SAND2011-5663C

SANDIA NATIONAL LABORATORIES

ASME Energy Sustainability 2011
Track 1-10-3 Solar Fuels via Two-Step TC with Metal Oxide Reactions
9 August 2011

Sunshine to Petrol: Oxide Materials for Thermochemical CO_2 Splitting Using Concentrated Solar Energy

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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Acknowledgements

- **SNL – S2P Team**
  - Ellen B. Stechel, PM
  - James E. Miller, PI
  - Richard B. Diver
  - Nathan P. Siegel
  - Eric Coker
  - Mark D. Allendorf
  - Gary L. Kellogg
  - Roy E. Hogan
  - Daniel Dedrick
  - Ivan Ermanoski
  - Tony McDaniel
  - Ken Chen
  - Terry Johnson
  - Chad Staiger

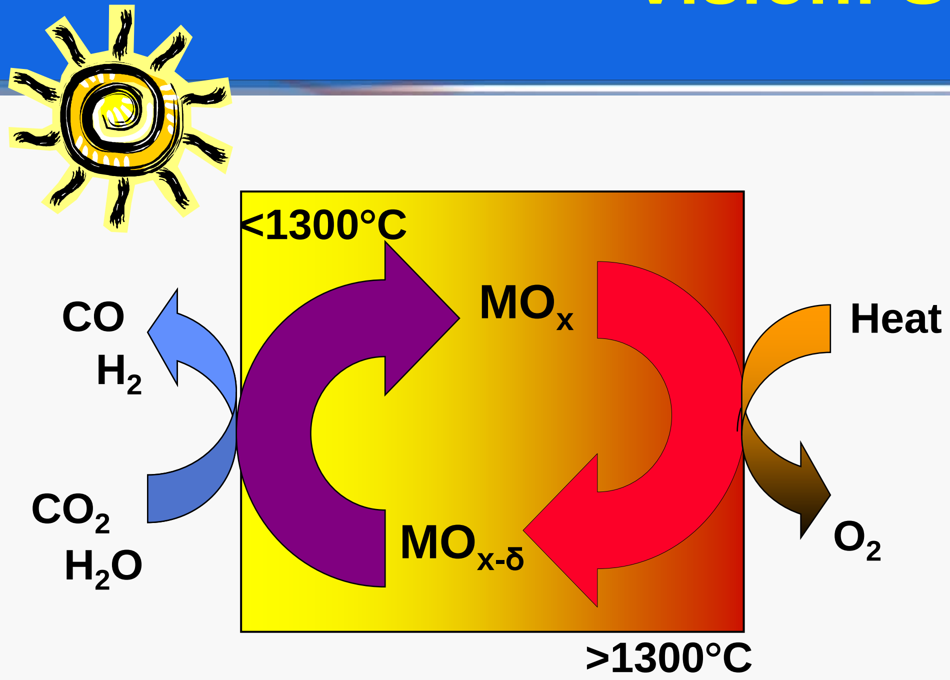
- **Special thanks:**
  - Bonnie McKenzie (SEM)
  - Tony Ohlhausen (SIMS)

- **University Partners**
  - Christos Maravelias, University of Wisconsin
  - Chris Wolverton, Northwestern University
  - Darryl James, Texas Tech University
  - Alan Weimer, University of Colorado

Funding: Sandia National Laboratories,

Lab Directed Research & Development

Vision: Sunshine to Petrol



Directly apply a solar energy source to effectively split CO_2 and H_2O into syn gas, utilizing redox-active metal oxides, in a process analogous to, but more efficient than, photochemical or biological processes.

Two step solar-thermochemical process utilizing redox reaction to split CO_2 or H_2O:

$MO_x + \text{Sunlight} \Rightarrow MO_{x-\delta} + \delta/2O_2$ (Thermal Reduction, TR)

$MO_{x-\delta} + \delta CO_2 \Rightarrow MO_x + \delta CO$ (CO_2-Splitting Oxidation, CDS)

$MO_{x-\delta} + \delta H_2O \Rightarrow MO_x + \delta H_2$ (H_2O-Splitting Oxidation, WS)

