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

DE-FE0031871

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2021 Carbon Management and Oil and Gas Research Project Review Meeting

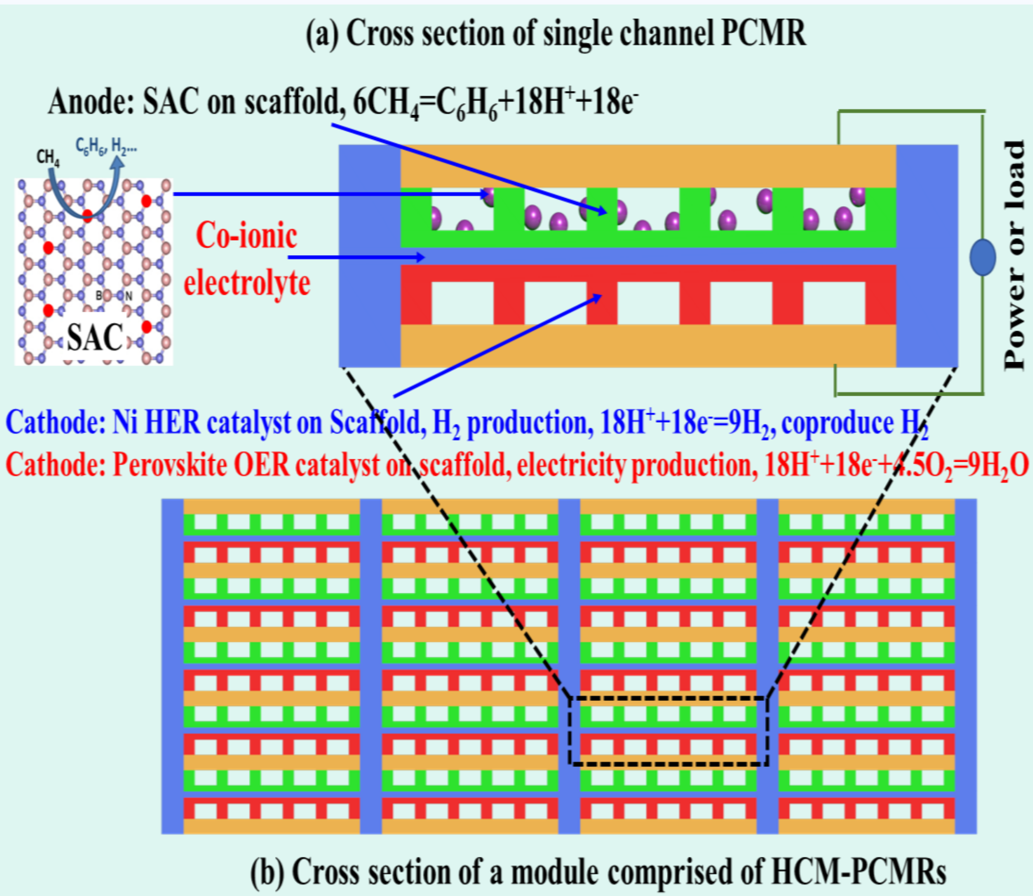
August 2021

Presentation Outline

- Technical Status
- Accomplishments to Date
- Lessons Learned
- Synergy Opportunities
- Appendix

Technical Status

Technology Concept



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

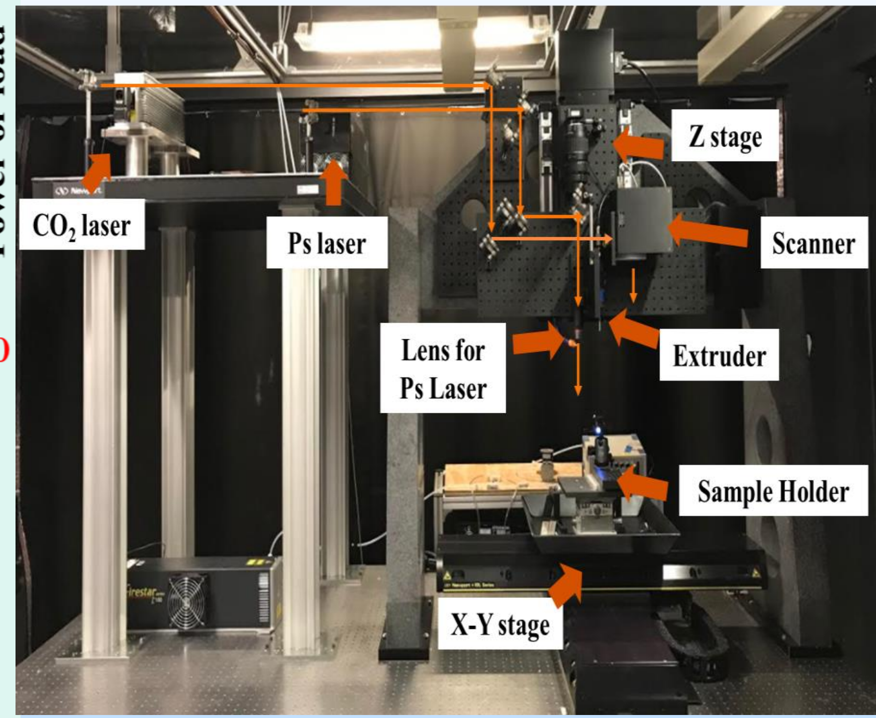


Photo of integrated additive manufacturing and laser processing (I-AMLP)

Technical Status

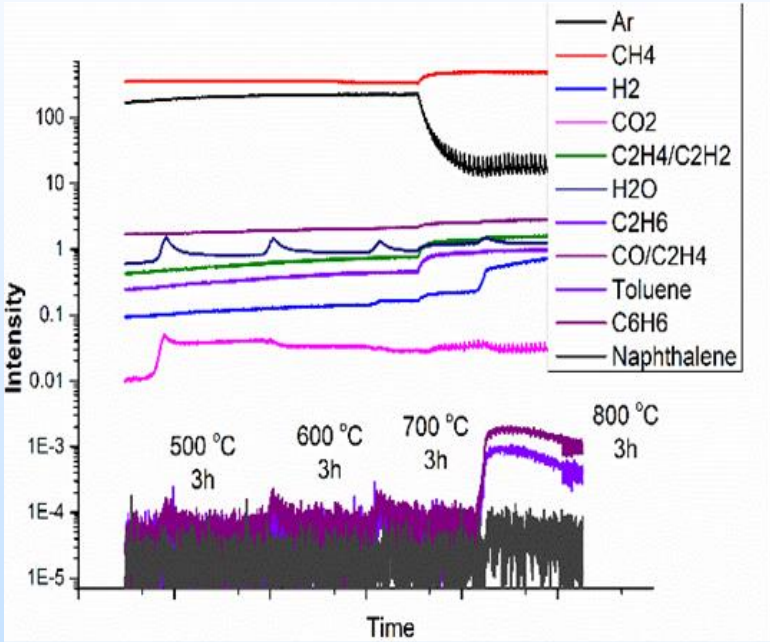
Research To Be Done

- Discovery of high surface area SAC for MDA
- Verification of the improved MDA performance in tubular PCMRs
- Discovery of high-performance PCMR component materials
- Manufacturing of HCM-PCMRs by I-AMLP technique
- Testing of MDA performance in HCM-PCMRs
- Estimation of the energy conversion efficiency of HCM-PCMRs

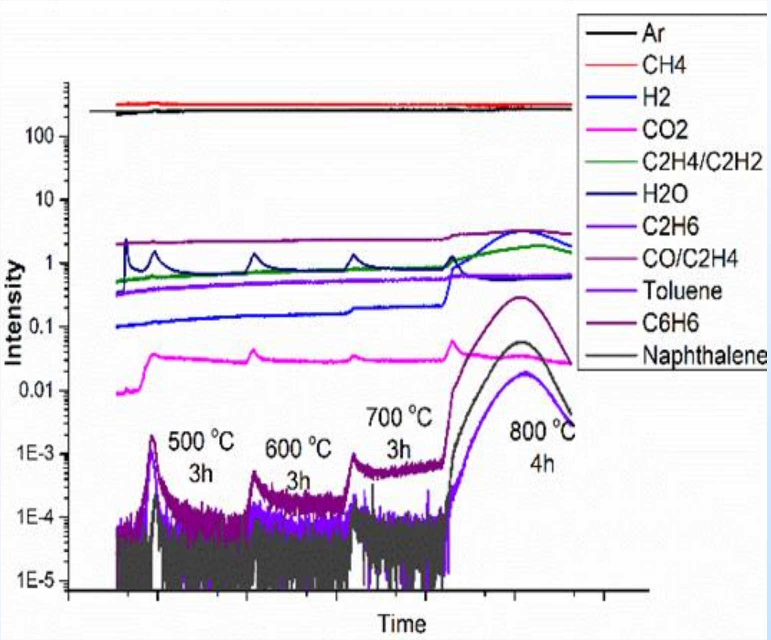
Technical Status

High Surface SAC for MDA

SAC Fe on mesoporous SiO_2



(a)



(b)

