Harnessing proton-conducting ceramics to produce methane and oxygen on Mars

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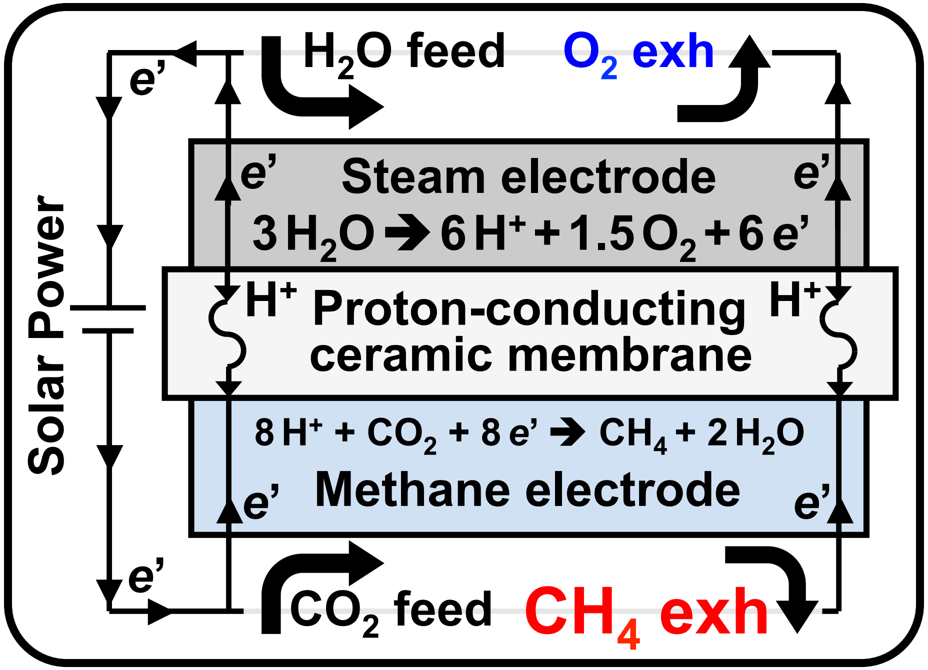
SCHOOL OF MINES COLORADO 1874

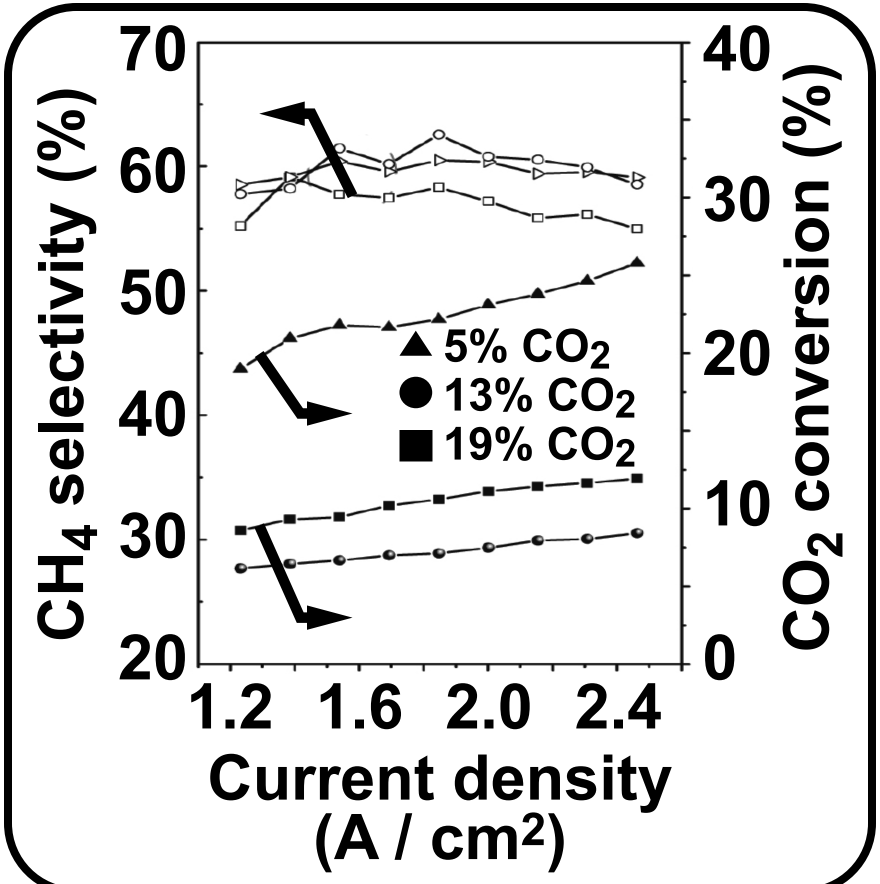
CFCC Colorado Fuel Cell Center

We are using proton-conducting ceramics to convert H_2O & CO_2 into CH_4 and O_2

Concept



Performance



We have been developing proton-conducting ceramics to convert natural gas into gasoline

