The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
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IAEA
International Atomic Energy Agency

2269-11

Workshop on New Materials for Renewable Energy

17 - 21 October 2011

SOLAR CELLS
(Solar-driven thermochemical dissociation of Co2 and H2O using ceria)

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Solar-Driven Thermochemical Dissociation of CO_2 and H_2O Using Ceria

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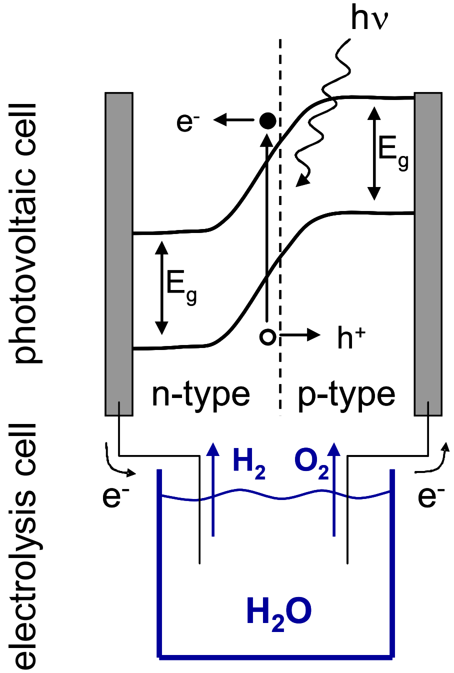
California Institute of Technology

"Capture and Conversion of CO_2 into Sustainable Fuels"
April 14-15, 2011; Riso, Denmark

Using the Sun to Make Fuels

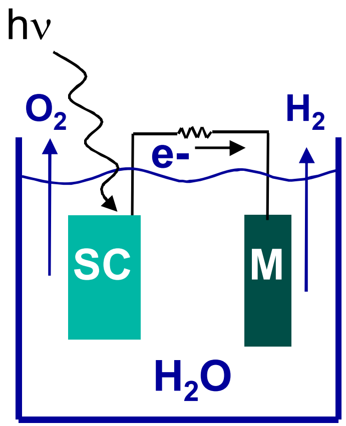
$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2 \qquad CO_2 \rightarrow CO + \tfrac{1}{2}O_2$$

- Solar electricity + electrolysis



- Separate components

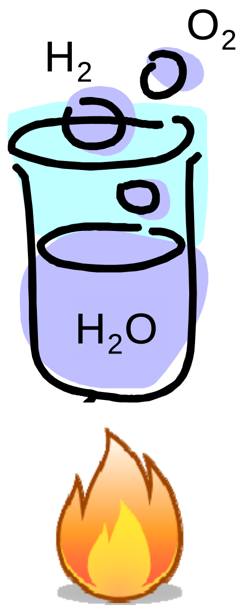
- Photolysis



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

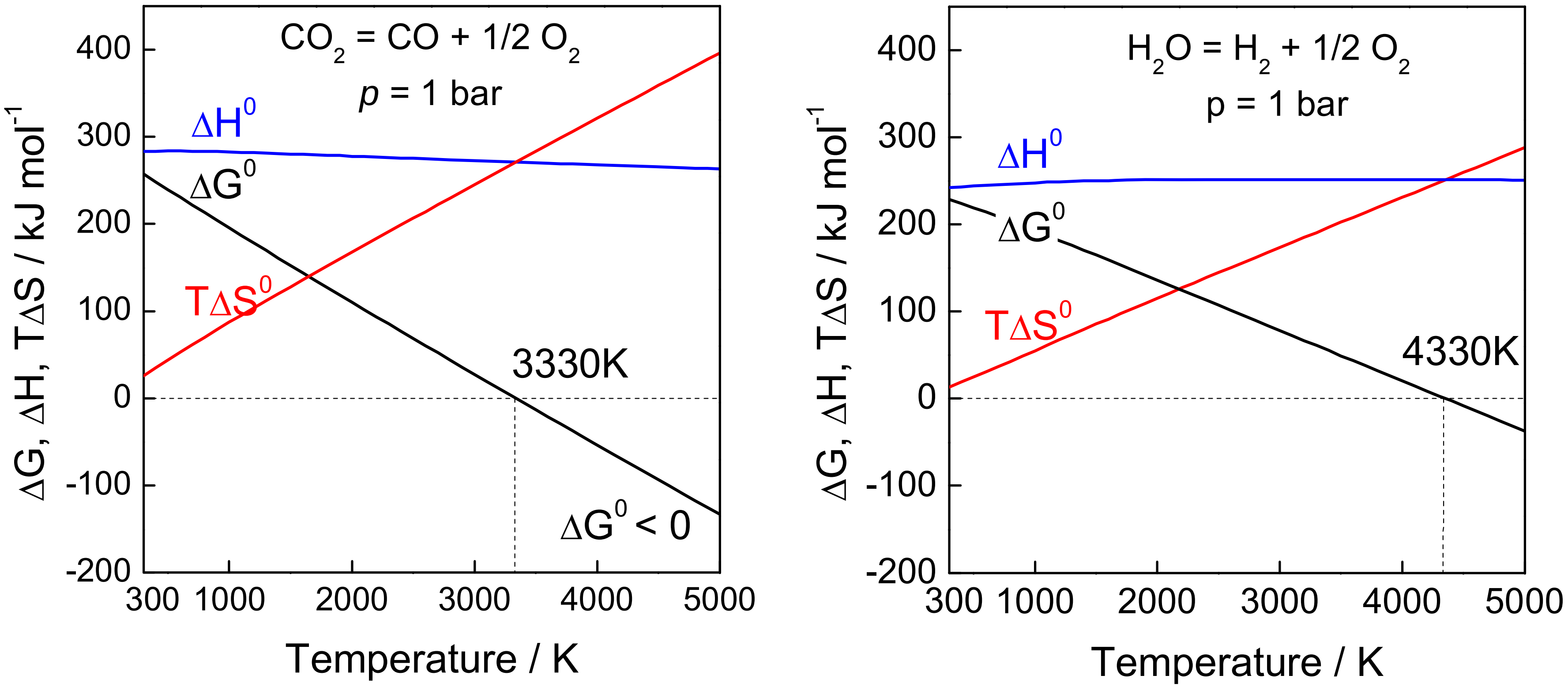
- Precious metal catalysts, poor rates
- Poor use of solar spectrum

- Thermolysis



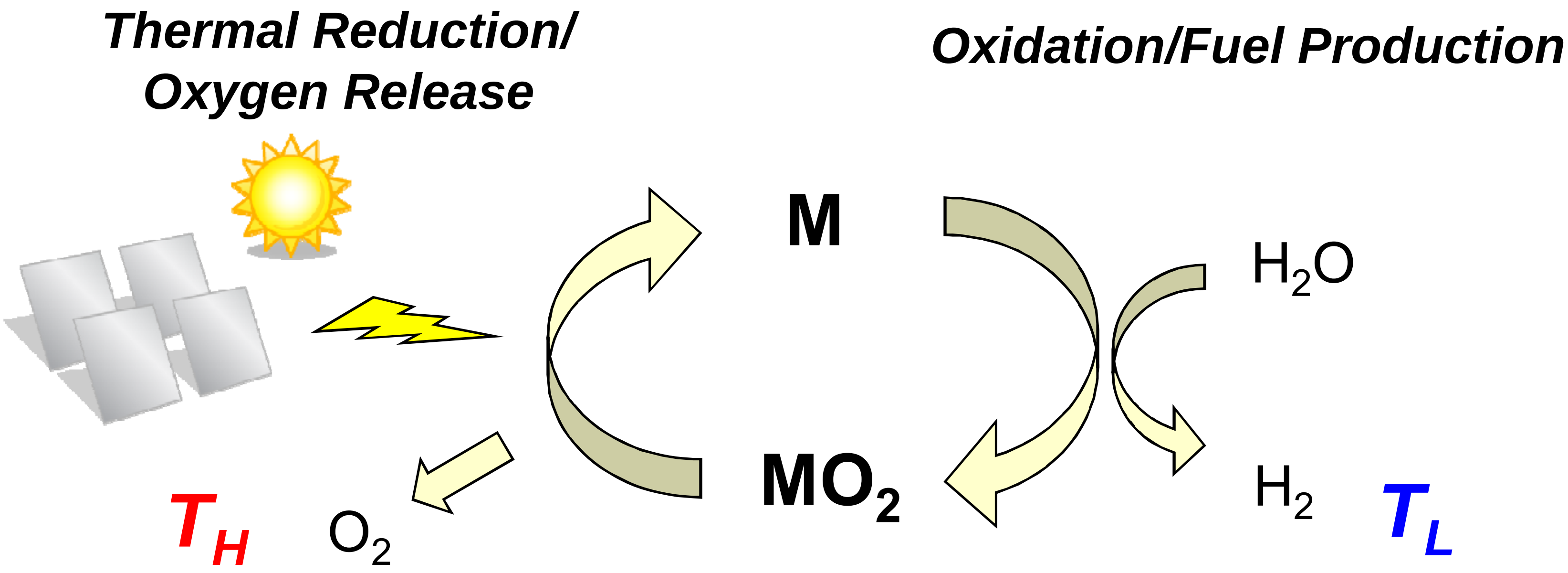
- Reaction at > 4,000 °C
- Requires separation

Direct Thermolysis



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

Metal Oxide Solar Thermochemical Cycle

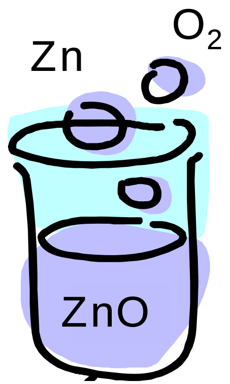


- Integrated solar capture and fuel production
- Oxygen and fuel produced in separate steps
- Challenges due to structural change & volatilization
- Fuel largely limited to hydrogen

State-of-the-Art

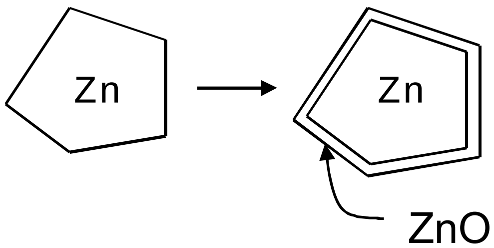
ZnO / Zn

907 °C



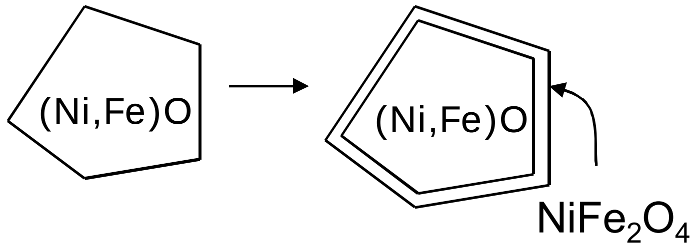
- Difficult Zn capture
  - Quench step required
- Slow oxidation kinetics

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



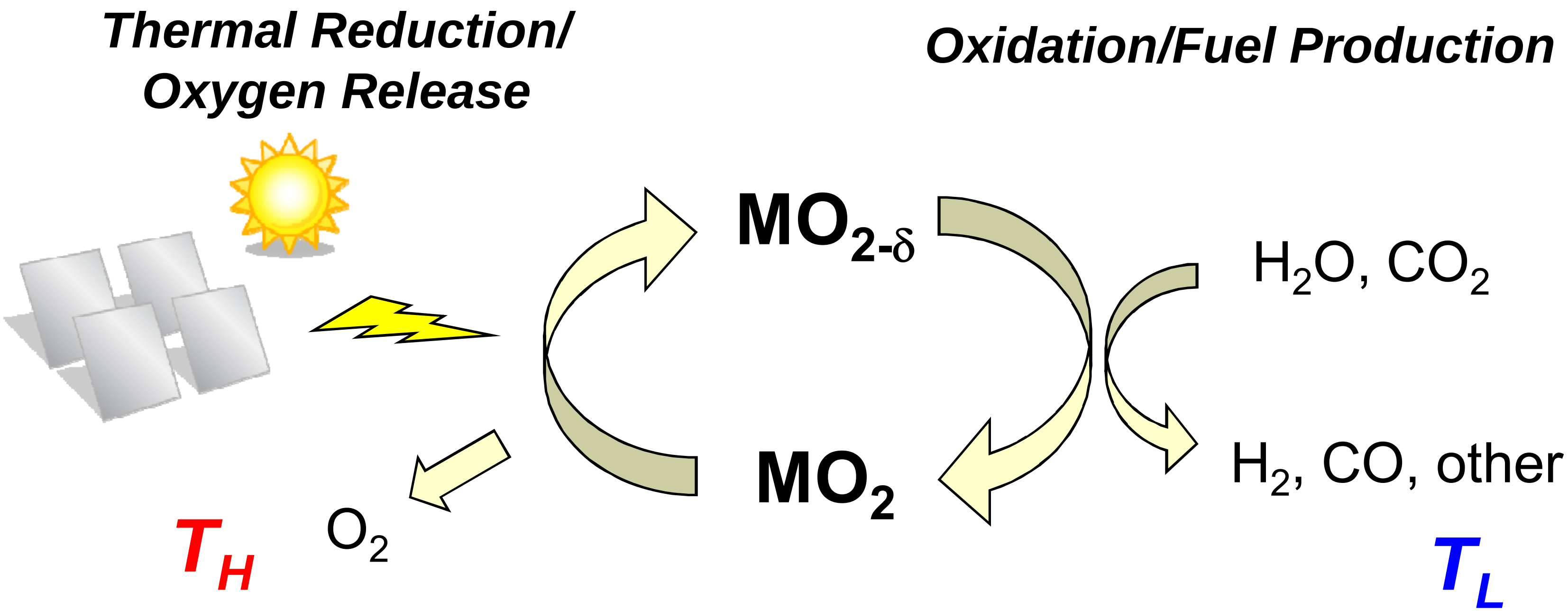
$NiFe_2O_4$ / $Ni_{1/3}Fe_{2/3}O$

- Solid state transformation
  - T_H ~ 1400°C
- Two distinct solid phases



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

Alternative Thermochemical Cycle



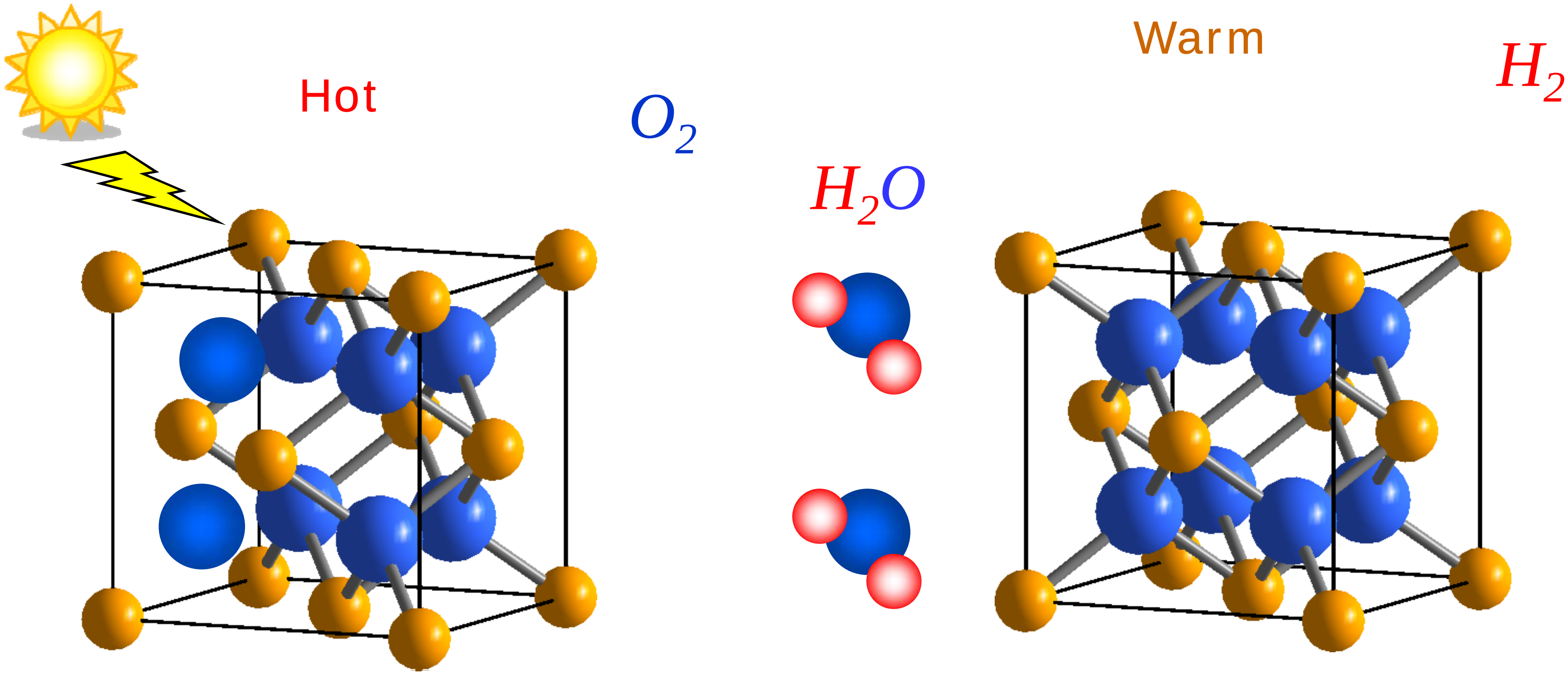
Metal oxide releases/incorporates oxygen

