CHANGING WHAT'S POSSIBLE

U.S. Department of Energy

Molten-Salt Methane Pyrolysis Optimization Through in-situ Carbon Characterization and Reactor Design

Fabrication & demonstration of a high temperature, high pressure molten salt methane pyrolysis reactor.

Total project cost:	$2.3M
Length	24 mo.

Binary Chloride Salts as Catalysts for Methane to Hydrogen and Graphitic Powder

Production and continuous removal of graphitic powder from a molten salt methane pyrolysis reactor.

Total project cost:	$1.2M
Length	24 mo.

Eric McFarland, C-Zero

Additional team members in attendance: Zach Jones, Sam Shaner, Fadl Saadi

The Concept

Idea

Decarbonize natural gas through Methane Pyrolysis

Key Challenges

- Reactor Design
- Monitor & Control Carbon Formation
- Carbon Removal
- Carbon Valorization
- Heat Integration
- Product Gas Cleanup

Goal

The Team

C||ZERO

Prof. Eric McFarland
Board Chair, CTO

Zach Jones
President & CEO

Fadl Saadi, Ph.D.
Director of Business Development & Operations

Brett Parkinson, Ph.D.
Senior Engineer

Sam Shaner, Ph.D.
Director of Engineering

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Collaborators

Prof. Mike Gordon
UCSB

Prof. Roya Maboudian
UCB

Prof. Horia Metiu
UCSB

Prof. Raphaele Clement
UCSB

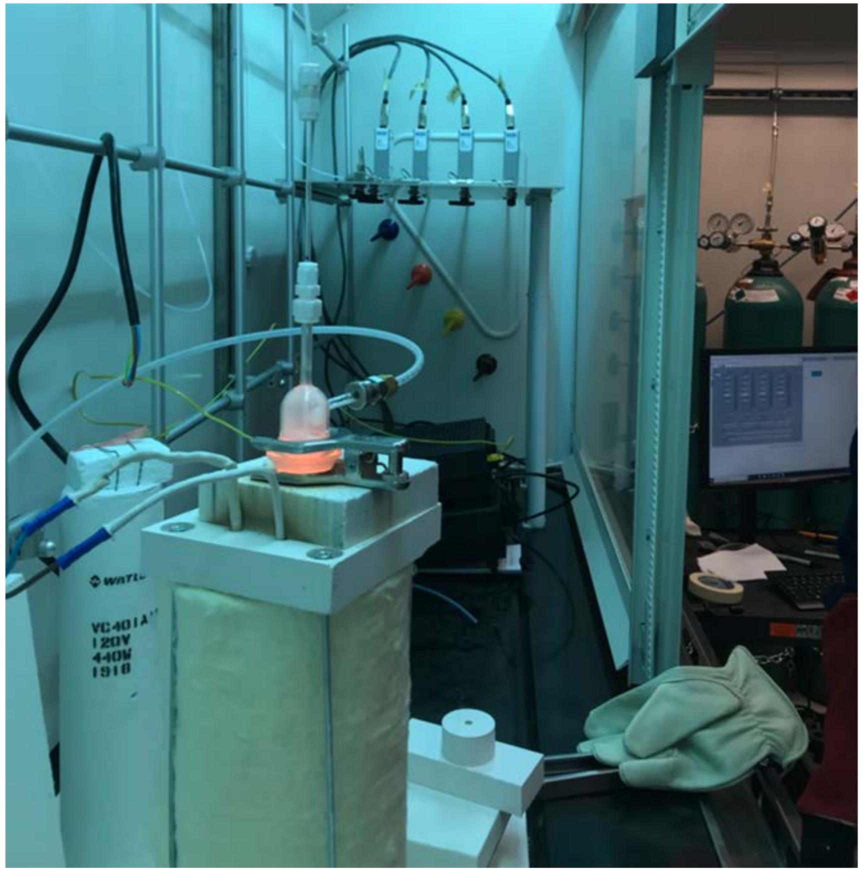
Advisory Board

Prof. Ches Upham
UBC

Arnie Smith
Fluor, Executive Director of Process Engineering

Philip Grosso
Kaiser Chemicals, Former Vice President

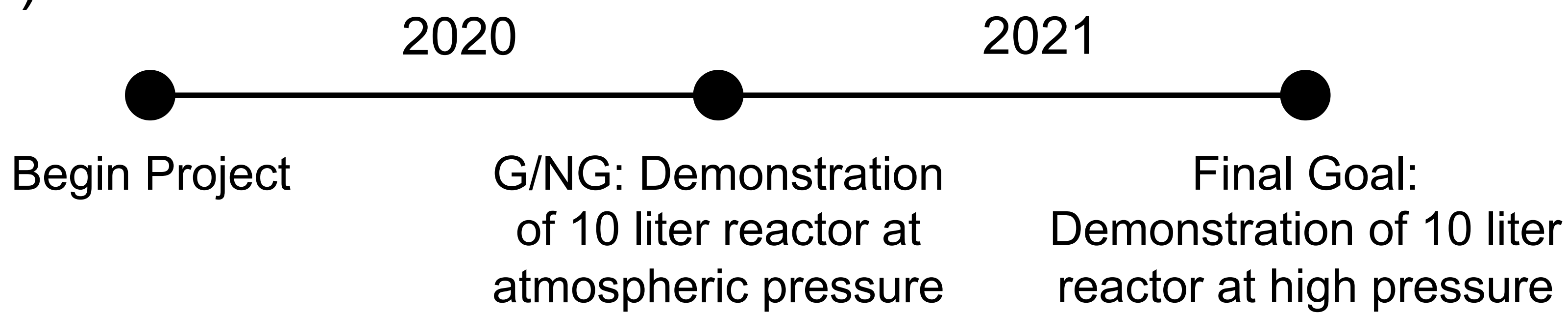
Lab & Setup



Objectives for ARPA-E Project

- Demonstrate in-situ spectroscopic measurements of carbon formation under methane pyrolysis reaction conditions.

