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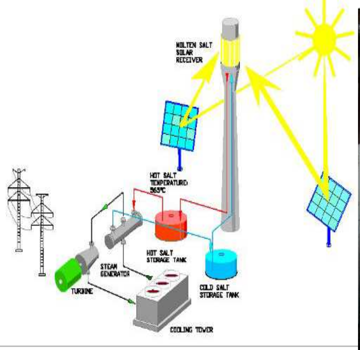
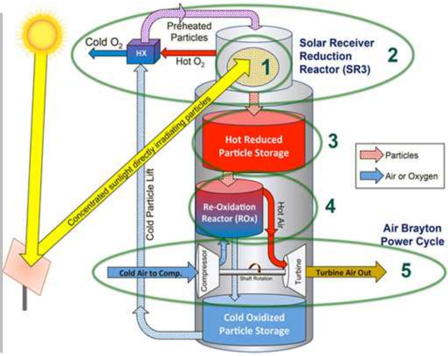




Solar-Thermal Energy Storage Options; from Phase-Change Materials to Thermochemical Systems

Eric N. Coker, Sean M. Babiniec, Andrea Ambrosini and James E. Miller

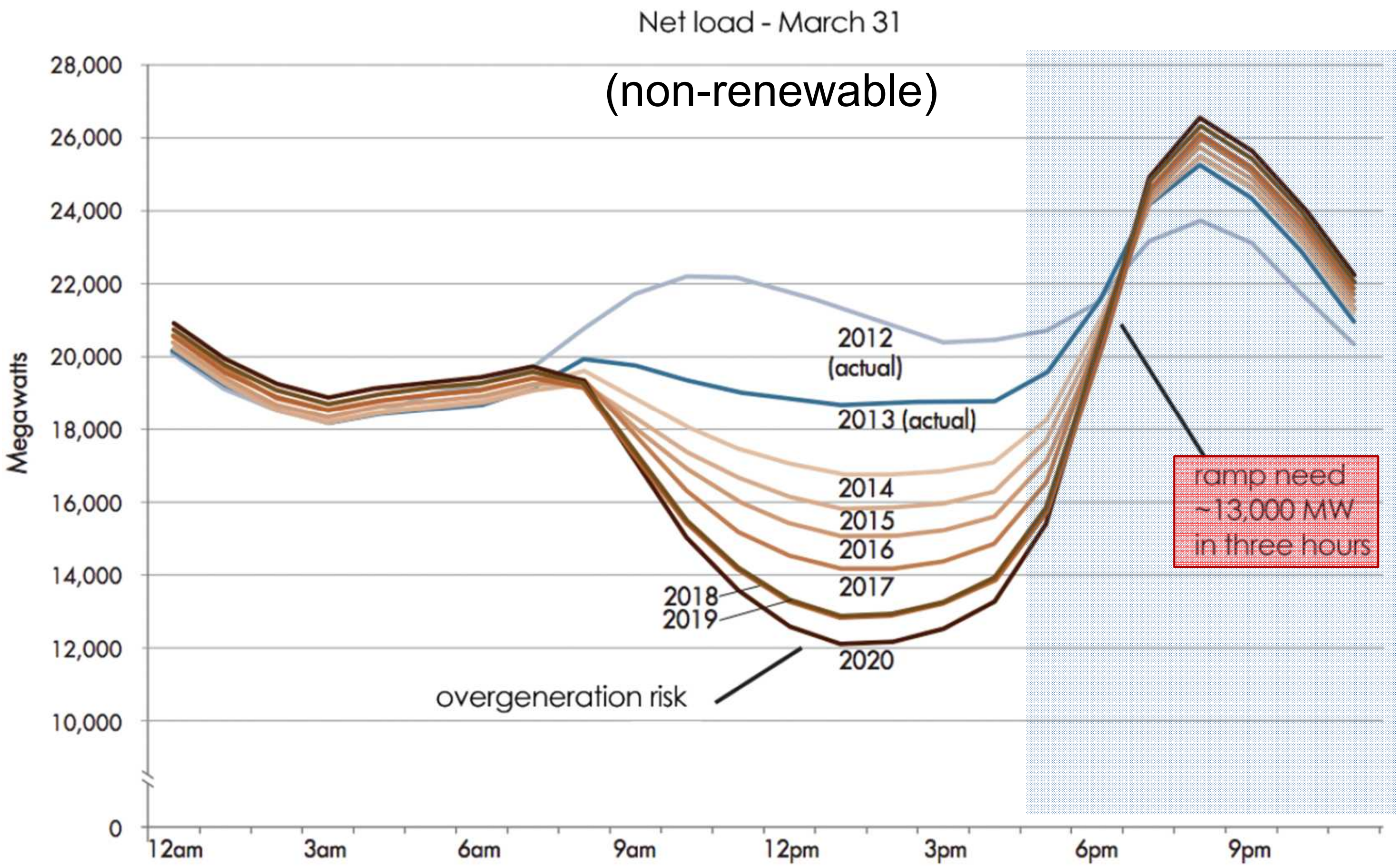
2nd Workshop on Thermal Analysis of Ceramics and Nuclear Materials,
Albuquerque, NM, May 10-12, 2016

Outline

- Need for energy storage (ES)
- Methods of ES
- Thermal ES options
- Thermochemical ES
    - Metal oxide TCES
- ES in liquid fuel form

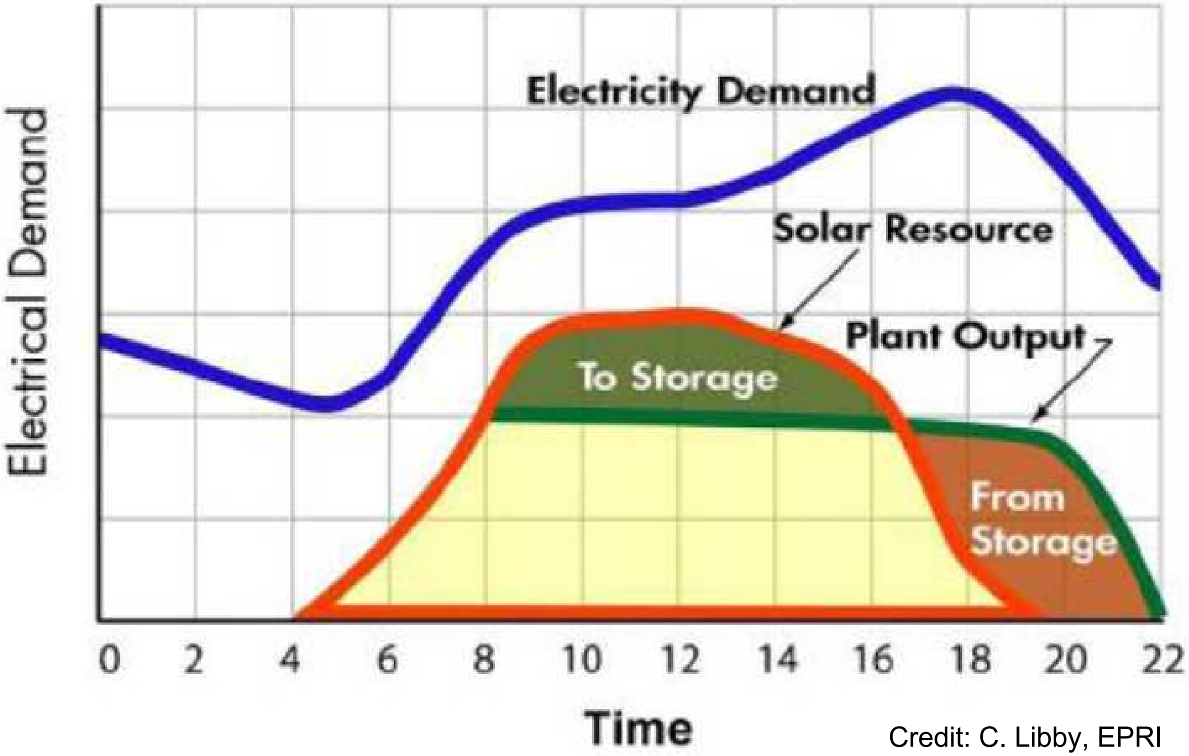
Electricity demand (California)

Credit: California Independent System Operator Corporation



Storage is critical for market penetration of solar energy into the grid

- Without storage, solar electricity is generated when least needed
- Shifting solar electricity generation to period of peak demand would have large implications on grid integration
- Decrease Levelized Cost of Electricity (LCOE) through better sizing/usage of power block

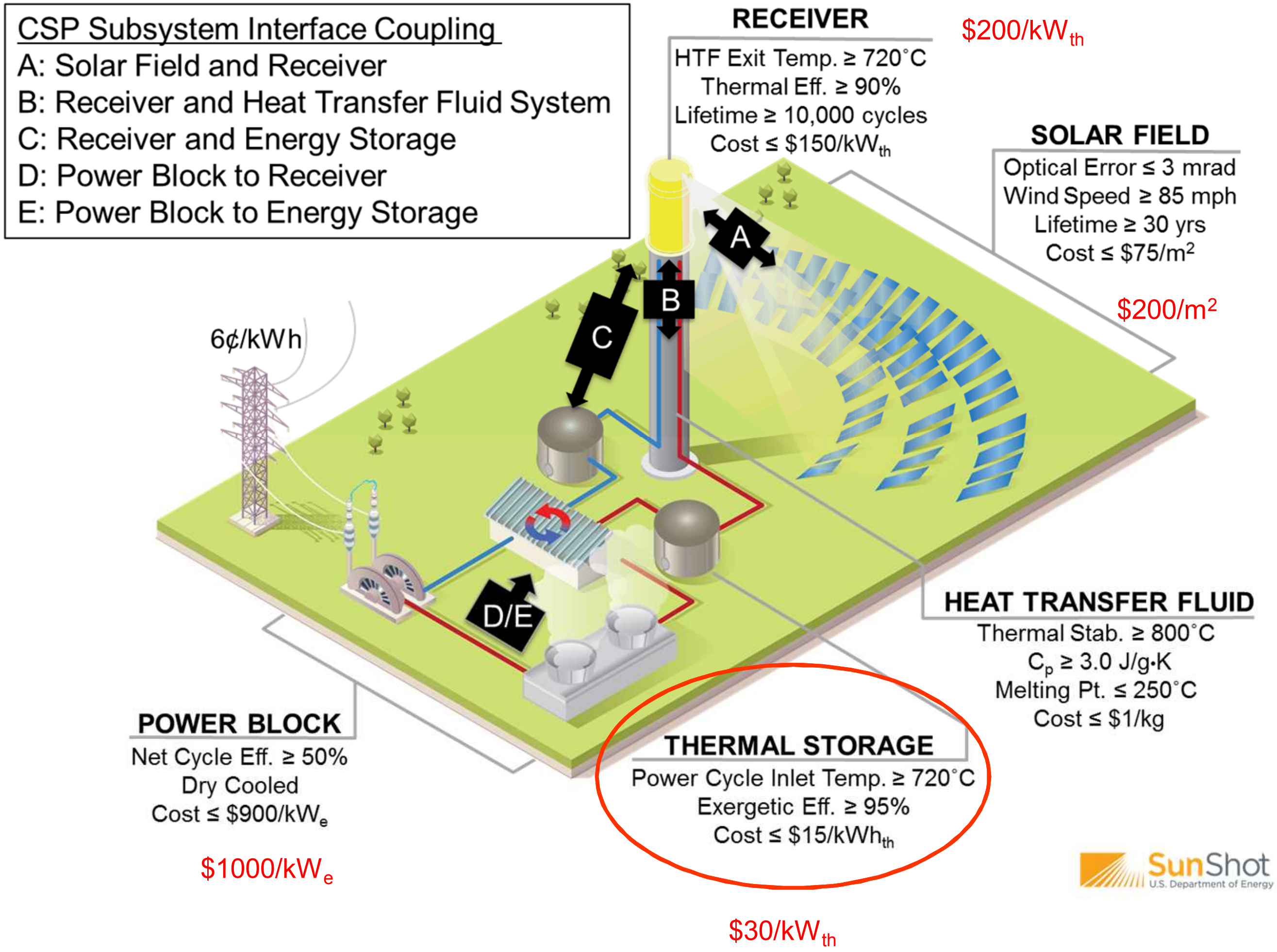


Credit: C. Libby, EPRI

Storage: Why thermal?

