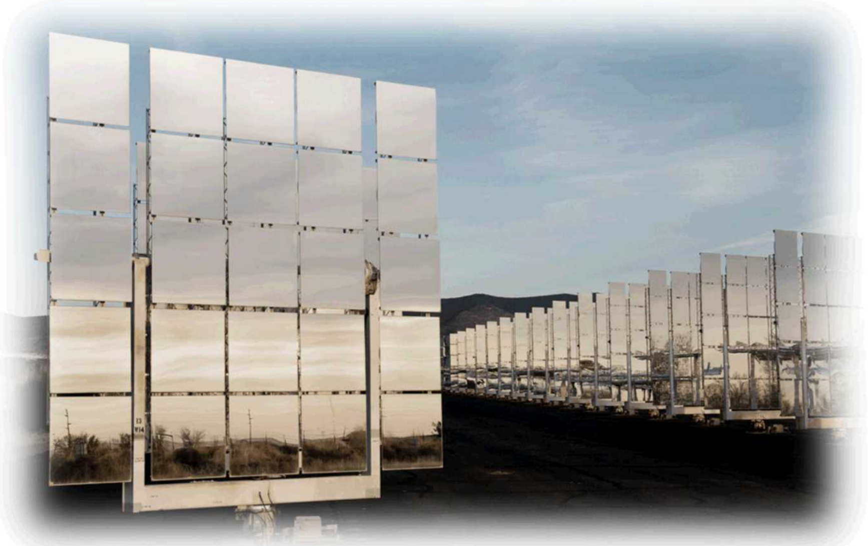
This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

SAND2018-7183C

# Hydrogen Production by Solar Thermochemical Water Splitting:
# Searching for Optimal Nonstoichiometric Perovskite Oxides

Anthony McDaniel
Sandia National Laboratories



255th ACS National Meeting
New Orleans, LA
March 2018

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and 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-NA-0003525.

# Acknowledgements

Colorado School of Mines

- Prof. Ryan O'Hayre
- Prof. Michael Sanders
- Ms. Debora Barcellos

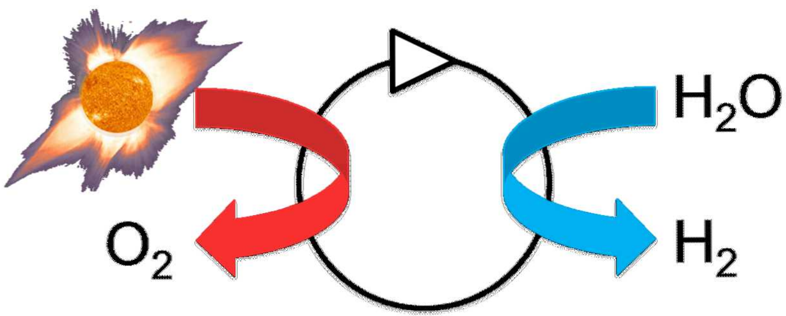
Sandia

- Dr. Joshua Sugar

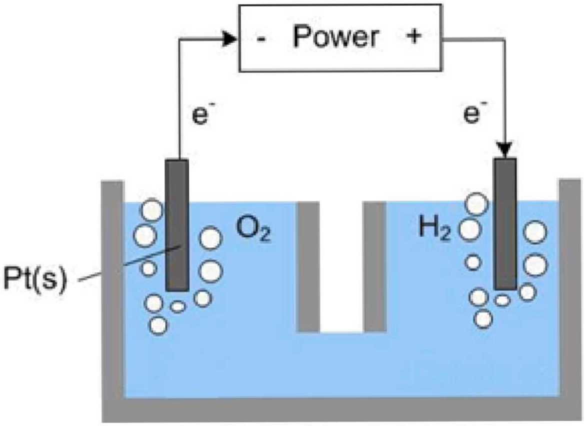
Funded by US DOE and LDRD

# Oh Those Many Water Splitting Ways

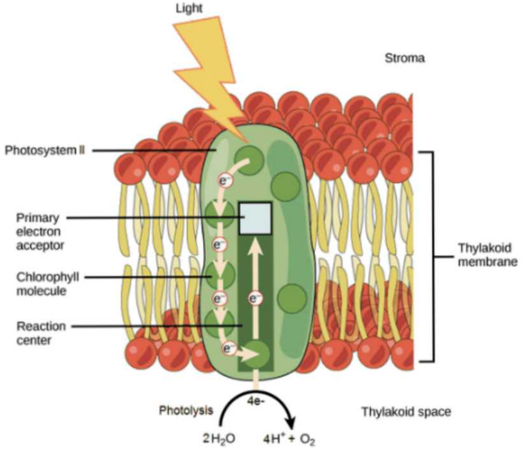
- Thermochemistry.




- Electrochemistry.




- Photochemistry.




- Hybrids.
  - photo + electro
  - thermo + electro
  - thermo + photo

# HydroGEN Advanced Water Splitting Materials Consortium

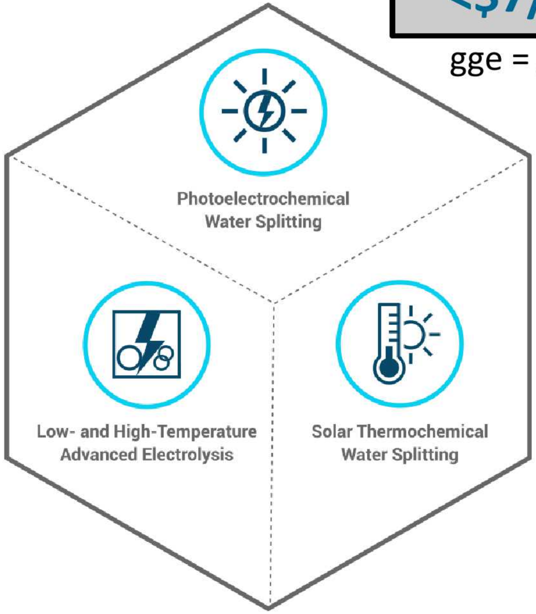
https://h2awsm.org (~$10M FY18)