- Design and construct a 10 liter methane pyrolysis molten salt reactor with:
  - ≥ 70% CH_4 conversion
  - ≥ 90% H_2 selectivity
  - ≥ 5 mol H_2/ m^3 s
  - ≤ 2.5% wt salt in carbon product
  - High Pressure (≥ 5 bar)



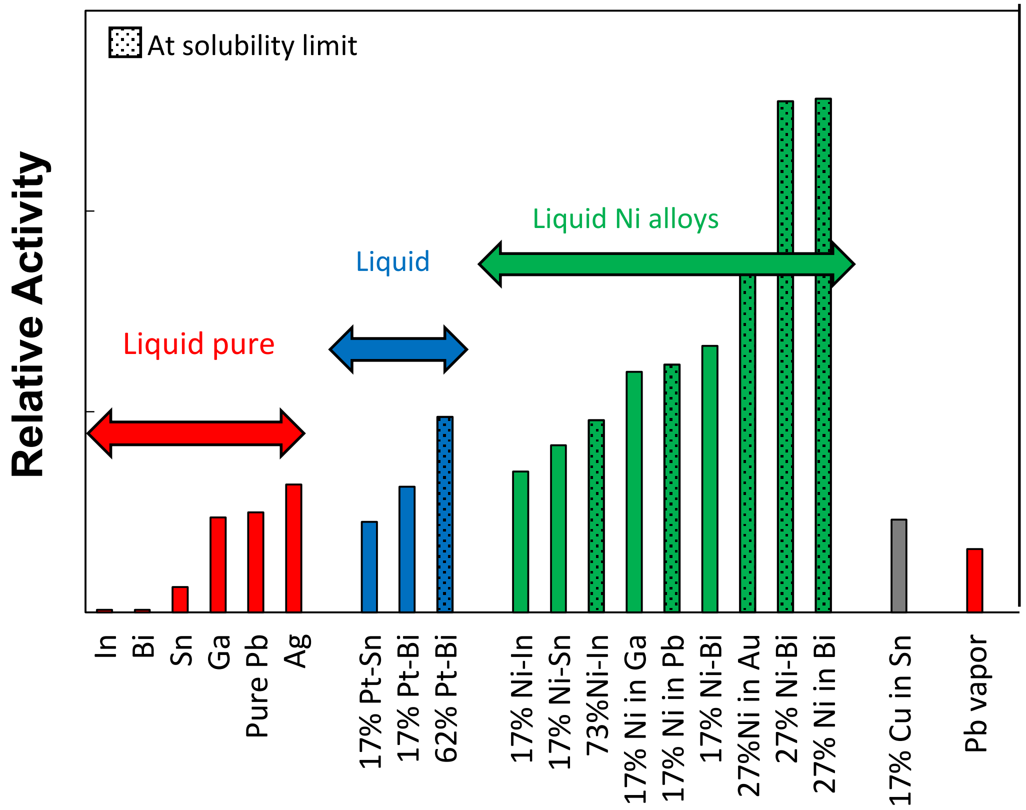
Objectives for H_2@Scale Project

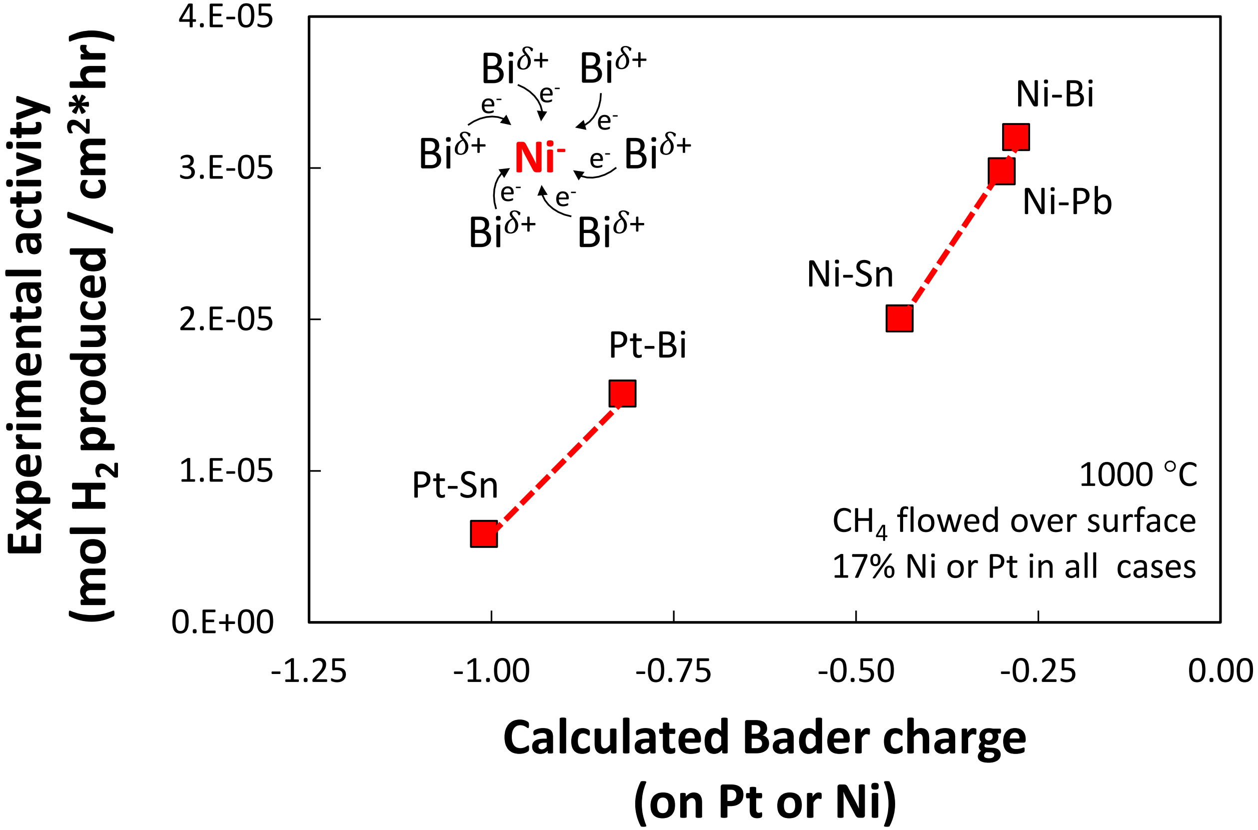
- Demonstration of stable, active, binary chloride melt system:
  - ≥ 90% H_2 selectivity
  - Graphitic carbon product that has properties favorable for battery anodes and additives

