Fuels from Sunlight, Water and Carbon Dioxide: A Thermochemical Approach

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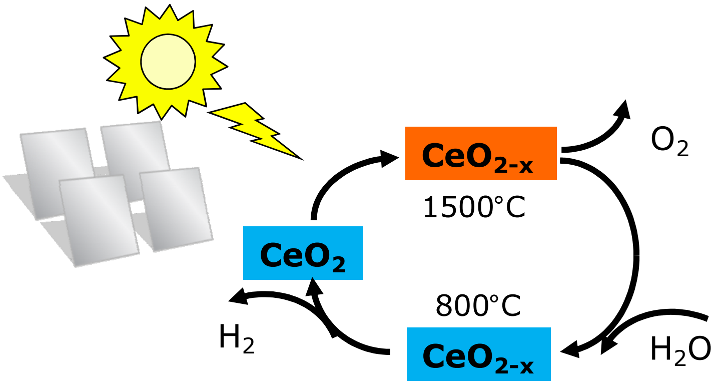


CeO_{2-x}

O_2

1500°C

CeO_2

800°C

H_2

CeO_{2-x}

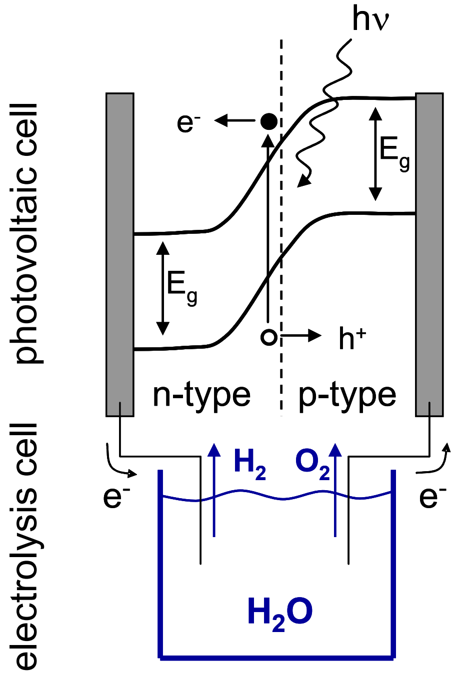
H_2O

ICMR Summer School
August 19-28, 2012; Santa Barbara, CA

Using the Sun to Make Fuels

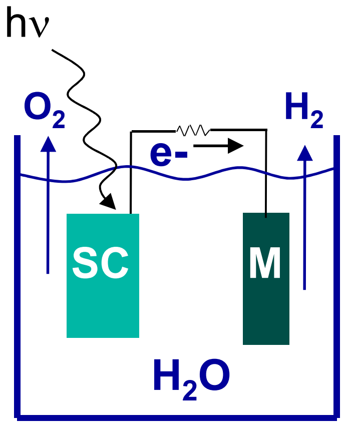
$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2 \qquad CO_2 \rightarrow CO + \tfrac{1}{2}O_2$$

- Solar electricity + electrolysis



- Separate components

- Photolysis

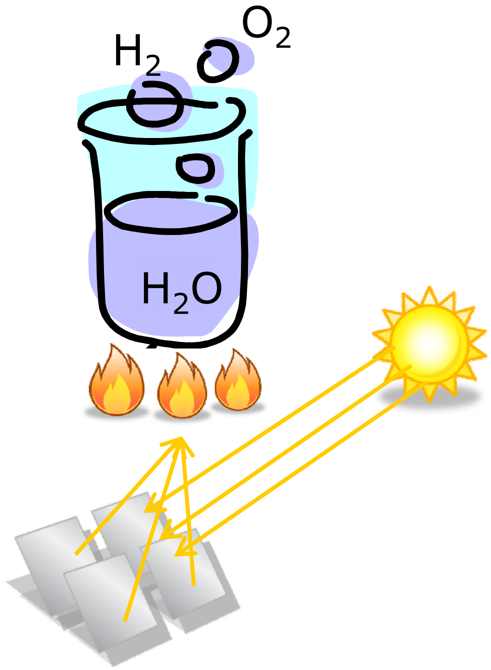


- Material corrosion

- Low CO_2 solubility
- Poor product selectivity
- Non-aqueous electrolyte

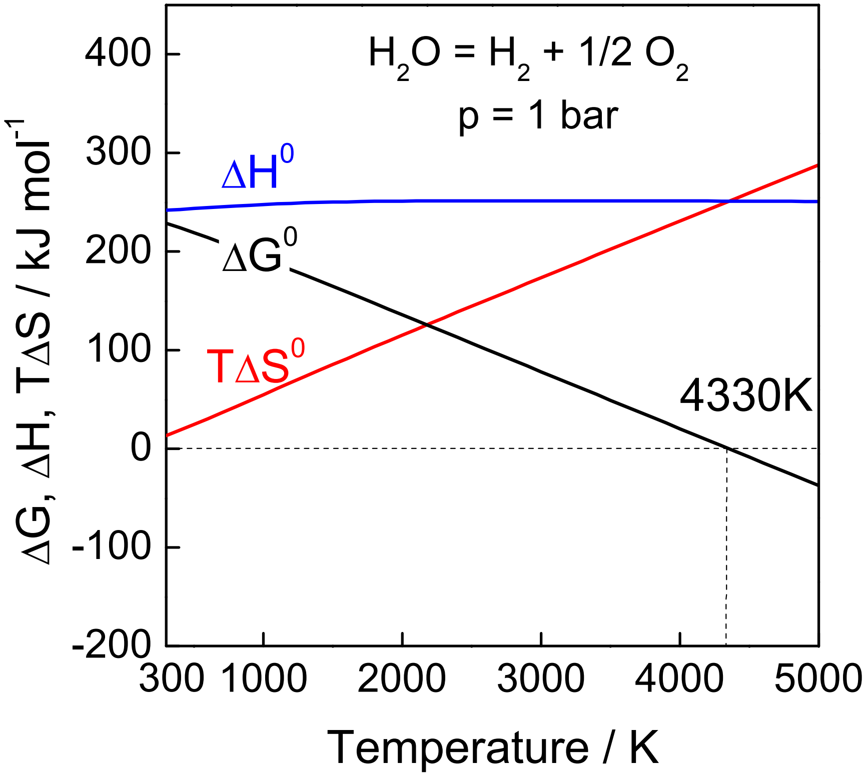
- Precious metal catalysts, poor rates
- Poor use of solar spectrum

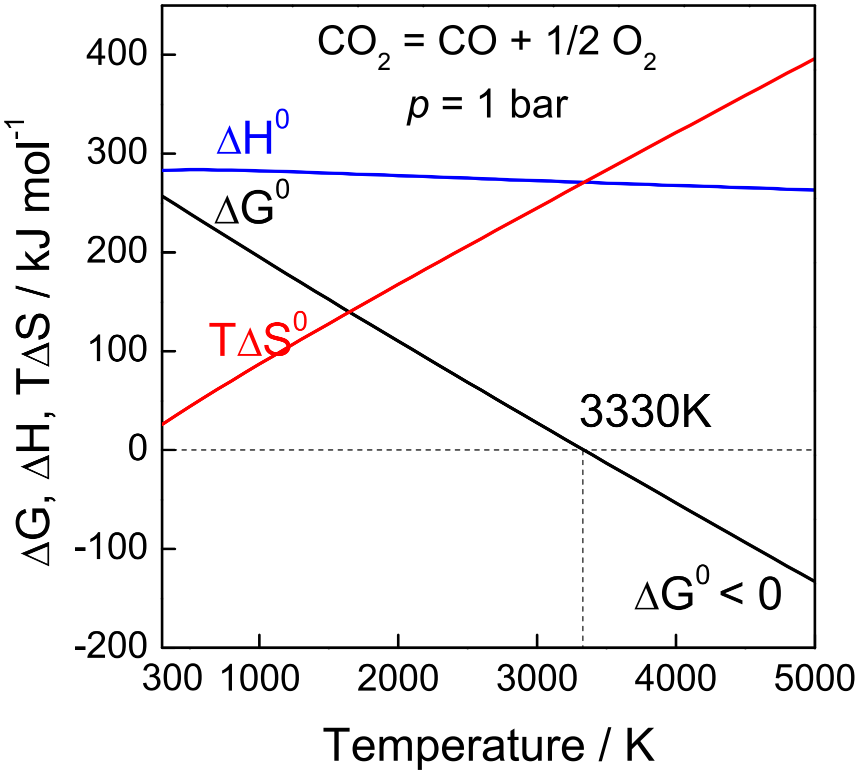
- Thermolysis



- Reaction at > 4,000 °C
- Requires separation

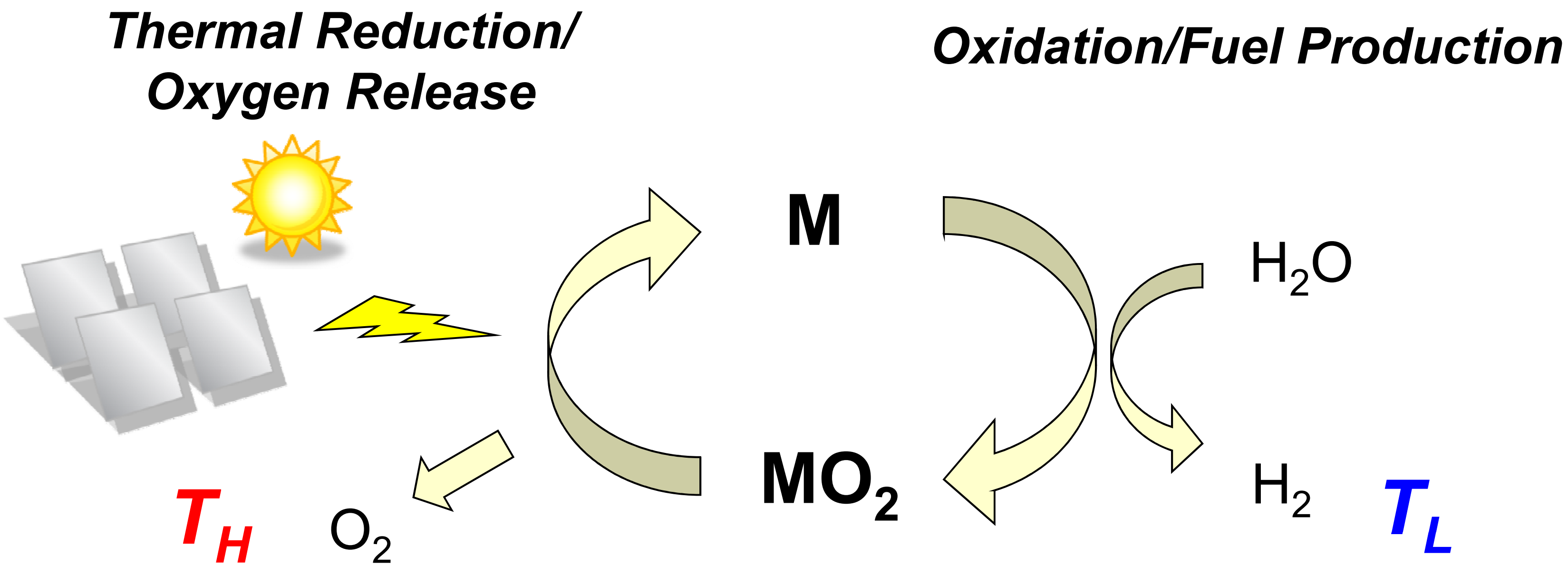
Direct Thermolysis





- Slightly easier for CO_2 dissociation than H_2O
- But still extremely challenging → multi-step reaction schemes

Metal Oxide Solar Thermochemical Cycle



Thermal Reduction/ Oxygen Release

Oxidation/Fuel Production

M

MO_2

H_2O

H_2

O_2

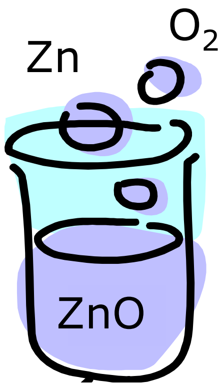
T_H

T_L

- Integrated solar capture and fuel production
- Oxygen and fuel produced in separate steps
- Challenges due to structural change & volatilization
- Fuel largely limited to hydrogen

State-of-the-Art

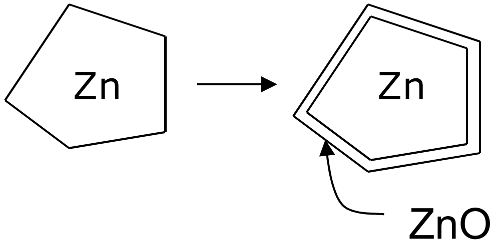
ZnO / Zn



900-1800 °C

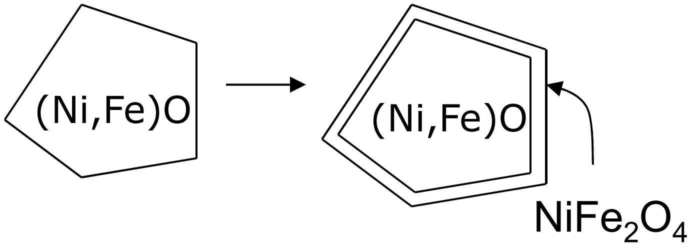
- Difficult Zn capture
  - Quench step required
- Slow oxidation kinetics

$$Zn + H_2O \rightarrow ZnO + H_2$$



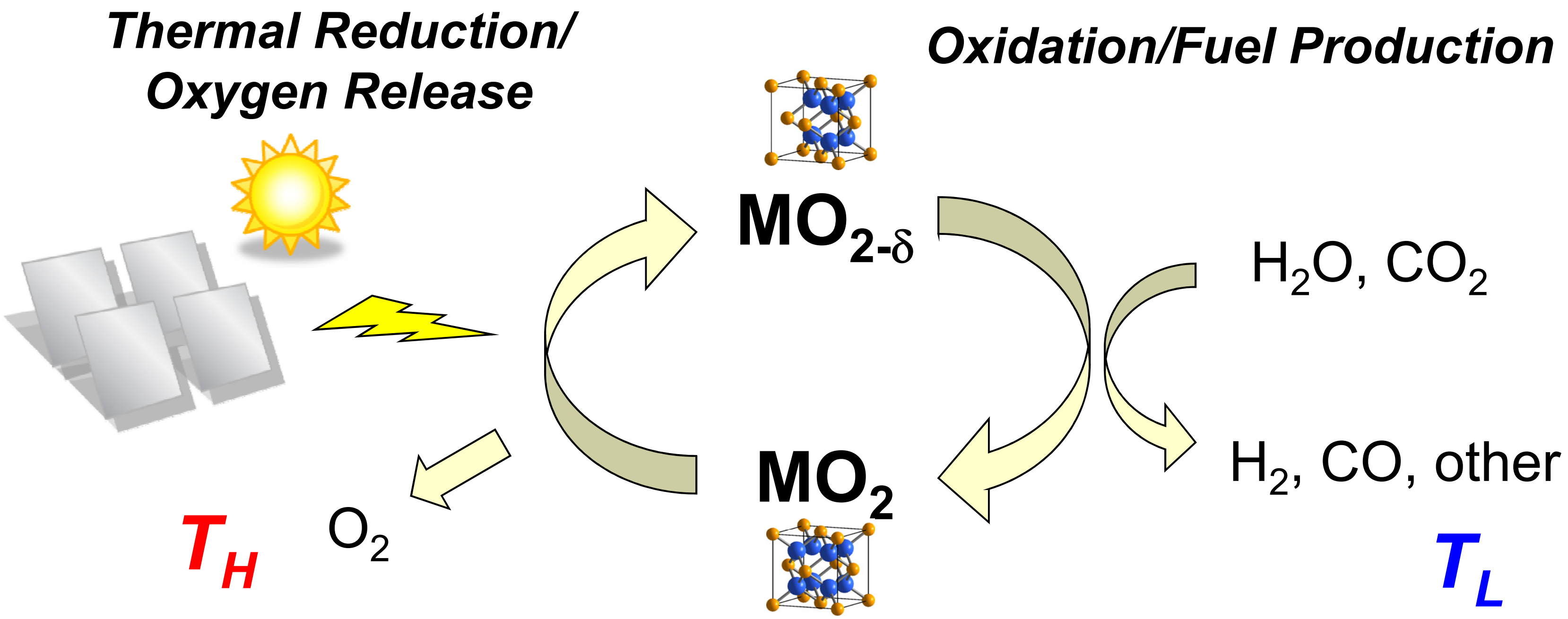
$NiFe_2O_4$ / $Ni_{1/3}Fe_{2/3}O$

- Solid state transformation
  - T_H ~ 1400ºC
- Two distinct solid phases



- Slow kinetics
  - Slow oxygen diffusion
  - Slow surface reaction
- Kinetics worsen
  - Loss of porosity (sinter)