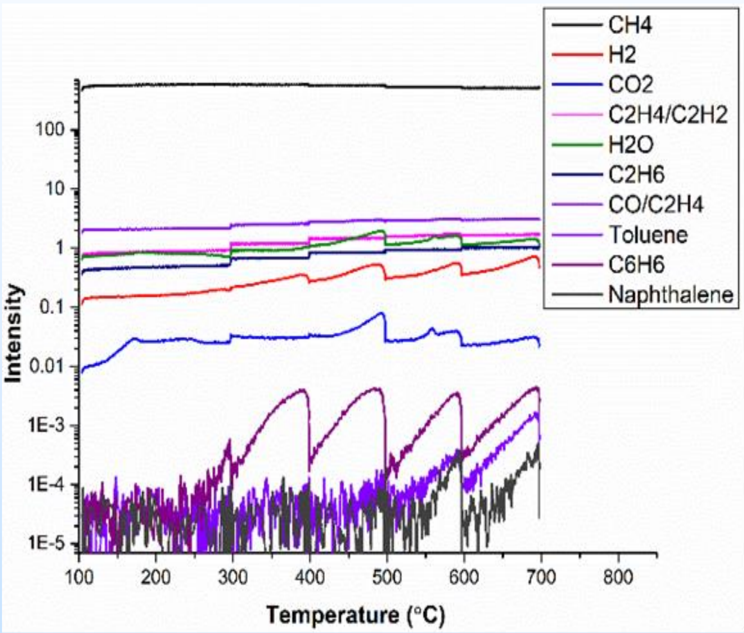
Methane conversion product of SAC Fe on mesoporous SiO_2 (0.2 wt% Fe) without (a)/with (b) ZSM-5.

Our new SAC Fe mesoporous SiO_2 catalyst showed benzene and toluene production at 800°C, which is 250°C lower than the reported Fe@SiO_2 catalyst. Mixed with ZSM-5, the benzene onset production decreased to 500°C. Higher production rate were obtained.

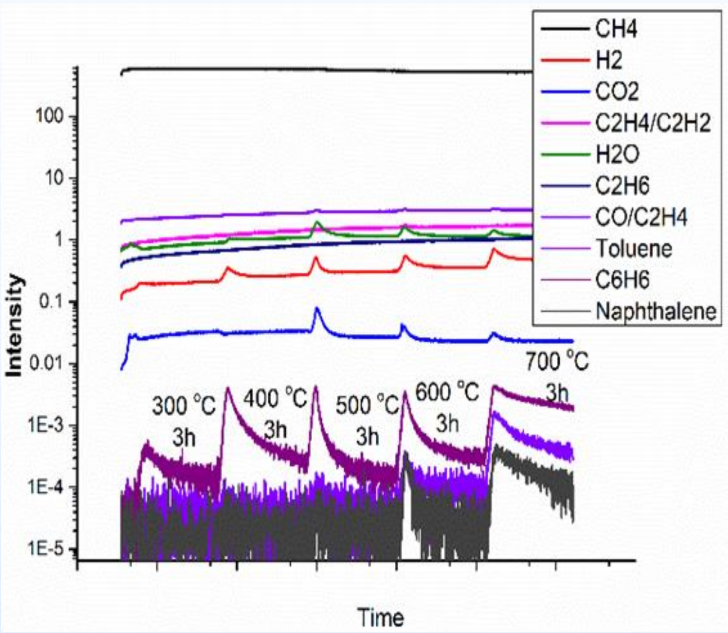
Technical Status

High Surface SAC for MDA

SAC Rh on mesoporous SiO_2 (0.33wt% Rh)



(a)



(b)

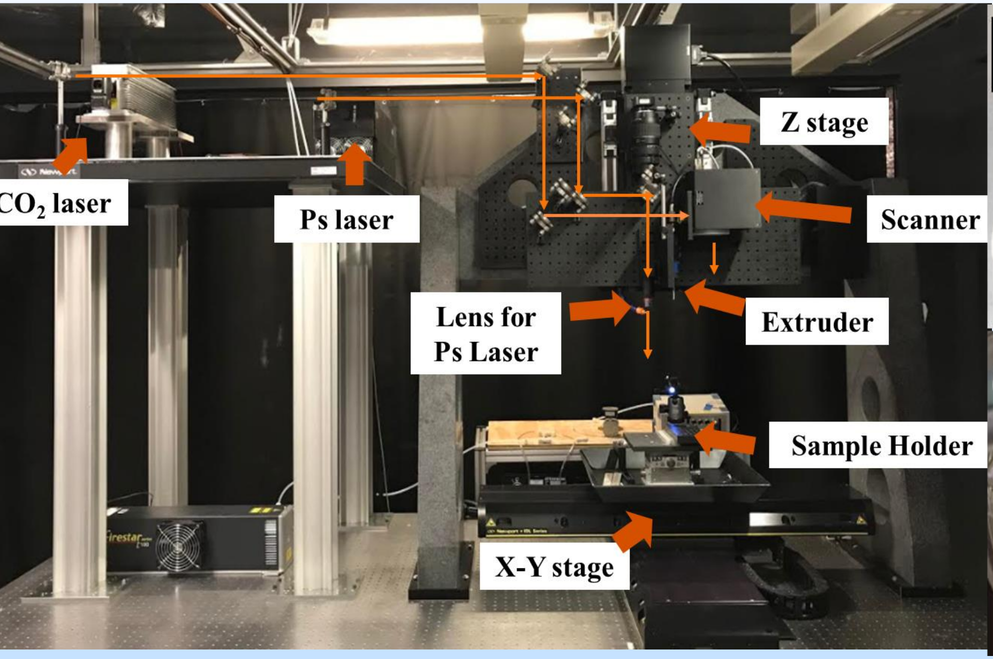
Methane conversion product of SAC Rh on mesoporous SiO_2 (0.33wt% Rh). (a) MS intensity *vs.* reaction temperature, and (b) MS intensity *vs.* reaction time.

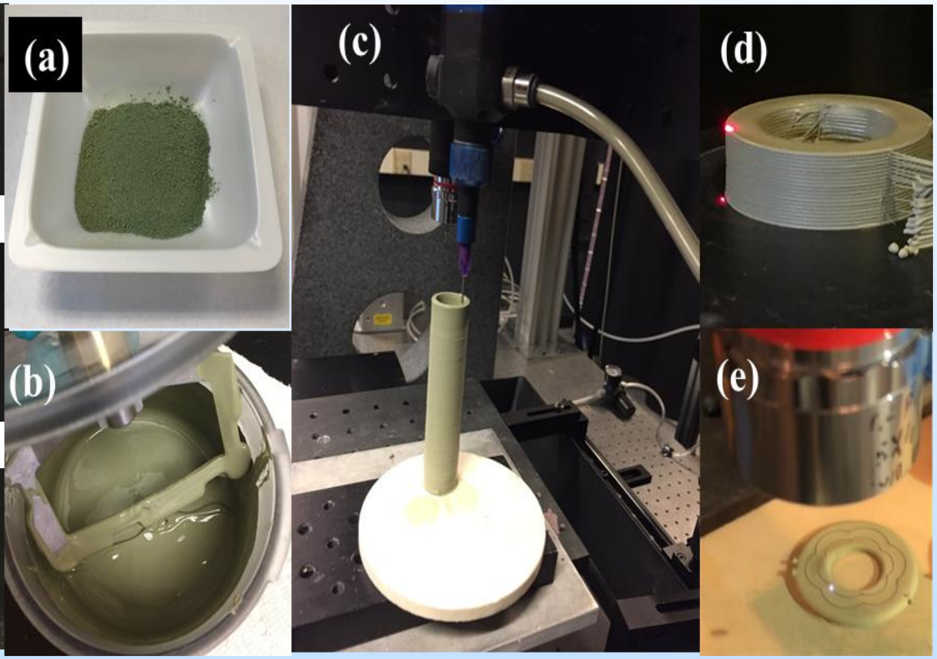
Our new SAC Rh mesoporous SiO_2 catalyst showed benzene production onset temperature of 250°C, which is significantly lower than the state-of-the-art Mo/Zeolite (700°C) and Fe@SiO_2 (1050°C)

