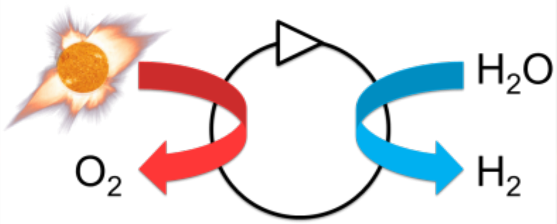
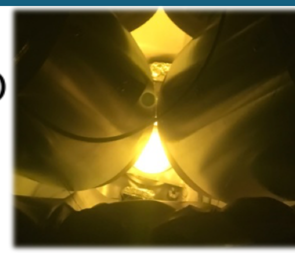
Pathways to Hydrogen Production Using Solar Heat

UC Solar Thermal Symposium
Davis, CA
November 15, 2019





PRESENTED BY

Anthony McDaniel(amcdani@sandia.gov)

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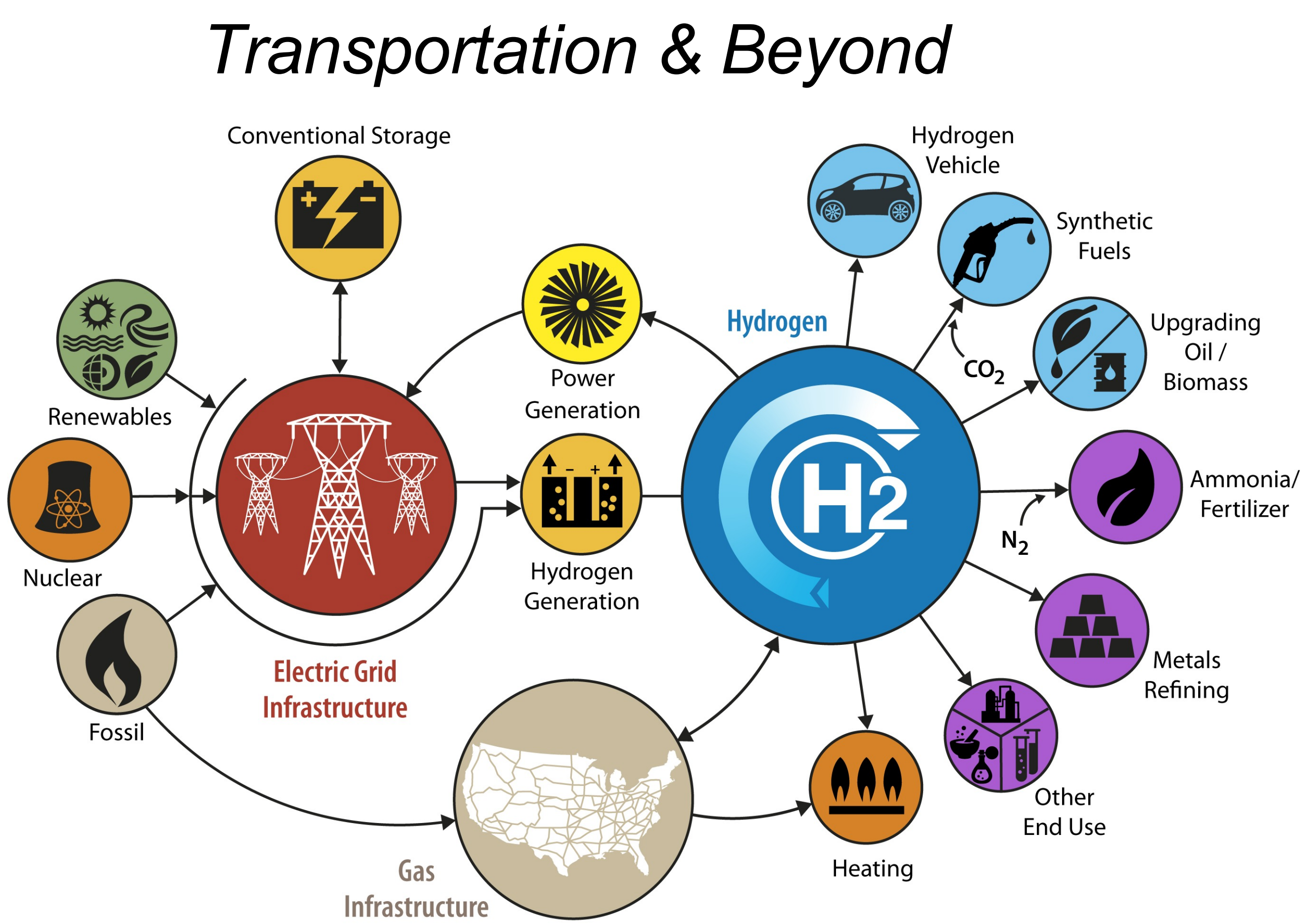
SAND2019-12068 PE

H2@Scale: Enabling Affordable, Reliable, Clean, and Secure Energy Across Sectors



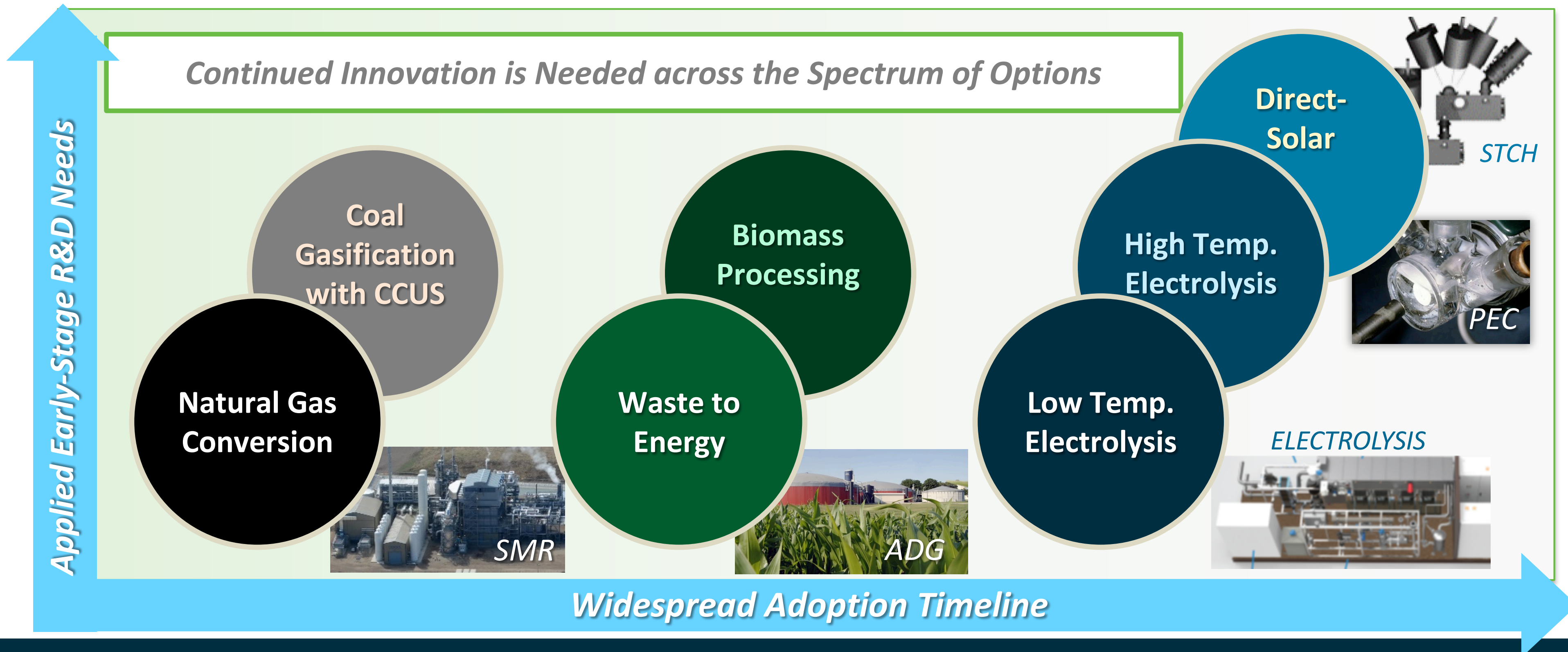
*Illustrative example, not comprehensive

