CO_2-to-fuels through novel electrochemical catalysis
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Carbon Management and Natural Gas & Oil Research Project Review Meeting

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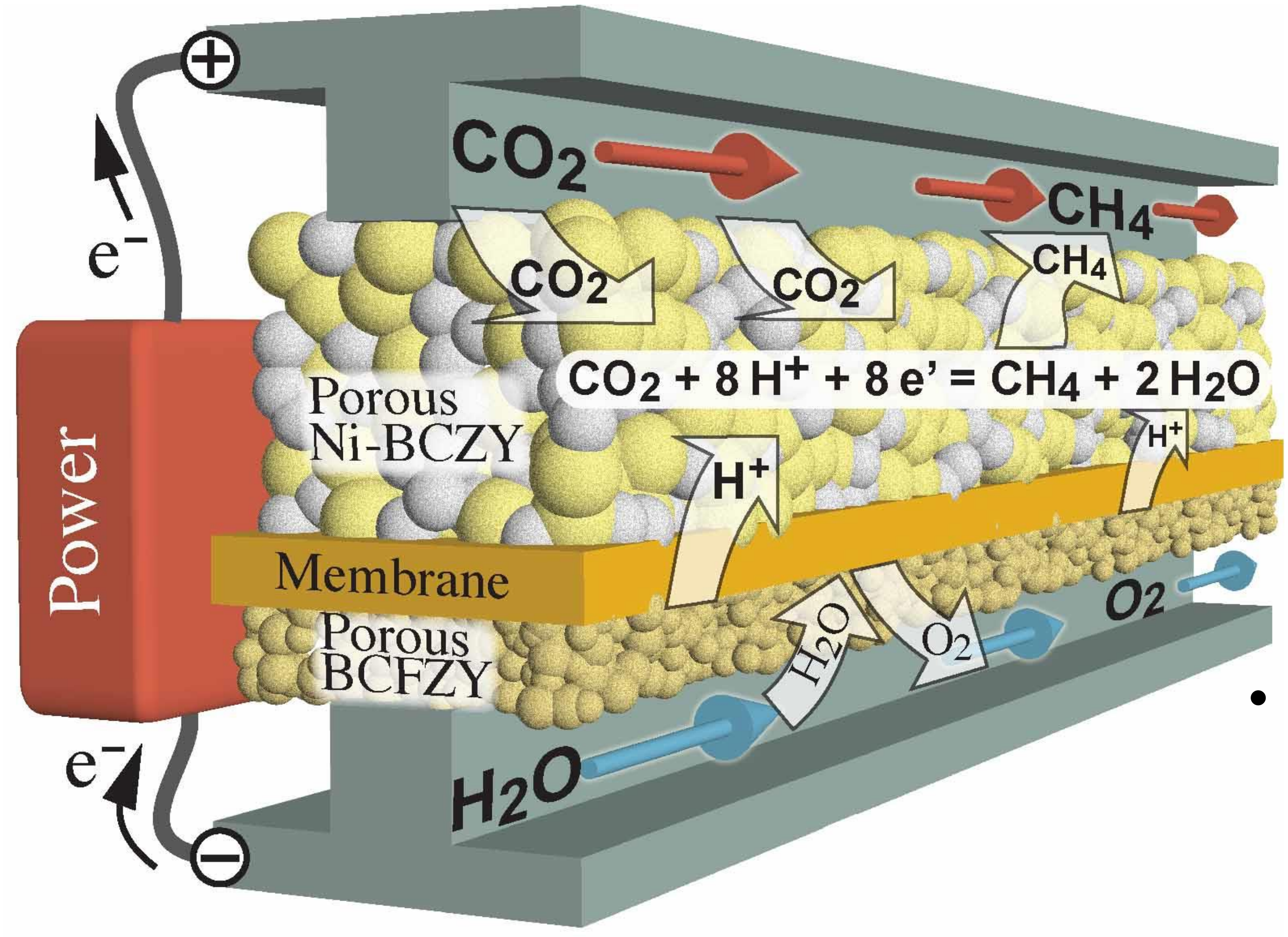
Project overview

- $800,000 in federal funding; $200,000 in cost share
- Duration: January 2019 – September 2021
- Participants
  - Colorado School of Mines (Mines)
    - Prof. Rob Braun, Mechanical Engineering
    - Prof. Robert J. Kee, Mechanical Engineering
    - Prof. Ryan P. O'Hayre, Metallurgical and Materials Engineering
    - Prof. Neal P. Sullivan, Mechanical Engineering
    - Post-doctoral fellow Zehua Pan, Materials scientist
    - Undergraduate student Tyler Pritchard, Techno-economic analyses
  - National Renewable Energy Laboratory (NREL)
    - Dr. Erick White, Chemical Reaction Engineer

Objective: Upgrade CO_2 to CH_4 using novel proton-conducting electro-ceramics…the "Sabatier Electrolyzer"

