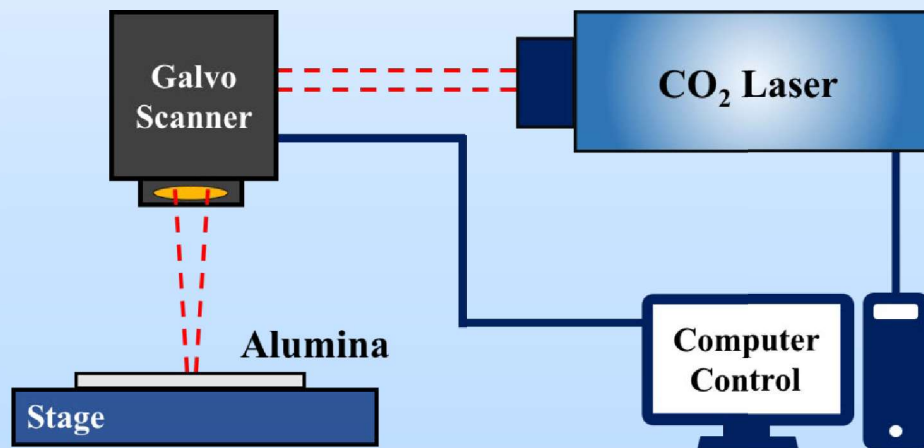
Technical Approach/Project Scope

Characteristics of CO₂ laser processing system

CO₂ laser: firestar v20, SYNRAD, Inc., WA, USA

Galvo scanner: intelliSCAN 14,
SCANLAB, Germany

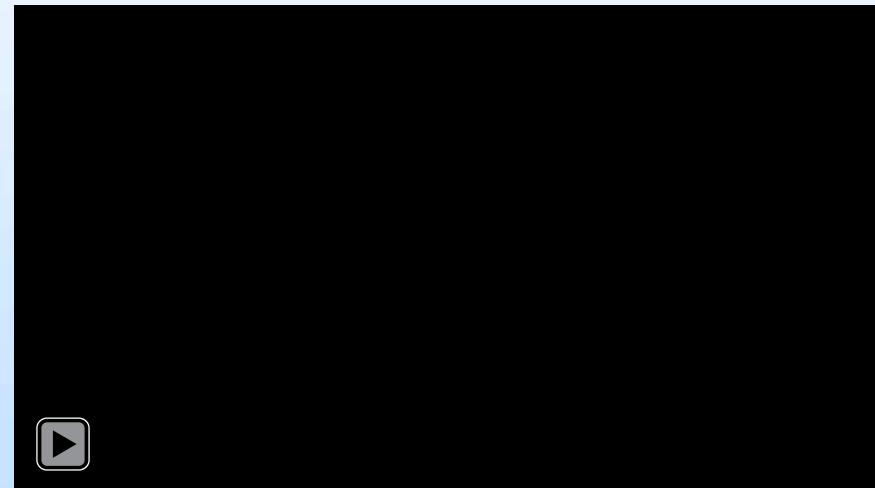
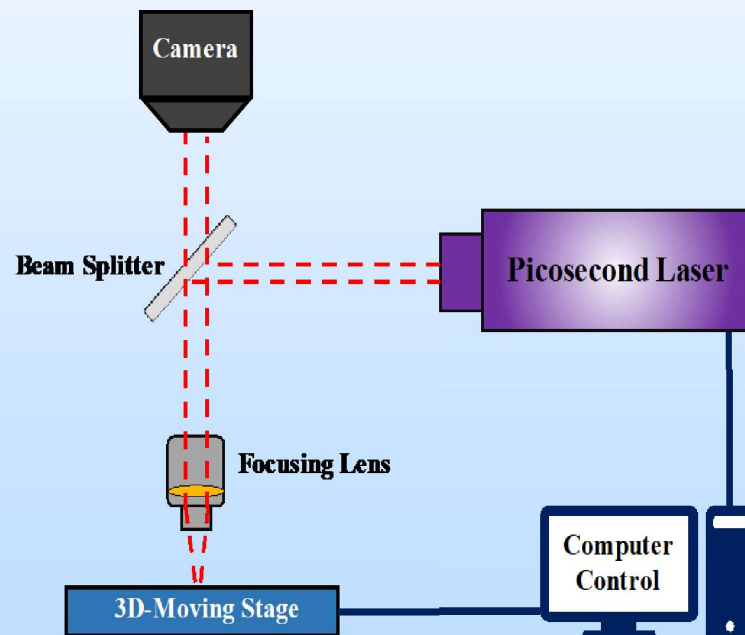
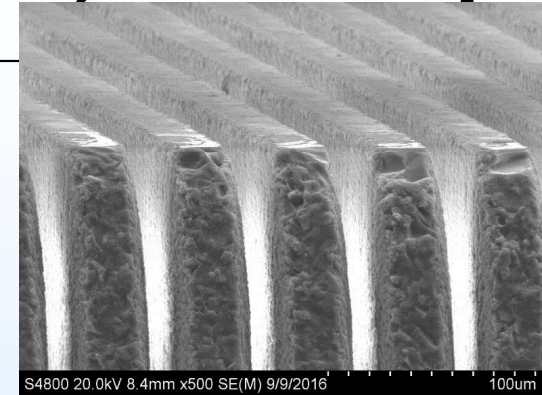
- ☐ Max output power: 20 W
- ☐ Operation: Continuous wave (CW)
- ☐ Mode quality: TEM₀₀, M₂ < 1.1
- ☐ Polarization: Linear
- ☐ Wavelength: 10.6 μm
- ☐ Beam diameter before focusing: 2.5 mm \pm 0.5 mm
- ☐ Beam diameter after focusing: 1 mm
- ☐ Marking speed: 2.5 m/s
- ☐ Positioning speed: 6.0 m/s
- ☐ Focal length: 200 mm
- ☐ Wavelength range: 9300 – 10600 nm



Schematic of the CO₂ laser processing system

Technical Approach/Project Scope

- ☐ Nd: YAG laser: APL-4000, Attodyne Inc., Canada
- ☐ Max. output power: 4 W
- ☐ Operation: Pulsed
- ☐ Mode quality: TEM00, M2 < 1.3
- ☐ Pulsed duration: 6 ps
- ☐ Beam diameter (using 5x objective): ~18 μm



Using PS- laser to machine a channel on an alumina substrate

Schematic of PS-laser machining system

Technical Approach/Project Scope

1. Discovery of high surface area 2D supported transition metal SAC for MDA

- Synthesis and testing of the state-of-the-art MDA catalysts
- Synthesis and test of M-SAC@2D catalyst for MDA

2. Verification of the improved MDA performance in tubular PCMRs

- Manufacture tubular PCMRs with a 3D printing technique
- Perform MDA in PCMRs integrated with Mo-HMCM-22 catalyst
- Perform MDA in PCMRs integrated with SAC of Fe@SiO₂

3. Discovery of high-performance PCMR component materials

- Develop co-ionic conducting electrolytes
- Develop triple-conducting cathodes
- Develop triple-conducting anode
- Develop cathode-supported PCMRs

4. Manufacturing of HCM-PCMRs by I-AMLPT technique

- 3D printing based on microextrusion
- Laser cutting of microchannels
- Sintering of multiple heterogeneous layers
- Infiltration
- Fabrication of HCM-PCMRs

Technical Approach/Project Scope

5. Testing of MDA performance in HCM-PCMRs

- Catalyst loading and assembling
- Perform MDA reaction in HCM-PCMRs
- Post-mortem analyses