- Mechanical
  - Flywheels, compressed air, hydrostatic
    - ✓ High capacities (large scale)
    - × Typically suffer from low efficiencies
- Electronic
  - Li-ion batteries
    - ✓ High efficiencies
    - × Expensive materials, limited charge/discharge rates
  - Supercapacitors
    - ✓ Fast charge/discharge rates
    - × Low energy densities
- Thermal
    - ✓ High efficiency
    - × Temperatures high to support new power cycles (~ 1200 °C)
      - ❖ ***Materials development crucial to feasibility of thermal storage at such temperatures***

Key CSP Technology Interfaces and Cost Targets to Achieve SunShot Goals



CSP Subsystem Interface Coupling
A: Solar Field and Receiver
B: Receiver and Heat Transfer Fluid System
C: Receiver and Energy Storage
D: Power Block to Receiver
E: Power Block to Energy Storage

RECEIVER
HTF Exit Temp. ≥ 720˚C
Thermal Eff. ≥ 90%
Lifetime ≥ 10,000 cycles
Cost ≤ $150/kW$_{th}$

$200/kW$_{th}$

SOLAR FIELD
Optical Error ≤ 3 mrad
Wind Speed ≥ 85 mph
Lifetime ≥ 30 yrs
Cost ≤ $75/m^2

$200/m^2

HEAT TRANSFER FLUID
Thermal Stab. ≥ 800˚C
C_p ≥ 3.0 J/g·K
Melting Pt. ≤ 250˚C
Cost ≤ $1/kg

POWER BLOCK
Net Cycle Eff. ≥ 50%
Dry Cooled
Cost ≤ $900/kW$_e$

$1000/kW$_e$

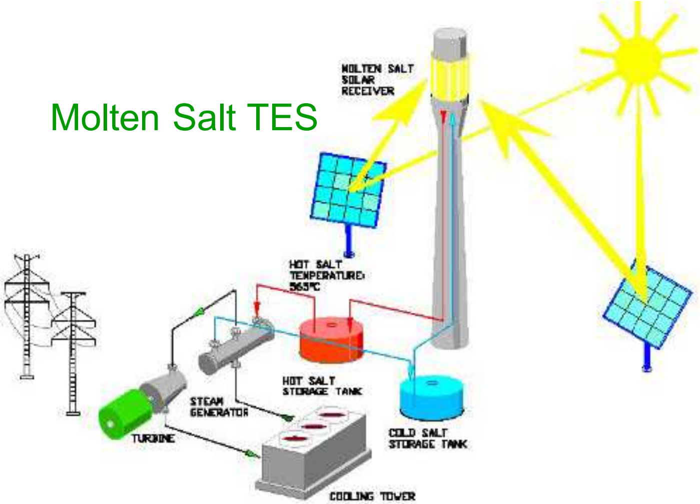
THERMAL STORAGE
Power Cycle Inlet Temp. ≥ 720˚C
Exergetic Eff. ≥ 95%
Cost ≤ $15/kWh$_{th}$

$30/kW$_{th}$

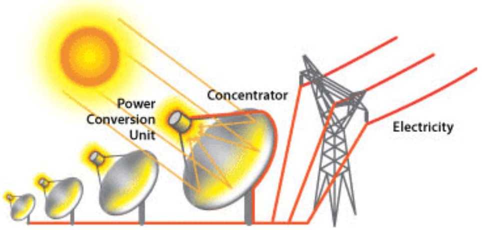
Solar energy used to heat storage media, drive thermal engine

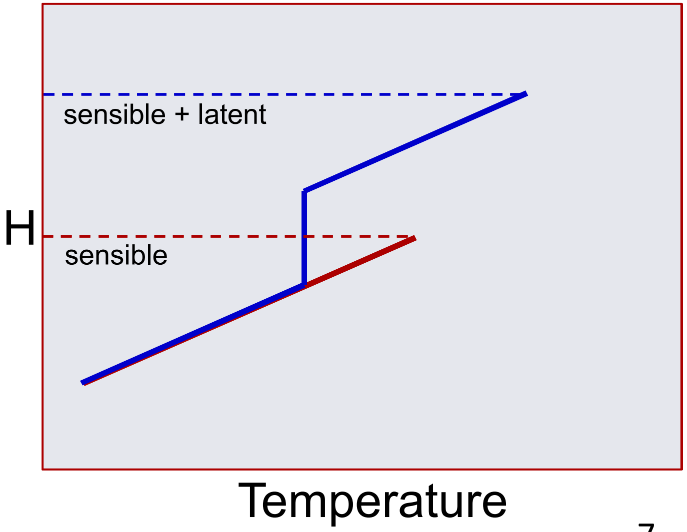
Thermal Energy Storage

- Sensible TES: Molten Salt Systems
  - Widely adopted
  - Temperature limited to < 650 °C
  - Low energy storage densities



- Sensible + latent heat TES: Metal Alloys
  - Eutectic mixtures
  - Temperatures up to ~ 850 °C
  - $\Delta H_f \sim 400\ \mathrm{kJ\ kg^{-1}}$ for CuMgSi ternary alloy
  - Dish Stirling application

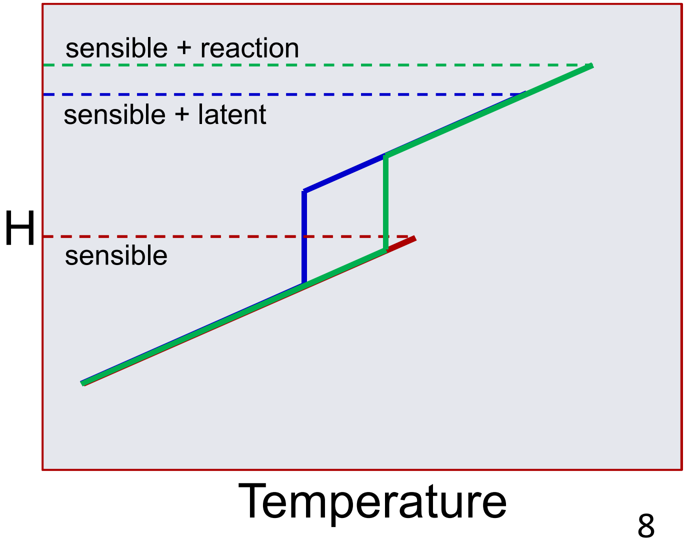




Thermal Energy Storage

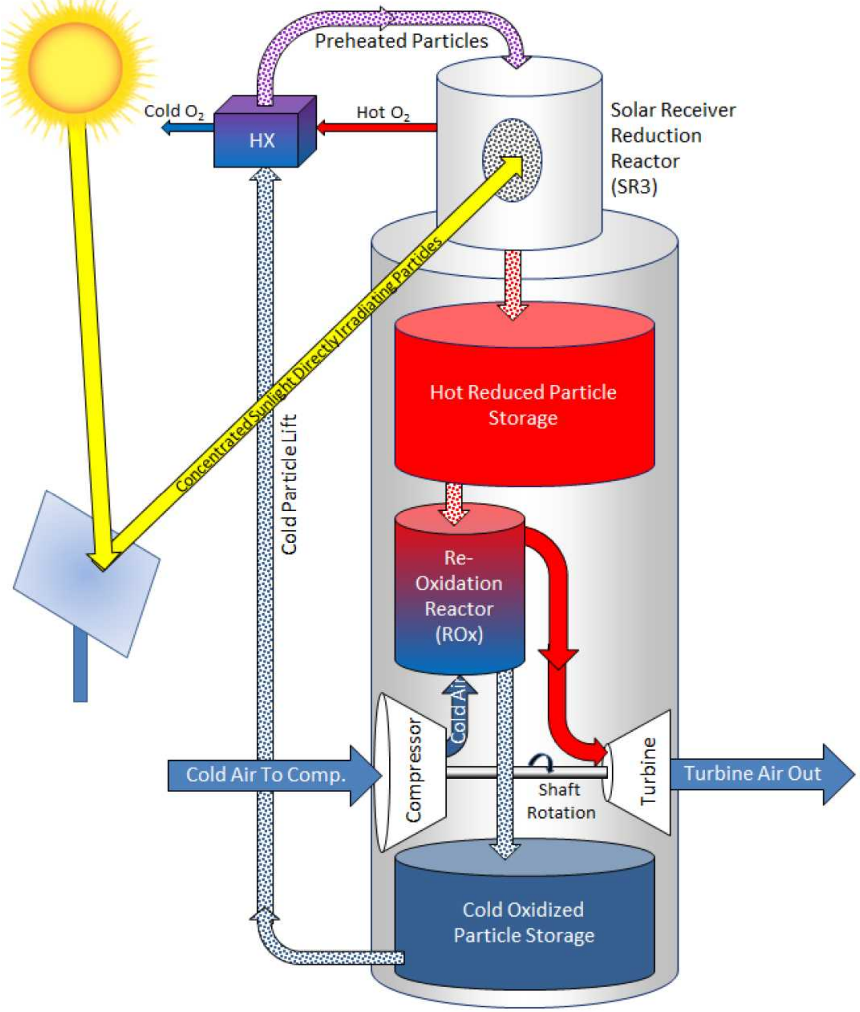
- Sensible + chemical-reaction heat TES: Metal oxide systems
  - Temperatures above 1000 °C achievable
  - $\Delta H_{reaction}$ above 800 kJ kg^{-1} possible

- Thermal Energy to Fuels
  - Multi-step thermochemical cycle; T > 1000 °C
  - “Re-energize” CO_2 and H_2O
  - Liquid fuels infrastructure already in place



Metal Oxide Based Thermal Energy Storage

- Redox particle-based systems offer advantages
  - High storage densities *via* (sensible + reaction) enthalpy
    - Thermochemical energy storage (TCES)
  - Cycle not limited by low decomposition temperatures
  - Direct irradiation of thermal storage media
  - Re-oxidation reaction directly off compressor outlet, favorably shifting thermodynamics



Materials requirements driven by Air-Brayton operating parameters

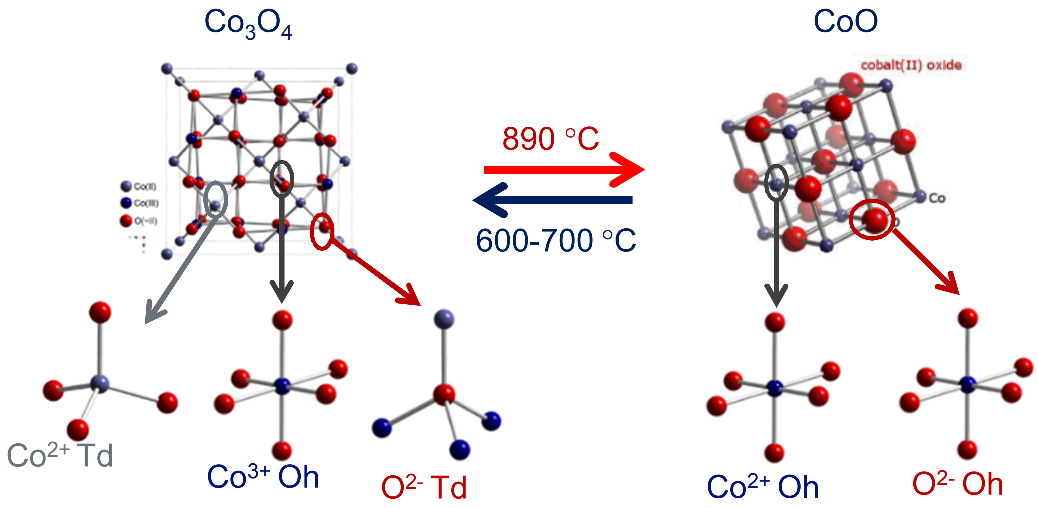
- High-efficiency Air-Brayton turbines are designed to operate at ~1200 °C
- Such temperatures are problematic for existing oxide TCES materials

- State-of-the-art cobalt oxide redox couple:

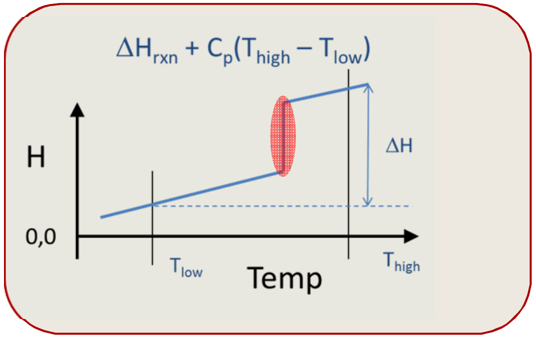
$2Co_3O_4 + \Delta \leftrightarrow 6CoO + O_{2(g)} \quad \Delta H_{theoretical} = 844\ \text{kJ kg}^{-1}\ Co_3O_4$

  - High theoretical ΔH occurring at one discrete transition
  - Reduction/oxidation in air occurs near 885 °C
  - Kinetics are slow at low temperatures
  - Cobalt is expensive

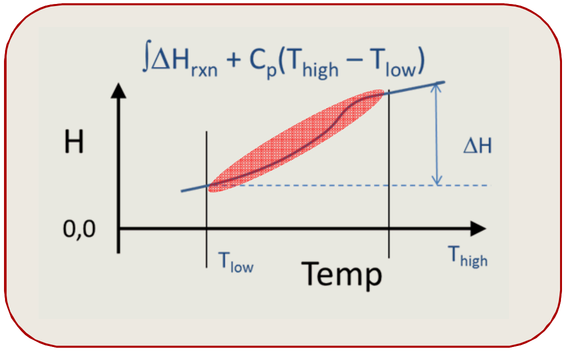
Cobalt oxide *vs.* Perovskites (ABO_3)

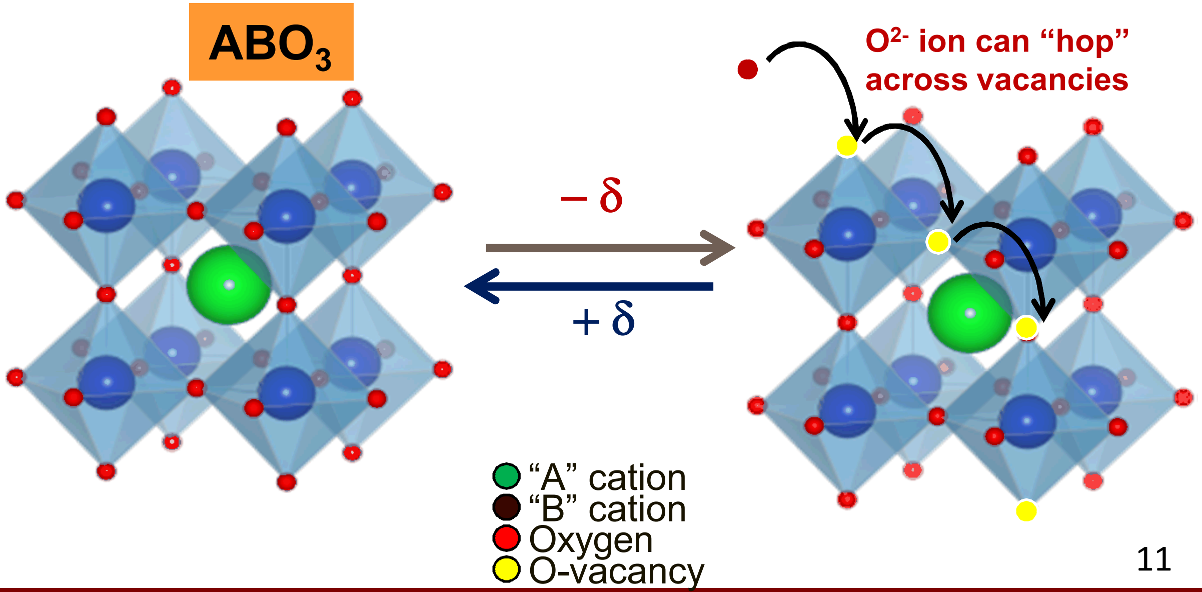


- Energetic phase change
- No O^{2-} transport
- Oxidation exotherm typically recovered at lower temperature than reduction