Large-scale, low-cost H_2 from diverse domestic resources enables an economically competitive and environmentally beneficial future energy system across sectors

Materials innovations are key to enhancing performance, durability, and cost of H_2 generation, storage, distribution, and utilization technologies key to H2@Scale

https://energy.gov/eere/fuelcells/h2-scale

DOE's Hydrogen Production R&D Strategy



Hydrogen Production

Research and Development

- Fossil fuels, biomass and waste
- Water electrolysis
- Solar water splitting
- Co-production of value-added products

Ultimate Goal

Less than $2/kg

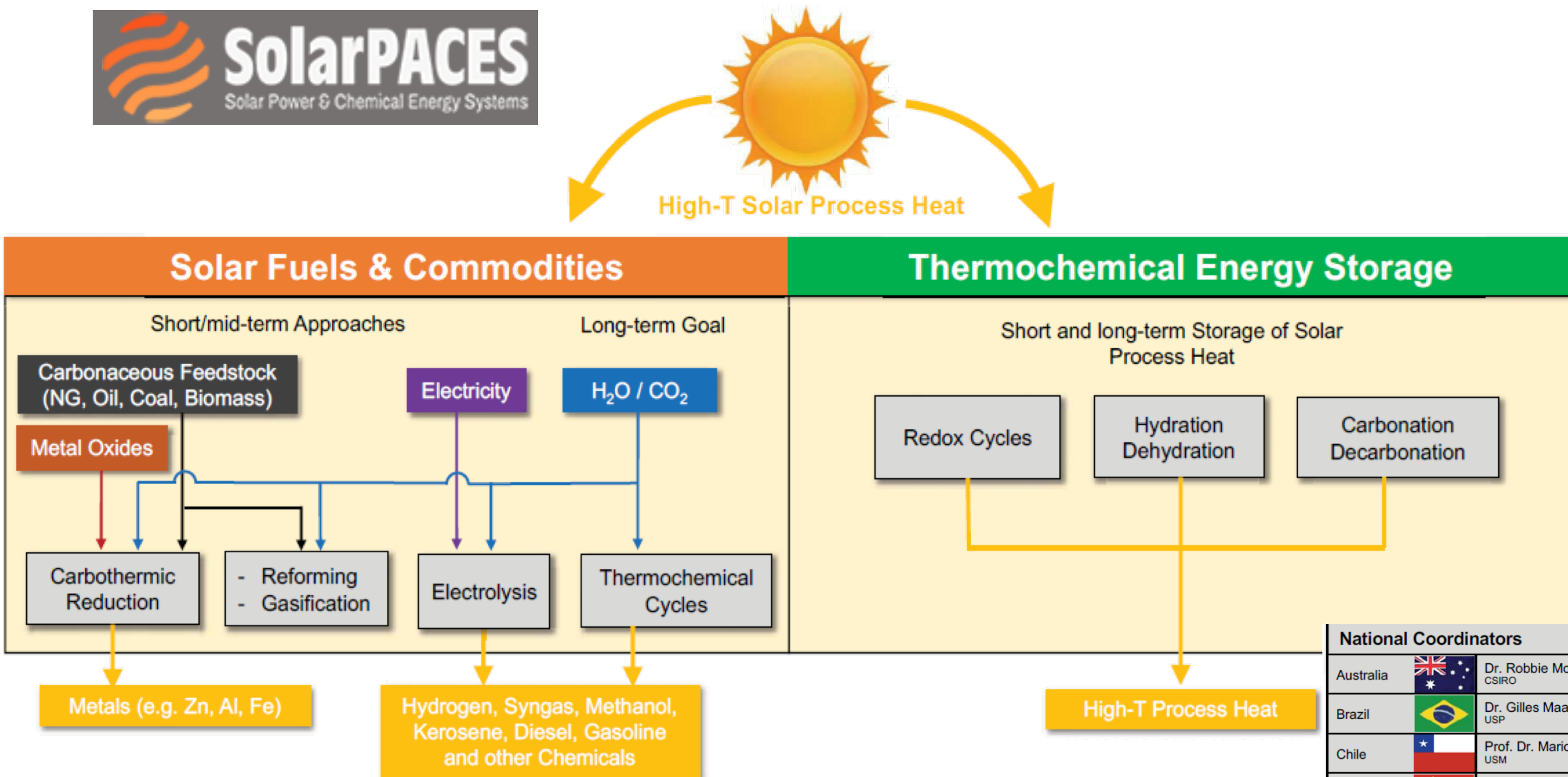
utilizing diverse, domestic feedstocks

Collaboration through Consortia

HydroGEN Advanced Water Splitting Materials — Advanced water-splitting materials

Innovative Concepts — Ex.: Leveraging biomass/waste for H_2 production

International Organization: TASK II—Solar Chemistry Research



SolarPACES Task II Activity:
Roadmap to Solar Fuels
Strategy for Industry Involvement and Market Penetration