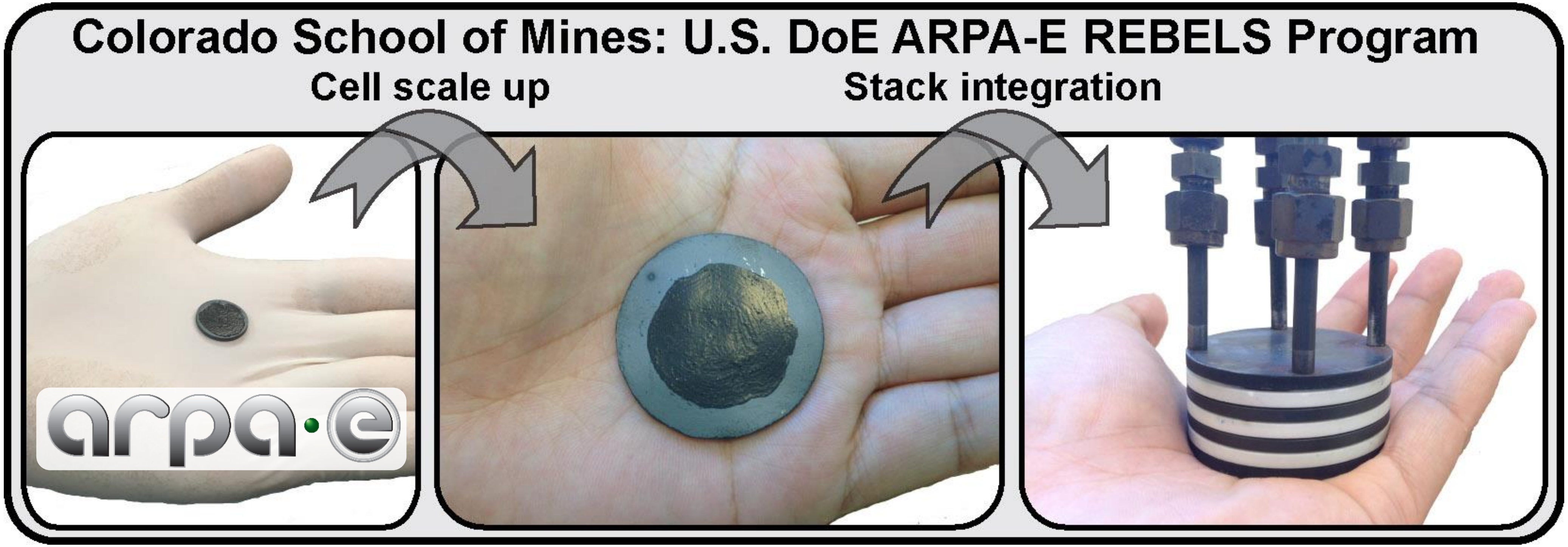
Illustration of the Sabatier Electrolyzer



- **Proton-conducting ceramic electrolyzer**
  - CO_2, H_2O, electricity inputs
  - CH_4 and O_2 outputs
  - Split H_2O in H^+ and O_2
  - Drive H^+ across membrane
  - CO_2 reacts with H^+ to form CH_4
  - Driven by external power source
    - Potential to store renewable electricity in the form of CH_4
    - Reduce carbon footprint while storing renewables
- **Results to date**
  - CO_2 conversion > 60%
  - CH_4 selectivity > 72%
  - Levelized cost of fuel production = \$104 / MW hr

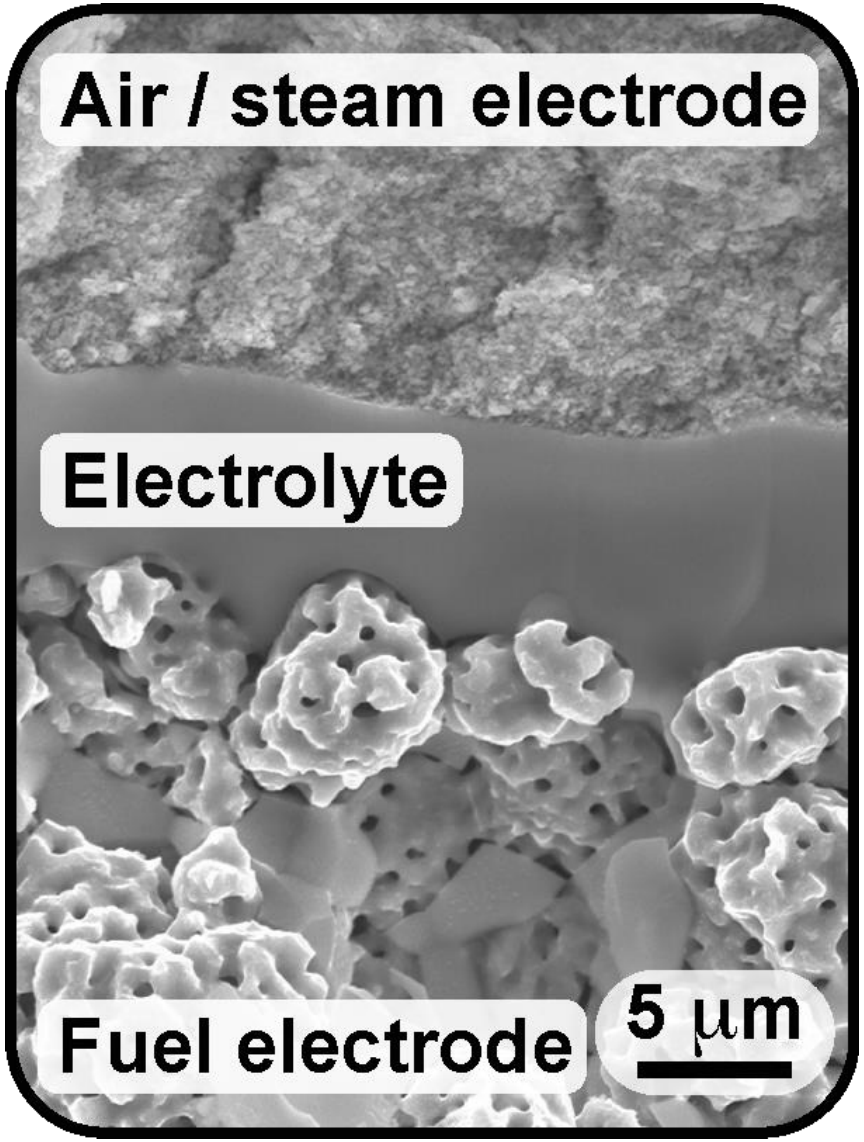
Mines is the nation's leader in protonic-ceramic electrolyzers: from button cells to multi-cell stacks