- Design and construct a carbon removal system capable of:
  - High Temperature (1000 C)
  - Continuous carbon removal (≥ 24 hours)
  - High Pressure (≥ 10 bar)

	2020		2021	
Begin Project		G/NG: Demonstration of carbon removal system at atmospheric pressure		Final Goal: Demonstration of carbon removal system at high pressure

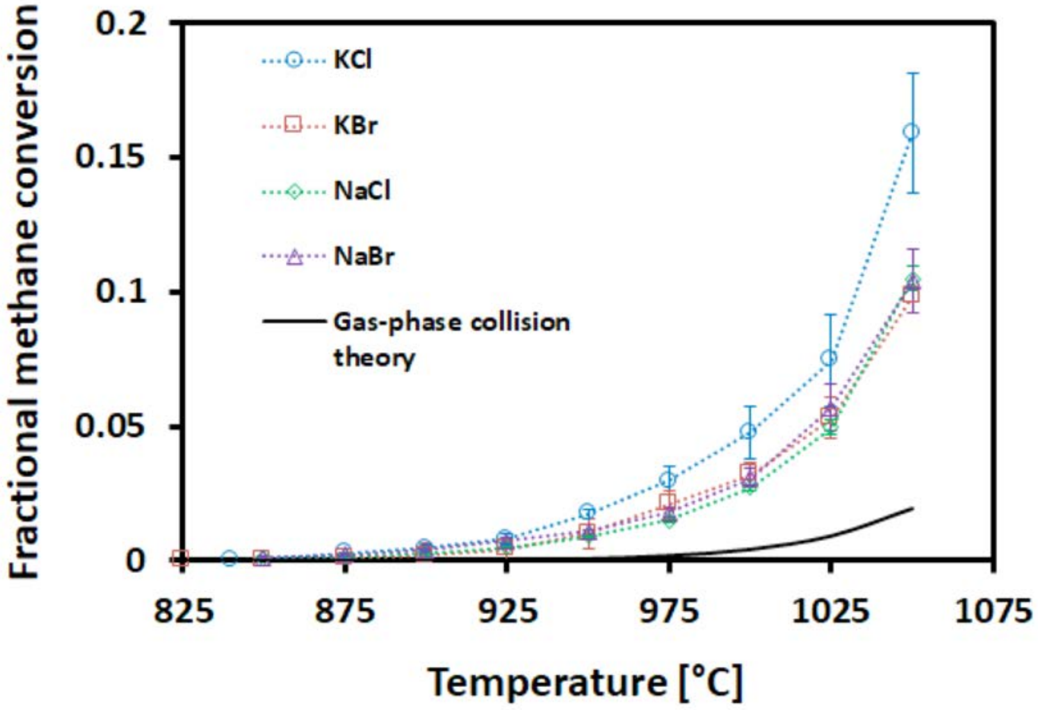
Liquid Catalysts: Molten Metals

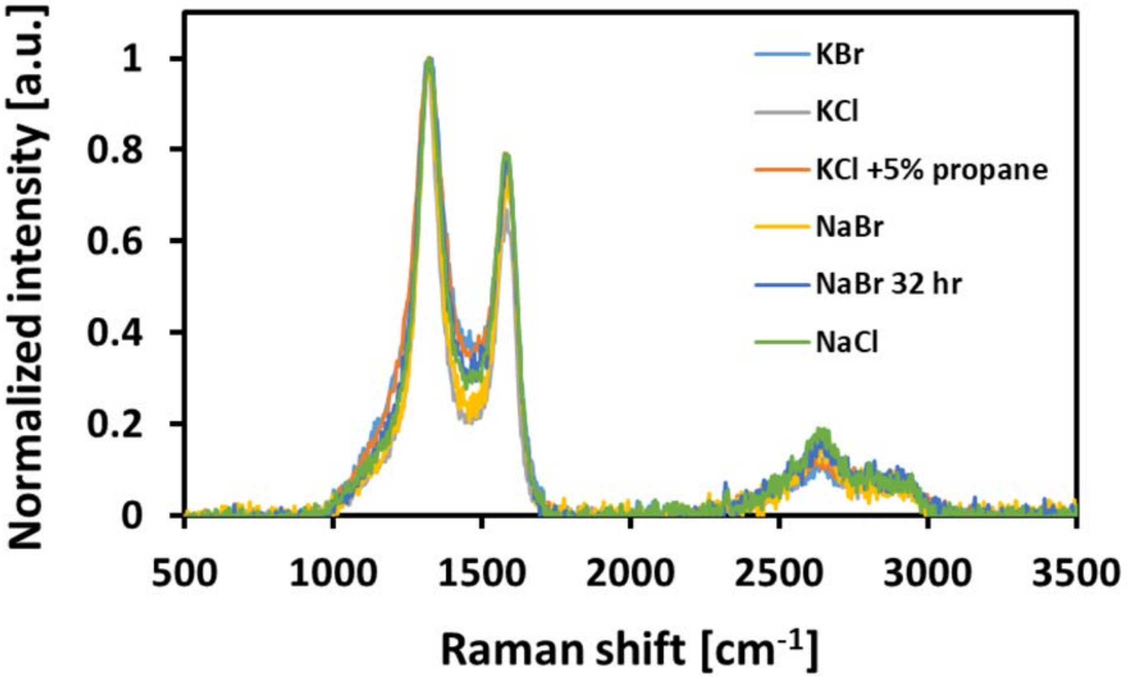




- Liquid metal catalysts showed very high activity for methane pyrolysis
- *Ab initio* molecular dynamics calculations support activation of host (Bi→Bi^+) by the electrophile (Ni→Ni^-)
- Carbon purity and catalyst recovery costs were identified as technical and economic challenges