2015 publication

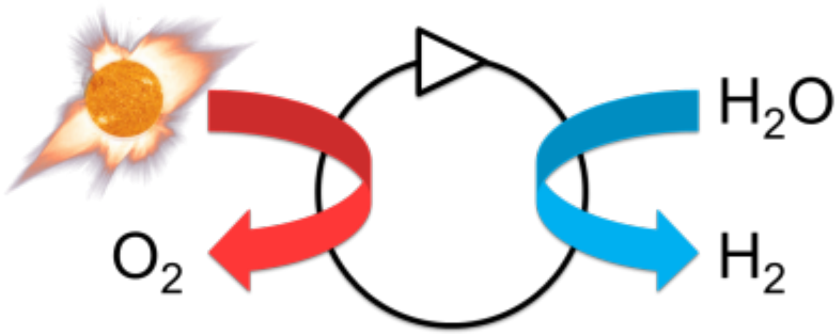
Roadmap to Solar Fuels

Strategy for Industry Involvement and Market Penetration

National Coordinators		
Australia	Dr. Robbie McNaughton CSIRO	robbie.mcnaughton@csiro.au
Brazil	Dr. Gilles Maag USP	gmaag@usp.br
Chile	Prof. Dr. Mario Toledo USM	Mario.Toledo@usm.cl
China	Prof. Dr. Jinjia Wei Xi'an Jiaotong Uni.	jjwei@mail.xjtu.edu.cn
France	Prof. Dr. Gilles Flamant CNRS	gilles.flamant@promes.cnrs.fr
Germany	Prof. Dr. Christian Sattler DLR	Christian.Sattler@dlr.de
Greece	Dr. George Karagiannakis CERTH	gkarag@cperi.certh.gr
Italy	Dr. Alberto Giaconia ENEA	alberto.giaconia@enea.it
Korea	Dr. Yong-Heack Kang KIER	yhkang@kier.re.kr
Mexico	Dr. Heidi I. Villafan Vidales UNAM	hivv@ier.unam.mx
South Africa	Dr. Gerhard Human NWU	Gerhard.hu@nwu.ac.za
Spain	Dr. Alfonso Vidal CIEMAT	alfonso.vidal@ciemat.es
Switzerland	Dr. Philipp Furler ETH Zurich	furlerp@ethz.ch
USA	Prof. Dr. Ivan Ermanoski Arizona State University	Ivan.Ermanoski@asu.edu
UAE	Prof. Dr. Khalid Al-Ali Khalifa University	Khalid.alali@ku.ac.ae

Thermochemical and Hybrid Water Splitting Technologies

Thermochemistry



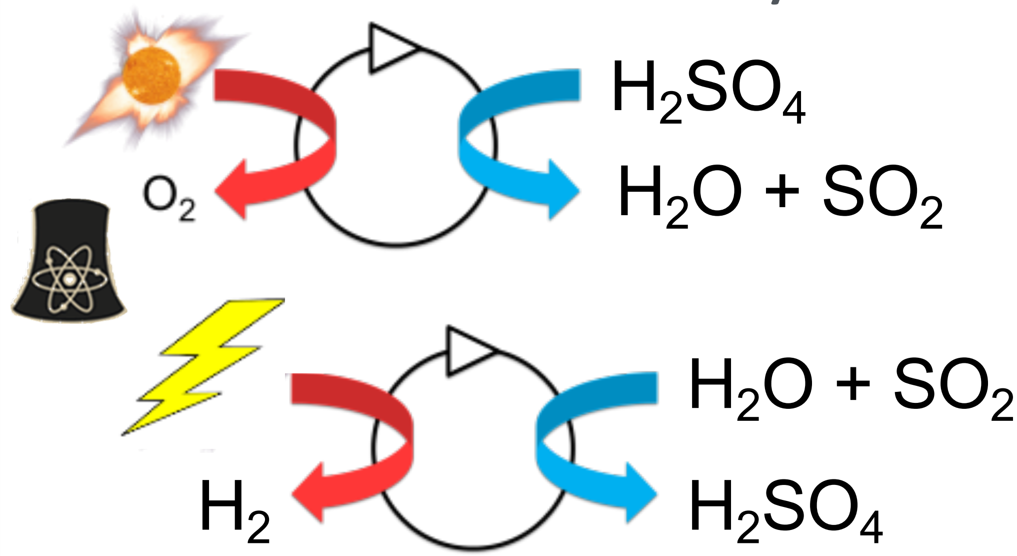
$$MO_x \rightarrow MO_{x-\delta} + \frac{\delta}{2} O_2 \quad \text{(1) Reduction}$$

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

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

- Metal cation is redox active element in two-step cycle

TC + Electrochemistry



$H_2SO_4 \leftrightarrow H_2O + SO_2 + ½ O_2$
(thermochemical; 800-900 °C)

$SO_2 + 2\,H_2O \rightarrow H_2SO_4 + H_2$
(electrochemical; 80-120 °C)

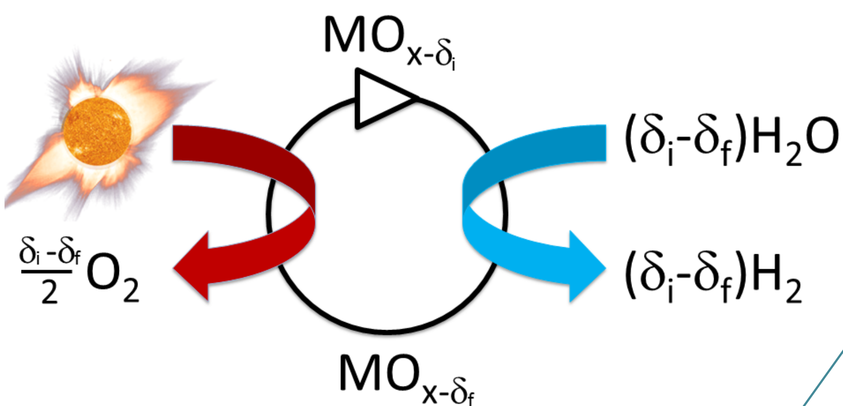
Net Reaction: $H_2O \rightarrow H_2 + ½ O_2$

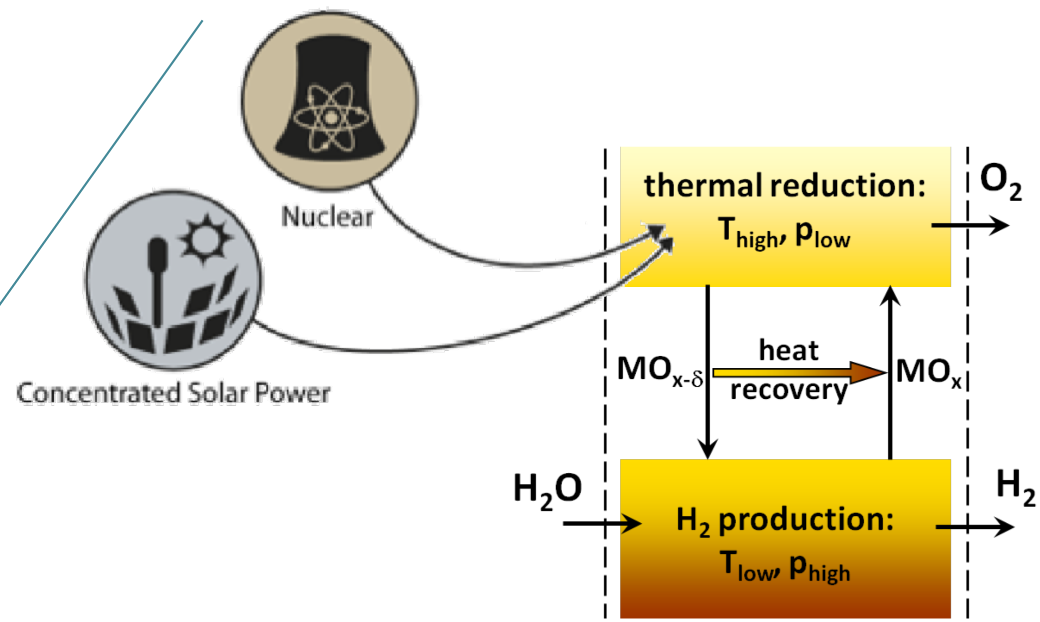
- Sulfur is redox active element in two-step cycle