6. Estimation of the energy conversion efficiency of HCM-PCMRs

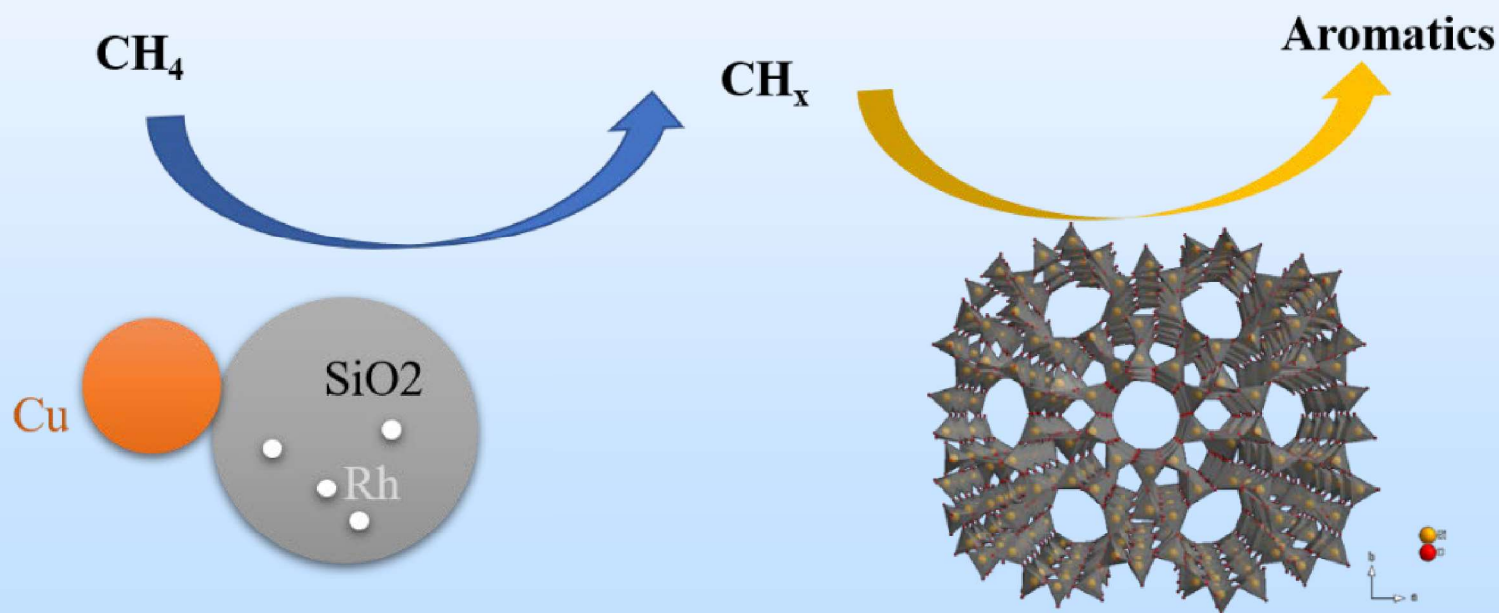
- Thermodynamics calculations and sequential reactor model
- Model simulations for the MDA process concept

- ❑ Demonstrate the transition metal-based high surface area SAC can be used for MDA. Verification for the tubular PCMRs based Fe@SiO₂ can have superior performance compared with Fe@SiO₂ in fixed bed reactors.
- ❑ Demonstrate the transition metal-based high surface area SAC can have much better performance than Fe@SiO₂. Demonstrate I-AMLP technique can manufacture microchannel PCMR.
- ❑ Demonstrate methane conversion > 50% with >90% selectivity for aromatics and light olefins at reaction temperatures ≤700°C. The durability test will be longer than 500 hours.

Progress and Technical Status

High Surface SAC for MDA

Propose new catalytic mechanism

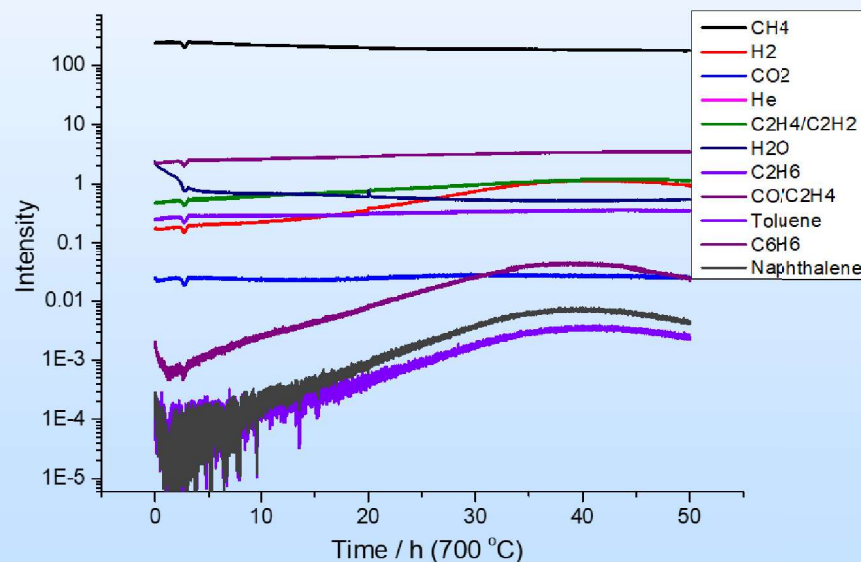
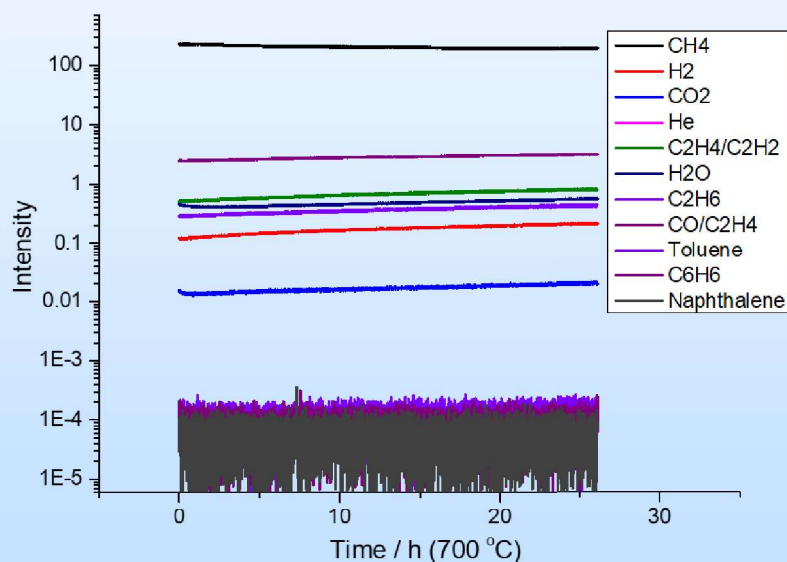


Progress and Technical Status

High Surface SAC for MDA

SAC Fe on mesoporous SiO₂

Verification of proposed catalytic mechanism for tandem catalyst

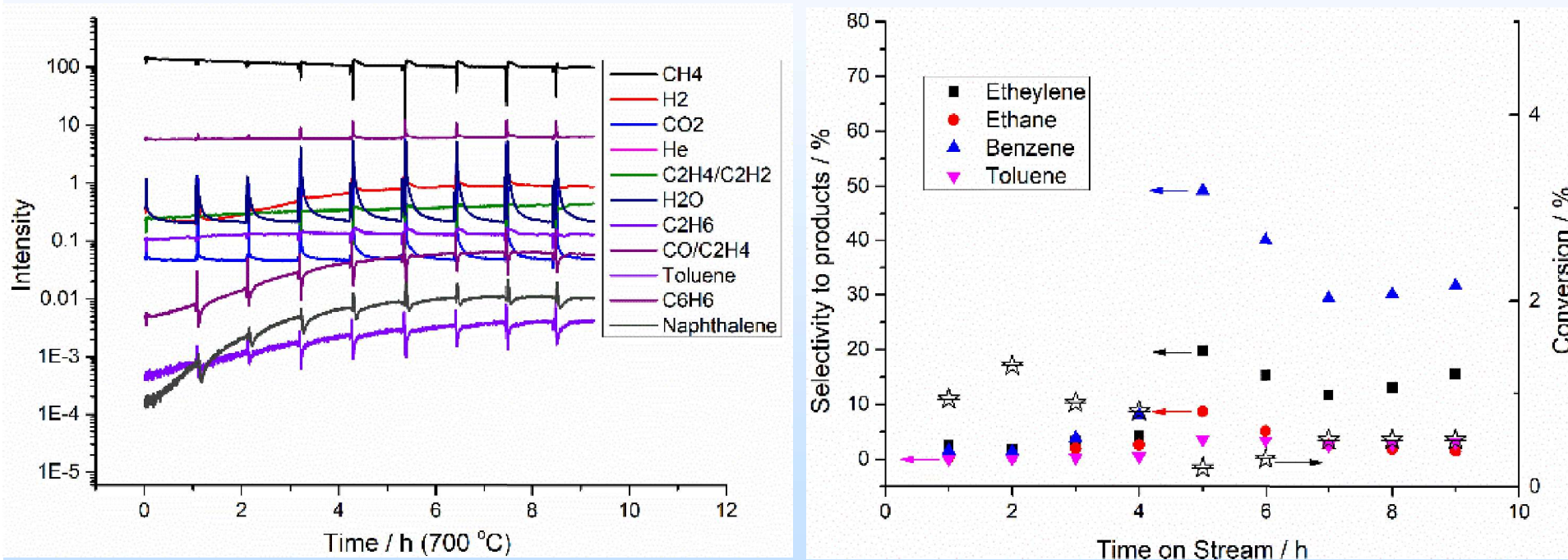


Methane conversion product of SAC Fe on mesoporous SiO₂ (0.2 wt% Fe) without (a)/with (b) ZSM-5.