Liquid Catalysts: Simple Salts

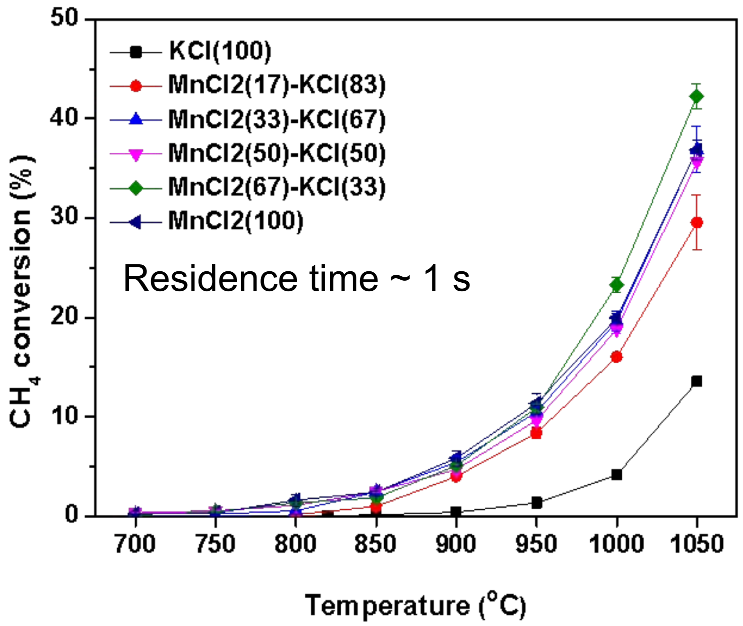


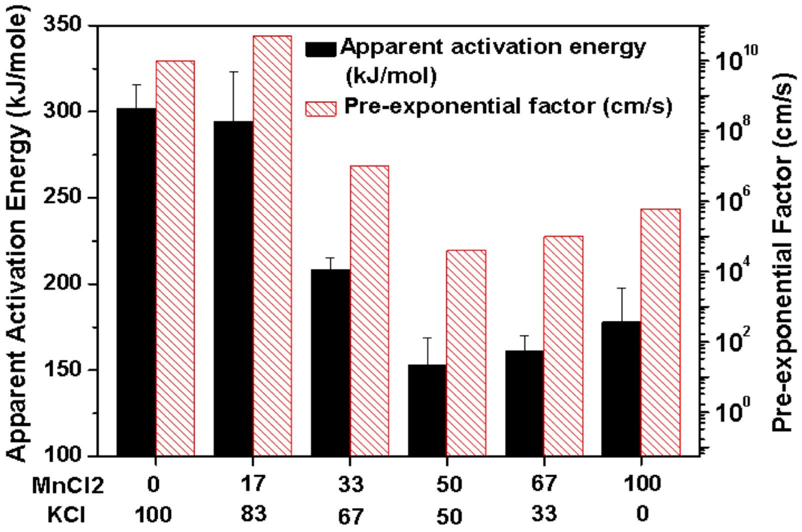


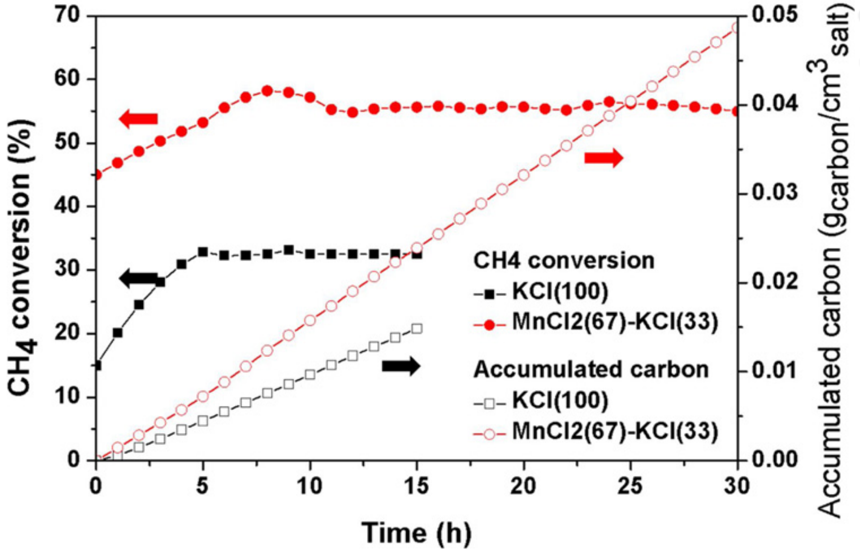
	KCl	NaBr	NaCl	KBr
Ea [kJ/mole]	280	270	300	330

- Monovalent salts have similar activities and produce similar disordered carbon
- Experiments in excellent agreement with gas-phase, radical mediated kinetic pathway