Technical Status

Verification of MDA in PCMRs

Description of Integrated Additive Manufacturing and Laser Processing



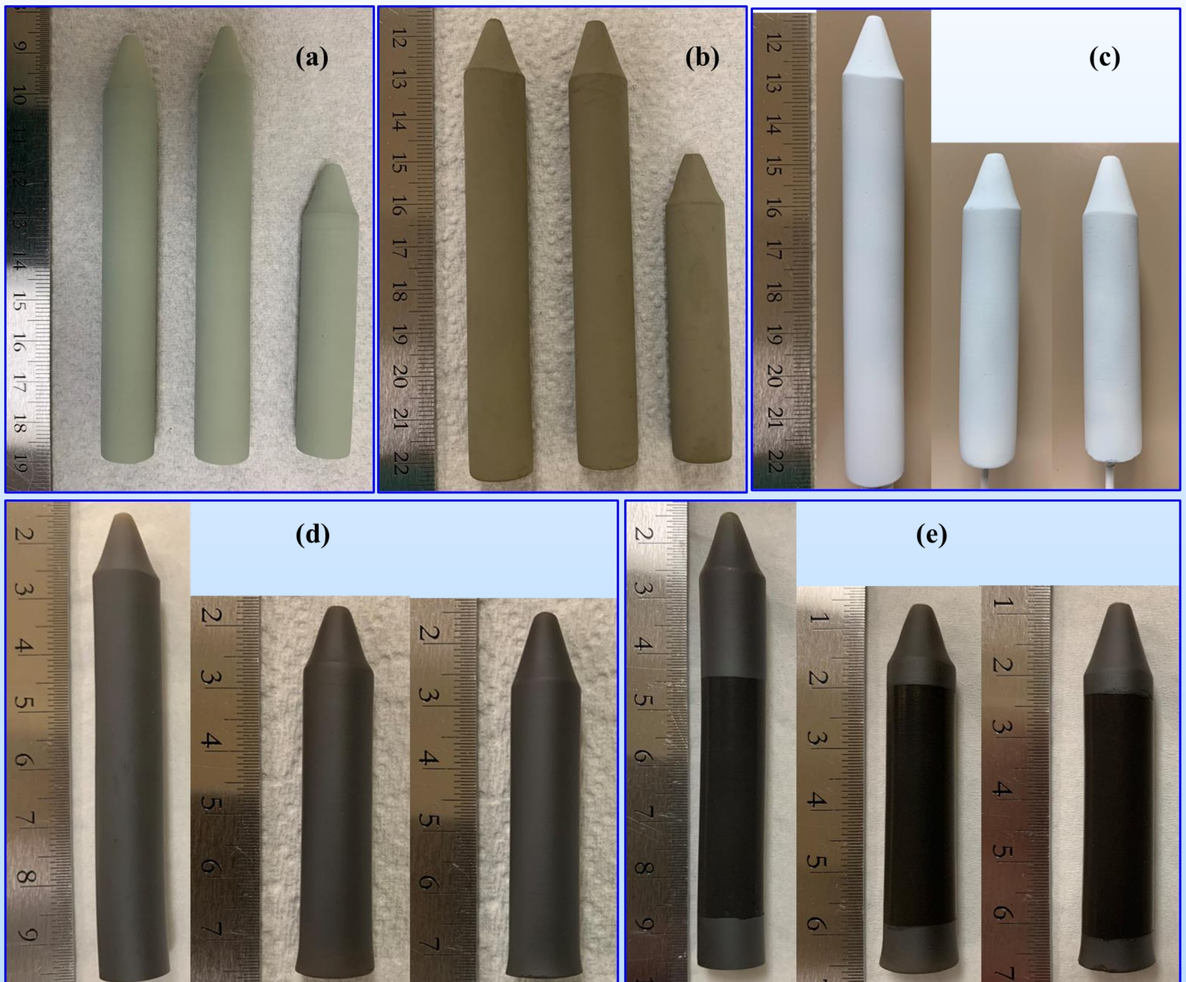


We have updated the I-AMLP technique for manufacturing PCMRs, which can print green layers with thickness 50-500μm. The utilization of low viscous paste and laser drying allow easy printing and bonding. The laser cutting allows introduction microchannels.

Technical Status

Verification of MDA in PCMRs

Tubular PCMRs Prepared by I-AMLP

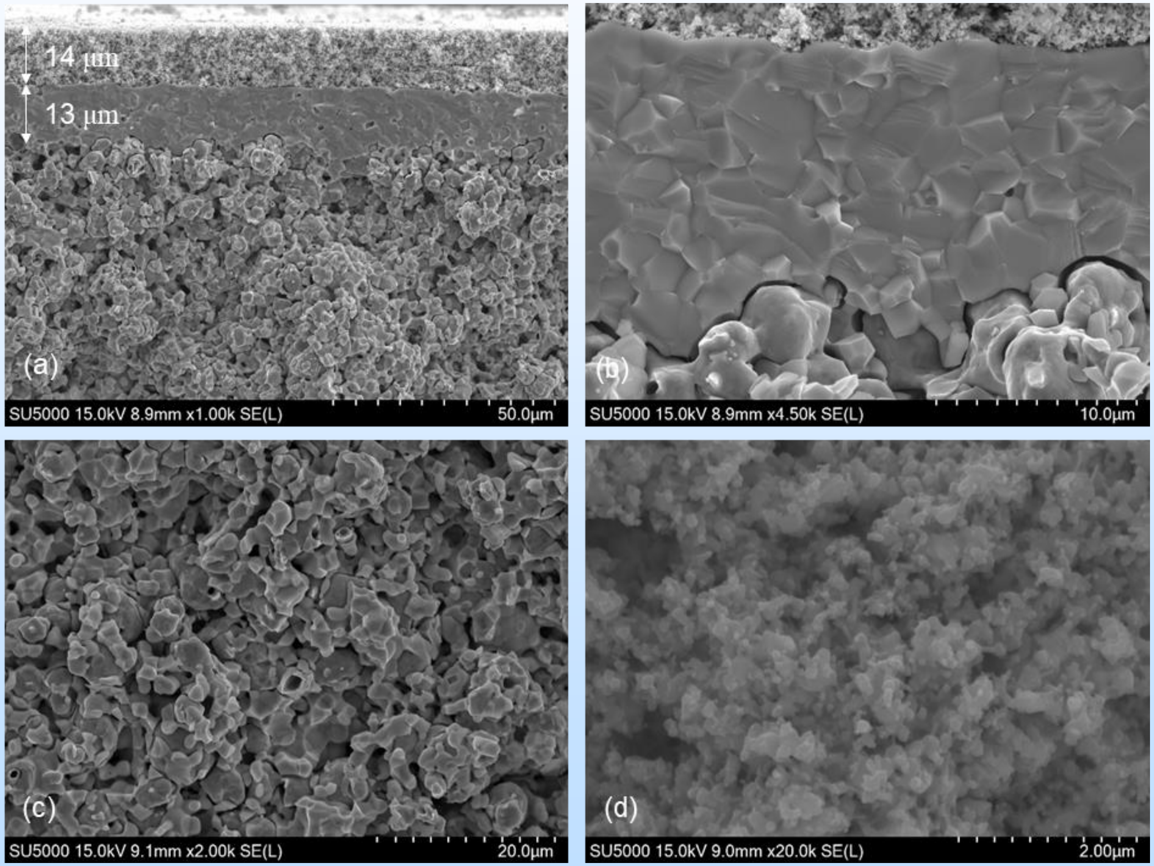


We can obtain tubular PCMRs with effective area larger than 25 cm^2 by I-AMLP method.

Technical Status

Verification of MDA in PCMRs

Microstructure of Tubular PCMRs fabricated by I-AMLP

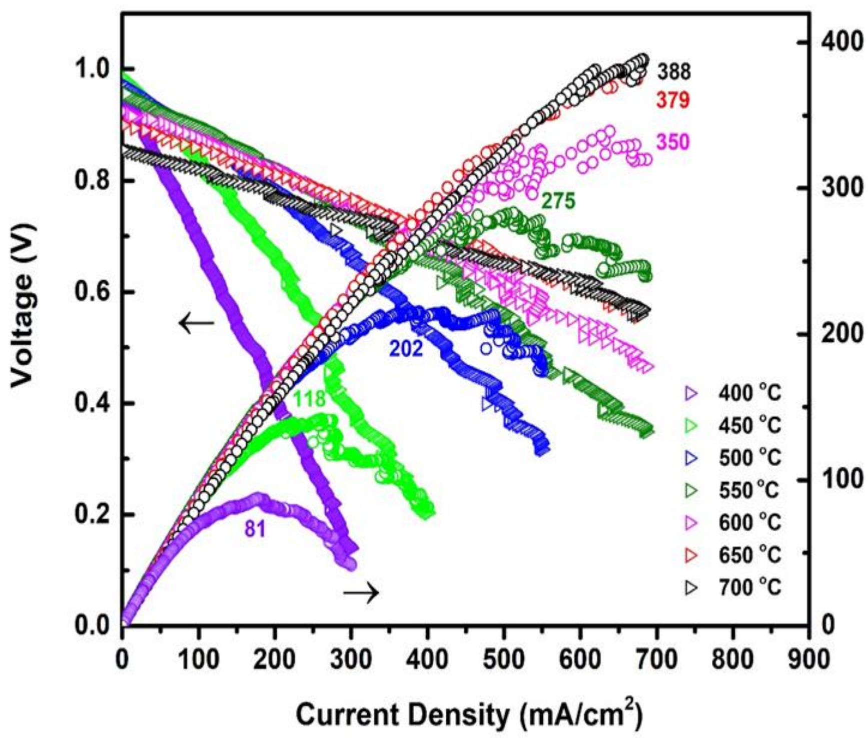


The PCMRs with fully densified thin electrolyte and highly porous electrode can be achieved by I-AMLP.