| $H_2$ Cost at Pump |
|---|
| <$4/gge |
| <$7/gge (early market) |

gge = gallon of gas equivalent

## $H_2$ as far as the eye can see…

+

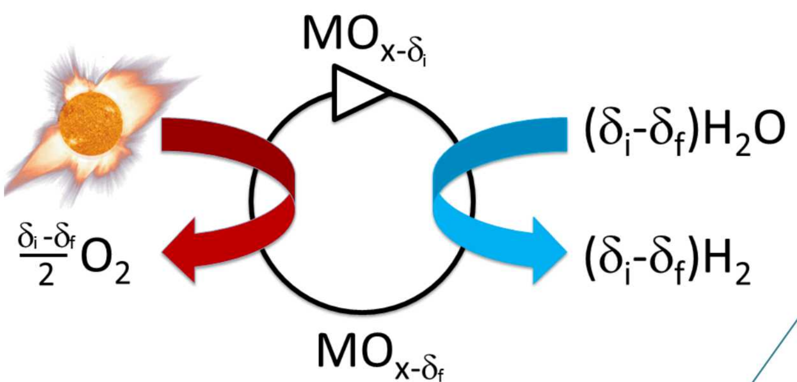


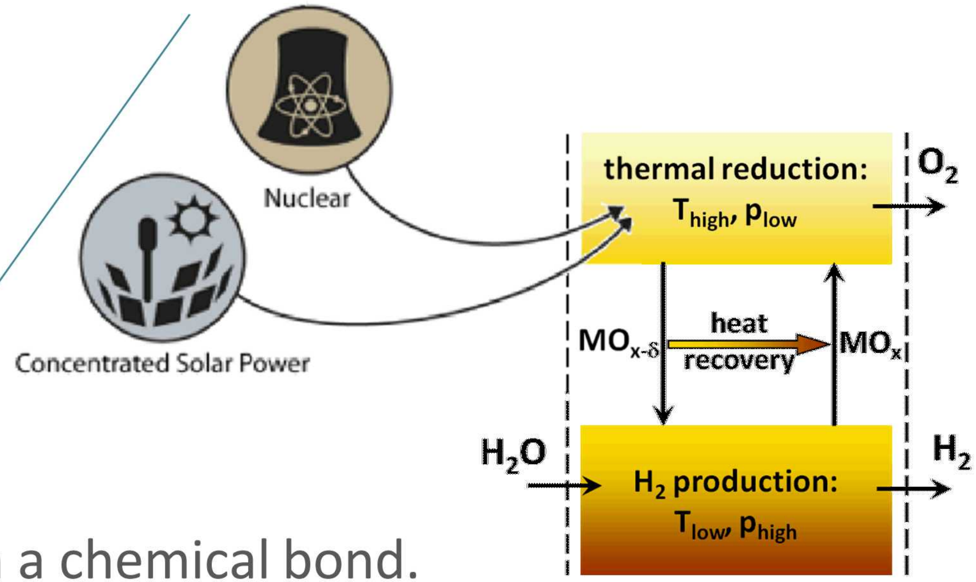

= $H_2$

- Multi-lab **consortium** investing in R&D of advanced water-splitting technology pathways.
  - Goal to produce $H_2$ renewably at large scale and low cost
  - Address KEY ***materials challenges*** to advancing TRL

# Simple Concept: Heat + $H_2O$ IN, $H_2$ + $O_2$ OUT

R. Perret, SAND Report (SAND2011-3622), Sandia National Laboratories, 2011.
G. J. Kolb, R. B. Diver, SAND Report (SAND2008-1900), Sandia National Laboratories, 2008.
S. Abanades, P. Charvin, G. Flamant, P. Neveu, *Energy*. **31**, 2805–2822 (2006).




- Direct storage of solar energy in a chemical bond.
- Many hundred cycles proposed.
  - Multi-phase, multi-step, thermochemical-electrochemical hybrids
- US DOE investments focused on two-step, non-volatile $MO_x$.

# STC $H_2$ vs Renewable Electrolysis

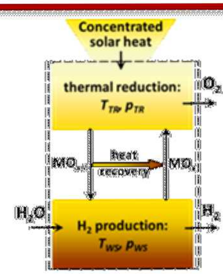
**STC offers a simpler technology development pathway to high efficiency.**

Assumptions

**THEORETICAL EFFICIENCY**

**72%**

+

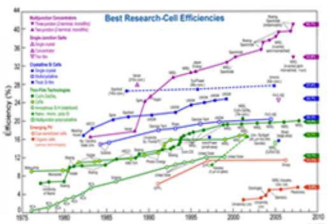



CSP 2-step Thermochemical

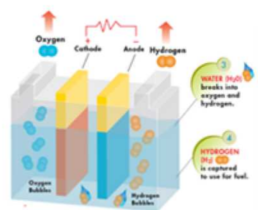
- $T_{reactor}$=1775K
- Blackbody receiver
- 3000 sun conc.

**THEORETICAL EFFICIENCY**

**78%**




+



PV electrolysis

- Infinite junction (86.8%)
- Ext. electrolysis (90%)
- Max sun conc. efficiency

**IMPOSSIBLE**

**POSSIBLE EFFICIENCY**

**21%**

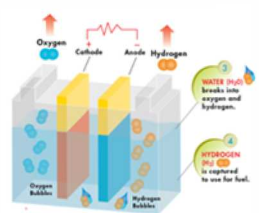
New world record for solar-to-grid conversion efficiency

February 13, 2008

Sandia and Stirling Energy Systems set new world record for solar-to-grid conversion efficiency. The record establishes a new solar-to-grid conversion efficiency of 31.25 percent. The old record, which has stood since 1984, was 29.4 percent. (Photo by Randy Montoya)

**On a perfect New Mexico winter day — with the sky almost 10 percent brighter than usual — Sandia National Laboratories and Stirling Energy Systems (SES) set a new solar-to-grid system conversion efficiency record by achieving a 31.25 percent net efficiency rate. The old 1984 record of 29.4 percent was toppled Jan. 31 on SES's "Serial #3" solar dish Stirling system at Sandia's National Solar Thermal Test Facility.**

+



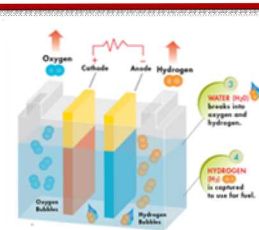
CSP electrolysis

- Stirling Engine
- 30% peak-to-grid
- Ext. electrolysis (70%)

**ACTUAL EFFICIENCY**

**8%**

+

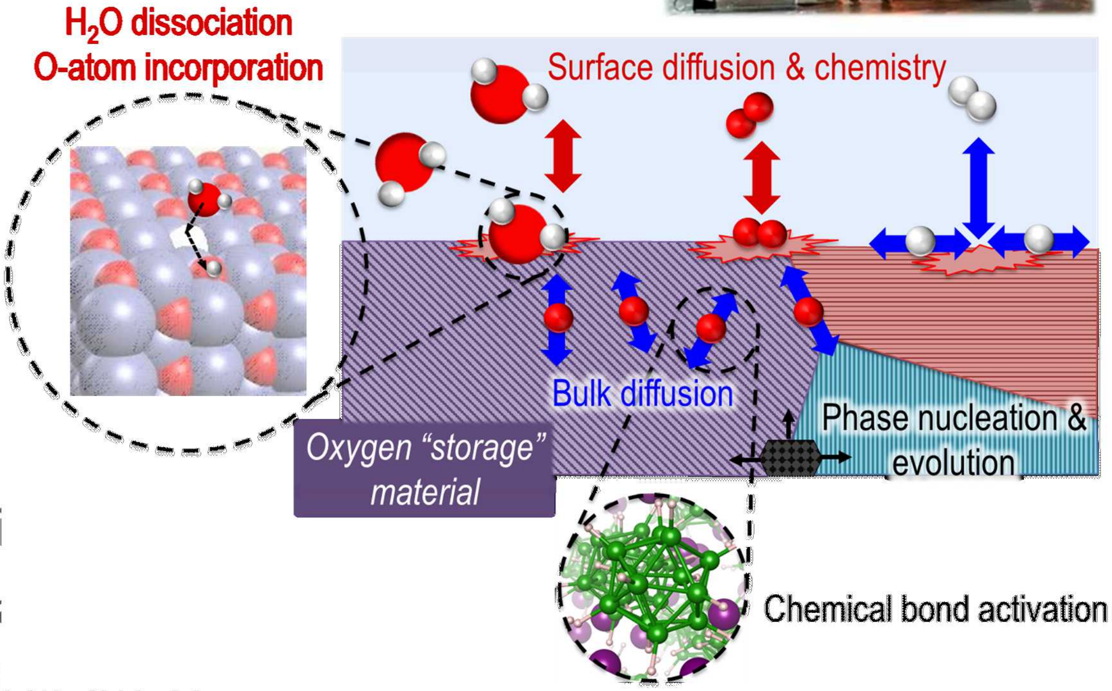


PV electrolysis

- Single junction (12%)
- Ext. electrolysis (70%)
- 1 sun conc.