Liquid Catalysts: Binary Salts

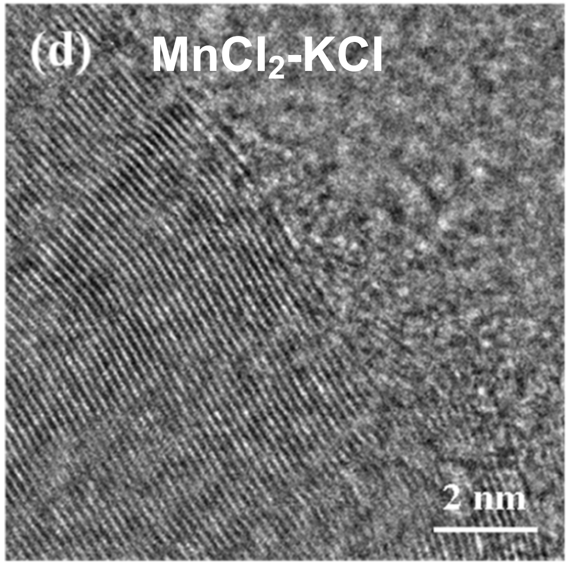


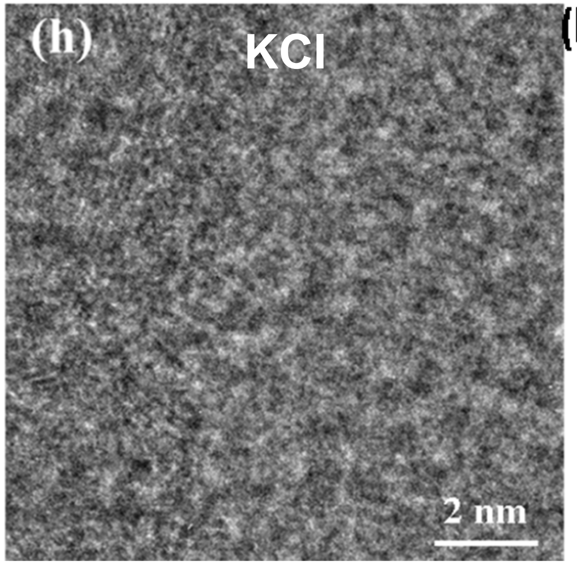


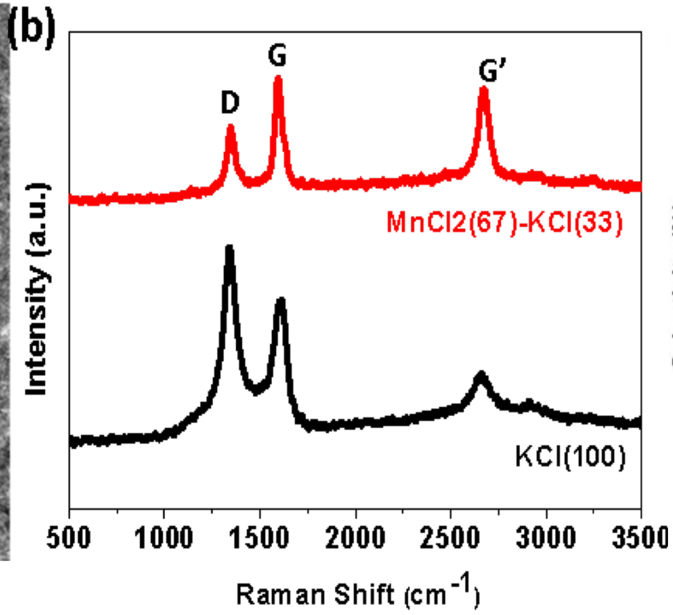


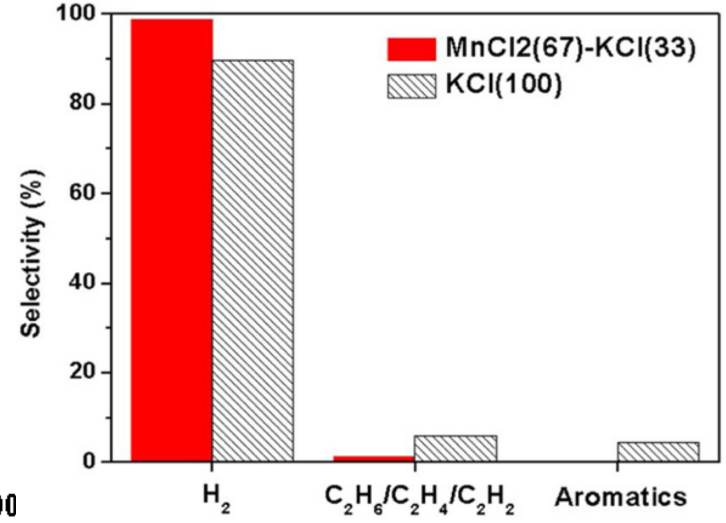
- Certain binary chloride salts show high catalytic activity for methane pyrolysis
  - Prolonged catalytic activity demonstrated (>24 hours)
- Activity of $MnCl_2$-KCl correlates to tetrahedrally coordinated $MnCl_4^{2-}$ molecular ion
- Surface mediated deep dehydrogenation demonstrated by isotope exchange

Liquid Catalysts: Binary Salts









- High hydrogen selectivity (>98%) at 40% methane conversion