- No phase change occurs
- Vacancies facilitate O^{2-} transport
- Redox activity continuous over variety of T and pO_2



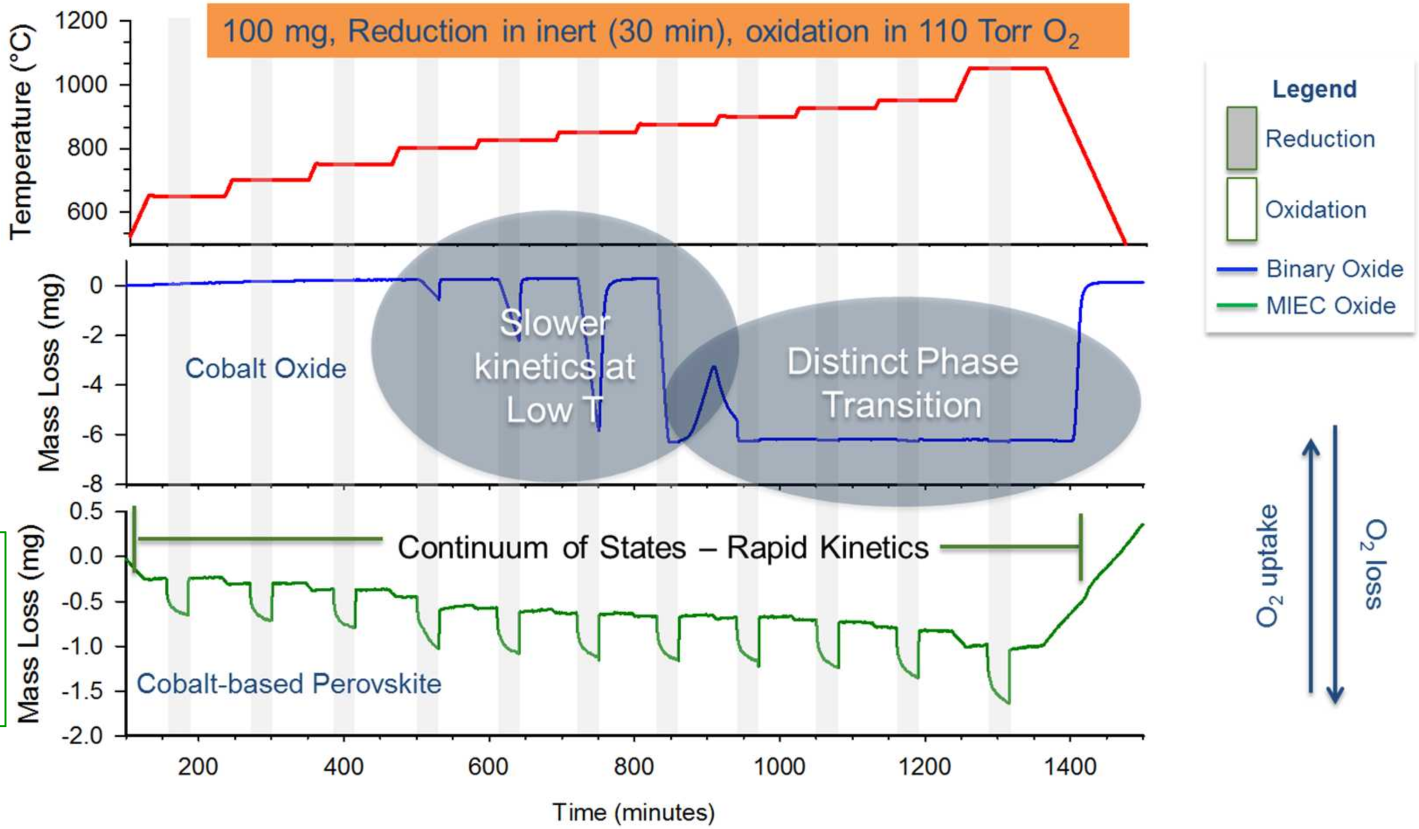


Perovskites offer a solution to increasing turbine inlet temperatures to ≥ 1200 °C

- Continuous reduction behavior as opposed to discrete reaction

Co_3O_4
↓
$3CoO + ½\ O_2$

ABO_3
↓
$ABO_{3-\delta} + \delta/2\ O_2$



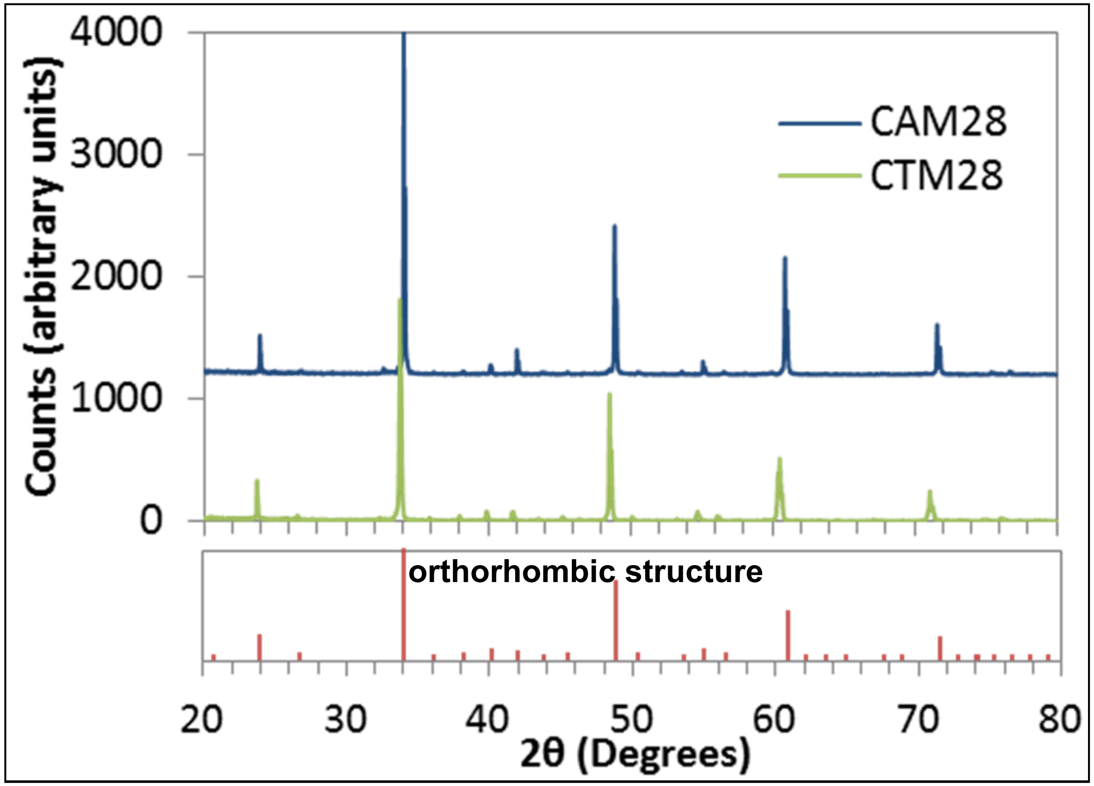
- Perovskites need to be engineered to increase capacity (mass loss) and reaction enthalpy

Perovskite compositions

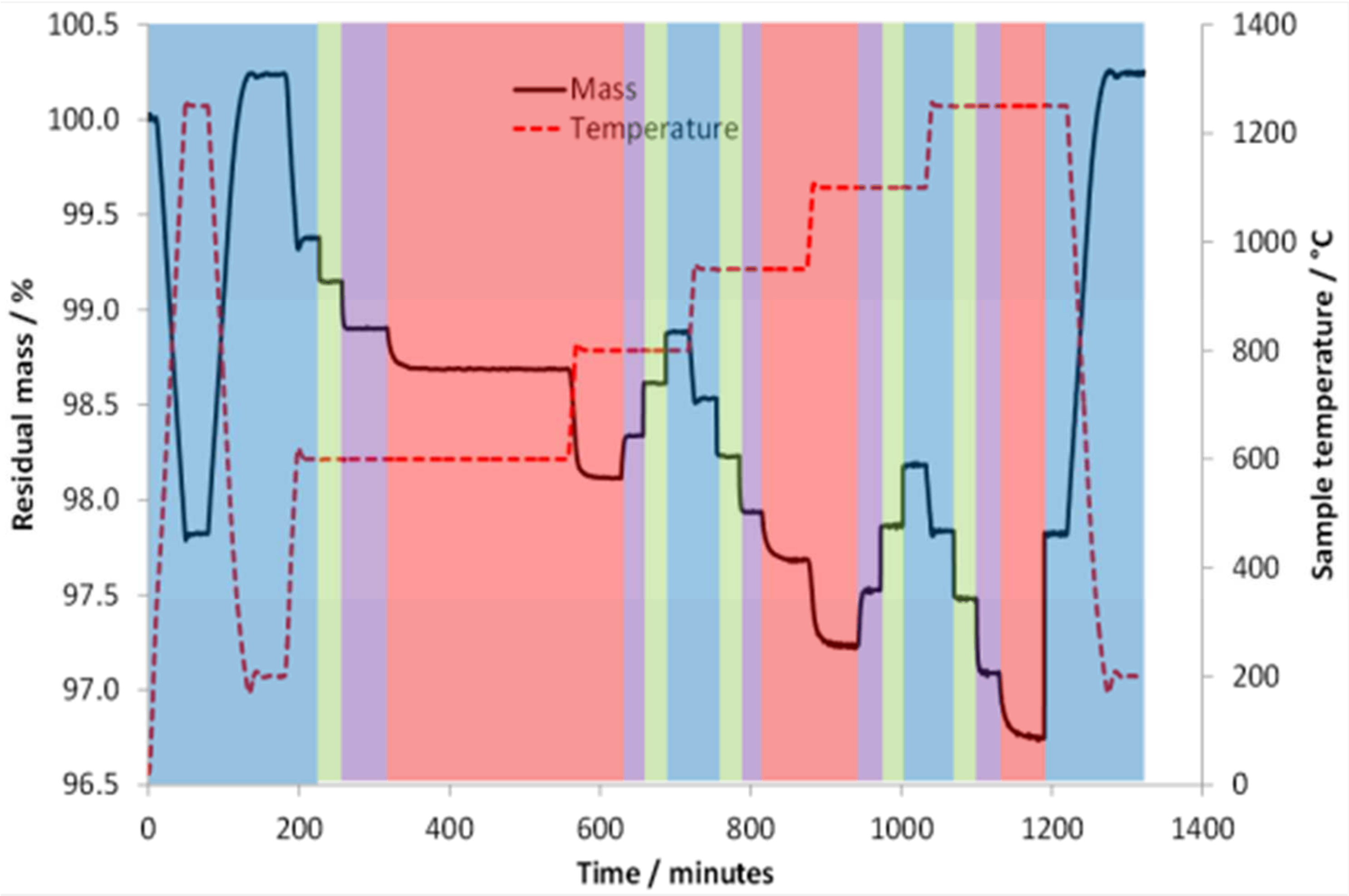
- $ABO_3 + \Delta \leftrightarrow ABO_{3-\delta} + \delta/2\ O_{2(g)}$
  - Gas species dominates entropy term (largest # degrees-of-freedom)
- At equilibrium (onset of reduction) $\Delta G_{red} = 0 = \Delta H_{red} - T\,\Delta S_{red}$
  - A change in reduction enthalpy necessitates a change in reduction temperature
- Previous studies focused on $La_xSr_{1-x}Co_yM_{1-y}O_{3-\delta}$, with M = Fe,Mn
  - High redox capacity (δ), but at low temperature (low reaction enthalpy)
- New materials aim to improve cost, reaction enthalpy:
  - Cost-effective, lightweight cations desired
  - A-site: Ca, B-site: Mn, Ti, Al

Synthesis and phase characterization

- Materials synthesized using an aqueous (Pechini) method
- X-ray diffraction used for phase identification
- Compositions:
  - CAM28 ($CaAl_{0.2}Mn_{0.8}O_{3-\delta}$)
  - CTM28 ($CaTi_{0.2}Mn_{0.8}O_{3-\delta}$)



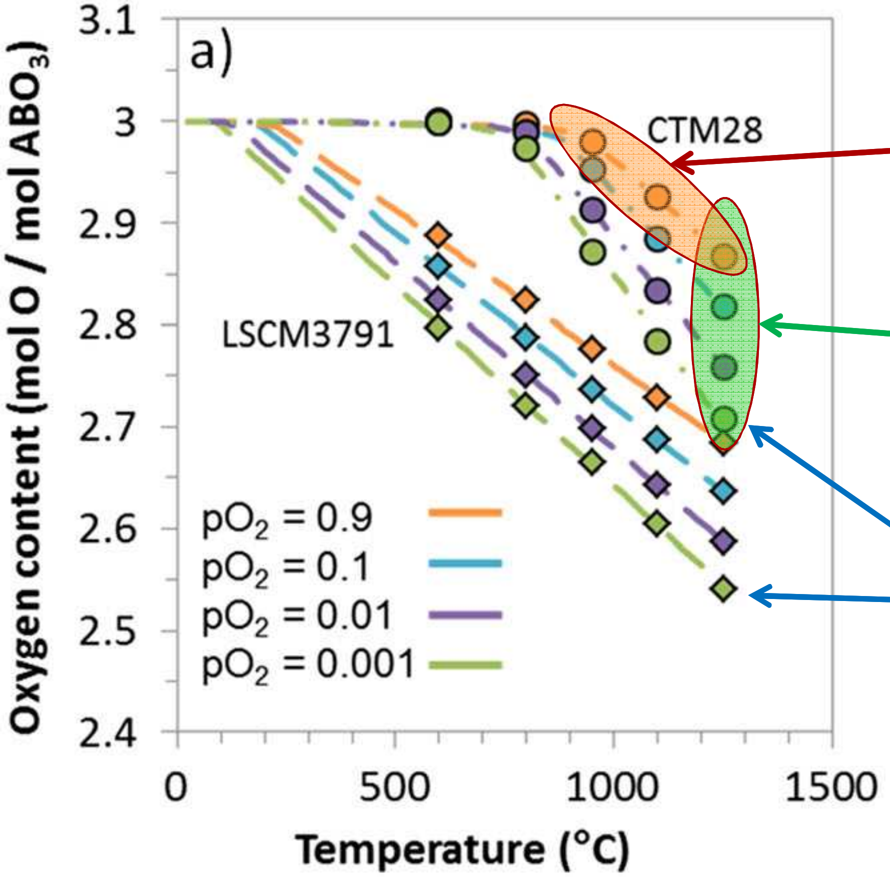
Thermogravimetric data acquired over range of temperatures and oxygen partial pressures



Oxygen pressure / atm

- pO_2= 0.9
- pO_2= 0.1
- pO_2 = 0.01
- pO_2 = 0.001

Equilibrium data taken from TGA experiments



Large changes in oxygen stoichiometry by changing temperature ….