Alternative Thermochemical Cycle



Thermal Reduction/ Oxygen Release

Oxidation/Fuel Production

$MO_{2-\delta}$

H_2O, CO_2

H_2, CO, other

T_H

O_2

MO_2

T_L

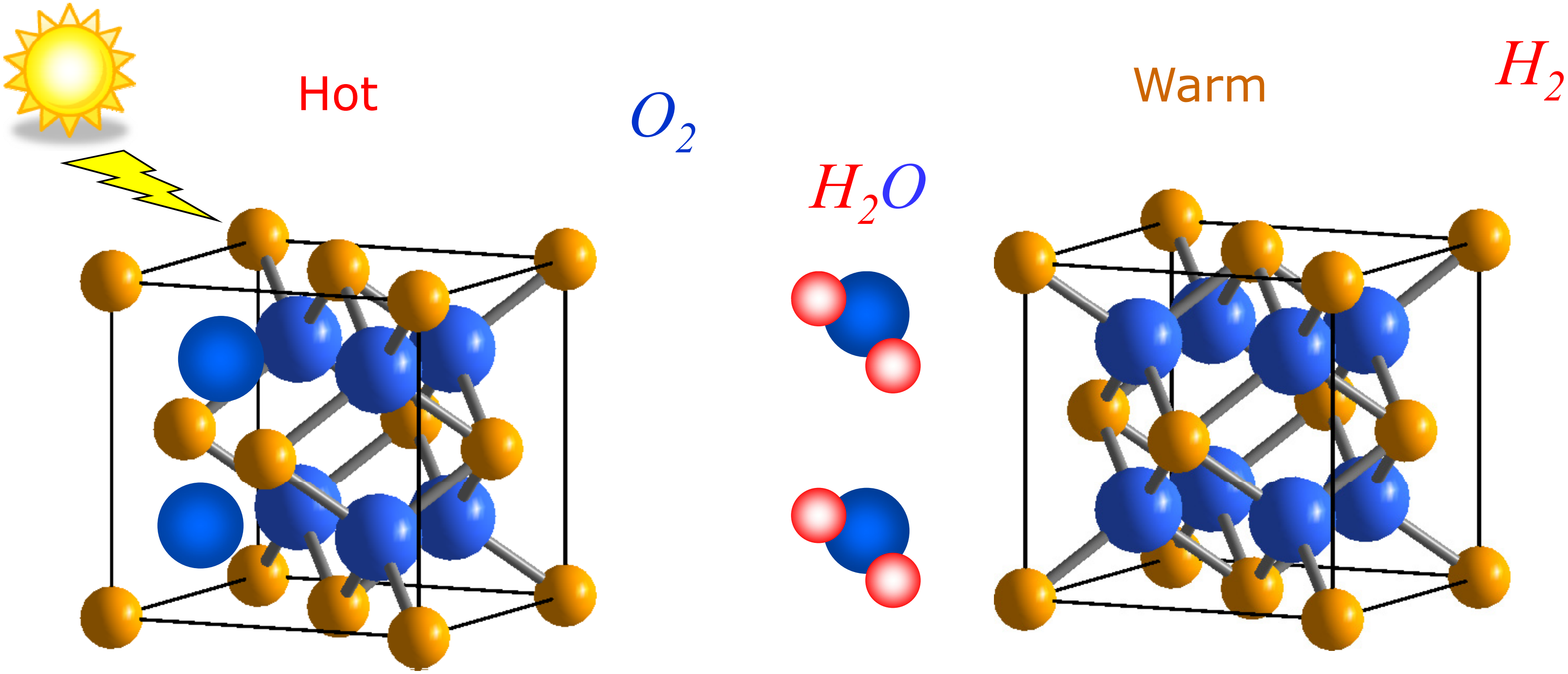
Metal oxide releases/incorporates oxygen

No phase change, large nonstoichiometry range

Rapid kinetics: bulk diffusion, surface reaction

Ideal candidate: *Ceria, $CeO_{2-\delta}$*

Ceria thermochemical cycle



$$CeO_2 \rightarrow CeO_{2-\delta} + {}^{\delta}\!/_{2} O_2$$

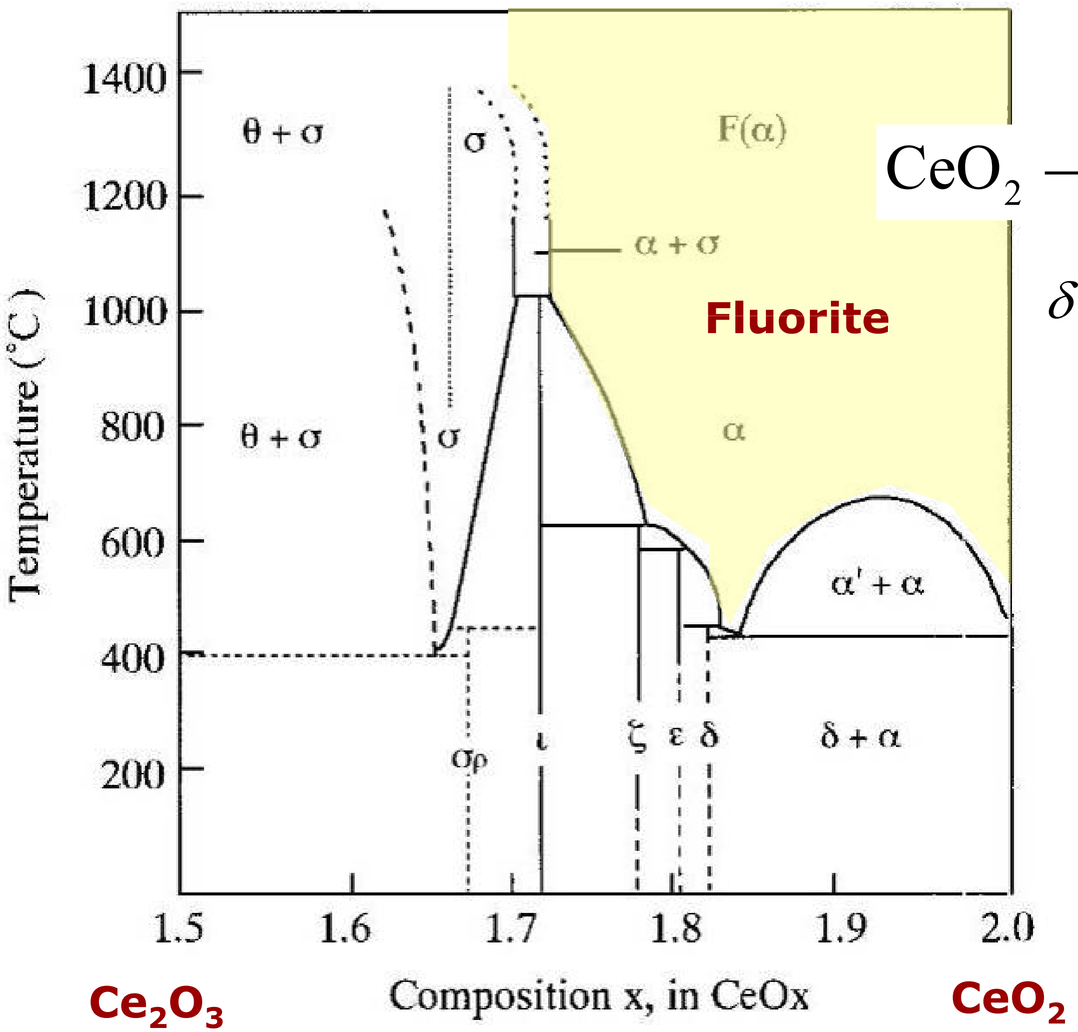
$$\delta H_2O + CeO_{2-\delta} \rightarrow \delta H_2 + CeO_2$$

- Ceria thermodynamics well-known
- Extremely refractory: T_m = 2477 °C, non-volatile

Outline

- Brief introduction
    - Thermodynamics
    - Kinetics
    - Preliminary evaluation of material requirement
- Experimental proof of principle
    - Water and carbon dioxide dissociation
    - Benchtop electric furnace → solar simulator
- Revisiting
    - Thermodynamics
    - Kinetics
    - Fundamental measurements
- Defining Efficiency

Ce_2O_3 – CeO_2 Phase Diagram



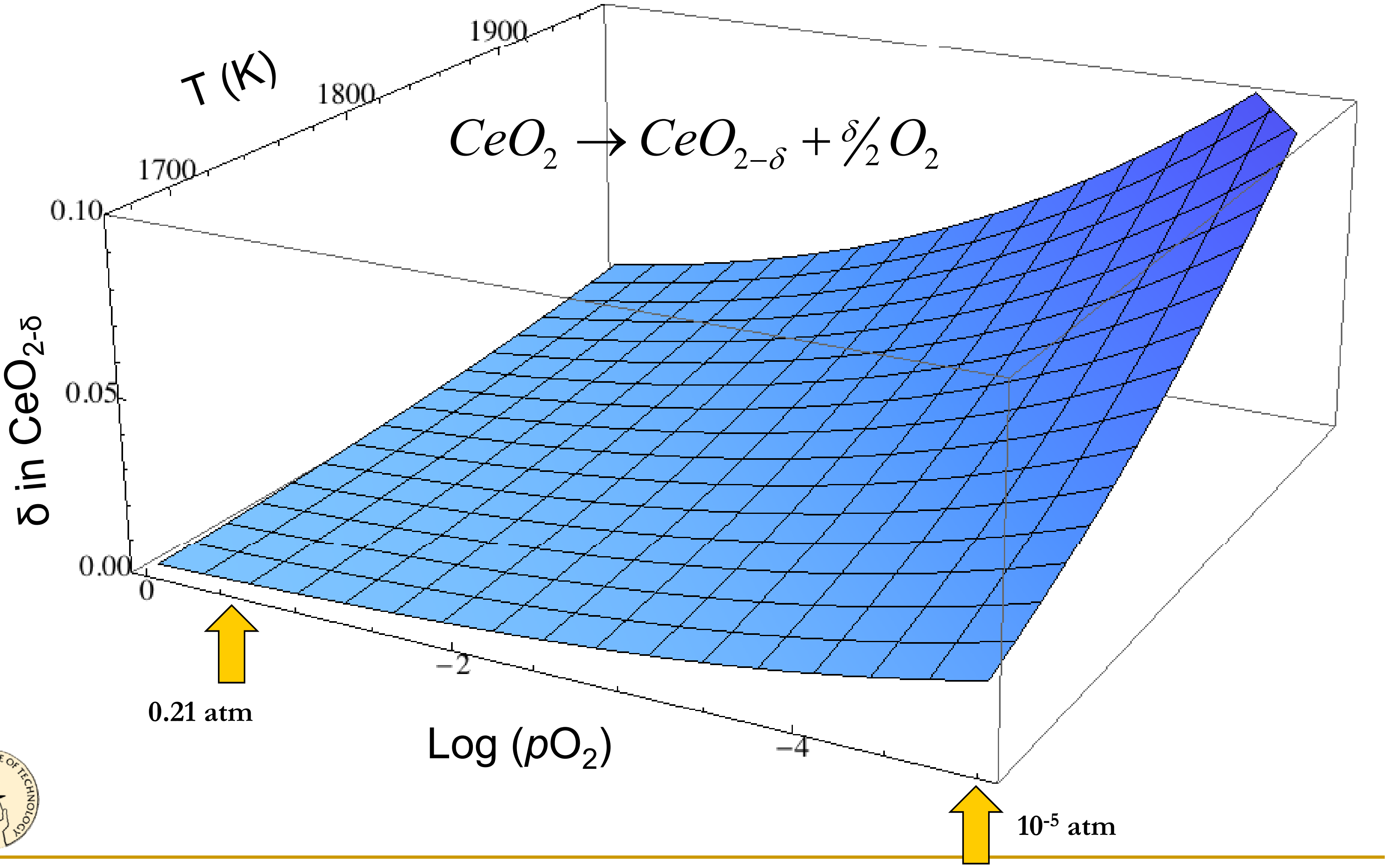
$$CeO_2 \rightarrow CeO_{2-\delta} + {}^{\delta}\!/_{2}\, O_2$$

$$\delta = f(T, pO_2)$$

G. Adachi and N. Imanaka, *Chem. Rev.*, **98,** 1479-1514 (1998).

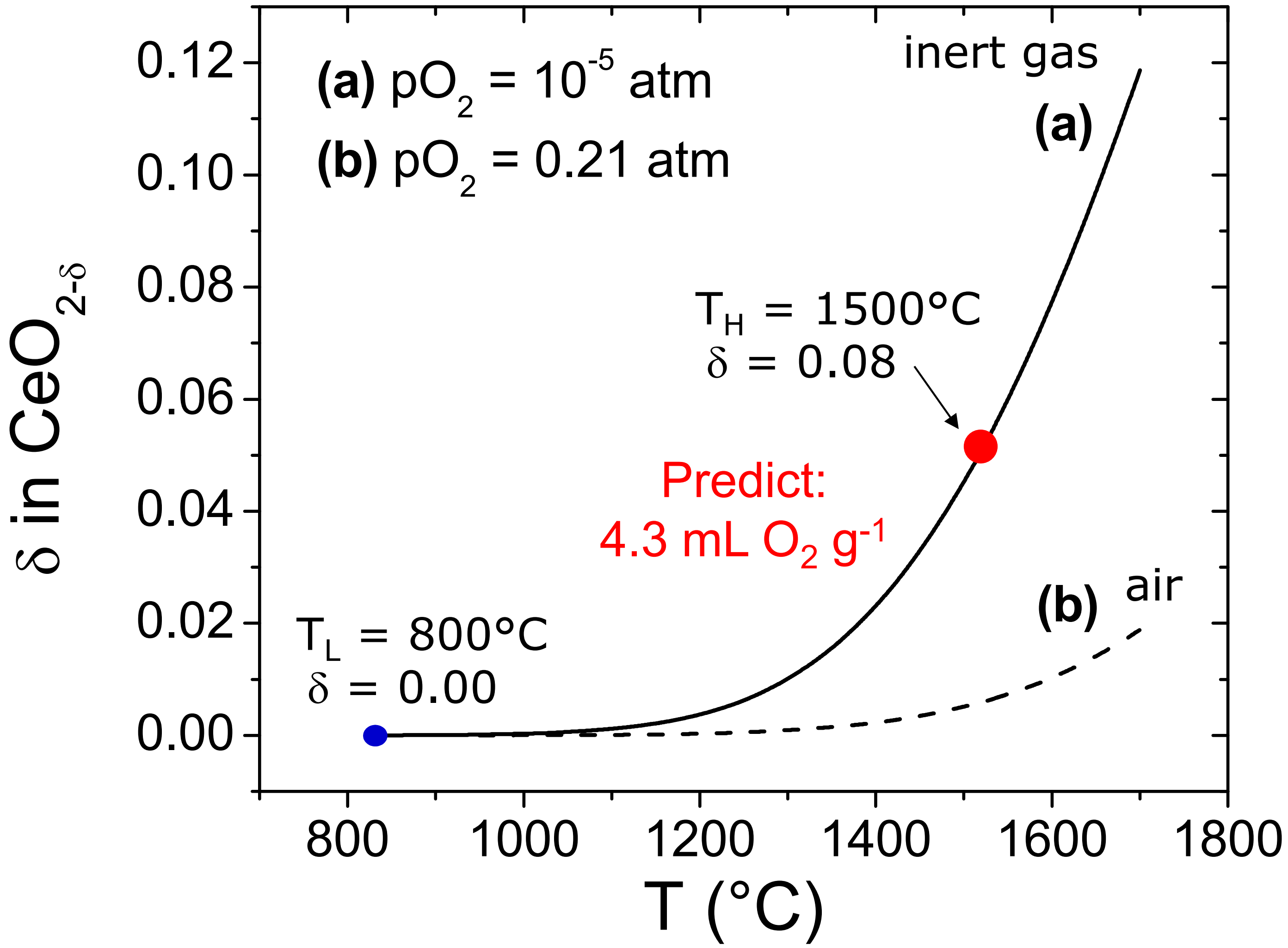
Thermodynamic Oxidation State

Can compute δ (T, pO_2) from material thermodynamic parameters



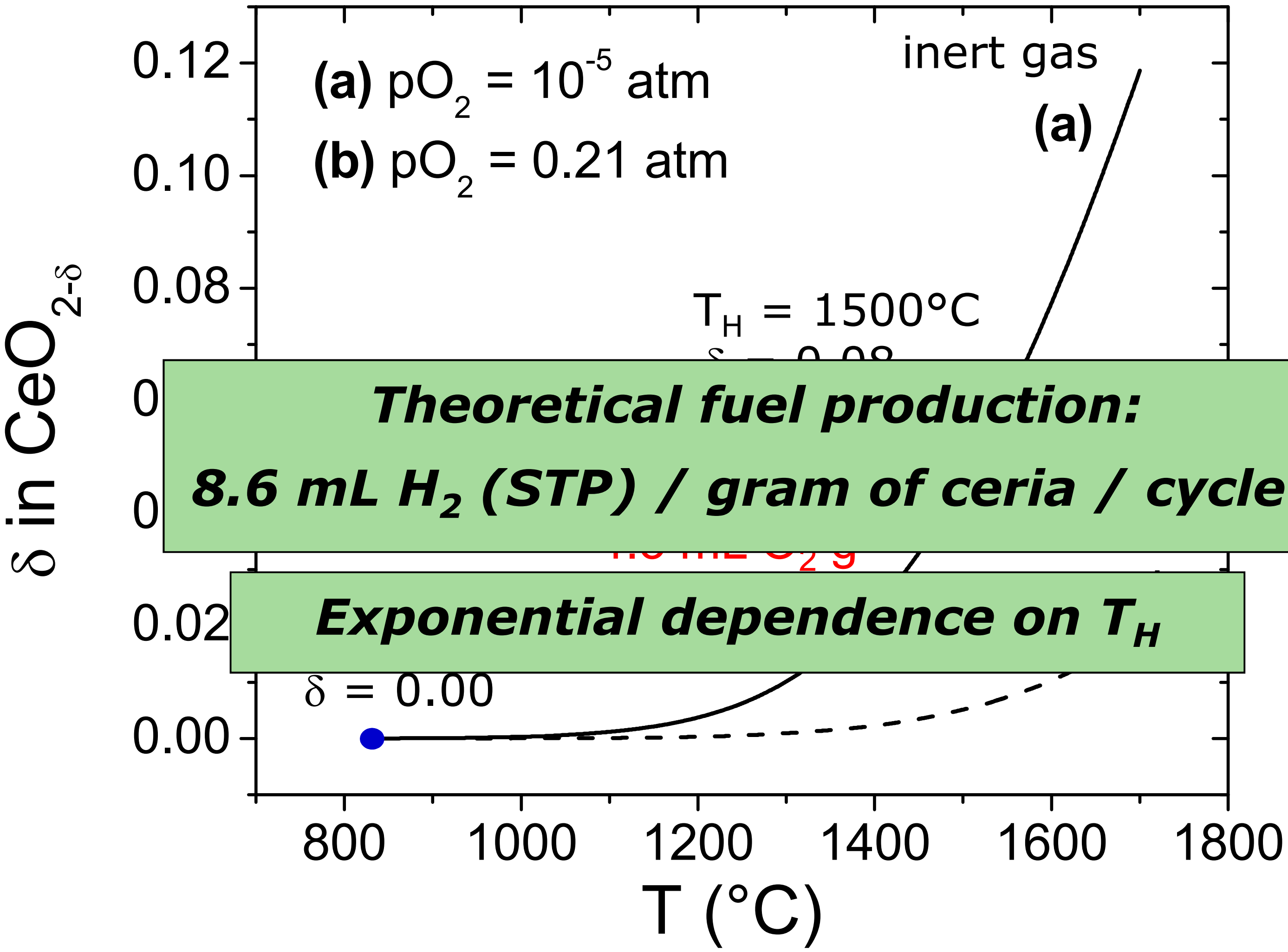
$$CeO_2 \rightarrow CeO_{2-\delta} + {}^{\delta}\!/_{2}\, O_2$$