- Pure H_2 product stream from H_2O and electricity inputs
- 500 ºC operating temperature well matched to CO_2 upgrading
  - Hot enough for facile electrochemistry
  - Cool enough for favorable CO_2-to-CH_4 thermodynamics
- Inherently high Ni-catalyst loading promotes Sabatier chemistry



The heart of our "Sabatier Electrolyzer" is the protonic-ceramic electrochemical cell

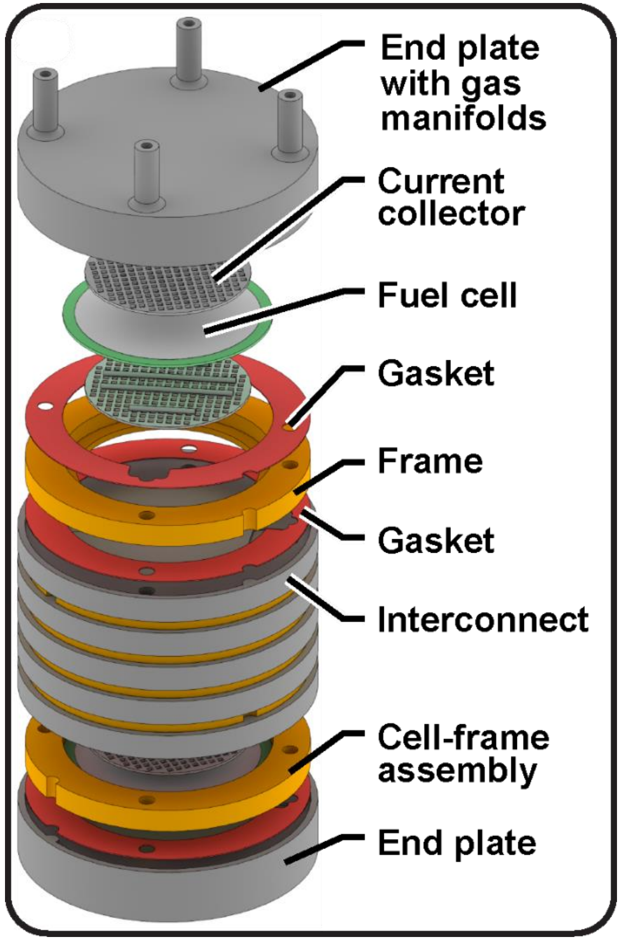
- Electrolyte material: $BaCe_{0.4}Zr_{0.4}Y_{0.1}Yb_{0.1}O_{3-d}$
  - Termed "BCZYYb"
  - Good stability, ruggedness
  - High H^+ conductivity at ~ 500 ºC
- Composite fuel electrode
  - Ni + BCZYYb "cermet"
  - Mechanical support
  - High catalytic activity
- Composite steam electrode
  - $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Yb_{0.1}O_{3-d}$
    - 80 wt-% BCFZY
    - 20 wt-% BCZYYb
- Cells fabricated using conventional techniques



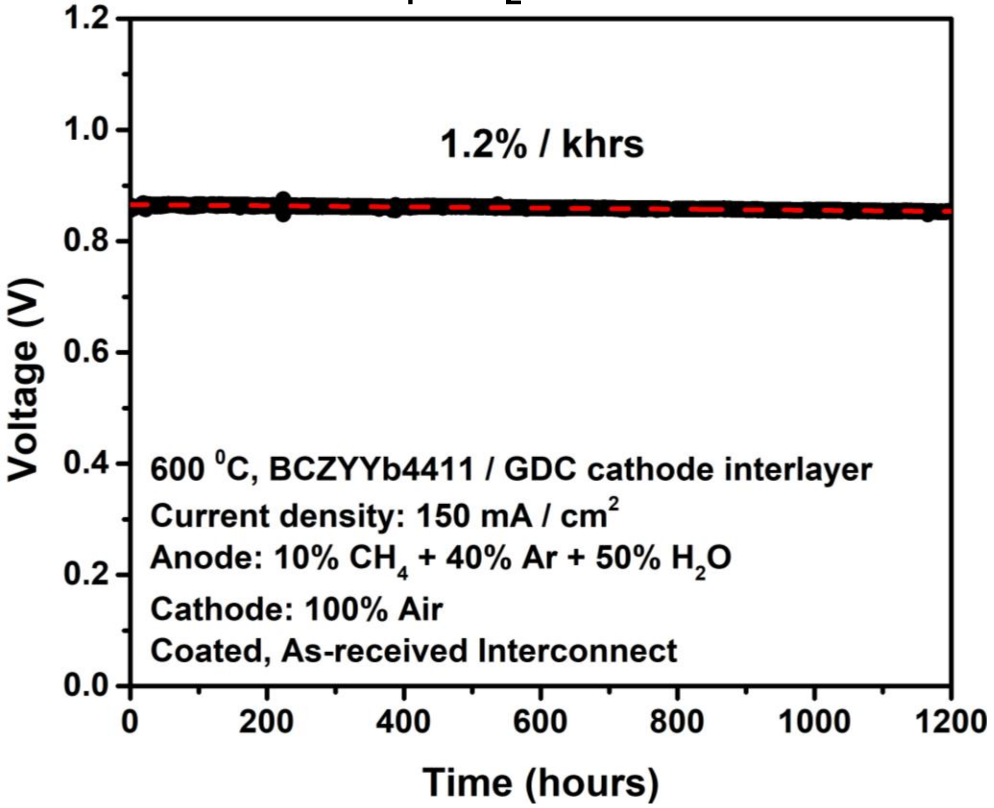
The heart of our “Sabatier Electrolyzer” is the protonic-ceramic electrochemical cell