# STC $H_2$ Materials Theme: Oxygen Exchange and Transport

- Oxygen storage materials with a **twist**.
  - Thermodynamics
  - Kinetics
  - Transport
  - Gas-solid interactions
  - Solid-solid interactions

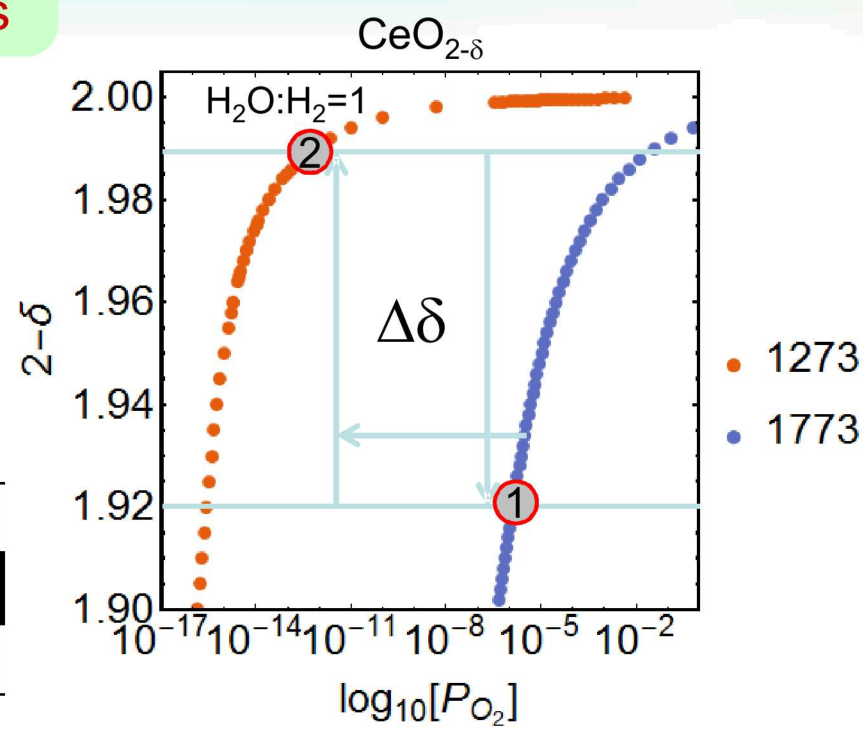



- Materials in extreme envi
  - High temperature and ra
  - High thermal and chemi

DOE is very interested in a "Materials Genome" approach to material discovery and optimization

# Cycle Thermodynamics: Challenge Process Economics

$\Delta\delta$ at target $T_{TR}$ too small for $CeO_2$ to meet cost and efficiency targets




## Process metrics (US DOE targets):

| | |
|---|---|
| $H_2$ production rate | 50-100mt/day |
| [redacted] | |
| $H_2$ production cost (US DOE) | ~$3/kg |

## Desired cycle metrics:

| | | |
|---|---|---|
| Reduction Temperature ($T_{TR}$) | ~1400ºC | |
| Oxidation Temperature ($T_{OX}$) | [redacted] | |
| "O" activity in reduction | $\mu_{gas} < \mu_{solid}$ | $\mu_{gas}$ ~$10^{-6}$atm |
| [redacted] | | |

Engineering challenge

Material challenge

# Cycle Thermodynamics: Tradeoffs Between $\Delta\delta$, $T_{TR}$, and $H_2O:H_2$

- Reduce at low $T_{TR}$ like (Sr,La)$Mn_{1-y}Al_yO_3$ ($\Delta H_{RED}$~300 kJ/mol O).
- Oxidize at low $H_2O:H_2$ ratio like $CeO_2$ ($\Delta S_{RED}$~250 J/K mol O).

## spinel

$Fe^{2+}/Fe^{3+}$ systems :

- High redox capacity ($\Delta\delta$>0.1).
- Slow $H_2O$ oxidation kinetics.
- Deep reduction at 1400 °C.
- Oxide matrix required.

## fluorite

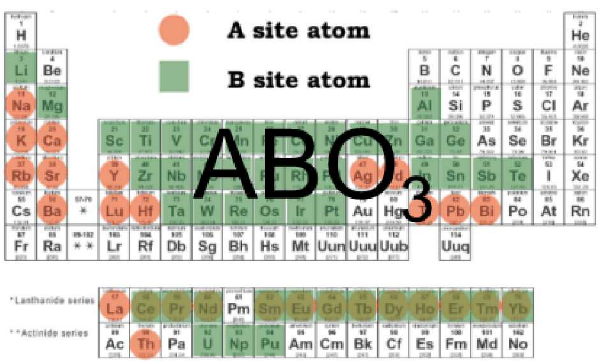
$Ce^{3+}/Ce^{4+}$ systems:

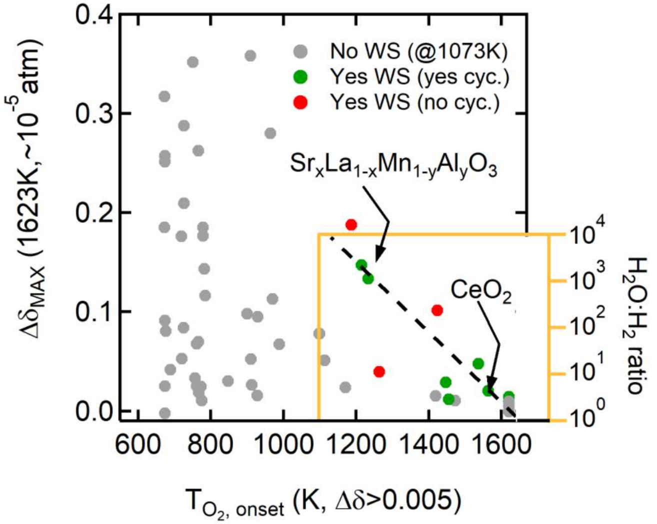
- Low redox capacity ($\Delta\delta$<0.08).
- Fast $H_2O$ oxidation kinetics.
- Shallow reduction at 1500 °C.
- Durable.

## perovskite

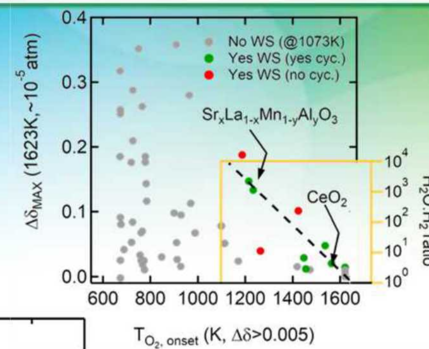
$TM^{2+}/TM^{3+}/TM^{4+}$ systems:

- High redox capacity ($\Delta\delta$>0.1).
- Promising $H_2O$ oxidation kinetics.
- Deep reduction at 1400 °C.
- Vast material space!