Predicted Oxygen Release / Fuel Production



** 7.0 mL for $Ce_{0.85}Sm_{0.15}O_{1.925-\delta}$*

Predicted Oxygen Release / Fuel Production



Theoretical fuel production:

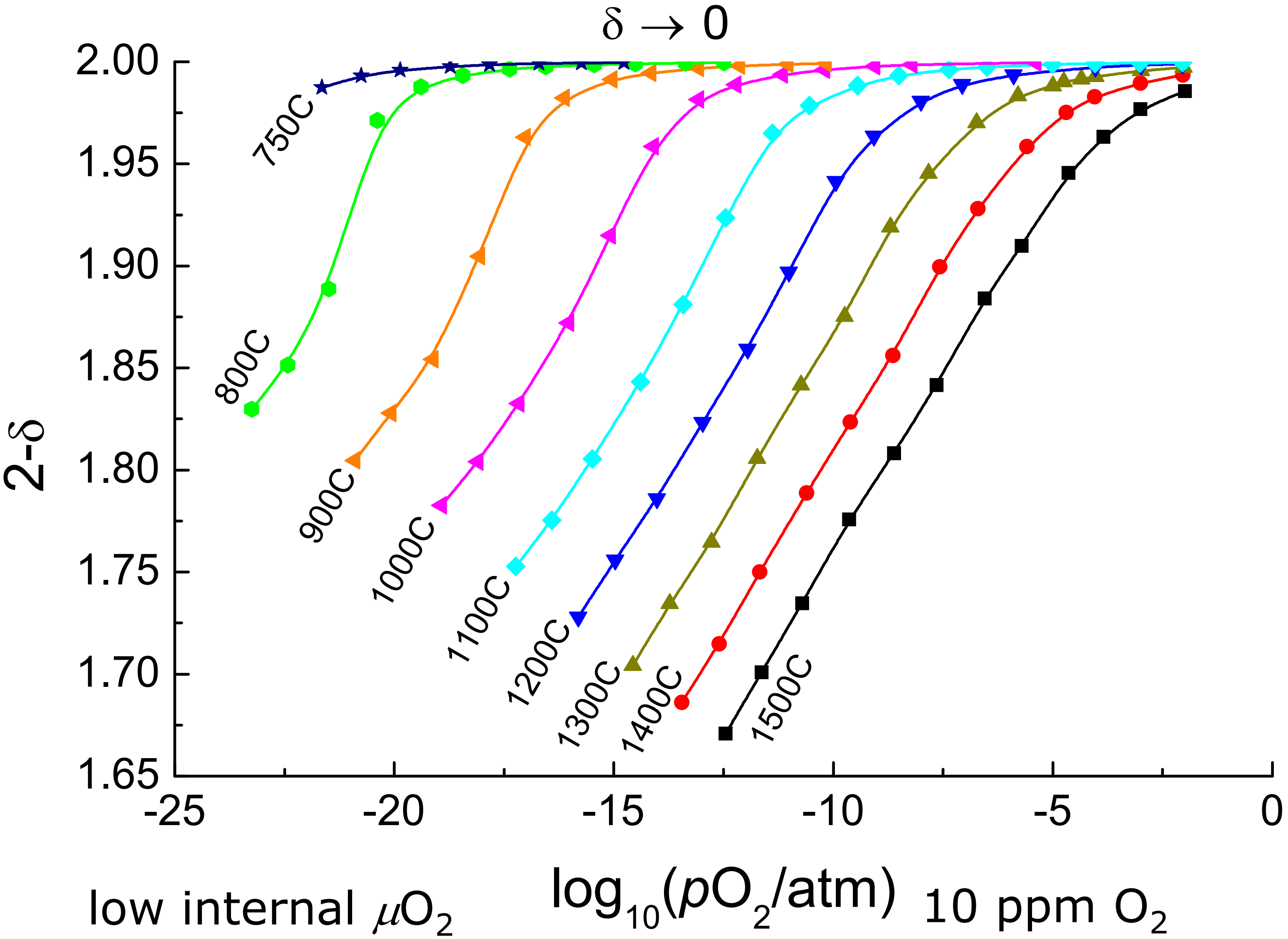
8.6 mL H_2 (STP) / gram of ceria / cycle*

Exponential dependence on T_H

*** 7.0 mL for $Ce_{0.85}Sm_{0.15}O_{1.925-\delta}$***

Nonstoichiometry in CeO_2

Panlener et al., *J Phys. Chem. Solids*, (1975).



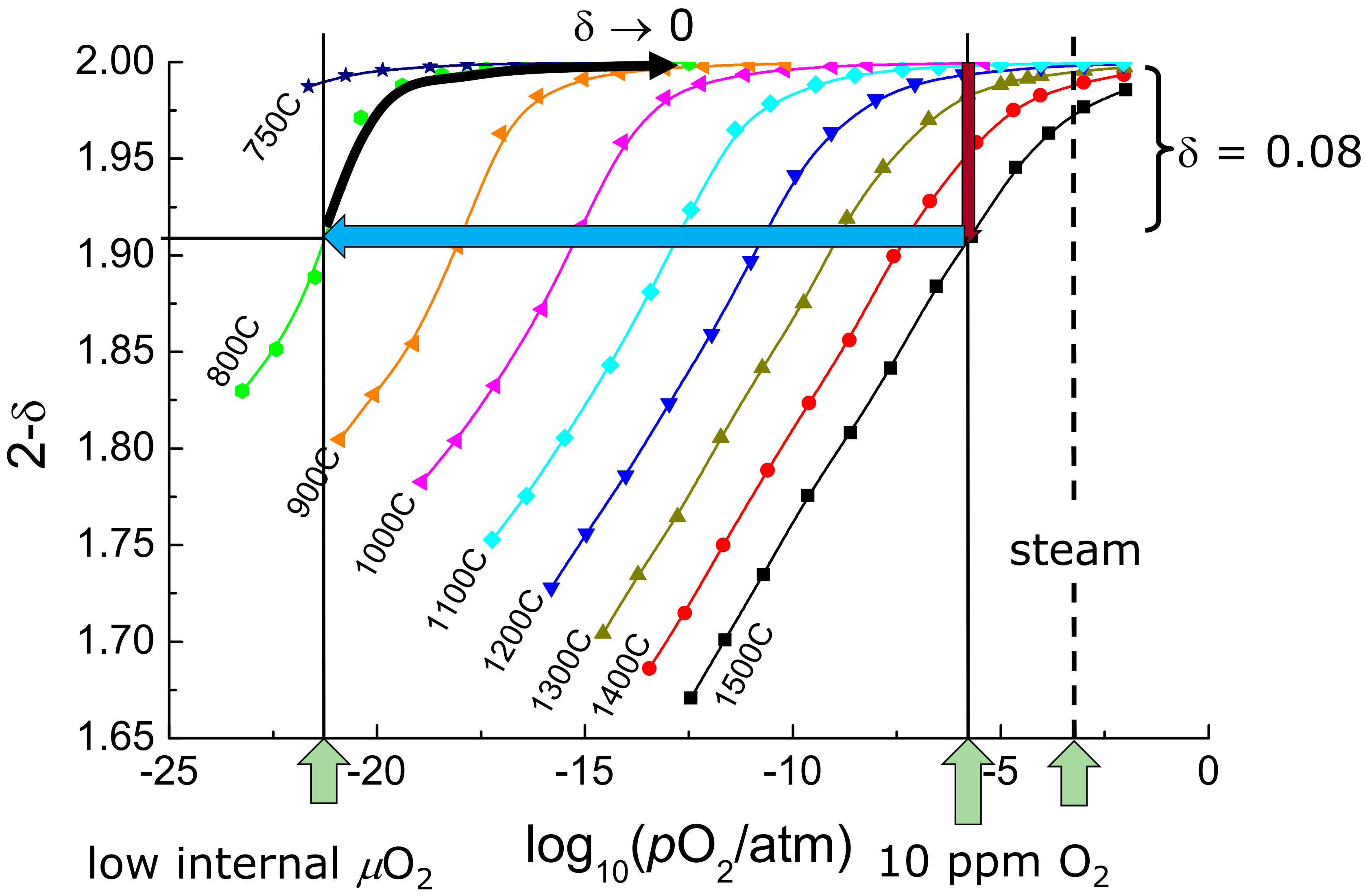
$\delta \to 0$

low internal μO_2

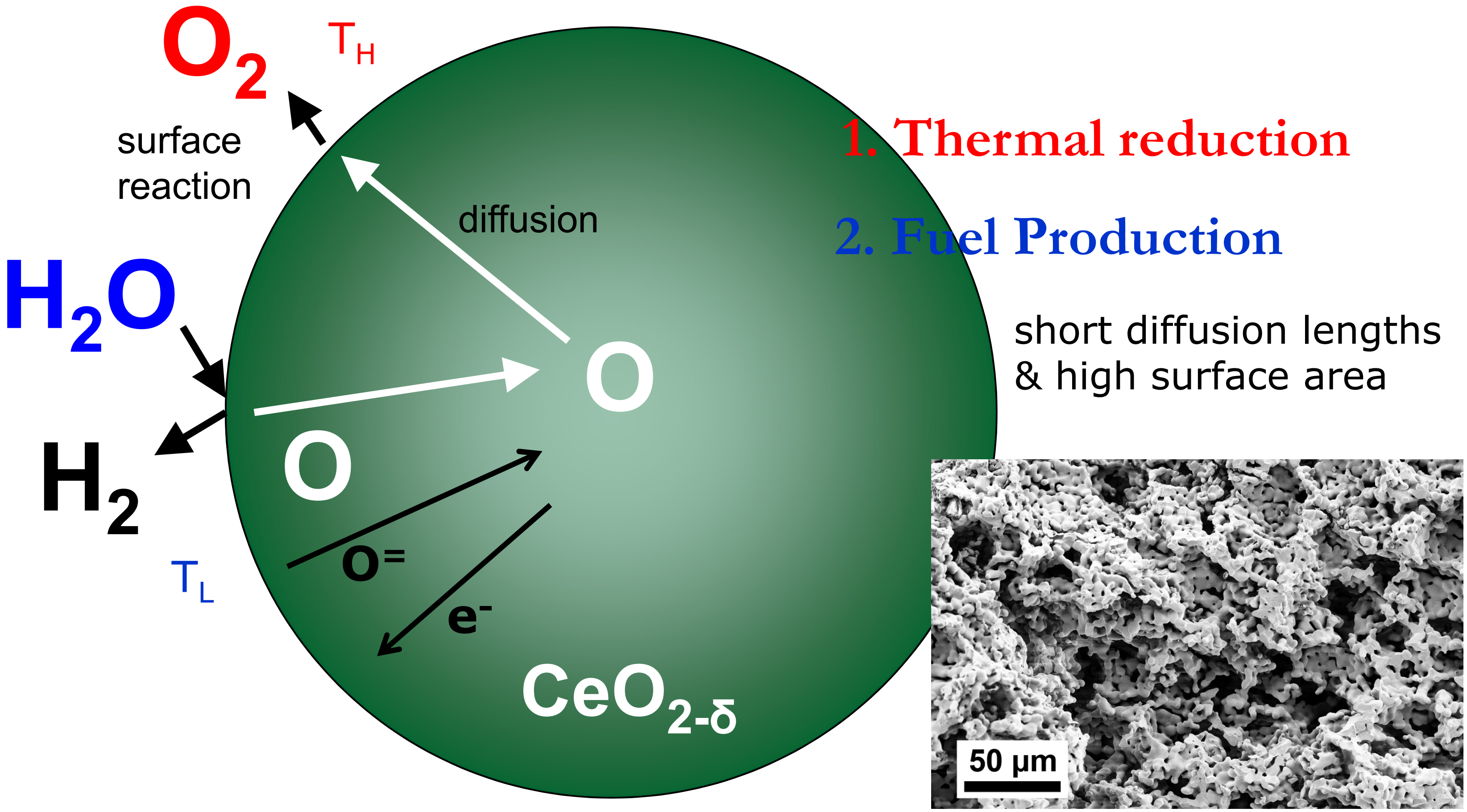
10 ppm O_2

Nonstoichiometry in CeO_2

Panlener et al., *J Phys. Chem. Solids*, (1975).



Kinetics of Reduction and Oxidation

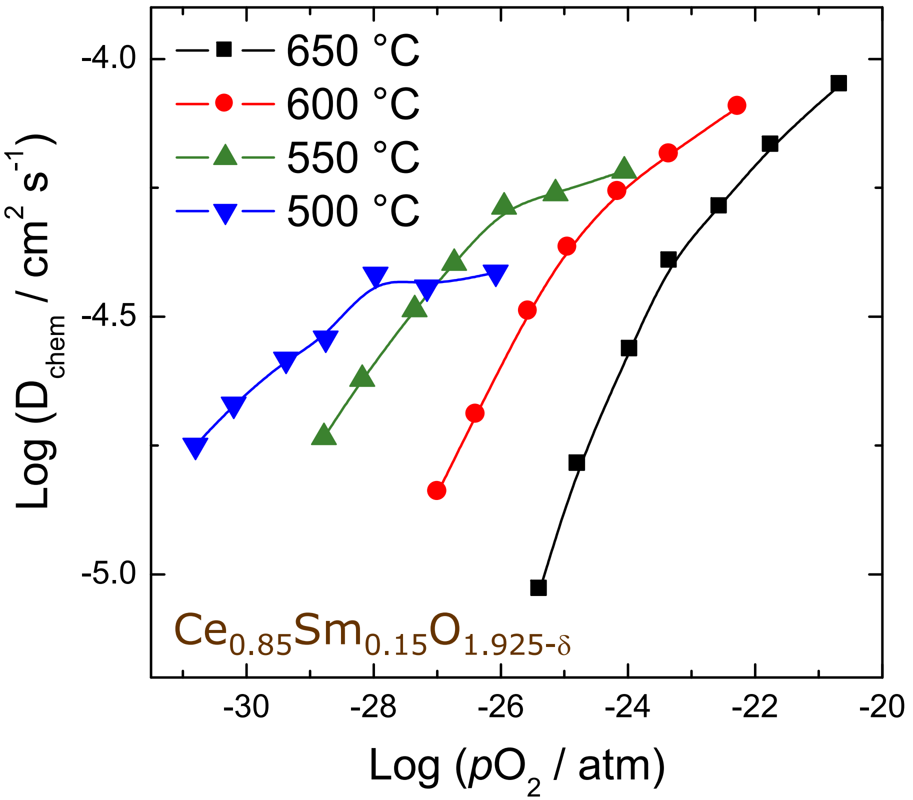


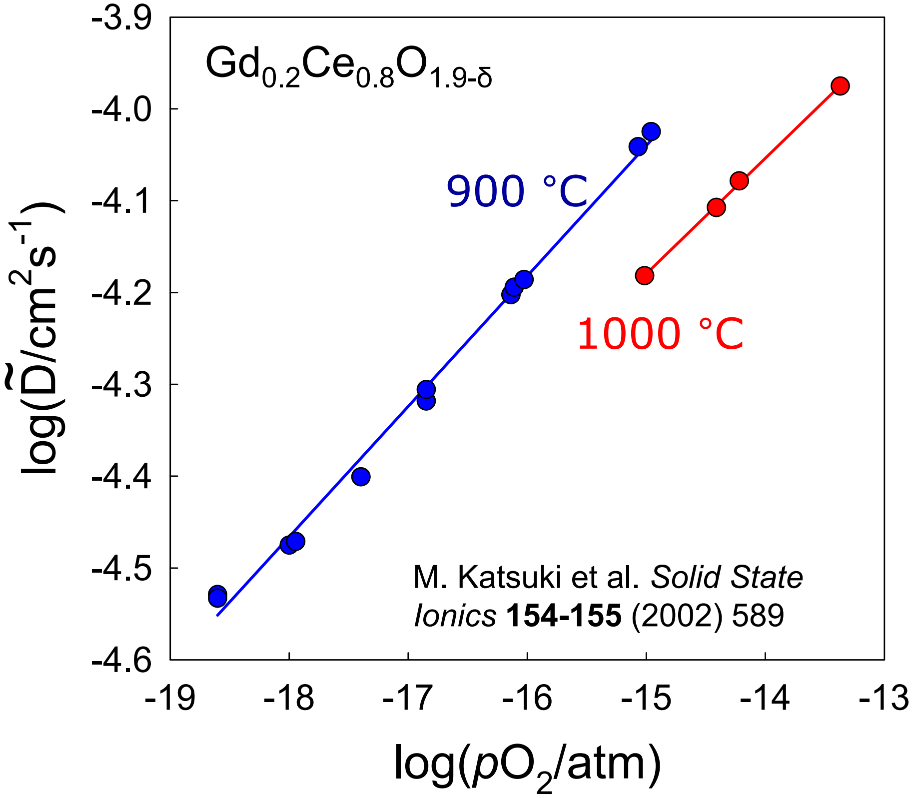
1. **Thermal reduction**

2. **Fuel Production**

short diffusion lengths
& high surface area

Kinetics of Oxygen Release





M. Katsuki et al. *Solid State Ionics* **154-155** (2002) 589

T = 1500 °C, $pO_2 = 10^{-5}$ atm

extrapolate: $\tilde{D} \sim 10^{-3}$ cm^2s^{-1}

$$t = l^2 / 4\tilde{D}$$

~2 μm particles

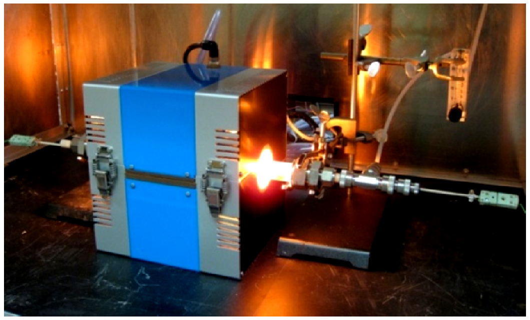
t ~ 10^{-5} s !!!