- Cell bonded to frame
- Metallic interconnect separated cells
- Metallic current collectors connect cells in series
- Assembly is compression sealed with Thermiculite gaskets
- Encouraging stability demonstrated

Stack schematic

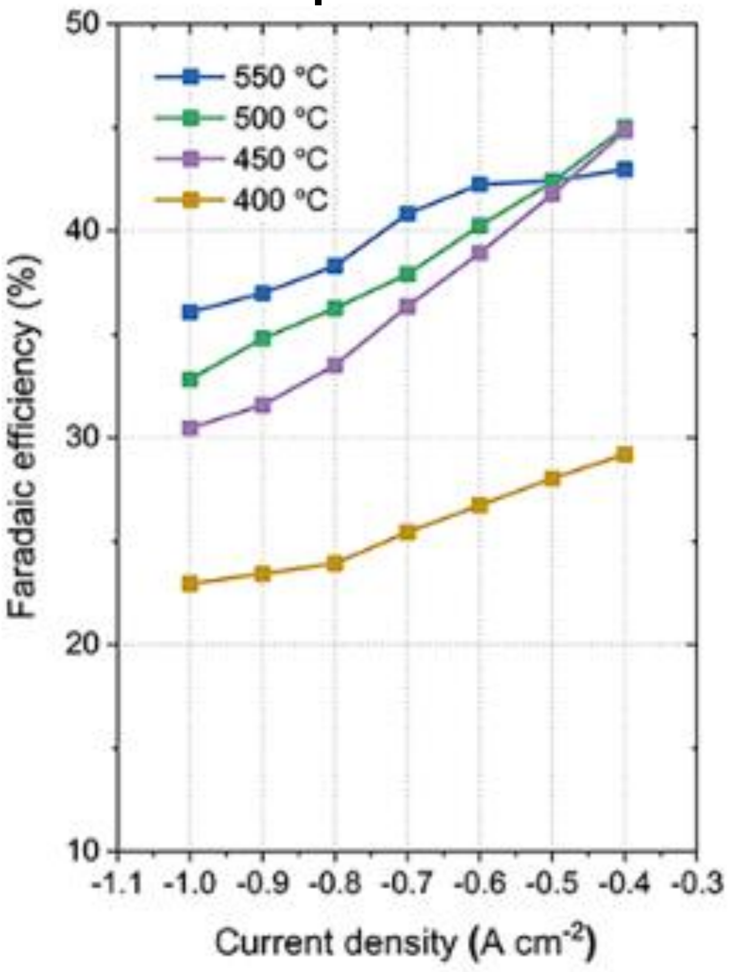


Stability of two-cell protonic-ceramic fuel-cell stack over 1200 hr under $CH_4 + H_2O$ fuel at 600 ºC

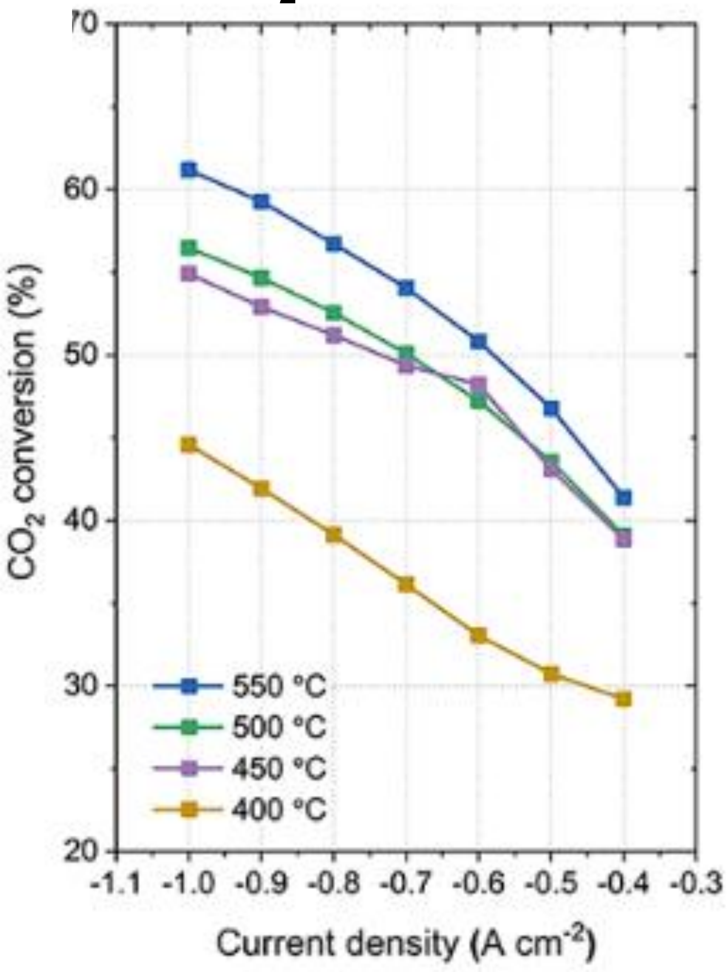


We are exploring operational tradeoffs that balance cell performance, CO_2 conversion, and CH_4 yield