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

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).





- Direct storage of solar energy in a chemical bond
- Multinational efforts focused on two-step, non-volatile MO_x

STC H_2 vs. Alternative Renewable Water Splitting Technologies

STC offers a simpler technology than alternatives and higher theoretical efficiency.

Theoretical vs. DOE Target Efficiency

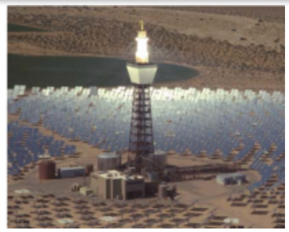
$$\eta_{STH} = LHV(H_2) / Q_{solar}$$

Theoretical Efficiency

Technical Simplicity

>40% vs. 26%

STC H_2



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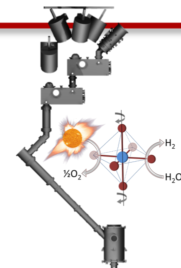


high temperature reactor

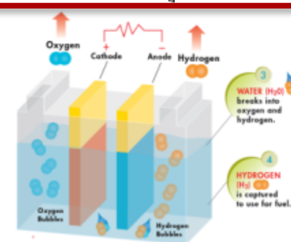
no bugs/wires/membranes

>1000 suns

~28% vs. 20%

Solar Thermal or PV+ Electrolysis

+

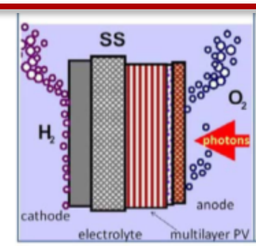


Stirling heat engine
conventional electrolyzer

>1000 suns

>40% vs. 25%

PEC



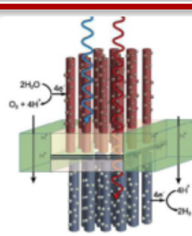
inorganic PV cells
complex, multi-layered

intrinsic electrolysis

1-15 suns

??% vs. 1%

Emerging Technologies
JCAP & Artificial Leaf

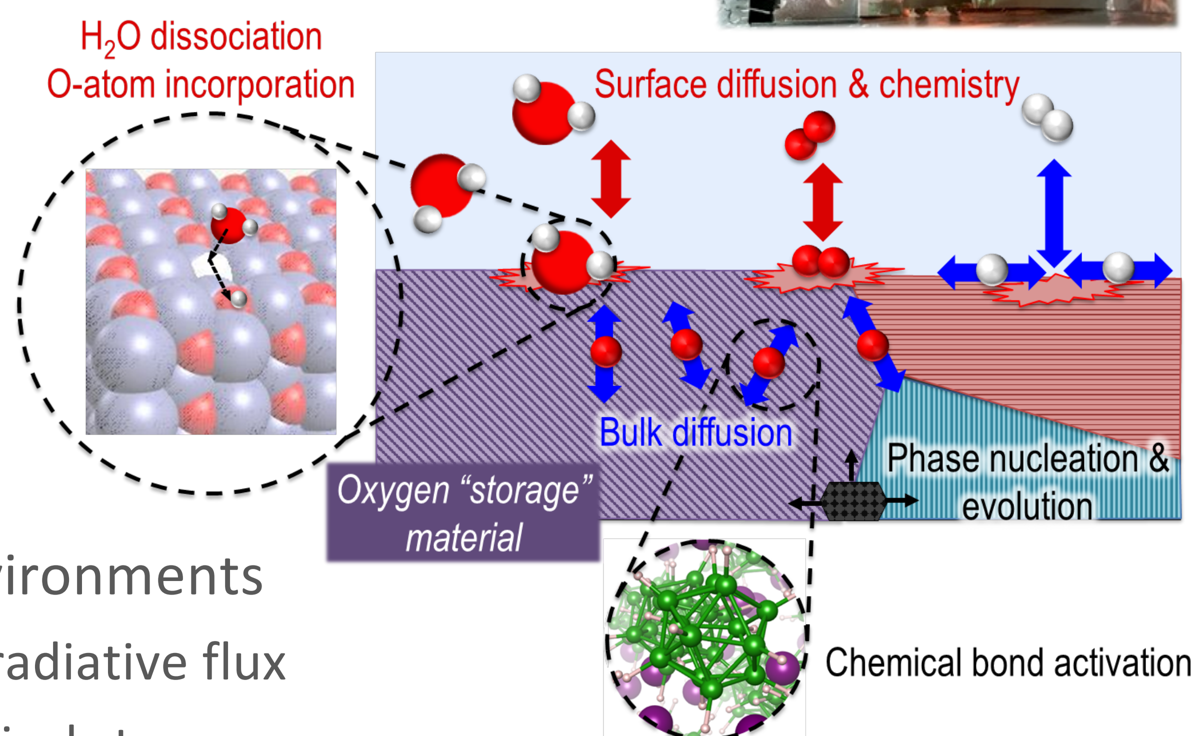


complex nano-engineered synthetic membranes

1 sun

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 environments
  - High temperature and radiative flux
  - High thermal and chemical stress