- First inspired by CoorsTek, Inc.
  - Dr. W. Grover Coors
  - Long history with Mines
- Methane dehydroaromatization (MDA)
  - Upgrade natural gas into benzene

$$6\ CH_4 \rightarrow C_6H_6 + 9\ H_2$$

  - Suffers from poor CH_4 conversion
  - Thermodynamic limitation
- Proton-conducting membrane
  - Remove H_2 from product stream
  - Shift thermo towards products
  - Increase CH_4 conversion
  - Produce more C_6H_6 and the like

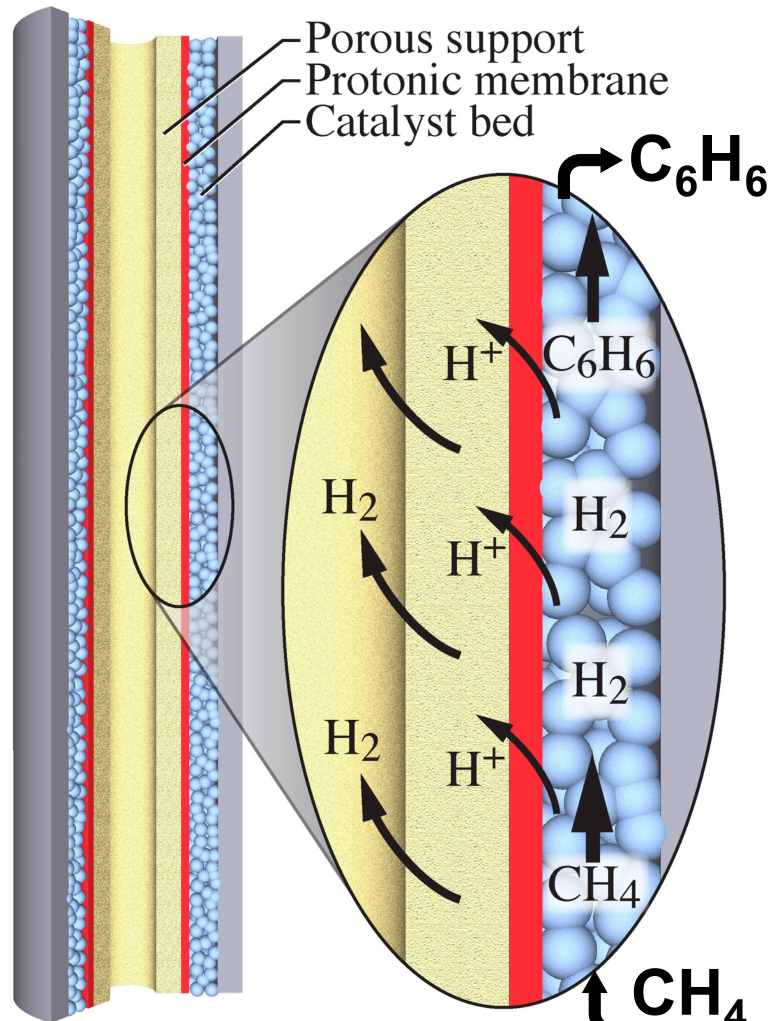
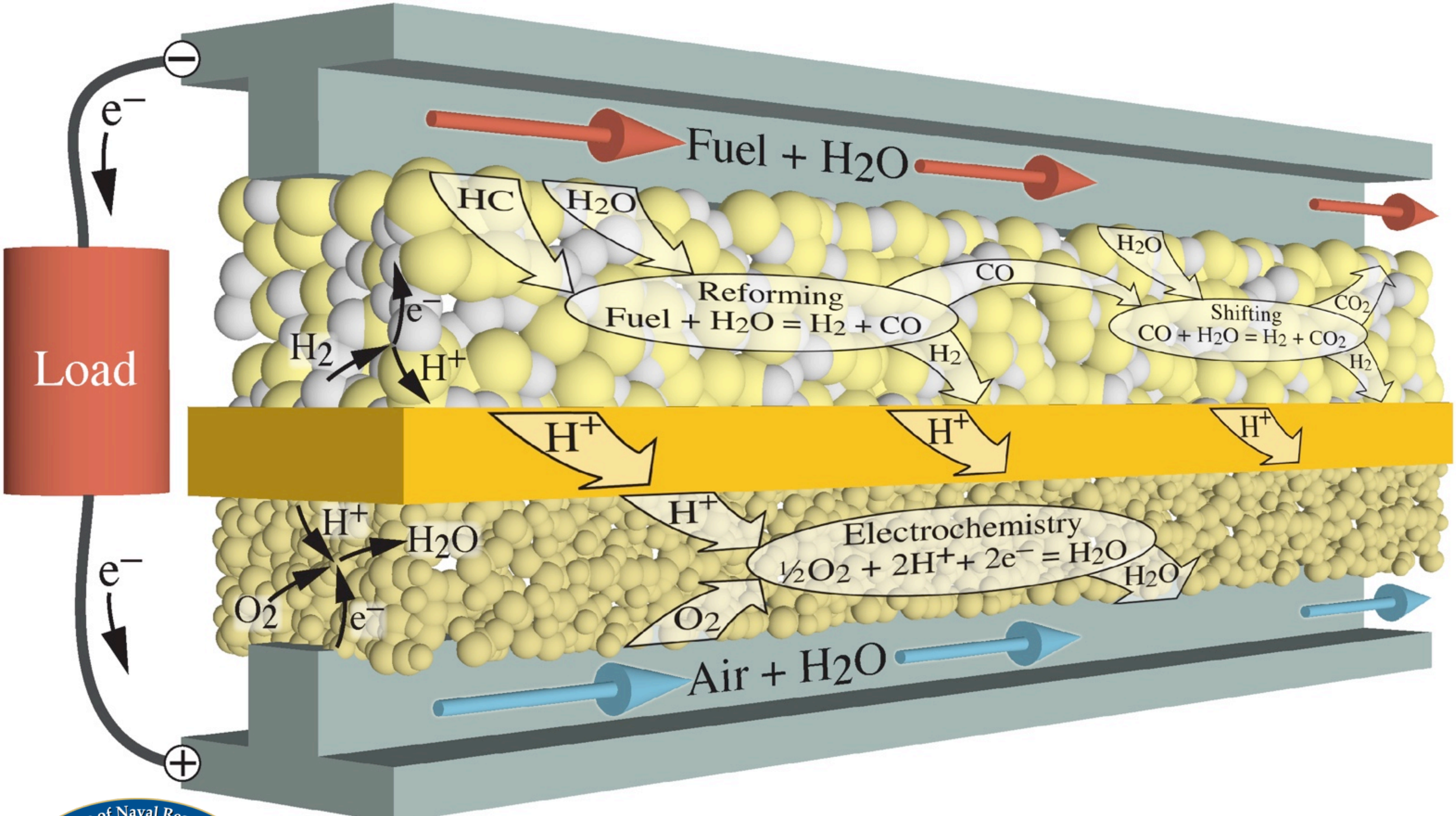