Progress and Technical Status

High Surface SAC for MDA

SAC Rh-Cu on mesoporous SiO₂ (0.2wt% Rh & 2wt% Cu)



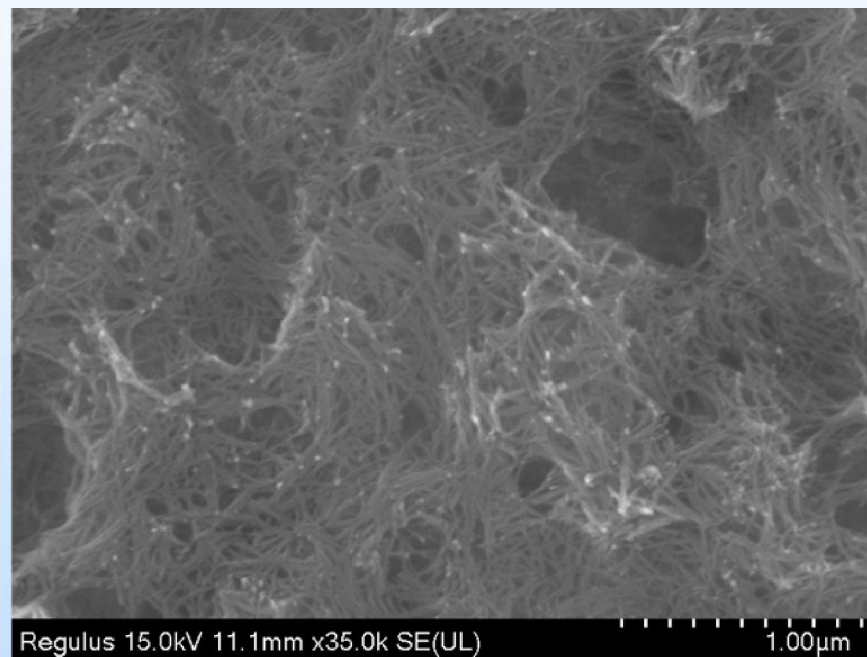
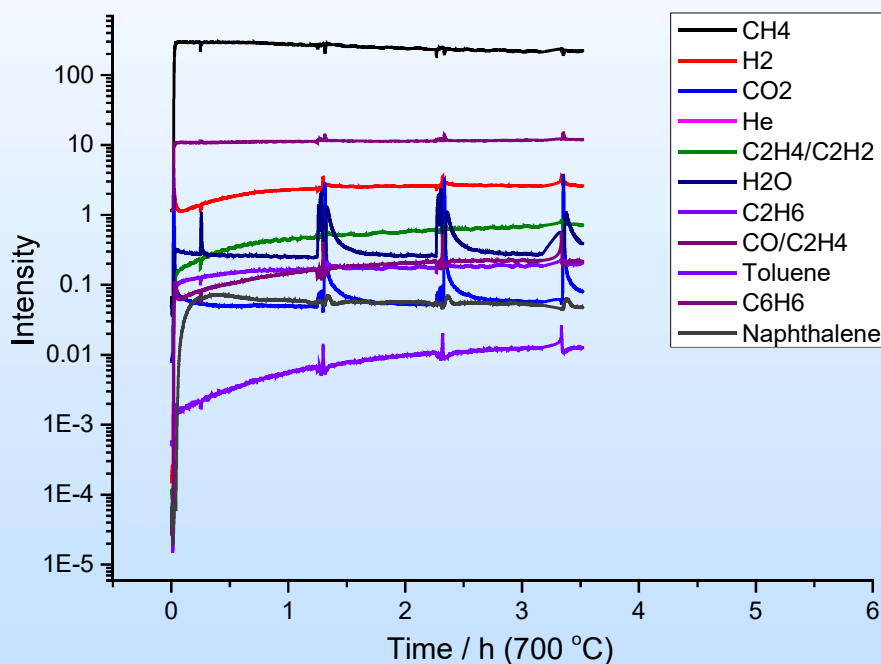
Methane conversion product of SAC Rh on mesoporous SiO₂ (0.2wt% Rh & 2wt%Cu). (a) MS intensity *vs.* reaction time, and (b) Selectivity and methane conversion *vs.* reaction time.

Our new SAC Rh-Cu mesoporous SiO₂ catalyst showed increasing benzene yield at 700°C over 10h operation.

Progress and Technical Status

High Surface SAC for MDA

SAC Rh on CuSiOx nanotube (0.5wt% Rh) +ZSM-5



Methane conversion product of SAC Rh on CuSiOx nanotube (0.5wt% Rh). (a) MS intensity *vs.* reaction temperature. (b) microstructure of CuSiOx nanotube

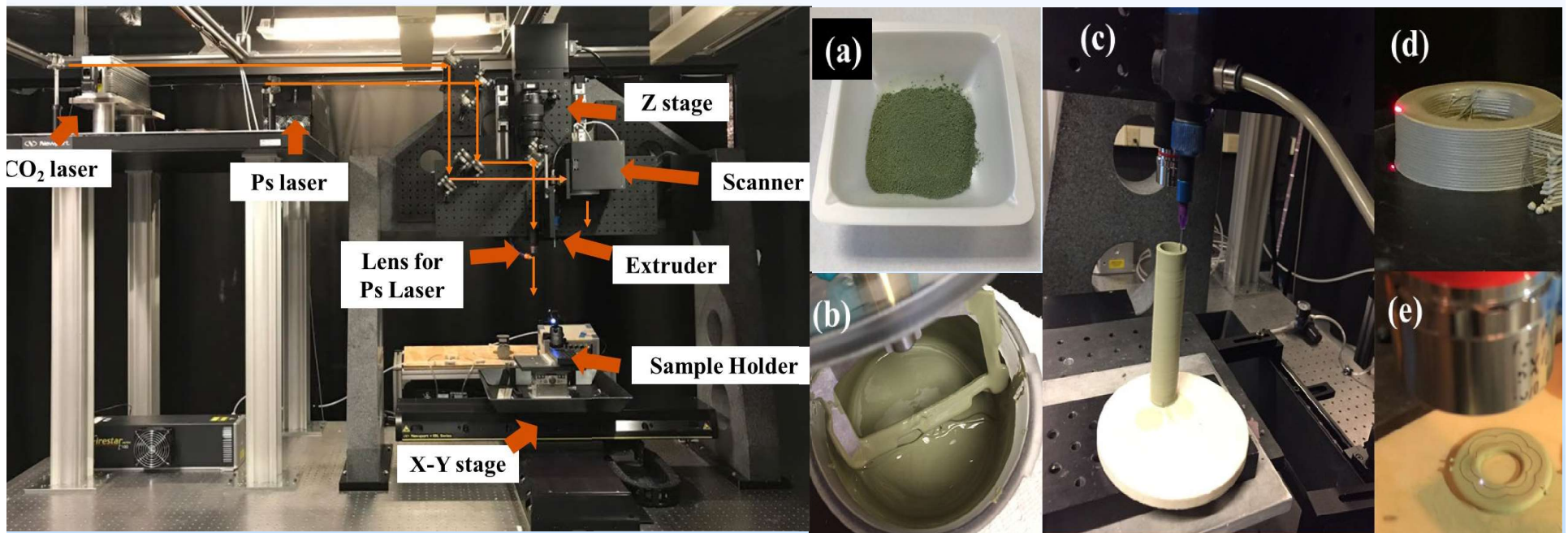
The intensity of products (such as benzene) doubled

**The selectivity: Benzene (25.1%), Ethylene (14%), Naphthalene (12.3%),
Toluene (4.9 %), total aromatics and olefin selectivity is 56.3%.**

Progress and Technical Status

Verification of MDA in PCMRs

Description of Integrated Additive Manufacturing and Laser Processing

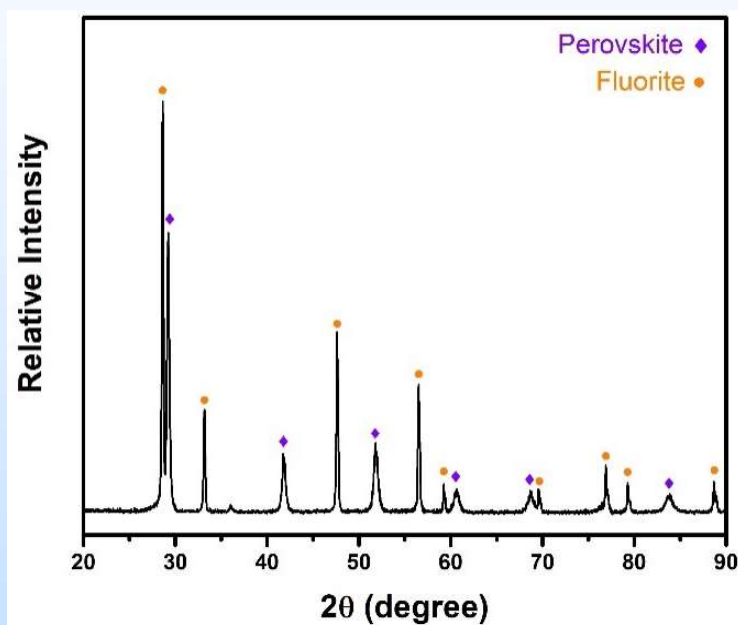


We have updated the I-AMLP technique for manufacturing PCMRs, which can print green layers with thickness 50-500 μ m. The utilization of low viscous paste and laser drying allow easy printing and bonding. The laser cutting allows introduction microchannels.