No phase change, large nonstoichiometry range

Rapid kinetics: bulk diffusion, surface reaction

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

Ceria thermochemical cycle

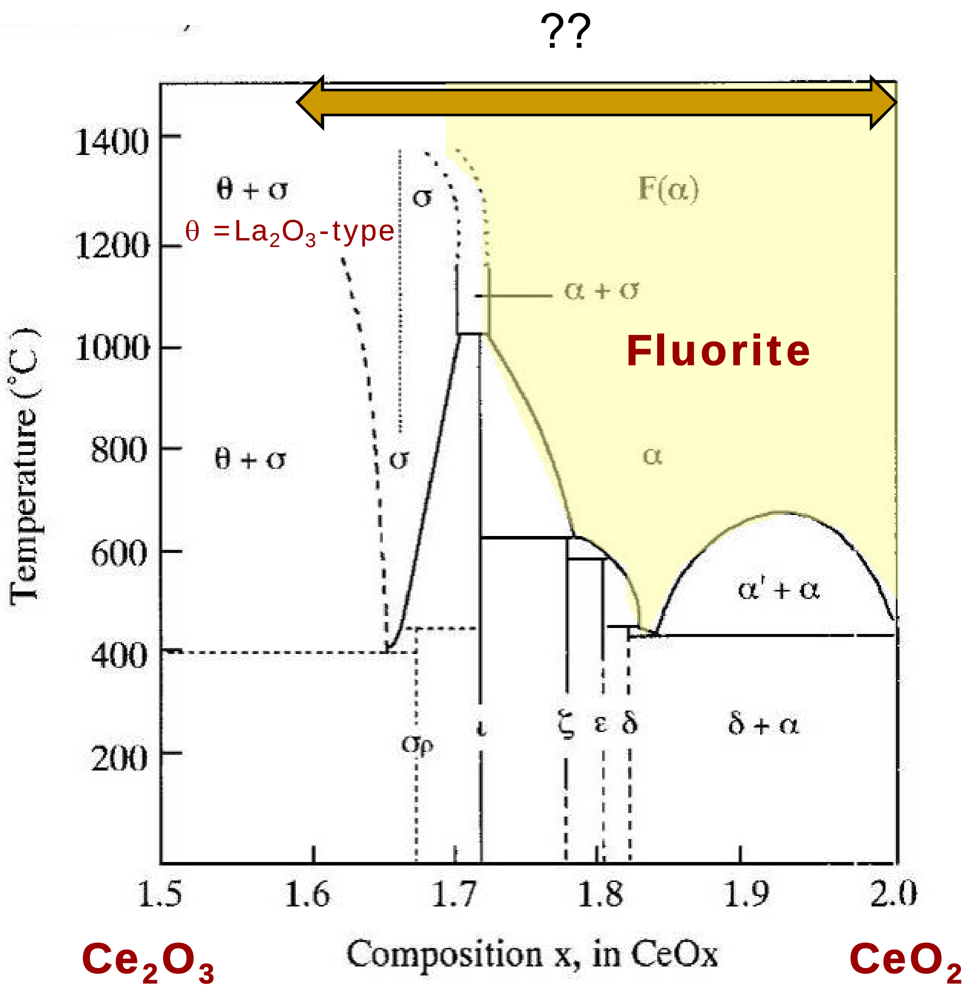


$$CeO_2 \rightarrow CeO_{2-\delta} + {}^{\delta}\!/_{2}\, O_2$$

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

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

Ce_2O_3 – CeO_2 Phase Diagram

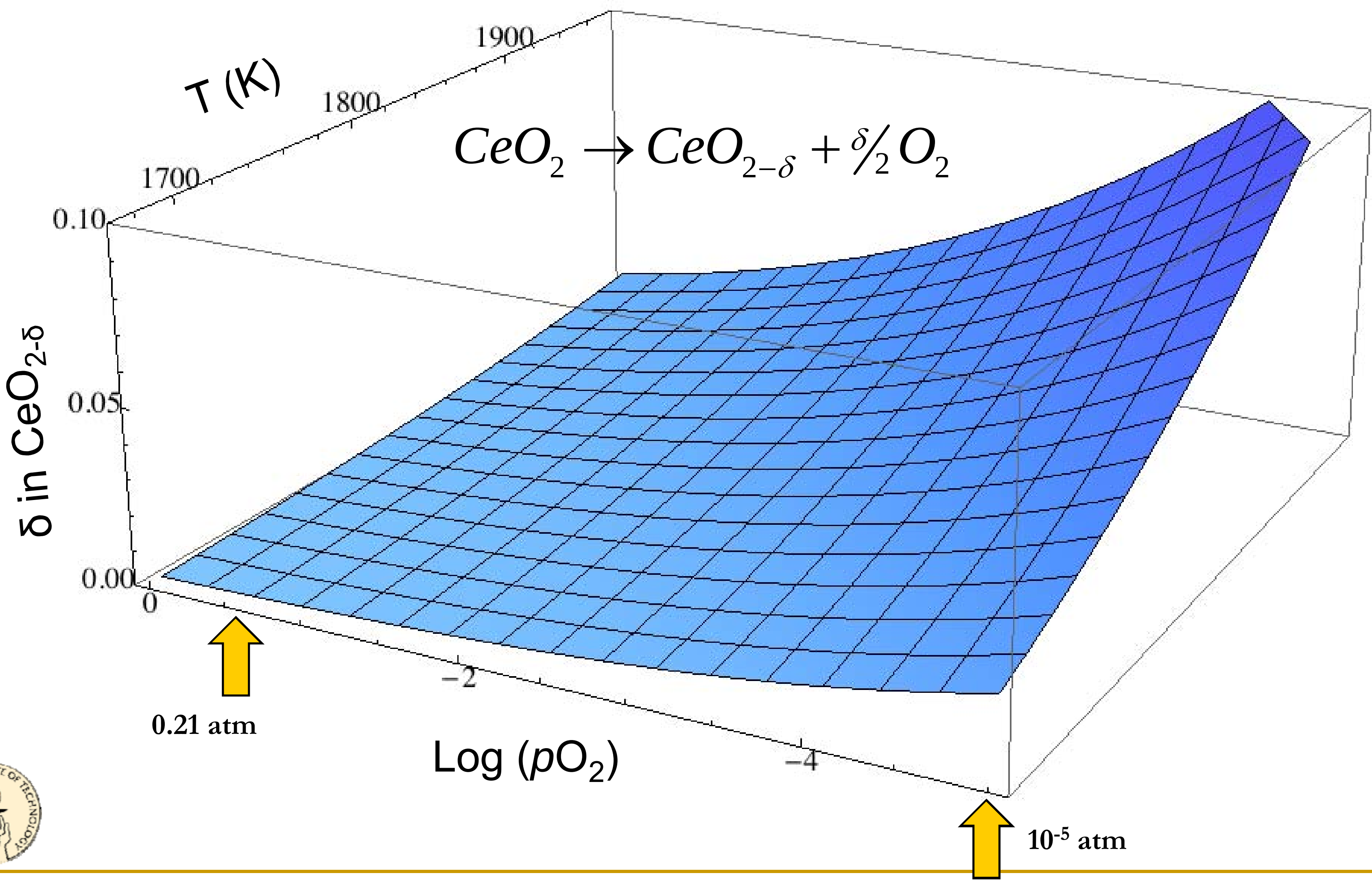


- Phase extent of fluorite unknown
- Favored at high T
- Favored by doping
- Ignore Ce_nO_{2n-m} ordered phases

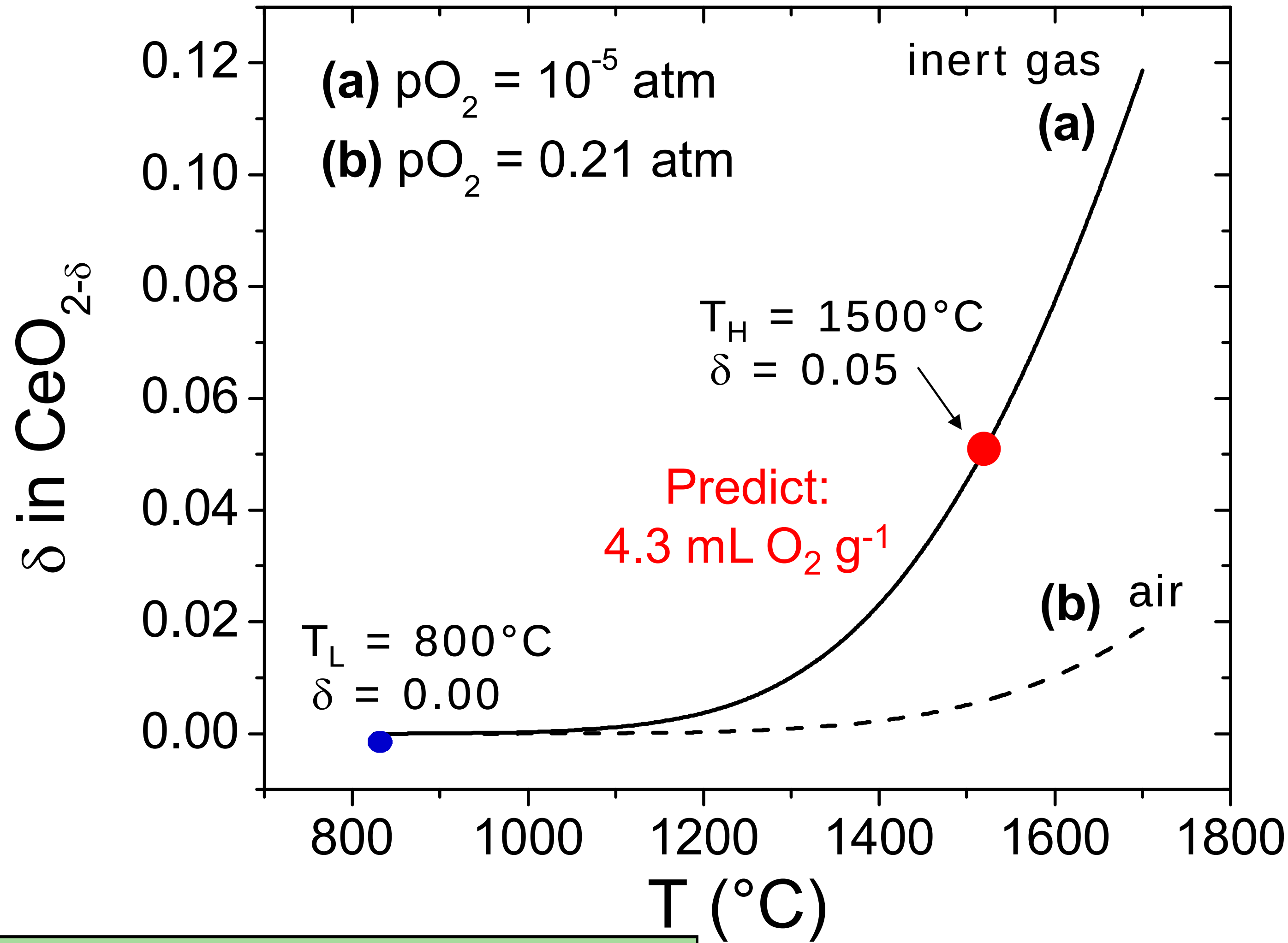
G. Adachi and N. Imanaka, *Chem. Rev.*, **98,** 1479-1514 (1998).

Thermodynamic Oxidation State

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



Predicted Oxygen Release / Fuel Production

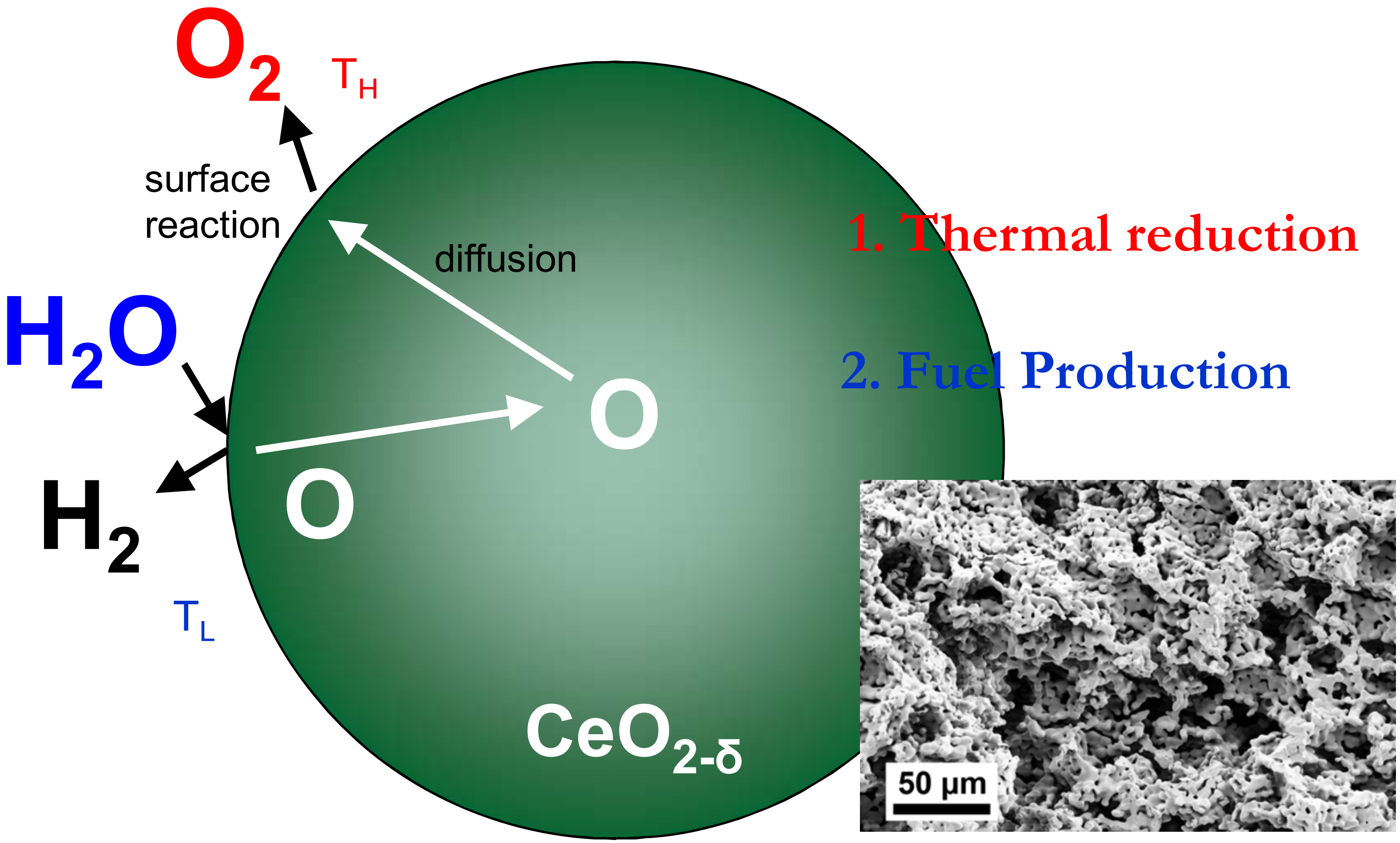


Theoretical fuel production:

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

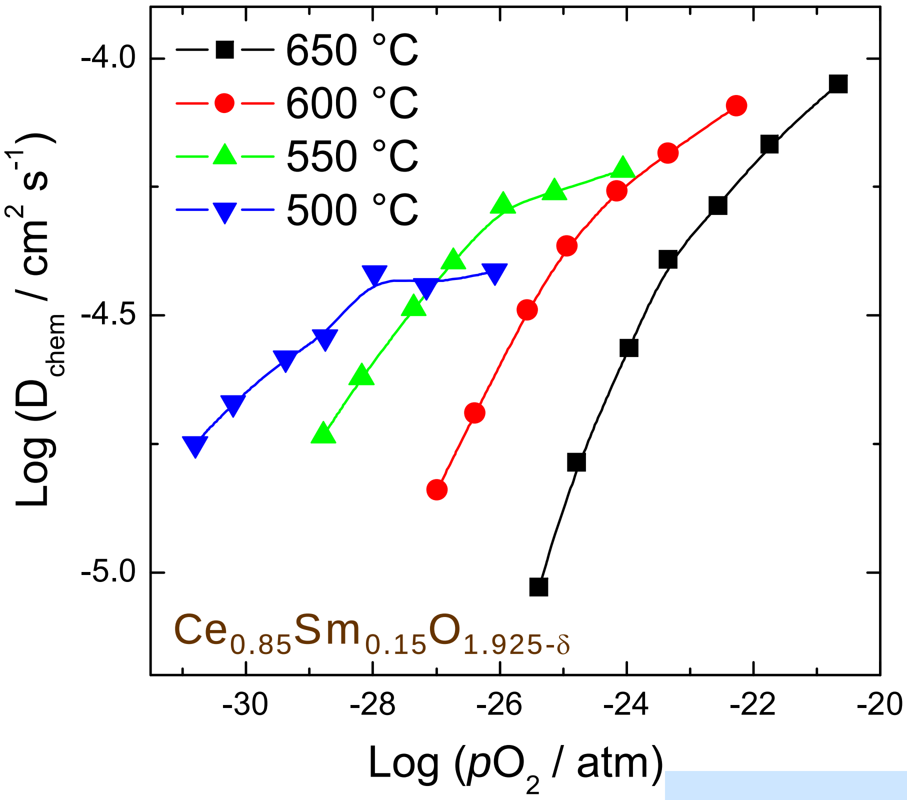
* 7 g for $Ce_{0.85}Sm_{0.15}O_{1.925-\delta}$

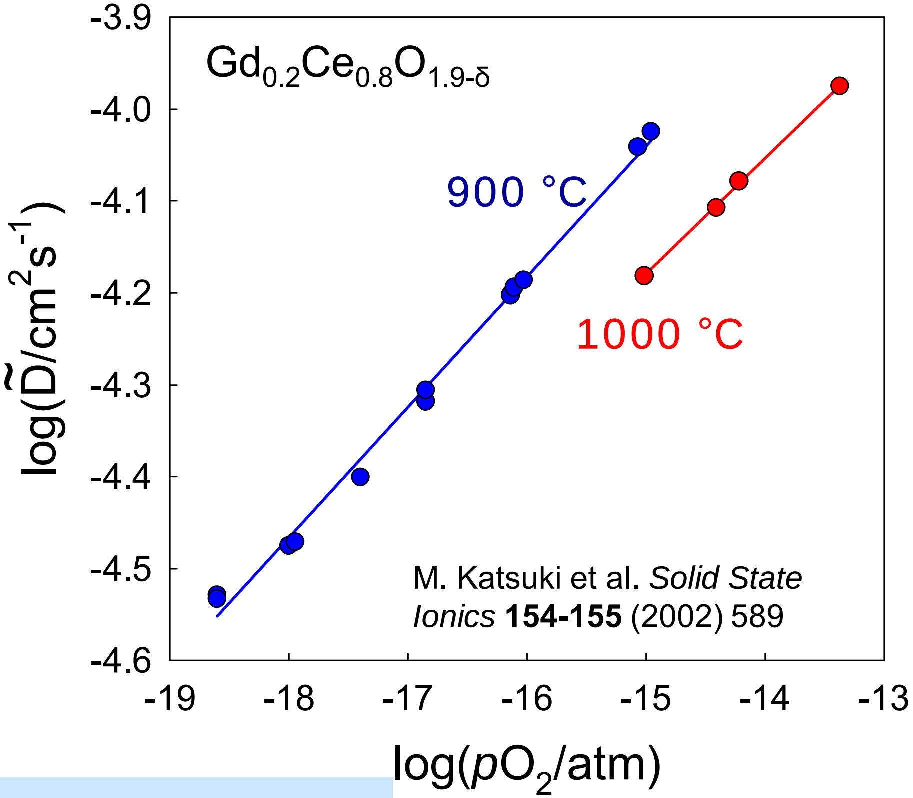
Kinetics of Reduction and Oxidation



Both bulk and surface kinetics can influence fuel production rate

Kinetics of Oxygen Release





T = 1500 °C, pO_2 = 10^{-5} atm

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

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

~2 μm particles

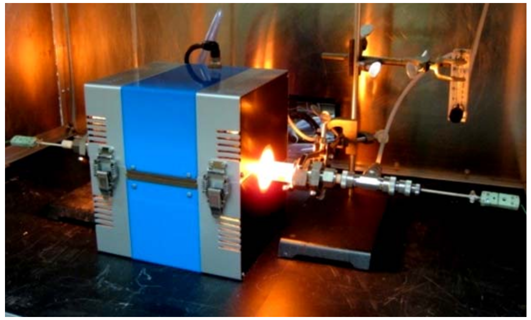
t ~ 10^{-5} s !!!

