SAND2017-10603PE

LDRD

Laboratory Directed Research and Development

LDRD Ending Project Review
Renewable hydrogen production via thermochemical/electrochemical coupling (Project #204724)

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FY17 (exploratory Express), $100k

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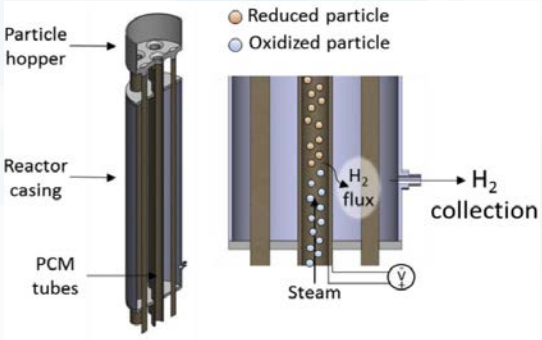
FY17 Ending Project Summary

Purpose, Goals & Approach

The practicality of current pathways of thermochemical hydrogen production is hampered by a thermodynamic-based ultra-high temperature requirement that impacts materials choices and materials reliability, efficiency, and ultimately costs. ***We propose that a novel coupled thermochemical/ electrochemical cycle using heat and power generated at a concentrating solar power facility can circumvent these issues.*** *This is the first time a combined system has been proposed and tested.*

Image and Caption



An electrochemical/thermochemical system that uses a reduced metal oxide to store thermal energy in the form of chemical energy, and then utilizes that energy to reduce the electrical demand in an electrochemical steam-splitting reaction. This coupling allows significant opportunity to decrease reduction temperatures while achieving higher renewable-to-H_2 efficiencies.

Key R&D Results and Significance

Milestone: Demonstration that the concept can provide a renewable thermal route to hydrogen from water at system thermal efficiency of > 20% (including thermal equivalent of electrical demand) and a peak system temperature of < 1200 C.

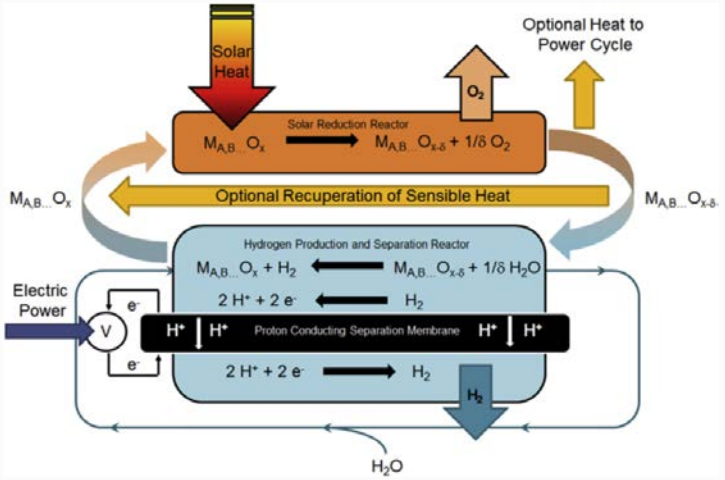
*Results: The constructed t*est stand is a new capability can be leveraged for testing solid oxide fuel cell/electrolyzer material, thermochemical H_2 production, thermodynamic measurements.

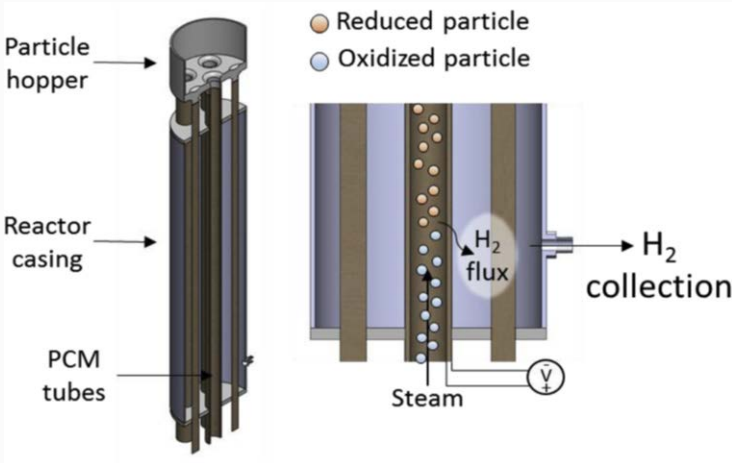
Mission relevance: SNL's SSEF mission space and DOE and EERE mission areas, e.g. DOE's HydroGEN Advanced Water Splitting Materials (Sandia is a core laboratory). *This project directly supports the DOE mission to promote America's energy security through reliable, clean, and affordable energy and the linked goal of support a more economically competitive, environmentally responsible, secure and resilient U.S. energy infrastructure.*