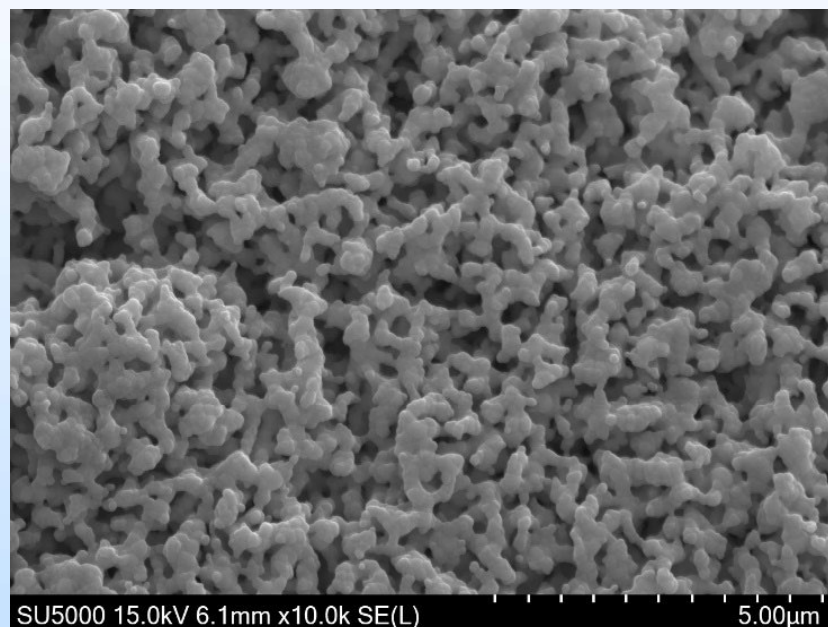
Progress and Technical Status

High-Performance PCMR Materials

Perovskite-Fluorite Composite Triple Conductors



(a)



(b)

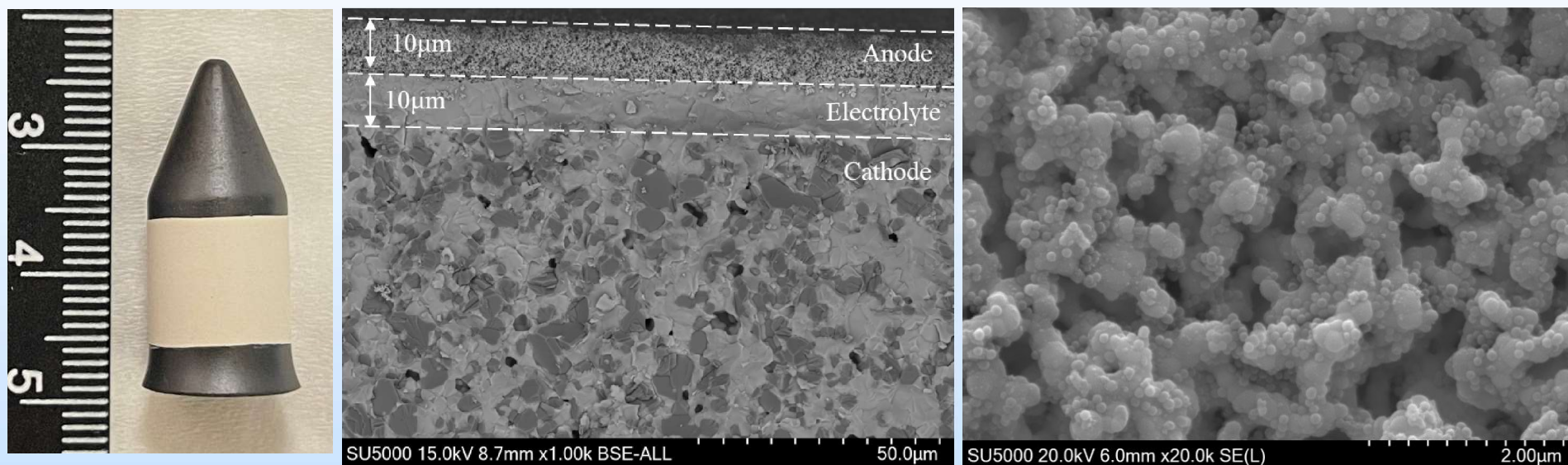
(a) XRD patterns of BCZYYb-YDC (1:2) composite powder (b) Microstructure of the BCZYYb-YDC electrode scaffold.

We can prepare porous BCZYYb-YDC perovskite-fluorite composite-based electrode scaffold by one-pot polymeric gelation method. The porosity and particle size were well controlled by polystyrene nanosphere as pore former.

Progress and Technical Status

High-Performance PCMR Materials

Perovskite-Fluorite Composite Triple Conductors loaded with SAC



(a)

(b)

(c)

(a) Photography of a tubular PCMR (b) Cross-sectional view of an untested tubular PCMRs (c) Microstructure of the anode scaffold loaded with SAC (Fe@SiO₂ nanosphere catalyst).

The Fe@SiO₂ nanosphere SAC can be well dispersed in the porous BCZYYb-YDC based triple-conducting (H⁺/O²⁻/e⁻) scaffold

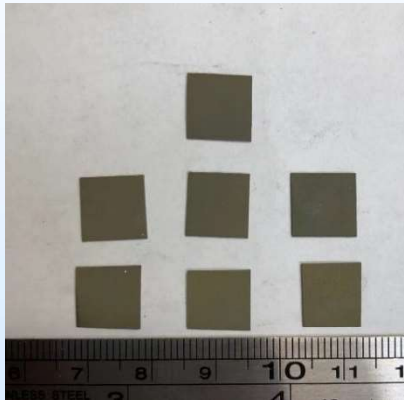
Progress and Technical Status

Manufacturing of HCM-PCMRs

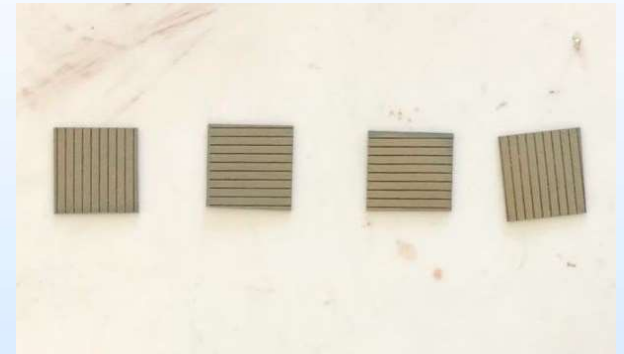
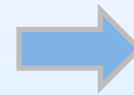
Preparation of multi-layer microchannel PCMR stacks



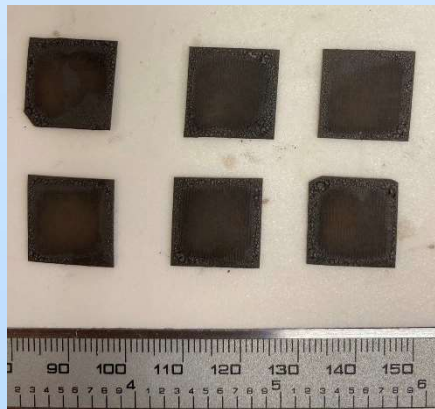
3D-printed green single cell



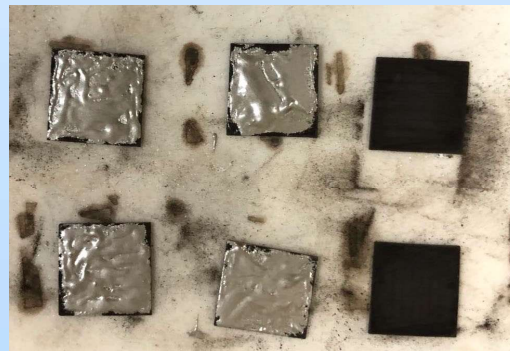
Sintered single cells cut by laser



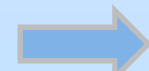
Single cells with microchannels by laser cutting