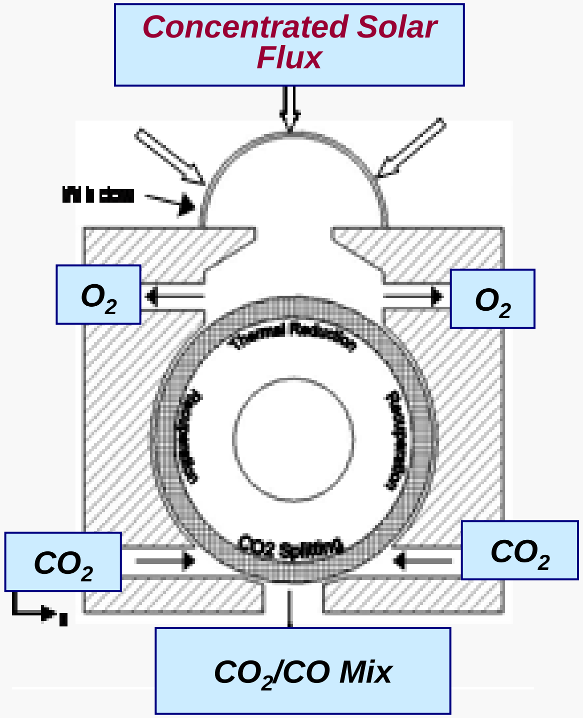
$$\boxed{\text{Sunlight} + CO_2 + H_2O \rightarrow \text{Fuel} + O_2}$$

Thermo-Chemical Splitting: The CR5

Counter Rotating Ring Receiver Reactor Recuperator

JE Miller et al, J Mater Sci (2008) 43:4714–4728

Cross-Section Illustration



Concentrated Solar Flux

O_2

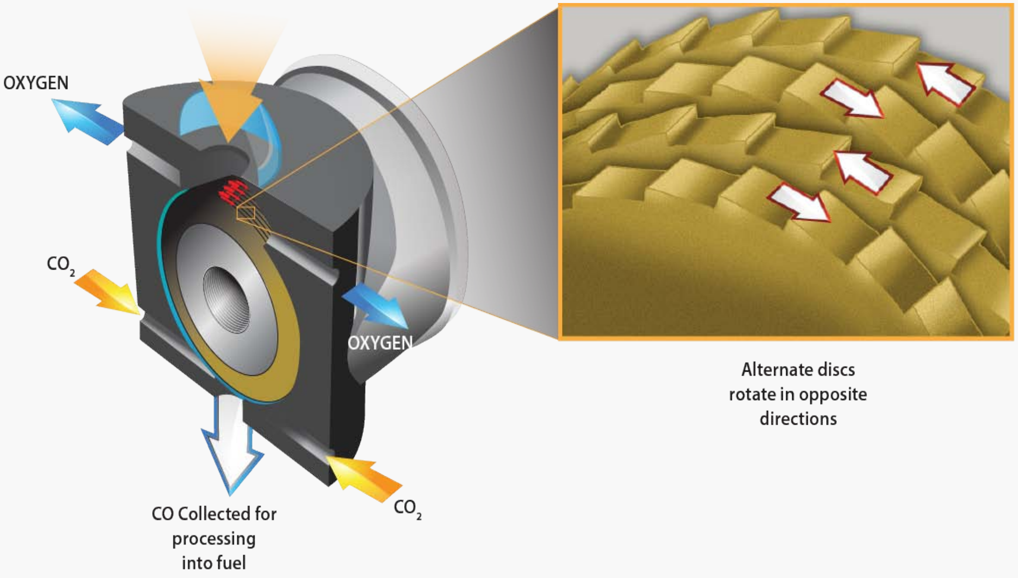
O_2

CO_2

CO_2

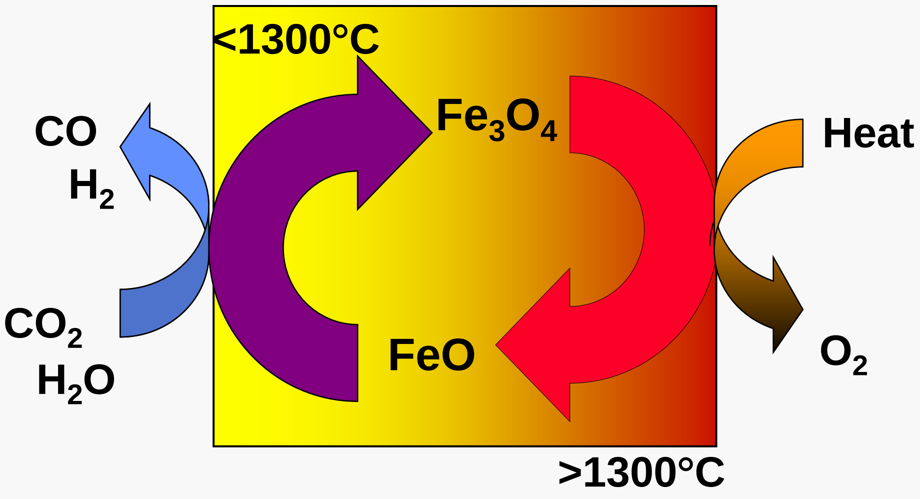
CO_2/CO Mix

Reaction Separation
Continuous Flow
Recuperation
High Efficiency



Alternate discs rotate in opposite directions

The Ferrite System



Two step solar-thermochemical process based on iron-oxide to split CO_2 (or H_2O):