Image courtesy of Prof. Robert J. Kee, CSM

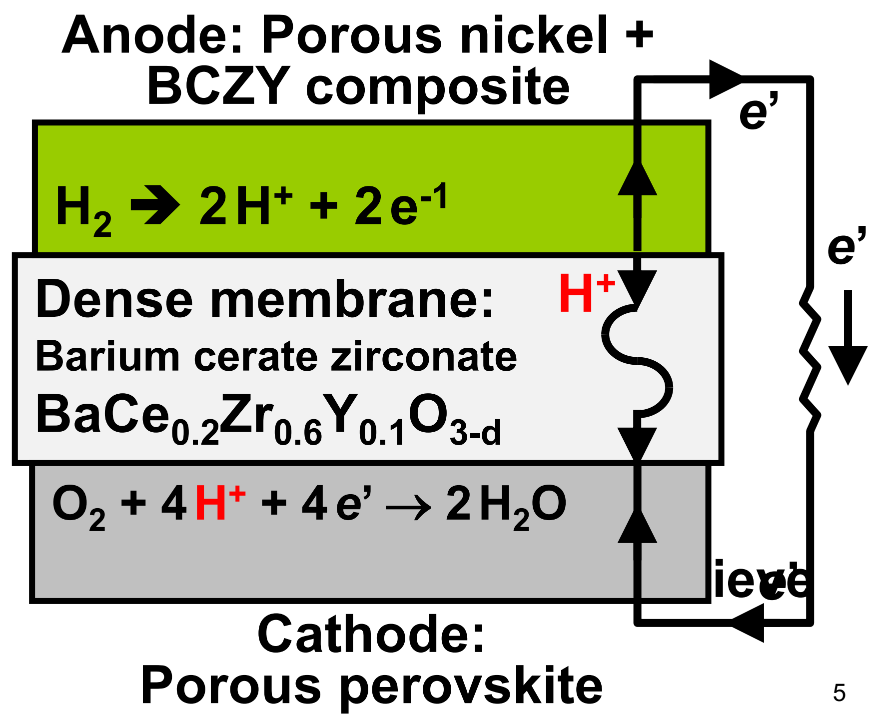
MDA produced breakthroughs in fuel-cell applications for efficient, distributed electricity generation



Proton-conducting ceramics are an emerging material with broad energy applications