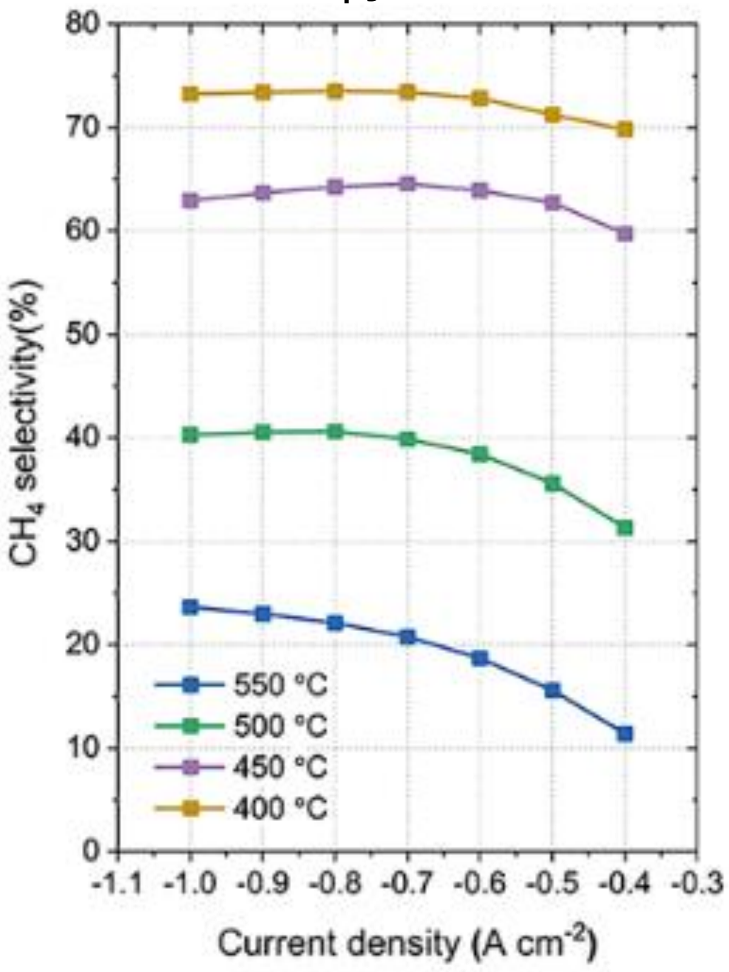
Higher temperature improves cell performance



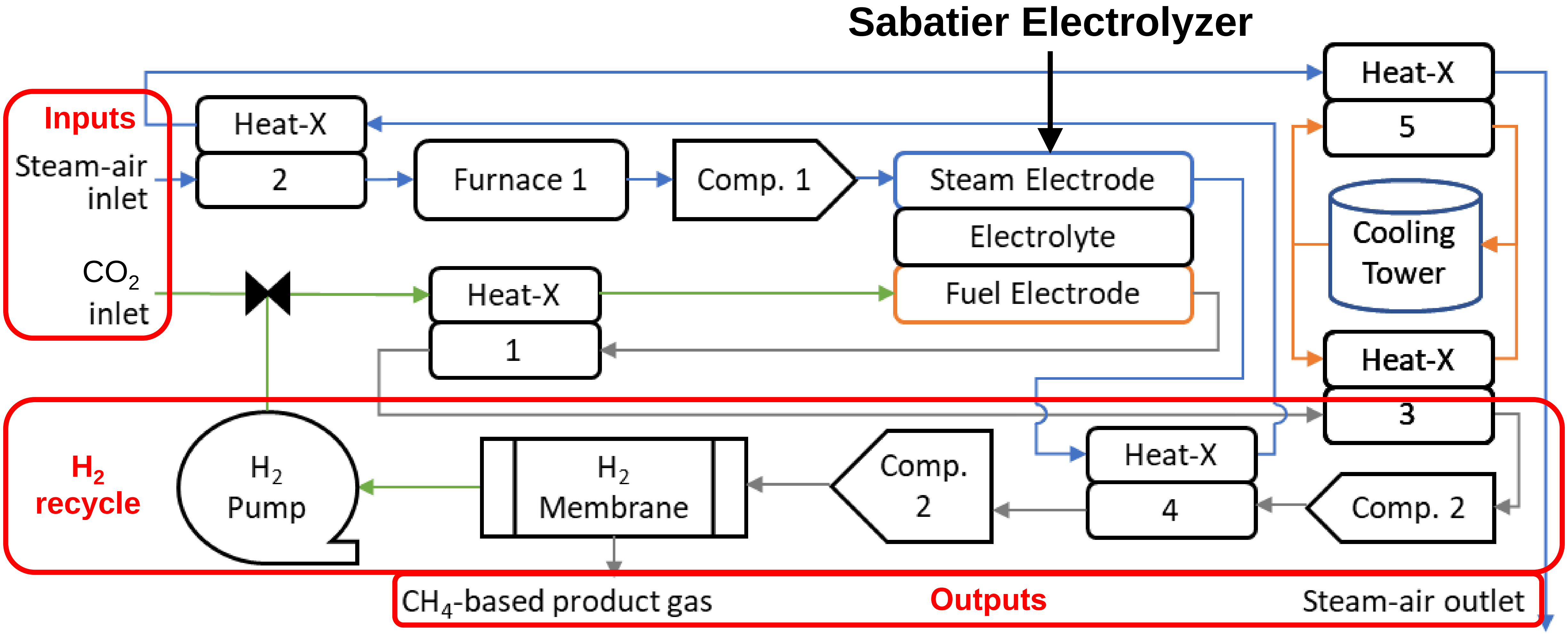
Higher temperature improves CO_2 conversion