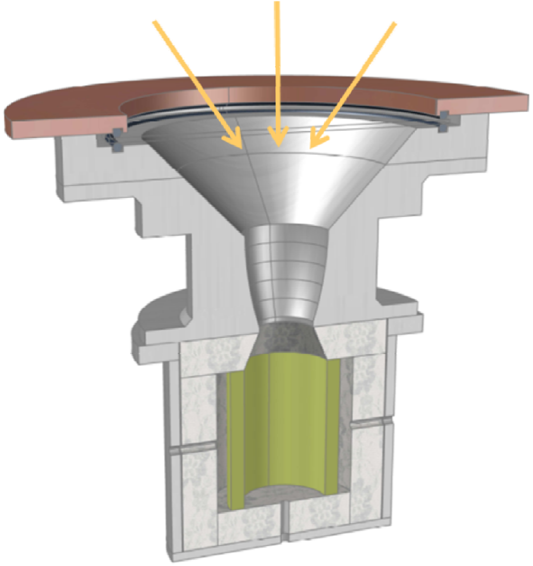
ZnO: 10^{-15} cm^2s^{-1}

$NiFe_2O_4$: 10^{-12} cm^2s^{-1}

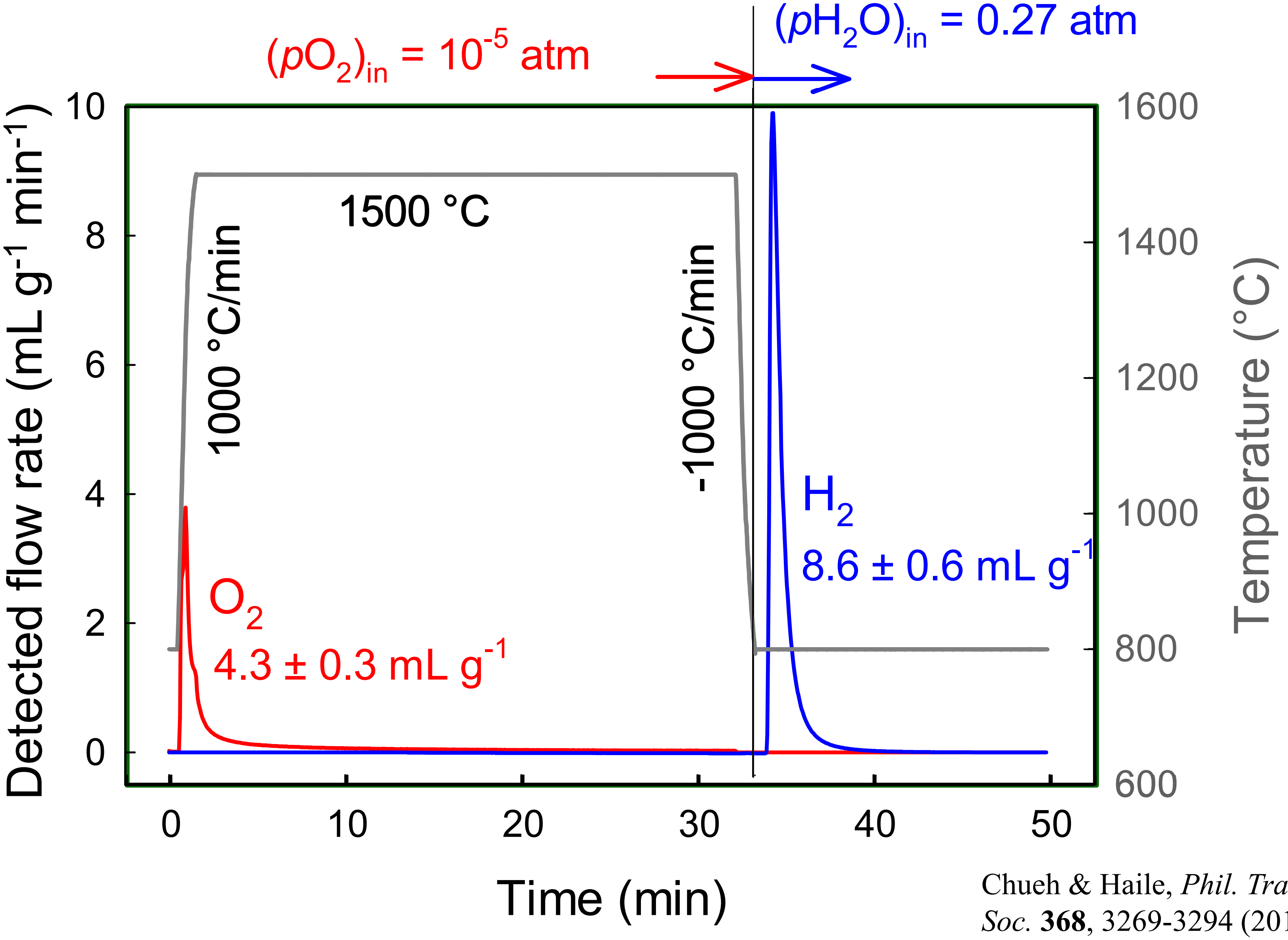
Progressive Demonstration

- Conventional Electric Furnace
  - Analysis by gas chromatography (quantitative)
  - Moderate temperatures, slow ramp rates
  - Surrogate reduction step using hydrogen
- IR Imaging Furnace
  - Analysis by mass spectrometry (rapid)
  - High temperatures and high ramp rates
  - Reduce under realistic gas conditions
- Solar Simulator Furnace
  - Almost direct fuels from sunlight
  - Exhaust gases to gas chromatograph
  - Challenging thermal design



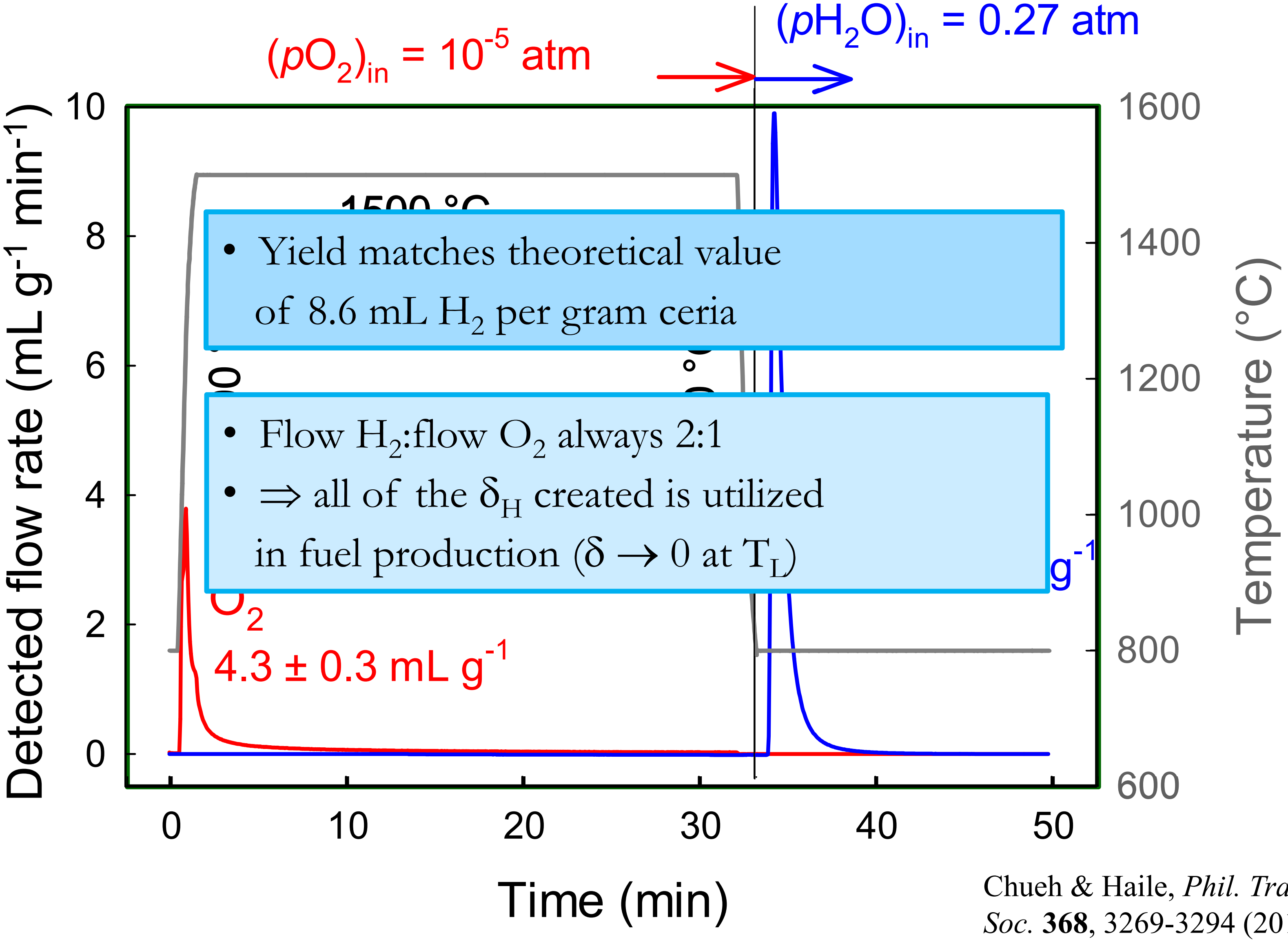


Thermochemical Cycling



Chueh & Haile, *Phil. Trans. R. Soc.* **368**, 3269-3294 (2010).

Thermochemical Cycling

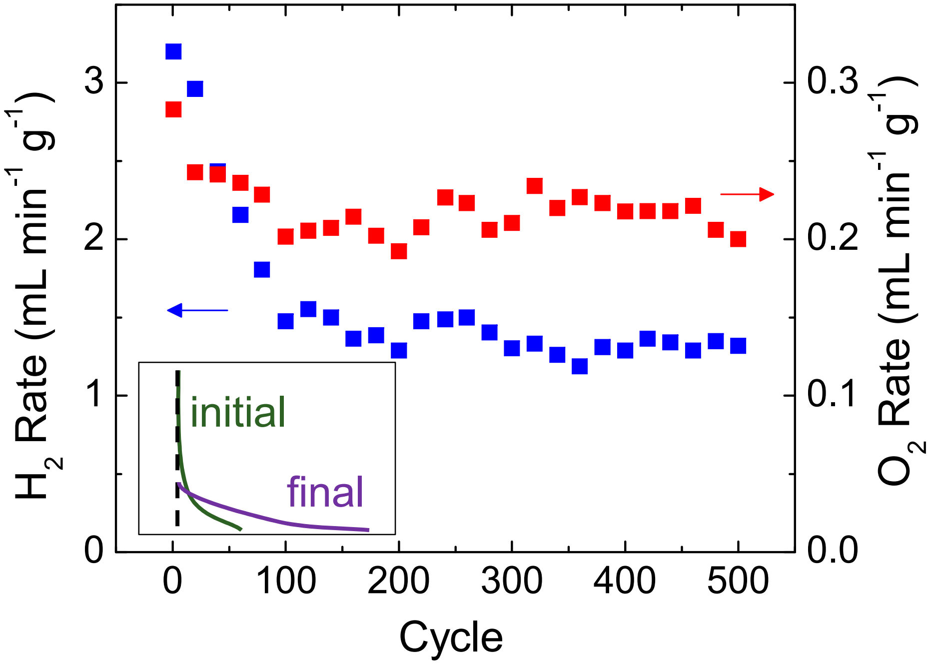


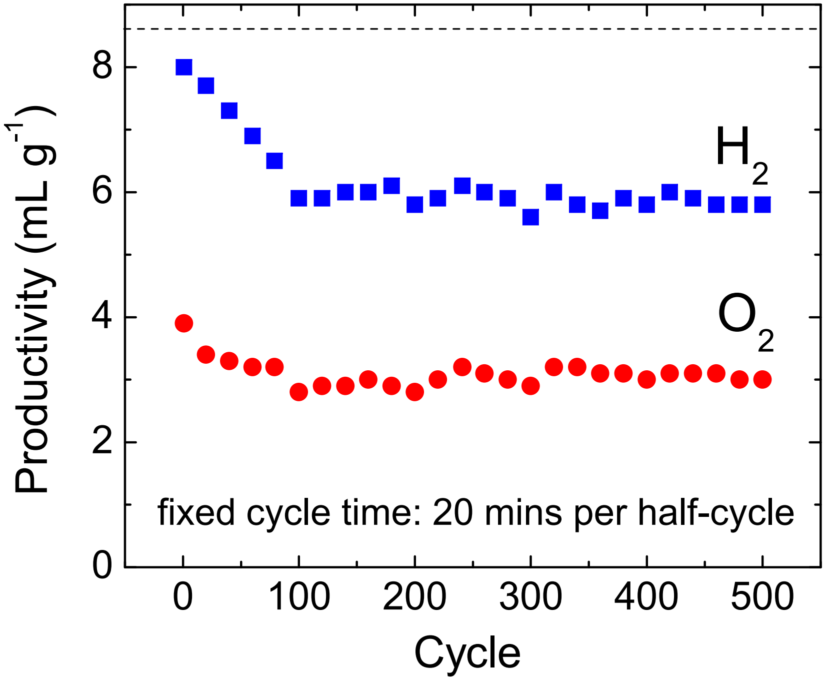
- Yield matches theoretical value of 8.6 mL H_2 per gram ceria

- Flow H_2:flow O_2 always 2:1
- ⇒ all of the δ_H created is utilized in fuel production ($\delta \rightarrow 0$ at T_L)

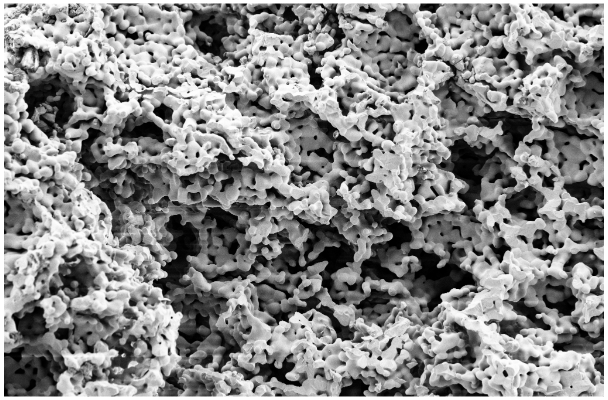
Chueh & Haile, *Phil. Trans. R. Soc.* **368**, 3269-3294 (2010).

Stability of Fuel Productivity



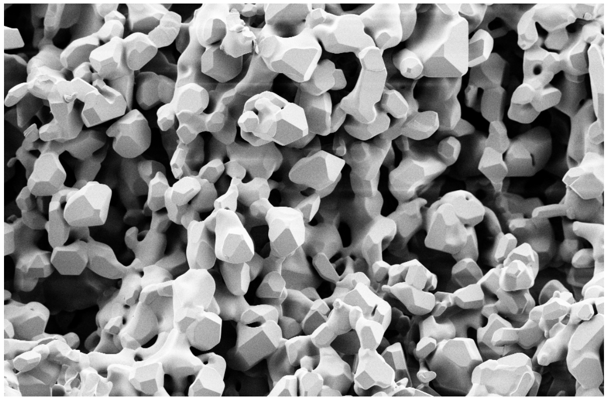


fixed cycle time: 20 mins per half-cycle



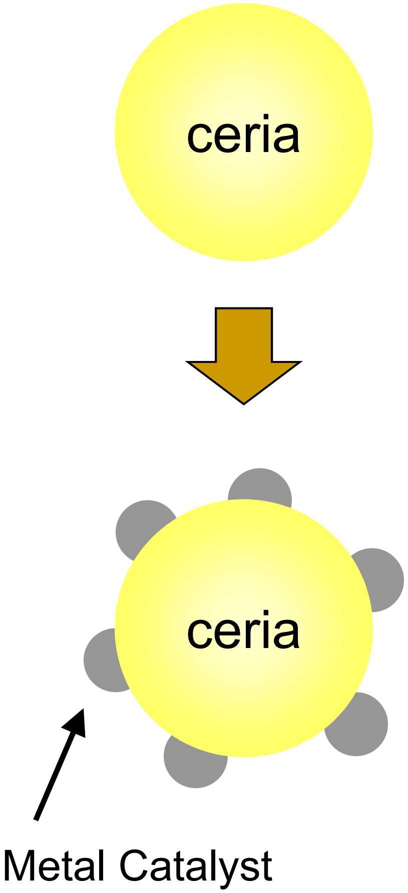
loss of surface area

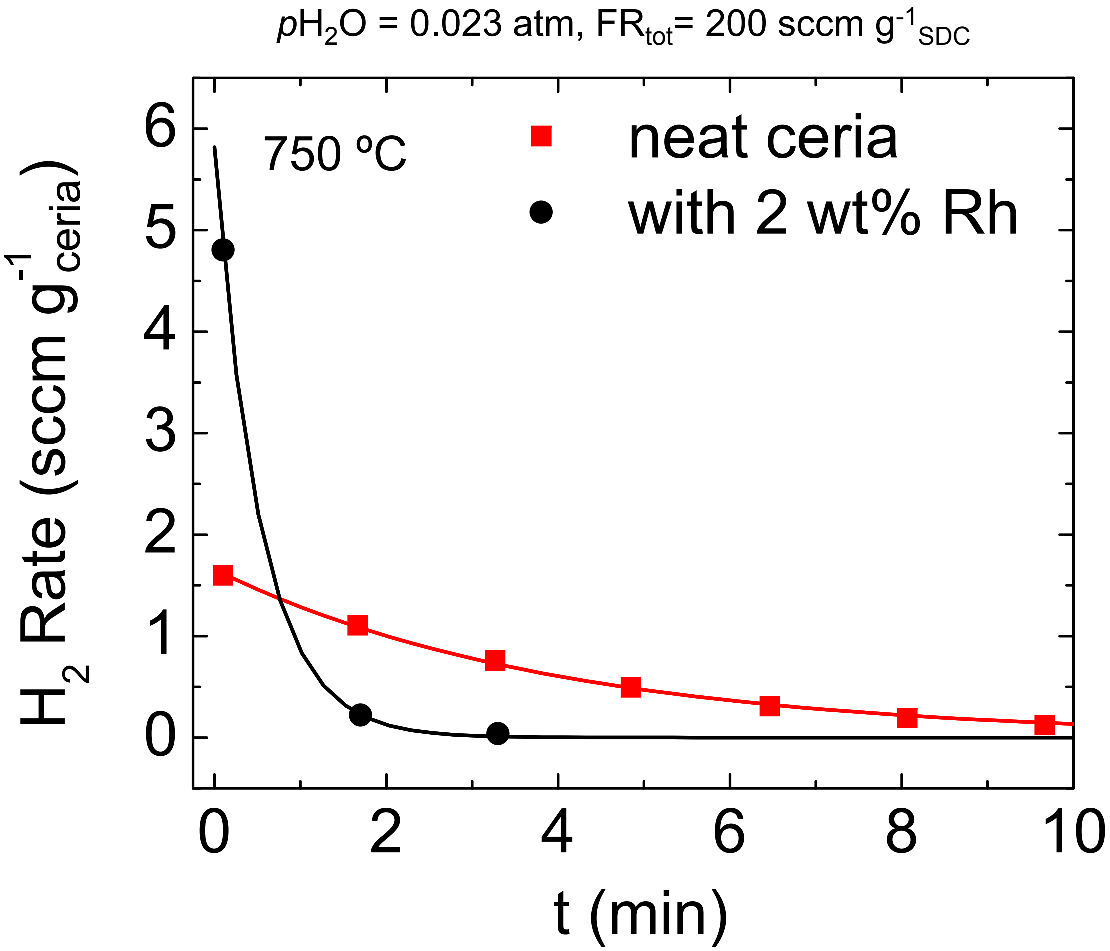
surface step is rate-limiting



Chueh & Haile, *Phil. Trans. R. Soc.* **368**, 3269-3294 (2010).