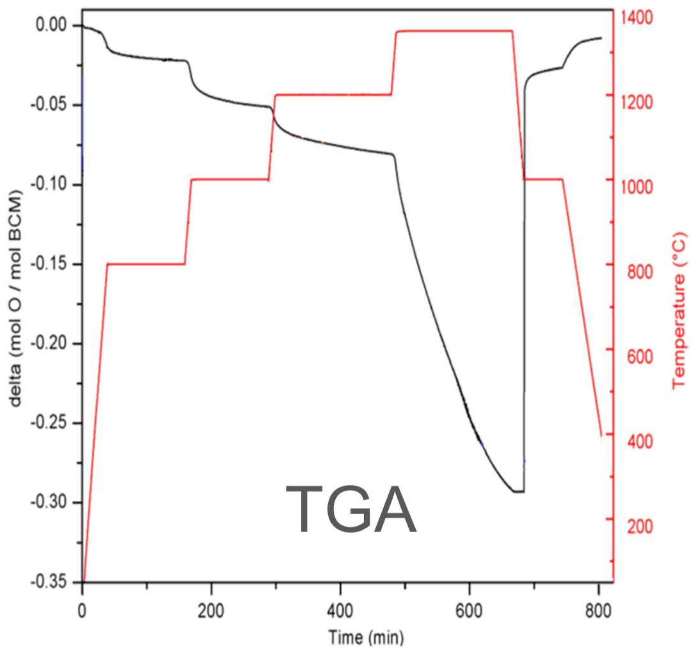



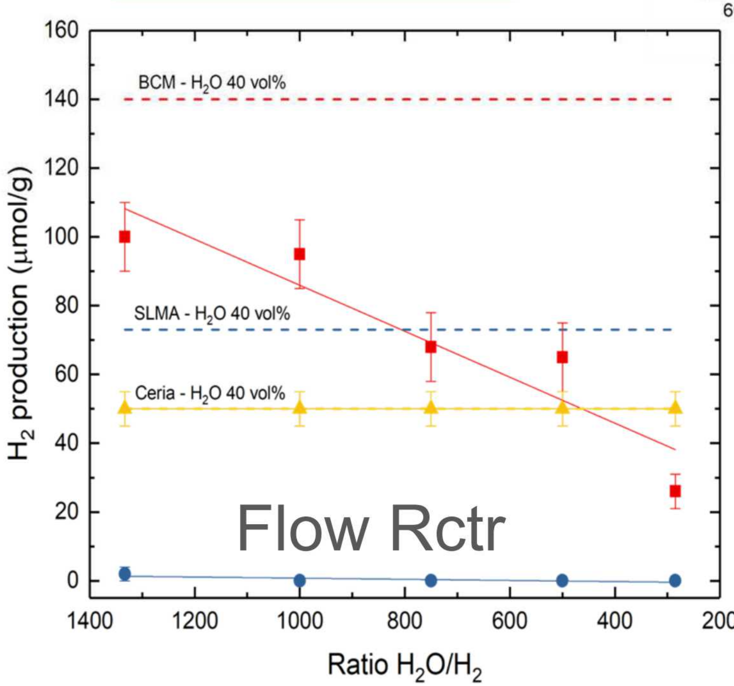
# A New Perovskite: $Ba_4CeMn_3O_{12}$ (BCM)



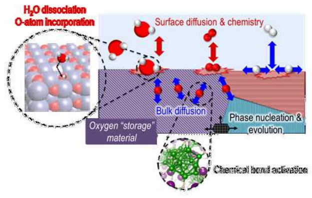

Significant $O_2$ loss ~1200 $^oC$

Splits water better than SLMA

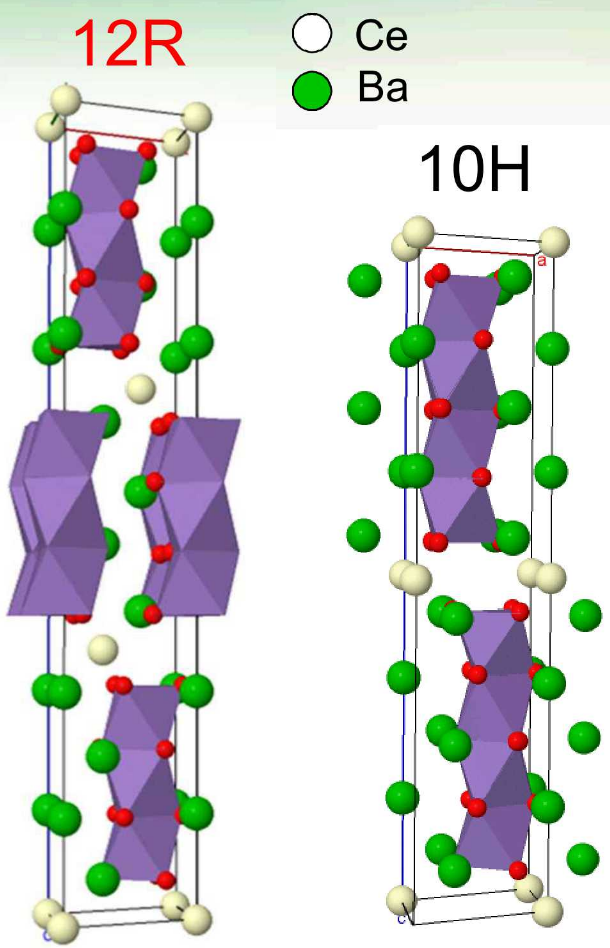


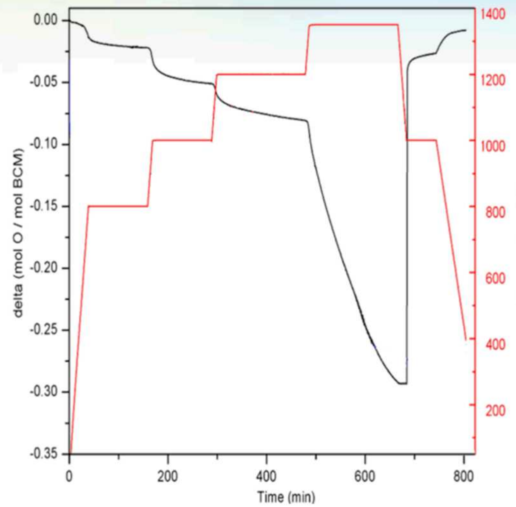



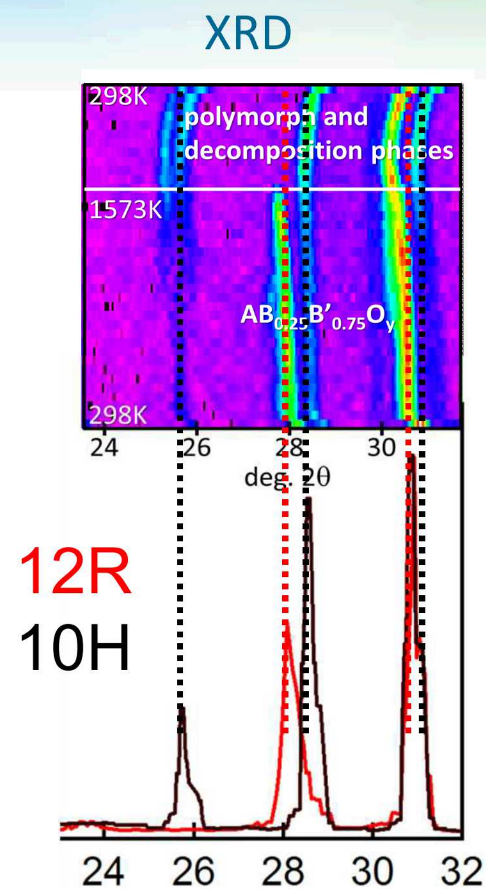

- BCM is UNIQUE when compared to known STCH perovskites.
  - Reduces at LOW $T_{TR}$ & oxidizes at LOW $H_2O:H_2$ ratio
  - It is a LINE COMPOUND not a solid solution
  - Cerium substitutes on the B-SITE