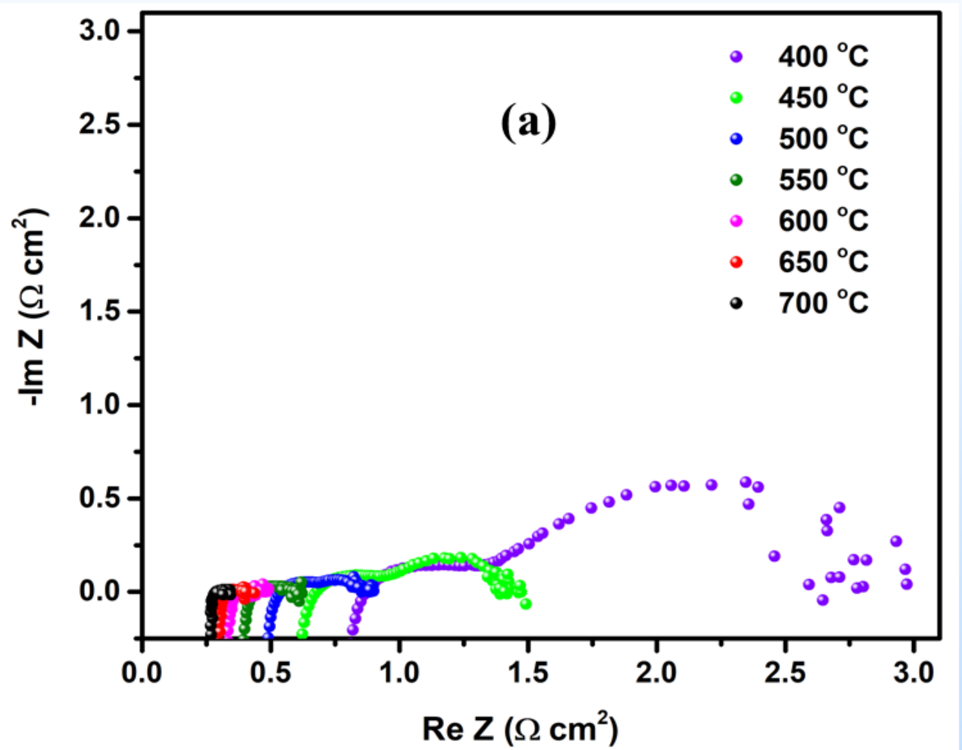
Technical Status

Verification of MDA in PCMRs

Fuel Cell Preformation of Tubular PCMRs



I-V and I-P curve of PCFC under air/H_2



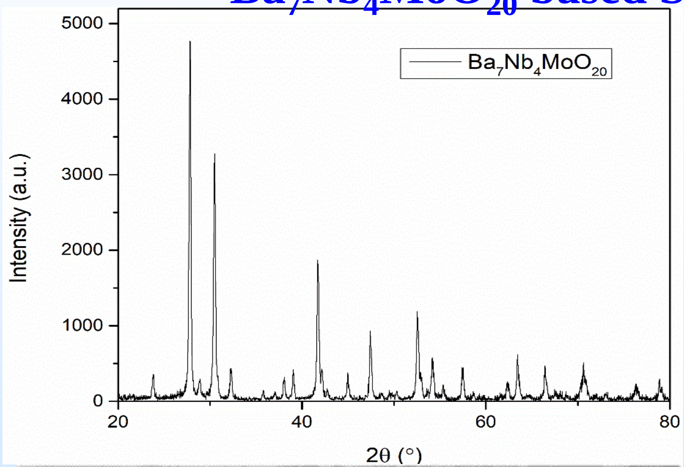
EIS spectra under of Air/H_2

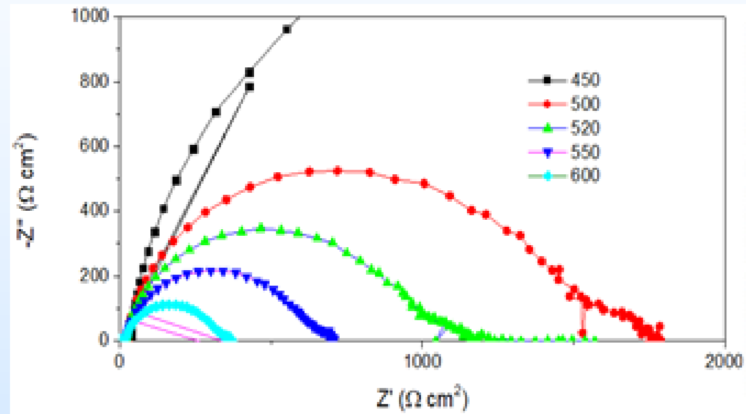
The tubular protonic ceramic fuel cell can achieve peak power density around 380 mW/cm^2 at 650^{o}C.

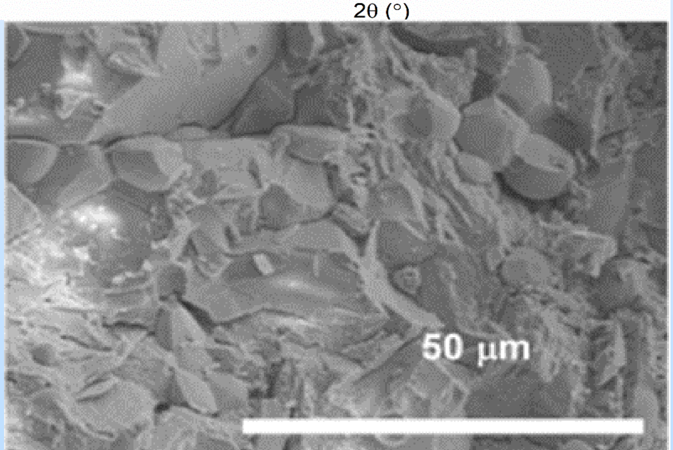
Technical Status

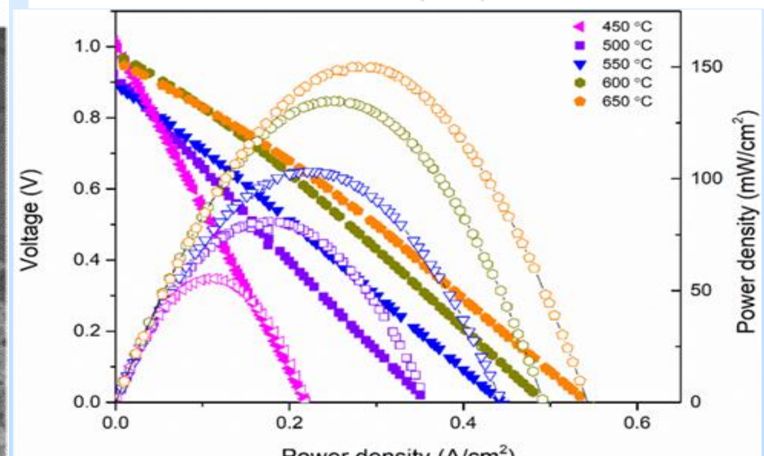
High-Performance PCMR Materials

$Ba_7Nb_4MoO_{20}$ based Single-Phase Co-ionic Conductor







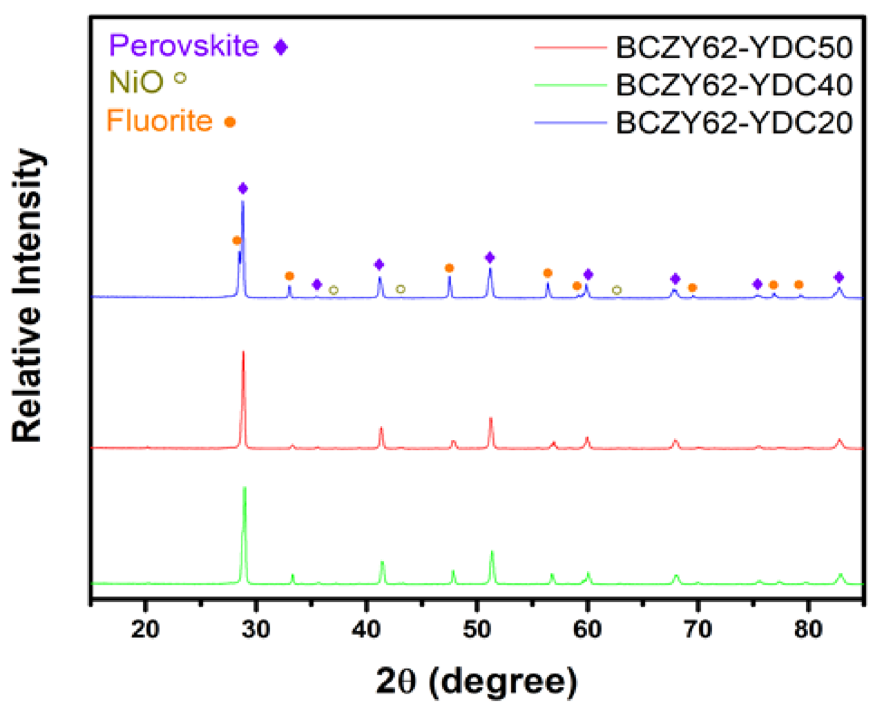


Synthesized state-of-the-art BNM co-ionic conductor, obtained the conductivity of 3.6 mS/cm², and achieved acceptable initial fuel cell result.

