



Renewable Hydrogen Production Via Thermochemical/ Electrochemical Coupling

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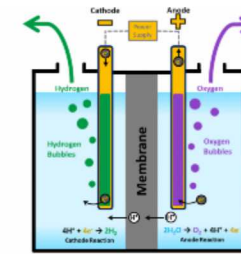
- National security and energy independence depend on a resilient energy infrastructure that must include reliable domestic fuel production from renewable energy sources to achieve sustainability and security
- Currently, H₂ is sourced mainly by reforming hydrocarbons, which is neither renewable nor environmentally friendly, as the process creates CO₂
- A myriad of renewable water splitting technologies exist, each with their own advantages and disadvantage

US Dept. of Energy envisions a massive scale-up of hydrogen utilization in transportation (air, rail, maritime, heavy duty and light vehicles) and industrial processes. Renewable production of H₂ is essential to that mission.

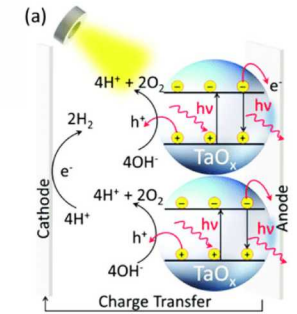
Renewable Water Splitting Technology Challenges



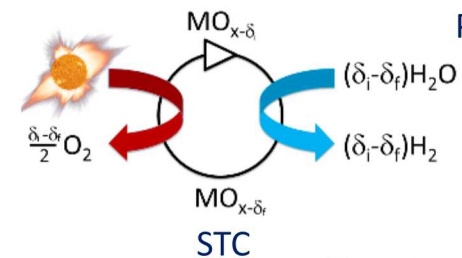
- Photoelectrochemical/Low-temperature electrolysis:** low efficiency, expensive catalysts, membrane challenges, scale up issues
- Solar-thermochemical water splitting:** low-efficiencies (despite high theoretical efficiency); ultra-high temperatures and low oxygen partial pressures require expensive building materials and exergy-killing pumping to maintain low pO_2
- High Temperature Electrolysis:** modestly higher theoretical efficiency than LTE, but cost and efficiency of renewable electricity generation limits practical efficiency (increasing T to 800 °C only lowers voltage requirement by 20%)
- Hybrid Technologies:**
 - Sulfur, Chlorine, Iodine, or Bromine Cycles:** temperatures too high for PWR or BWR reactors, uses highly caustic materials
 - Solar-thermal decoupled water electrolysis:** requires large temperature swings and complex solution chemistry



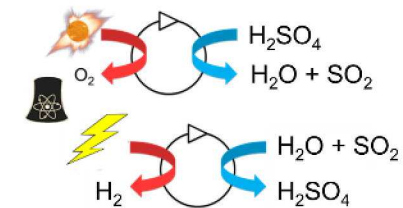
LT electrolysis



PEC



STC



Hybrid SI

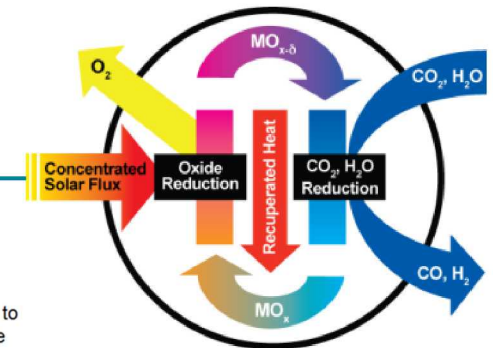
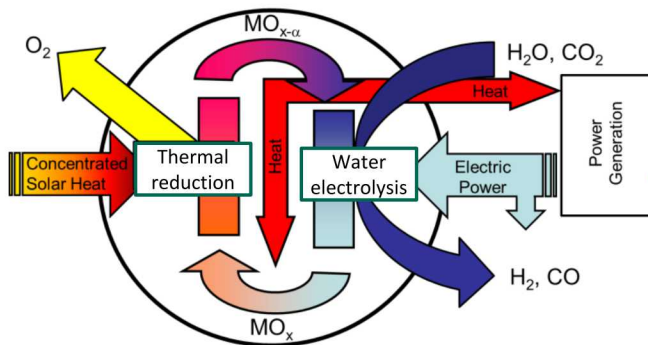