…. or by changing pO_2.

δ_{max}, observed at pO_2 = 0.001 atm, T = 1250 °C

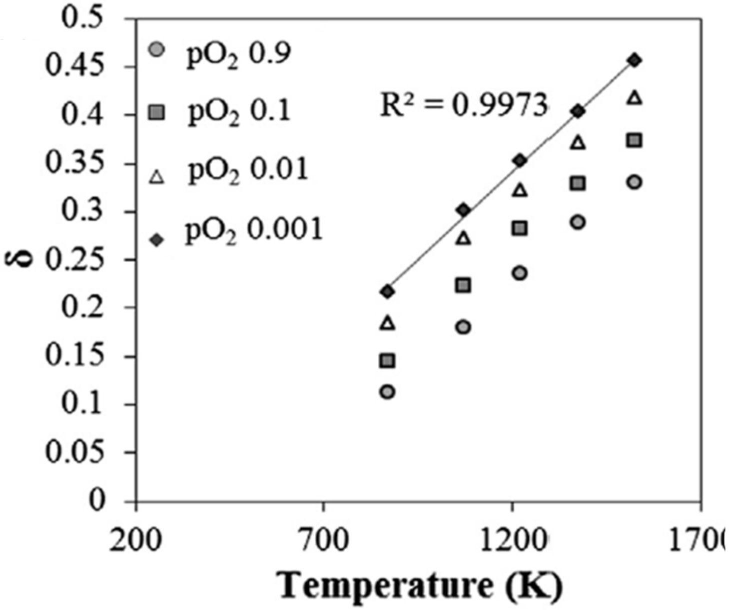
Thermodynamic parameters extracted from this data by van ’t Hoff approach

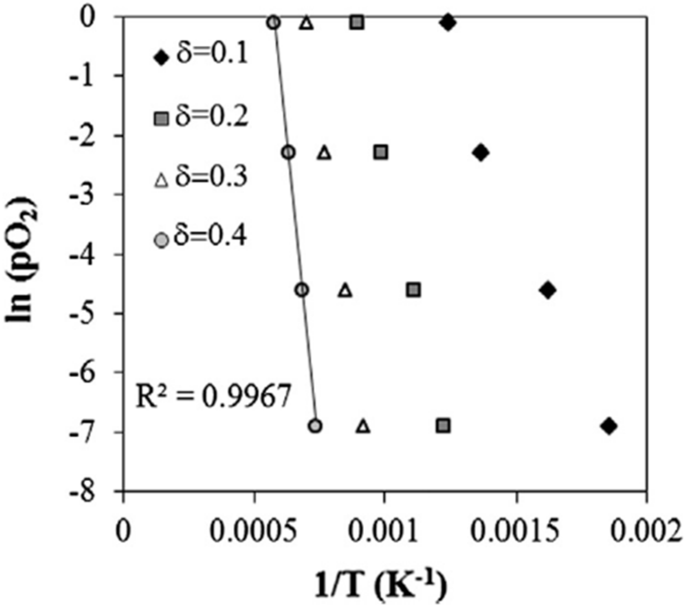
Equilibrium TGA data used to estimate thermodynamic parameters

- **van ’t Hoff approach**

  $K = \frac{[ABO_{3-\delta}]^{1/\delta}\, pO_2^{1/2}}{[ABO_3]^{1/\delta}}$, assume ratio of solid activities is ≈unity

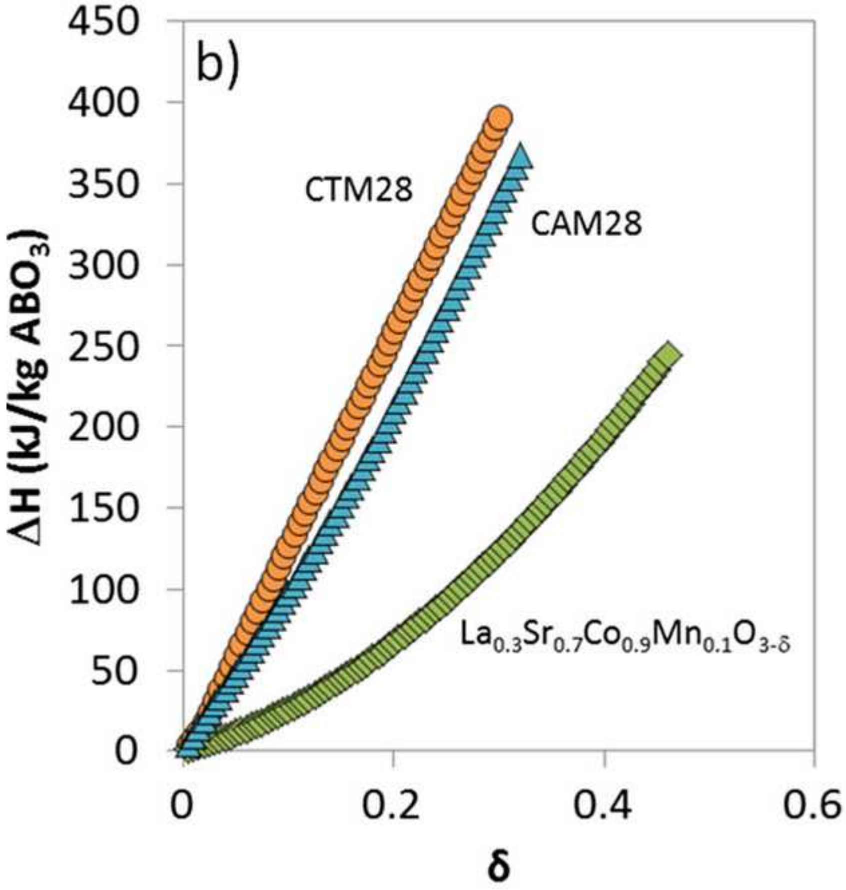
  - $\ln(pO_2) = 2\frac{-\Delta G_{rxn}}{RT} = 2\left(\frac{1}{T}\cdot\frac{-\Delta H_{rxn}}{R} + \frac{\Delta S_{rxn}}{R}\right)$
    - Enthalpy determined by slope, entropy by intercept for each value of δ





Enthalpies from van ’t Hoff are given for a specific oxygen non-stoichiometry

- Describe energy to remove a mole of O_2 at a specific δ

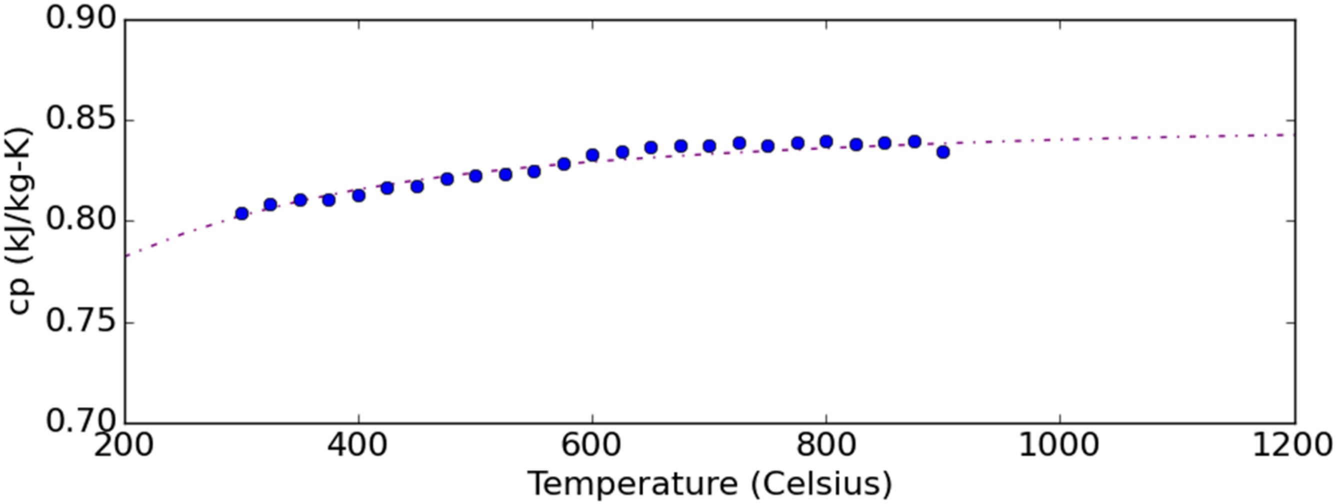


Material	Reduction onset (°C)	Maximum δ	Enthalpy at δ_{max} (kJ/kg)
LSCM3791	352	0.461	240 [a]
CTM28	901	0.293	390 [b]
CAM28	759	0.322	370 [b]

[a] S.M. Babiniec, et al., *Solar Energy*, **118**, 451–9, (2015).
[b] S.M. Babiniec, et al., *Int. J. Energy Res.*, **40**, 280–4, (2016).

Heat capacity as a function of temperature is needed to calculate sensible heat

- Einstein heat capacity model used to fit data for CAM28, converted to polynomial fit for ease of integration
  - CTM28 expected to be similar due to same structure and similar molecular weight



$$c_p = a_5 * T^5 + a_4 * T^4 + a_3 * T^3 + a_2 * T^2 + a_1 * T + a_0$$

	a_5	a_4	a_3	a_2	a_1	a_0
CAM28	8.066E-18	-7.169E-14	2.455E-10	-4.070E-7	3.346E-4	7.329E-1

$\Delta H_{sens} = \int_{T1}^{T2} C_p(T)dT$ = 871 kJ/kg between 200 and 1250 °C

$$\Delta H_{total} = \Delta H_{sens} + \Delta H_{reaction} = 871 + 370 = 1241\ kJ/kg$$

TCES Summary & Conclusions

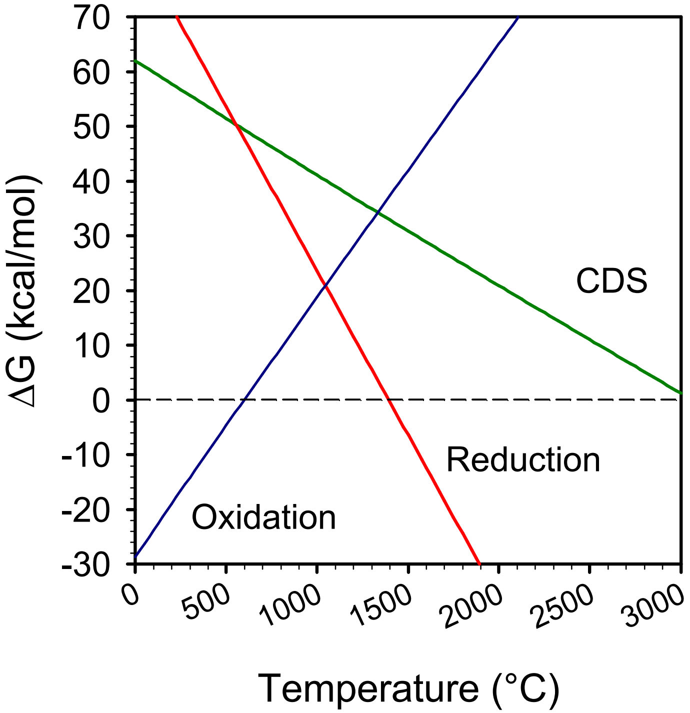
- CAM28 and CTM28 show high storage enthalpy
  - Sensible + reaction enthalpy approx. 1200 kJ/kg
  - Reaction enthalpy of CTM28 & CAM28 60% greater than LSCM
    - Increase in reduction temperature → larger reaction enthalpy
    - Molecular mass of CTM28 and CAM28 ~ 35% lower than LSCM
  - Reaction enthalpy extraction up to 1250 °C possible
    - Applicable to high-efficiency Air Brayton cycle
  - Earth-abundant components brings materials cost down

PART 2

Thermochemical Production of Liquid Fuels

- Thermal Energy used to drive multi-step thermochemical cycle
  - Convert CO_2 and H_2O to liquid fuel
  - Syngas intermediate
  - "Solar Fuels"

$$2CO_2 + \Delta \rightarrow 2CO + O_2 \quad \text{(CDS)}$$



Single-step CDS: > 3000 °C
Two-step cycle achievable < 1500 °C

Re-energizing CO_2 and H_2O

Focus on the following critical conversions:

$4H_2O + \text{energy} \rightarrow 4H_2 + 2O_2$ (water splitting)
$2CO_2 + \text{energy} \rightarrow 2CO + O_2$ (carbon dioxide splitting)

$2CO_2 + 4H_2O + \text{energy} \rightarrow 2CO + 4H_2 + 3O_2$

Capitalize on decades of Synfuel technology, *e.g.*,

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$$

WS and CDS are linked by the Water Gas Shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