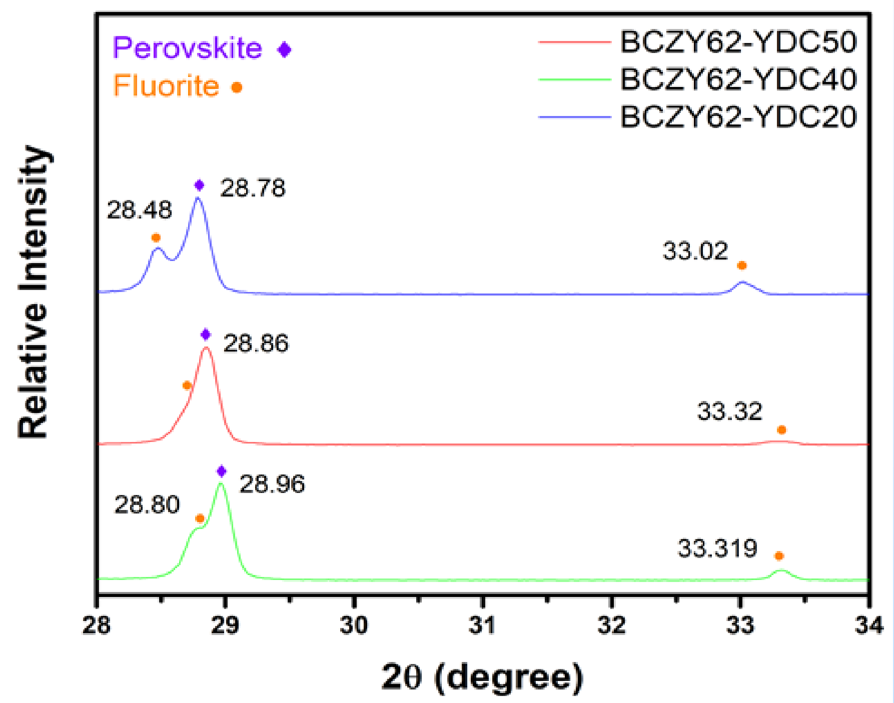
Technical Status

High-Performance PCMR Materials

Perovskite-Fluorite Composite Co-Ionic Conductors



(a)



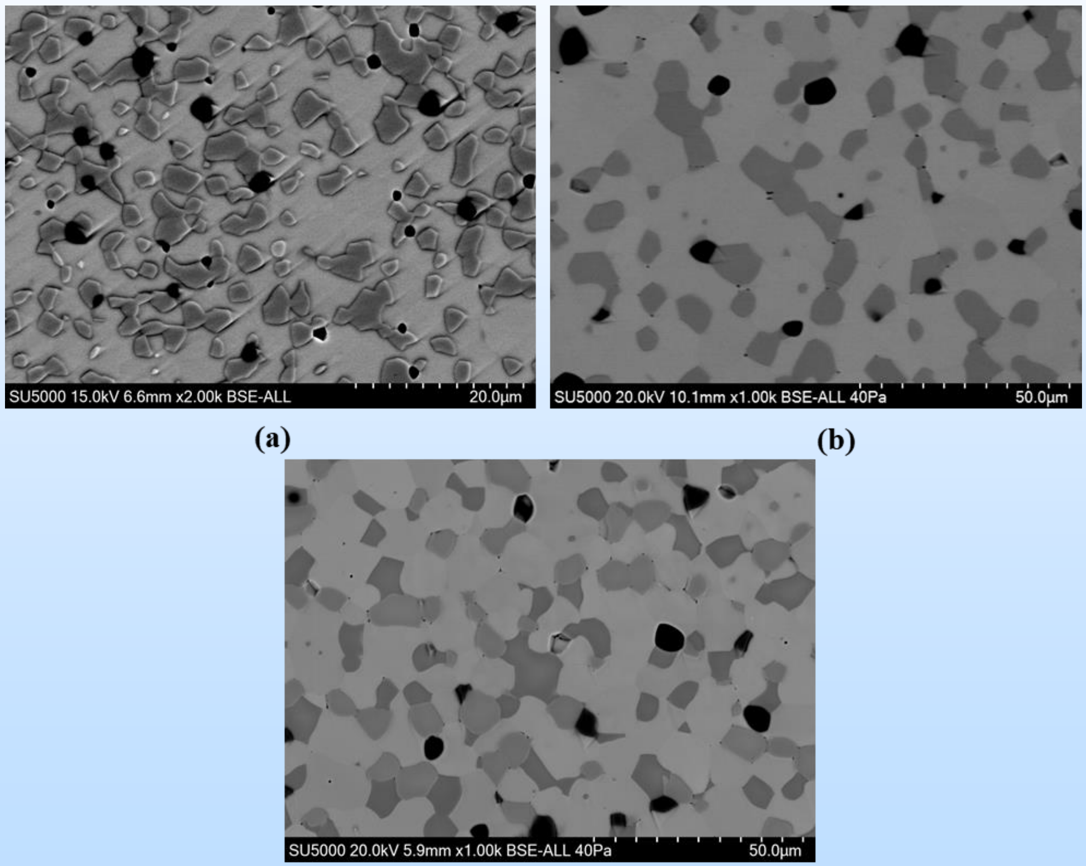
(b)

We can synthesize stable BCZY-YDC perovskite-fluorite composites by one-pot polymeric gelation method.

Technical Status

High-Performance PCMR Materials

Perovskite-Fluorite Composite Co-Ionic Conductors



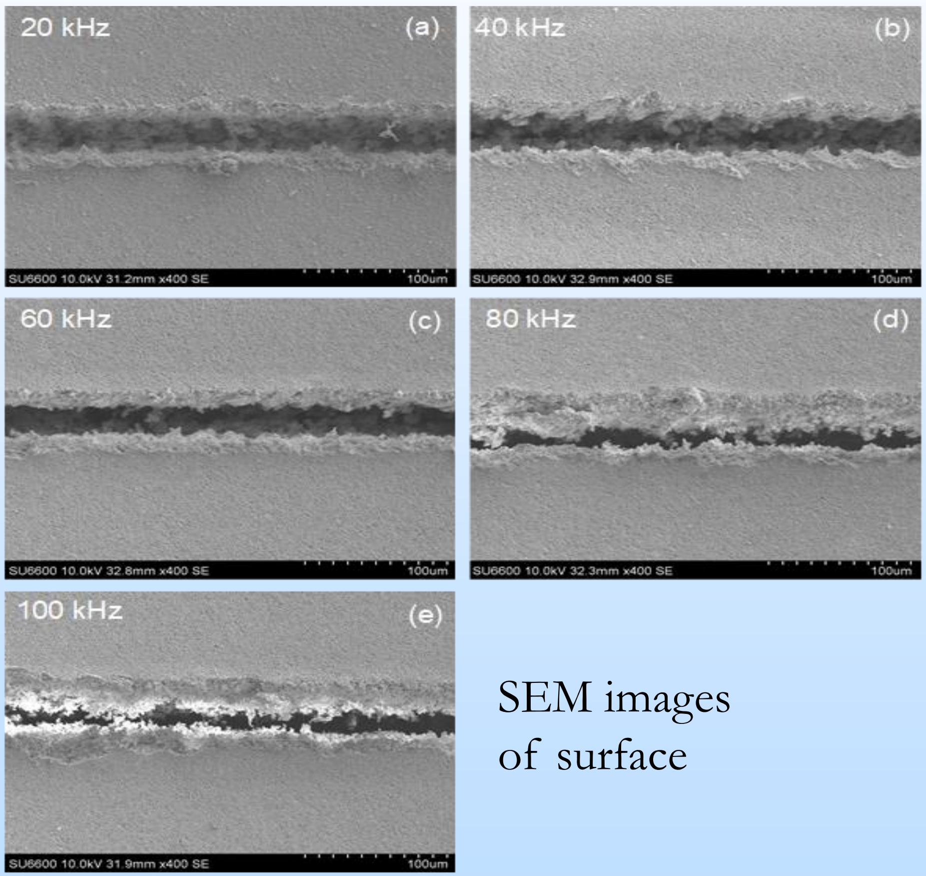
(a) (b) (c)

The perovskite and fluorite phase can be well dispersed to form homogenous composite co-ionic conductor