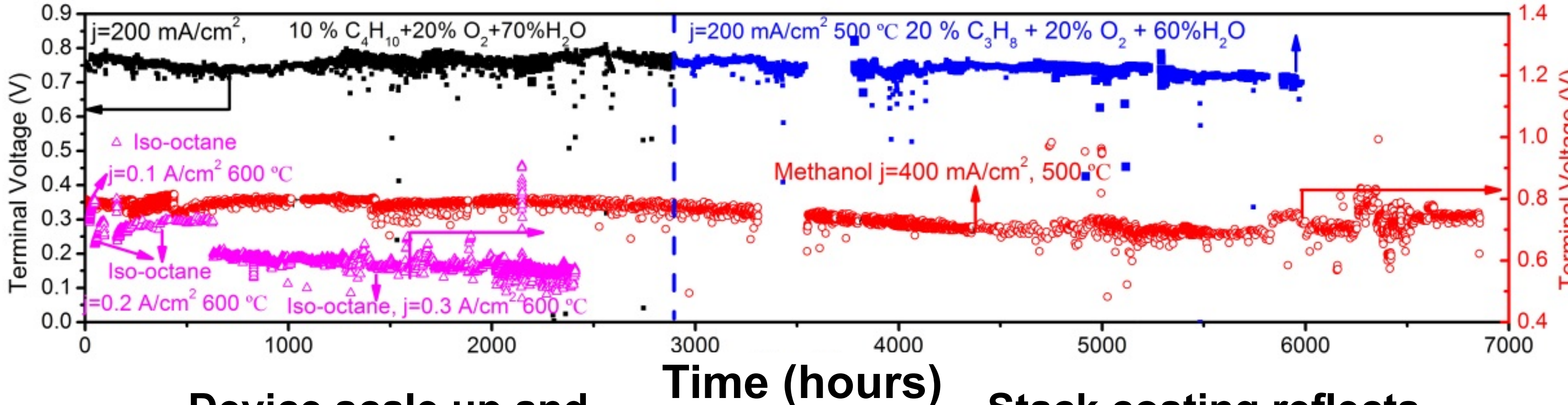
- Ceramic ion conductors are an active area of research
  - Yttria-stabilized zirconia (YSZ) is the current state-of-the-art
  - Oxygen ions (O^{2-}) serve as charge carriers
  - Require 700 – 850 ºC operation
- Protonic ceramics have a number of performance benefits
  - Small charge carrier (H^+)
  - Higher ionic conductivity
  - Lower-temperature operation
    - 500 – 600 ºC operation
    - Lower degradation rates
    - Lower cost balance of plant
- ABO_3 perovskite structure
  - $BaCe_xZr_yY_{1-x-y}O_{3-d}$
    - Tune stoichiometry to desired properties

Protonic Ceramic Fuel Cell

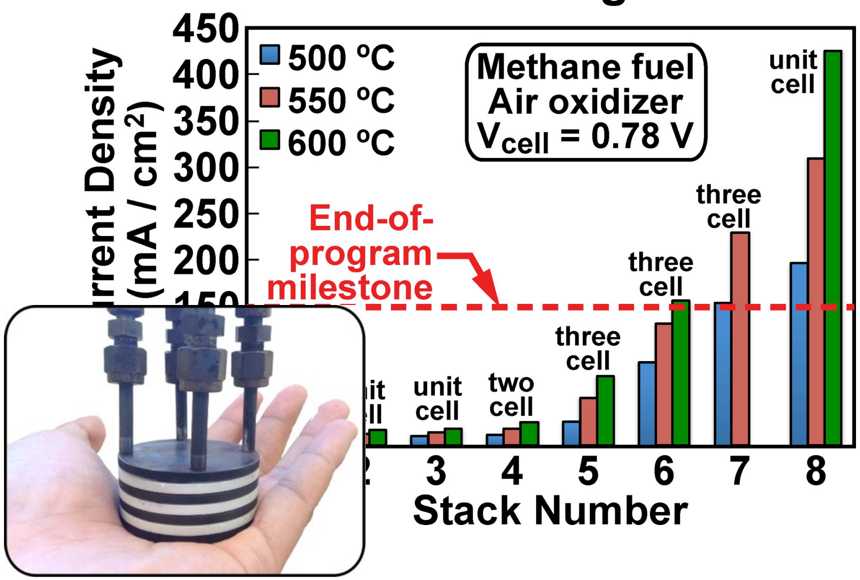


Our Phase I REBELS effort led to breakthroughs in intermediate-temperature fuel-cell performance

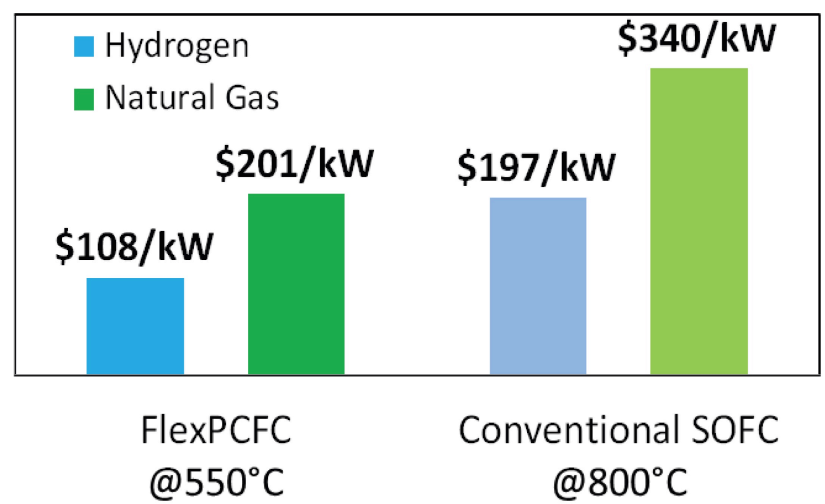
Long-term operation under direct hydrocarbon fuels (no pre-reforming)