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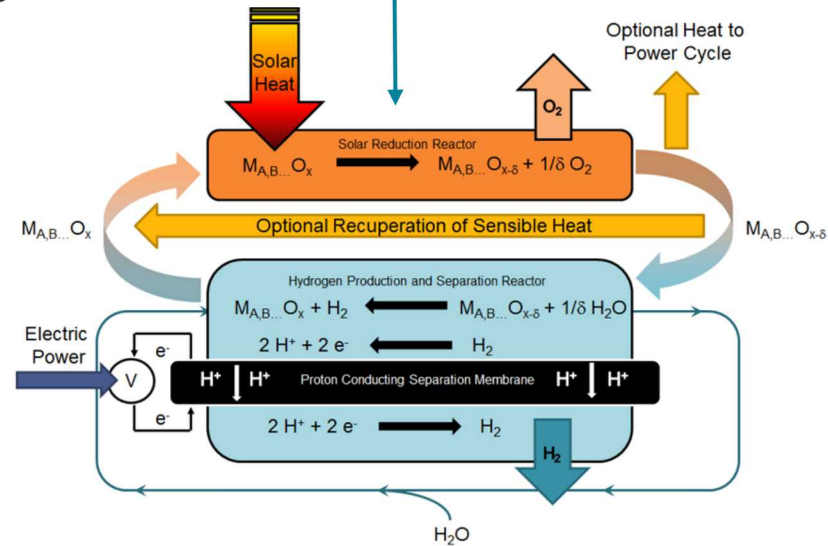
Electrically-enhanced Thermochemical Hydrogen Production (EETHP)



Improve on the current state-of-the-art by developing a coupled electrochemical/thermochemical system that uses a reduced metal oxide to **store thermal energy in the form of chemical energy**, and then carry that energy to reduce the electrical demand in an electrochemical steam-splitting reaction. We hypothesize that this coupling allows significant opportunity to **decrease reduction temperatures while achieving higher renewable-to-H₂ efficiencies**.



US 92188 B2 and US 9556528 B2
shared by SNL and Valparaiso79

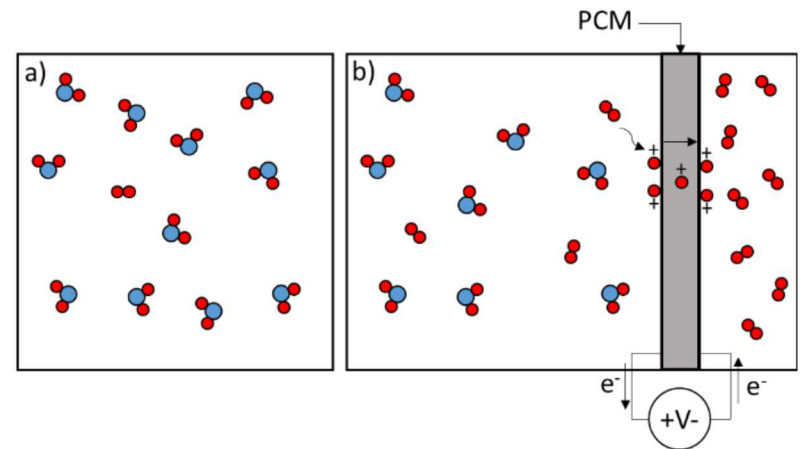


5 Coupled Cycle Concept



Concept enables renewable hydrogen production via steam splitting *without requiring thermochemical spontaneity* (ΔG does not need to be < 0)