Higher temperature decreases CH_4 yield



Techno-economic analyses provide insight on "optimal" operating points



CO_2-to-CH_4 System sized for six (6) metric tons of CO_2 per day

Four system operating cases were compared from the perspective of Levelized Cost of CH_4 Fuel Production (LCoFP)

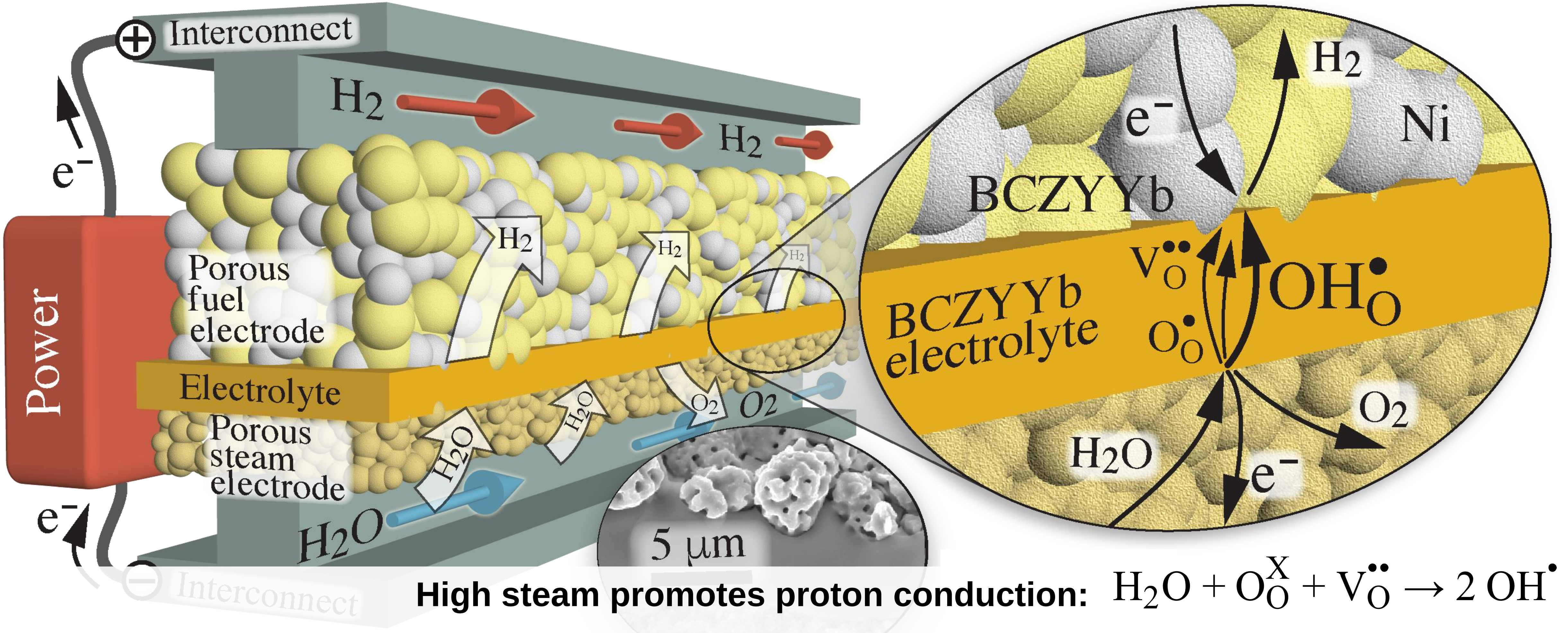
	Case 1	Case 2	Case 3	Case 4*
Current density	1 A cm^{-2}	1 A cm^{-2}	0.4 A cm^{-2}	0.4 A cm^{-2}
Applied voltage	1.63 V	1.72 V	1.50 V	1.50 V
Temperature	450 ºC	450 ºC	450 ºC	450 ºC
CH_4-yield ratio	34.6%	40.9%	65.6%	65.6%
Faradaic efficiency	30.6%	39.8%	62.1%	90%
H_2 recycle?	No	No	Yes	Yes

Operational cost parameters

Parameter	Value
Installation factor	130%
Capacity factor	100%
Cost of O&M	0.0743 \$ kWh^{-1}

Parameter	Value
Price of electricity	0.05 \$ kWh^{-1}
Price of CO_2	40.00 \$ t^{-1}
Price of H_2O	0.69 \$ t^{-1}
PCEC stack life	5 years
Plant life	20 year

Protonic ceramics demonstrate mixed ionic-electronic conduction and internal shorting, lowering efficiency; H_2 recycle mitigates this problem