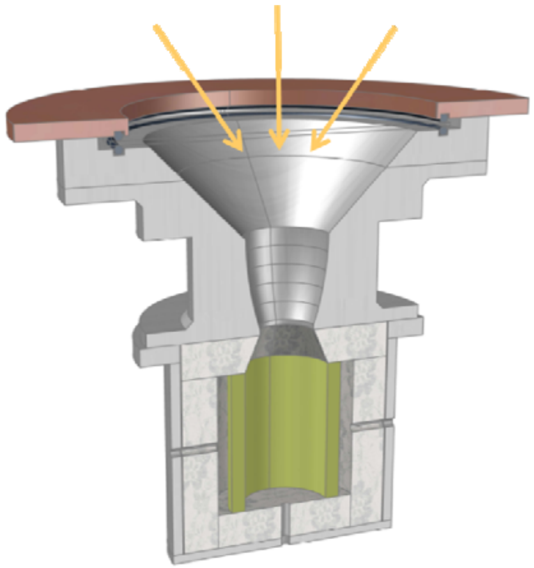
ZnO: 10^{-15} cm^2s^{-1}

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

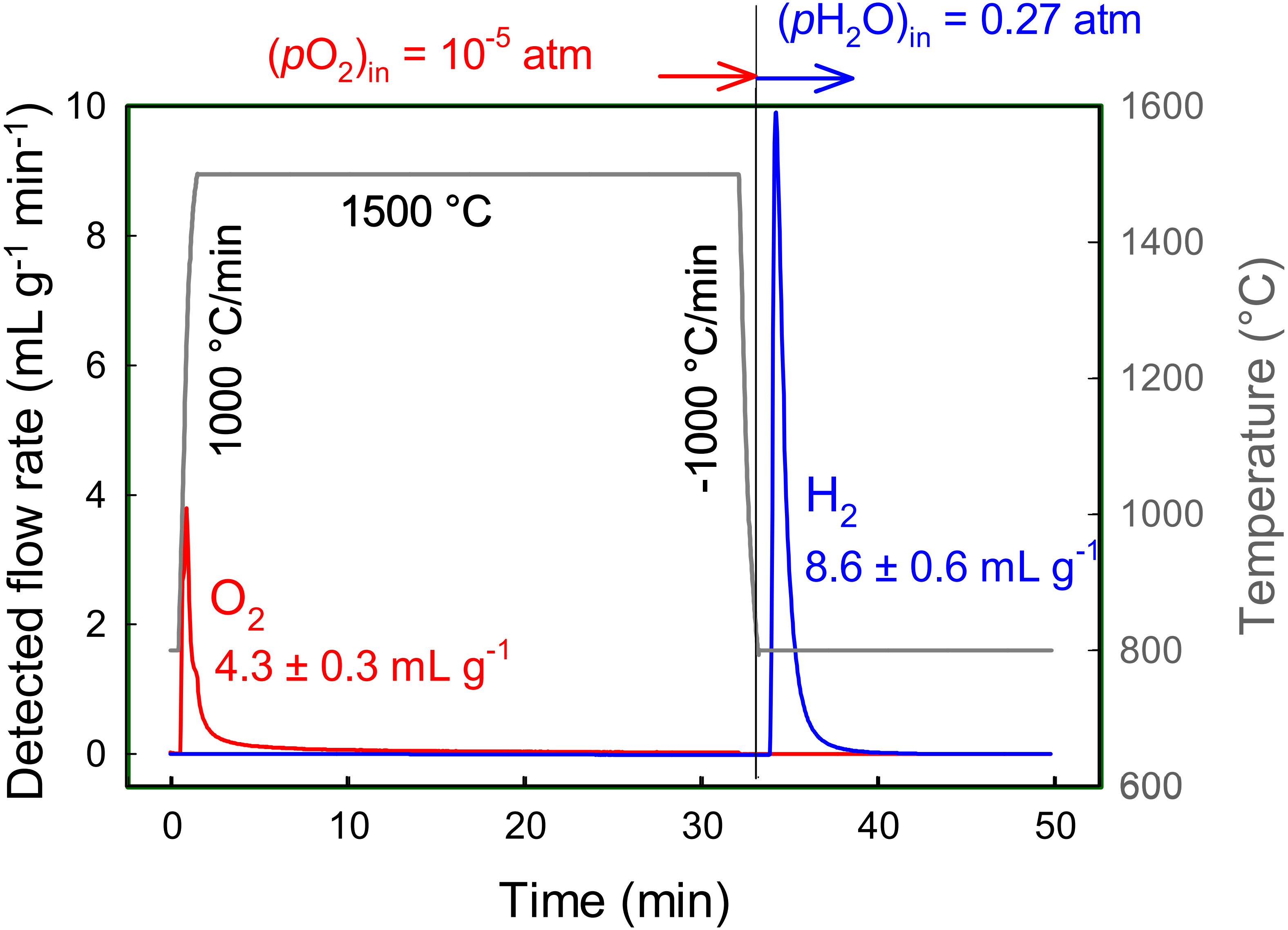
Progressive Demonstration

- 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

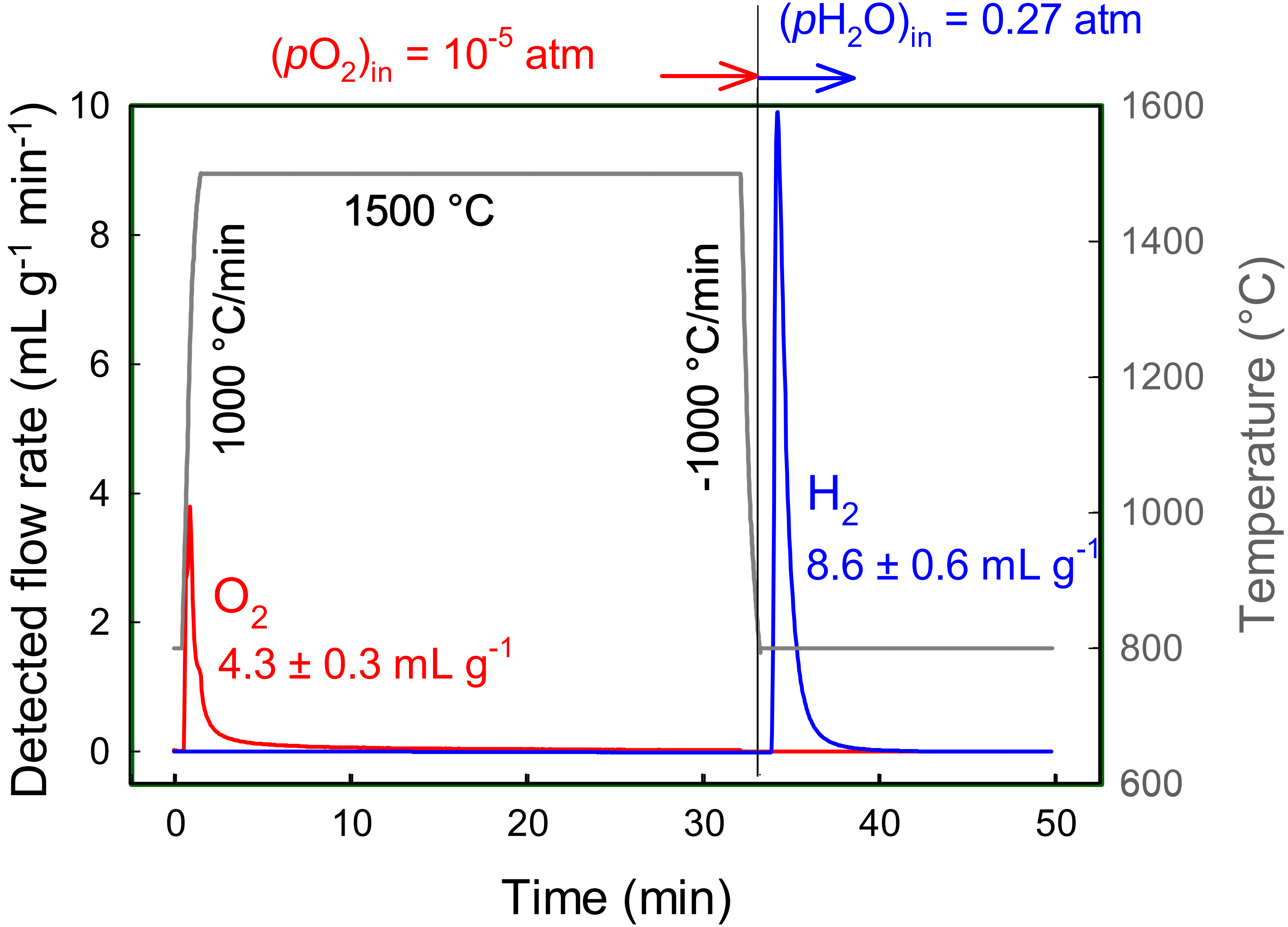




Thermochemical Cycling



Thermochemical Cycling

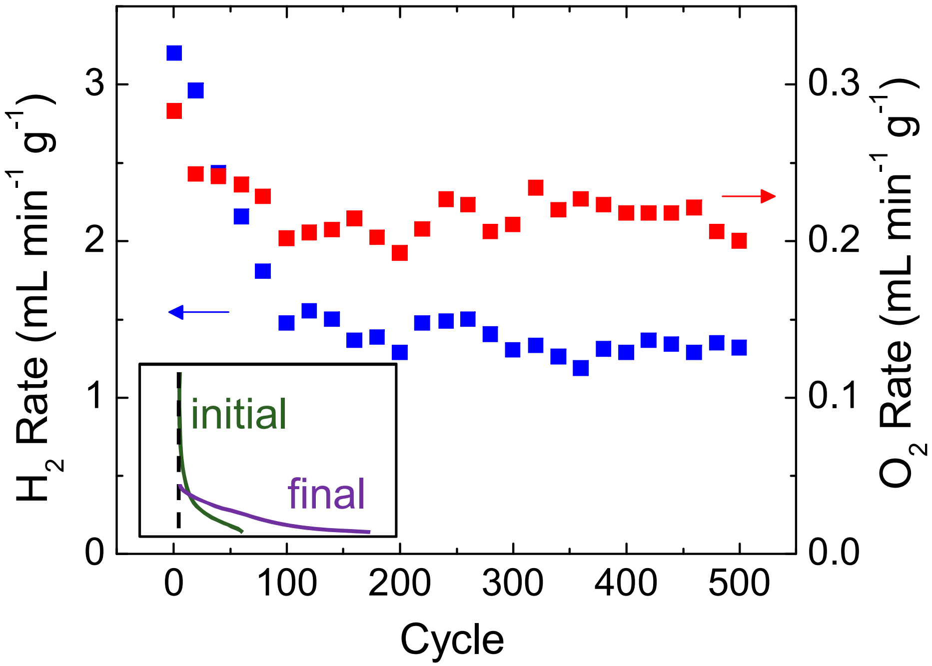


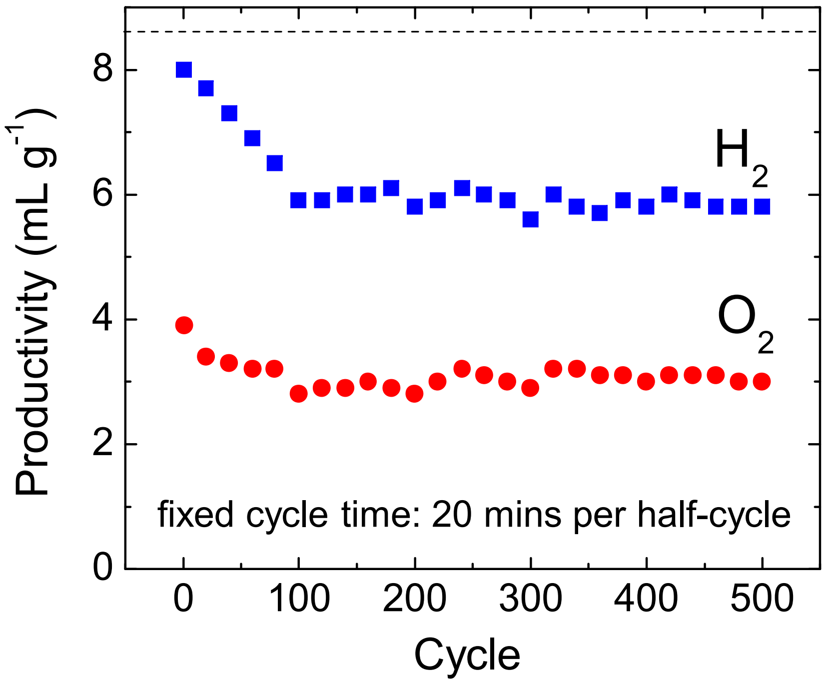
Thermochemical Cycling

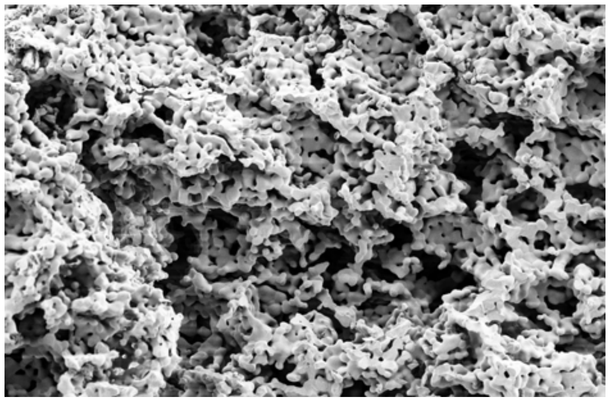
- Yield matches theoretical value of 8 mL H_2 per gram ceria

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

Stability of Fuel Productivity

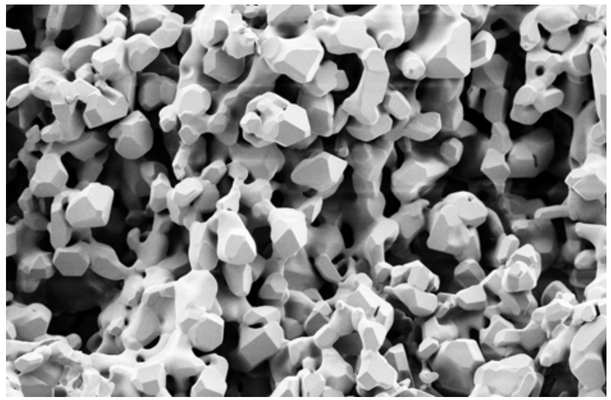




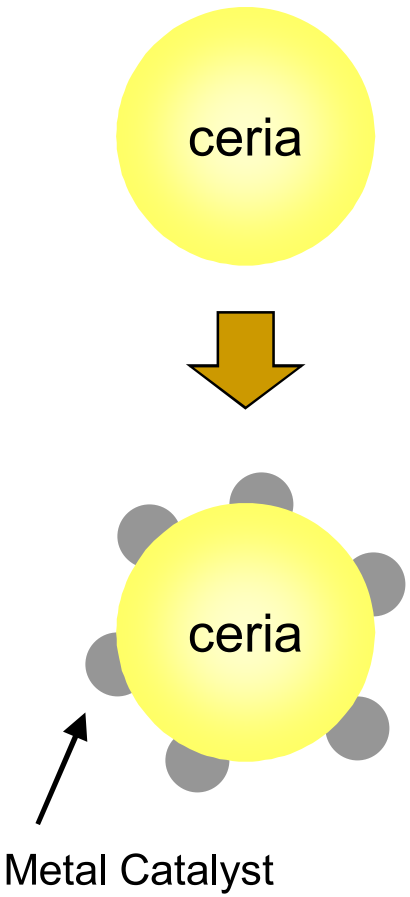


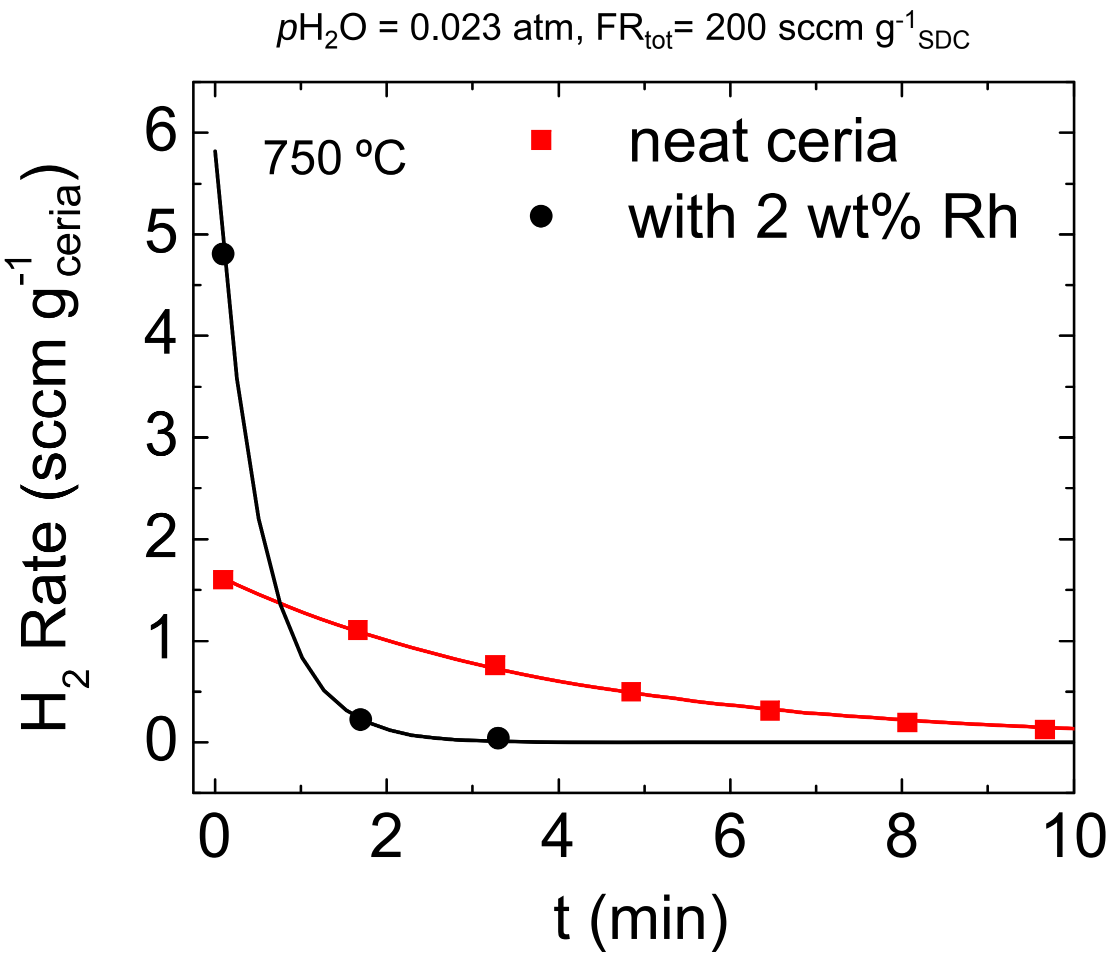
loss of surface area

surface step is rate-limiting



Rate Limiting Step

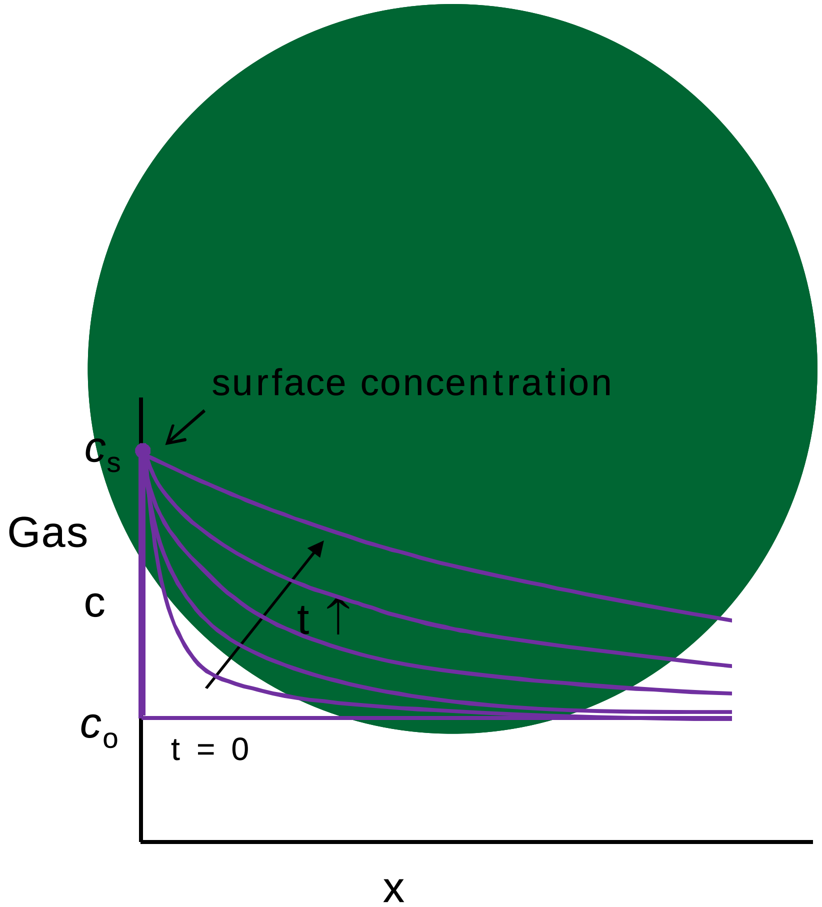




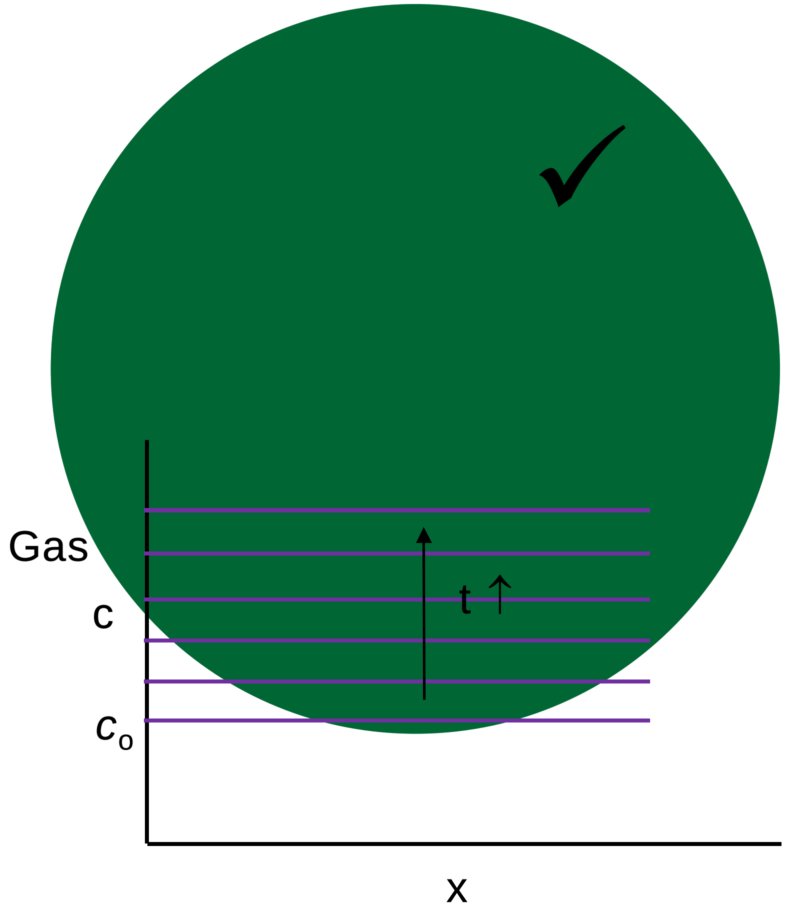
Catalyst improves kinetics → surface limited process