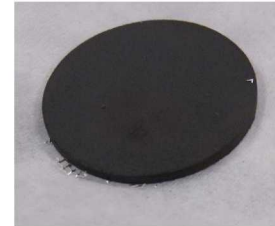
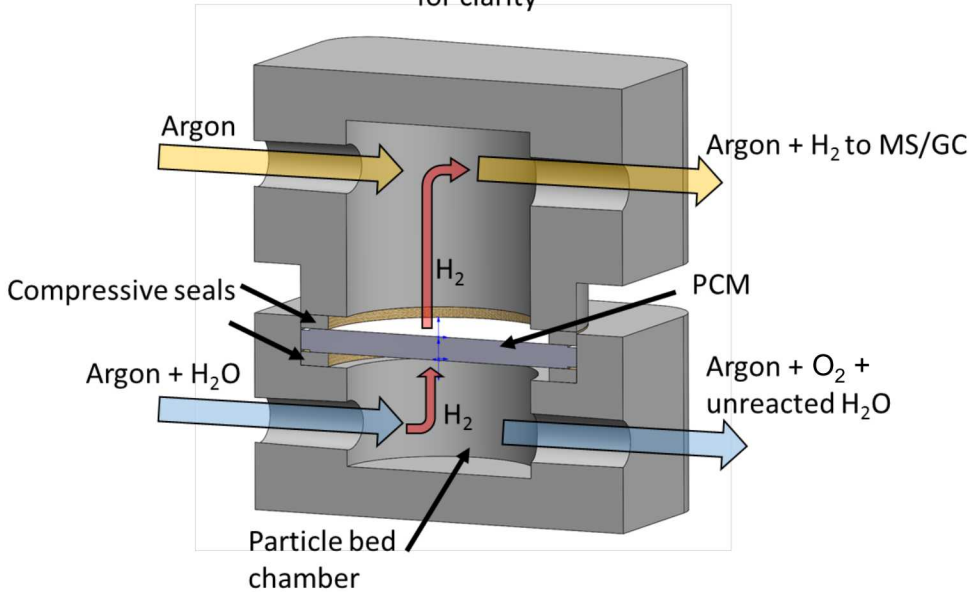
- Electrochemical energy using proton conducting membrane (PCM) makes up energy deficit while providing in-situ hydrogen separation, which maintains a non-equilibrium state (Le Chatlier's Principle)
 - Can take advantage of higher pressure operation not realized in purely thermodynamic systems
- Lower oxidation enthalpy unlocks several benefits
 - Lower solar receiver temperatures and pressures
 - Wider range of materials can be used
 - Less expensive, more abundant element can reduce capital costs
- All-solid (non-solution) process allows for
 - Smaller temperature swing
 - No phase changes
 - More facile separations



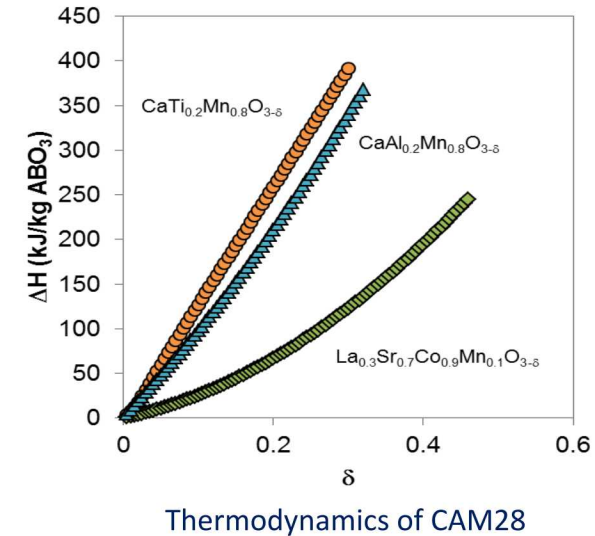
Non-spontaneous oxidation in steam (a) without coupled PCM, and (b) with coupled PCM.



Electrode wires not shown
for clarity

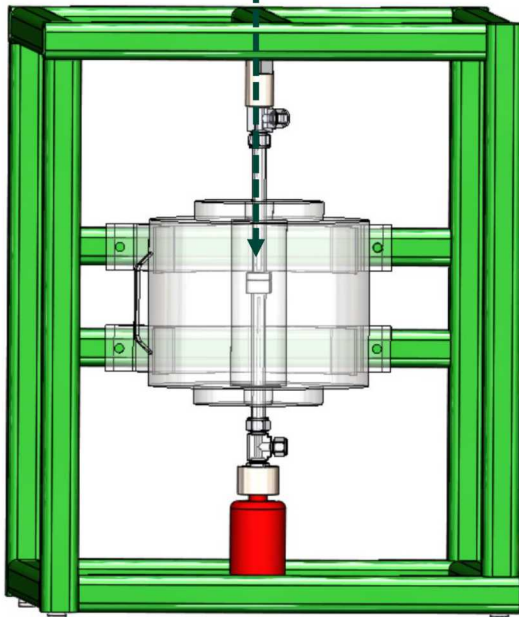
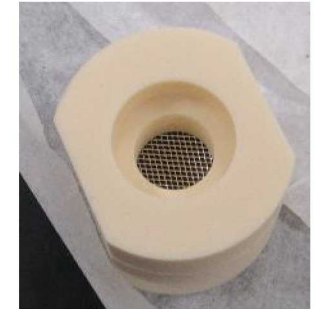
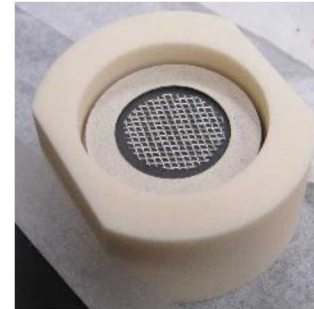
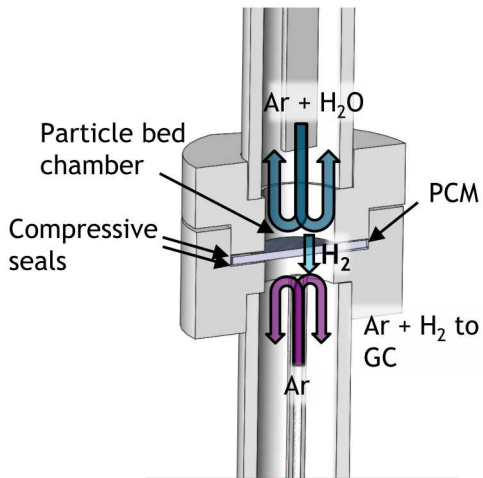