Applying interconnect



Stacking



700 ° C
4 hrs

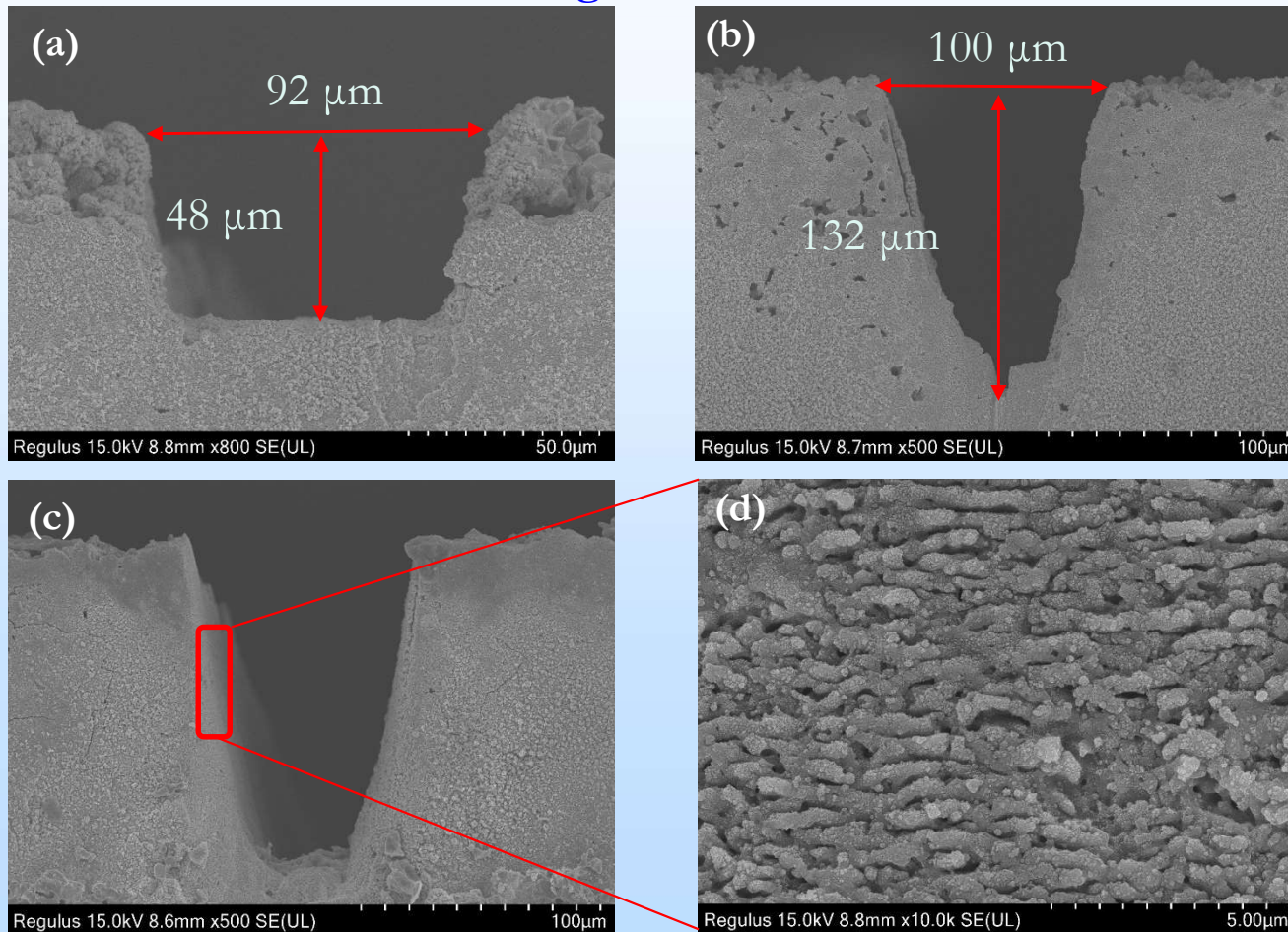


Infiltrating catalysts in microchannels

Progress and Technical Status

Manufacturing of HCM-PCMRs

Sintered single microchannels

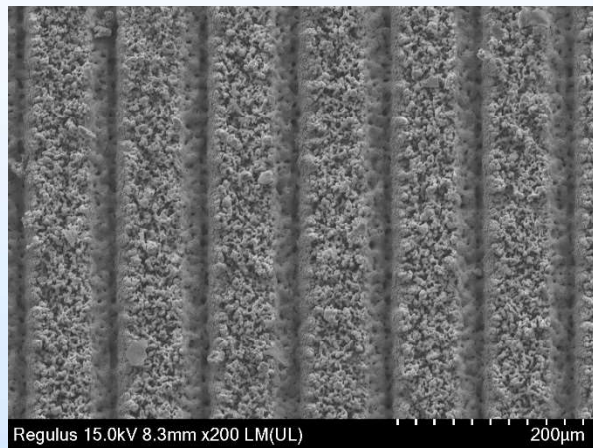


Flexible channel size can be cut via changing laser cutting parameters

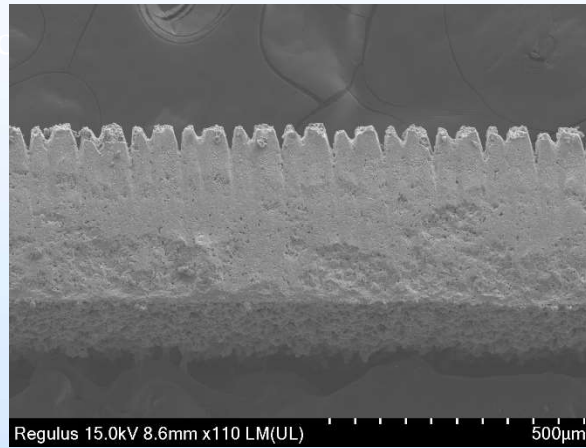
Progress and Technical Status

Manufacturing of HCM-PCMRs

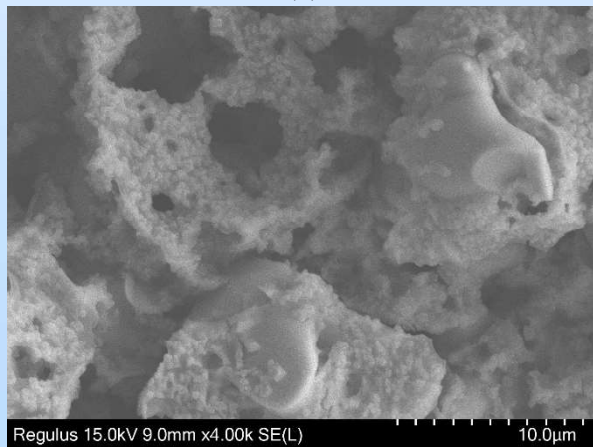
Sintered microchannel single PCMRs



(a)



(b)



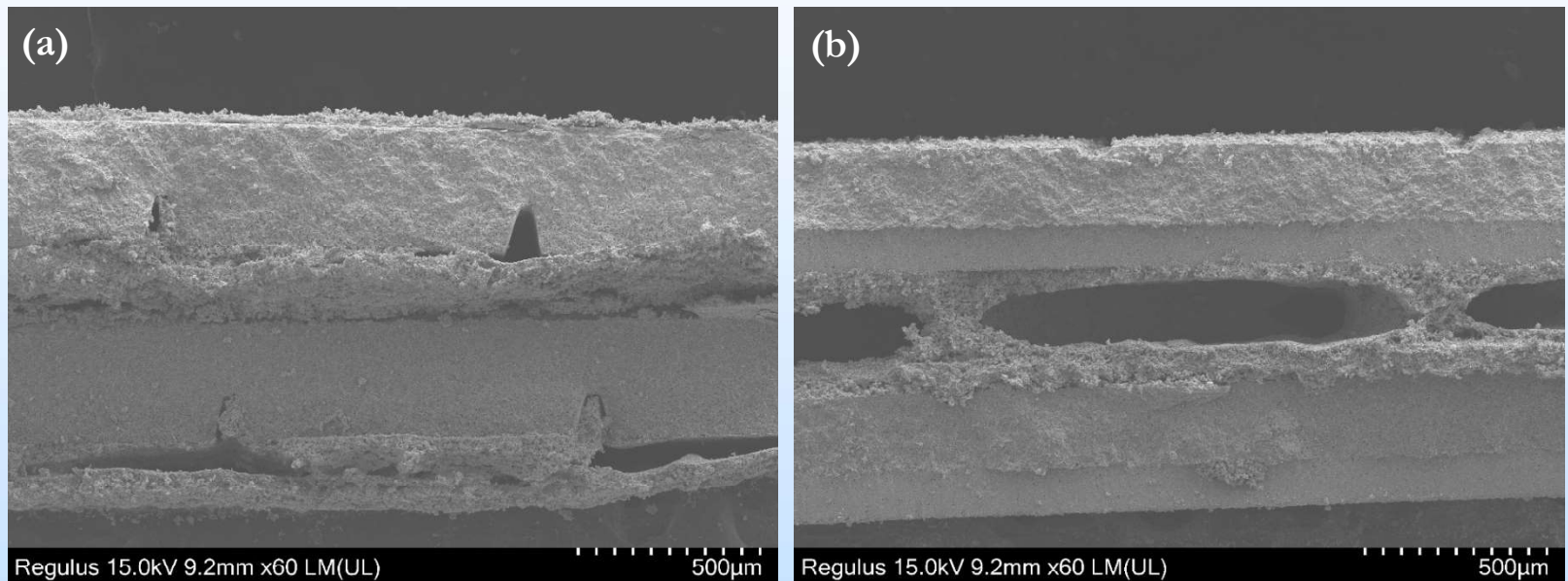
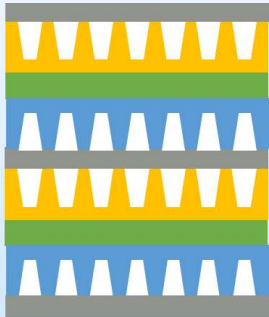
(c)