Rate Limiting Step

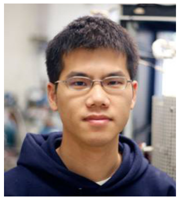


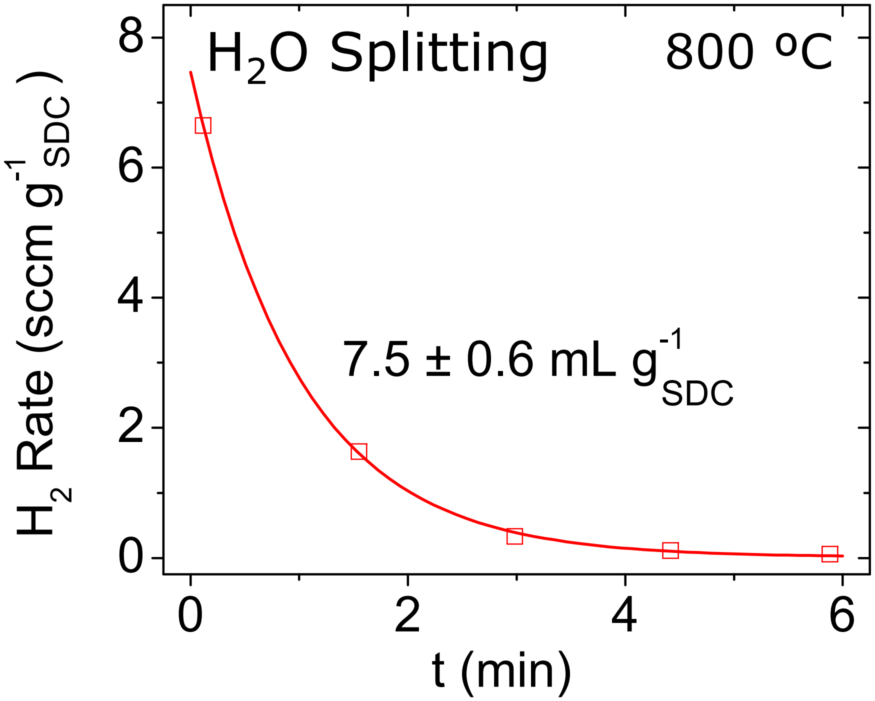


Catalyst improves kinetics → surface limited process

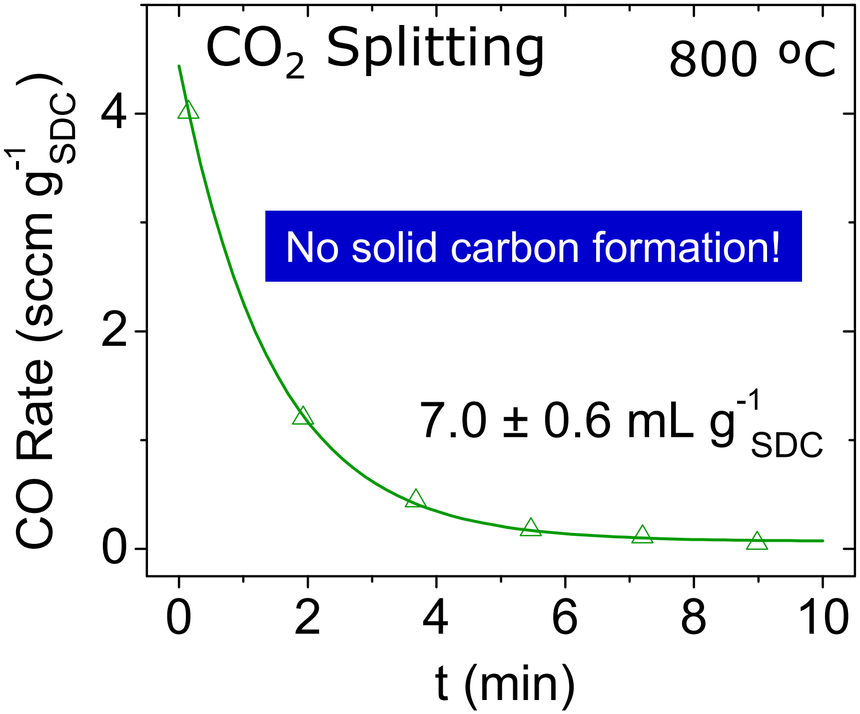
Chueh & Haile, *Phil. Trans. R. Soc.* **368**, 3269-3294 (2010).

Making the Fuel of Choice





pH$_2$O = 0.064 atm, FR$_{tot}$= 380 sccm g$^{-1}_{SDC}$



No solid carbon formation!

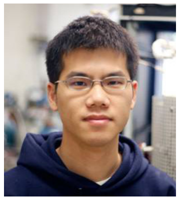
pCO$_2$ = 0.032 atm, FR$_{tot}$= 300 sccm g$^{-1}_{SDC}$

Complete utilization of ceria non-stoichiometry for fuel production

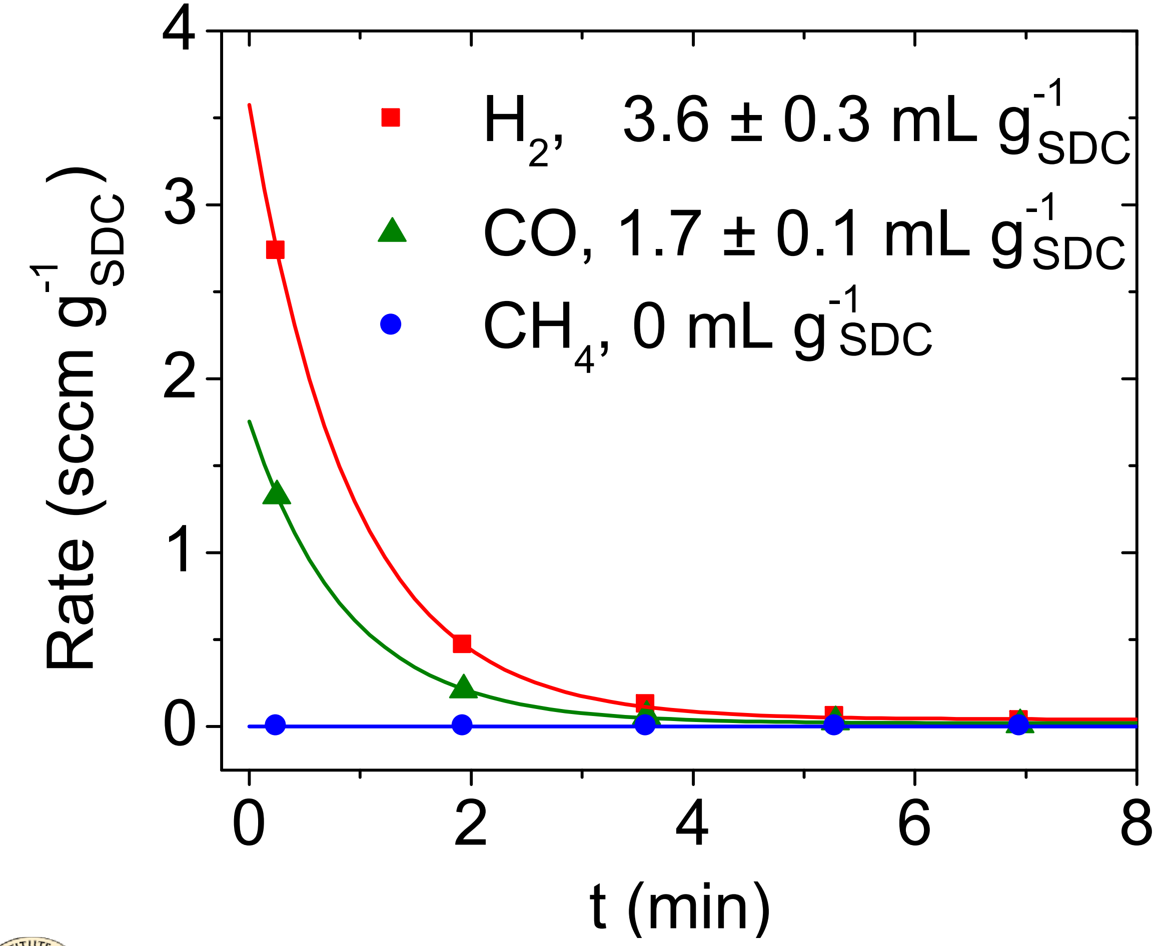
SDC = samaria doped ceria

Chueh & Haile, *Phil. Trans. R. Soc.* **368**, 3269-3294 (2010).

Making Syngas



pH_2O = 0.132 atm, pCO_2 = 0.066 atm, FR_{tot} = 40 sccm g^{-1}_{SDC}, 900 ºC



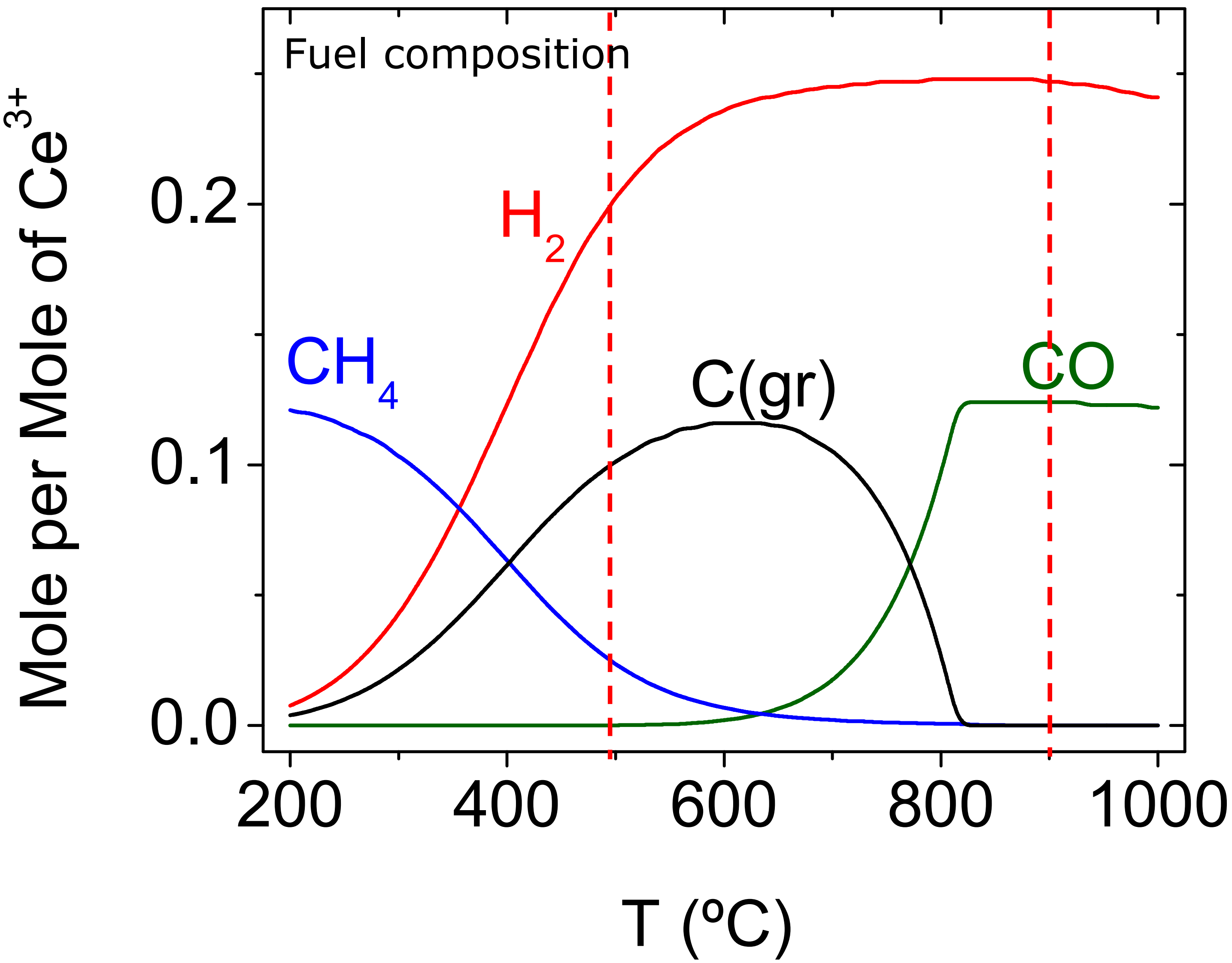
~ 20 mL min^{-1} g^{-1}

900 ºC; 0.66 atm pH_2O; 0.34 atm pCO_2

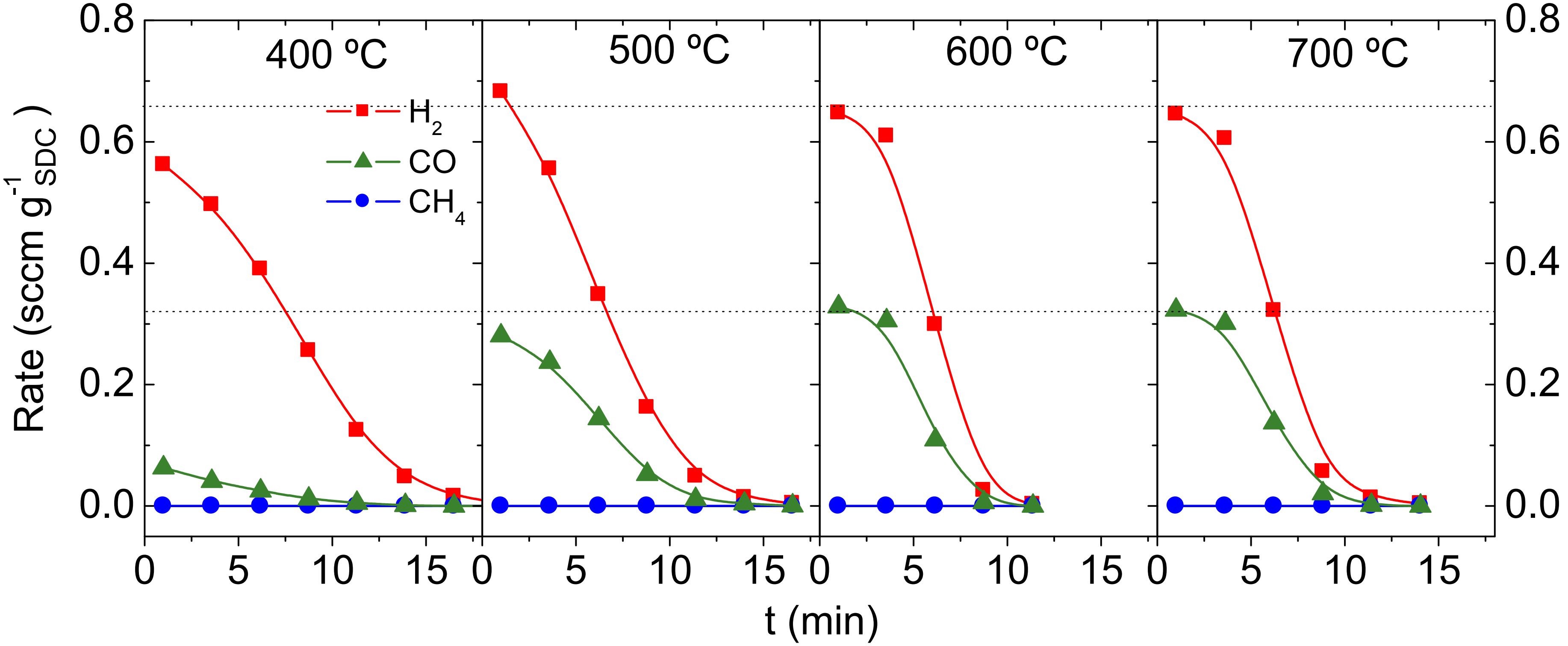
Chueh & Haile, *ChemSusChem*, **2**, 735-769 (2009).