We are only <u>required</u> to carry out *one* reaction - WS or CDS

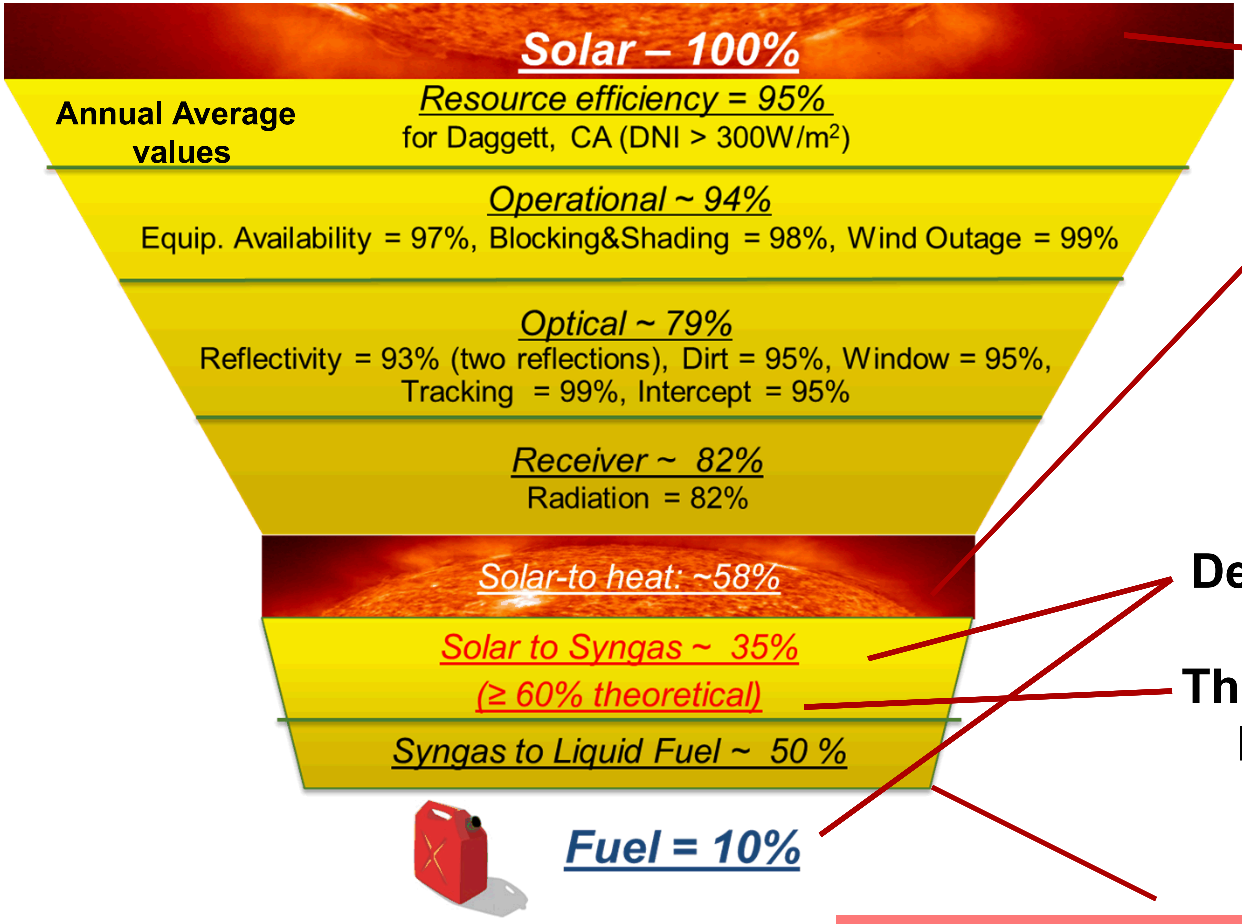
Solar Fuels Impact:

Meeting a significant fraction of transportation fuel demand with solar fuels is certainly plausible!

- ***High solar to fuel efficiency (>10% Annual Average) is absolutely required.***
  - Cost
  - Scale (land, materials of construction (embedded energy))
- *Water, CO_2 are not limiting –*
  - Water consumption/cost relatively low (water rights?)
  - High impact opportunity for CO_2 utilization – long term requires air capture.
- *Consistent with other human activities occurring over multiple decades.*

E.B. Stechel and J.E. Miller “Re-energizing CO_2 to fuels with the sun: Issues of efficiency, scale, and economics” Journal of CO_2 Utilization, 1 (2013) 28–36.

Solar Thermal Heat In, Fuel Out



Solar – 100%

Annual Average values

Resource efficiency = 95%
for Daggett, CA (DNI > $300 W/m^2$)

Operational ~ 94%
Equip. Availability = 97%, Blocking&Shading = 98%, Wind Outage = 99%

Optical ~ 79%
Reflectivity = 93% (two reflections), Dirt = 95%, Window = 95%, Tracking = 99%, Intercept = 95%

Receiver ~ 82%
Radiation = 82%

Solar-to heat: ~58%

Solar to Syngas ~ 35%
(≥ 60% theoretical)

Syngas to Liquid Fuel ~ 50 %

Fuel = 10%

Use entire solar spectrum

Convert heat directly to chemical energy. Avoid conversion to mechanical or electrical work.

Desired outcome defines minimum efficiency. Theoretical value must be higher to account for losses.

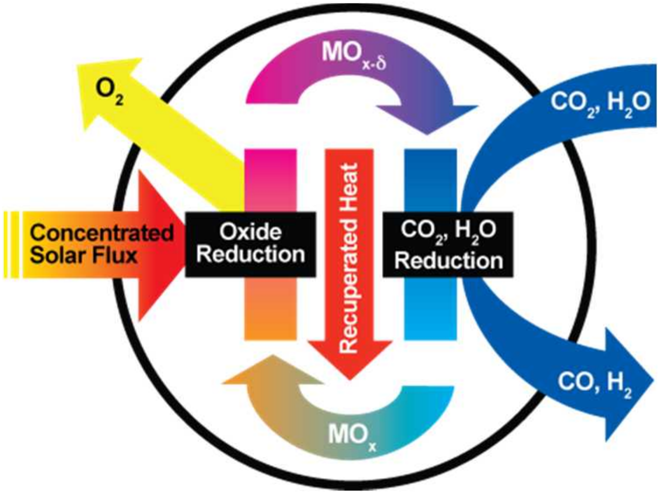
Capitalize on decades of Synfuel technology, e.g.

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$$

Siegel, Miller, Ermanoski, Diver, Stechel, Ind. Eng. Chem. Res., 2013, 52 , 3276.

A Simple Concept: Heat in, Fuel Out

1) $1/\delta\ MO_x \rightarrow\ 1/\delta\ MO_{(x-\delta)} + ½\ O_2$



2) $1/\delta\ MO_{(x-\delta)} + CO_2 \rightarrow 1/\delta\ MO_x + CO$

---

3) $CO_2 \rightarrow CO + ½\ O_2$

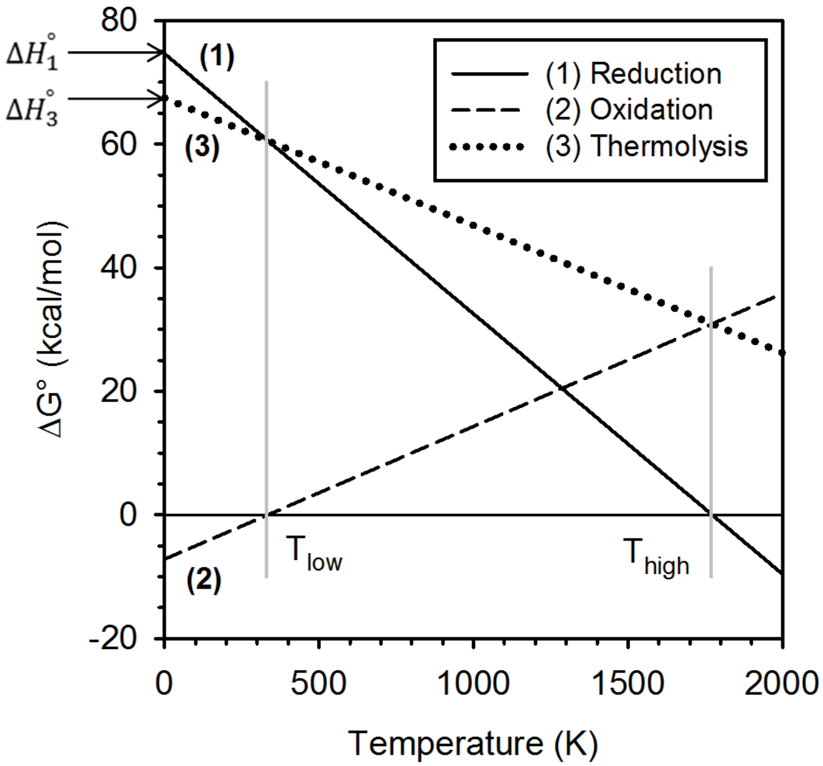
A thermochemical cycle is essentially an engine that converts heat into work in the form of stored chemical energy. ***Efficiency gains are possible as initial conversion to mechanical work and electricity are avoided.***

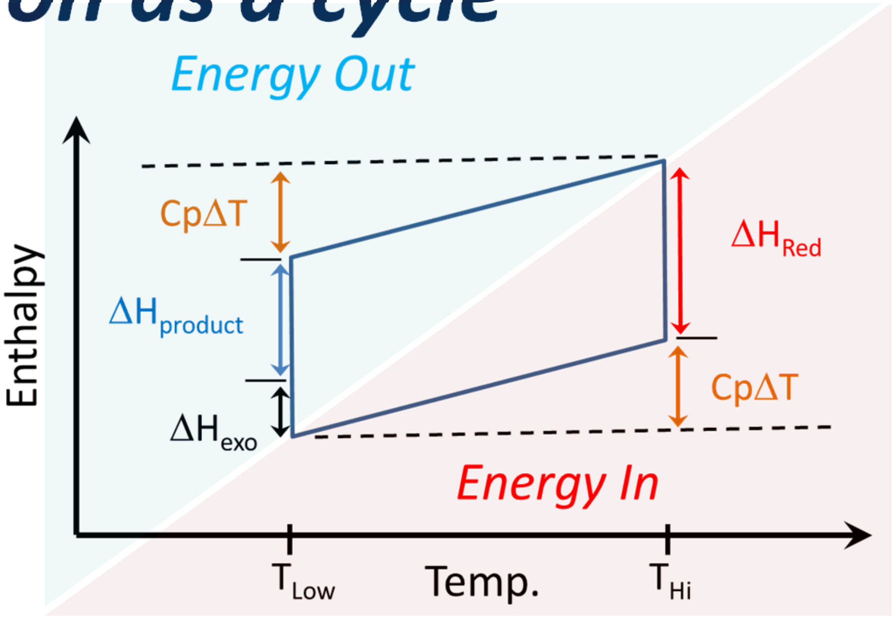
Of interest here are two-step, metal oxide-based processes.

Divide an unfavorable endothermic reaction ($H_2O \rightarrow H_2 + ½\ O_2$, or $CO_2 \rightarrow CO + ½\ O_2$) into two thermodynamically favorable reactions.

The thermodynamic cost implementing a reaction as a cycle

$$\Delta H_{\text{red endotherm}} - \Delta H_{\text{oxid exotherm}} = \Delta H_{\text{fuel}}$$



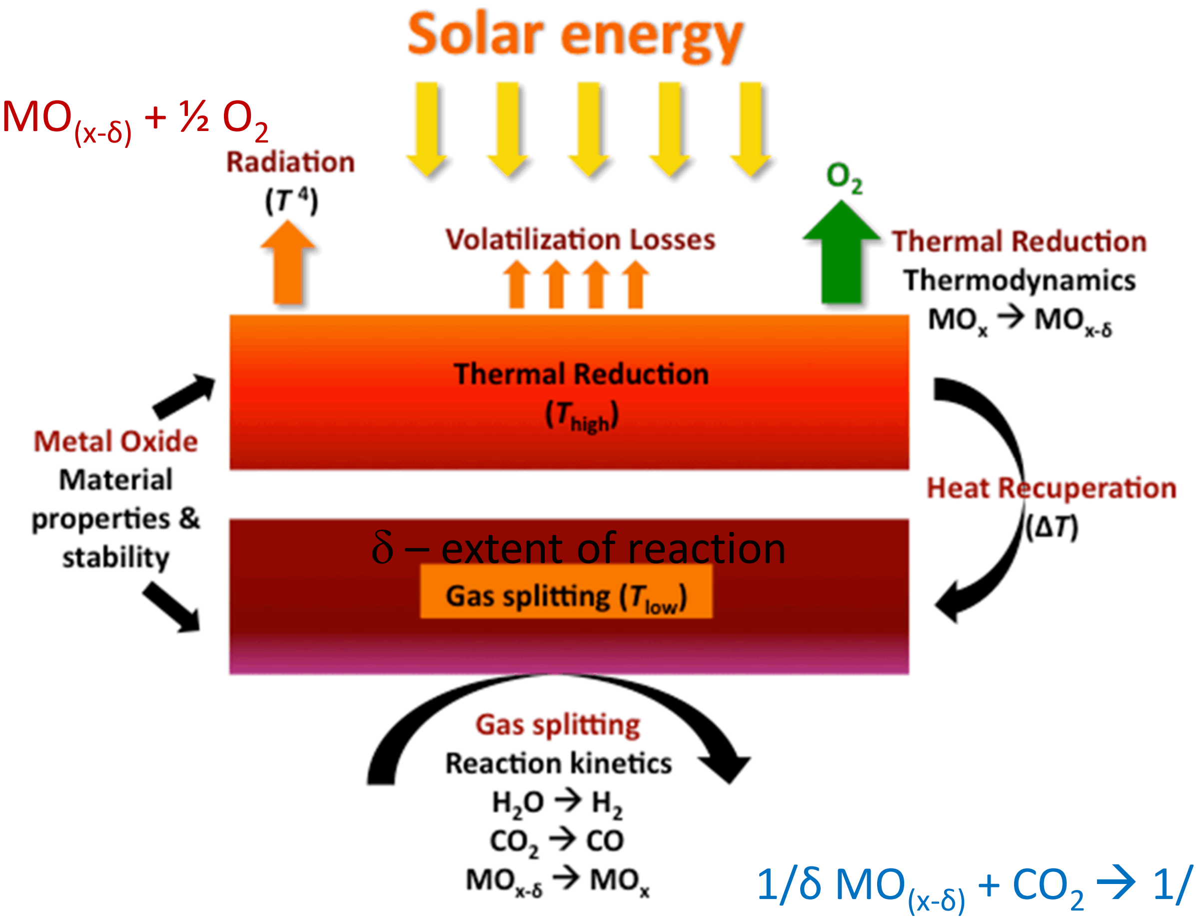


$$\frac{\Delta H_{\text{fuel product}}}{\Delta H_{red} + C_p \Delta T_{net}} = \text{Max. thermal eff.}$$