- Graphitization of carbon in $MnCl_2$-KCl significantly higher compared to KCl
  - Indicative of carbon formation on the catalytic surface
- Moving Forward: Further investigation of binary chloride salts focused on identifying melt systems that are:
  - Highly catalytic
  - Produce graphitic carbon
  - Low cost and non-toxic

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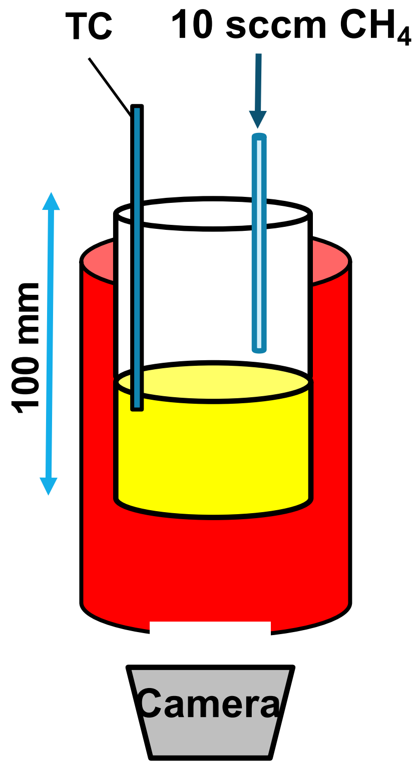
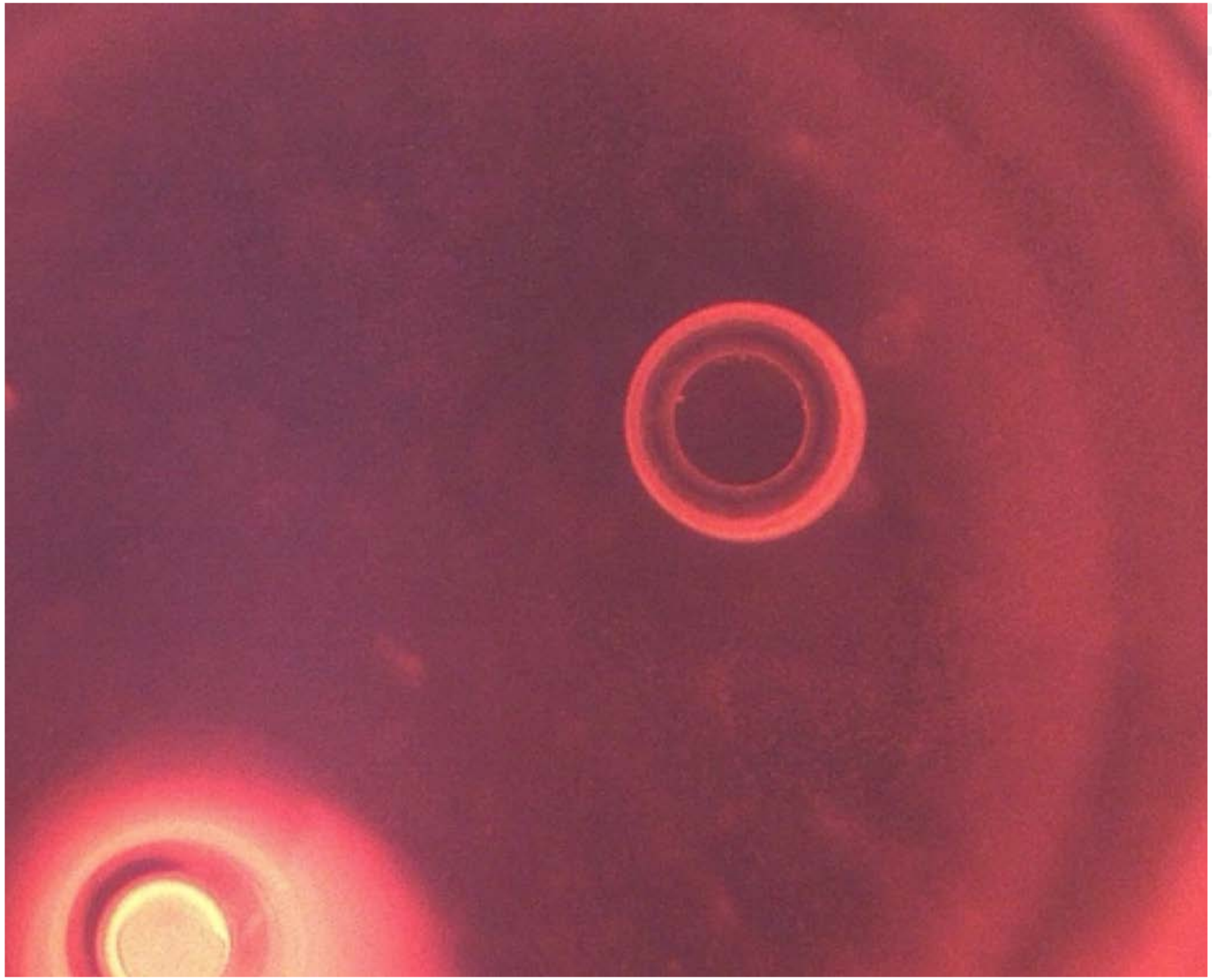
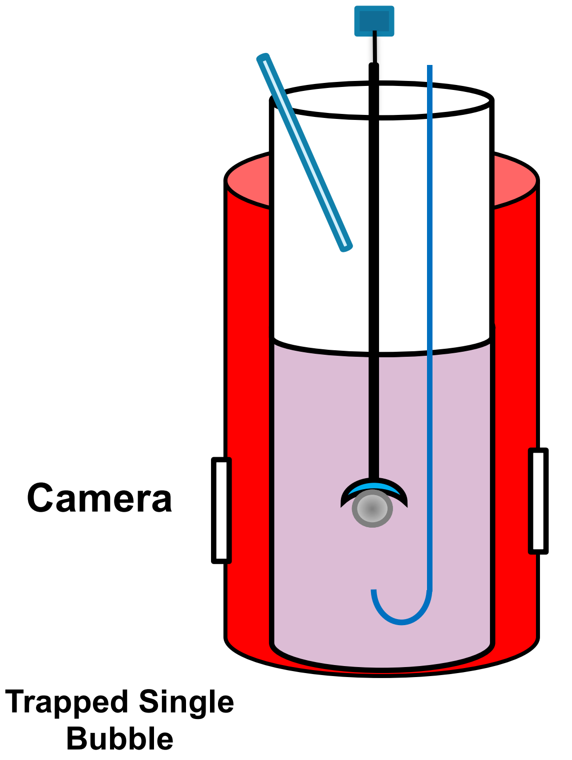
Direct Visualization of Carbon Deposition on Salt Surfaces