BCZY18 PCM from
Sandia (top) and CSM
(bottom)



- Proton Conducting Membrane (PCM): $\text{BaCe}_{0.1}\text{Zr}_{0.8}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BCZY18)
 - Well-characterized PCM
 - Sandia-synthesized (via solution methods) membranes initially too porous
 - Dense PCM provided by Colorado School of Mines (Sullivan group)
 - Reduced in Ar to $\sim\delta=0.25$
- Thermochemical working material: $\text{CaAl}_{0.2}\text{Mn}_{0.8}\text{O}_{3-\delta}$ (CAM28)
 - Reducible metal oxide developed initially for TCES
 - Thermodynamics well-characterized
 - Not a spontaneous water-splitter

7 Cell and Test Stand Construction



Top: assembly of membrane cell

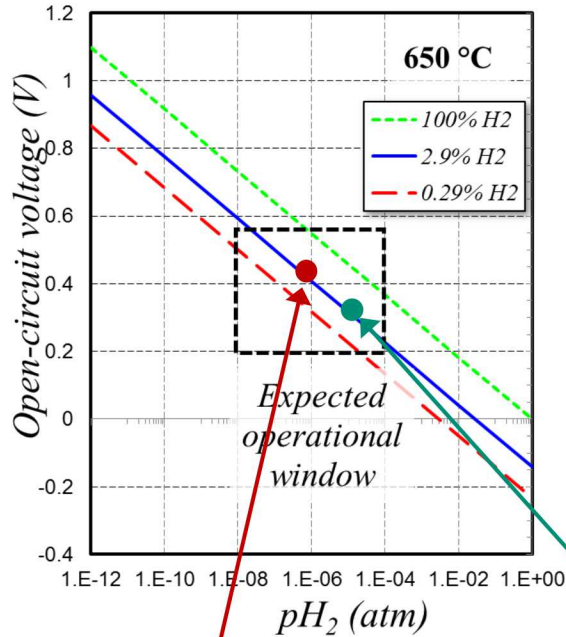
Middle: test cell

Bottom: assembled test cell plumbed and in furnace

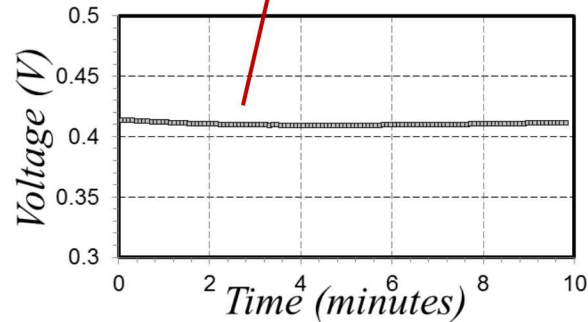
8 Open-Circuit Operation



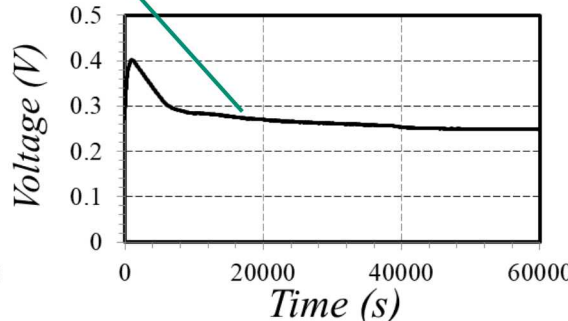
OCV as a function of p_{H_2} on sweep side