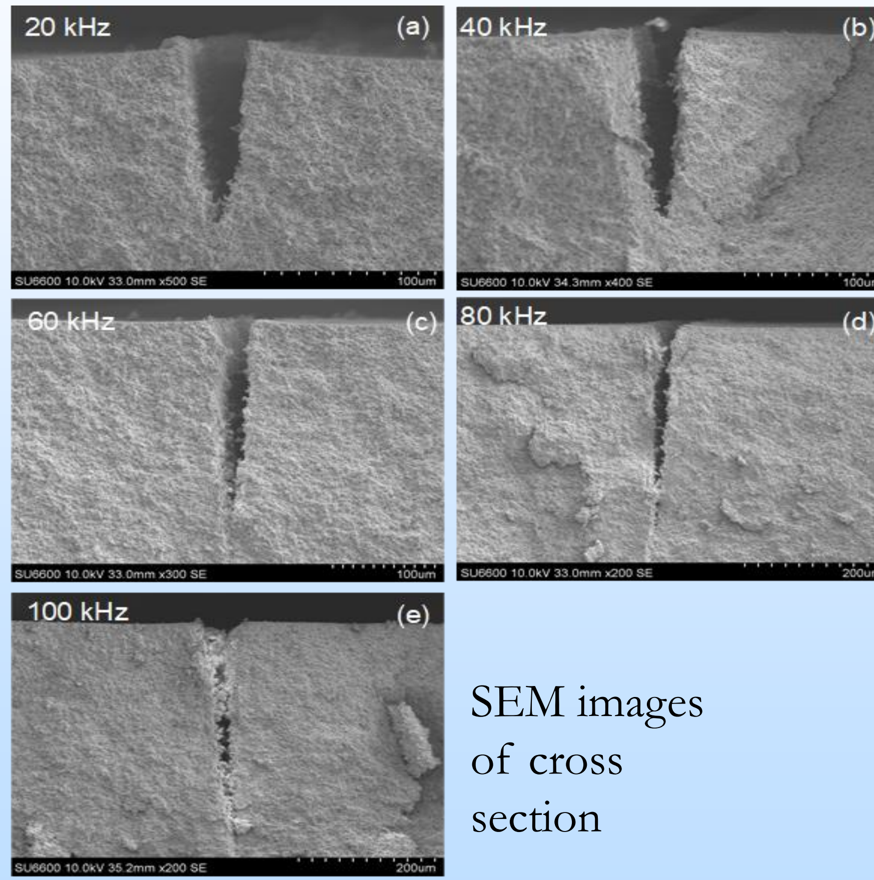
Technical Status

Manufacturing of HCM-PCMRs

Cutting Microchannel by Picosecond Laser



SEM images of surface



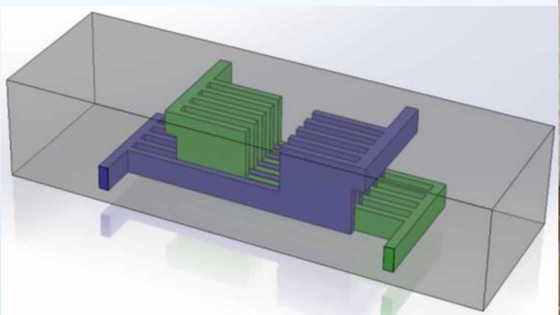
SEM images of cross section

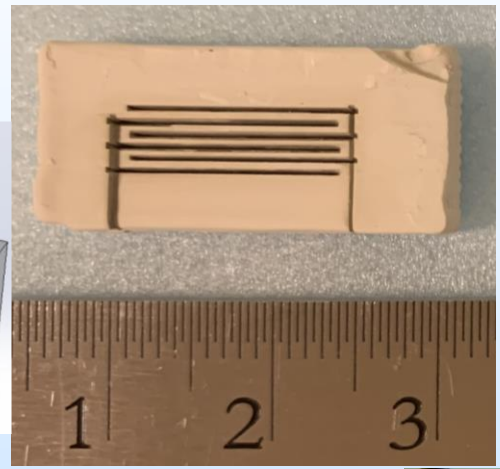
Picosecond laser can cut microchannels as small as 50 μm and the aspect ratio can reach to 5-6. Multiple cutting can result in large and deep channels.

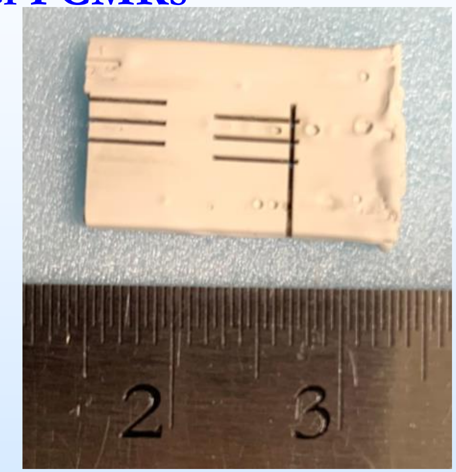
Technical Status

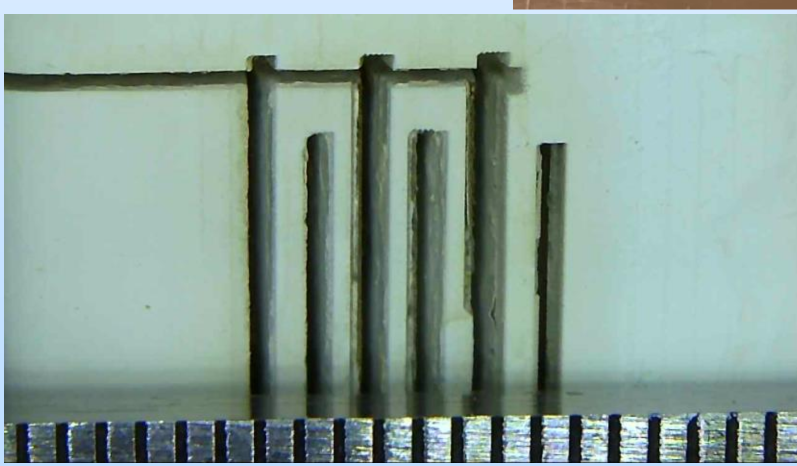
Manufacturing of HCM-PCMRs

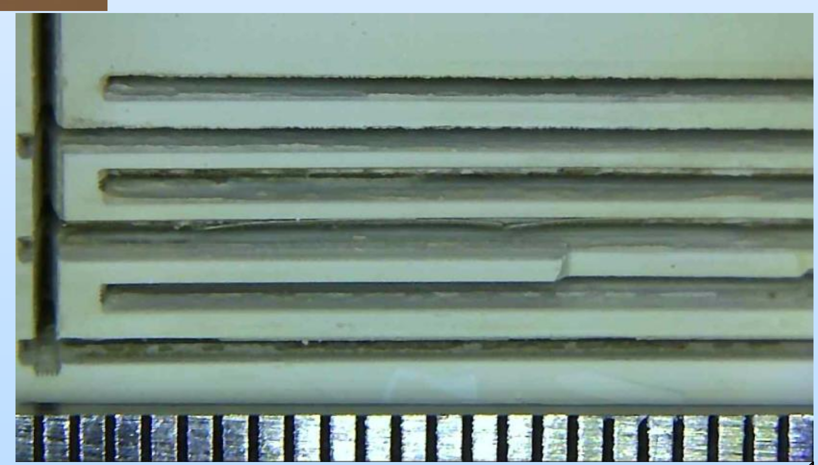
Preparation Microchannel PCMRs









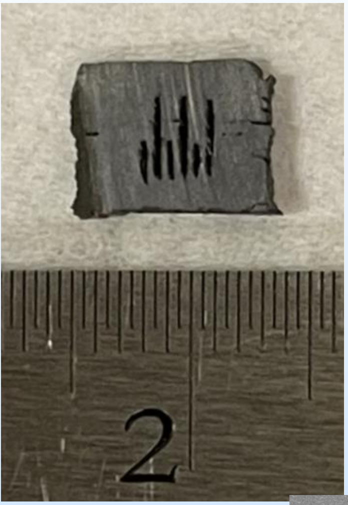


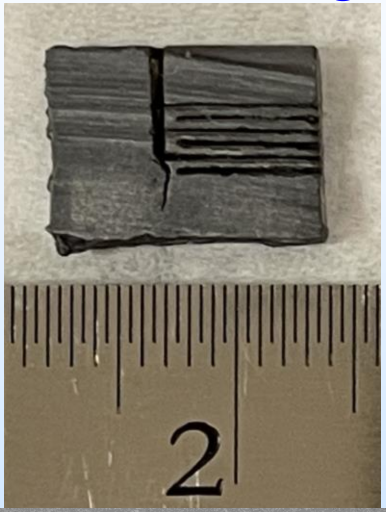
We can prepare microchannel PCMR with one material by I-AMLP with interdigital channels

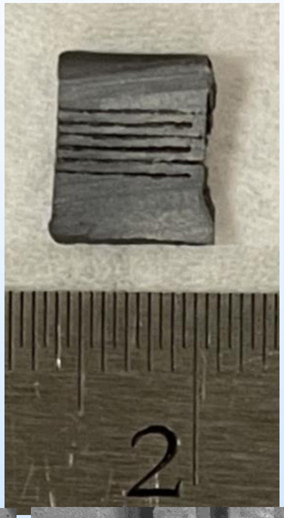
Technical Status

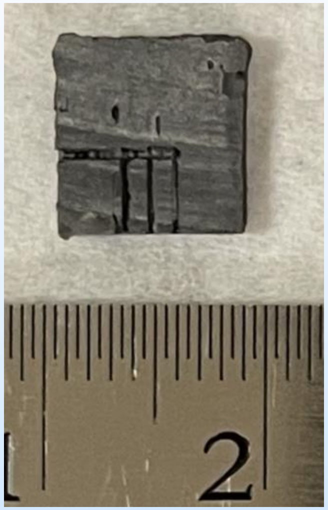
Manufacturing of HCM-PCMRs

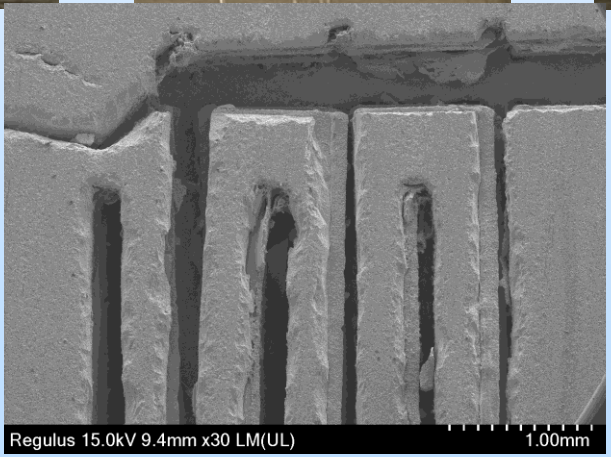
Sintered Interdigital Microchannel PCMRs

