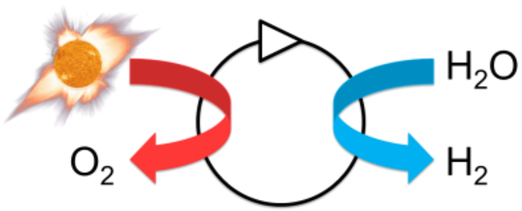
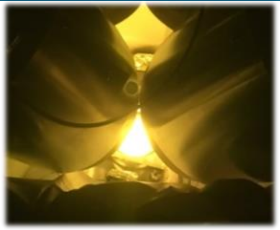
Sandia National Laboratories

Pathways to Hydrogen Production Using Solar Heat

Unlocking Solar Thermochemical Potential: Receivers, Reactors, and Heat Exchangers SETO webinar-workshop
December 3, 2020





PRESENTED BY

Anthony McDaniel(amcdani@sandia.gov)

U.S. Department of Energy   NNSA

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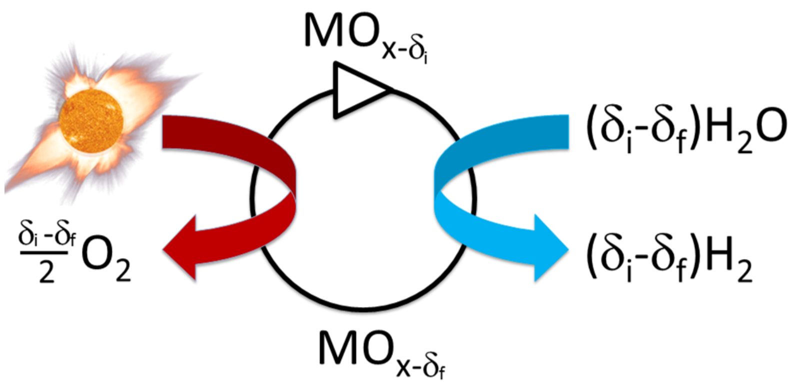
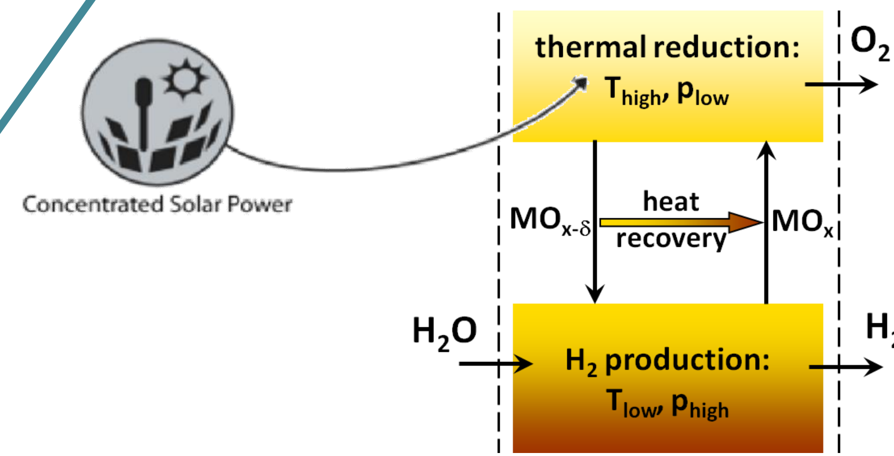
SAND2020-13487 PE

Thermochemical Water Splitting is a 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).





$$MO_x \rightarrow MO_{x-\delta} + \frac{\delta}{2}O_2$$ (1) Reduction

$$MO_{x-\delta} + \delta\cdot H_2O \rightarrow MO_x + \delta\cdot H_2$$ (2) Oxidation

$$\delta\cdot H_2O \rightarrow \frac{\delta}{2}O_2 + \delta\cdot H_2$$ (3) Thermolysis

Direct storage of solar energy in a reduced metal oxide.