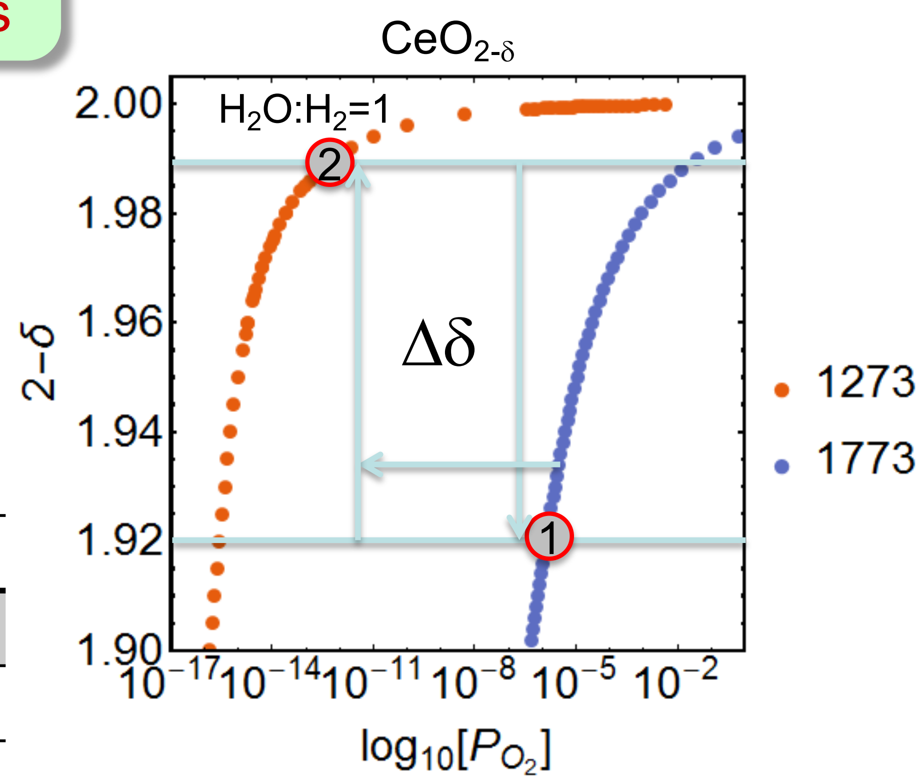
Cycle Thermodynamics Challenge Process Economics

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

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

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

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



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

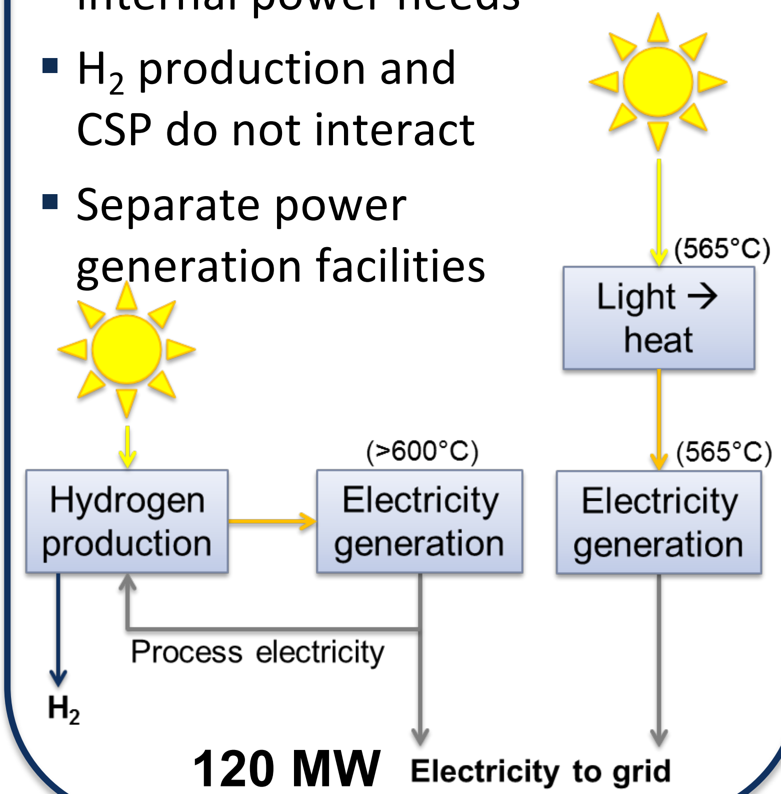
Engineering challenge

Material challenge

Thought Experiment: Adjacent H_2 and CSP Plants

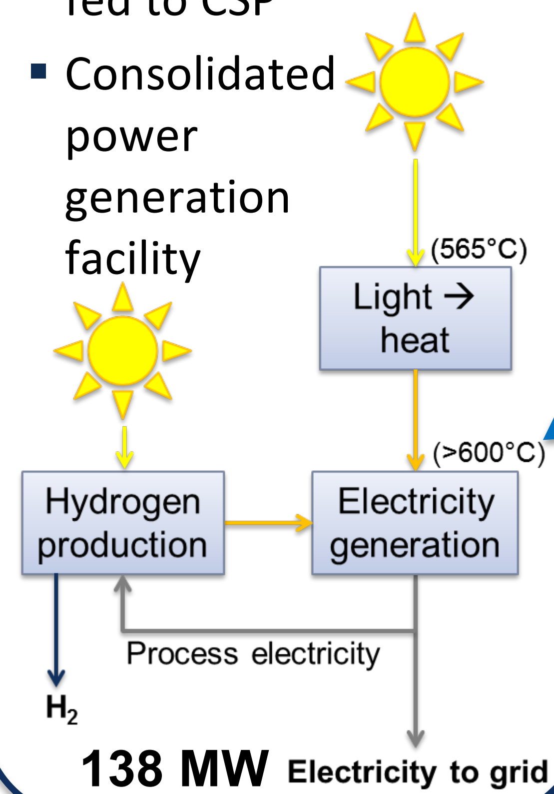
No integration

- Waste heat supplies internal power needs
- H_2 production and CSP do not interact
- Separate power generation facilities



CSP-H_2 integration

- Waste heat is fed to CSP
- Consolidated power generation facility



Electricity generation efficiency increases from **42%** to **48%** at higher T

****All heat*** is converted to electricity more efficiently, not only heat from H_2 production

CSP-H_2 integration increases electricity generation by 15% (relative), with lower total capital costs

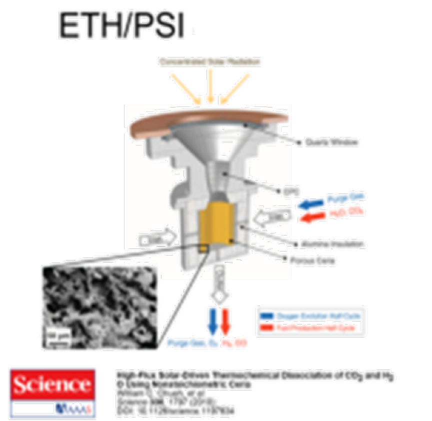
https://www.energy.gov/eere/fuelcells/downloads/potential-strategies-integrating-solar-hydrogen-production-and

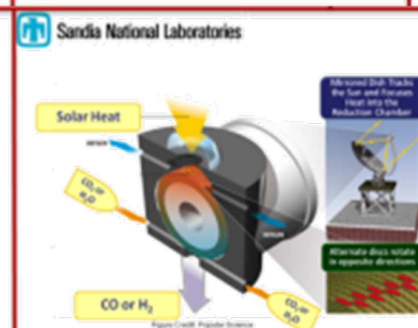
MO_x WS Cycle Demonstrated: From Watts to Kilowatts