Kinetics of Reduction and Oxidation

Diffusion controlled

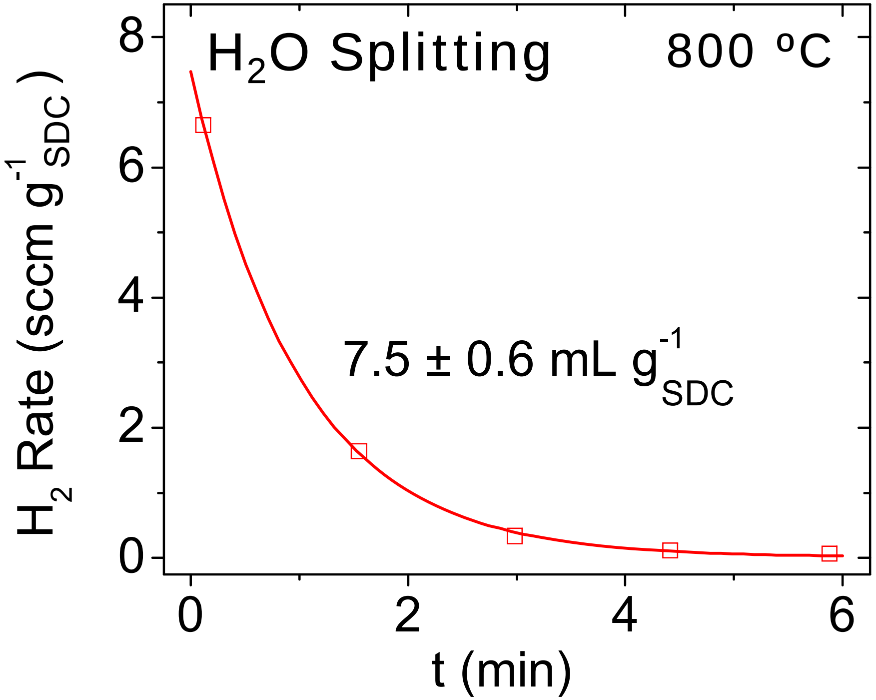


Surface reaction controlled

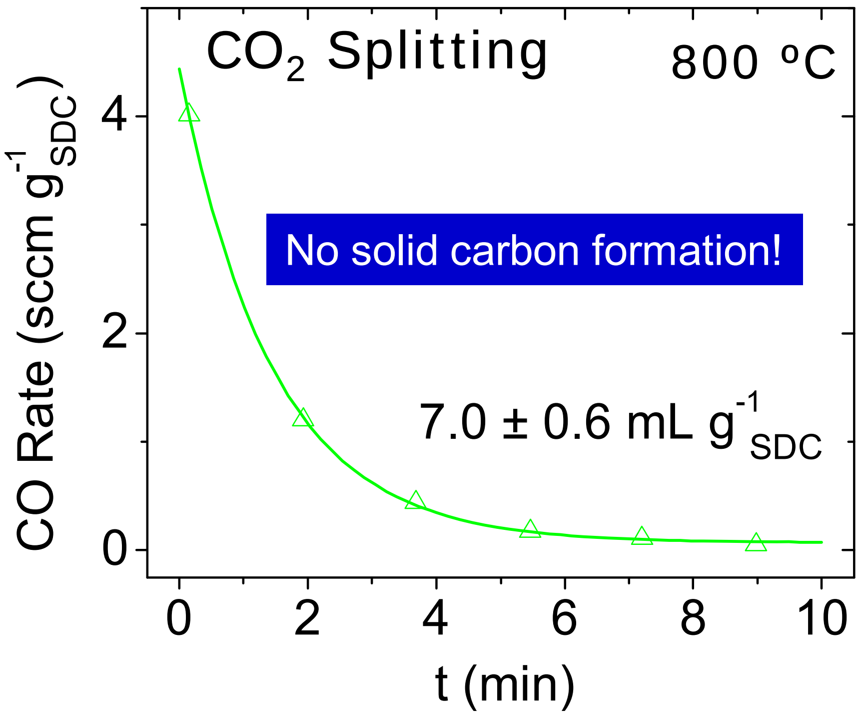


Process is dominated by surface reaction rate

Making the Fuel of Choice



pH_2O = 0.064 atm, FR_{tot}= 380 sccm $g^{-1}{}_{SDC}$

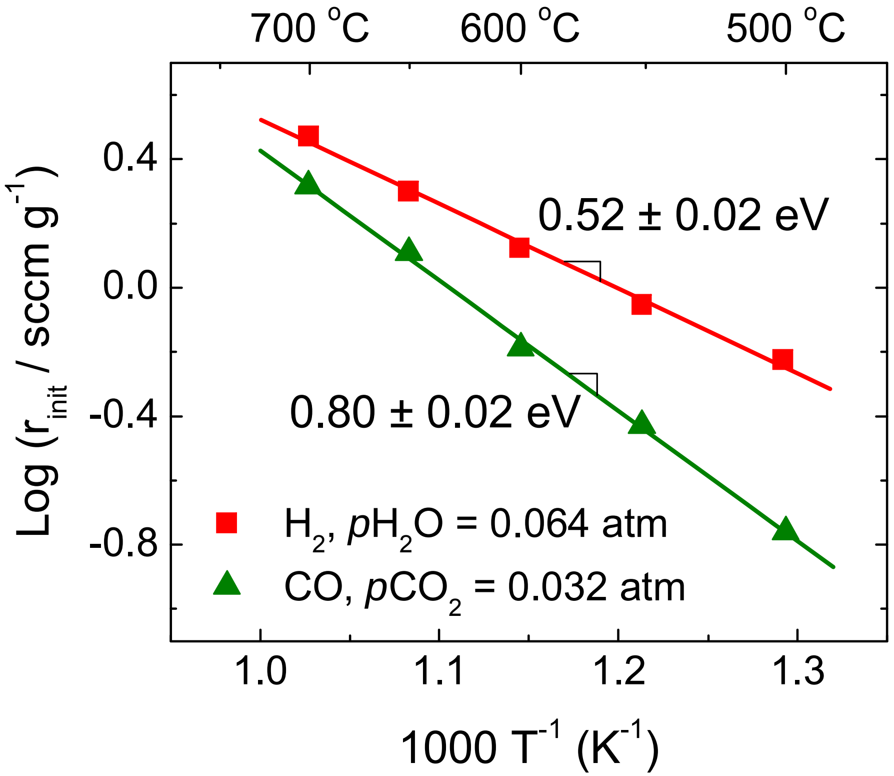


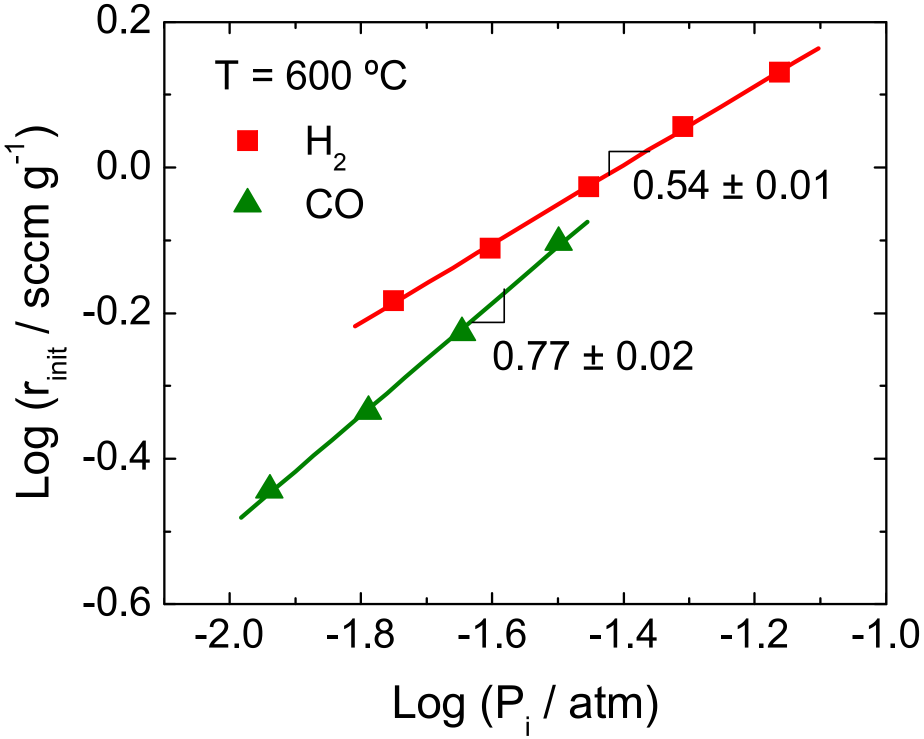
pCO_2 = 0.032 atm, FR_{tot}= 300 sccm $g^{-1}{}_{SDC}$