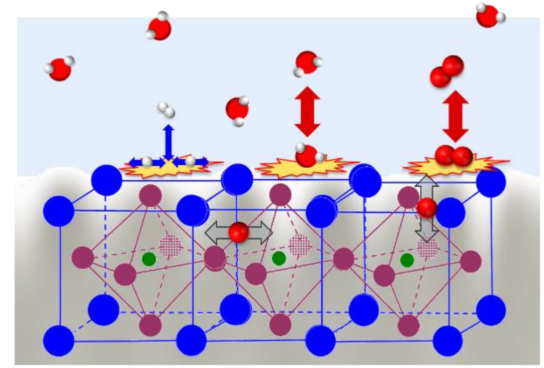
Hundreds of cycles proposed.

- Multi-phase, multi-step, thermochemical-electrochemical hybrids

Multinational R&D efforts have gravitated towards two-step, non-volatile MO_x

STC H_2 Materials Theme: Oxygen Exchange and Transport

Challenge: decrease T_R and increase $\Delta\delta_{OX}$

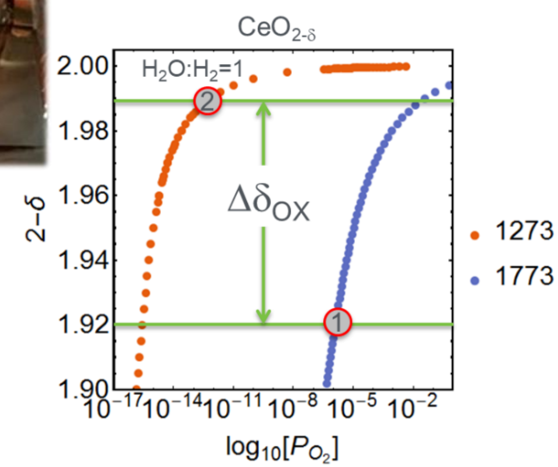


Oxygen **storage** materials with a **twist**.

- O-atom "harvested" from H_2O not air
- Bulk phenomena largely govern O-atom exchange with environment
- Understanding thermodynamics, kinetics, transport, gas-solid interactions, solid-solid interactions is important

Material subject to **extreme** environments.

- Redox cycling on the order of seconds
- Large thermal stress per cycle
  - 800 °C< T <1500 °C; ΔT_{RATE} ~100 °C/sec
- Large chemical stress per cycle
  - 10^{-14} atm< p_{O2} <10^{-1} atm



Water splitting at extremely **low p_{O2}**.

- Strongly reducing "oxidizing" atmosphere

"O" activity in $H_2O:H_2$	$\mu_{gas} > \mu_{solid}$	$\mu_{gas} <10^{-13}$atm

Receiver/Reactor and Material R&D must not evolve in "isolation"

J. E. Miller, A. H. McDaniel, M. D. Allendorf, *Advanced Energy Materials*. **4**, 1300469 (2014).

A Brief History of Non-Stoichiometric STC Water Splitting Materials

Cycle thermodynamics: tradeoff between $\Delta\delta$, T_{TR}, and $H_2O:H_2$

spinel

<u>Fe^{2+}/Fe^{3+} (unsupported) systems:</u>

High redox capacity ($\Delta\delta>0.1$)

Moderate T_R <1400 °C

WS-UNTESTED in $H_2O:H_2$ atm

perovskite

<u>$TM^{2+}/TM^{3+}/TM^{4+}$ (Mn, Fe, Co) systems:</u>

High redox capacity ($\Delta\delta>0.1$)