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]	[illegible]

Efficiency is a key metric for US R&D

High cost of solar collection





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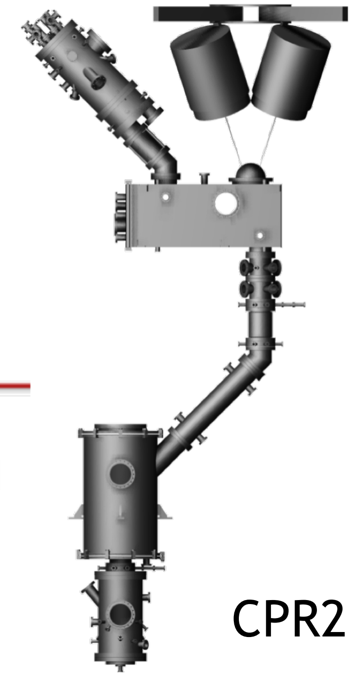
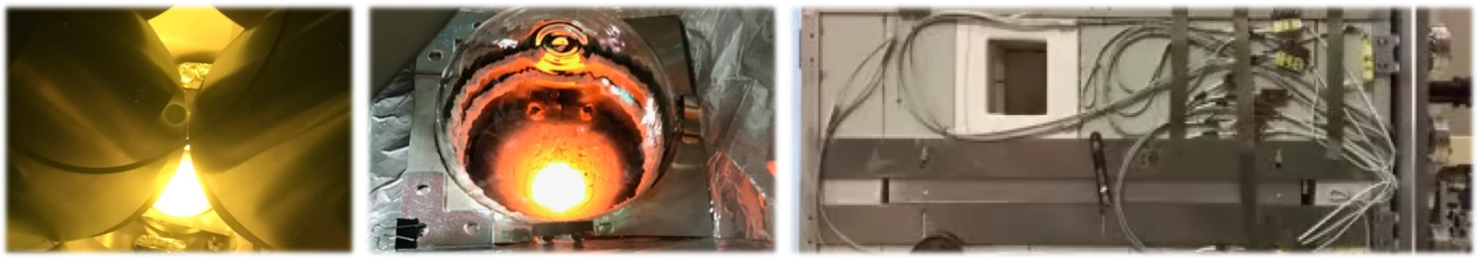


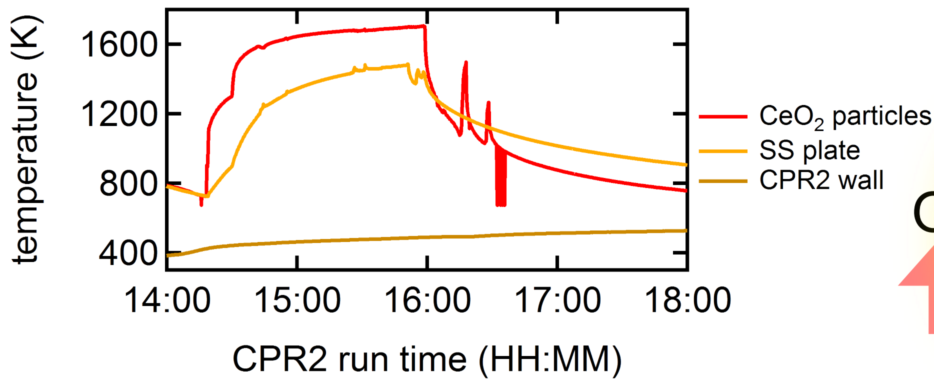
CPR2

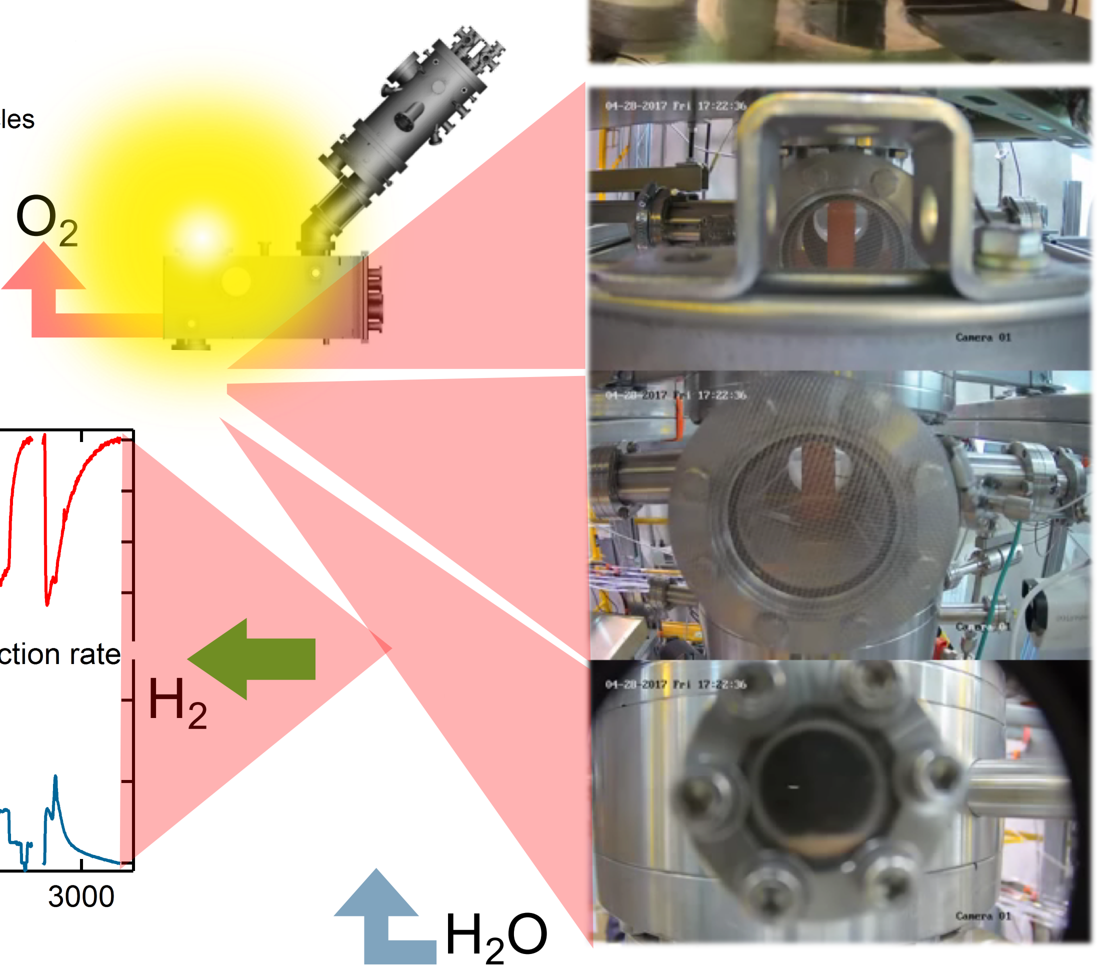
- Many different reactor designs have been explored