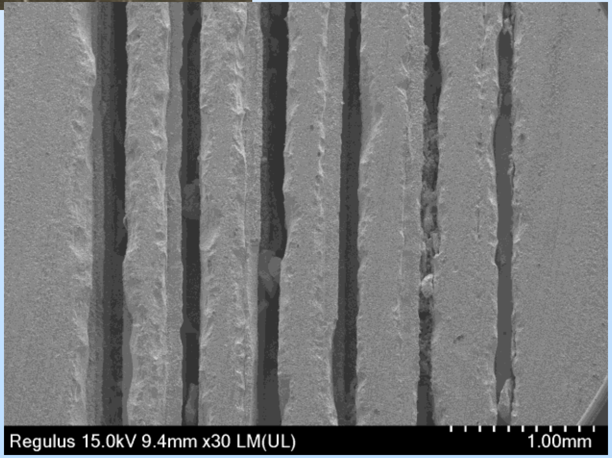










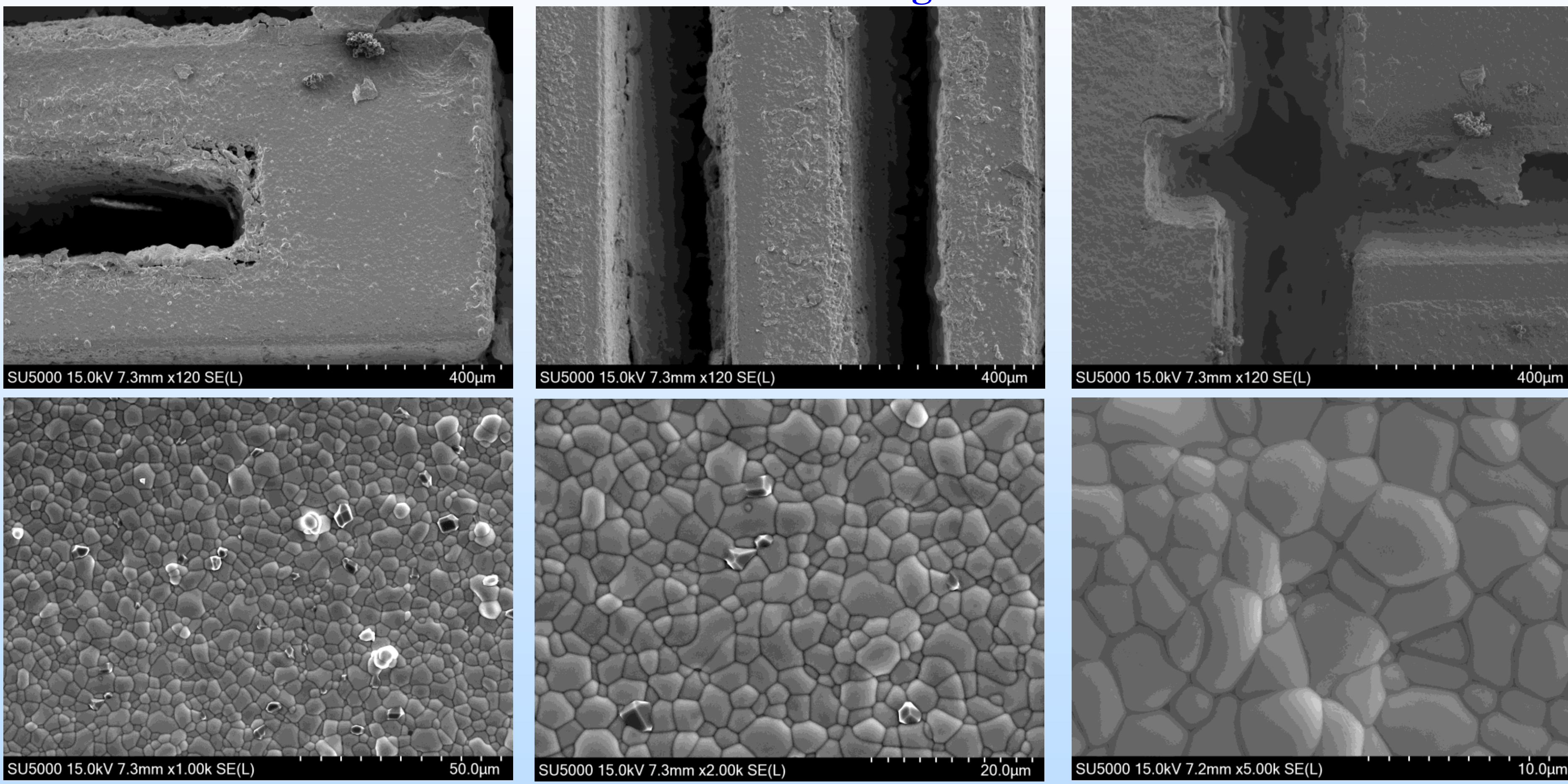


The interdigital channels kept well after high-temperature sintering

Technical Status

Manufacturing of HCM-PCMRs

Microstructures of Sintered Interdigital Microchannel PCMRs



The BCZY-YDC based microchannel were fully densified. The channel width is around 200μm with acceptable accuracy.

Accomplishments to Date

Catalysts/Materials Synthesis and Characterization

1) Synthesized Mo-HMCM-22 for MDA reaction

2) Synthesized boron nitride nanosheet with the desired crystal structure, morphology, and high surface (~290m^2/g).

3) Synthesized SAC Fe on mesoporous SiO_2. The onset reaction temperature to produce benzene was as low as 700^oC, 350^oC lower than the reported Fe@SiO_2 catalyst.

4) 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.

5) Rh@SiO_2 (mesoporous) catalyst could lower the benzene production onset temperature to 250^oC-300^oC. The mesoporous SiO_2 could significantly improve the aromatic production rate.

6) Synthesized phase-pure tetragonal perovskite oxide $Ba_7Nb_4MoO_{20}$ and achieved a total conductivity of 3.6×10^{-3} S/cm under a wet air atmosphere reached, which is even higher than that in the literature.

7) Perovskite-fluorite dual-phase composites with different Y amounts in the YDC phase could be prepared by the one-pot SSRS method. The XRD, BSE-SEM, and EDX characterization indicate that the perovskite-fluorite composites were formed.

Accomplishments to Date

Manufacturing and Testing of PCMRs

1) Prepared appropriate paste/slurry for the 3D printing of anode, electrolyte, and cathode.

2) Developed a new microextrusion and CO_2 laser drying combined method, allowed successfully printing one end closed anode tube with a surface area greater than $25 cm^2$.

3) I-AMLP technique could reproducible, high-quality, and large-surface-area tubular PCMRs with a functional area larger than $25 cm^2$.

4) Demonstrated a maximum power density of 325.6 mW/cm^2 at 650℃ with a large effective area of 12.45 cm^2 in a tubular PCMR.

5) Fabricated BNM + NiO | BNM | BCFZY0.1 single cells based on new BNM co-ionic electrolyte The peak power density of this cell is about 150 mW/cm^2 at 650°C.

6) By optimizing picosecond laser cutting parameters, we have achieved the anode microchannel with an open width of less than 50μm and aspect ratios close to 7.

7) Manufactured interdigital microchannel PCMRs based on BCZY-YDC material. Showed fully dense microstructure, accurate control of microchannel size and good sintering behavior.

Lessons Learned

- The direct MDA is challenging work. The development of 2D catalyst has challenge. However, the mesoporous materials with high surface and porous pore 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
- Some proposed compositions of materials may need change. The 2D catalyst substrates may need to change to mesoporous substrates.

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/SiO_2 (mesoporous) and Rh/SiO_2 (mesoporous) SAC for MDA, which can significantly lower MDA reaction temperature. The addition of ZSM-5 can significantly improve MDA rate.
- The phase-pure and perovskite-fluorite composite co-ionic electrolyte or electrode scaffold were found.
- The I-AMLP method can successfully fabricate tubular PCMRs, which demonstrated excellent fuel cell performance.
- The I-AMLP method can successfully make interdigital PCMRs with desired microchannels.