Microstructure of microchannel PCMRs. (a) cross-sectional view of PCMRs with microchannels on anode scaffold. (b) surface view of microchannels on anode scaffold. (c) microstructure of anode scaffold loaded with BCFZY0.1 catalyst

Progress and Technical Status

Manufacturing of HCM-PCMRs

Sintered Microchannel PCMR two-cell stacks



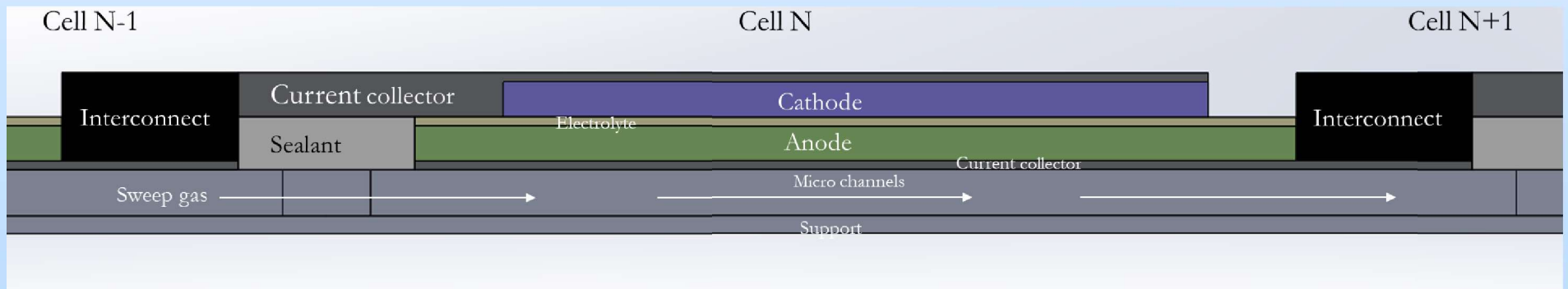
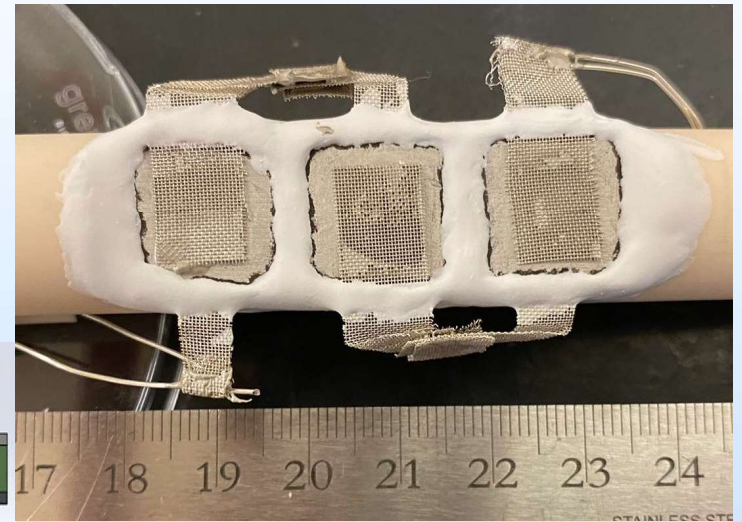
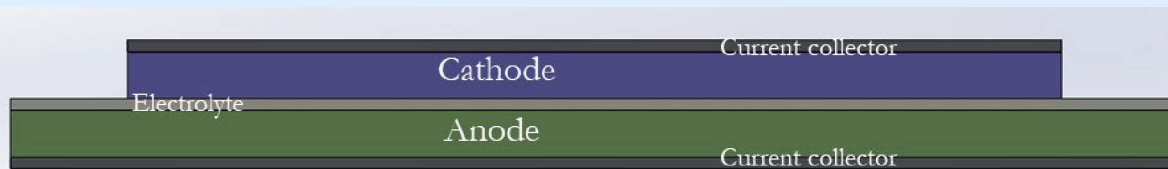
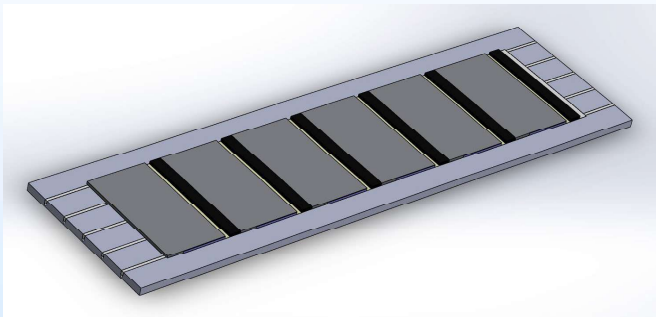
Microstructure of a microchannel PCMR stack. (a) cross-sectional view of the PCMR shown with cathode microchannels. (b) cross-sectional view of the PCMR shown with anode microchannels.

The silver was still porous, which was not good as interconnect for this type stacks. So, we change the stack design to segment-in-series type.

Progress and Technical Status

Manufacturing of HCM-PCMRs

A segment-in-series stack design

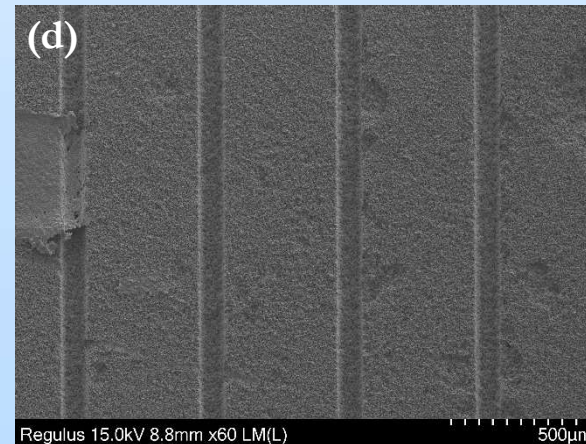
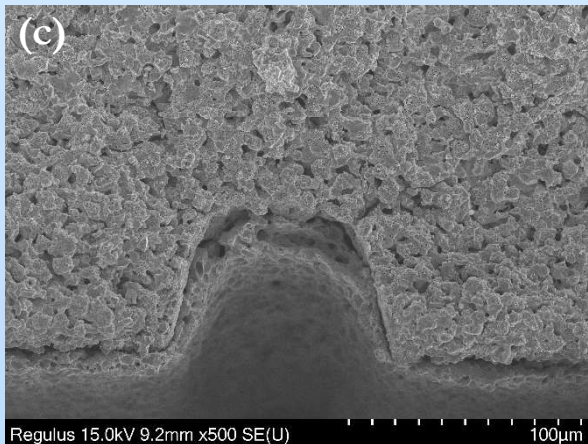
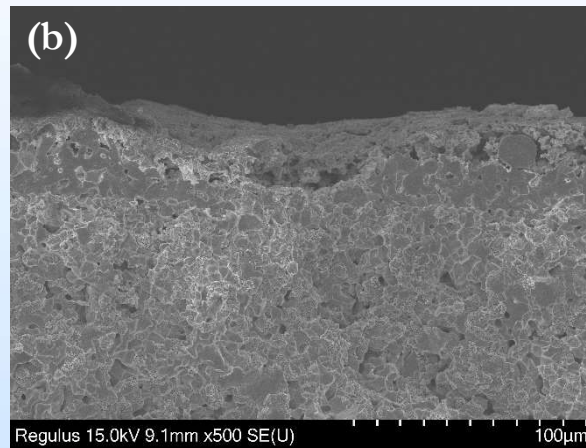
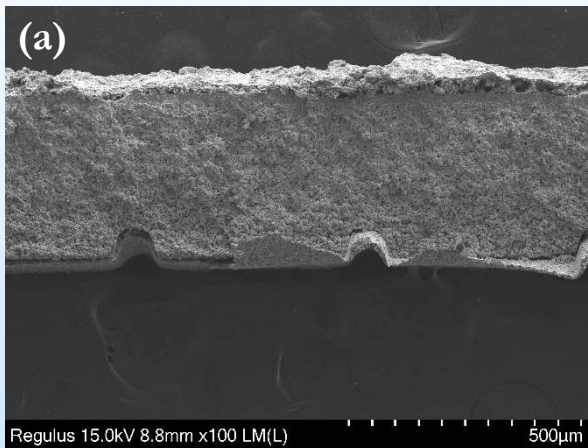