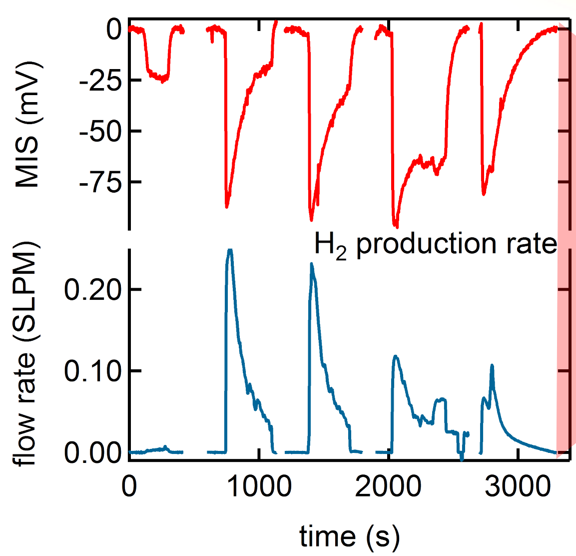
J. E. Miller, A. H. McDaniel, M. D. Allendorf, *Advanced Energy Materials*. **4**, 1300469 (2014).

Sandia's Flowing Particle Receiver Reactor









T_{TR}~1700 K

0.25 SLPM peak H_2 rate

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

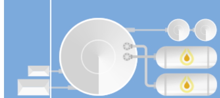
Source: reneweconomy.com.au

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

HydroGEN
Advanced Water Splitting Materials

AWSM Consortium Six Core Labs:

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

Accelerating R&D of innovative materials critical to advanced water splitting technologies for clean, sustainable, and low cost H_2 production, including:

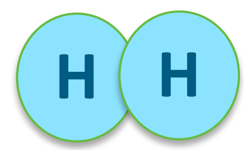
Water

Photoelectrochemical (PEC)

Solar Thermochemical (STCH)

Low- and High-Temperature Advanced Electrolysis (LTE & HTE)

H_2 Production target <$2/kg



Hydrogen

HydroGEN consortium supports early stage R&D in H_2 production

What Would it Take for Solar Thermal Technologies to Deliver…

Renewable H_2 by splitting the water molecule (or solar fuels in general)

- R&D to discover and advance functional materials
- R&D to discover and advance alternative cycle chemistry
  - both pure thermochemical and hybrid cycles
- R&D to develop solar reactors and synergistic system concepts (H_2+Electricity)
  - 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

Nature's Thermochemical Water Splitting Process

Source: iStock

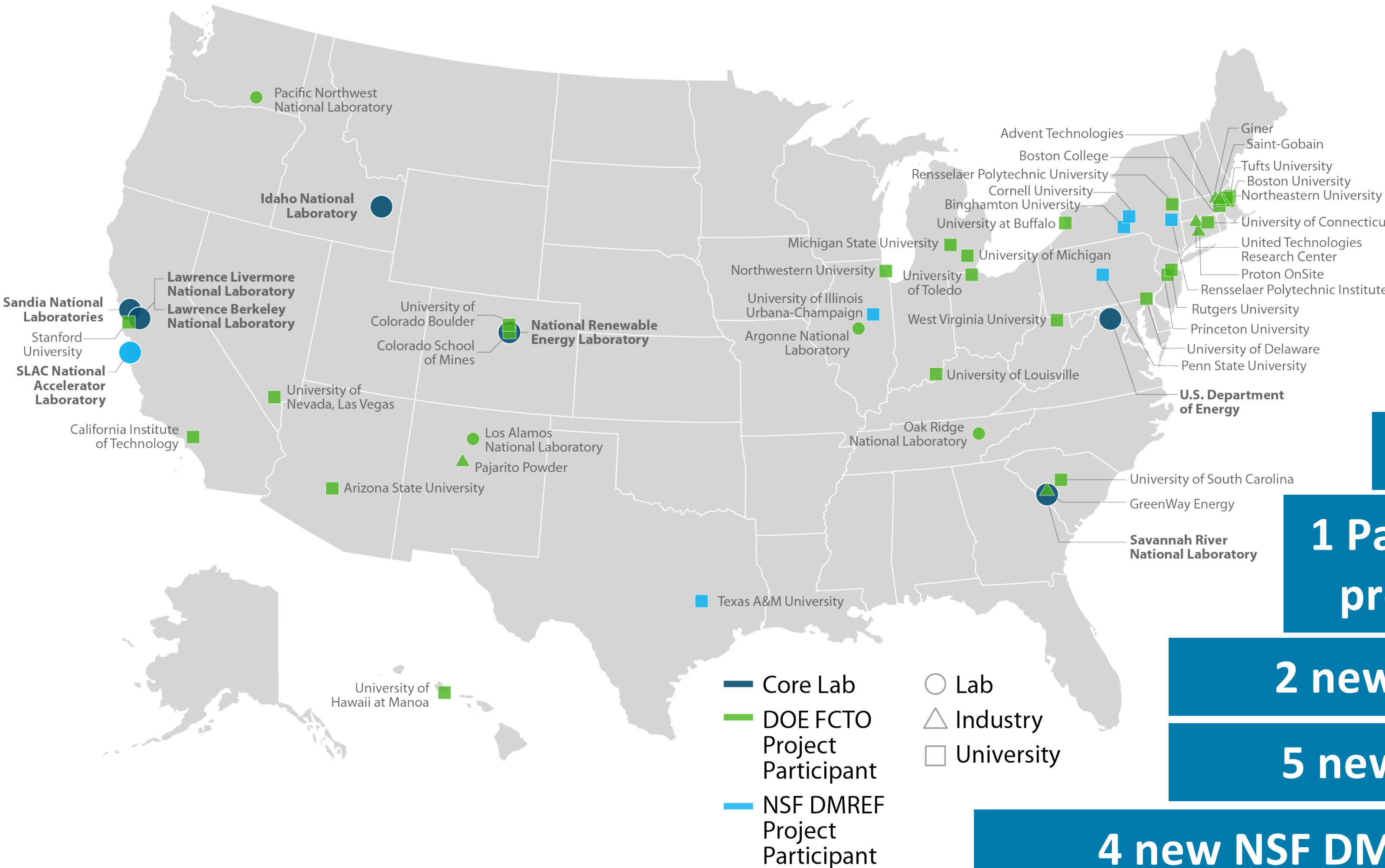
Our challenge is to develop efficient and scalable *solar*-powered reactors producing 100,000 kg H_2/day without melting houses