Low-to-moderate T_R <1400 °C

WS-PROMISING in $H_2O:H_2$ atm

fluorite

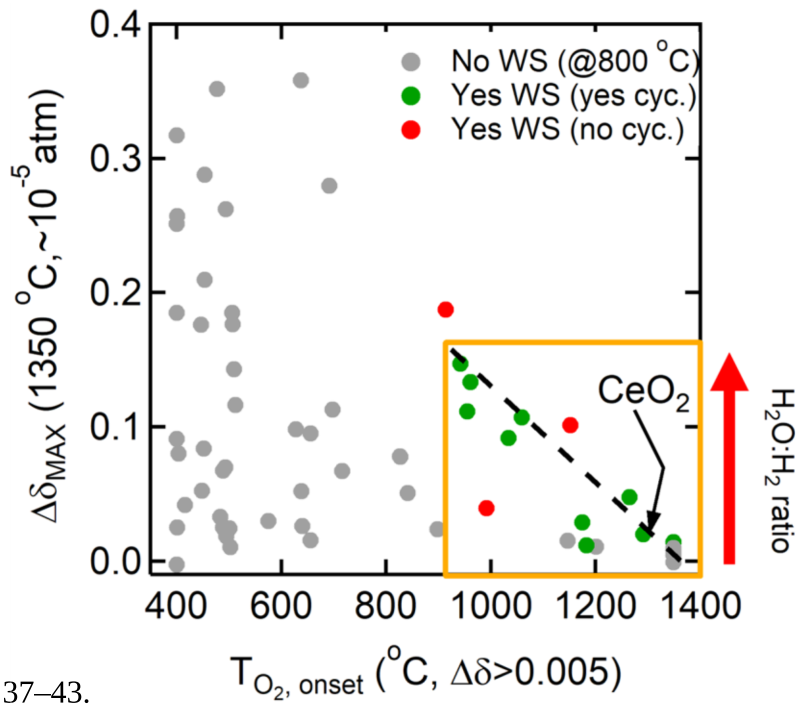
<u>Ce^{3+}/Ce^{4+} systems:</u>

Low redox capacity ($\Delta\delta<0.08$)

High T_R >1500 °C

WS-"BEST IN CLASS" in $H_2O:H_2$ atm

WS inactive at $T_{O2,onset}$ <850 °C
High $H_2O:H_2$ ratio at $T_{O2,onset}$ <1200 °C



A.H. McDaniel, *Current Opinion in Green and Sustainable Chemistry*, 2017, **4**, 37–43.

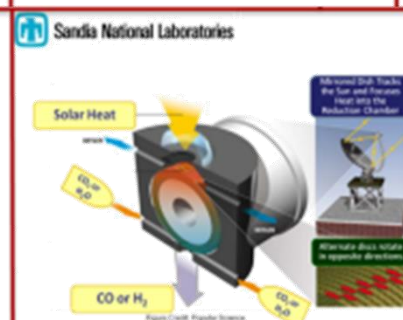
A Brief History of Reactor Design Concepts

Table 3.1.7 Technical Targets: Solar-Driven High-Temperature Thermochemical Hydrogen Production [a]

Characteristics	Units	2011 Status	2015 Target	2020 Target	Ultimate Target
Solar-Driven High-Temperature Thermochemical Cycle Hydrogen Cost [b]	\$/kg	NA	14.80	3.70	2.00
Chemical Tower Capital Cost (installed cost) [c]	\$/TPD H_2	NA	4.1MM	2.3MM	1.1MM
Annual Reaction Material Cost per TPD H_2 [d]	\$/yr.-TPD H_2	NA	1.47M	89K	11K
Solar to Hydrogen (STH) Energy Conversion Ratio [e,f]	%	NA	10	20	25%
1-Sun Hydrogen Production Rate [g]	kg/s per m^2	NA	8.1E-7	[illegible]	2.1E-6

Efficiency is a key metric for US R&D

High cost of solar collection



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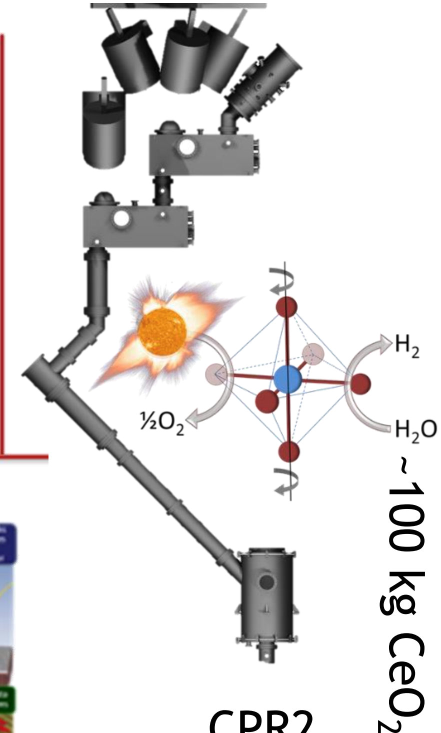


CPR2

Different reactor designs have been explored.