- *Each reaction favorable at a different temperature*
- *Some heat will be rejected as an exotherm*
- *Temperature gap and exotherm are a function of the active material*

Materials Challenges

$1/\delta\ MO_x \rightarrow 1/\delta\ MO_{(x-\delta)} + ½\ O_2$

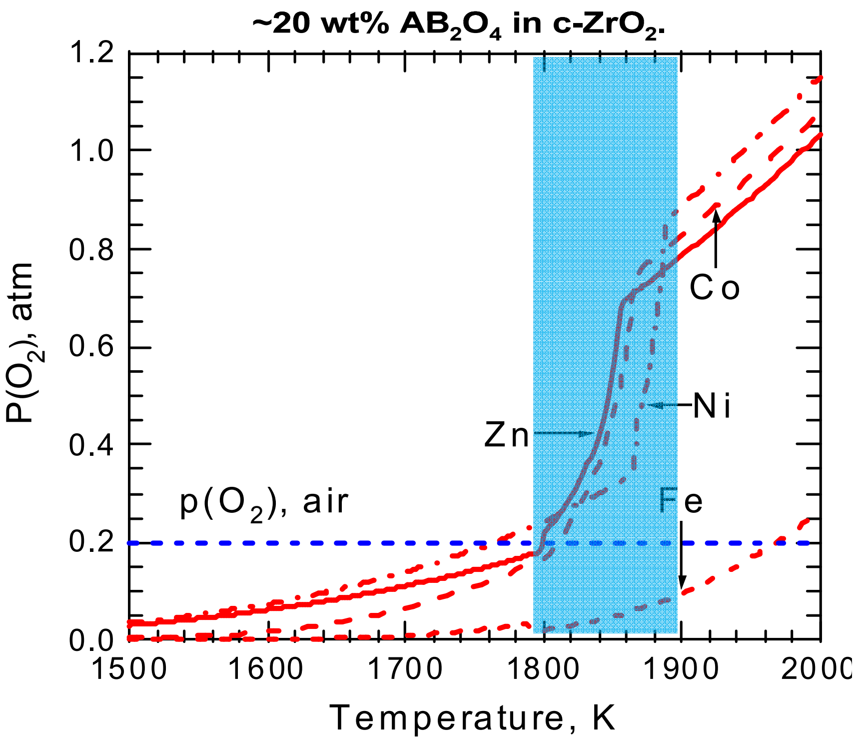


δ – extent of reaction

$1/\delta\ MO_{(x-\delta)} + CO_2 \rightarrow 1/\delta\ MO_x + CO$

Metal Oxide TC Begins with Ferrites

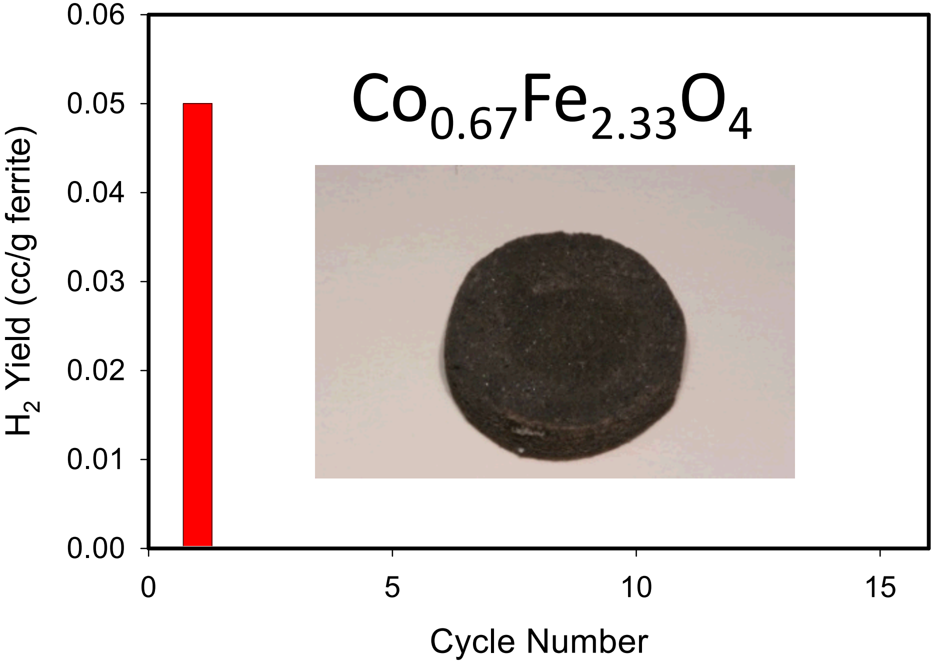
Ferrite metal oxide cycle (Nakamura 1977).



Favorable temperature range (thermodynamics) can be manipulated via metal substitutions in Fe_3O_4.

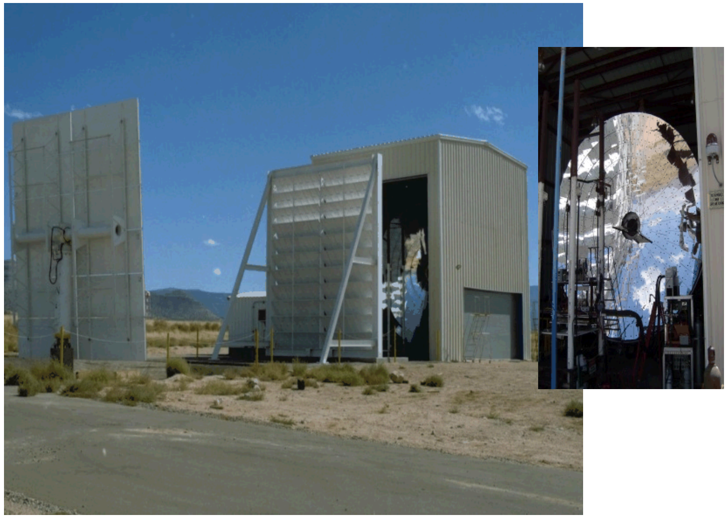
Partial conversion now possible.

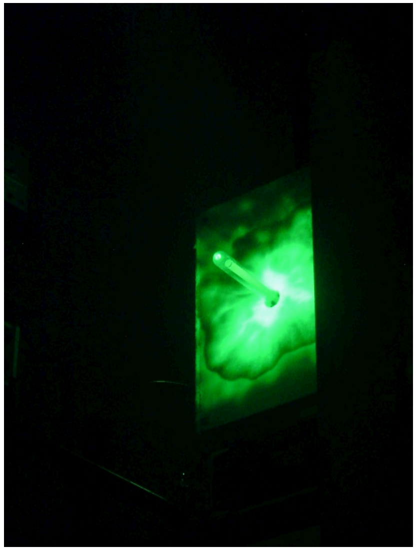
"Bulk" doped ferrites do not live up to thermodynamic expectations



Porous disk of cobalt ferrite produced small amount of H_2 for only one cycle.

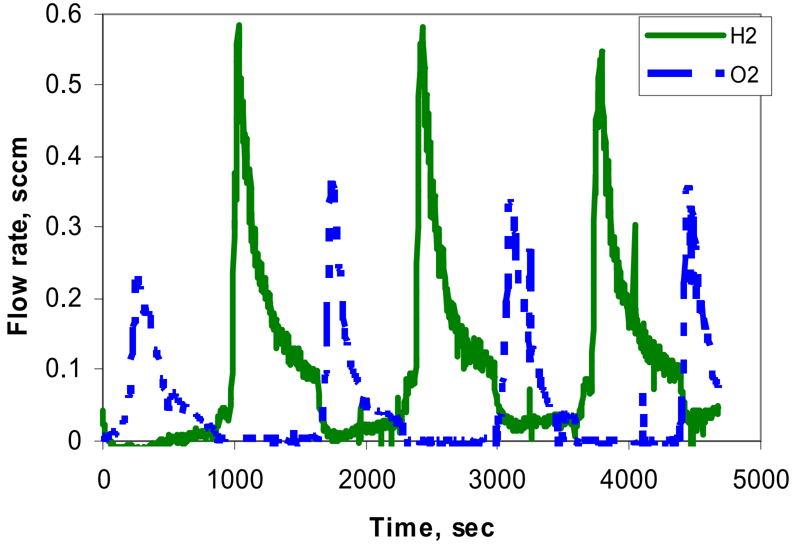
Ferrites work … when you add Zirconia





On-Sun Test:
$Co_{0.67}Fe_{2.33}O_4$/YSZ (1:4)

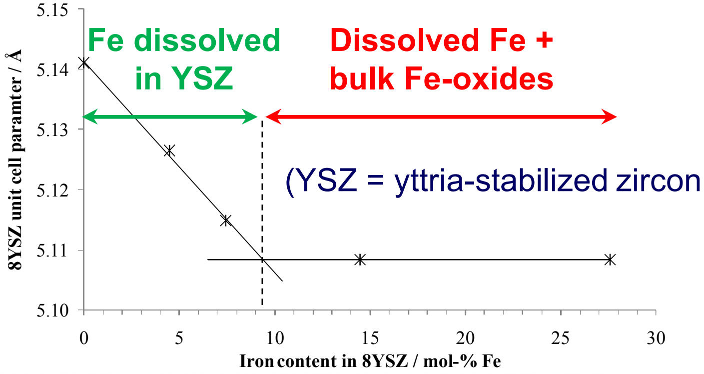
T_{TR} 1580 °C, T_{OX} 1050 °C
H_2 = 3.5-4 scc/g ferrite each cycle



Pioneered by Kodama et. al. (ISEC) 2004, ISEC2004-65063, Portland, OR.

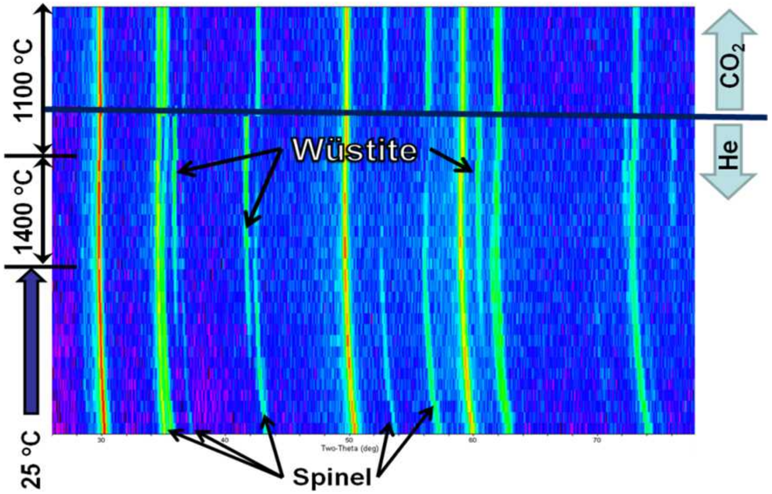
Monolithic composites with YSZ are cyclable – Why?

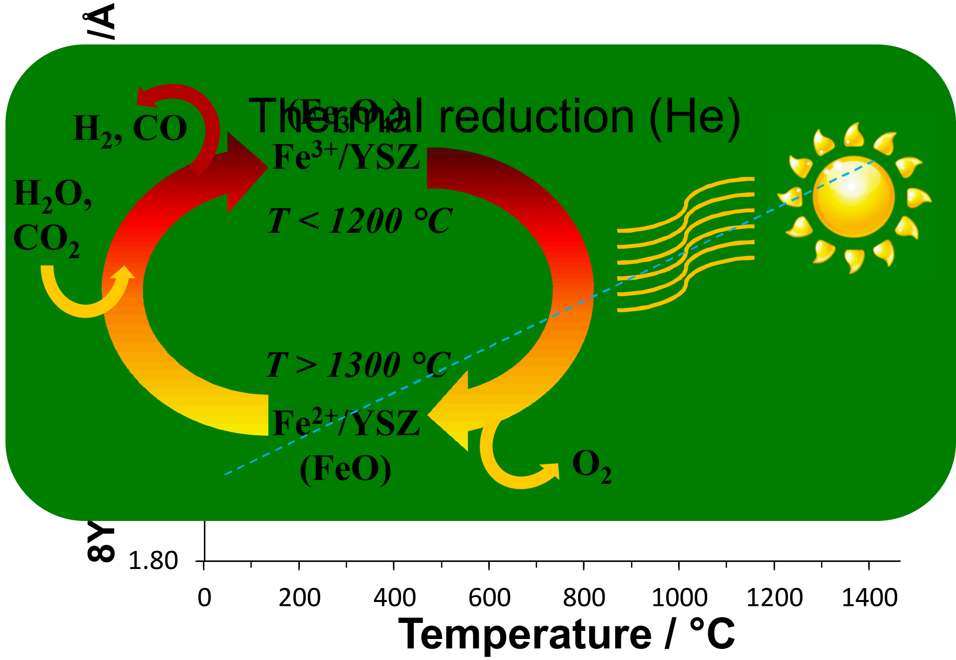
Structural characterization: X-ray diffraction



(YSZ = yttria-stabilized zirconia)

- Fe is soluble in YSZ
- Solubility is a function of both temperature and oxidation state.