Backup Slides

National Innovation Ecosystem

HydroGEN Advanced Water Splitting Materials

11 Labs **7** Companies **30** Universities **2** Funding Agencies



A Community Benchmarking Workshop

2 MRS Symposia

17 papers published

85 presentations

1 Patent filed, 1 SLAC proposal accepted

2 new HTE projects

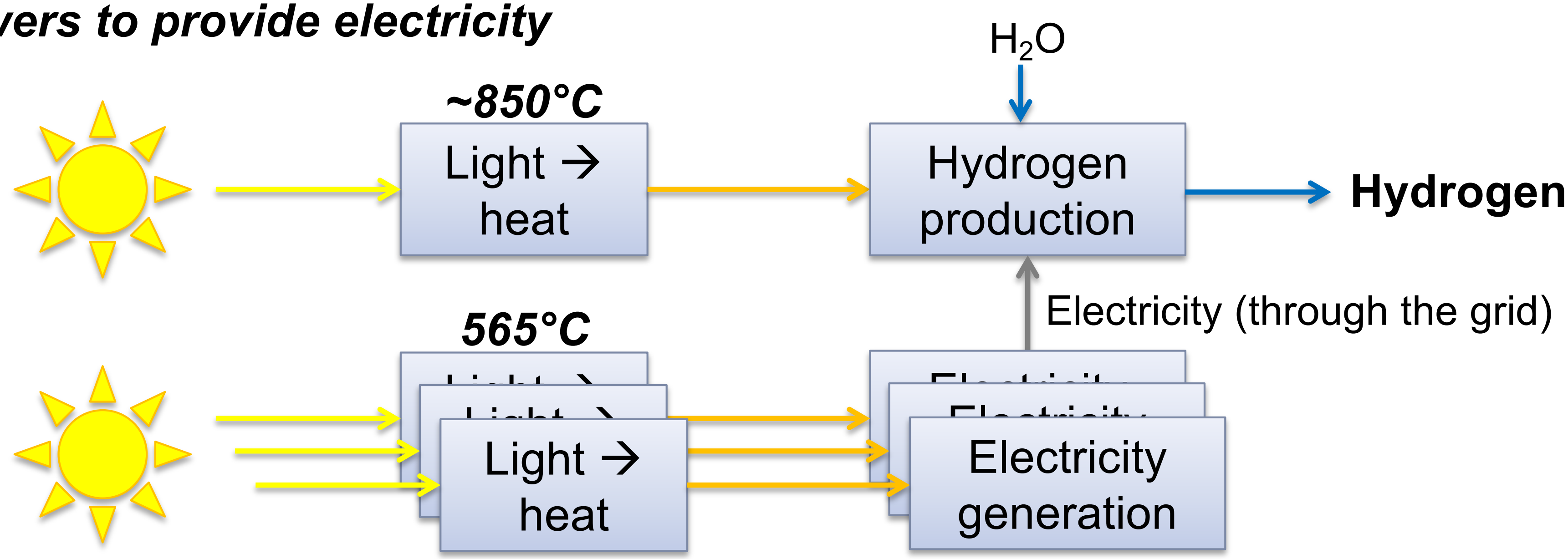
5 new Supernodes

4 new NSF DMREF projects

HydroGEN is vastly collaborative, has produced many high value products, and disseminating them to the R&D community.

Thought Experiment: High-temperature Electrolysis & CSP

Single tower dedicated to providing thermal energy, multiple additional CSP towers to provide electricity



11 additional CSP towers would be necessary to supply electricity for each tower supplying exclusively heat for H_2 production

→ No process-level integration of H_2 production and CSP

Heat and electricity provided by solar energy

https://www.energy.gov/eere/fuelcells/downloads/potential-strategies-integrating-solar-hydrogen-production-and

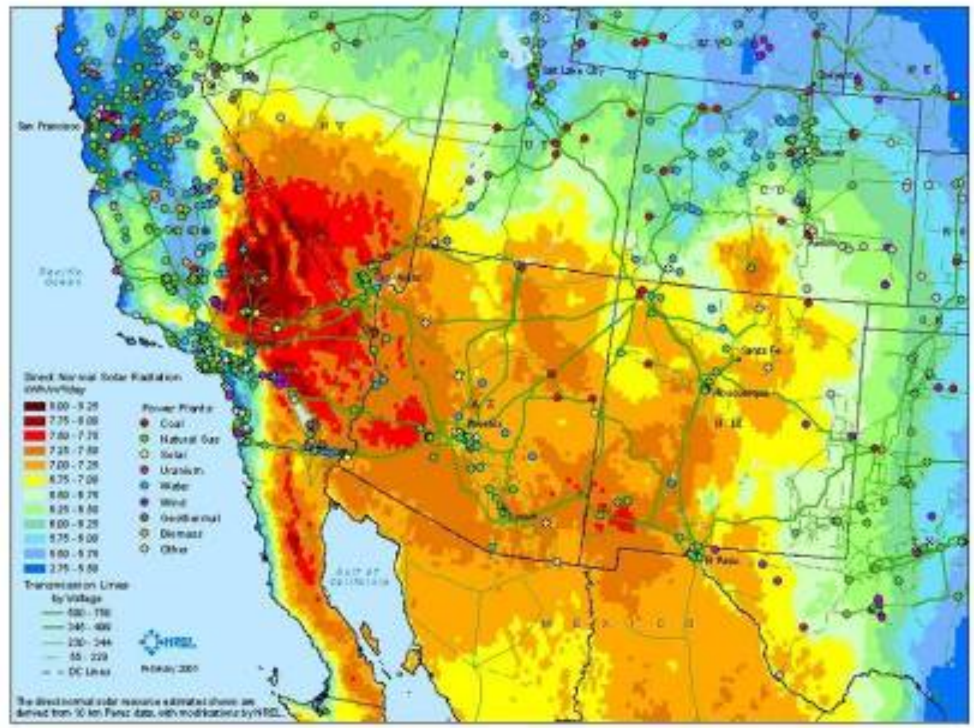
Domestic Solar Resources are Capable of Supplying Entire US Demand

- US consumes > 21 mb/d petroleum

Filters applied (Resource analysis by NREL):

- Sites > 6.75 kWh/m^2/day.
- Exclude environmentally sensitive lands, major urban areas, etc.
- Remove land with slope > 1%.
- Contiguous areas > 10 km^2.

State	Land Area (10^9 m^2)	Solar Capacity (TW)	Fuel Capacity (GW)	Fuel Capacity (mb/d)
AZ	49.9	3.37	421	5.9
CA	17.7	1.20	150	2.1
CO	5.5	0.37	46	0.7
NV	14.5	0.98	122	1.7
NM	39.3	2.65	331	4.7
TX	3.0	0.20	25	0.4
UT	9.2	0.62	78	1.1
Total	139.2	9.39	1,174	16.6



- 139×10^9 m^2 is 1.5% of total US land area.