# $Ba_4CeMn_3O_{12}$...or is it...$Ba_5Ce_{1.25}Mn_{3.75}O_{15}$?

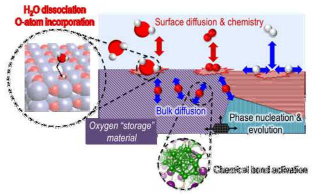


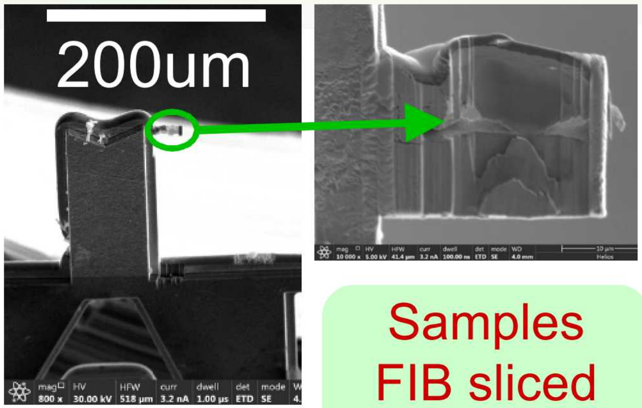




Significant $O_2$ loss ~1200 °C accompanied by **POLYTYPE** phase transition

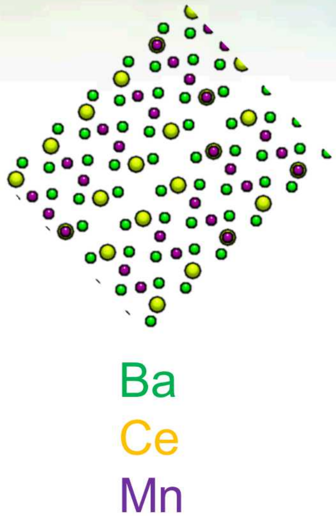
- Reduction may be dependent on phase composition.
  - Nonstoichiometric behavior is not known in this system

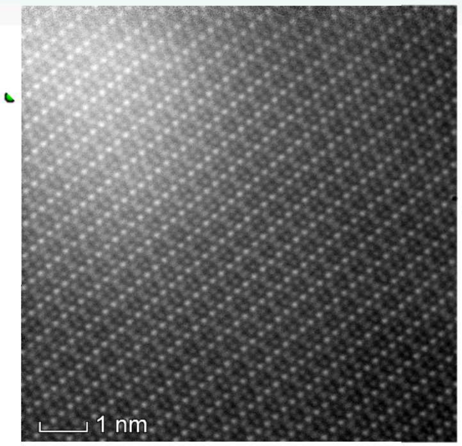


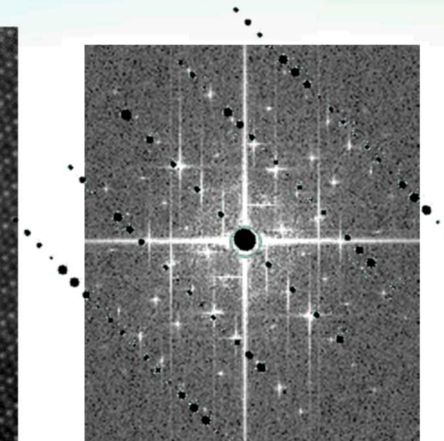
# Core-hole Spectroscopy: Reveal Redox Behavior with EELS



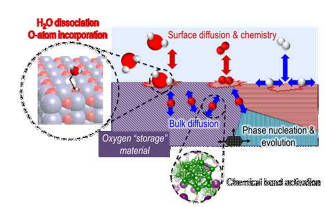

Samples FIB sliced for HRTEM



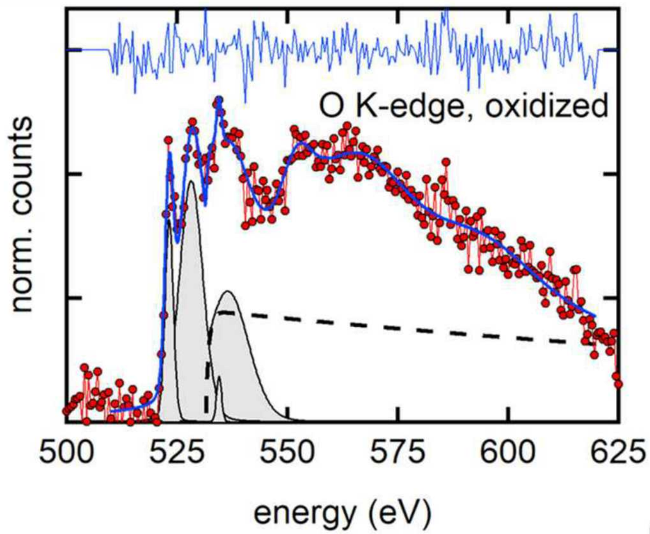



- Probe electron DOS for 12R and 10H "quenched" phases.
  - Discover where electrons go when O atoms vanish
  - Does cerium participate in redox chemistry?
- Derive fundamental understanding of redox behavior.
  - Explain known materials
  - Engineer better materials



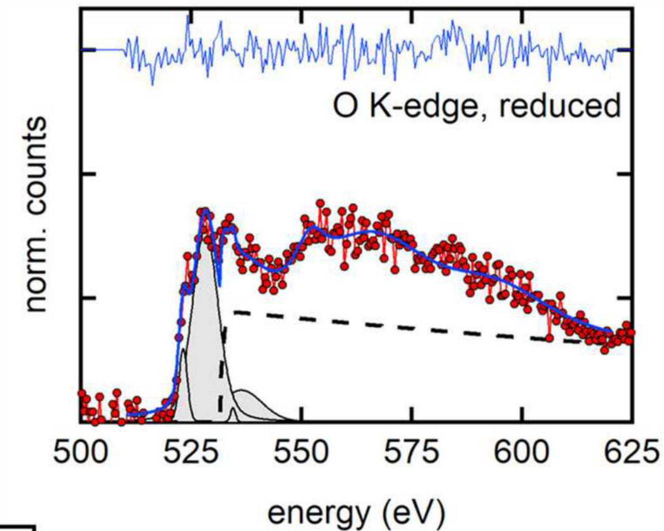
# EELS Reveals: Effect of Thermal Reduction on O-M Bonding