Impact: Successful completion will provide experimental evidence to support the transition of IP from provisional (expected to be submitted to USPTO by 02/16/2017) to full patent; offer a game-changing alternative for conducting thermochemistry at lower temperatures – a research priority identified by DOE task force; and provide a high solar-to-hydrogen efficiency process (a key to decreasing the cost and scaling to impactful sizes) to enhance and secure America's energy future.

Motivation: Coupled cycle concept

- Thermochemical hydrogen production via water
  - Splitting water requires high oxidation enthalpy in oxygen carrier material
    - Results in very high reduction temperatures and/or low reduction pressures
- Electrochemical hydrogen production via steam using solar resources (PV to electrochemical cell) typically show low efficiencies due to low photovoltaic efficiencies
- ***Coupled thermochemical/electrochemical cycle using heat and power generated at a concentrating solar power facility is proposed as a solution to these issues***
  - Electrochemical energy used to facilitate steam splitting without needing a material that spontaneously splits steam ($\Delta G > 0$)
    - Lower oxidation enthalpy unlocks several benefits
      - Lower solar receiver temperatures and pressures
      - Wider range of materials can be used
      - Less expensive, more abundant elements can be utilized to bring capital costs down

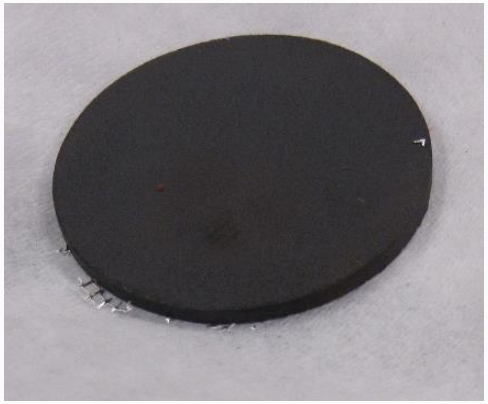




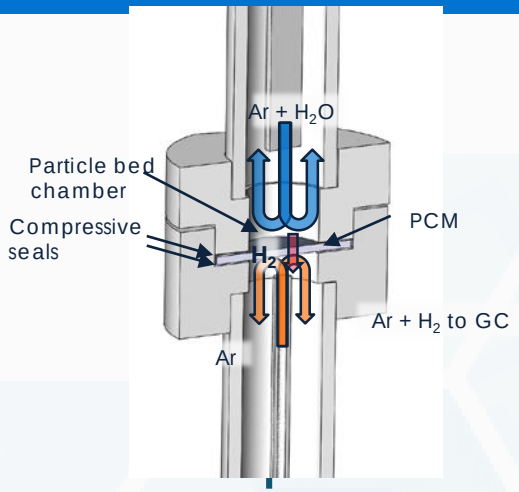
Proton Conducting Membrane

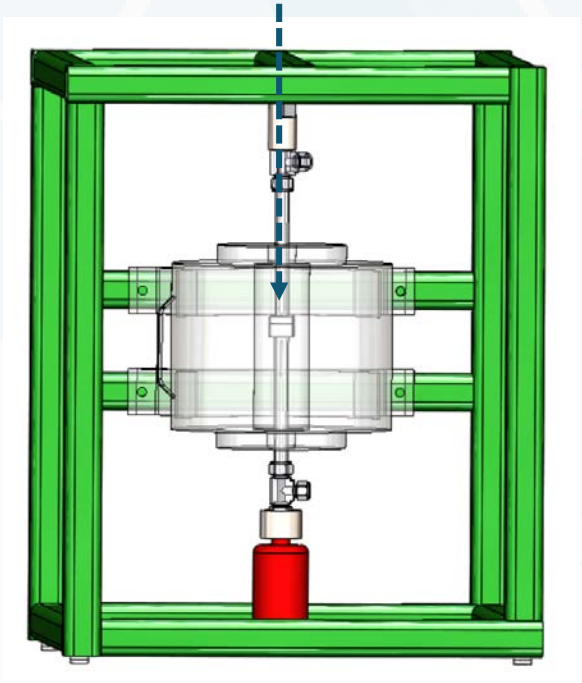
$BaCe_{0.1}Zr_{0.8}Y_{0.1}O_{3-\delta}$ (BCZY18)