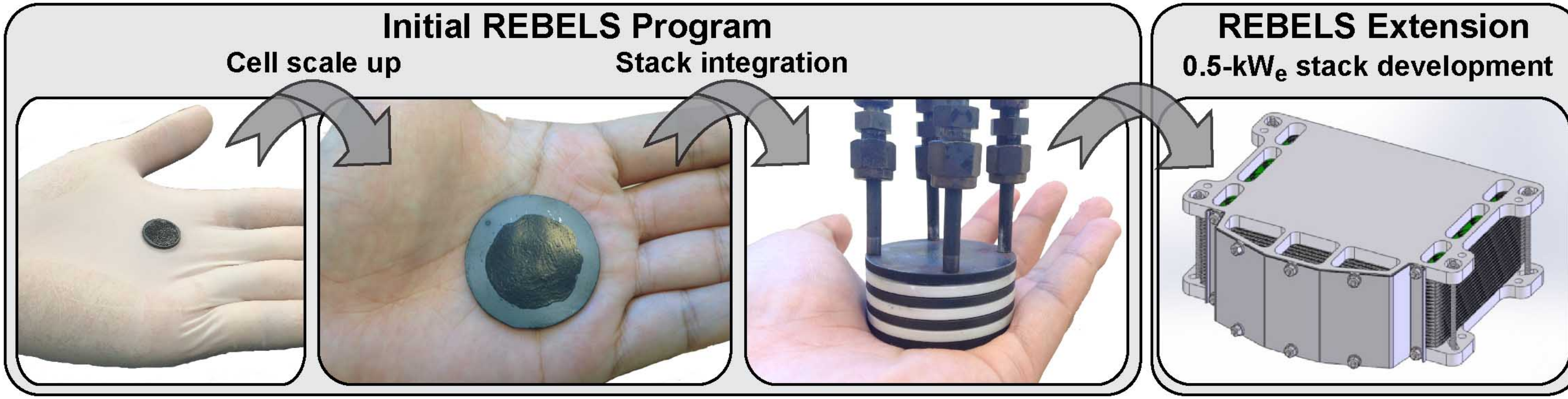
Device scale up and multi-cell stack integration



Stack costing reflects protonic-ceramic advantages



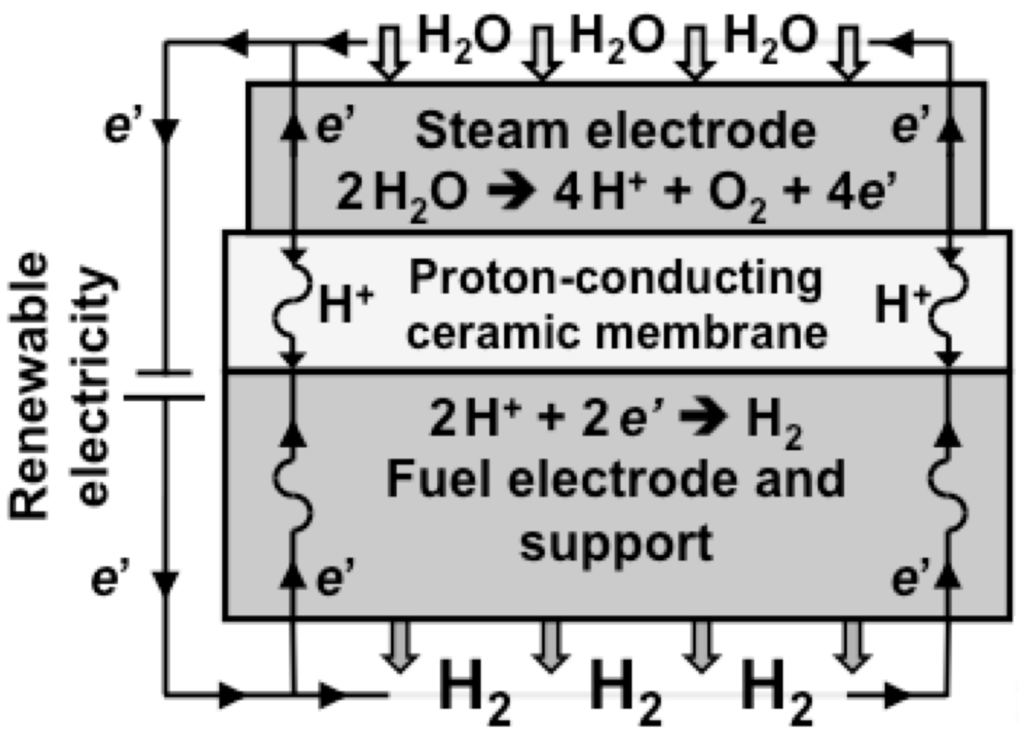
Promising results justify further protonic-ceramic fuel-cell scale up to the 500-W stack level in Phase II



- New industrial partner: FuelCell Energy (Danbury, Connecticut, USA)
- Further scale up of cell size by order of magnitude
- Explore and mitigate degradation
- Optimize hydrocarbon internal reforming conditions
- Understand “value proposition” of protonic-ceramic fuel cells