Project Summary

Next Steps

- Further improve Fe/SiO_2 and Rh/SiO_2 SAC based on mesoporous silica. Further check zeolite effect. Quantify the MDA performance.
- Demonstrate high-performance based on the phase-pure and perovskite-fluorite composite co-ionic electrolyte or electrode scaffold were found.
- Verify superior MDA in tubular PCMRs
- Improve the manufacturing of microchannel PCMRs and test the performance of 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 CH_4) 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 CO_2 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

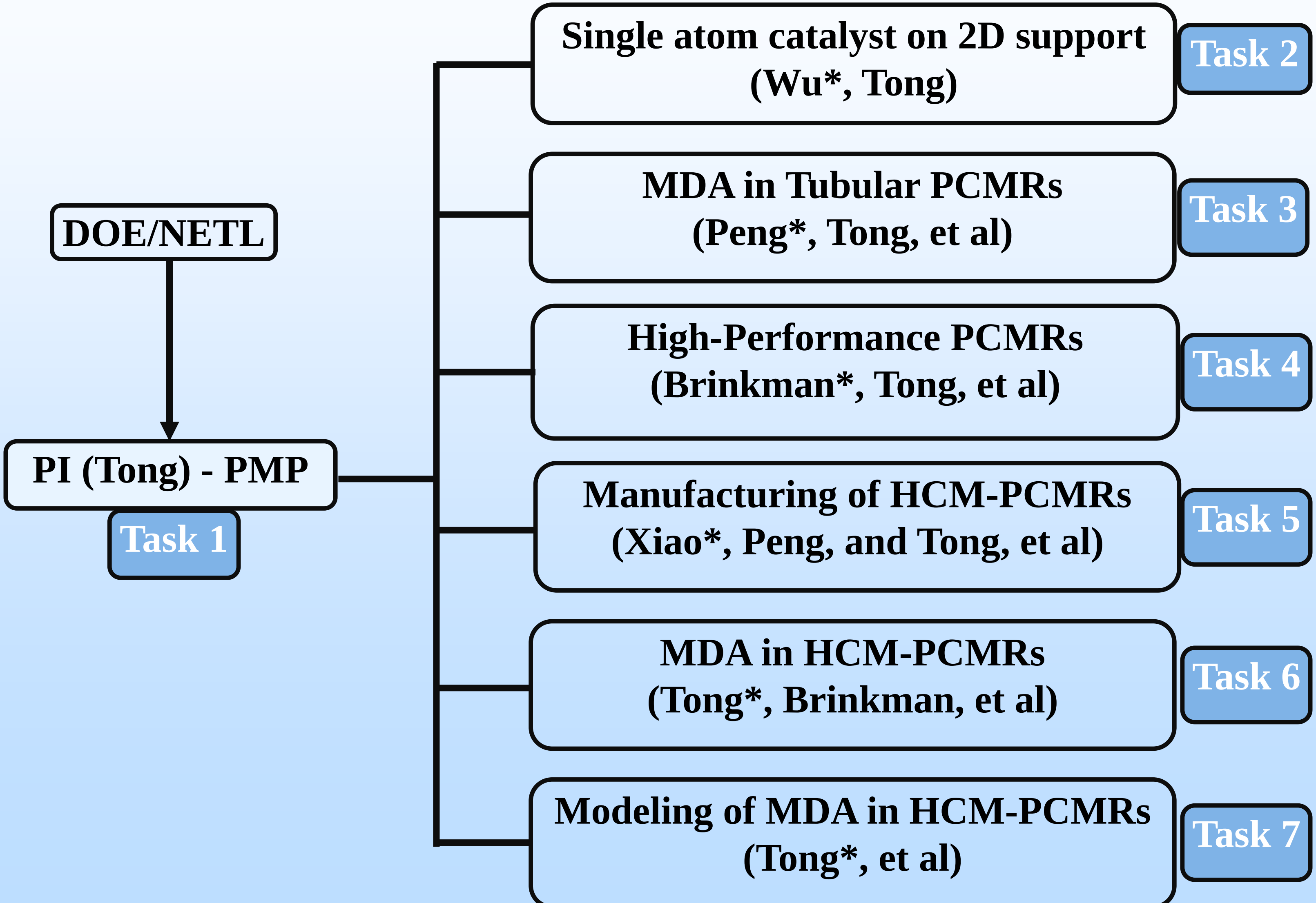
The overarching goal is to develop a highly compacted microchannel protonic ceramic membrane reactors (HCM-PCMRs) for efficient and cost-effective methane dehydrogenation to aromatics (MDA, e.g., benzene).

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@SiO_2, Mo-HZSM-5, and Mo-HMCM22; and show the feasibility to apply new laser 3D printing technique for manufacturing microchannel PCMRs.

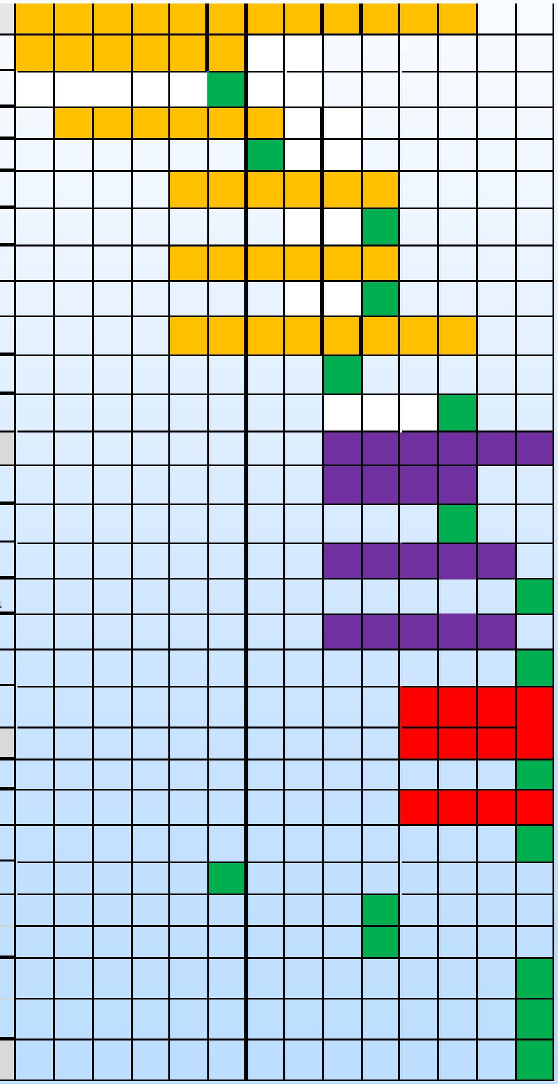
BP3: Manufacture modules of HCM- PCMRs by laser 3D printing technique and prove the long-term stable and efficient production of benzene from methane with new 2D SACs.

Organization Chart



Gantt Chart

Task 5.0	**Manufacturing of HCM-PCMRs by I-AMLP technique**
Subtask 5.1	3D printed green parts
Milestone 5.1	Desired parts by 3D printing
Subtask 5.2	Laser cutting microchannels
Milestone 5.2	Microchannel width close to 50μm, depth >50μm
Subtask 5.3	Sintering of multilayered parts
Milestone 5.3	Crack-free and integrated sintering for more 12 layers
Subtask 5.4	Infiltration optimization
Milestone 5.4	Achieve active phase particles less than 100nm
Subtask 5.5	Fabrication of HCM-PCMRs
Milestone 5.5.1	Single microchannel PCMR
Milestone 5.5.2	HCM-PCMR with area >20cm^2
Task 6.0	**Testing of MDA performance in HCM-PCMRs**
Subtask 6.1	HCM-PCMR assembling
Milestone 6.1	Successfully loading of MDA catalyst into anode channels
Subtask 6.2	MDA in HCM-PCMR
Milestone 6.2	MDA performance in HCM-PCMR, 50% conversion at 700°C for 500h
Subtask 6.3	HCM-PCMR analysis
Milestone 6.3	Fully understand the catalyst and PCMR
Task 7.0	**Estimation of the energy conversion efficiency of HCM-PCMRs**
Subtask 7.1	Models for HCM-PCMRs
Milestone 7.1	Establish reasonable model
Subtask 7.2	Estimation of process efficiency
Milestone 7.2	Achieve methane conversion efficiency higher than other MDA process
BP1 GNG point	Verification of the improved MDA performance in tubular PCMRs
BP2 GNG point	SAC@2D catalyst has performance better than Fe@SiO_2
	show feasibility to manufacture by I-AMLP
Final goal	Methane conversion >50%, aromatics/olefine selectively >90%,
	reaction temperature <700°C, stability >500h
	Final Technical Report



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 singe 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 result														
Task 3.0	**Verification of the improved MDA performance in tubular PCMRs**														
Subtask 3.1	I-AMLP of tubular PCMRs														
Milestone 3.1	PCMR, >10cm2, >300mV/cm2, 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														
Milesteone 4.3	ASR<0.1Ω·cm2 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														

Bibliography

1. Zeyu Zhao, Minda Zou, Hua Huang, Harrison Wofford, and Jianhua Tong, Stable Perovskite-Fluorite Dual-Phase Composite s Synthesized by One-Pot Solid-State Reactive Sintering for Protonic Ceramic Fuel Cells. Ceramics International, 2021, accepted.