12R

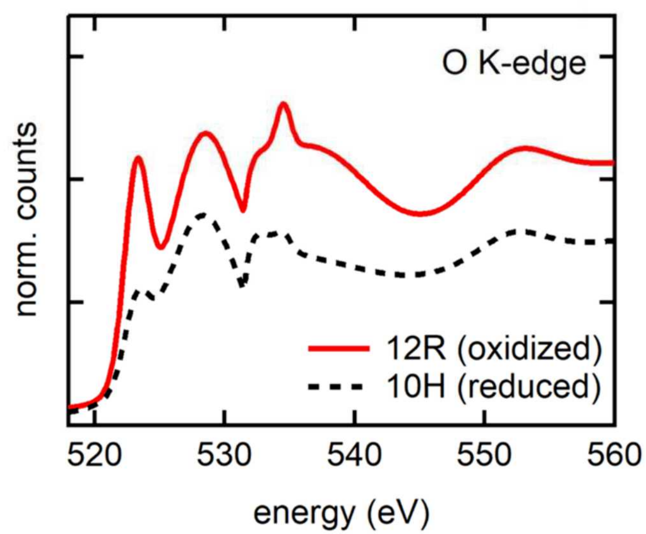



e⁻ charge transferred to hybridized 2p system decreases hole DOS

10H



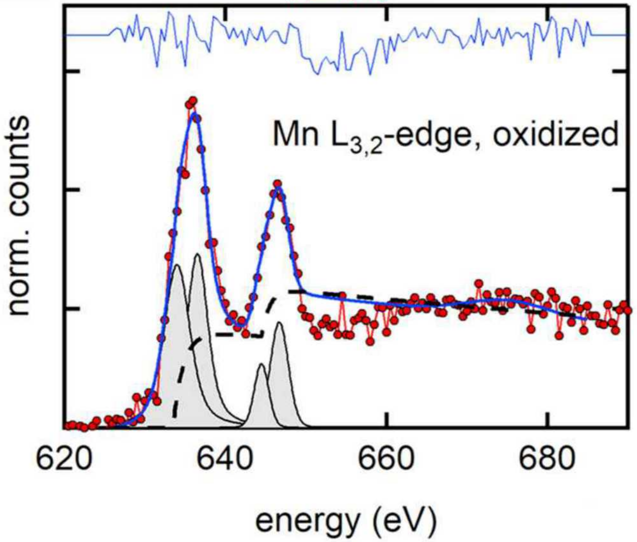

Ab inito theory required to fully interpret spectra




Subtle variation in extended edge oscillations

# EELS Reveals: Manganese Oxidation State Changed?

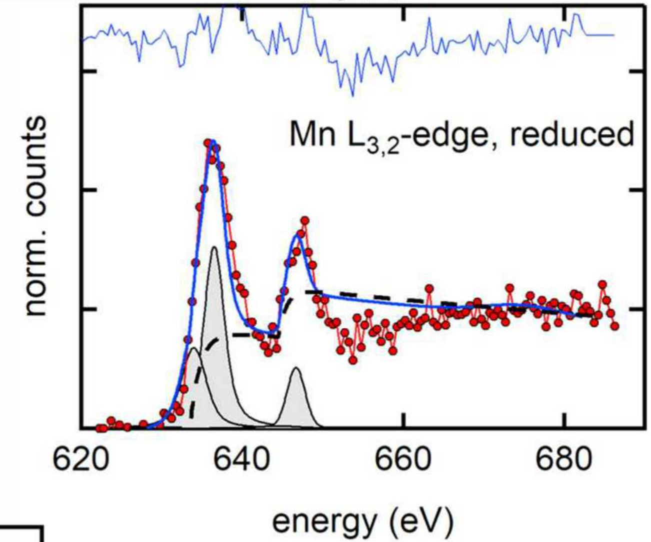
12R



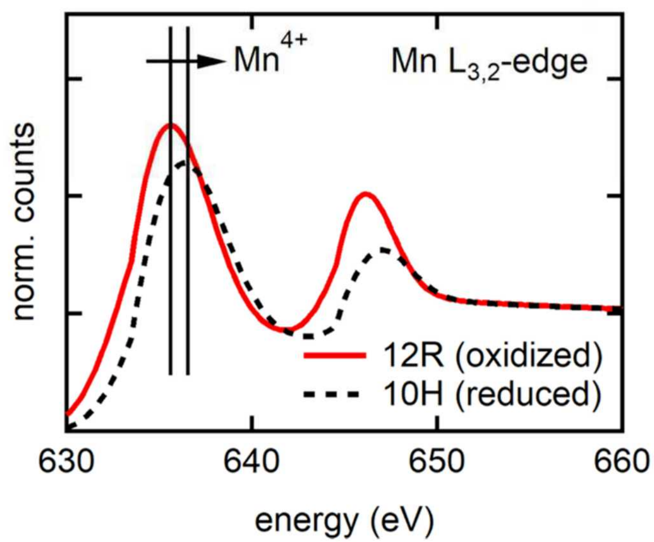

$e^-$ charge transferred to hybridized 3d system decreases hole DOS

branching ratio = Mn **REDUCED**

10H



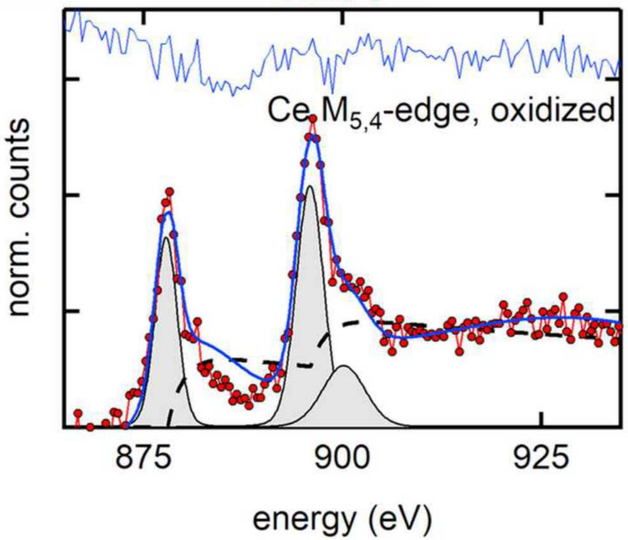

Ab inito theory required to fully interpret spectra



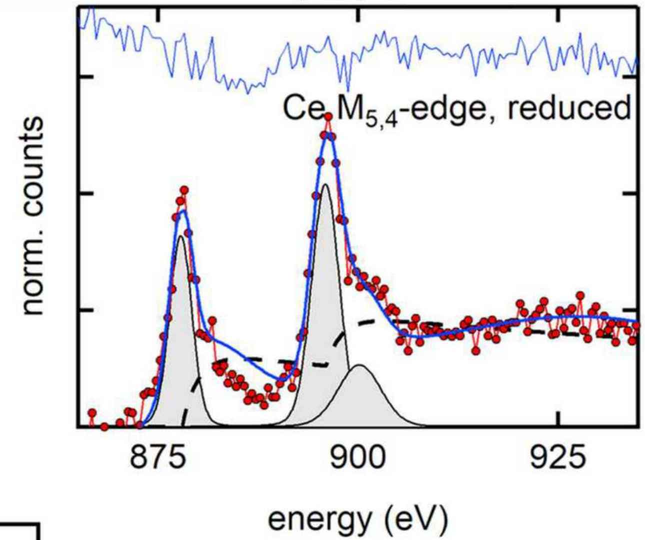

Peak shift = Mn **OXIDIZED**

# EELS Reveals: Cerium Not Likely Redox Active on B-site

12R

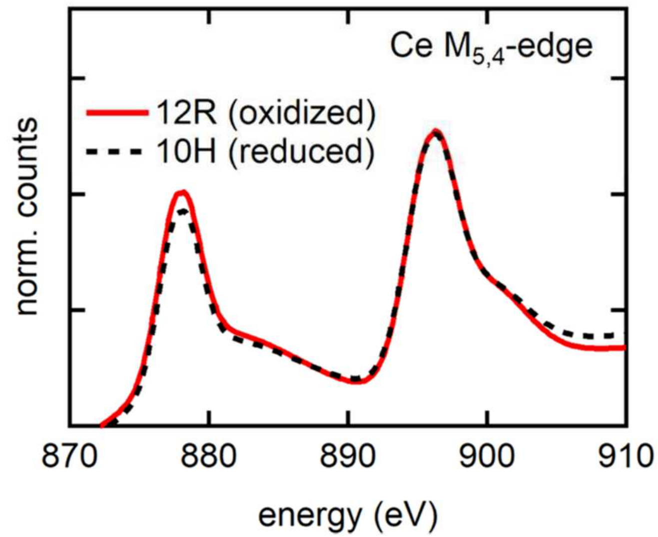



10H




4f system does not show significant changes in hole DOS

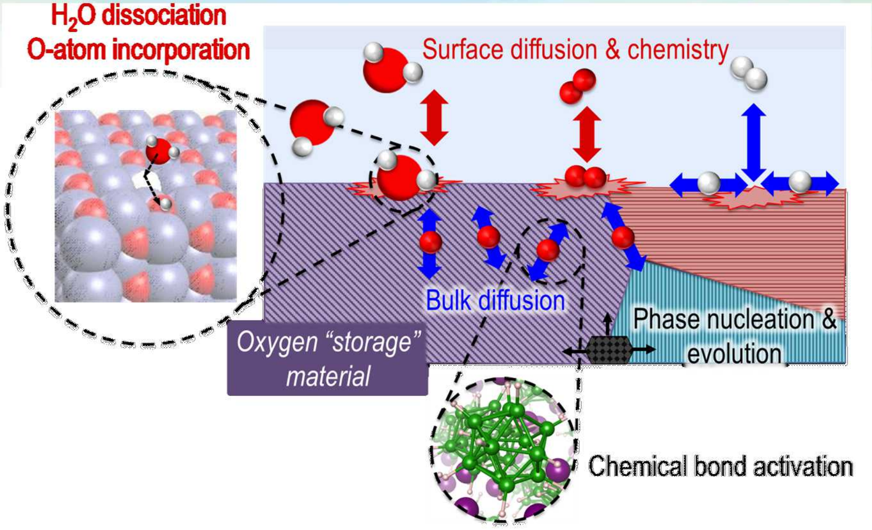
Ab inito theory required to fully interpret spectra




4f DOS is a very strong indicator of Ce oxidation state

# Much of the STCH Perovskite Story Yet to be Told

SLOWLY marching towards developing holistic design rules for STCH materials based on first principles




- Structural transformations.
  - Exploit large entropy changes to promote water splitting favorability
  - Exploit high $[V_O^{\cdot\cdot}]$ defect concentration to promote high $H_2$ production