Complete utilization of ceria non-stoichiometry for fuel production

SDC = samaria doped ceria

Fuel Production Rates

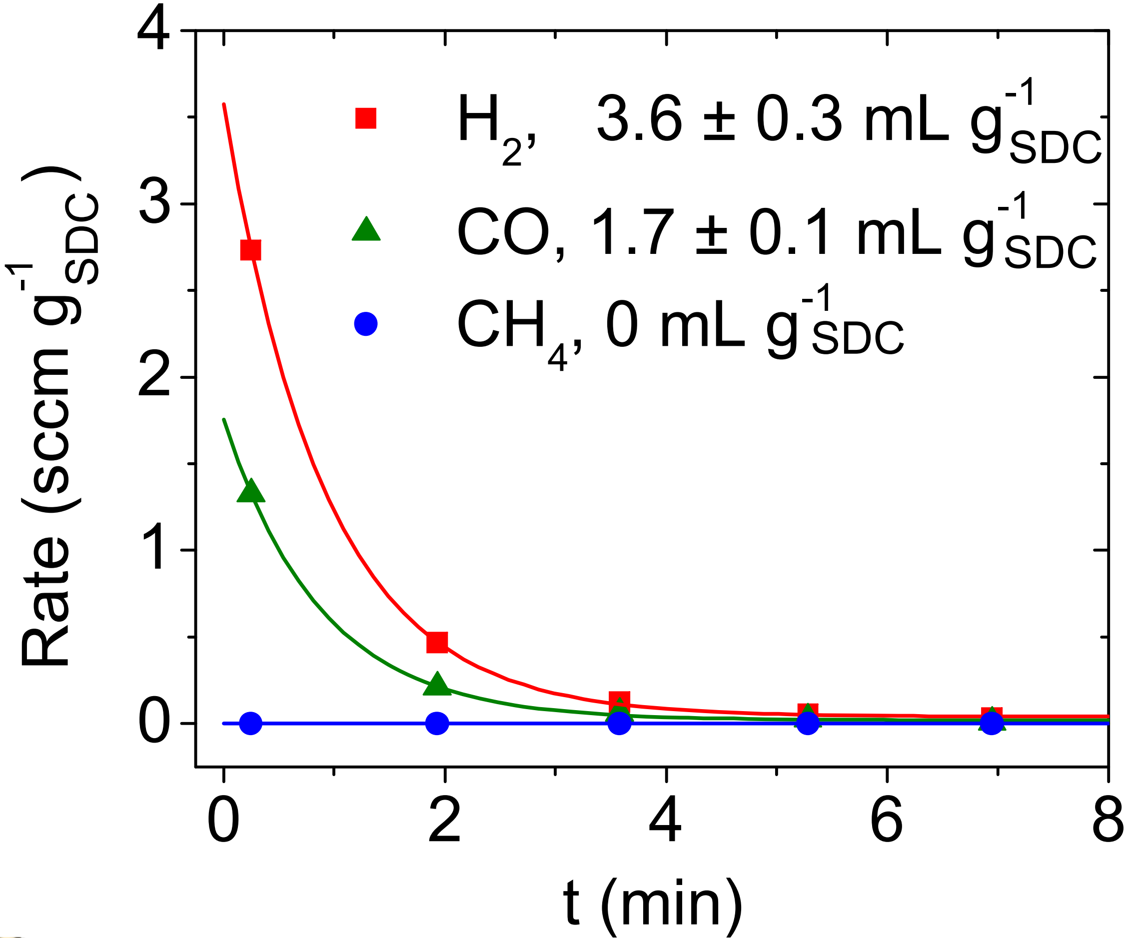




Rate depends on gas species $\rightarrow$ confirms surface reaction limited

Making Syngas

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



~ 20,000 μL min^{-1} g^{-1}

900 °C; 0.66 atm pH_2O; 0.34 atm pCO_2

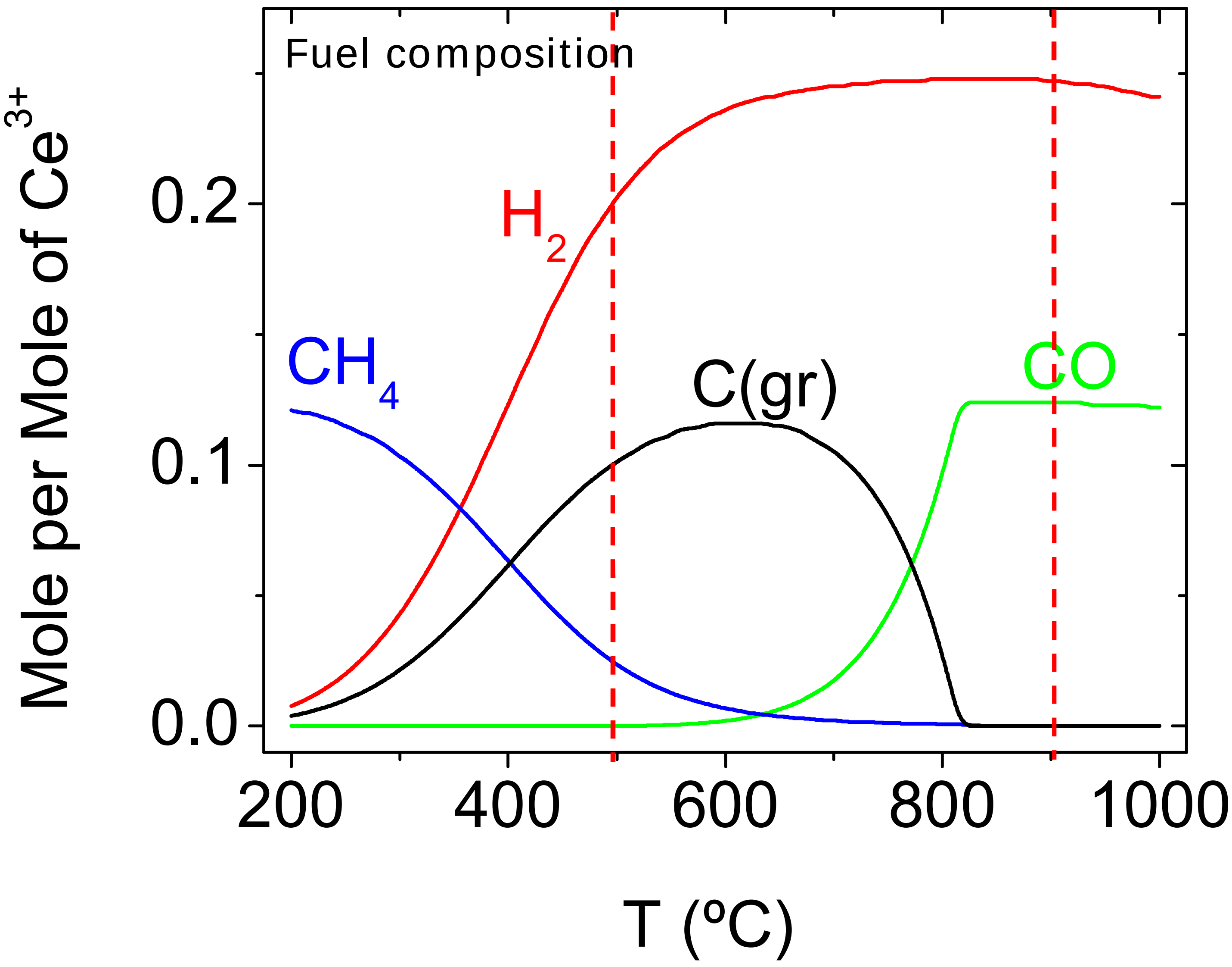
~ 2 μL min^{-1} g^{-1}

N-doped TiO_2 nanotubes

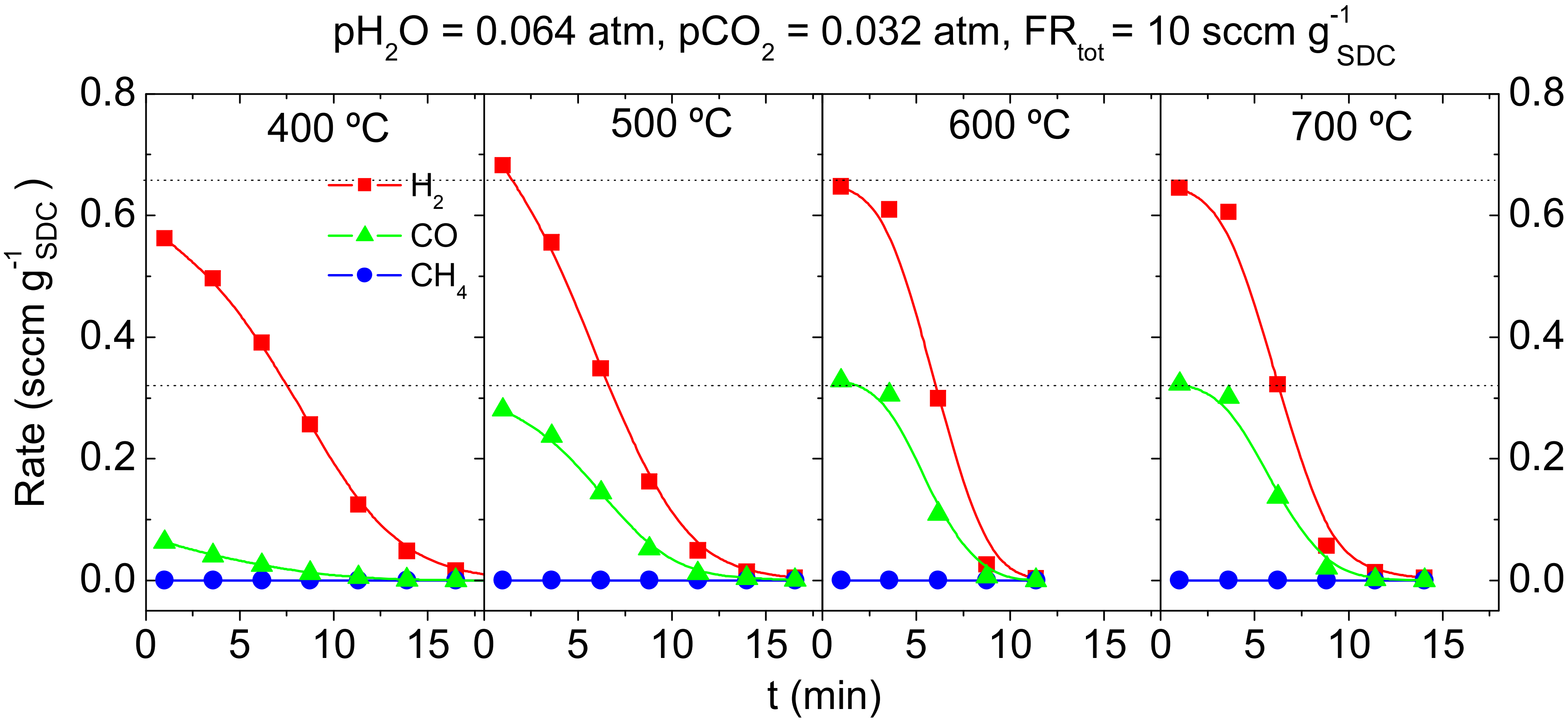
Grimes, Nano Lett., 2009, 9 (2), pp 731–737

Complete utilization of ceria nonstoichiometry

Thermodynamic Prediction

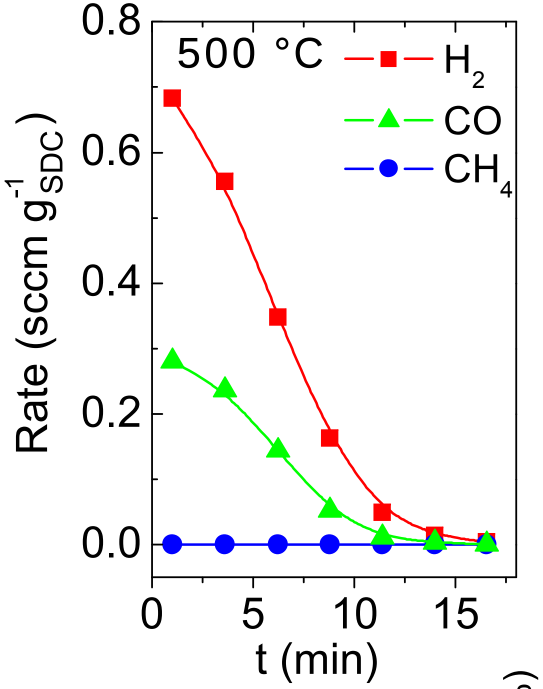


Measured Fuel Composition

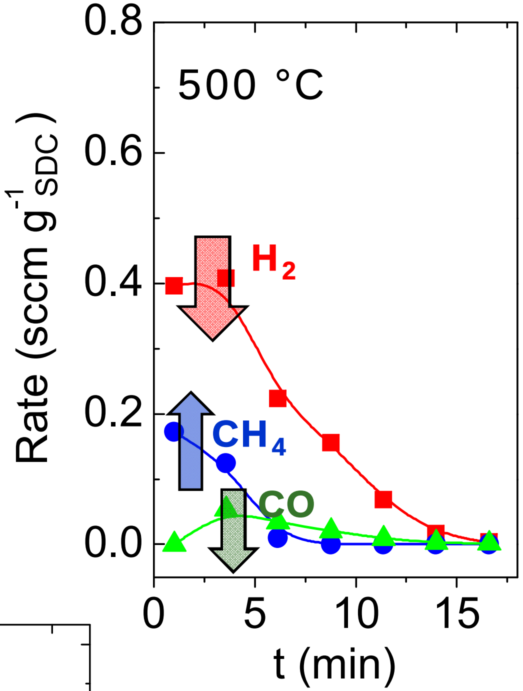


100% syngas selectivity – no methane produced

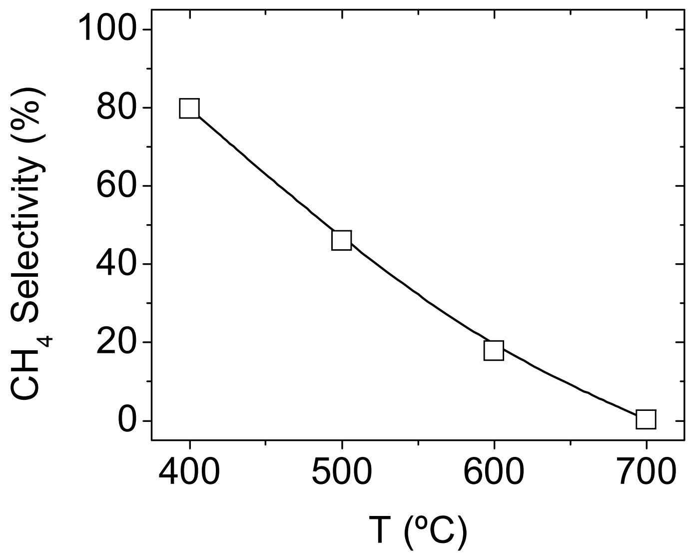
Producing Methane?