- Fixed material bed, moving material bed, inert gas sweep, vacuum, temperature swing, pressure swing

Increasing solar-to-hydrogen efficiency largely drives R&D.

MO_x WS cycle has been demonstrated at scales from watts to kilowatts

Sandia's Receiver/Reactor Design Philosophy

R. B. Diver *et al.*, *J. Solar Energy Engineering*. **130**, 041001(1)–041001(8) (2008).
J. E. Miller *et al.*, SAND2012-5658 (2012)
I. Ermanoski, *International Journal of Hydrogen Energy*. **39**, 13114–13117 (2014).
A. Singh *et al.*, *Solar Energy*. **157**, 365–376 (2017)

High solar-to-hydrogen conversion **efficiency**.

- Continuous on-sun operation
- Direct solar absorption
- Temperature and product separation
- Heat recovery between T_{TR} and T_{WS}

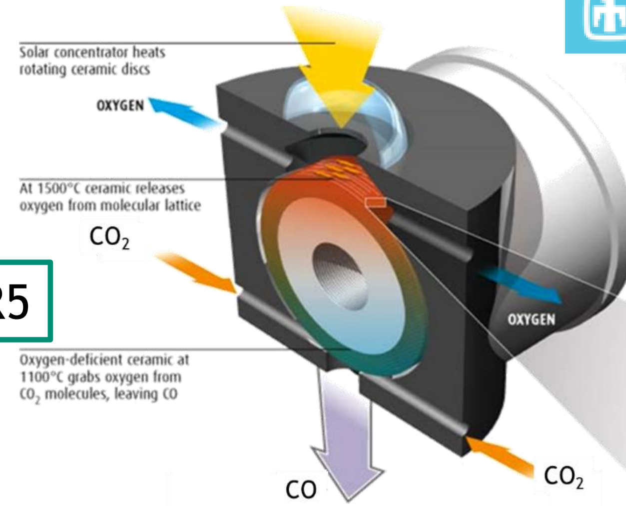
Moving particle bed design advantages:

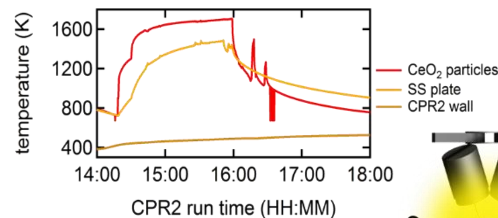
- Small reactive particles (~100µm) not monoliths
- Only particles are thermally cycled
- Independent component optimization
- Reaction kinetics decoupled from reactor mechanics

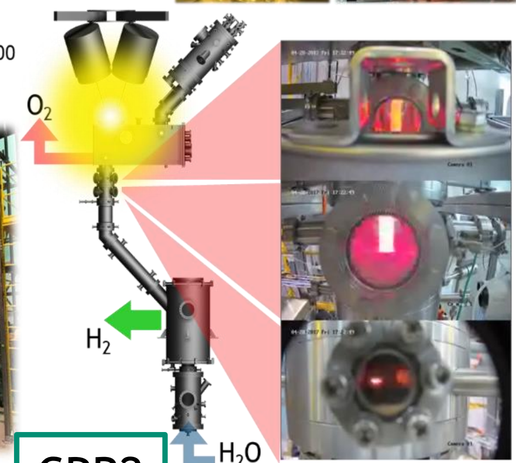
Cascading pressure design advantages:

- Ultra-low reduction pressure by chamber isolation
- Decreased pump work requirement

CR5







CPR2

CO_2 (CR^5) and H_2O (CPR^2) splitting demonstrated at power levels 5-10kW_{th}

Desired Material Behavior Defined by Process Economics

Commercial viability key driver when competing against steam methane reforming and fossil fuels

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	MOD	$>10^1/10^6$ Si
T_{TR} @ Reduction	LOW	<1400°C
H_2O/H_2 @ Oxidation	LOW	<10:1 ($H_2O:H_2$)
Durability	HIGH	>10 years

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).