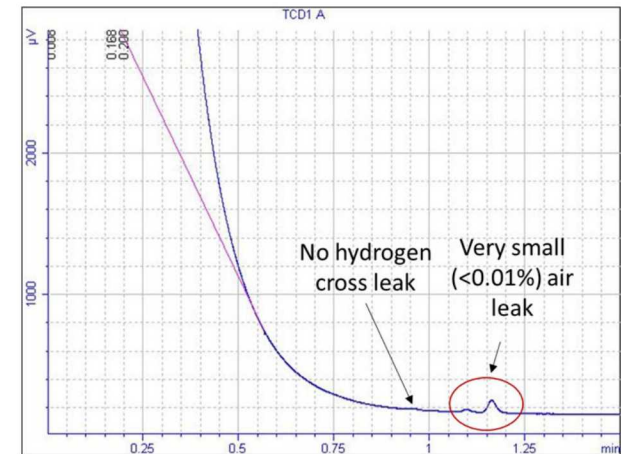
- To test for electrochemical activity, a potential at varying p_{H_2} vs Ar was applied
- Open-circuit voltage (OCV) was observed under (Ar + steam + H_2) vs. Ar
 - Indicates electrochemical activity
 - Both Sandia and CSM membranes operate in expected voltage regimes
 - Sandia cell had large air leak, reducing p_{H_2} on sweep side and increasing OCV



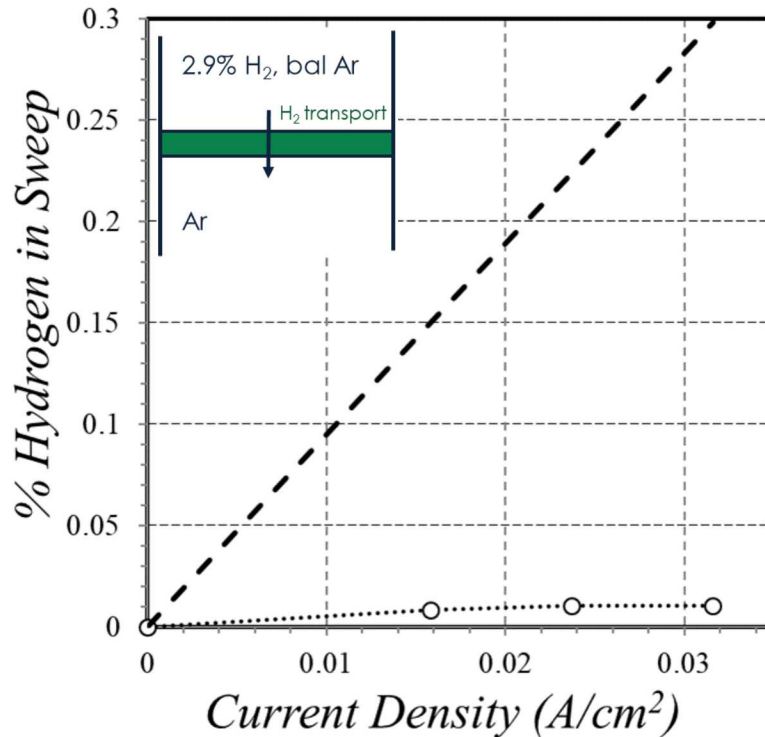
Measured open-circuit voltage (Sandia membrane)



Measured open-circuit voltage (Colorado School of Mines membrane)