The 3-cell stack has over 12 layers structure with microchannels on anode and cathode

Progress and Technical Status

Manufacturing of HCM-PCMRs

A sintered microchannel PCMRs from the segment-in-series stack



(a) cross-sectional view of microchannels PCMRs
(b) zoom in image of the cross-sectional view, showing a microchannel on anode. (c) cross-sectional microstructure of a microchannel on cathode (d) surface microstructure of microchannels on cathode

Progress and Technical Status

Accomplishments to Date

Catalysts/Materials Synthesis and Characterization

- 1) Synthesized SAC Fe on mesoporous SiO_2 . The onset reaction temperature to produce benzene was as low as 700°C , 350°C lower than the reported Fe@SiO_2 catalyst.
- 2) Fe@SiO_2 (mesoporous) catalyst mixed with ZSM-5 could significantly increase the aromatic production rate. It provides a new strategy to make highly active DMA catalysts.
- 3) Rh-Cu@SiO_2 (mesoporous) catalyst with ZSM-5 could significantly improve the aromatic production rate and operating stability.
- 4) Rh @ CuSiO_x nanotube catalyst mixed with ZSM-5 could double benzene yields.
- 5) Perovskite-fluorite dual-phase composites could be prepared by the one-pot sol-gel method. The porosity and particle size were well controlled by using polystyrene nanosphere as pore former. The XRD, SEM, and EDX characterization indicate that the perovskite-fluorite composites were formed.

Progress and Technical Status

Accomplishments to Date

Manufacturing and Testing of PCMRs

- 1) Prepared appropriate paste/slurry for the 3D printing of anode, electrolyte, and cathode.
- 2) By optimizing picosecond laser cutting parameters, we have achieved the anode/cathode microchannel with an open width of $\sim 100\mu\text{m}$ and depth of $50\text{-}150\mu\text{m}$.
- 3) Infiltrated SAC catalysts into porous electrodes with microchannels. Showed well dispersion, good adhesion, and nano-sized catalyst particle.
- 4) Manufactured tubular PCMRs with triple-conducting perovskite-fluorite composite anode scaffold and infiltrated Fe@SiO_2 SAC catalyst.
- 5) Manufactured microchannel PCMRs stacks with over 12 layers. Showed fully dense electrolyte, porous electrodes, accurate control of microchannel size.

Progress and Technical Status

Lessons Learned

- The direct MDA is challenging work. The development of 2D catalyst has challenge. However, the mesoporous materials with high surface area can help improve this problem.
- The integration the MDA catalyst with PCMR electrode has some challenge based on zeolite powder. We solved this problem by using mesoporous silica sol-gel process.
- The sealing of PCMRs has challenge. We are trying to search different type sealants

Progress and Technical Status

Synergy Opportunities

- This project was performed by four PI/Co-PI from Clemson University and one Co-PI from ORNL.
- The PI/Co-PIs communicates extensively during the budget period 1, which integrated catalyst preparation, additive manufacturing, and electrochemical characterization together for establishing project for efficient and clean conversion natural gas.
- Some of these team members explored other fund sources inspired by the current work.
- The team is trying to submit more related proposals based on electrocatalytic protonic ceramic membrane reactors for other chemical manufacturing.

Project Summary

Key Findings

- We found new Fe/SiO₂ (mesoporous), Rh-Cu/SiO₂ (mesoporous), Rh/CuSiO_x nanotube SAC for MDA, which can significantly lower MDA reaction temperature. The addition of ZSM-5 can significantly improve MDA rate.
- The perovskite-fluorite composite triple-conducting electrode scaffold loaded with SAC catalyst was prepared for the tubular PCMRs via I-AMLPP method.
- The I-AMLPP method can successfully make multilayer PCMRs stacks with desired microchannels.
- Demonstrate the performance of feasibility to fabricate HCMC-PCMRs.

Project Summary

Next Steps

- Further check the zeolite effect. Quantify the MDA performance and achieve a high-performance catalyst.
- Demonstrate high performance based on the perovskite-fluorite composite triple-conducting electrode scaffold with SAC catalysts.
- Improve the manufacturing of microchannel PCMRs and test the performance of PCMRs for MDA.
- Demonstrate the improved MDA performance in HCMC-PCMRs

Appendix

The following slides are appendix.

Benefit to the Program

One of the main areas of interest of DOE's Natural Gas Infrastructure Program is to develop process-intensified technologies for the upcycling of flare/venting gas (mainly CH₄) into transportable, value-added liquid products. However, the current technologies for natural gas to liquid (GTL) are facing significant challenges: **1)** the deployment and intermittent operation at isolated sites often lack convenient access to electricity, make-up water, and other required services; and **2)** the GTL technologies (e.g., indirect catalytic conversion of methane to liquid chemicals via synthesis gas) are confirmed to be complicated, inefficient, and environment unfriendly (enormous CO₂ emission), requiring large economies of scale to compete in existing commodity markets, and relying on extensive supporting infrastructure to be available. **Thus, indirect GTL technologies are presently impractical for meeting the program's objectives.**

- **Development of new catalysis materials**
- **Highly efficient conversion at a lower temperature and 2) as separation.**
- **Highly efficient conversion at a lower temperature.**
- **Long-term efficient conversion.**
- **Convenient access to electricity and make-up water and highly efficient conversion at a lower temperature.**
- **Modular, compact, integrated, and transportable technologies.**
- **Technology platform capable of producing a variety of products**

Project Overview

Goals and Objectives

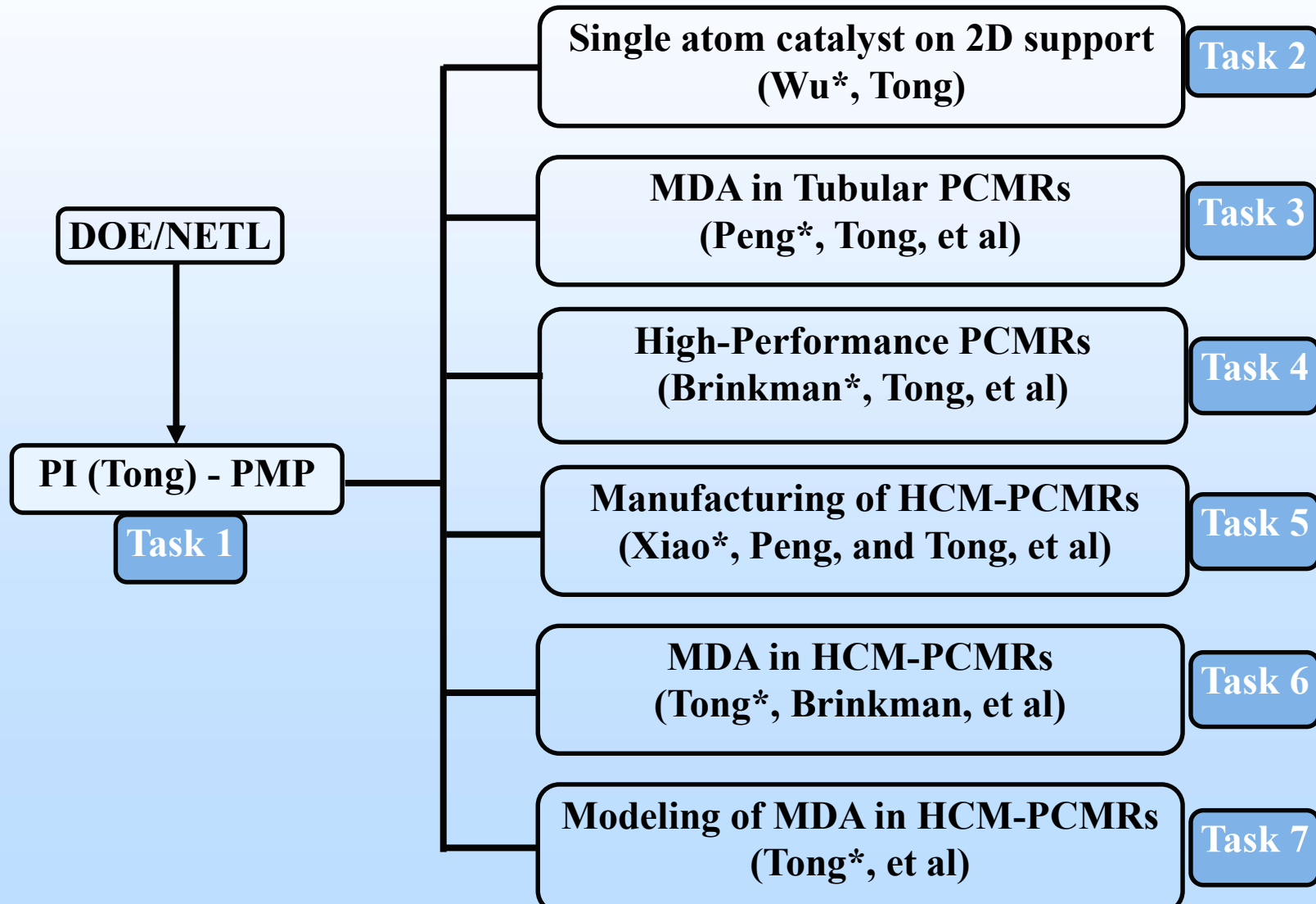
The overarching goal is to develop a highly compacted microchannel protonic ceramic membrane reactors (HCM-PCMRs) for efficient and cost-effective methane dehydrogenation to aromatics (MDA, e.g., benzene).