Navigating A Highly Constrained Space: Thermodynamic Tradeoffs Affect Process Efficiency and Economics

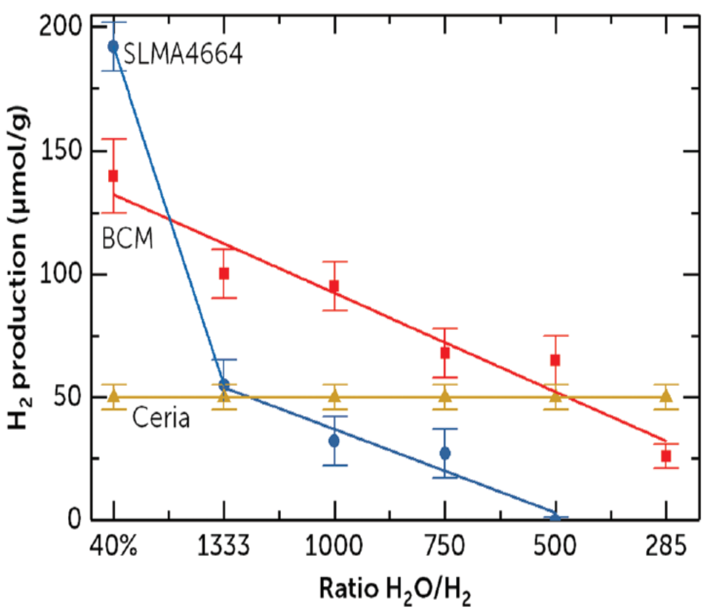
Process metrics (US DOE targets):

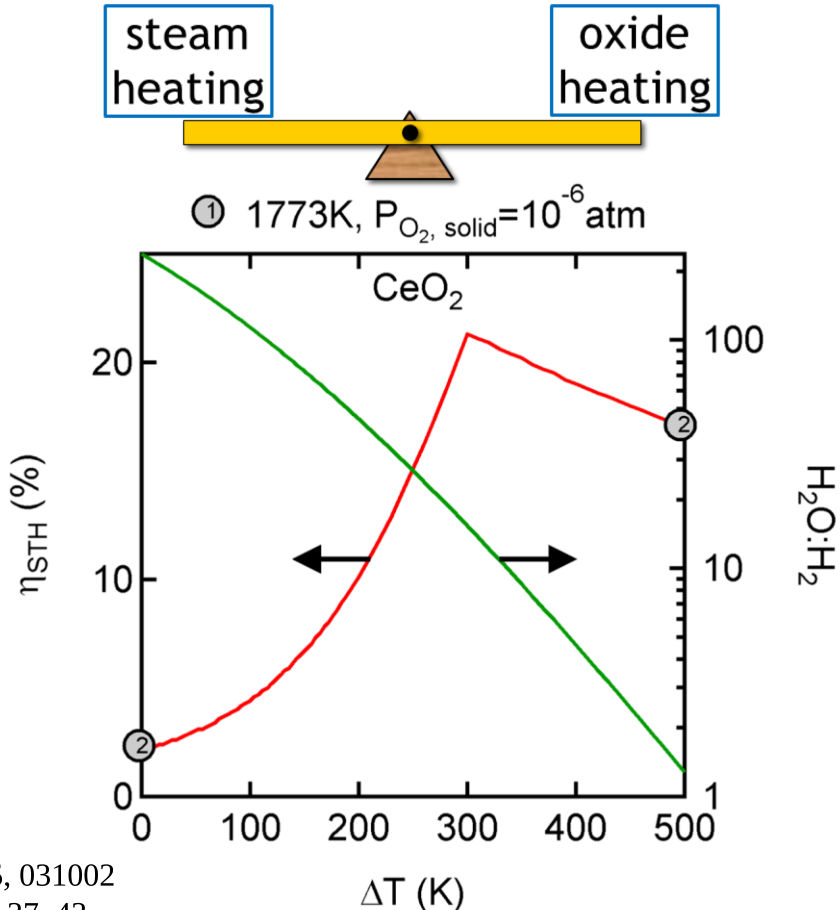
H_2 production rate	50-100mt/day
Solar-to-H_2 efficiency	>25%
H_2 production cost (US DOE)	~$3/kg