Sweep side gas composition: Improved sealing



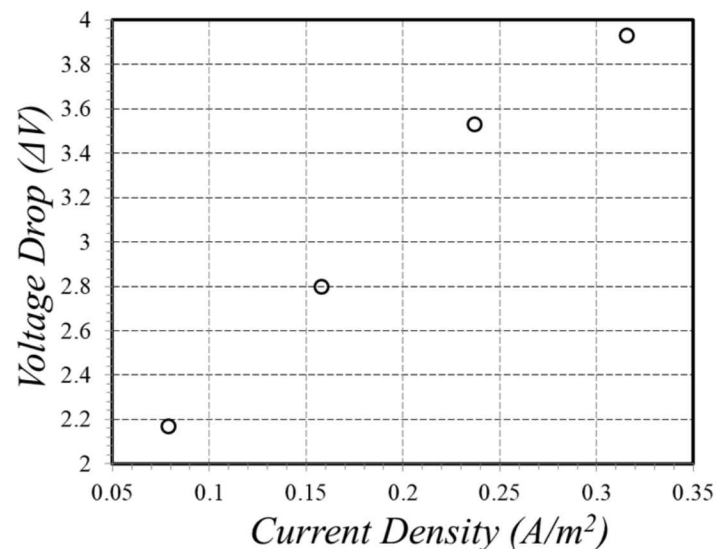
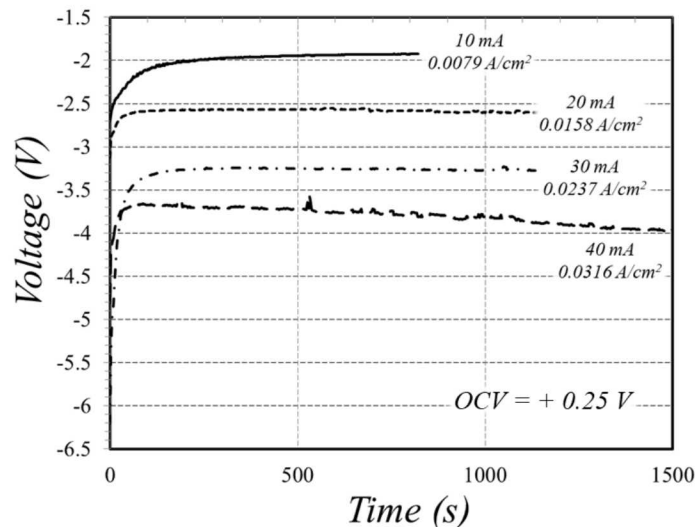
Hydrogen transport performance:
2.9% H₂/bal. Ar vs. Ar , 650 °C

- To analyze electrochemical cell performance proton transport was measured across the 2 mm membrane
- Varied current density from a 2.9% H₂/Ar stream to the Ar sweep side
- Observed proton transport << theoretical
- Low Faradaic efficiency likely due to high voltages required to drive current across **2 mm** thick PCM

10 Membrane Degradation



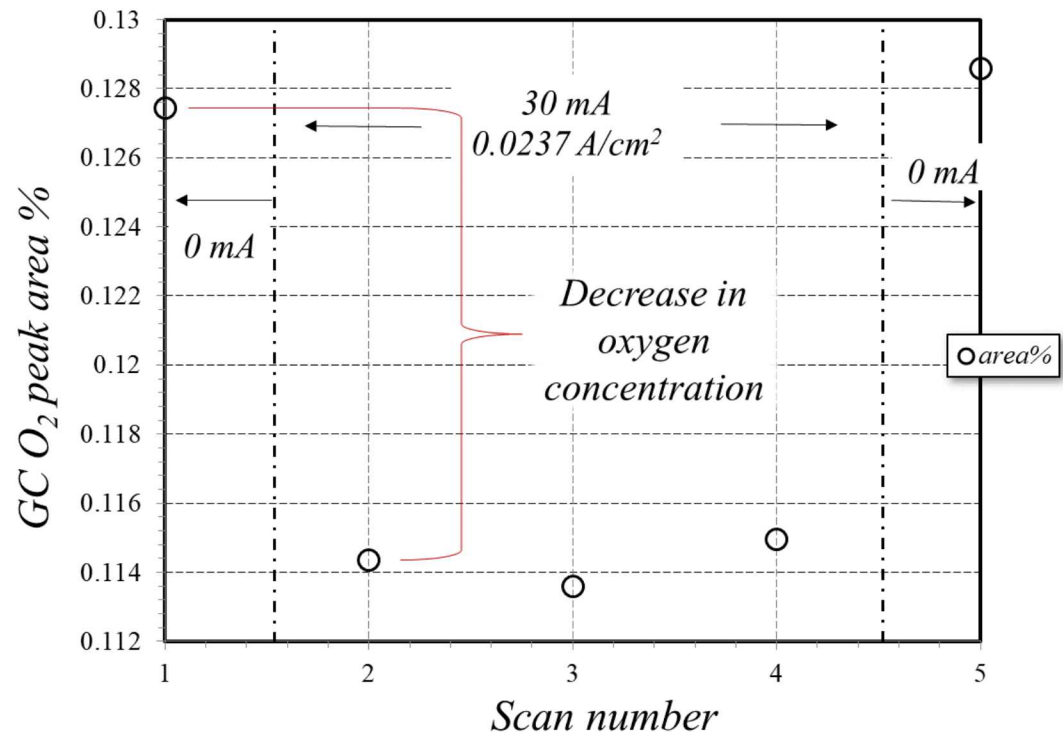
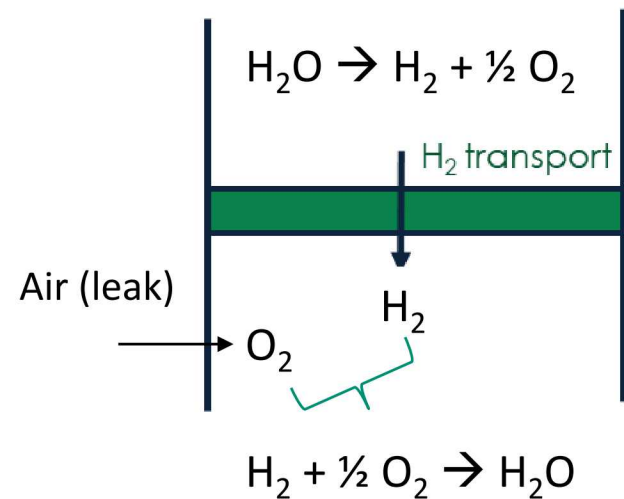
- Possible electronic leakage: e^- , h^+ , O^{2-} , and H^+ charge carriers depend on gas environment and applied voltage
 - Reduction of $Ce^{4+} \rightarrow Ce^{3+}$ results in electronic defect formation
 - Voltage drop for 2mm membrane calculated at $\Delta V \sim 4.8 V$
 - 40 mA current resulted in $\sim 4 V$ of overpotential (close to theoretical)
- 40 mA voltage shows a clear decrease as a function of time, indicating that degradation or crystallographic changes may be occurring in the membrane
- Conclusion: Membrane is too thick for this application (need $<50 \mu m$)