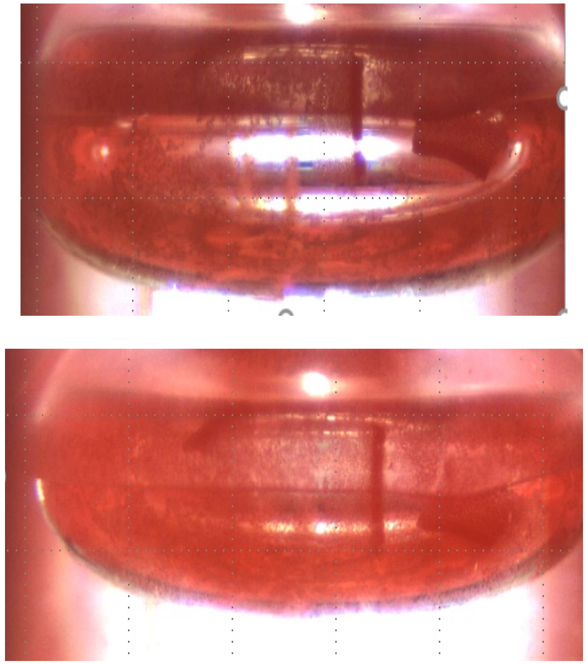
Carbon nucleation and growth on the surface of the molten salt, 1000 C