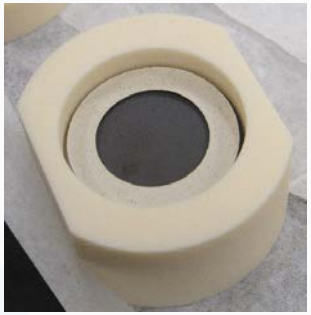
- Known proton conducing electrolyte
- Synthesized vis Pechini solution method (nitrate precursors)
- NiO (1 wt%) added as a sintering agent
- Pressed into 1" membranes and initially sintered at 1375 °C/48h
- Initial membranes came out extremely warped and fragile
  - Sieved precursor particles (≤ 90 μm) to reduce size distribution
  - Pressed thicker membranes (result in less warping, but longer proton diffusion path)
  - Added additional sinter at 1650 °C (Eric Coker, AML)
- New batch much less warped, better sintered
  - Still exhibited some porosity
  - Due to time constraint, we went forward with these

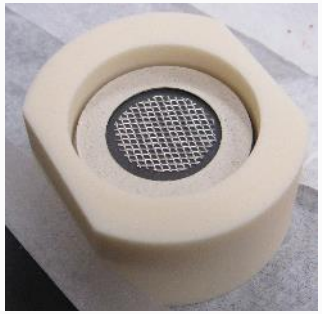


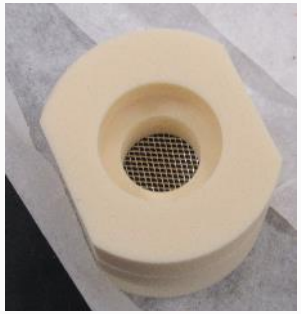
Cell and test stand











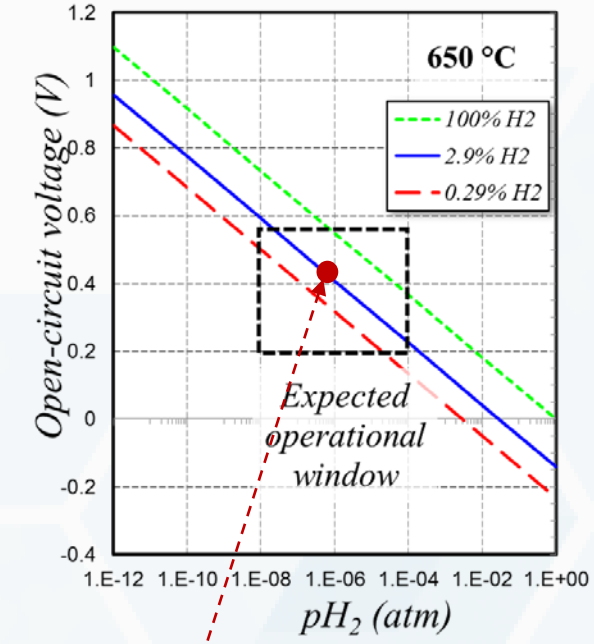
Top: assembly of membrane cell

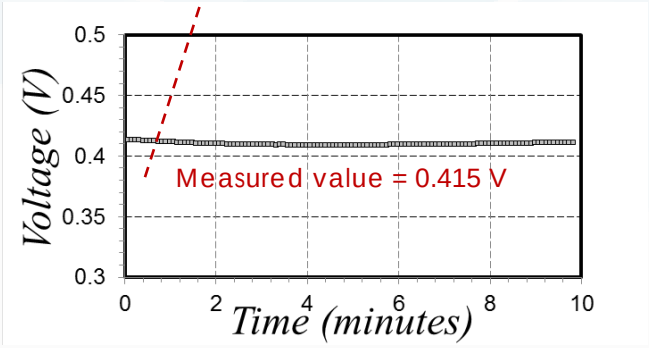
Middle: test cell

Bottom: assembled test cell plumbed and in furnace

Open-circuit behavior

OCV as a function of pH_2 on sweep side



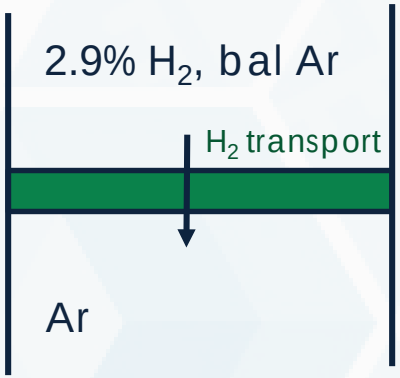