- Surface reaction and bulk transport kinetics.
  - Enhance gas-exchange rates to promote fast cycle times
  - Enhance bulk oxygen diffusion rates for to promote fast cycle times
- Material degradation.
- Material – radiation interactions.

Sandia National Laboratories

$H_2FC$ Hydrogen and Fuel Cells Program

# HydroGEN is an Energy Materials Network (EMN)

## https://energy.gov/eere/energy-materials-network/energy-materials-network

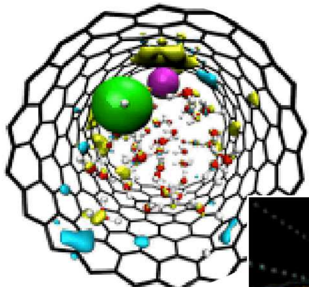
HydroGEN Advanced Water Splitting Materials

NREL · Berkeley Lab · Sandia National Laboratories · INL Idaho National Laboratory · Lawrence Livermore National Laboratory · SRNL

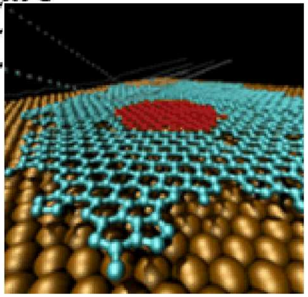
**Core Labs**

***Comprising more than 80 unique, world-class capabilities/expertise in materials theory/computation, synthesis, and characterization & analysis:***

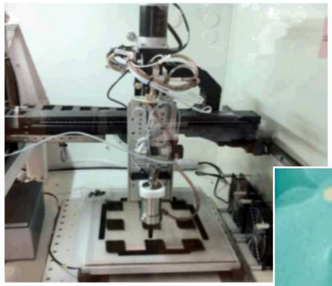
| ***Materials Theory/Computation*** | ***Advanced Materials Synthesis*** | ***Characterization & Analysis*** |
| --- | --- | --- |



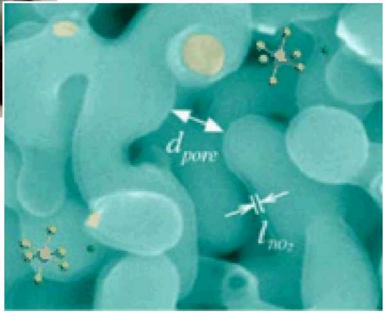
*Bulk and interfacial models of aqueous electrolytes*



*LAMMPS classic molecular dynamics modeling relevant to $H_2O$ splitting*



*High-throughput spray pyrolysis system for electrode fabrication*



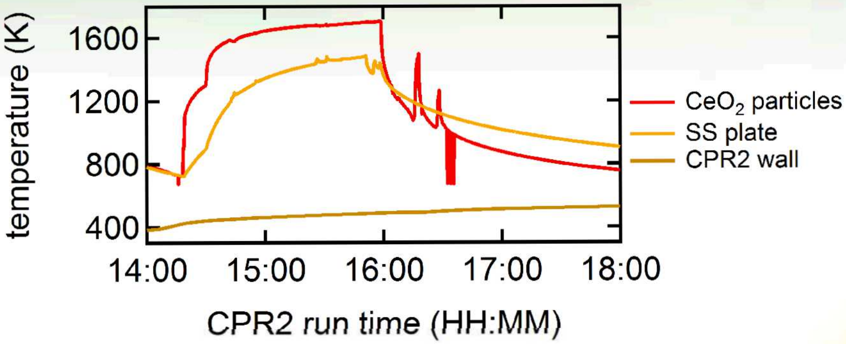
*Conformal ultrathin $TiO_2$ ALD coating on bulk nanoporous gold*