We are extending protonic ceramics for steam electrolysis, H_2 generation, and energy storage

- Pure H_2 product stream is formed, unlike O^{2-} electrolyzers
- Eliminates costly downstream H_2-separation processes
- Serves to store intermittent renewable energy in form of hydrogen
- Recent award from DOE Fuel Cell Technologies Office
  - Two-year program; target start date of August 2018

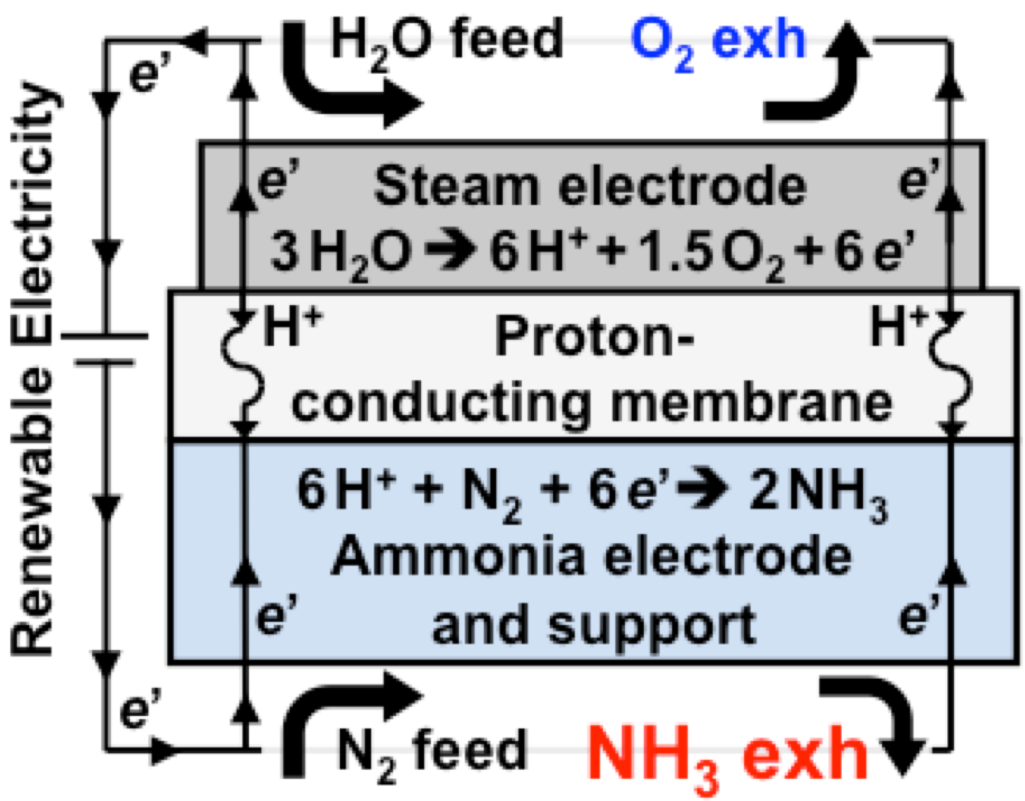


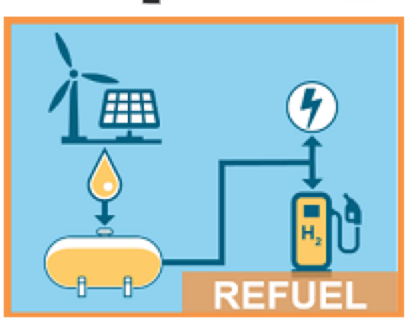
We are now extending protonic ceramics to chemicals synthesis for renewable-energy storage

- **Ammonia presents an effective energy-storage solution**

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3$$

- **Create carbon-neutral liquid fuel to store intermittent renewables**





Central objective is operation under 100% internal reforming of natural gas fuel premixed with steam