Desired cycle metrics:

Reduction Temperature (T_{TR})	~1400ºC	
Oxidation Temperature (T_{OX})	~800ºC	
"O" activity in reduction	$\mu_{gas} < \mu_{solid}$	μ_{gas} ~10^{-6}atm
"O" activity in oxidation	$\mu_{gas} > \mu_{solid}$	μ_{gas} ~10^{-13}atm

Receiver/Reactor engineering and material challenges must be addressed simultaneously





I. Ermanoski, N.P. Siegel, E.B. Stechel, *J. Solar Energy Engineering*, 2013, **135**, 031002
A.H. McDaniel, *Current Opinion in Green and Sustainable Chemistry*, 2017, **4**, 37–43
D. R. Barcellos *et al.*, *Energy & Environmental Science* (2018) doi:10.1039/C8EE01989D

Opportunities for Material Discovery

Ideal material is not unobtainium.

- Desired thermodynamic properties sandwiched between known compounds

DOE EMN Consortium

HydroGEN Advanced Water Splitting Materials

HydroGEN Seedling Projects Taking Up the Challenge

Non-stoichiometric oxide community needed to bring expertise into this field.

- Ideas needed for entropy and enthalpy engineering

Continued development and application of DFT.

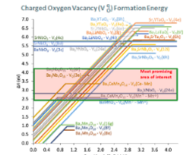
- Descriptors beyond vacancy formation energy

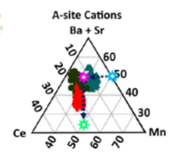
Advanced experimental methods.

- High throughput synthesis and characterization
- Electrochemical approaches
- Operando X-ray spectroscopies

- Find RP phases that modify redox thermo.
  - DFT screening of defect formation energy
  - Thin film combinatorics for compound discovery
  - High throughput colorimetric screening

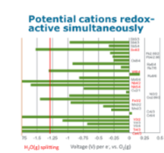
COLORADO SCHOOL OF MINES

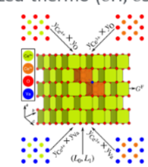




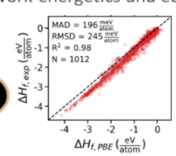
- Incorporate second redox active sublattice to modify thermo.
  - DFT method to predict $\Delta\delta_{OX}$ a priori using simple sublattice model formulations
  - Discover compounds with optimized thermo (δH, δS)

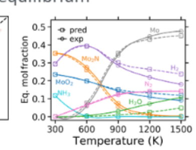
ASU Arizona State University





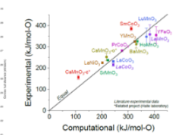
- Use machine-learned models coupled to DFT to discover new redox materials.
  - Rapidly screen materials based on machine-learned predicted stability
  - Formulate descriptor(s) for predicting reaction network energetics and equilibrium





- Use high-throughput Density Functional Theory to discover new redox materials.
  - Screen >10^4 known compounds for ground state stability/synthesizability and favorable thermo at reduction T<1400 °C

Northwestern University



What will it Take for Solar Thermal Technologies to Deliver…

Renewable H_2 or solar fuels in general

- R&D to discover and advance functional materials
- R&D to discover and advance alternative cycle chemistry
- R&D to develop solar reactors and synergistic system concepts
  - extremely high temperatures
  - high efficiency heat recuperation
  - hermetically sealed
  - CSP integration
- R&D to develop efficient collectors for high concentration and high temperature

Large scale demonstrations

- public—private partnerships

New policies and regulation to incentivize and drive private investment

Global Initiatives Gaining Momentum

Article in March 2018 issue of Chemical Engineering (www.chemengonline.com) titled "Solar Chemistry Heats Up" written by staff editor Gerald Ondrey