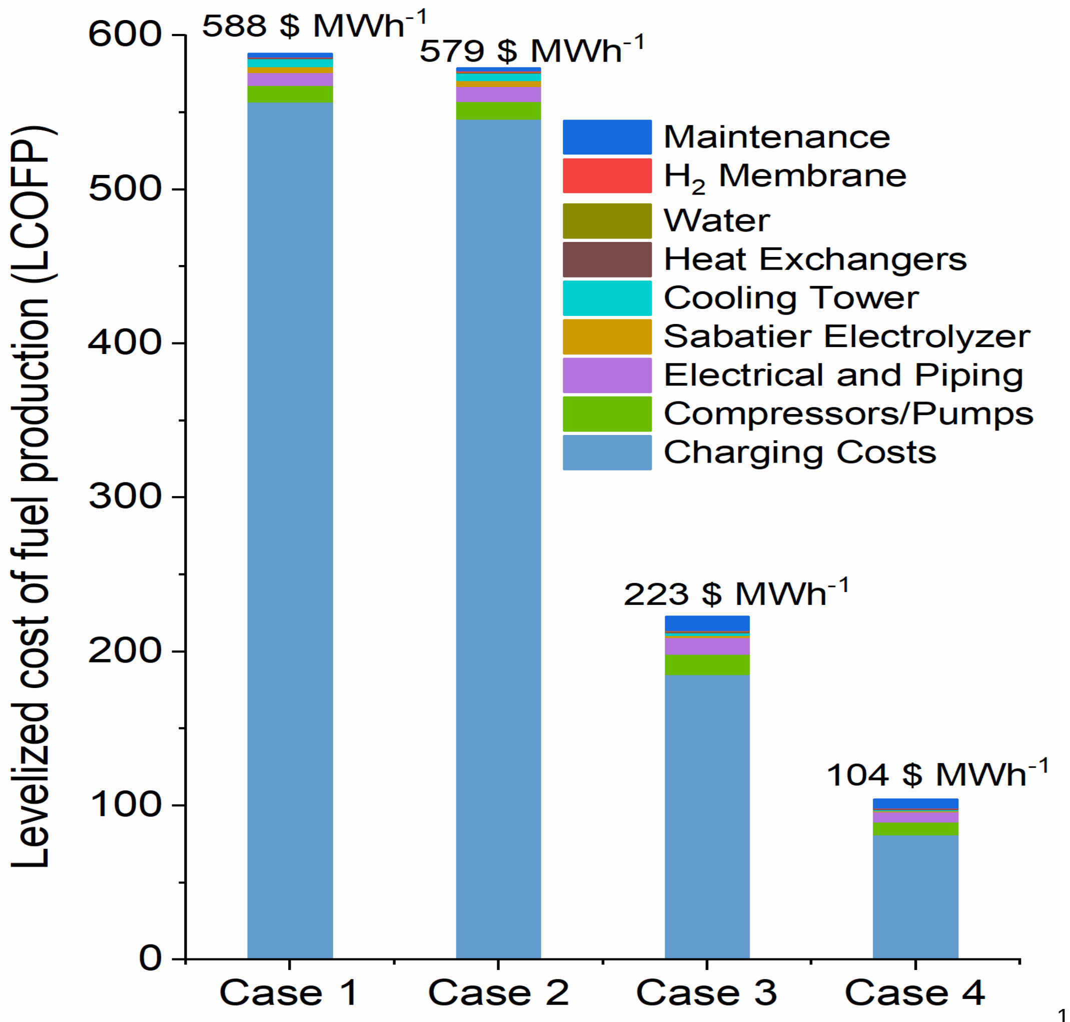
High steam promotes proton conduction: $H_2O + O_O^X + V_O^{\bullet\bullet} \rightarrow 2\,OH^{\bullet}$

High oxygen promotes hole conduction, lowering Faradaic efficiency: $\frac{1}{2}O_2 + V_O^{\bullet\bullet} \rightarrow 2\,h^{\bullet} + O_O^X$

Four system operating cases were compared from the perspective of Levelized Cost of CH_4 Fuel Production (LCoFP)

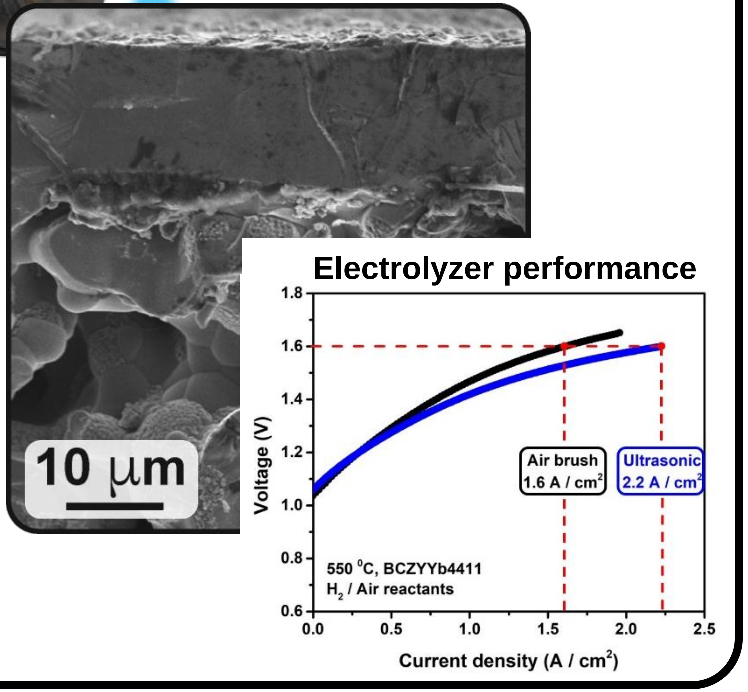
- Charging costs, or price of electricity, drives the cost of CO_2-to-CH_4 system
- Case 4 blends high Faradaic efficiency (90%) and low electricity cost ($0.02 / kW hr)
- Case 4 operational state point results in LCoFP = $104 / MW hr
  - Lower than cost of town gas in Singapore, with similar composition
- Impact of materials properties (Faradaic efficiency) on cost is pronounced