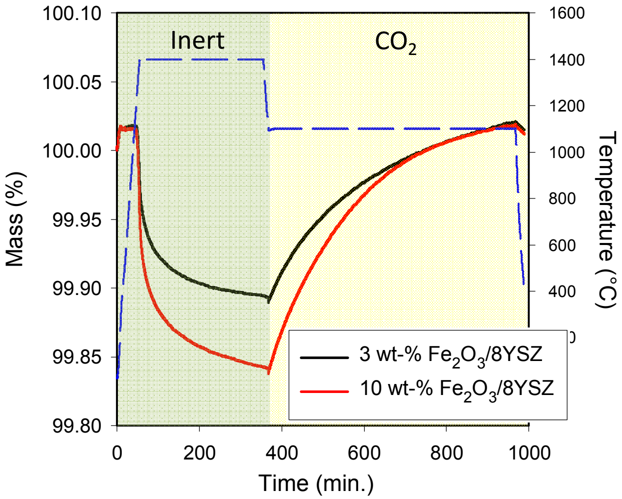


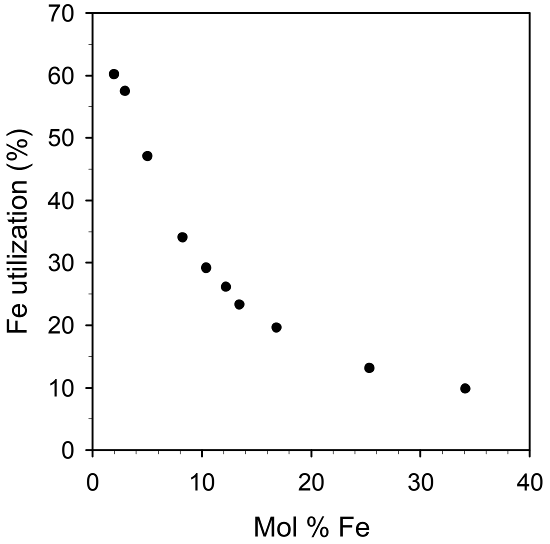
In situ observation of phases and YSZ lattice parameters reflect complex migration of Fe in/out of solid solution.

E.N. Coker, *et al.*, *J. Mater. Chem.*, **21**, 10767-76, (2011).

Monolithic composites with YSZ are cyclable – Why?

Fe dissolution and oxygen transport are the keys

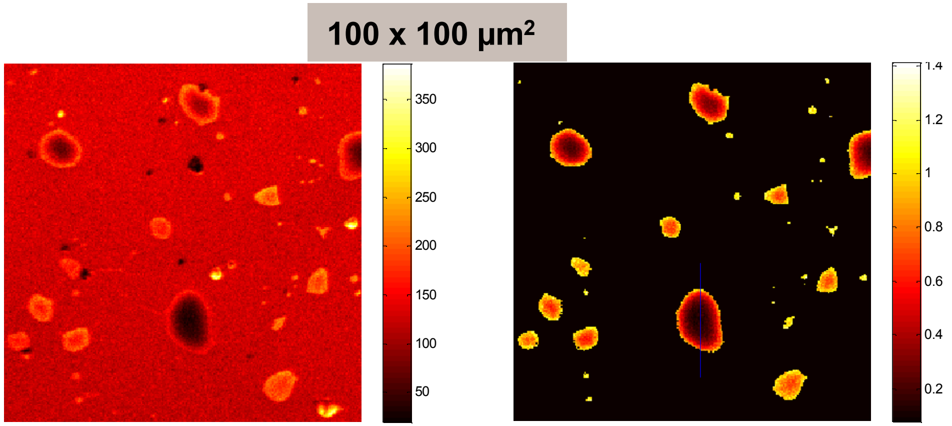




Beyond the solubility limit, Fe contributes little to the overall gas yield.

Re-oxidation with ^{18}O-labelled CO_2 confirms limited utilization of bulk Fe-oxide relative to Fe/YSZ.

^{18}O Secondary Ion Mass Spectrometry (SIMS)



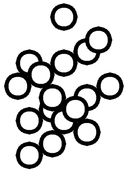
Raw image
(all ^{18}O visible)

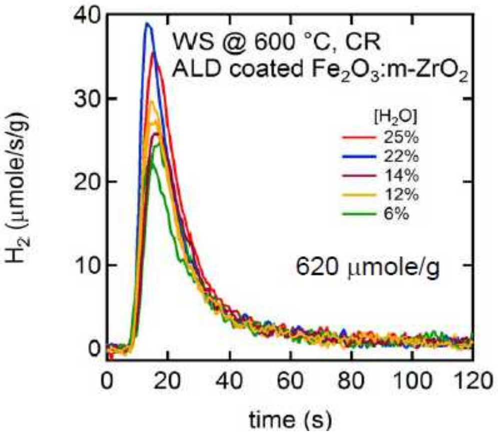
Masked image
(only ^{18}O in FeO_x)

E.N. Coker, J.A. Ohlhausen, A. Ambrosini, and J.E. Miller J. Mater. Chem., 2012, 22, 6726. DOI:10.1039/C2JM15324F.

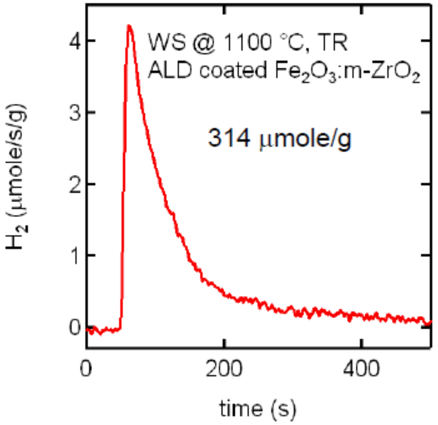
Small Dimension Structures

ALD thin film peak production rate ~ 100X faster than bulk

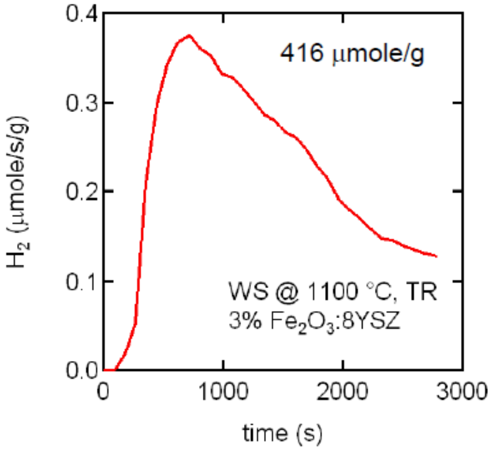




Chemically reduced ALD
Fe:ZrO_2 nanoparticles

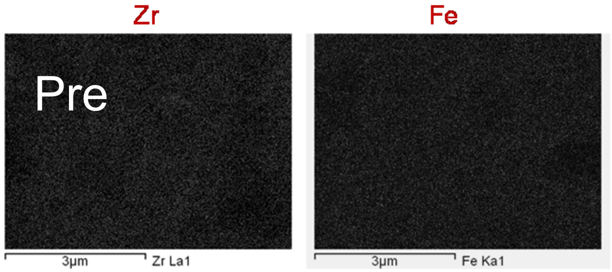


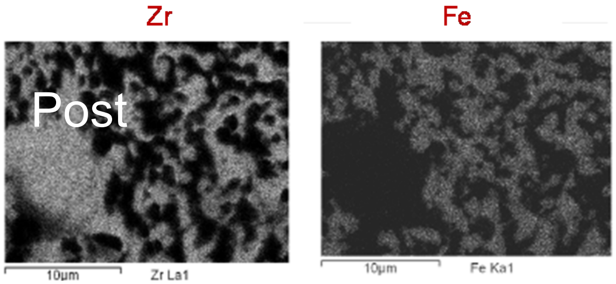
Thermally reduced
ALD particles



Bulk Fe:YSZ

- CO_2-splitting activity improves dramatically for particles of ZrO_2 coated with *nanometer scale* layers of Fe_2O_3

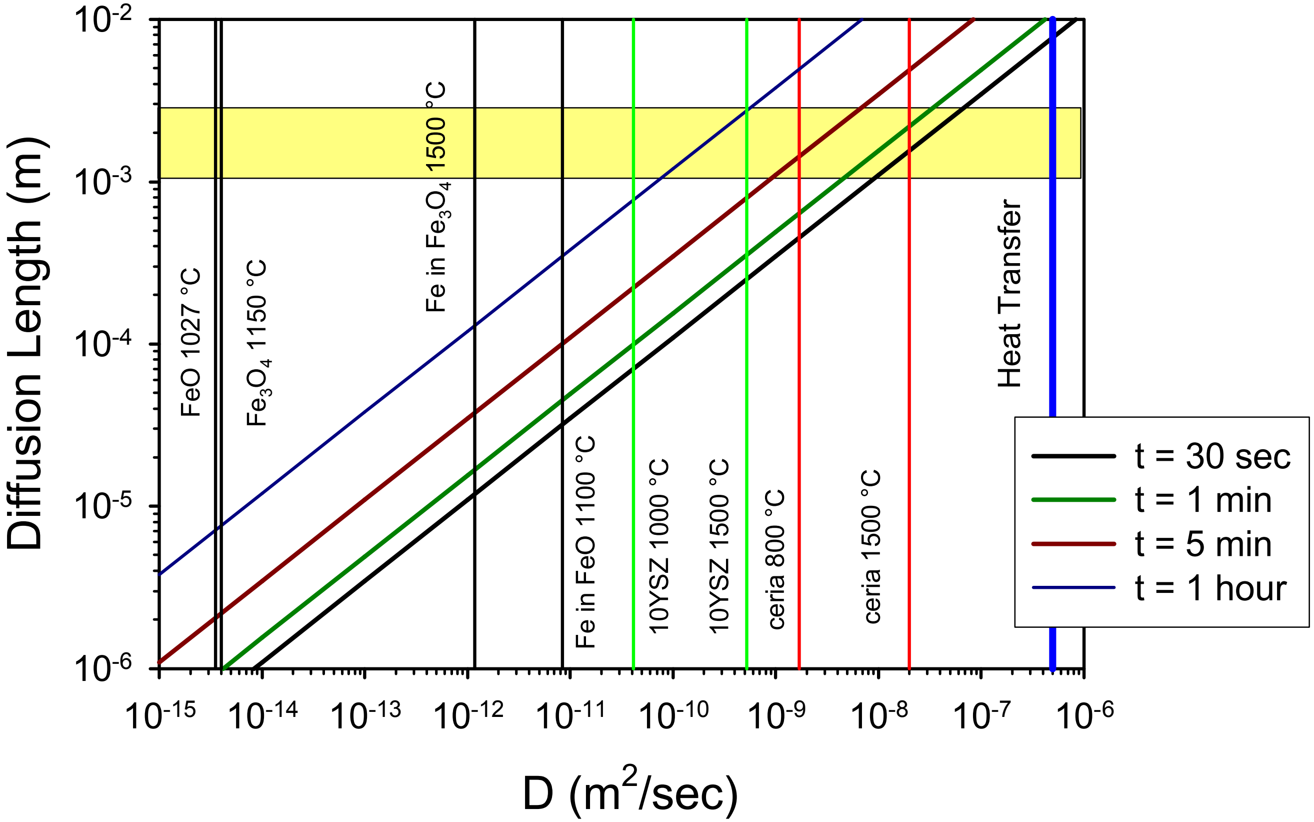




J.R. Scheffe, *et al.*, *Chem. Materials* **23 (8)**, 2030-2038.

Perspective on Ion Transport

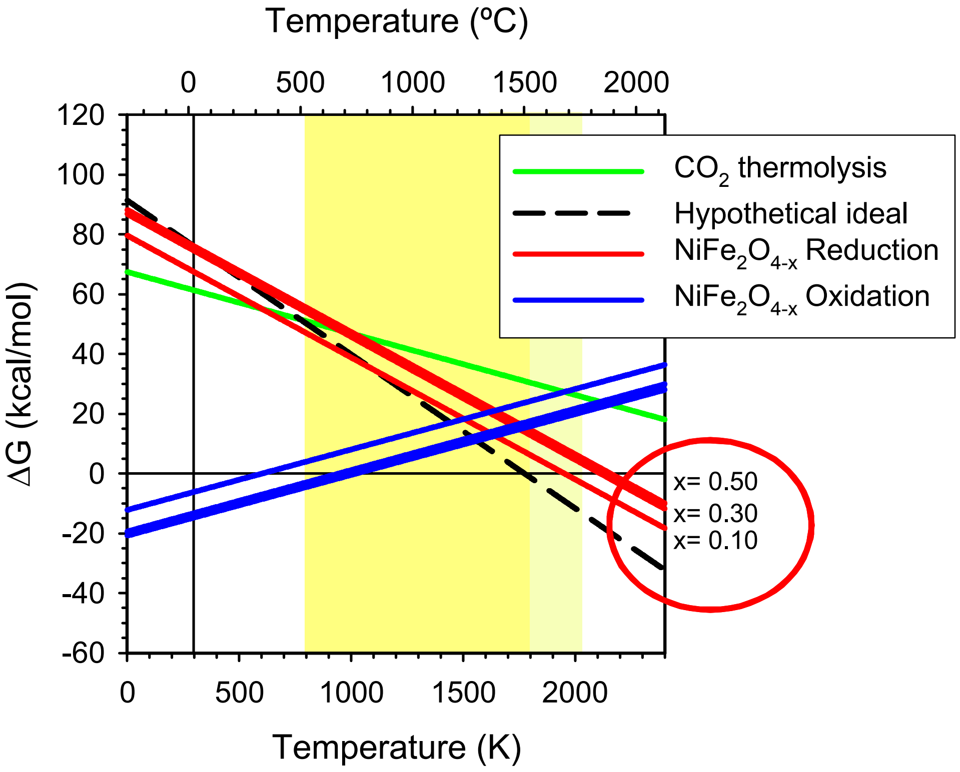
$$diffusion\ length = 2\sqrt{Dt}$$



Heat> Ceria > YSZ >> Fe_3O_4

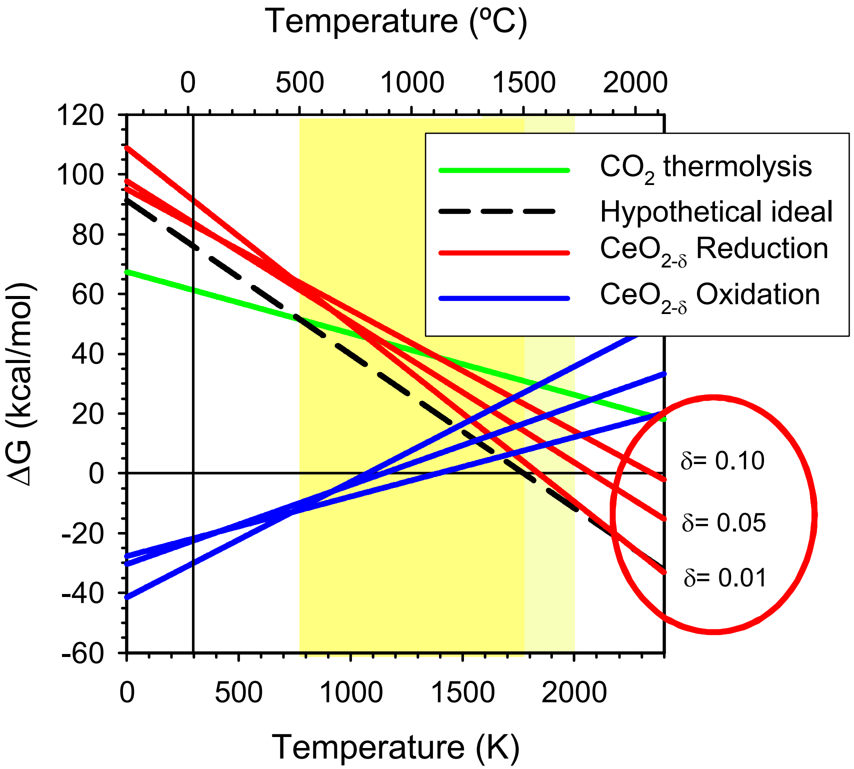
Ion (oxide) diffusion lengths are materials- and temperature-dependent.