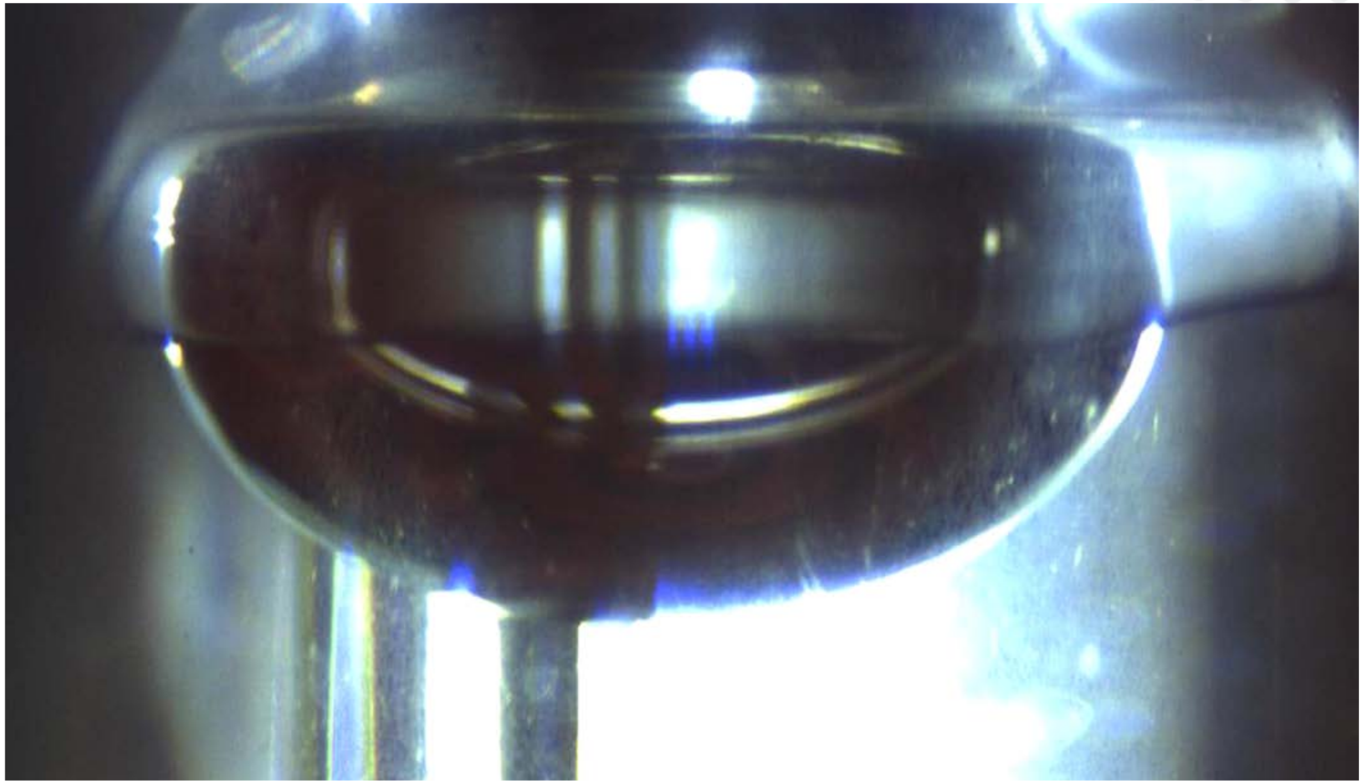




Direct Visualization of Carbon Deposition on Salt Surfaces



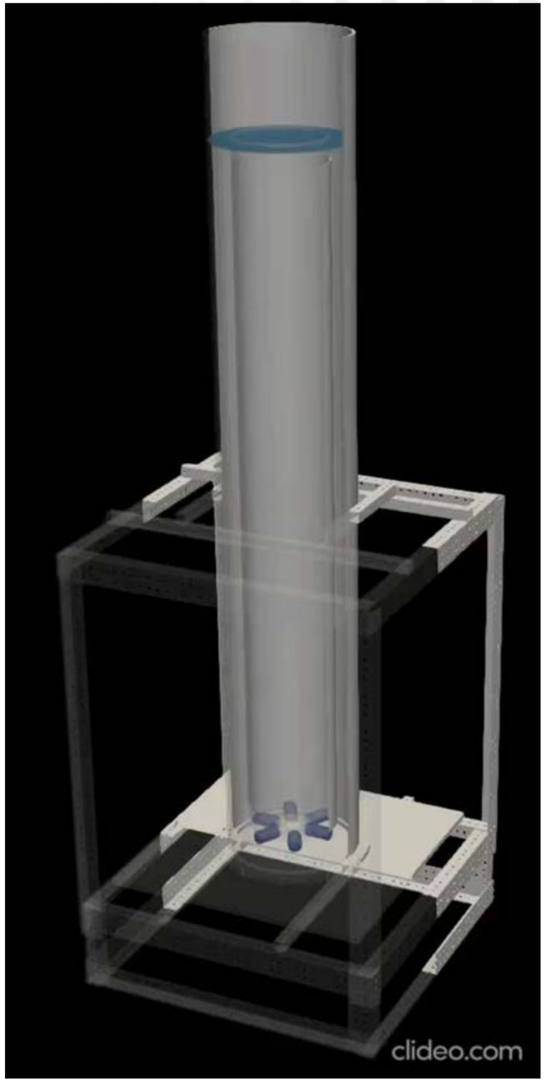




- Insulating properties of molten salts allow for direct imaging of methane pyrolysis and carbon formation
- Moving Forward: Extend apparatus capabilities for *in situ* spectroscopic analyses of molten salt during methane pyrolysis by Raman, IR, and UV/Vis
  - Help elucidate pyrolysis mechanisms for different systems
  - Allow for rational design of reaction conditions for optimized hydrogen and specific carbon production

Reactor Modeling & Design

- Constructed aqueous circulating fluid bubble column of sufficient size to avoid wall/entrance effects.
- Evaluated multiple gas sparger designs.
- Moving Forward: Continue building Eulerian multiphase CFD model to enable a verified predictive capability for building and scaling up methane pyrolysis bubbly flow reactor. Construct model system with continuous solid particulate removal capabilities.



Challenges and Potential Technical Partnerships

- Biggest challenge to date has been the generation of a clean carbon product
  - Metal contamination was a major issue early on
  - Moved to molten salt catalysts which have the advantage of:
    - Lower catalyst cost
    - Ability to tune carbon morphology
- Another challenge is identifying suitable materials of construction (MOC)
  - Designing rapid MOC testing of several different potential materials.
- Looking for technical partnerships with entities that have expertise in carbon modification and characterization

T2M

- C-Zero is working on the design and commercialization of its methane pyrolysis technology
- C-Zero plans to complete the full design of the commercial reactor by 2022
- We are looking for partnerships/collaborations with:
  - Current consumers of natural gas
  - Experts in delayed cokers
  - Hydrogen producers and consumers
  - Refineries (especially in California)

Production Unit

6000 kg H_2 / day
10 MW Thermal