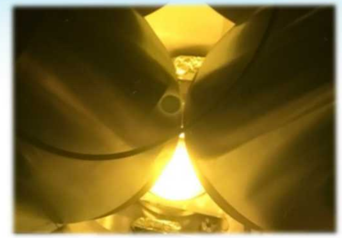
*Stagnation flow reactor to evaluate kinetics of redox material at high-T*

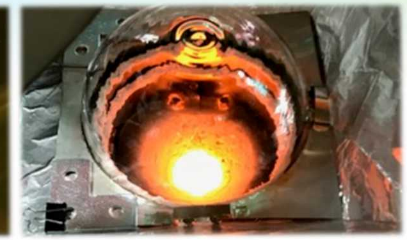
*TAP reactor for extracting quantitative kinetic data*

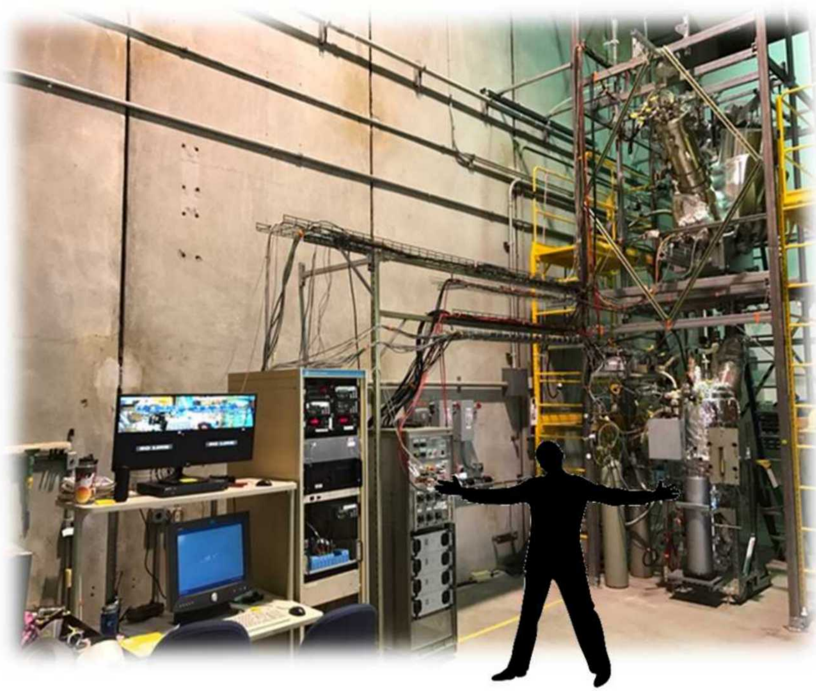
HydroGEN fosters cross-cutting innovation using ***theory-guided applied materials R&D*** to advance all emerging water-splitting pathways for hydrogen production

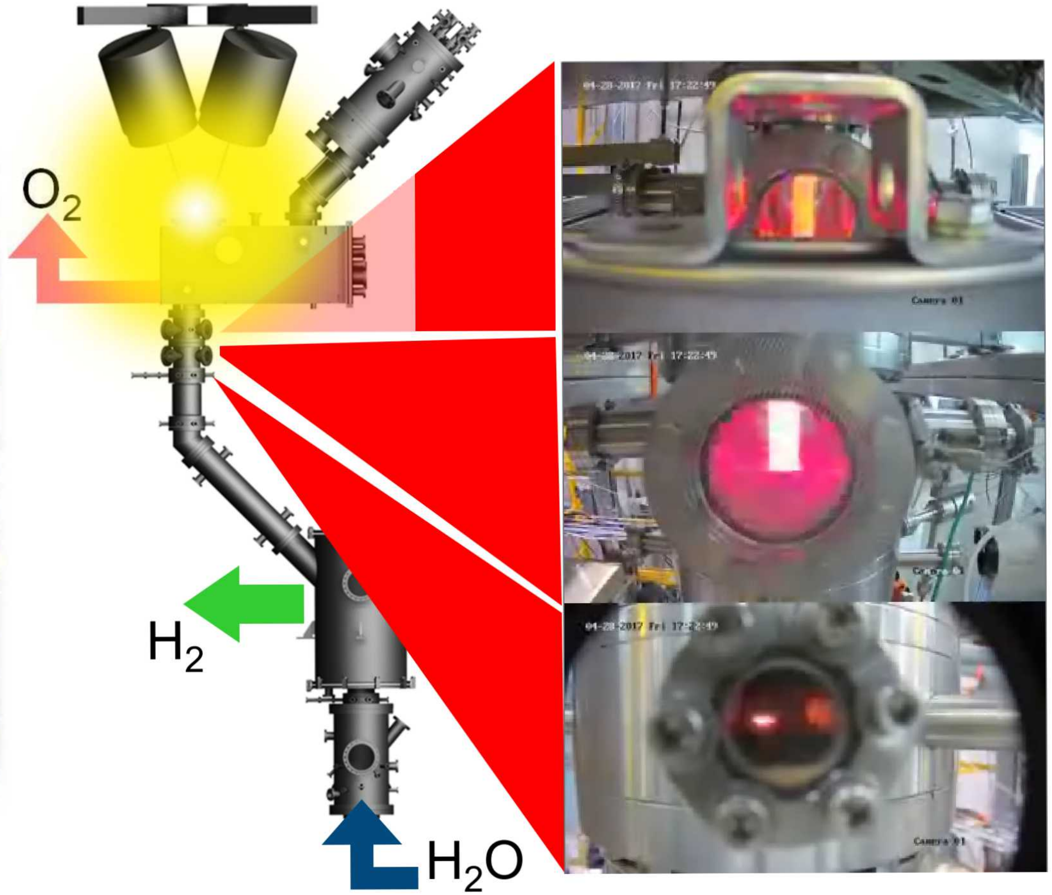
# STC $H_2$ Production Reactor Test Facility at Sandia









# THANK YOU

# QUESTIONS?

# Desired Material Behavior Defined by Process Economics

- Redox capacity ($MO_x/H_2$).
  - Oxide heating and material inventory
- Redox kinetics.
  - Cycle time and material inventory
- Earth abundance.
  - Raw materials
- Reduction temperature ($T_{TR}$).
  - Heliostats (solar concentration)
  - Reactor construction materials
- Steam requirement ($H_2O:H_2$).
  - Steam heating and water use
- Durability.
  - Material replacement

| PROPERTY | IDEAL | |
|---|---|---|
| Redox Capacity | HIGH | <10:1 ($MO_x/H_2$) |
| Redox Kinetics | FAST | ~sec (match flux) |
| Earth Abundance | HIGH | >$10^3/10^6$ Si |
| $T_{TR}$ @ Reduction | LOW | ~1400°C |
| $H_2O/H_2$ @ Oxidation | LOW | <5:1 ($H_2O:H_2$) |
| Durability | HIGH | >10 years |

Commercial viability key driver when competing against steam methane reforming or electrolysis.

J. E. Miller, A. H. McDaniel, M. D. Allendorf, *Advanced Energy Materials*. **4**, 1300469 (2014).
I. Ermanoski, J. E. Miller, M. D. Allendorf, *Physical Chemistry Chemical Physics*. **16**, 8418 (2014).