TABLE 1. RECENT SOLAR-THE

Project (timeframe)	Partners*	Aims
Indiref: Indirectly solar-heated reformer (2016–2019)	Solar Institut Jülich, Hilger GmbH, Hille & Müller	Using solar thermal energy (at 700–1,000°C) to reform CH_4, with CO_2 and H_2O, into syngas
Astor: Automized thermochemical water splitting (2017–2020)	Rheinische Fachhochschule Köln, Stausberg & Vosding GmbH, AWS-Technik e.K.	Using solar-thermal energy (at 800–1,400°C) to make H_2 from reaction of water with metal oxides
Sun-to-Liquid (2016–2019)	Bauhaus Luftfahrt, ETH Zurich, IMDEA Energy, Hygear B.V., Abengoa S.A., Arttic	Synthesize liquid hydrocarbons from H_2O and CO_2, via formation of syngas and subsequent Fischer-Tropsch (F-T) synthesis
Hydrosol: Solar thermochemical water splitting (2014–2017)	CIEMAT, Hygear B.V., Hellenic Petroleum, APTL	Using solar-thermal energy (at 800–1,400°C) to make H_2 from reaction of water with metal oxides
Sophia: Solar integrated pressurized high-temperature electrolysis (HTE) (2014–2017)	CEA, HyGear B.V., VTT, Engie, HTceramix S.A., SolidPower	Decomposition of steam by a combination of electrical and high-temperature (700–800°C) heat into carbon-free H_2 and O_2
Solpart: High-temperature solar-heated reactors for industrial production of reactive particles (2016–2020)	CNRS, Cemex, Abengoa Research, Universit of Manchester, EPPT, comessa, eurovia, New Lime Development, Université Cadi Ayyad, OPC	To utilize solar-thermal energy to perform the calcination step used in the lime, phosphate and cement industries
Pegasus: Renewable power generation by solar-particle-receiver-driven sulfur-storage cycle (2016–2020)	APTL/Certh, KIT, Baltic Ceramics, Processi Innovativi	Using sulfur to store energy in an $S\text{-}SO_2\text{-}H_2SO_4$ cycle (for more information, see *Chem. Eng.*, June 2017, p. 10)
Düsol: Sustainable fertilizer production from sun, air and water (2016–2019)	GTT Gesellschaft für Technische Thermochemie- und physik mbH, aixprocess GmbH	Making nitrogen fertilizers via a Haber-Bosch process in which the H_2 is derived from water splitting, and the N_2 from a solar-thermochemical air-separation process
Solam: Solar aluminum smelting (2015–2018)	aixprocess GmbH, CSIR, NFTN, Eskom, DST (last four South African)	An effort to decarbonize the aluminum smelting process using solar-thermal energy
Virtual Institute SolarSynGas: Thermochemical research for CO_2-neutral renewable fuels (2012–2017)	ETH Zurich, KIT, TU Clausthal	To produce CO_2-neutral fuels via a thermochemical route
HEST-HY: High efficiency solar-thermal hydrogen (2014–2017)	Sandia National Laboratories, Colorado School of Mines, Northwestern University, Stanford University, Bucknell University, Arizona State University	To develop new methods and reactors for operating thermochemical looping cycles to make H_2 by splitting

*Source: DLR, Institute of Solar Research; DLR is a partner in all projects listed

Newsfront

Solar Chemistry Heats Up

Major efforts are underway to develop new process technology for making chemicals using sunlight and the products of combustion

No one can deny that the sun provides more than enough energy to supply the world's energy and materials needs. After all, Mother Nature has been using sunlight for millennia, making myriads of chemicals from carbon dioxide and water via photosynthesis. And the fact is, fossil fuels are the remnants of sun-to-chemical production, which humans have been exploiting for the last few centuries as alternatives to the biomass our ancestors used to meet their synthesis gas (syngas; H_2 and CO), which is then used for making ammonia, liquid fuels, alcohols and more (see Table 1).

Understand the limits

When it comes to making chemicals from CO_2, water and sunlight, there are basically three possibilities, explains Christian Sattler,

https://hydrogeneurope.eu/project/hydrosol-plant

Project HYDROSOL-PLANT

Thermochemical HYDROgen production in a SOLar monolithic reactor: construction and operation of a 750 kWth PLANT

Solar fuels could be Australia's biggest energy export

Solar fuels could be Australia's biggest energy export

Posted on October 16, 2015. **Australasian News.**

Author: Giles Parkinson

Source: reneweconomy.com.au

China Conducts Massive Synthesis of Liquid Solar Fuel

http://english.cas.cn/newsroom/archive/news_archive/nu2018/201807/t20180709_194849.shtml

A 1,000-tonne industrialization of liquid solar fuel synthesis project has been launched in Lanzhou, capital city of northwest China's Gansu Province.