Measured open-circuit voltage

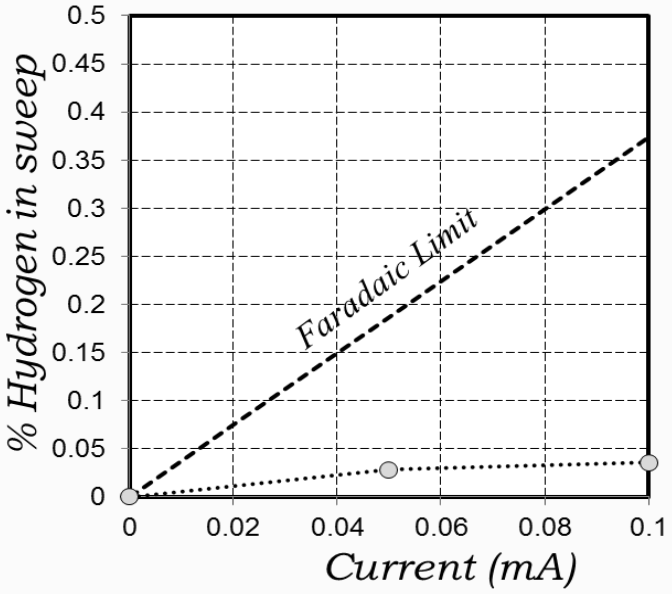
- Open-circuit voltage was also observed under (Ar + steam) vs. Ar
  - Indicated small presence of hydrogen, confirming activity of thermochemical material
  - With denser membranes, OCV with and without thermochemical material could provide analysis of the change in thermodynamic state due to the presence of thermochemical material

Hydrogen transport experiments used to analyze electrochemical cell performance

H_2 transport measured by observing decreasing hydrogen concentration on the H2/Ar side as a function of current



Hydrogen transport performance: 2.9% H_2/bal. Ar vs. Ar , 650 °C



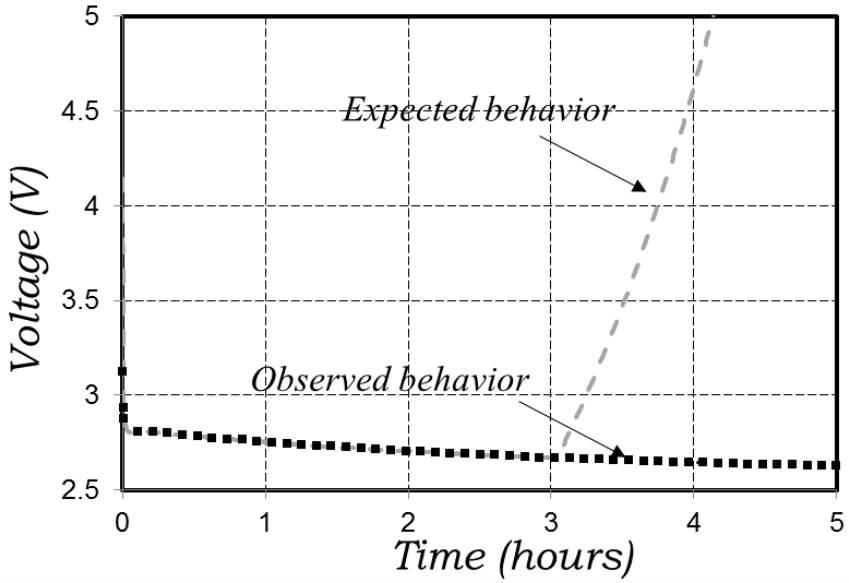
- Low Faradaic efficiency suggests issues with cell assembly:
  - Likely large electronic leakage: e^-, $h^\bullet$, O^{2-}, and H^+ all charge carriers depending on gas environment and applied voltage
  - Membrane porosity
  - Poor seal
    - Seal on Ar side was poor, seal on H_2/Ar side was very good
    - Slight warpage in membrane may account for poor seal