Complete utilization of ceria nonstoichiometry

Thermodynamic Prediction

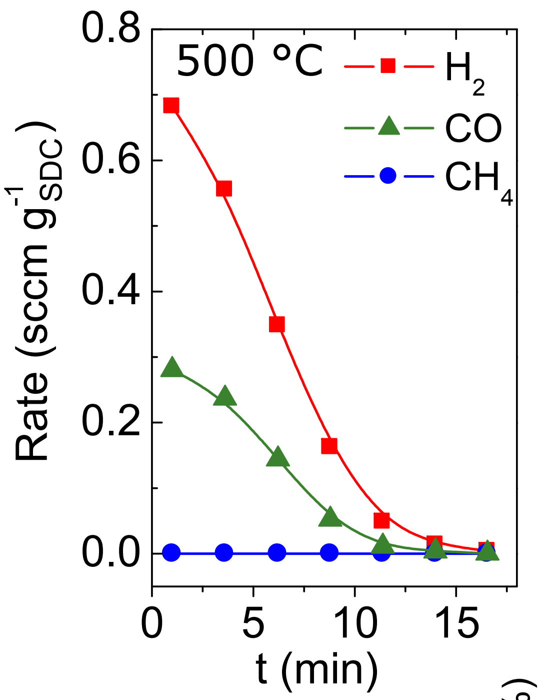


Measured Fuel Composition


pH_2O = 0.064 atm, pCO_2 = 0.032 atm, FR_{tot} = 10 sccm g^{-1}_{SDC}

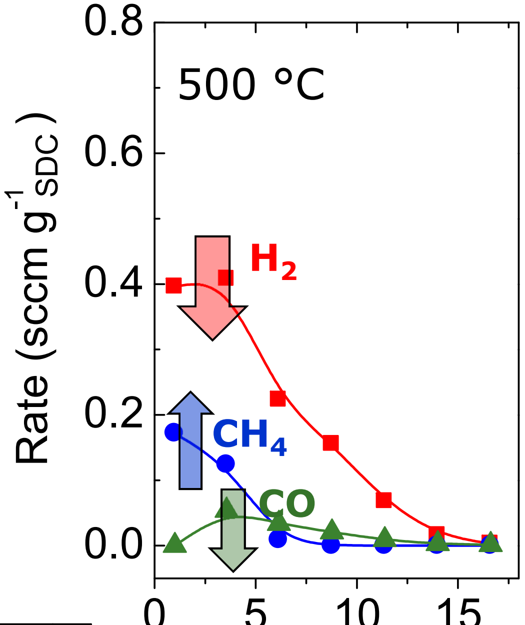
100% syngas selectivity – no methane produced

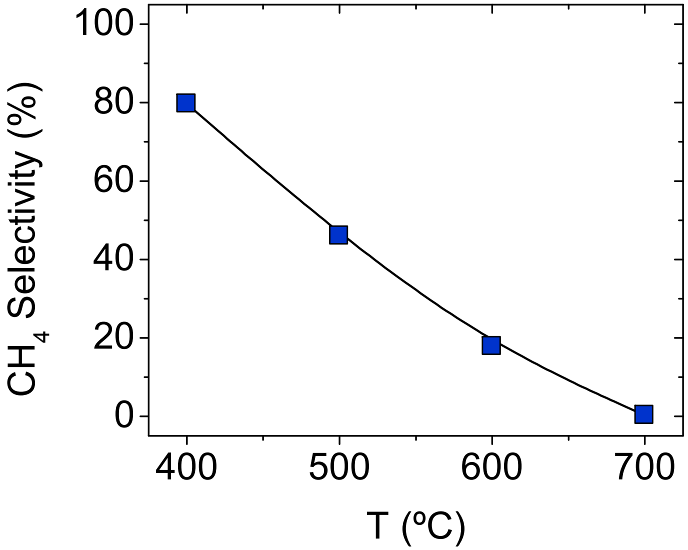
Producing Methane?



pH_2O = 0.064 atm
pCO_2 = 0.032 atm
FR_{tot}= 10 sccm g^{-1}_{SDC}

Add Ni catalyst

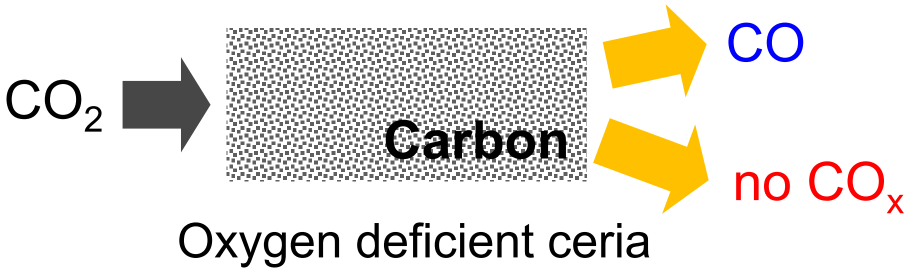




due to "transient" carbon deposition

Chueh & Haile, *ChemSusChem*, **2**, 735-769 (2009).