Add Ni catalyst

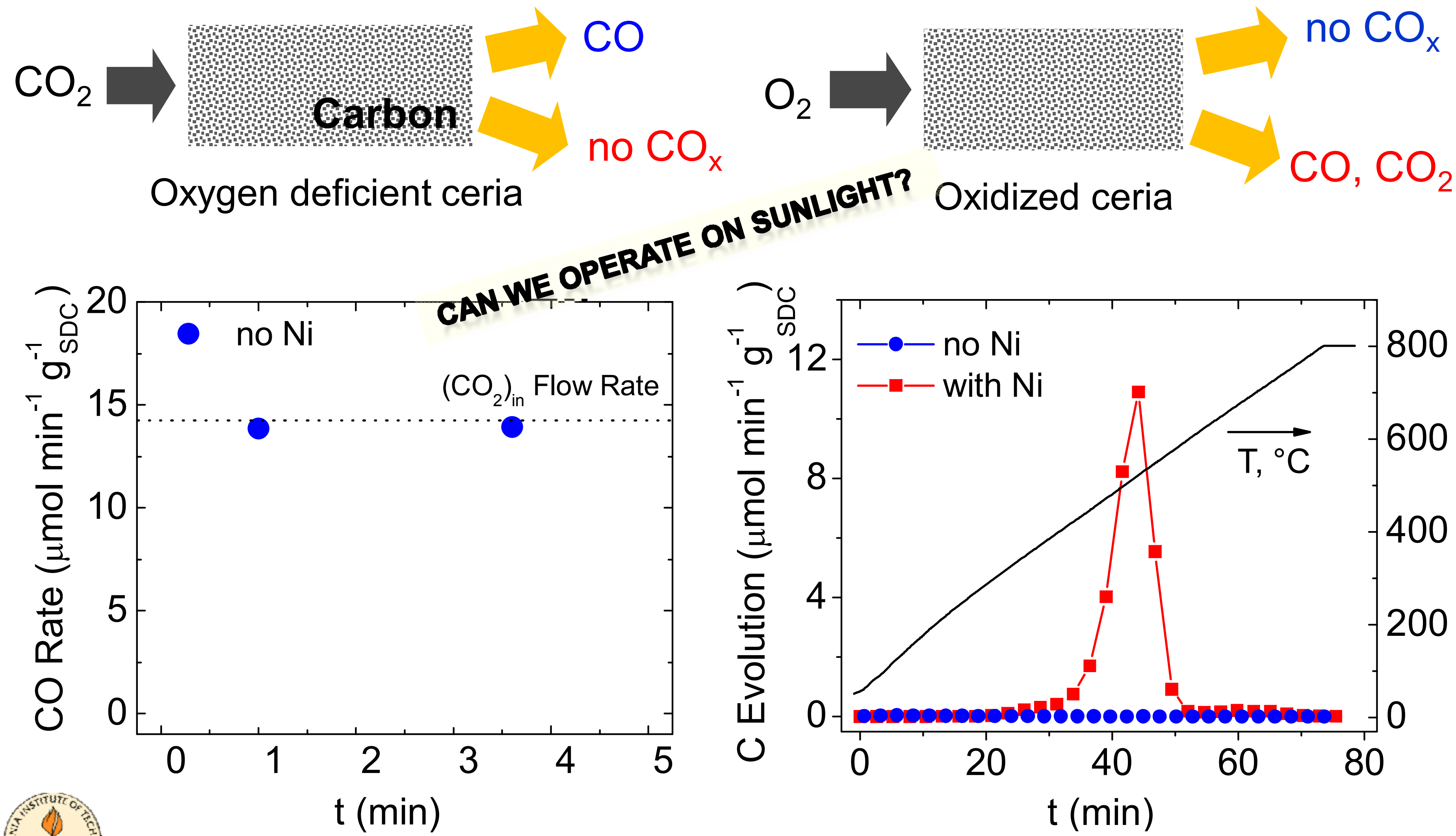


pH_2O = 0.064 atm
pCO_2 = 0.032 atm
FR_{tot} = 10 sccm g^{-1}_{SDC}



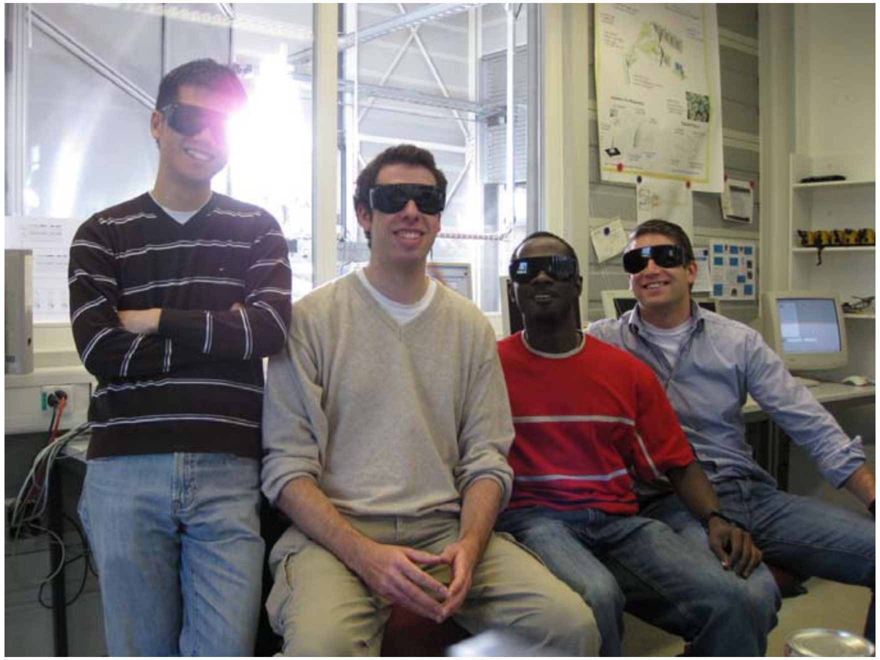
due to "transient" carbon deposition

Ni induces Carbon Deposition



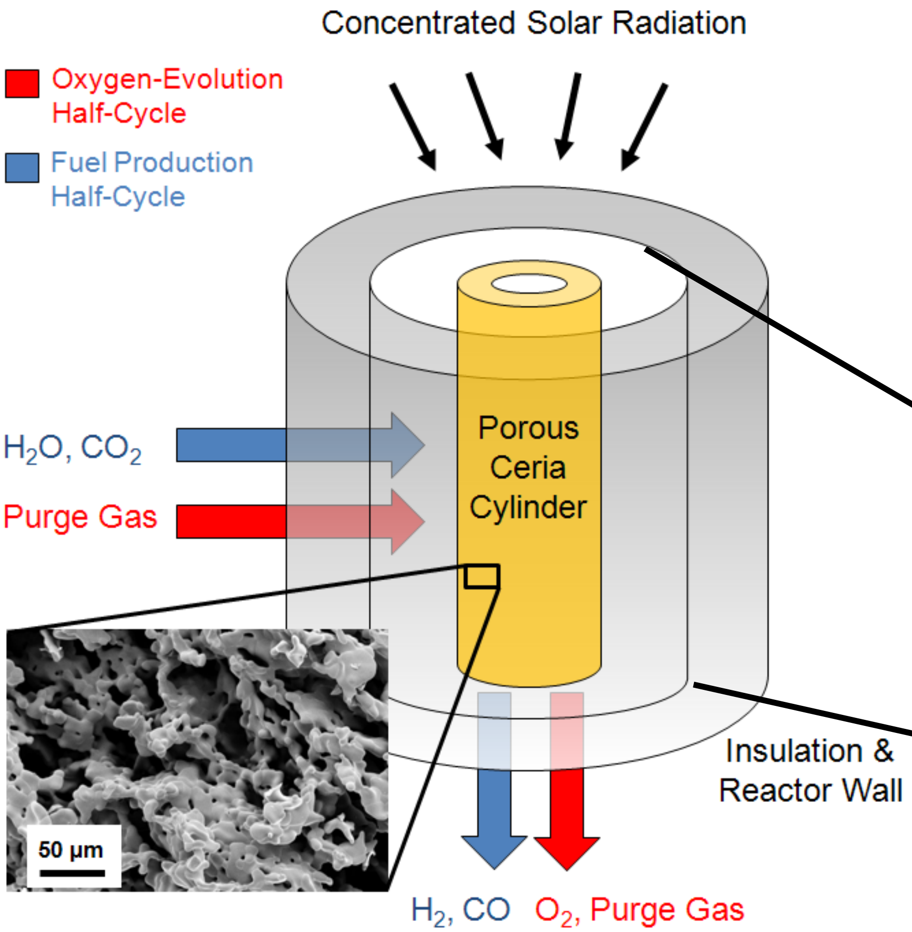
Operating on Photons

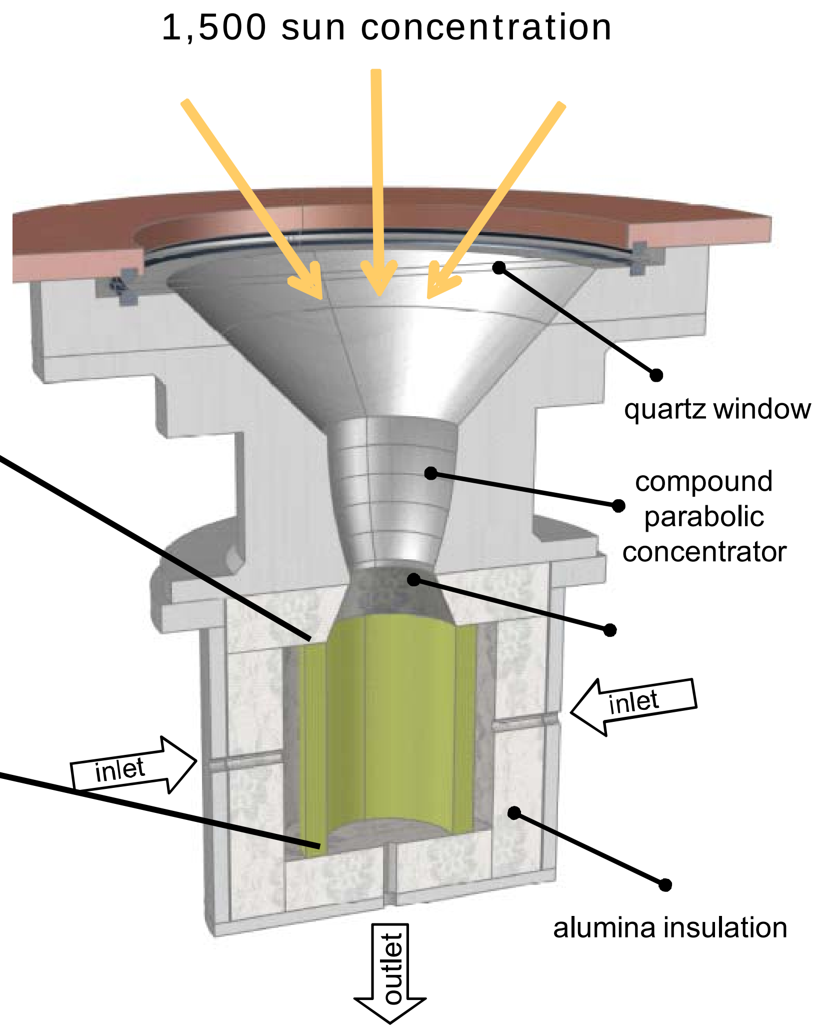
Switzerland in March



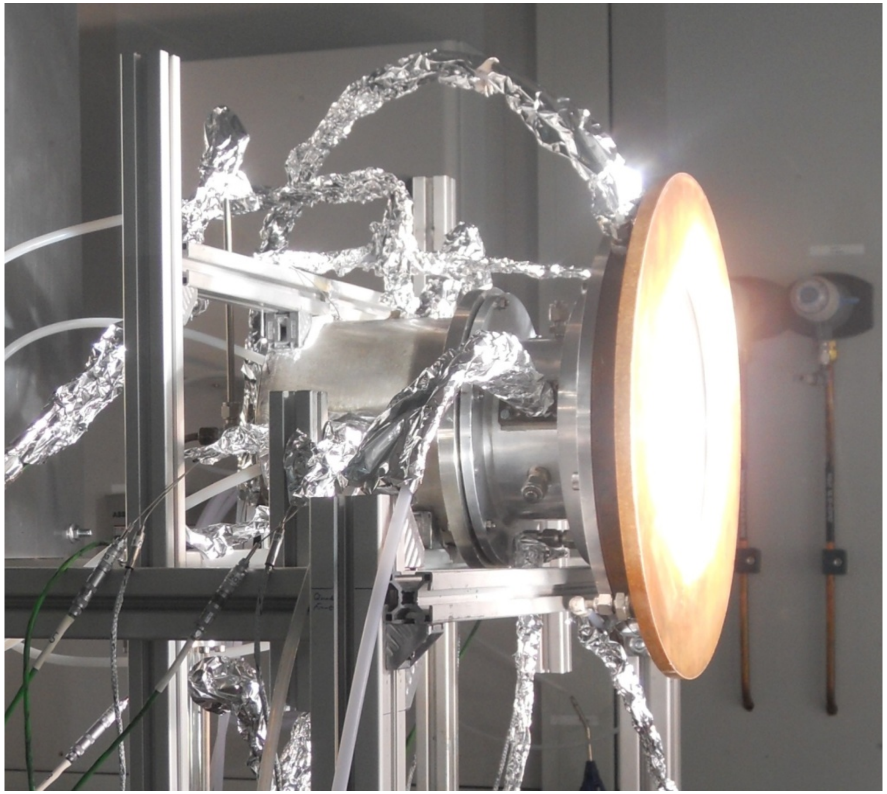
Collaboration with Aldo Steinfeld, ETH Zurich and the Paul Scherer Institute