Investigation of thermochemically-assisted hydrogen production

- Air leak on bottom chamber resulted in compromised μGC measurements of hydrogen
- *New experiment: observe voltage as a function of current over a long duration*
  - If hydrogen production is thermochemically assisted, voltage should increase when available thermochemical inventory is consumed
  - Amount of thermochemical material estimated to last for 3 hours of hydrogen production

- Expected behavior not observed
- Three possible reasons:

1. Low faradaic efficiency resulted in less hydrogen transported, thus thermochemical material not oxidized by end of experiment
2. Thermochemical material did not adequately reduce
3. Kinetic limitations hinder thermochemical assistance



Challenges and Lessons Learned

Challenges:

- GC (power source and column)
- Membrane synthesis
  - Cell cracking – mitigated by tightening particle size distribution before pressing
  - Porosity – not yet mitigated - causes gas permeability
  - Warpage – note yet mitigated – results in difficulty achieving cell-to-manifold seal
- Sealing/leakage in cell
- Retirement/manpower
- Inconclusive data: *could not prove hypothesis (yet) , but did not disprove it either*

Lessons Learned:

- Sintering temperature and importance of particle size in membrane synthesis
- Leak testing at room temperature is essential to detect problems before the cell is heated
- Nothing goes according to plans the first time around

Accomplishments and Impact

Accomplishments:

- Design/built novel thermochemical/electrochemical test stand
- Demonstrated proton-conduction across PCM
- Measured OCV response in presence of steam, implying chemical activity of some sort

Impact:

- Test stand is a new capability can be leveraged for testing solid oxide fuel cell/electrolyzer material, thermochemical H_2 production, thermodynamic measurements
- Mission relevance: SNL's SSEF mission space and DOE and EERE mission areas, e.g. DOE's HydroGEN Advanced Water Splitting Materials (Sandia is a core laboratory)
- Successful demonstration can enable increased efficiency of H_2 production utilizing renewable resources (CSP, PV, H_2O)

Project Metrics

- Intellectual Property
  - Provisional patent: Patent No. 62/461,141
    - Plan to use current and future results to move this provisional patent to full patent

- Publications
  - S.M. Babiniec, A. Ambrosini, J.E. Miller, “Thermodynamic assessment of an electrically-enhanced thermochemical hydrogen production (EETHP) concept for renewable hydrogen generation”, *Int. J. Hydrogen Energy* 42, 14380-14389, 2017

  - Follow-on paper planned after more data is accumulated
    - Another “sweat equity” effort is planned to continue analysis of this concept

Path Forward

- Use lessons-learned to fabricate better membranes
  - Porosity
  - Warpage
  - Sintering temperature
- Solve sealing issues
  - Top manifold seal functioned properly but must investigate why bottom seal was compromised
- Repeat and expand on experimental set
  - Improve seals; test for H_2 on Ar side
  - Vary applied current, reduction extent of working material, reaction temperature
- Analyze steam/H_2O concentrations (current μGC configuration does not detect H_2O)
  - Mass spectrometry could be utilized to fully characterize gas compositions

Capabilities Development

- Establishment of Capabilities expected to impact future work
  - New capability: Test stand for high-temperature electrochemical analyses
  - Increased knowledge base
    - Electrochemical test methods
      - Test procedures
      - Thermodynamic calculations
      - Electrode deposition and current delivery
      - Cell assembly/sealing
    - Synthesis and fabrication of proton-conducting membranes

- Early Career Development
  - Junior staff (Sean Babiniec) mentored as team member

Project Legacy (to be completed by the PM)

What are the key results from this research that will be useful to other current and future projects?

- Notable technical accomplishments, S&E impacts to the research community

How did this project contribute to IA strategic goals and objectives?

- Potential mission-relevant Impacts and timeframe
- IA metrics *(if not already mentioned by PI)*
  - Capabilities
  - Partnerships **see Notes section*
  - Staff Development

What are next steps? Who will do what and when?

Summarize any important lessons learned, good or bad – What was learned from any "failure?"