Water Splitting



- Small air leak in sweep side combined with very low hydrogen production/diffusion precluded direct measurement of hydrogen
- However, a decrease in oxygen concentration *without* a corresponding decrease in nitrogen suggests that **hydrogen was produced**, transported across the membrane, and reacted with oxygen
- Hydrogen was produced from steam, but not quantifiable
- Quantification difficult due to insufficient gas chromatograph oxygen peak calibration





Accomplishments:

- Design/built novel thermochemical/electrochemical test stand
- Demonstrated proton-conduction across PCM
- Measured OCV response in presence of steam, implying chemical activity
- Observed indirect evidence of H₂ production, using dense PCM from Mines, via change in O₂:N₂ ratio on sweep side vs. applied current
- Could not prove whether H₂ was thermochemically or electrolytically produced

Lessons Learned:

- Sintering temperature and importance of particle size in membrane synthesis
- PCM thickness is important: future experiments should utilize PCM < 100 μm
- Leak testing at room temperature is essential to detect problems before the cell is heated



- Use lessons-learned to fabricate better membranes
 - Porosity
 - Warpage
 - Sintering temperature
- Solve sealing issues
- Repeat and expand on experimental set
 - Improve seals; test for H₂ on Ar side
 - Vary applied current, reduction extent of working material, reaction temperature
- Analyze steam/H₂O concentrations (current μ GC configuration does not detect H₂O)
- Mass spectrometry could be utilized to fully characterize gas compositions



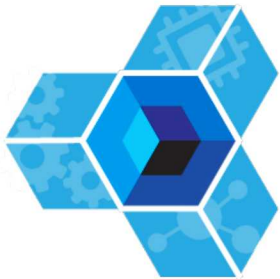
- Palumbo, R., Diver, R. B., Larson, C., Coker, E. N., Miller, J. E., Guertin, J., Schoer, J., Meyer, M., and Siegel, N. P., 2012, "Solar thermal decoupled water electrolysis process I: Proof of concept," *Chemical Engineering Science*, **84**, pp. 372-380.
- S.M. Babiniec, A. Ambrosini, J.E. Miller, "Thermodynamic assessment of an electrically-enhanced thermochemical hydrogen production (EETHP) concept for renewable hydrogen generation", *Int. J. Hydrogen Energy* 42, 14380-14389, 2017
- S.M. Babiniec, E.N. Coker, J.E. Miller, Andrea Ambrosini "Doped calcium manganites for advanced high-temperature thermochemical energy storage" *International Journal of Energy Research*, 2016, 40, 280-284. DOI:10.1002/er.3467
- Babiniec, S. M., Ricote, S., and Sullivan, N. P., 2015, "Characterization of ionic transport through BaCe_{0.2} Zr_{0.7}Y_{0.1}O_{3-δ} membranes in galvanic and electrolytic operation," *Int J Hydrogen Energ*, **40**(30), pp. 9278-9286.
- Full patent on EETHP: Patent No. 15/899,295 filed on 19 February, 2018

Acknowledgements



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LDRD

Laboratory Directed Research and Development



Thank You



Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.