Transient Carbon Deposition on Ni



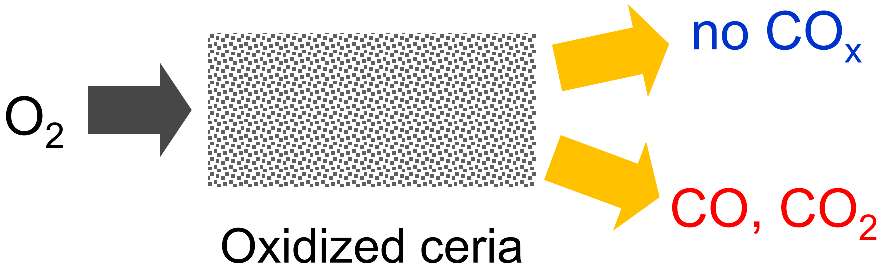
CO_2

Carbon

CO

no CO_x

Oxygen deficient ceria

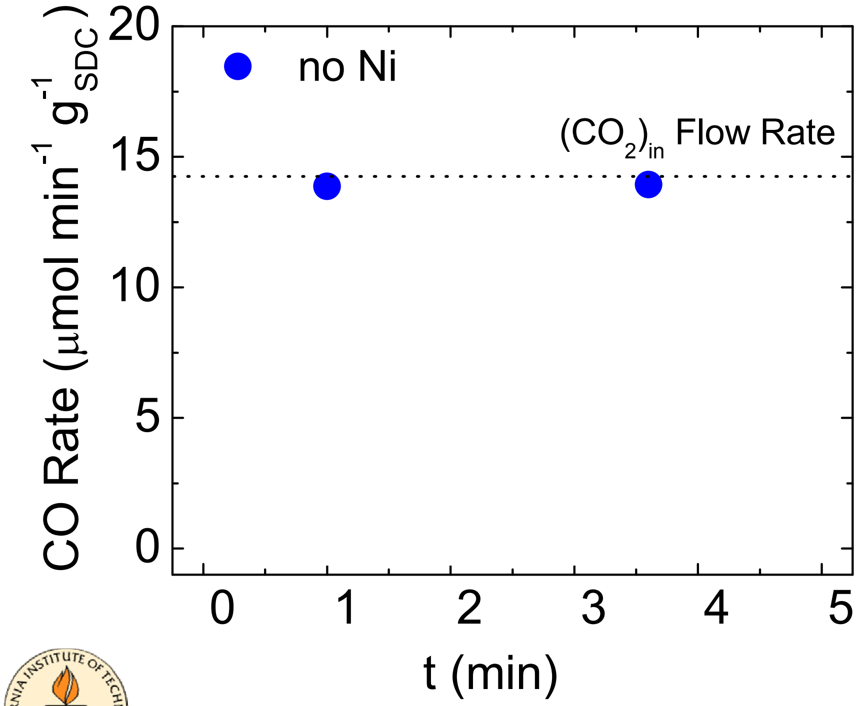


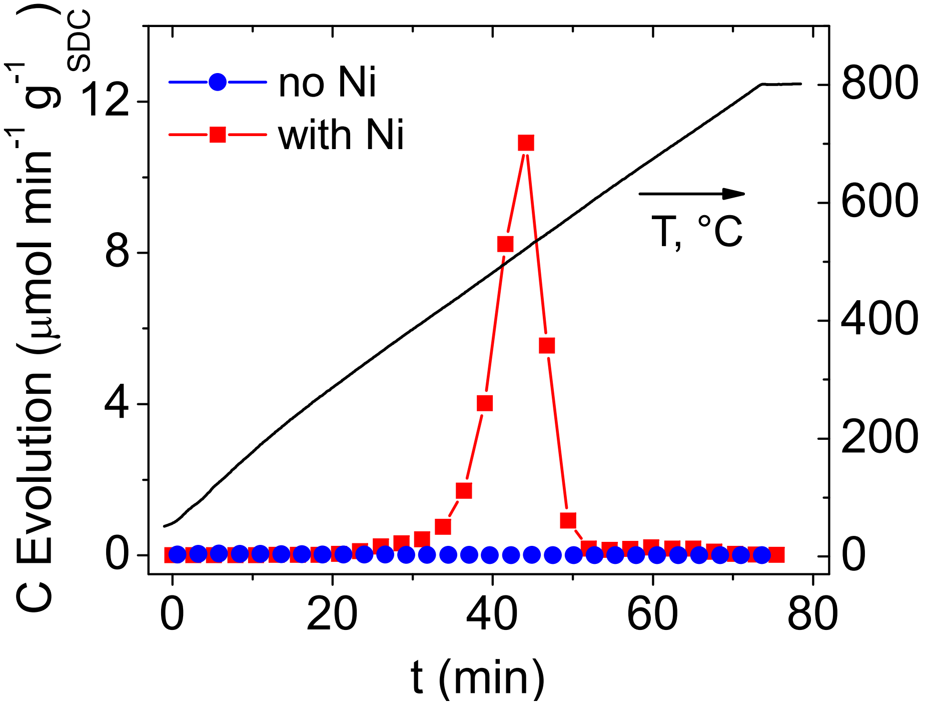
O_2

no CO_x

CO, CO_2

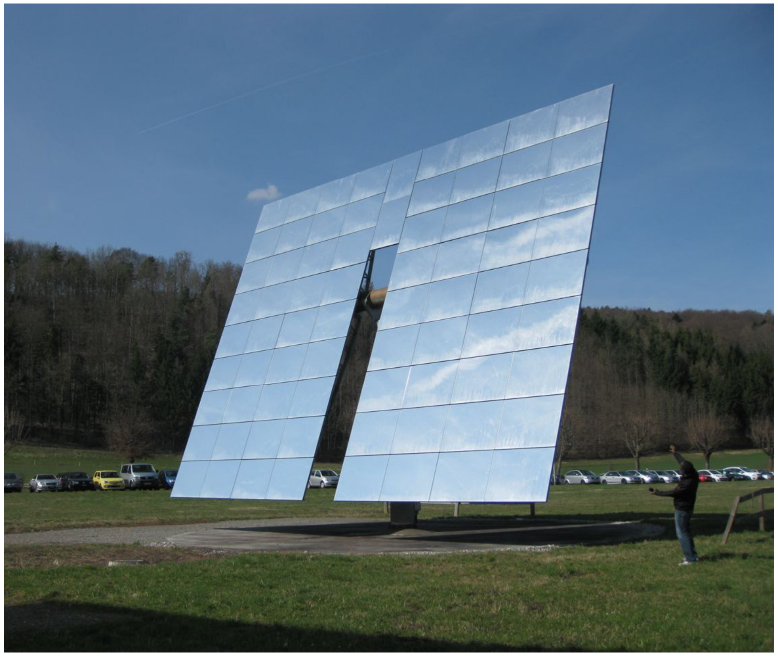
Oxidized ceria

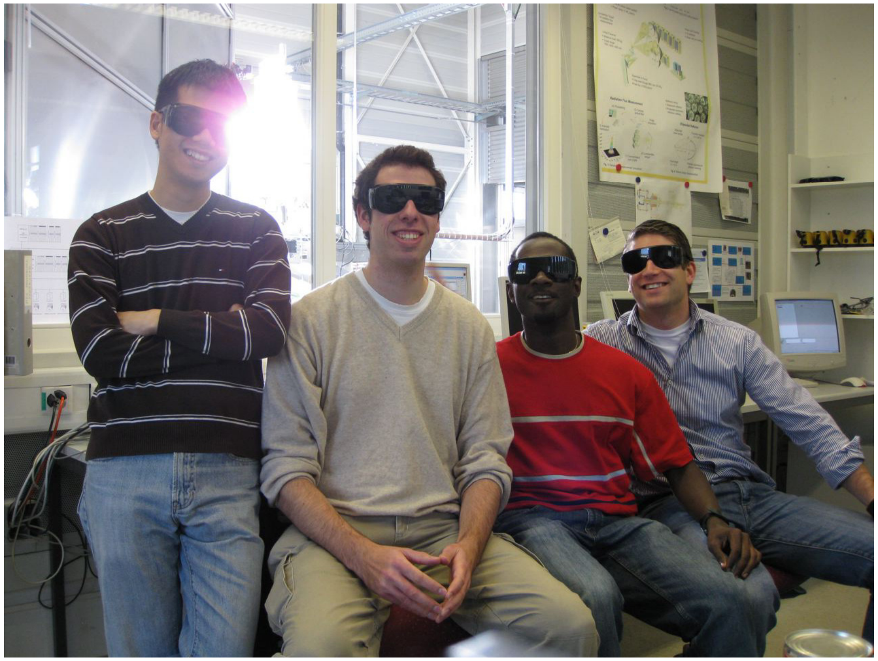




Operating on Photons

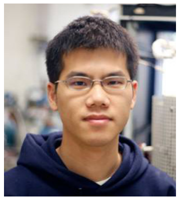
Switzerland in March

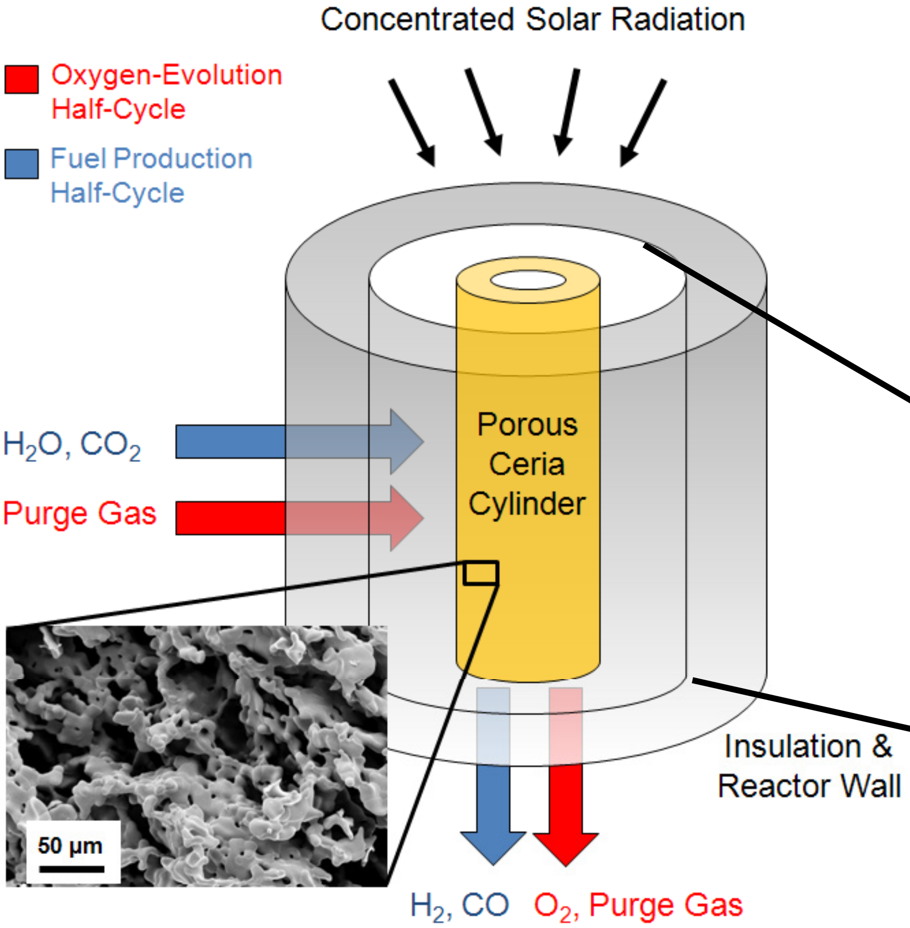


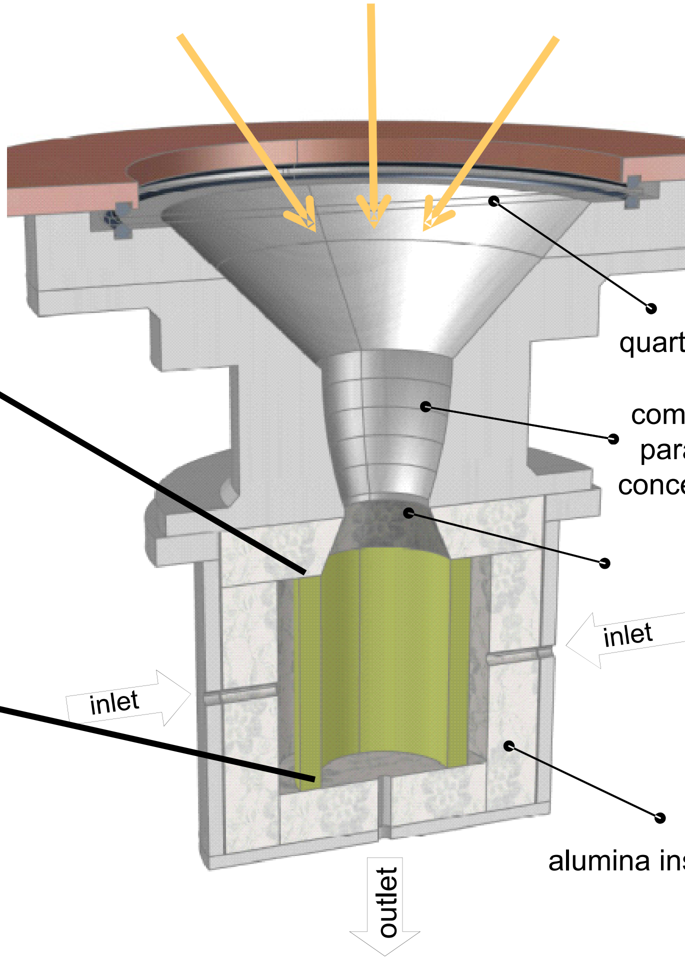


Collaboration with Aldo Steinfeld, ETH Zurich and the Paul Scherer Institute

Under Simulated Solar Radiation

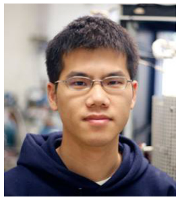


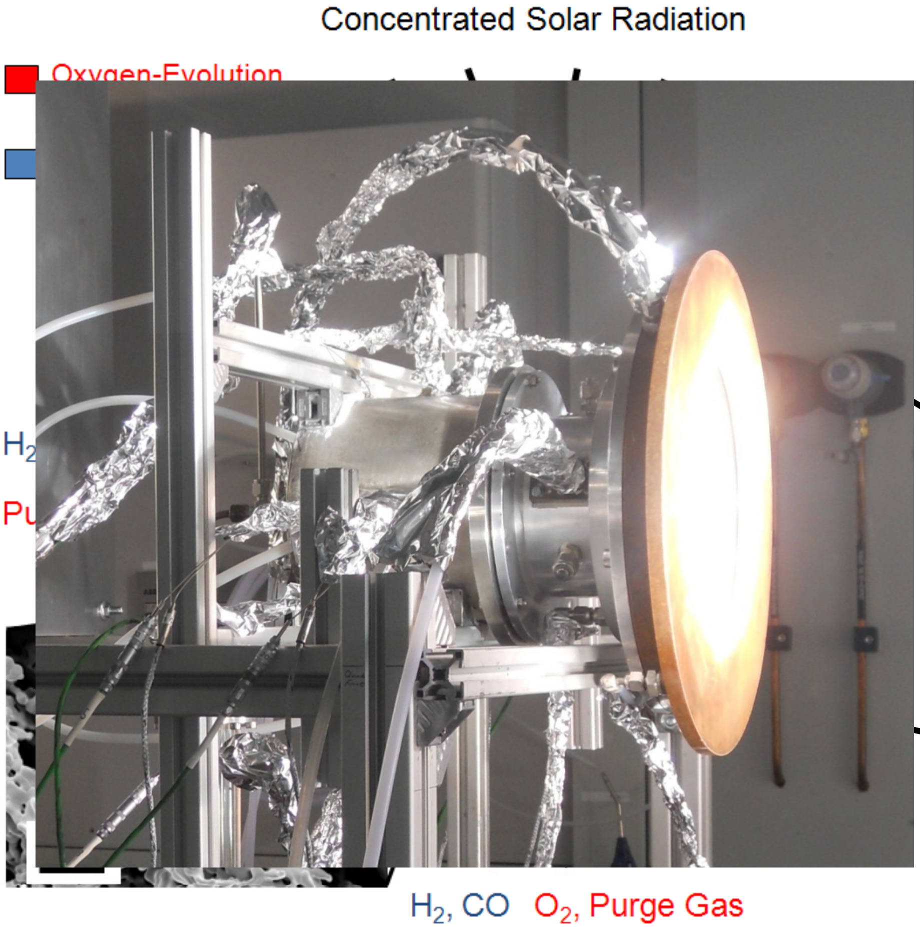


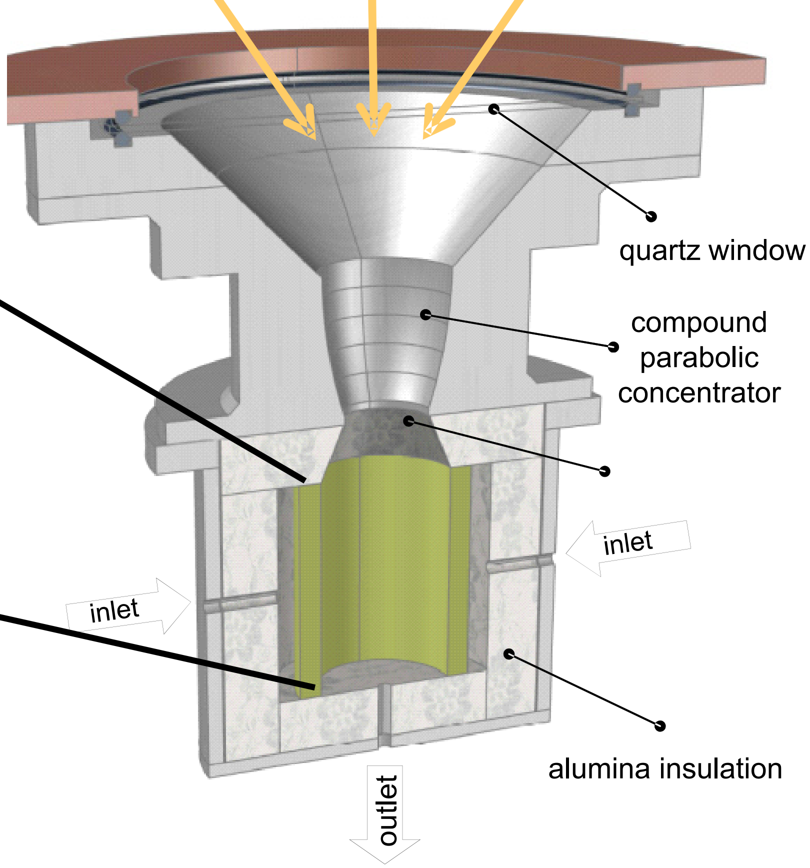


Chueh et al. *Science* **330**, 1797-1801 (2010).

Under Simulated Solar Radiation

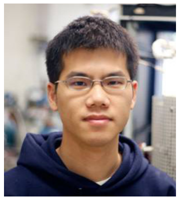




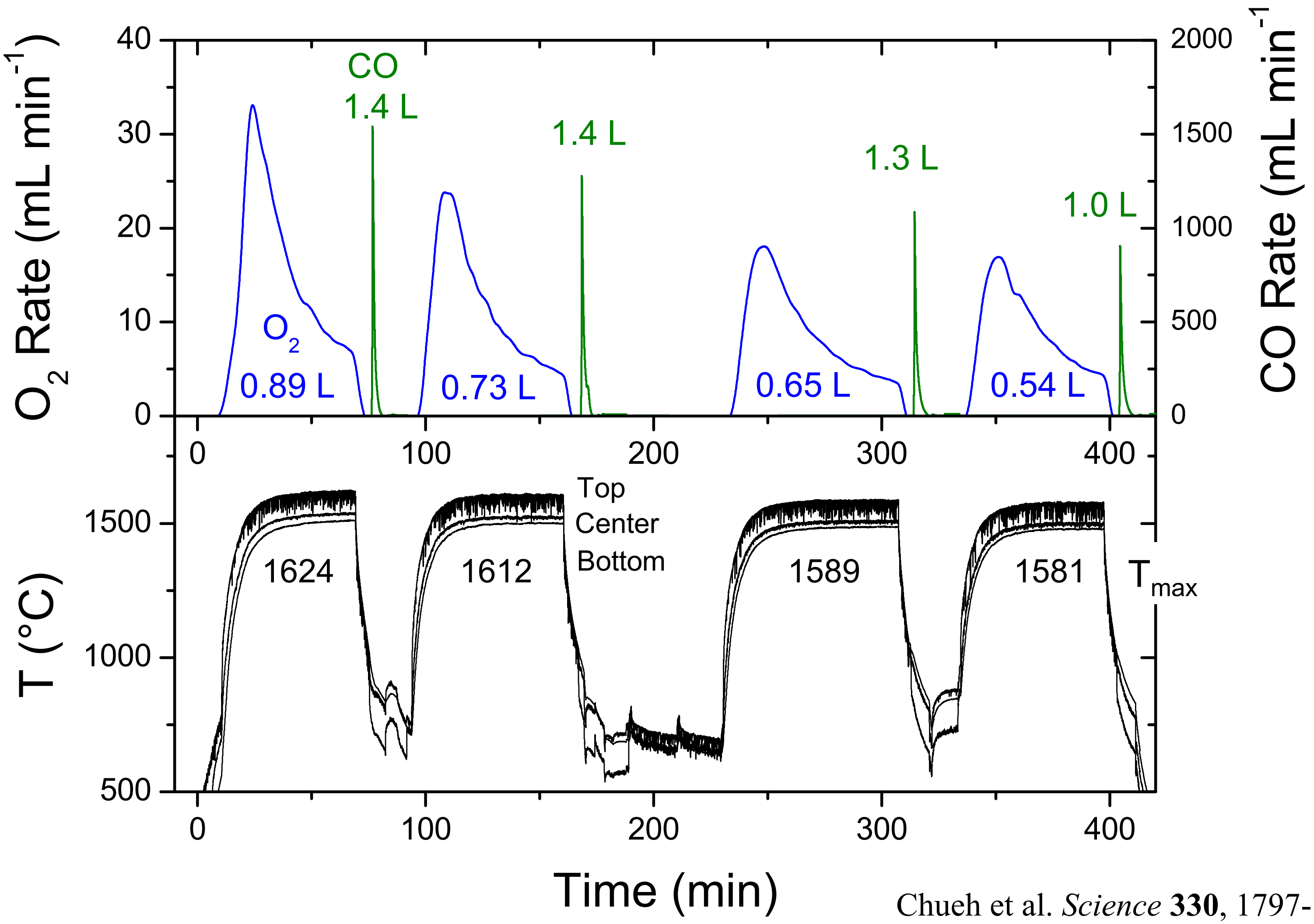


Chueh et al. *Science* **330**, 1797-1801 (2010).

Under Simulated Solar Radiation



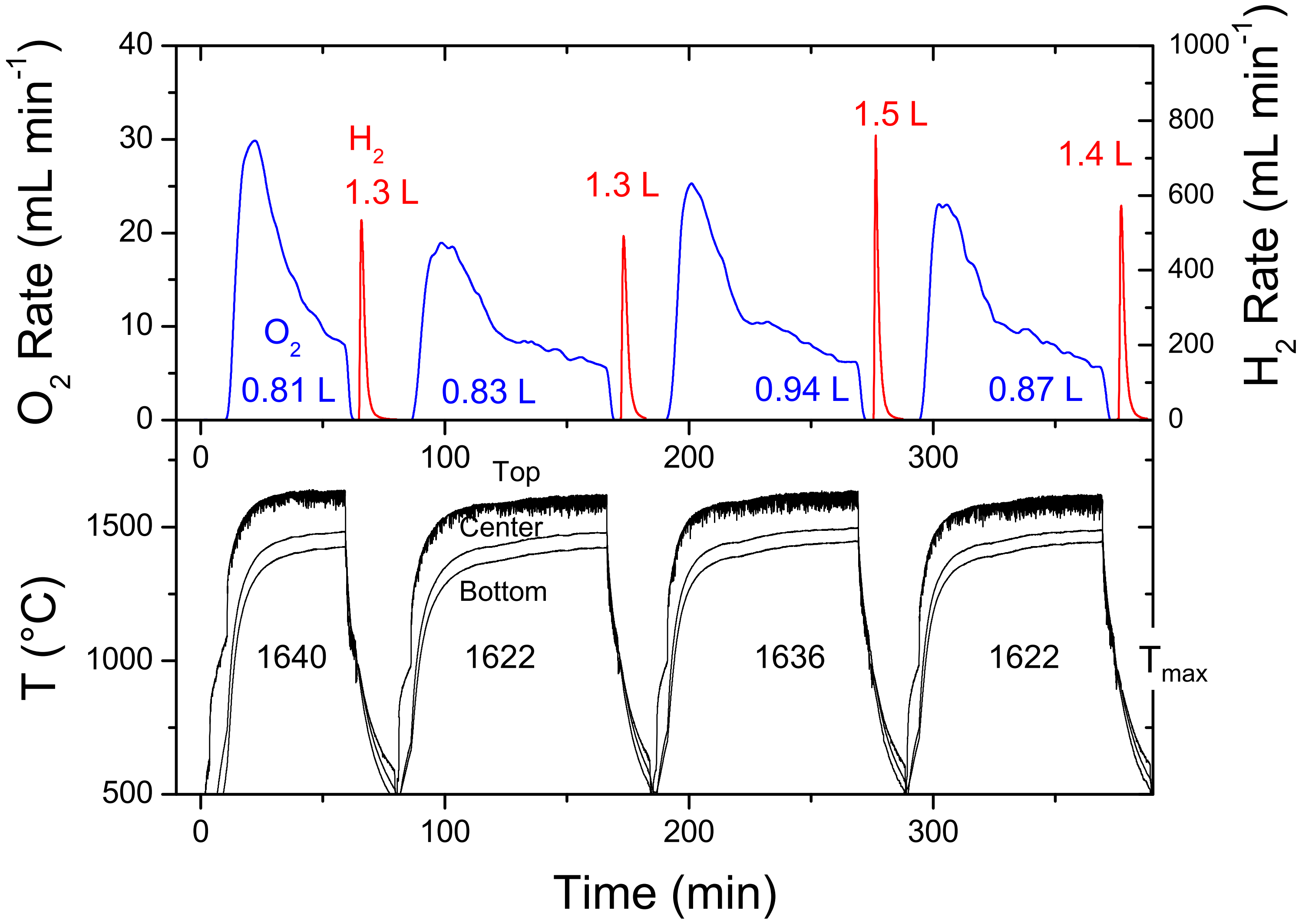
CO_2 dissociation



Chueh et al. *Science* **330**, 1797-1801 (2010).

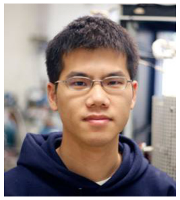
Under Simulated Solar Radiation

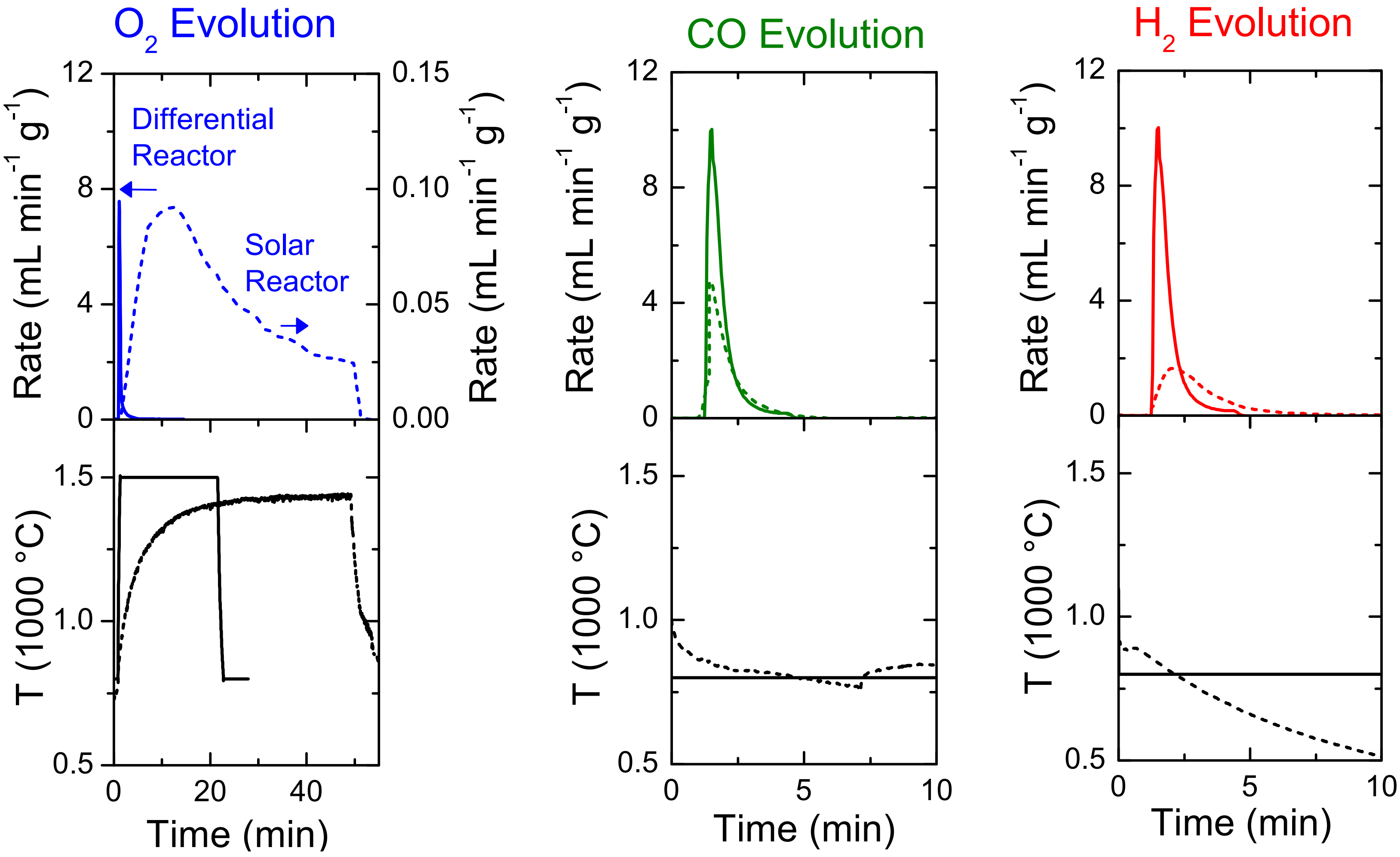
H_2O dissociation



Impact of Thermal Management

Chueh et al. *Science* **330**, 1797-1801 (2010).





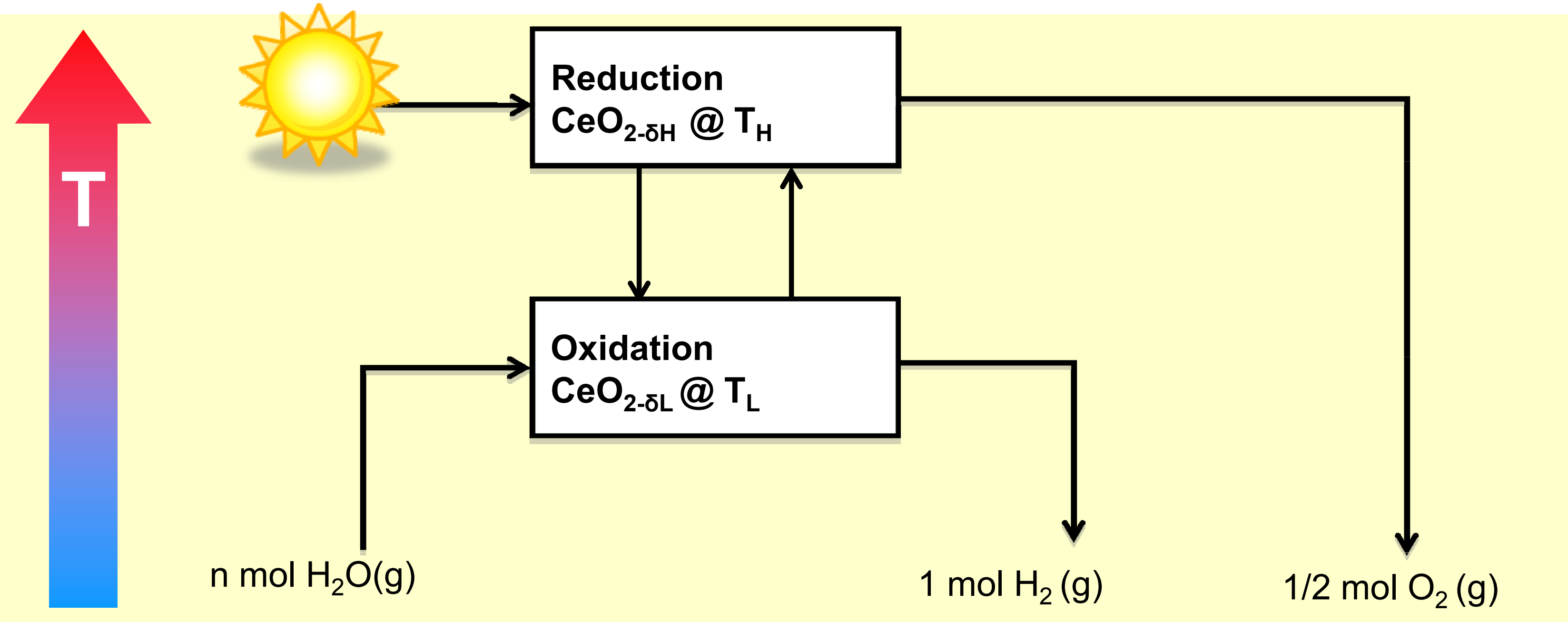
Heat losses in solar reactor have major detrimental impact on efficiency