The problem with ceria – reaction extent



From a thermodynamic viewpoint, ferrites are superior to ceria (larger δ in target temperature range).

ΔH and ΔS (ΔG) are functions of redox state (δ or x). With each increment of reduction, materials become harder to reduce, easier to oxidize.



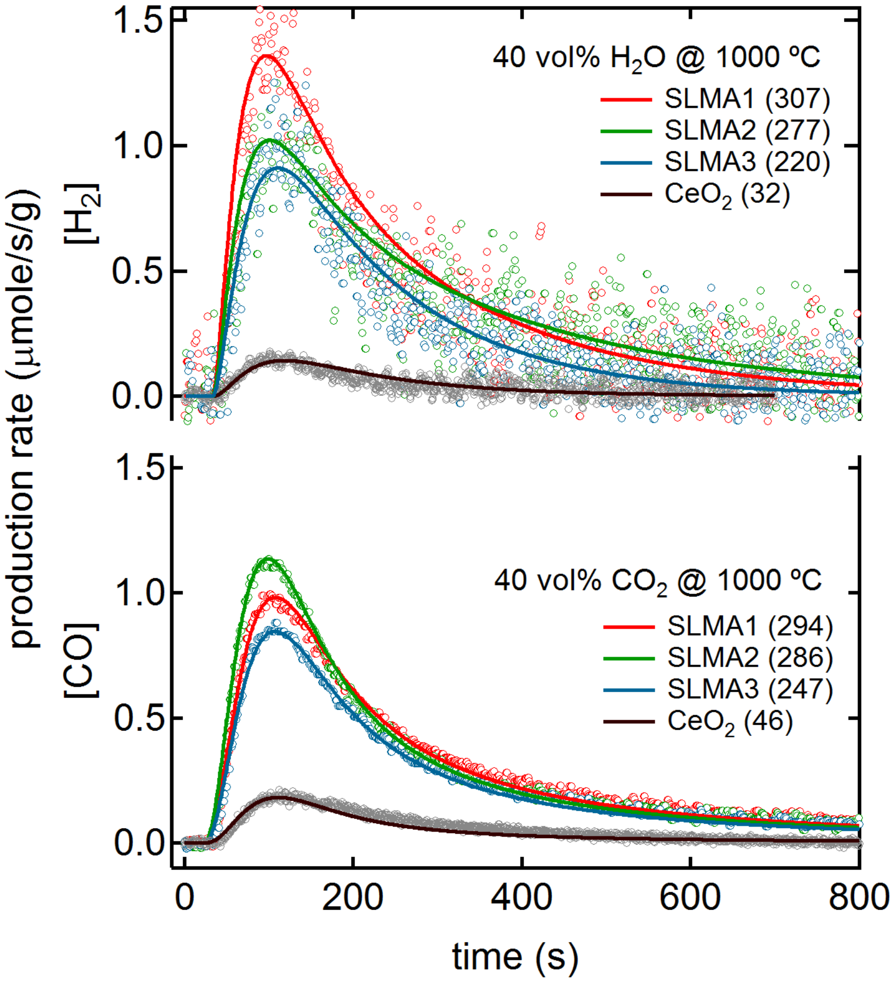
Miller, McDaniel, Allendorf *Adv. Energy Mater 2013.*

One Path Forward: Tailored MIECs for Thermo and Transport

- $Sr_xLa_{1-x}Mn_yAl_{1-y}O_{3-\delta}$ oxidize to split H_2O and CO_2 with lower T_{TR}
- Comparable kinetics to ceria, but higher utilization.

9× more H_2, 6× more CO

compound	CO (µmole/g)	H_2 (µmole/g)
LSAM1	294	307
LSAM2	286	277
LSAM3	247	220
$CeO_{2-\delta}$	46	32

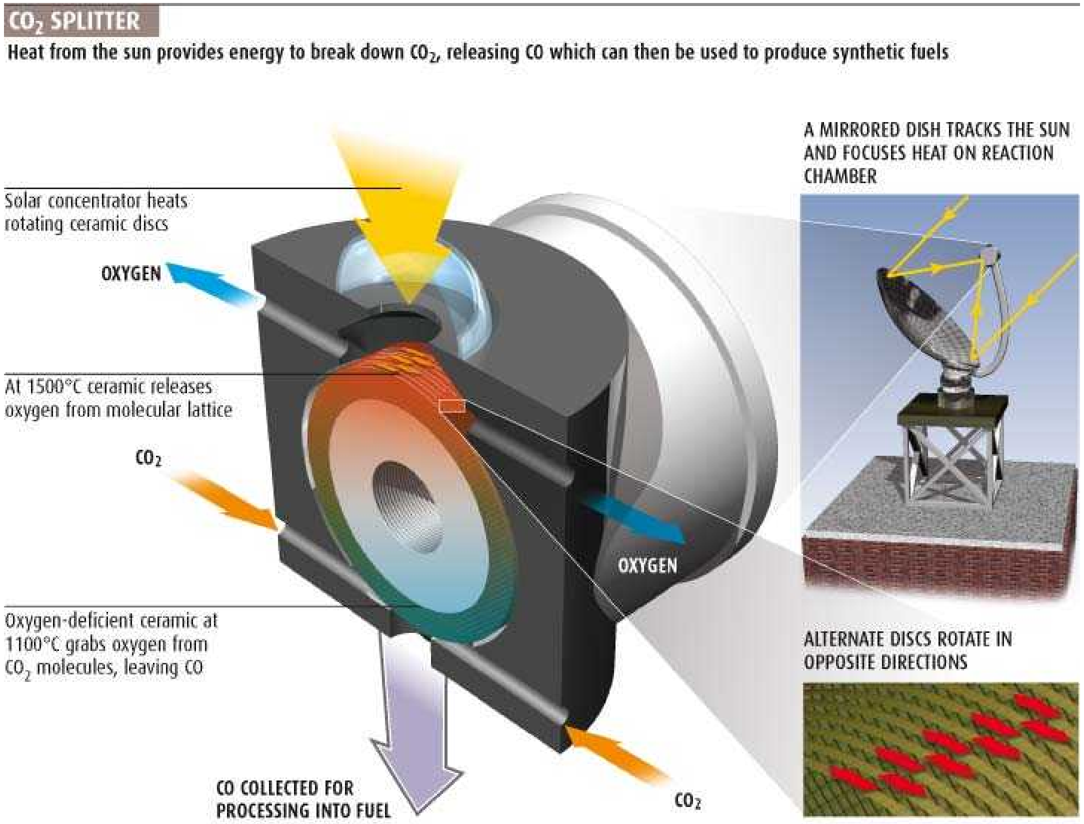


80 cycle durability demonstrated

A.H. McDaniel, Elizabeth C. Miller, Arifin, A. Ambrosini, E.N. Coker, R. O'Hayre, W.C. Chueh and J. Tong, Energy Environ. Sci., 2013,6, 2424-2428.

CR5 : First-of-a-kind approach and our attempt to apply the lessons.

Counter-Rotating-Ring Receiver/Reactor/Recuperator (CR5)



CO_2 SPLITTER

Heat from the sun provides energy to break down CO_2, releasing CO which can then be used to produce synthetic fuels

Solar concentrator heats rotating ceramic discs

At 1500°C ceramic releases oxygen from molecular lattice

Oxygen-deficient ceramic at 1100°C grabs oxygen from CO_2 molecules, leaving CO

CO COLLECTED FOR PROCESSING INTO FUEL

A MIRRORED DISH TRACKS THE SUN AND FOCUSES HEAT ON REACTION CHAMBER

ALTERNATE DISCS ROTATE IN OPPOSITE DIRECTIONS

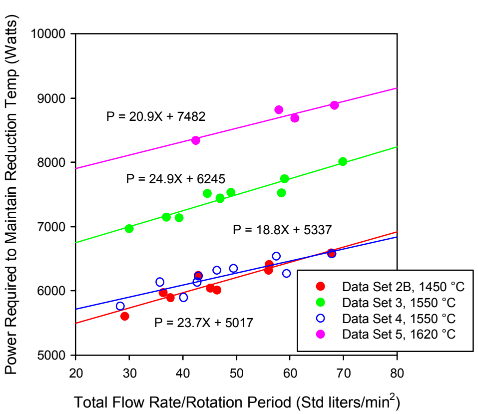
"Reactorizing a Countercurrent Recuperator"

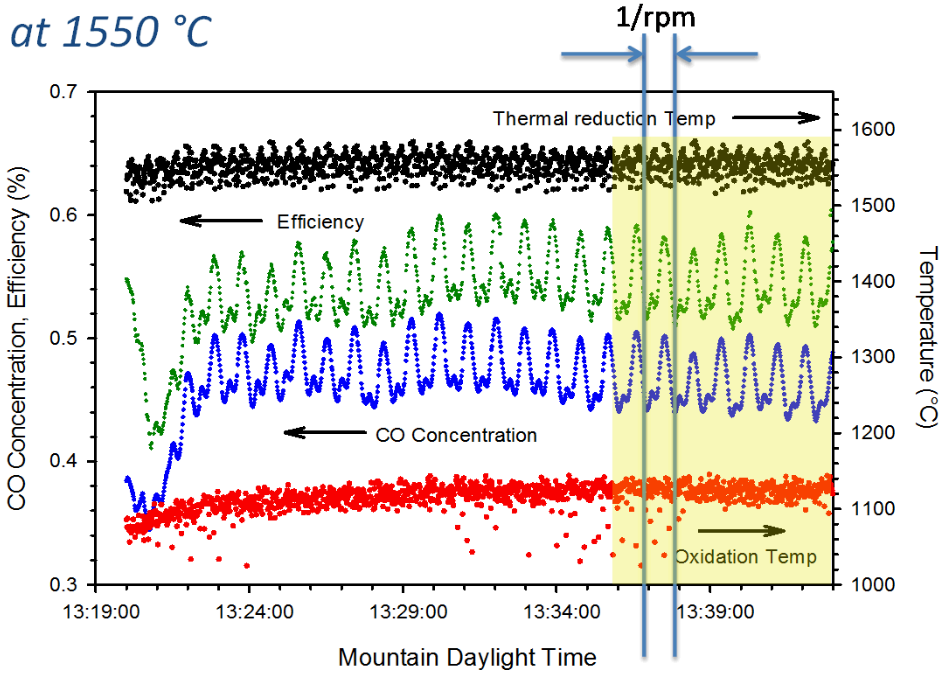
Continuous flow, Spatial separation of products, Thermal recuperation

Performance Map of Gen-1 Prototype

Collect data to validate models, guide improvements

- *Ceria-based fins on rings*
- *6 Data Sets: Cold, 2@ 1450 °C, 2@ 1550 °C, 1620 °C*
- *3 ring rotation speeds, 3 CO_2 flow rates for each*
- *Constant Ar flow, Pressure = 0.5 atm*
- *Floating Pressure at 1550 °C*





Miller, Allendorf, Ambrosini, Coker, Diver, Ermanoski, Evans, Hogan, McDaniel “Development and Assessment of Solar-Thermal-Activated Fuel Production: Phase 1 Summary” SAND2012-5658, July 2012

Take-home points

- For any approach to Solar Fuels- Efficiency is key for cost and scalability – 10% solar to fuel minimum (lifecycle)
  - Often it is unappreciated that sunlight is a “high cost” feedstock (capital cost)
  - Low efficiencies increase scale, further challenge efficiency and stretch resources.
  - CO_2 and water (and associated energy costs) are not limiting
- Thermochemical approaches have potential for high efficiency and thus high impact
  - TE studies support eventual economic viability – difficult, but not implausible
  - Small global community has made significant advances in recent years
- Materials, Reactors, Systems all areas of opportunity and need
  - All impact efficiency, all relatively immature for this technology.
  - Adjacency to other technologies (e.g. solar electric, solar reforming) can help move technology forward, but focused cross-discipline efforts are also needed.

Materials are challenging, but we have barely begun to explore the possibilities.

Acknowledgements

- TCES work was supported by the U.S. Department of Energy SunShot initiative under award number DE-FOA-0000805.

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