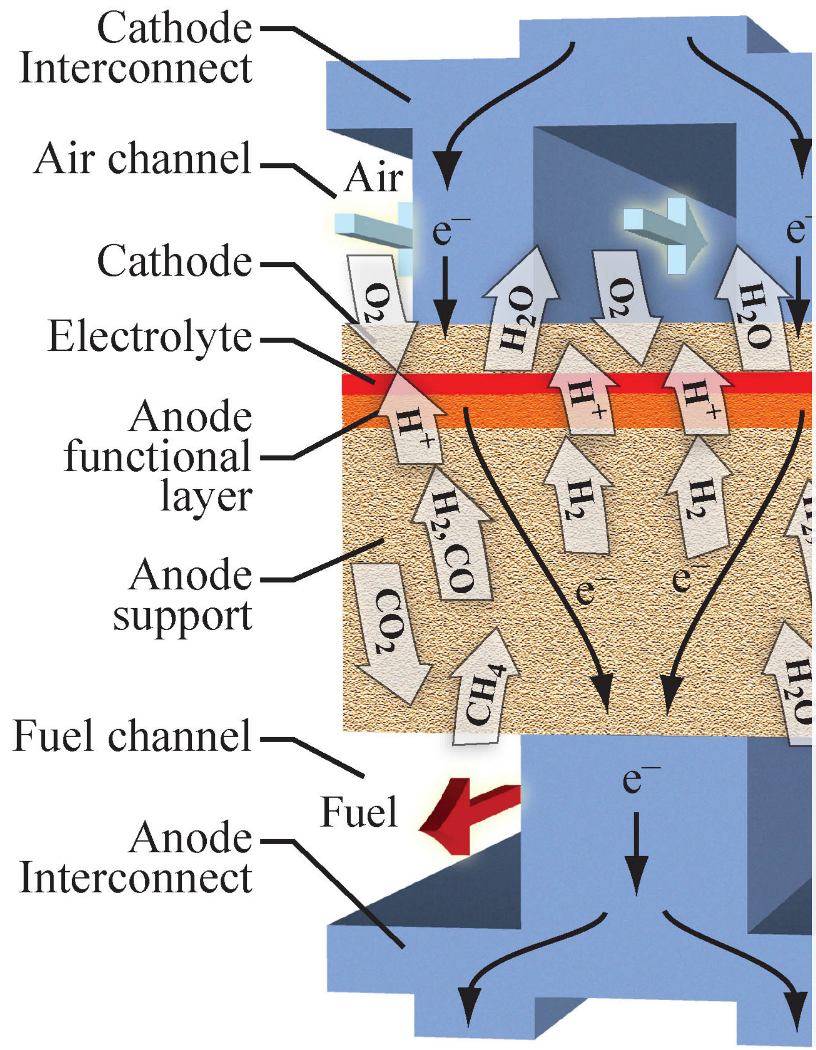


Image courtesy of Prof. R.J. Kee

- Steam injected with CH_4 fuel
- H_2 consumption shifts chemistry

  $$CH_4 + 2\,H_2O \rightarrow 4\,H_2 + CO_2$$

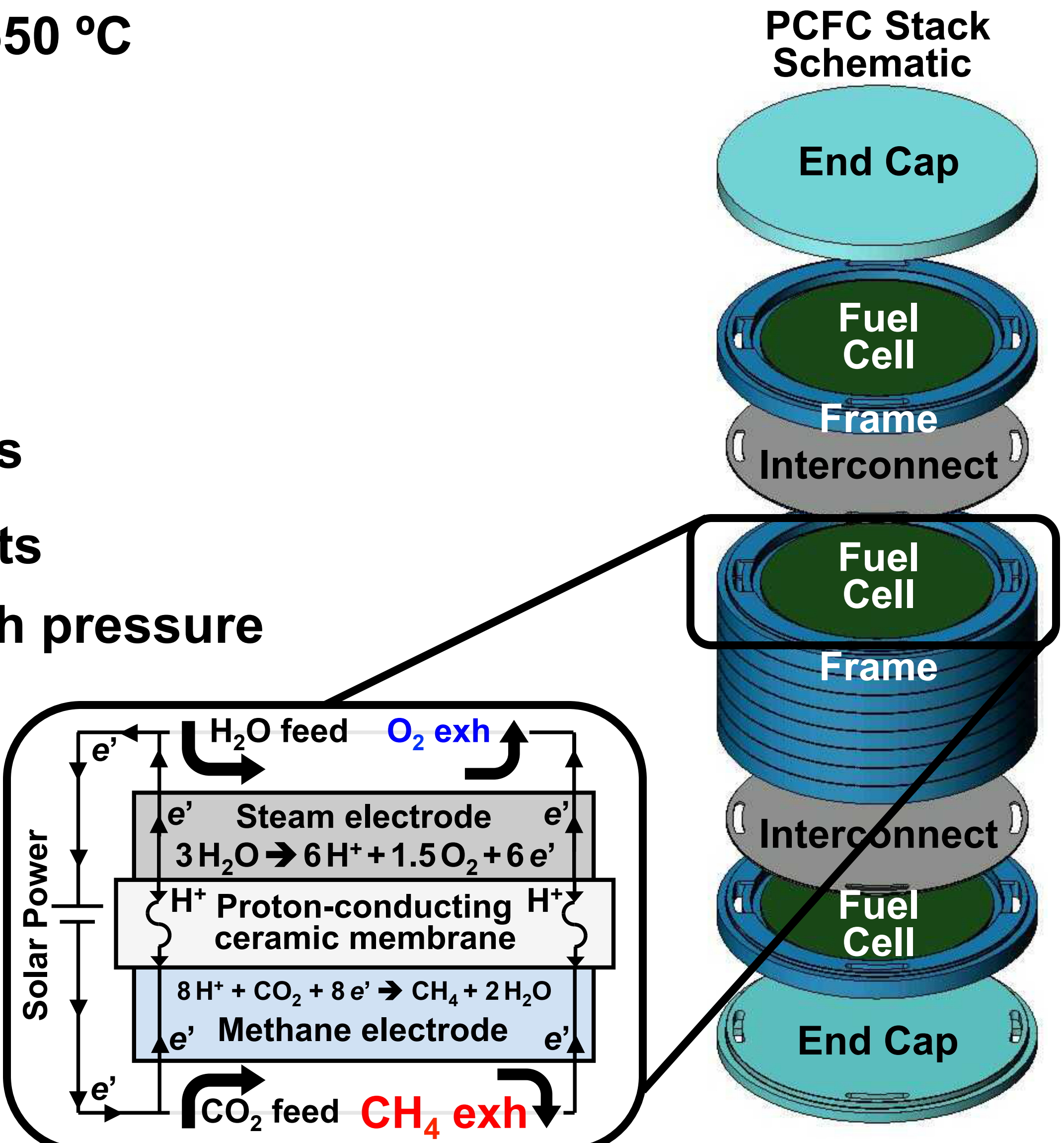
- Gas transport through porous anode
  - Optimal anode morphology
    - High porosity
    - Large pore diameters
    - Open microstructure
- Hydrocarbon internal reforming
  - Catalytic processes
  - Optimal anode morphology
    - High catalyst surface area
    - Lower porosity
    - Tight microstructure
- Conflicting anode-design objectives