Levelized cost of CH_4 fuel production across the four cases

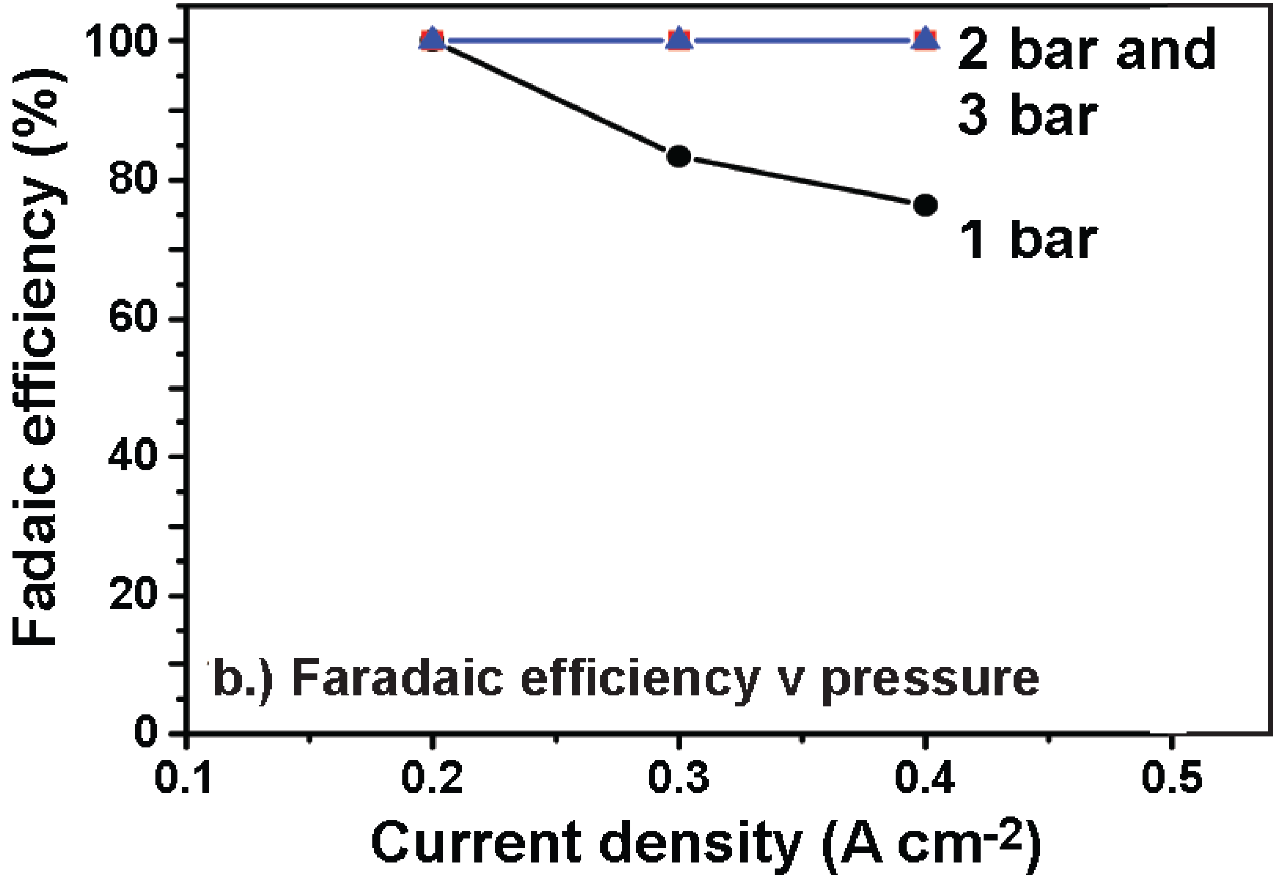


Going forward, Mines is harnessing recent laboratory advancements, including pressurized operation, to drive down cost and boost yield

New fabrication tools boost electrolyzer performance by 50%



Pressurized operation boosts Faradaic efficiency to 100%



In summary, we've found proton-conducting ceramic electrolyzers to be impactful in upgrading CO_2 to CH_4, at reasonable cost

- Critical to define optimal operating condition to achieve lowest cost
  - Higher-temperature operation near 600 ºC
    - Improves electrochemical performance and H_2 production
    - Increases chemical kinetics and CO_2 conversion
  - Lower-temperature operation near 400 ºC
    - Promotes CH_4 formation over CO + H_2 production
    - Reduces electrolyzer internal shorting, enables higher efficiency
  - Our best state point: ~ 450 ºC, 55% CO_2 conversion, 62% CH_4 selectivity
  - H_2 recycle proves critical to achieving high Faradaic efficiency
- Techno-economic analyses identify key cost drivers and attractive operating conditions
  - Charging costs drive OPEX
  - High Faradaic efficiency (~ 90%) minimizes charging costs
  - Levelized Cost of CH_4 Fuel Production can be as low as \$104 / MW hr

Acknowledgements

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