6 Experimental Approach

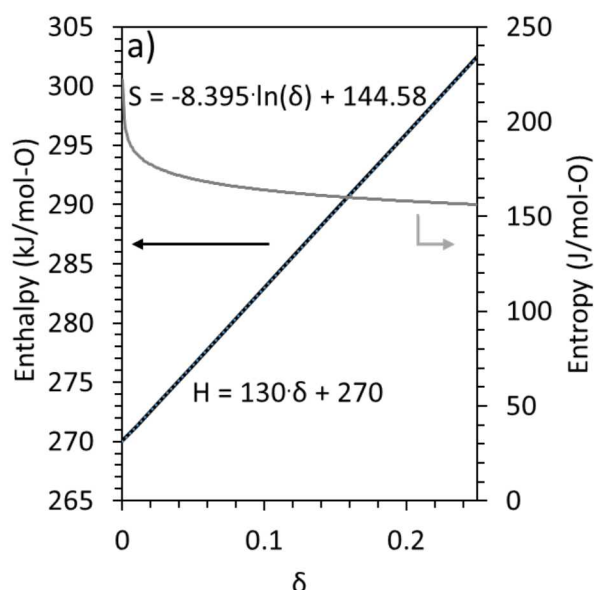


- Preliminary characterization
 - Characterize ohmic resistance of PCM via EIS
 - Demonstrate hydrogen transport across membrane
- Cell characterization
 - Load pre-reduced (to known reduction state) perovskite material into particle chamber (or reduce in-situ)
 - Characterize ohmic resistance via EIS prior to and after each test
 - Apply voltage – record current trace until current tails to zero, signifying material is fully oxidized
 - Simultaneously record hydrogen concentration in argon sweep line
 - Repeat experiment set at different conditions (e.g. steam concentration, steam oxidation temperature, extent of reduction)

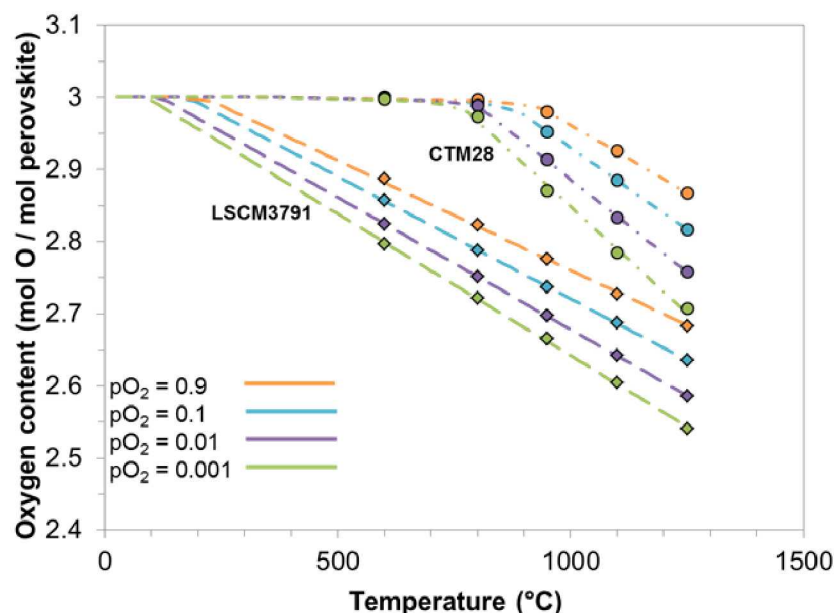
The Team has extensive experience in synthesizing and characterizing both the reducible metal oxides and the PCMs

Reducible Metal Oxides

- Currently developing these materials for other applications
- Thermodynamic data and some materials are in hand



$\text{SrMnO}_{3-\delta}$: Example used in the analysis



- Babiniec, Coker, Miller, Ambrosini, “Investigation of $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{M}_{1-y}\text{O}_{3-\delta}$ ($M = \text{Mn, Fe}$) perovskite materials as thermochemical energy storage media”, *Solar Energy* 118, 451-459 (2015).
- S.M. Babiniec, E.N. Coker, J.E. Miller, Andrea Ambrosini “Doped calcium manganites for advanced high-temperature thermochemical energy storage” *International Journal of Energy Research*, 2016, 40, 280-284. DOI:10.1002/er.3467