Actual Reactor Efficiency

$$\eta = \frac{r_{fuel}\Delta H_{fuel}}{P_{solar} + r_{inert}E_{inert}}$$

- Estimate at 0.5 to 1%
  - Reactor heat-up is slow ⇒ P_{solar} is large
    - Heat loss through insulation
    - Re-radiation losses through quartz window
  - Material keeps up with heating rate
    - Immediate efficiency improvements from better reactor design
    - No need to enhance surface reaction rates
  - Material with lower temperature cycling
    - Would ease requirements on reactor design

Thermodynamic Efficiency



T

Reduction
$CeO_{2-\delta H}$ @ T_H

Oxidation
$CeO_{2-\delta L}$ @ T_L

n mol H_2O(g)

1 mol H_2 (g)

1/2 mol O_2 (g)

$$\eta = \eta_{solar-thermal} \times \eta_{thermal-fuel} = \eta_{solar-thermal} \times \frac{285.8kJ}{\Delta H_{input}}$$

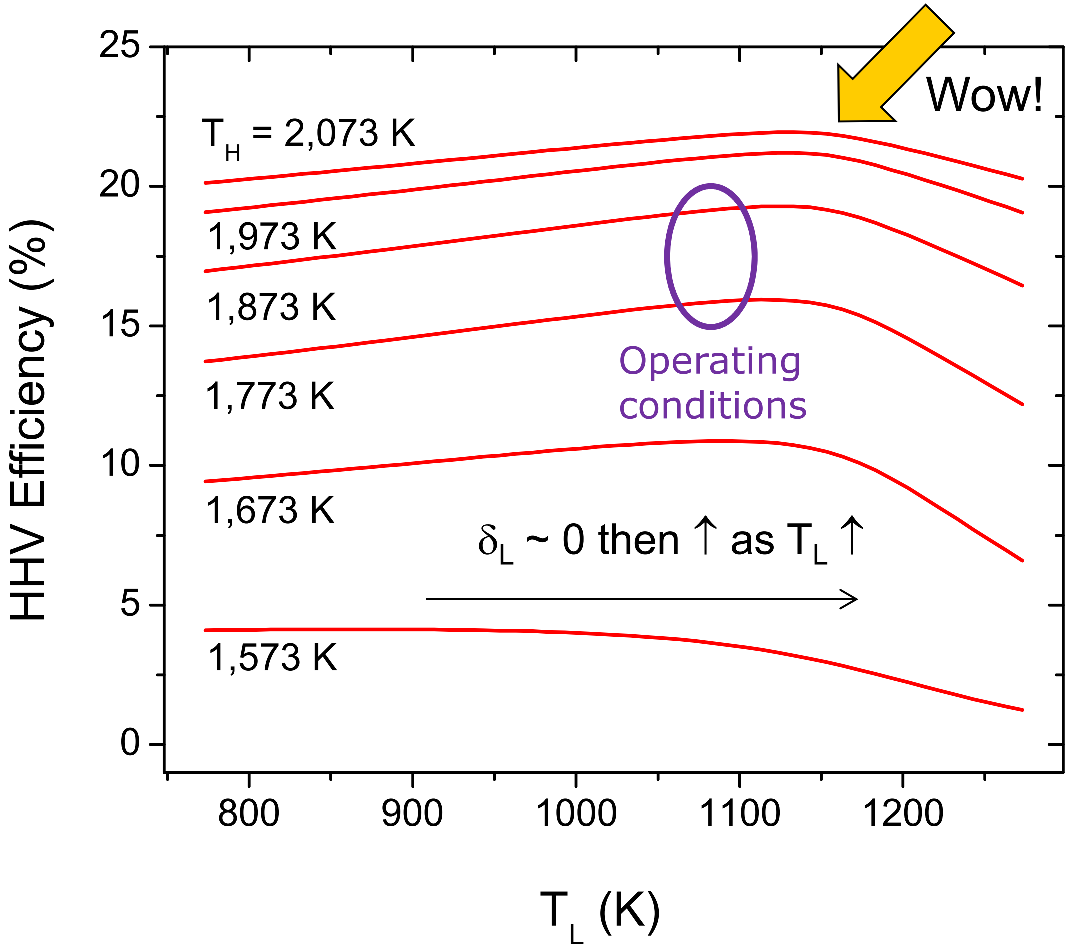
$\Delta H_{input} =$ Boil and heat water to T_L + Heat ceria from T_L to T_H + Reduce ceria

Influence of Cycling Parameters

decreasing ΔT lowers waste heat

too small ΔT generates too little fuel

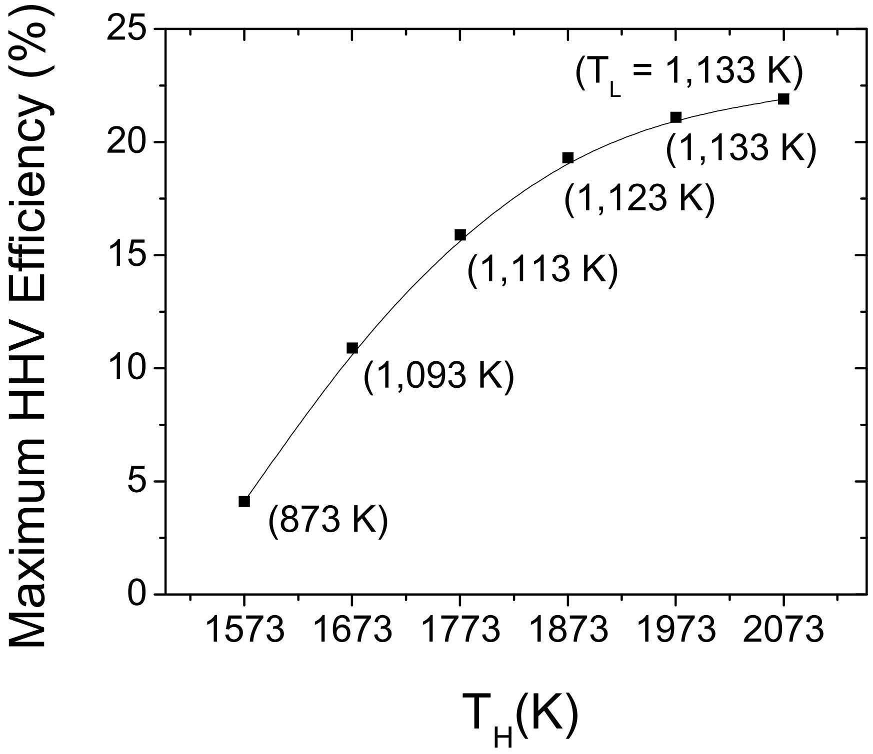
δ_H ↑ as T_H ↑

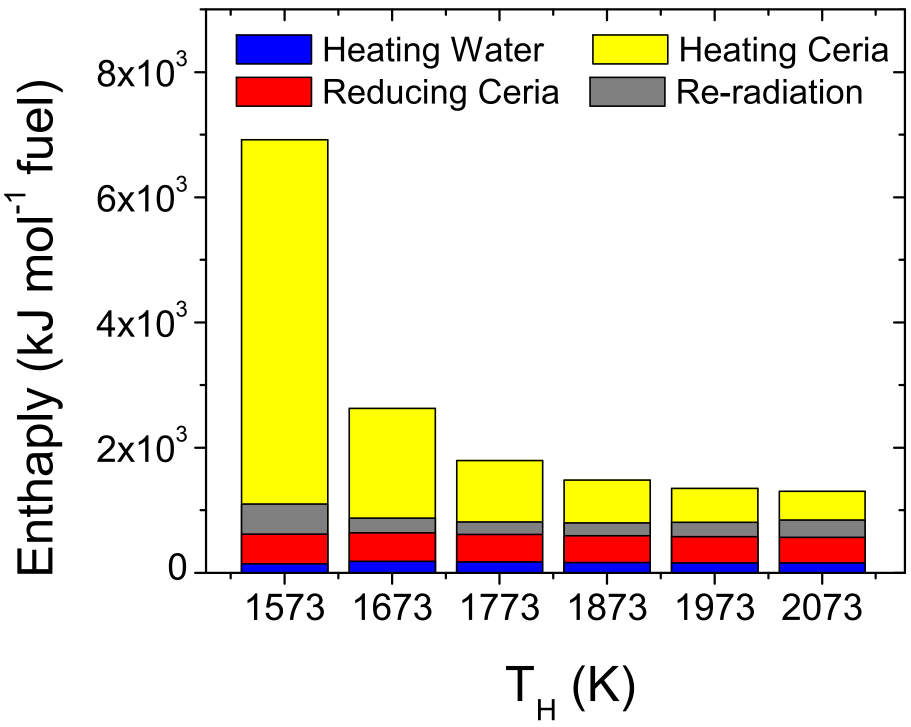


Analysis ignores potential of heat recovery

Maximal Efficiency

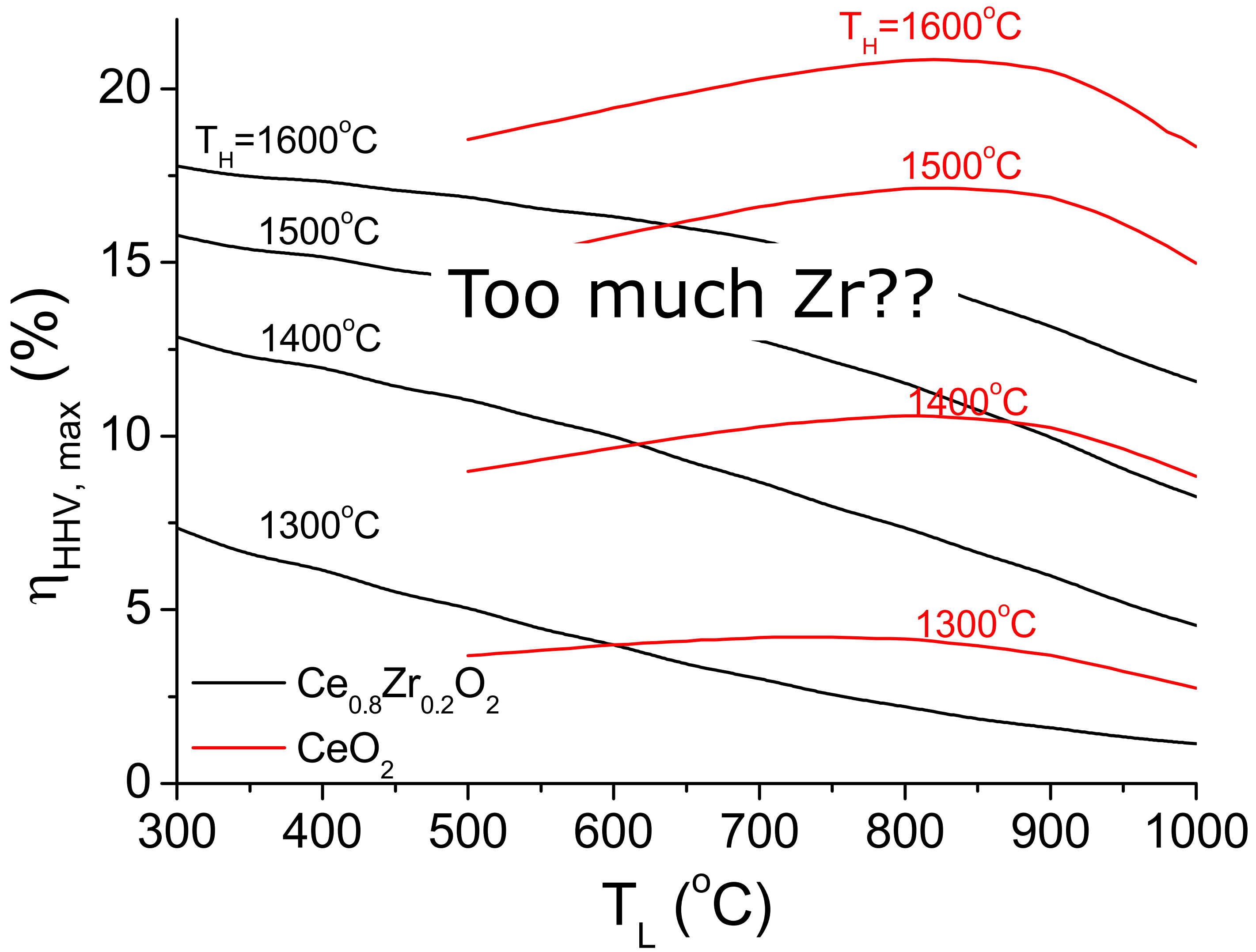
Increasing T_H increases fuel output per cycle, increases efficiency



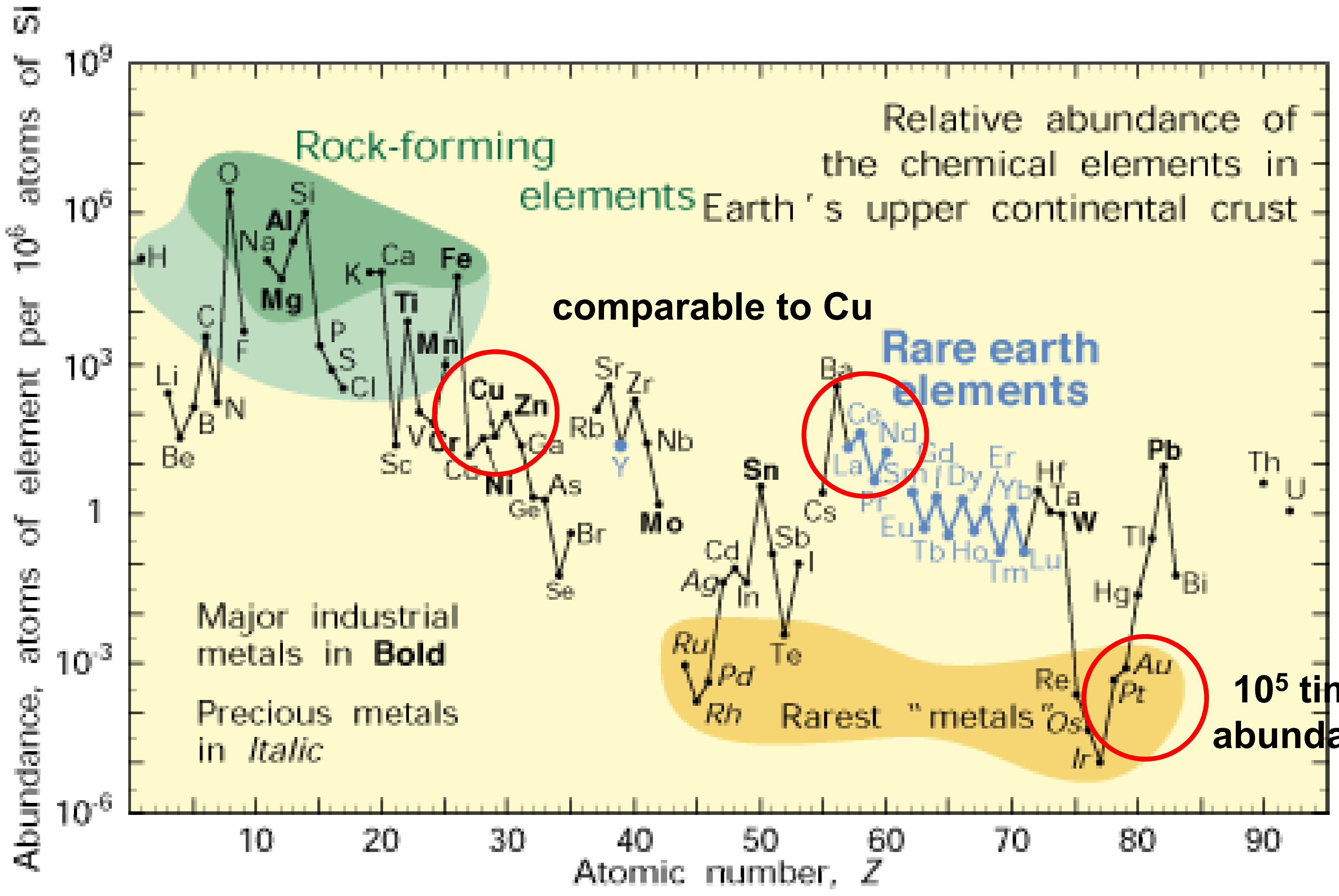


Diminishing returns due to “fixed costs” on a per mole fuel basis

Influence of Zr on Efficiency



Earth Abundance



comparable to Cu

10^5 times more abundant than Pt

Source: USGS

~ 40 MT world reserve

Conclusions & Challenges

Conclusion: *Ceria based materials work *very* well*

Chemical Challenge

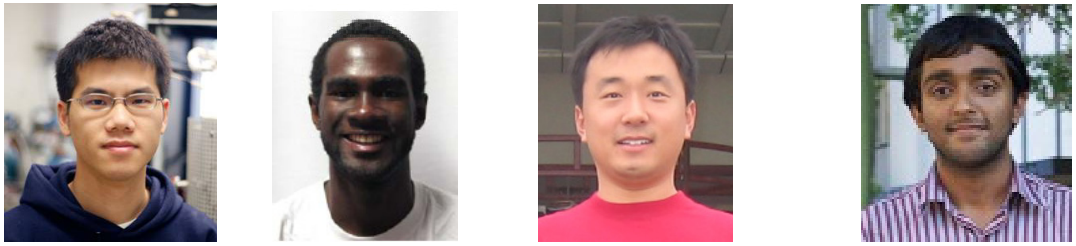
- Design of new materials
  - Operability at lower temperature
  - Wider nonstoichiometry range
  - Maintain structural stability, non-volatility?
- Forays into ZrO_2-CeO_2 system
  - Zr enhances reducibility, but not necessarily fuel productivity
  - Zr dramatically lowers oxygen chemical diffusivity

Engineering Challenges

- Reactor design: solar, thermal, fluid, mass transfer
- Efficiency requires high degree of heat recovery
- …

Acknowledgments

- William, Danien, Yong, Chirranjeevi (BG)



- Aldo Steinfeld & students

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