We have a new program with NASA for harnessing protonic ceramics to make fuel on Mars

- Convert CO_2 and H_2O into O_2 and CH_4

Operation of ceramic electrochemical devices on Mars presents "balance-of-plant" challenges

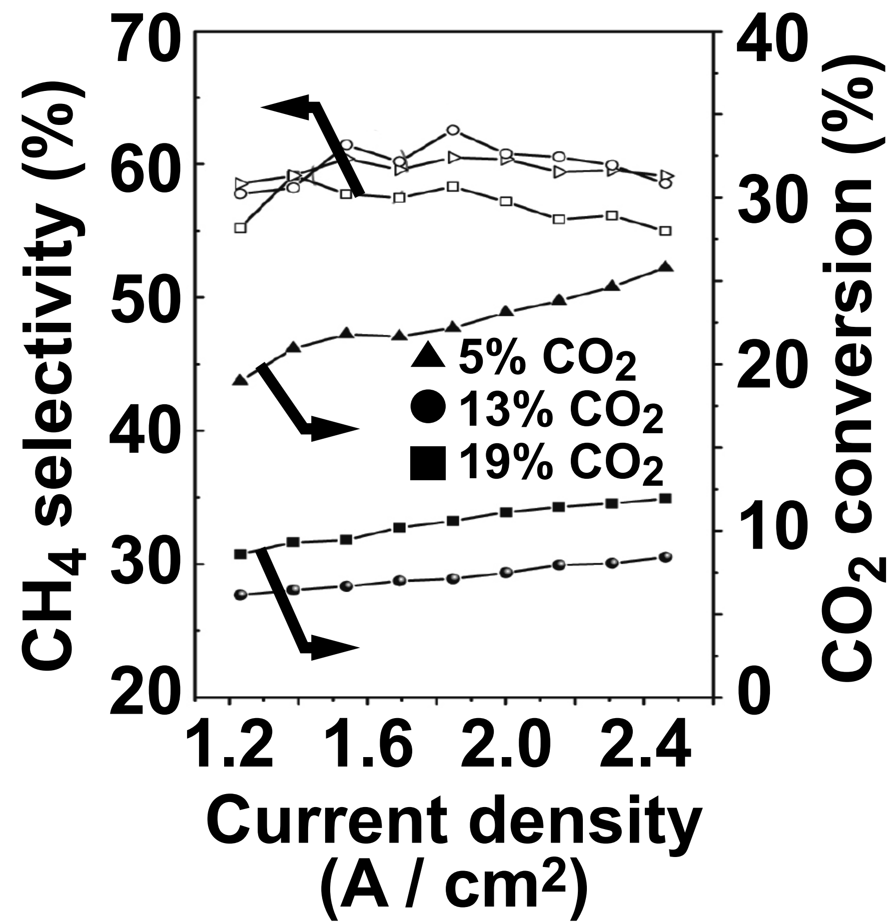
- Operating temperature = 550 ºC
  - Start-up challenges
  - Insulation materials
- CO_2 and H_2O reactants
  - Need preheating
  - Need pumps / blowers
- Methane – oxygen products
  - Must be stored at high pressure
- Dynamic control system



Initial studies on CO_2 hydrogenation and methane production shows reasonable selectivity to CH_4

- CO_2 conversion is modest
  - Generally < 25%
  - Necessitates large blowers
- CH_4 selectivity is encouraging
  - Approaches 60%
  - Independent of current density
- Increasing current density
  - Drives H^+ across membrane
  - Promotes CH_4 formation
  - Requires more solar power

CO_2 conversion and CH_4 selectivity as a function of current density



In summary, protonic-conducting ceramics could play a role in manned missions to Mars

- Convert Martian-derived CO_2 into fuel and oxygen
  - Next-generation MOXIE
- Early stage of technological development
  - TRL 3-4?
- Development leveraged by terrestrial applications
  - Fuel cells for efficient electricity generation
  - Membrane reactors for renewable energy storage
  - Significant DOE support
- Could also serve as electric generator
  - Reversible operation is possible
- Industrial partner is moving technology to pre-commercial scale
  - FuelCell Energy, Danbury, CT

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