BP1: Show the feasibility to apply new high surface area 2D matrix confined single transition metal catalysts for MDA; verify the improved MDA performance by tubular PCMRs with state-of-the-art catalysts.

BP2: Discover new 2D single-atom catalysts showing much better performance than the state-of-the-art Fe@SiO₂, Mo-HZSM-5, and Mo-HMCM22; and show the feasibility to apply new laser 3D printing technique for manufacturing microchannel PCMRs.

BP3: Manufacture modules of HCM-PCMRs by laser 3D printing technique and prove the long-term stable and efficient production of benzene from methane with new 2D SACs.

Organization Chart



Gantt Chart

[illegible]

Gantt Chart

	TECHNICAL TASKS	YEAR 1						YEAR 2				YEAR 3			
		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12	Q13	Q14
Task 1.0	Project management and planning														
Task 2.0	Discovery of high surface area 2D supported transition metal SAC for MDA														
Subtask 2.1	Mo-HMCM-22 and Fe@SiO ₂														
Milestone 2.1	MDA performance comparable to state-of-the-art results														
Subtask 2.2	2D single atom catalyst for MDA														
Milestone 2.1.1	MDA performance comparable to state-of-the-art results														
Milestone 2.1.2	MDA performance increase by 50% compared to the state-of-the-art results														
Task 3.0	Verification of the improved MDA performance in tubular PCMRs														
Subtask 3.1	I-AMLP of tubular PCMRs														
Milestone 3.1	PCMR, >10cm ² , >300mV/cm ² , and >200h														
Subtask 3.2	MDA in PCMRs with Fe@SiO ₂														
Milestone 3.2	PCMR for MDA has performance better than Fe@SiO ₂														
Subtask 3.3	MDA in PCMRs with 2D SAC														
Milestone 3.3	PCMR for MDA has performance better than new 2D SAC														
Task 4.0	Additively manufacture the sensor module prototypes														
Subtask 4.1	Co-ionic electrolyte														
Milestone 4.1	conductivity>0.01S/cm, degradation <2% per 1000h														
Subtask 4.2	Triple conducting anode														
Milestone 4.2	ASR<0.1Ω·cm ² and degradation <2% per 1000h at 650°C														
Subtask 4.3	Triple conducting cathode														
Milestone 4.3	ASR<0.1Ω·cm ² and degradation <5% per 1000h at 650°C														
Subtask 4.4	Performance of new PCMRs														
Milestone 4.4	Cathode supported single cells with performance comparable to the state-of-the-art results														

Milestones Title & Description	Planned Compl. Date	Actual Compl. Date	Verification method	Comments
Task 1: Project management and planning				
Project Management Plan	Q1	Q1	Manager approval	
Technology Maturation Plan	Q1	Q1	Manager approval	
Techno-Economic Analysis	Q1	Q1	Submission	Continuous
Task 2: Discovery of high surface area 2D supported transition metal SAC for MDA				
MS-2.1: Obtain Mo/HMCM-22 and Fe@SiO₂ catalysts with MDA performance comparable to the literature for integrating with PCMRs and comparing with new M-SAC@2D catalysts		Q6	RPPR	100%
MS-2.2: Obtain highly efficient, stable, and coke-resistant M-SAC@2D catalysts that increase 50% in the CH₄ conversion to aromatics/olefins compared with Fe@SiO₂ catalyst.		Q10	RPPR	92%
Task 3: Verification of the improved MDA performance in tubular PCMRs				
MS-3.1: Print tubular PCMRs with an area >10cm², peak power density > 300mW/cm², and stability >200h at 650°C under Air/H₂ and demonstrate large-area cathode supported tubular PCMRs can achieve performance comparable to the small-area button cells (with an area ~0.5cm²).		Q6	RPPR	100%
MS-3.2: Establish tubular PCMRs based on Mo/HMCM-22 and run MDA in electricity and hydrogen co-production modes to achieve better MDA performance than the fixed bed reactor.		Q8	RPPR	91%
MS-3.3: Proves the PCMRs based on SAC of Fe@SiO₂ to have better performance than the Fe@SiO₂ in fixed bed reactor and the PCMRs with Mo-HMCM-22 catalyst.		Q10	RPPR	62%

Milestones Title & Description	Planned Compl. Date	Actual Compl. Date	Verification method	Comments
Task 4: Discovery of high-performance PCMR component materials				
MS-4.1: Obtain co-ionic conducting electrolytes with the desired proton and oxygen ion conductivity ratio. The conductivity should be >0.01 S/cm, and the conductivity degradation rate should be <2% per 1000h in a 5% H₂ atmosphere.	Q8		RPPR	92%
MS-4.2: Obtain triple conducting ORR and HER cathodes with ASR less than 0.1 Ω·cm² and degradation rate less than 5% per 1000 h at 650°C	Q8		RPPR	87%
MS-4.3: Obtain triple conducting anodes with ASR less than 0.1 Ω·cm² and degradation rate less than 5% per 1000h at 650 °C. The MDA reaction atmosphere should not show a marked effect on anode stability. The excellent compatibility with MDA catalysts should also be satisfied.	Q8		RPPR	87%
MS-4.4: Obtain cathode-supported button single cells with performance comparable to anode-supported single cells from the newly developed materials, showing the compatibility with the MDA reaction.	Q8		RPPR	100%
Task 5: Manufacturing of HCM-PCMRs by I-AMLPT technique				
MS-5.1: Obtain green films with a thickness of 100μm 1mm and an area near 100cm². The single wall has a width of < 500μm and a height of < 2mm. The printed channels between the wall can be down to 500μm. The bonding between different layers and filament should be indistinguishable.	Q6		RPPR	100%
MS-5.2: Obtain microchannels with a width of 50μm and a depth of 50μm after firing for both cathode and anode scaffolds.	Q7		RPPR	100%
MS-5.3: Obtain the crack-free integrated multiplayer structure comprised of electrolyte, cathode scaffold, anode scaffold, and interconnect for more than 12 layers.	Q10		RPPR	55%

Milestones Title & Description	Planned Compl. Date	Actual Compl. Date	Verification method	Comments
MS-5.4: Obtain the proper infiltration procedures to introduce nanoparticles less than 100nm in cathode and anode scaffolds.	Q10		RPPR	100%
MS-5.5: Obtain HCM-PCMRs with active area >20cm² and electrochemical properties and microstructure good enough for MDA testing.	Q12		RPPR	70%
Task 6: Testing of MDA performance in HCM-PCMRs				
MS-6.1: Obtain HCM-PCMRs with desired MDA catalyst loading and prepare for MDA.	Q12		RPPR	Not started
MS-6.2: Obtain conversion > 50% with >90% selectivity for aromatics and light olefins at reaction temperatures ≤700°C. The durability test should be longer than 500h.	Q14		RPPR	Not started
MS-6.3: Understand catalysts and HCM-PCMR for further improvement of the performance.	Q14		RPPR	Not started
Task 7: Estimation of the energy conversion efficiency of HCM-PCMRs				
MS-7.1: Establish reasonable models	Q14		RPPR	Not started
MS-7.2: Achieve reasonable process efficiency of HCM-PCMR and show superiority to other MDA processes.	Q14		RPPR	Not started
BP1: Demonstrate the transition metal-based high surface area SAC can work for MDA. Verification for the tubular PCMRs based on Fe@SiO₂ can have superior performance than Fe@SiO₂ in fixed bed reactors.	Q6		RPPR	98%
BP2: Demonstrate that the transition metal-based high surface area SAC can have much better performance than Fe@SiO₂, and the I-AMLP technique can manufacture microchannel PCMR.	Q10		RPPR	50%
BP3: Achieve CH₄ conversion > 50% with >90% selectivity for aromatics and light olefins at reaction temperatures ≤700°C; the durability >500h, conversion > 50% with >90% selectivity for aromatics/olefins at reaction temperatures ≤700°C; the durability test longer than 500h.	Q14		RPPR	
Final report				