OBJECTIVES https://www.sun-to-liquid.eu/

SUN-to-LIQUID will design, fabricate, and experimentally validate *a large-scale, complete* ***solar fuel production plant***

The preceding EU-project SOLAR-JET has recently demonstrated the first-ever solar thermochemical kerosene production from H_2O and CO_2 in a laboratory environment (*6). A total of **291 stable redox cycles** were performed, yielding **700 standard litres of high-quality syngas**, which was compressed and further processed via Fischer-Tropsch synthesis to a mixture of naphtha, gasoil, and kerosene (*7).

As a follow-up project, **SUN-to-LIQUID will design, fabricate, and experimentally validate a more than 12-fold scale-up of the complete solar fuel production plant and will establish a new milestone in reactor efficiency**. The field validation will integrate for the first time the whole production chain from sunlight, H_2O and CO_2 to liquid hydrocarbon fuels.

In ASTOR a reactor will be developed, which is based on the ones of the HYDROSOL project family. It will have a thermal capacity of 250 kW. As REDOX-material Ceroxide is used.

Reactor for thermochemical hydrogen generation in SynLight

Acknowledgements

Sandia Labs:

- Andrea Ambrosini
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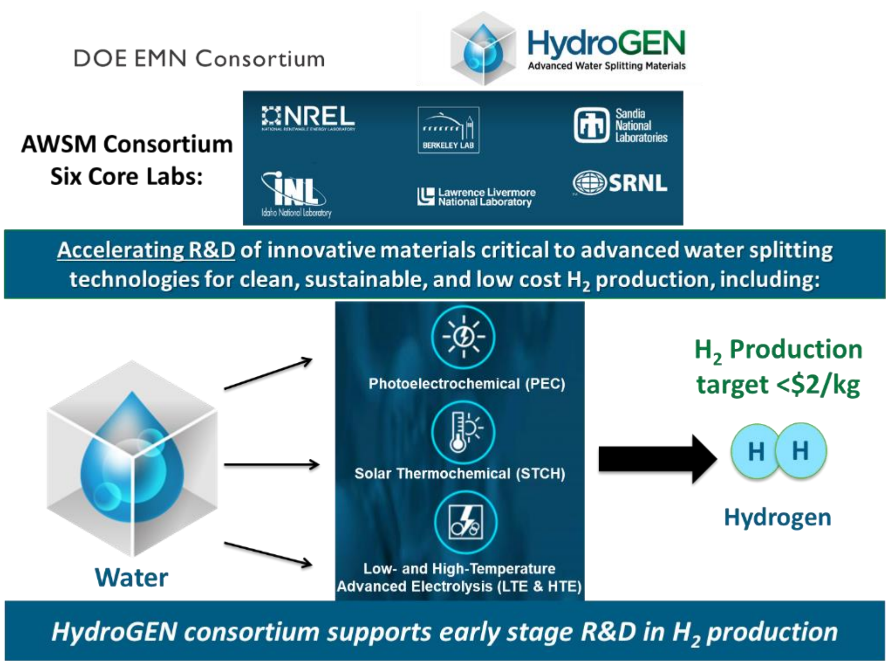
- Josh Sugar



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- Christian Sattler (DLR)
- Martin Roeb (DLR)
- Nathan Siegel (Bucknell)
- Ryan O'Hayre (CSM)
- Michael Sanders (CSM)
- Jianhua Tong (Clemson)
- William Chueh (Stanford)
- Ellen Stechel (ASU)
- Ivan Ermanoski (ASU)
- Jim Miller (ASU)
- Chris Wolverton (NWU)

Deutsches Zentrum für Luft- und Raumfahrt
German Aerospace Center

Nature's Thermochemical Water Splitting Process

Source: iStock

Our challenge is to develop efficient and scalable *solar*-powered reactors producing 100,000 kg H_2/day without melting houses