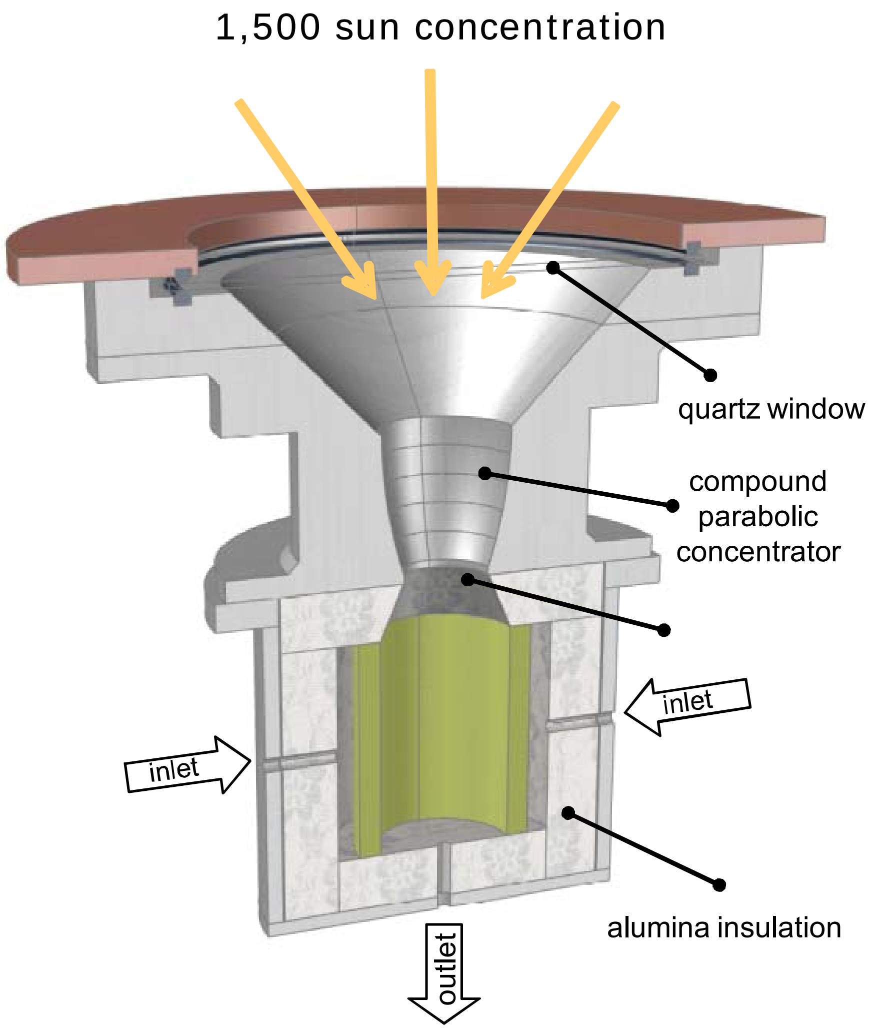
Under Simulated Solar Radiation





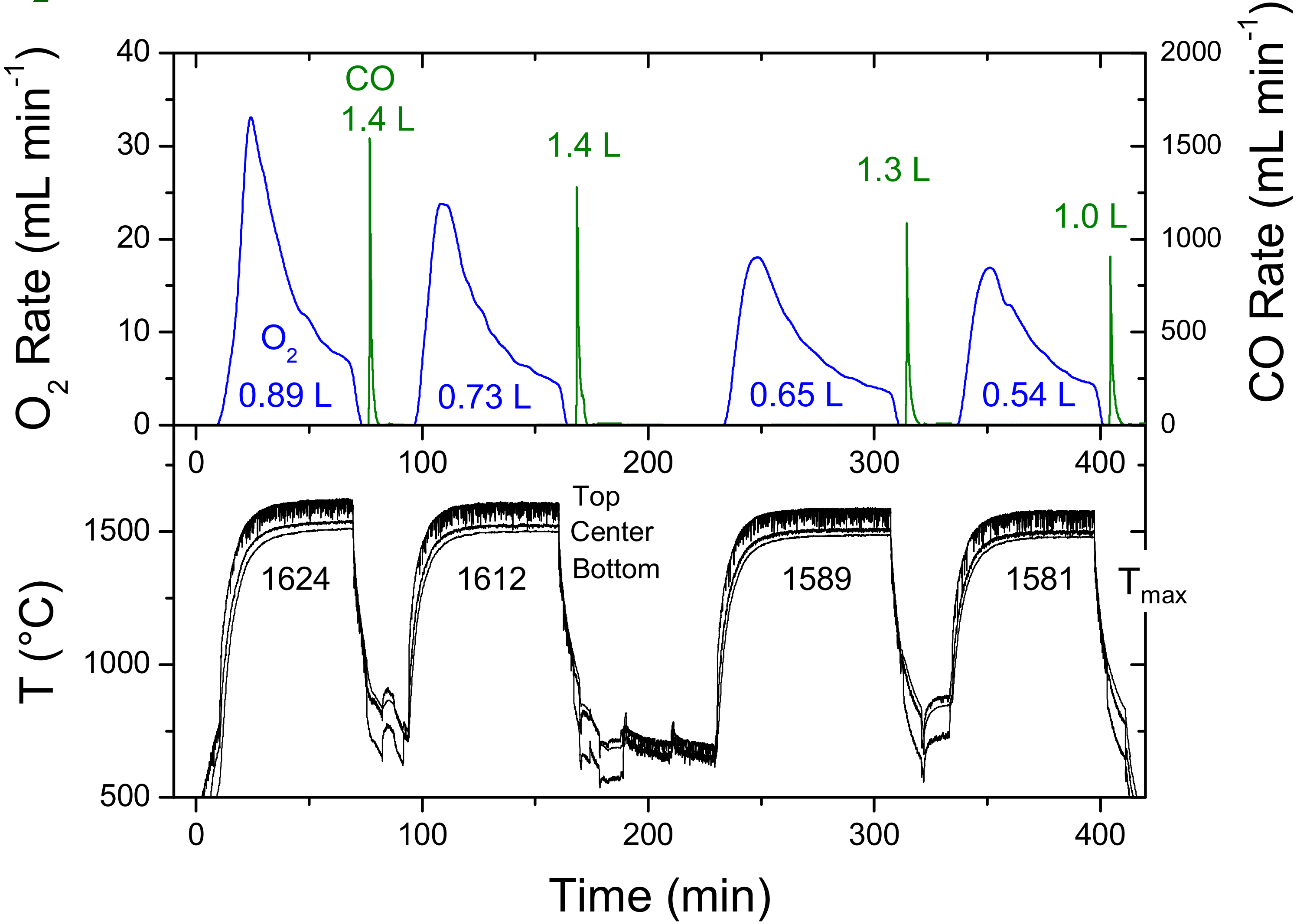
Under Simulated Solar Radiation





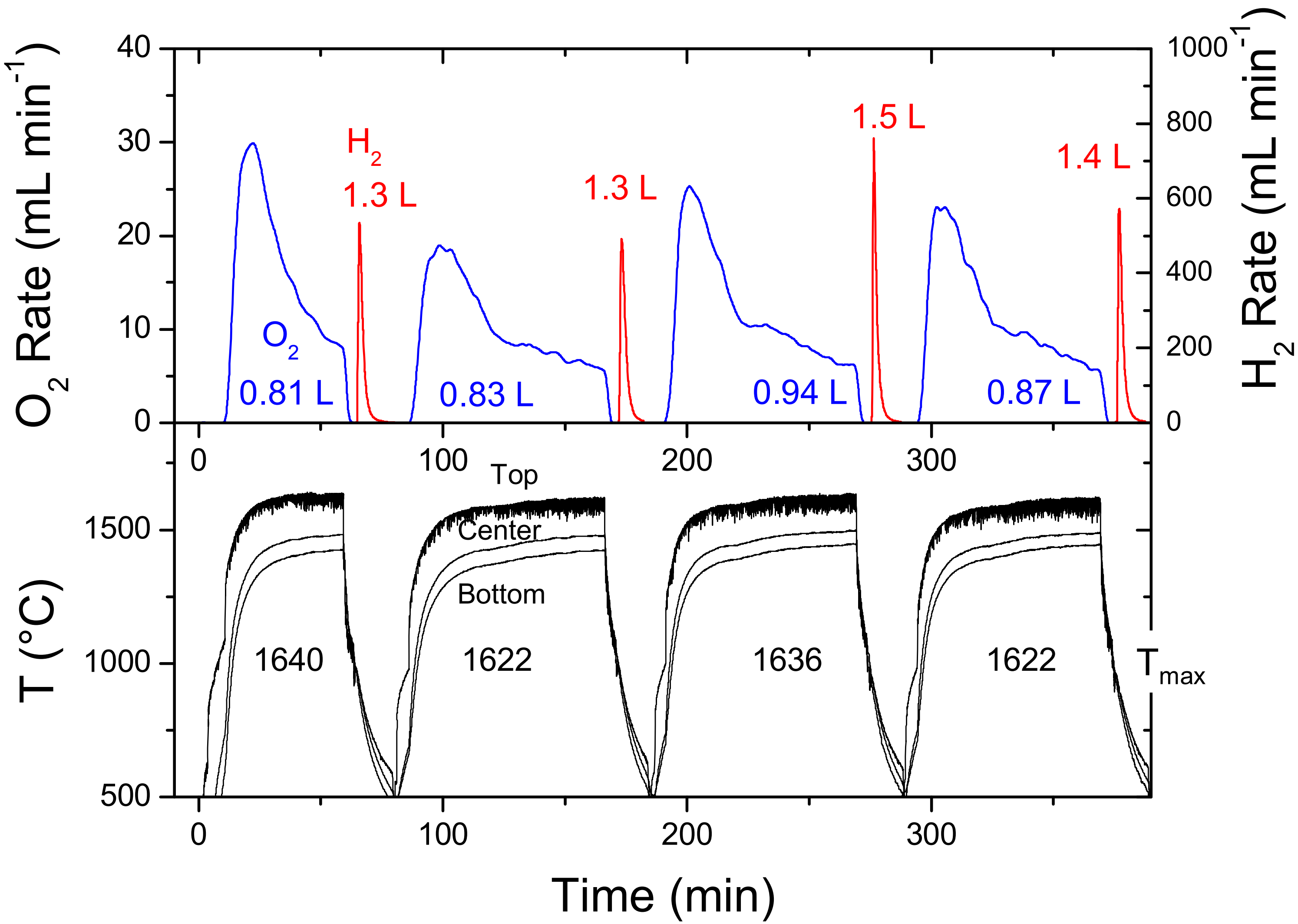
Under Simulated Solar Radiation

CO_2 dissociation

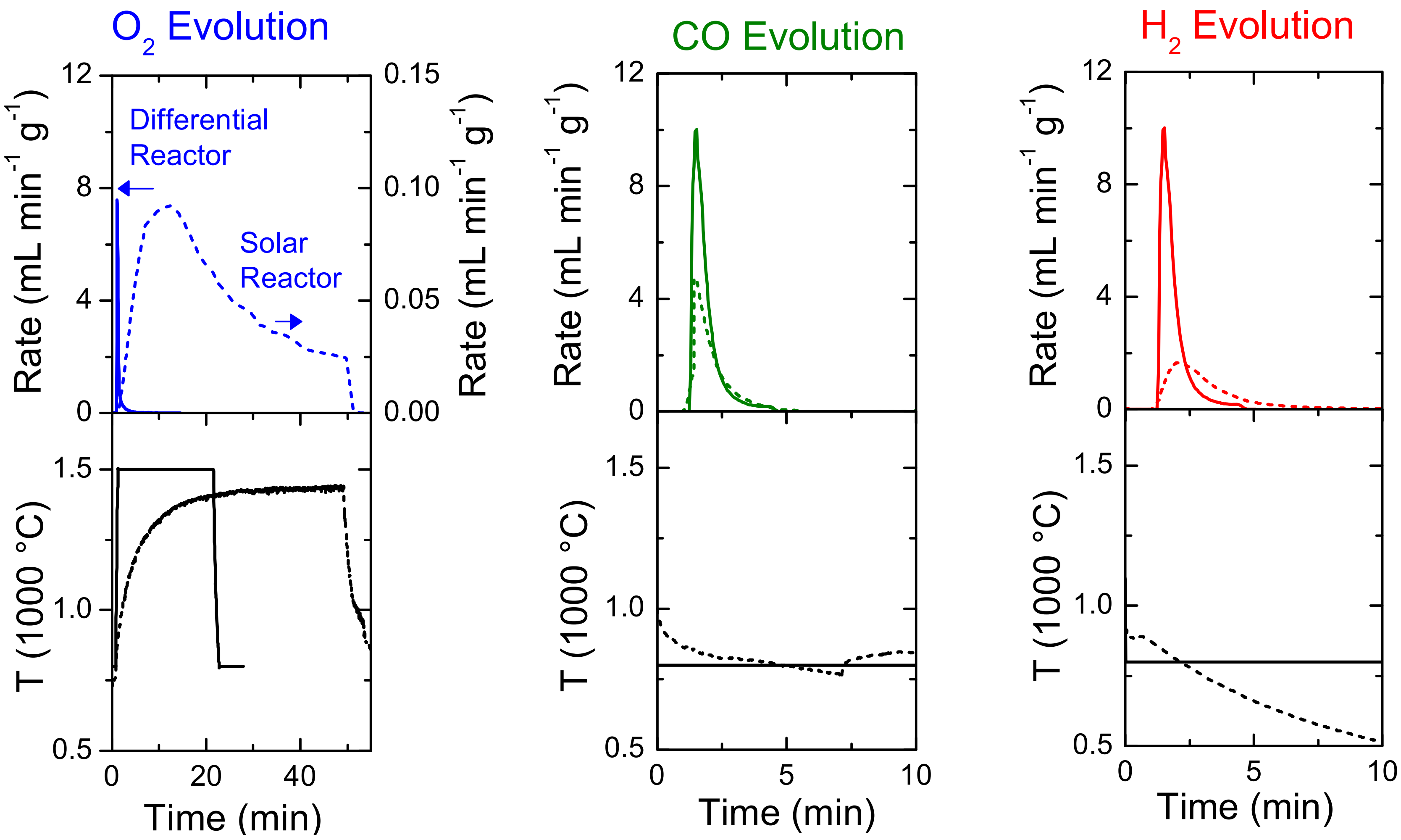


Under Simulated Solar Radiation

H_2O dissociation

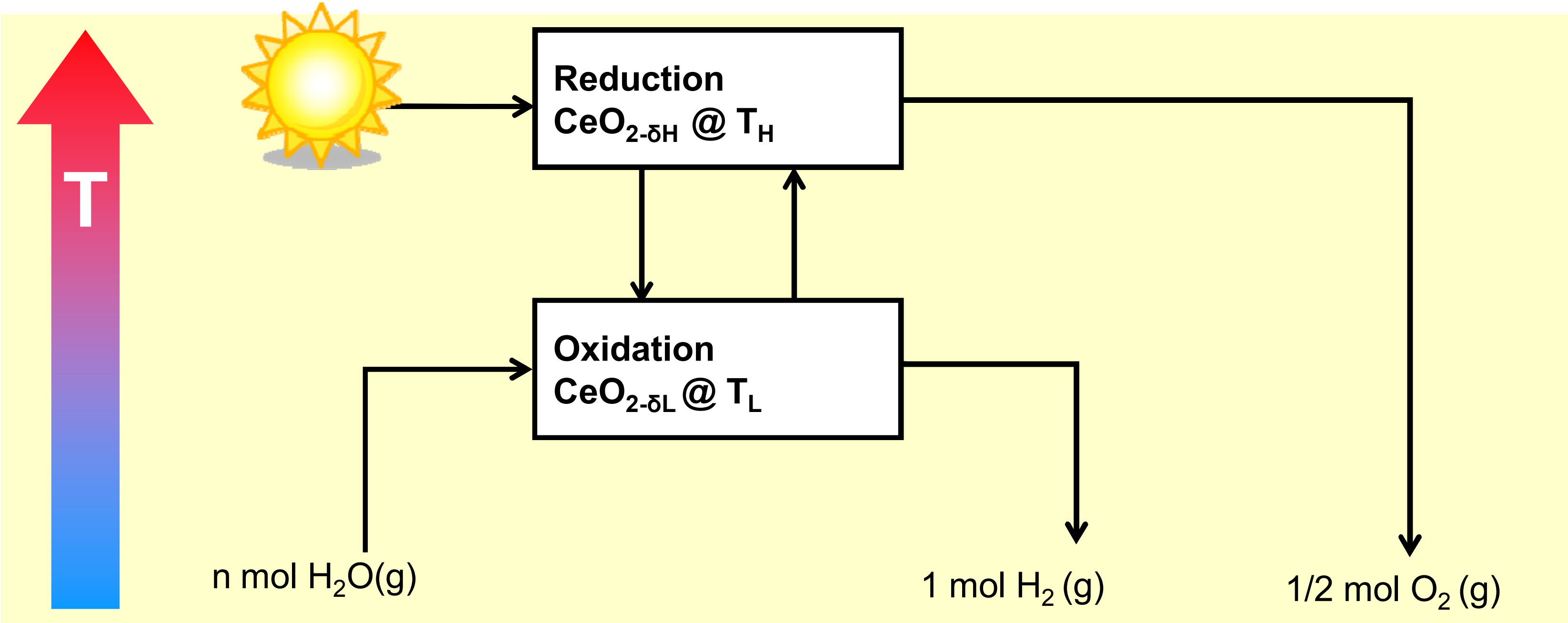


Impact of Thermal Management



Heat losses in solar reactor have major detrimental impact on efficiency

Thermodynamic Efficiency

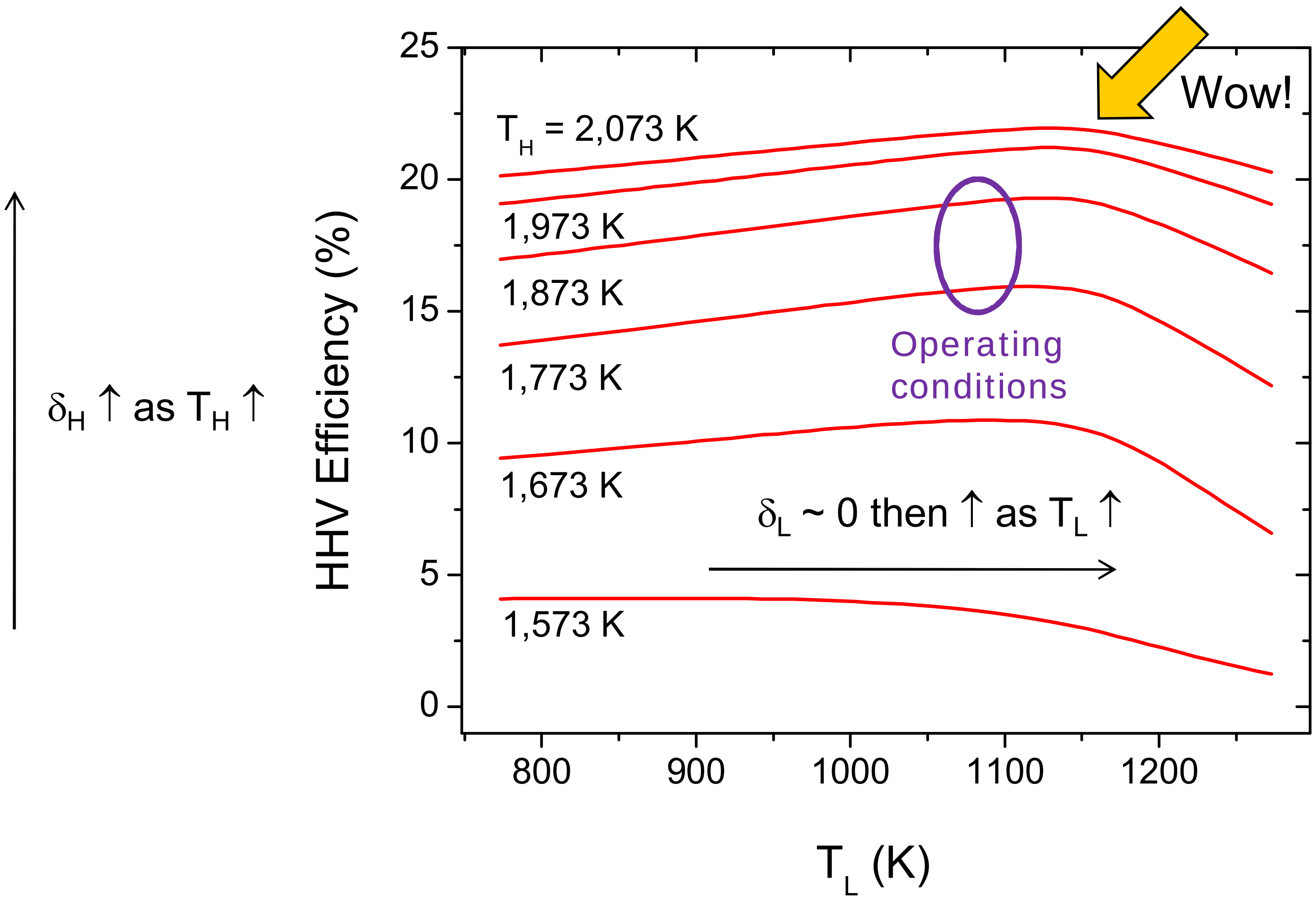


$$\eta = \eta_{solar-thermal} \times \eta_{thermal-fuel} = \eta_{solar-thermal} \times \frac{285.8kJ}{\Delta H_{input}}$$

$\Delta H_{input} =$ 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



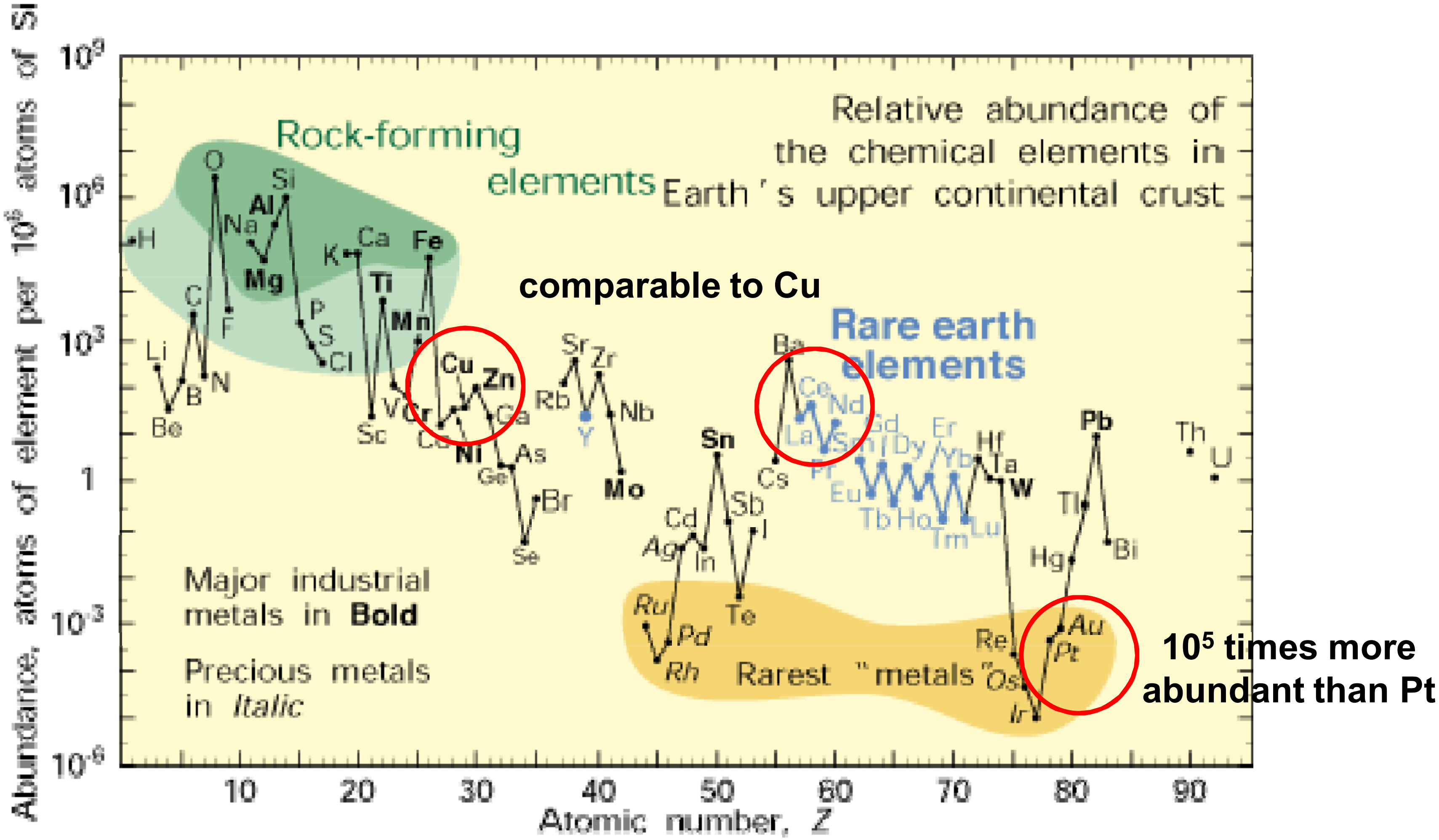
Analysis ignores potential of heat recovery

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 $\Rightarrow$ 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

Earth Abundance



Source: USGS

~ 40 MT world reserve

Conclusions & Challenges

Conclusion: *Ceria works really, really well!*

Scientific Challenges

- Thermodynamic measurements at very high temp

Engineering Challenges

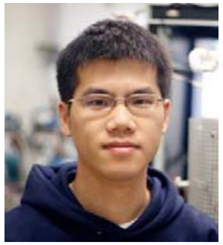
- Thermal management
- How to flush high temperature oxygen?
- Efficiency (cost!) tied to $\Delta\delta$

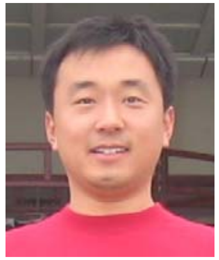
Grand Challenge

- Design of new materials
  - Wider nonstoichiometry range (CeO_2-ZrO_2 solid solutions)
  - Maintain structural stability, non-volatility?

Acknowledgments

- William, Danien, Yong
- Aldo Steinfeld & students
- National Science Foundation
- Gordon and Betty Moore Foundation
  - Caltech Center for Sustainable Energy Research
- eSolar (Philip Gleckman)






- W.C. Chueh and S. M. Haile, "Ceria as a Thermochemical Reaction Medium for Selectively Generating Syngas or Methane from H_2O and CO_2," *ChemSusChem*, **2**, 735-769 (2009).
- W. C. Chueh and S. M. Haile, "A Thermochemical Study of Ceria: Exploiting an Old Material for New Modes of Energy Conversion and CO_2 Mitigation," *Phil. Trans. R. Soc.* **368**, 3269-3294 (2010).
- W.C. Chueh, C. Falter, M. Abbott, D. Scipio, P. Furler, S. M. Haile and A. Steinfeld, "High-Flux Solar-Driven Thermochemical Dissociation of H_2O and CO_2 Using Nonstoichiometric Ceria," *Science*, **330**, 1797-1801 (2010).