1) **Fe_3O_4 + Heat $\Rightarrow$ 3FeO + ½ O_2 (Thermal Reduction, TR)**

2) **3FeO + $CO_2 \Rightarrow Fe_3O_4$ + CO (CO_2-Splitting Oxidation, CDS)**

Net: $CO_2 \Rightarrow CO + ½O_2$

- Ferrites, AFe_2O_4 (A=Fe, Ni, Co, Mn), are redox active

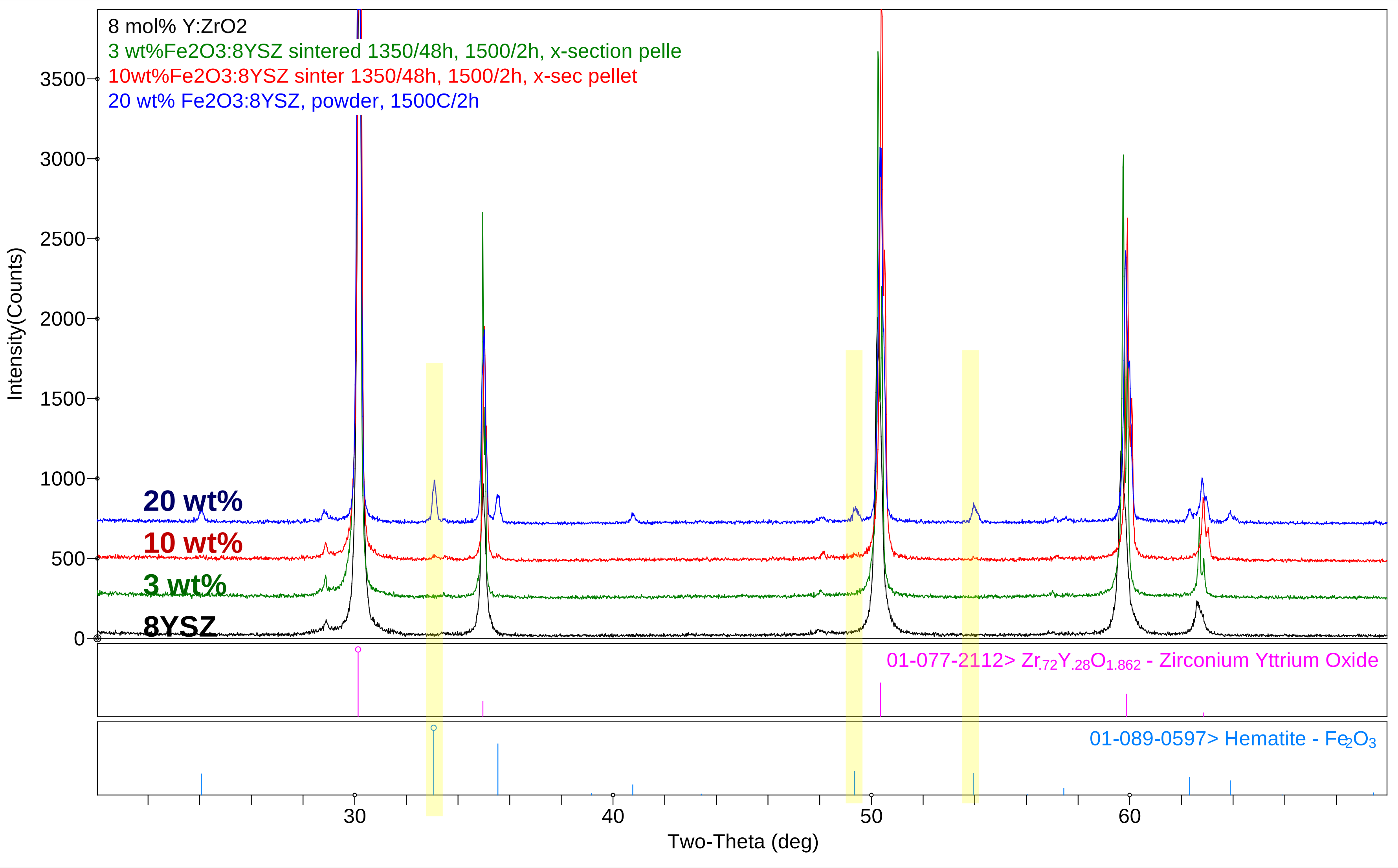
- Operate in the temperature regime of concentrated solar thermal

- Require a "support" material, e.g. ZrO_2 or YSZ, for efficient long-term cyclability (Tamaura, Kodama)

- Behavior of the ferrite systems at the high temperatures and conditions present in these repeated cycles is not well understood

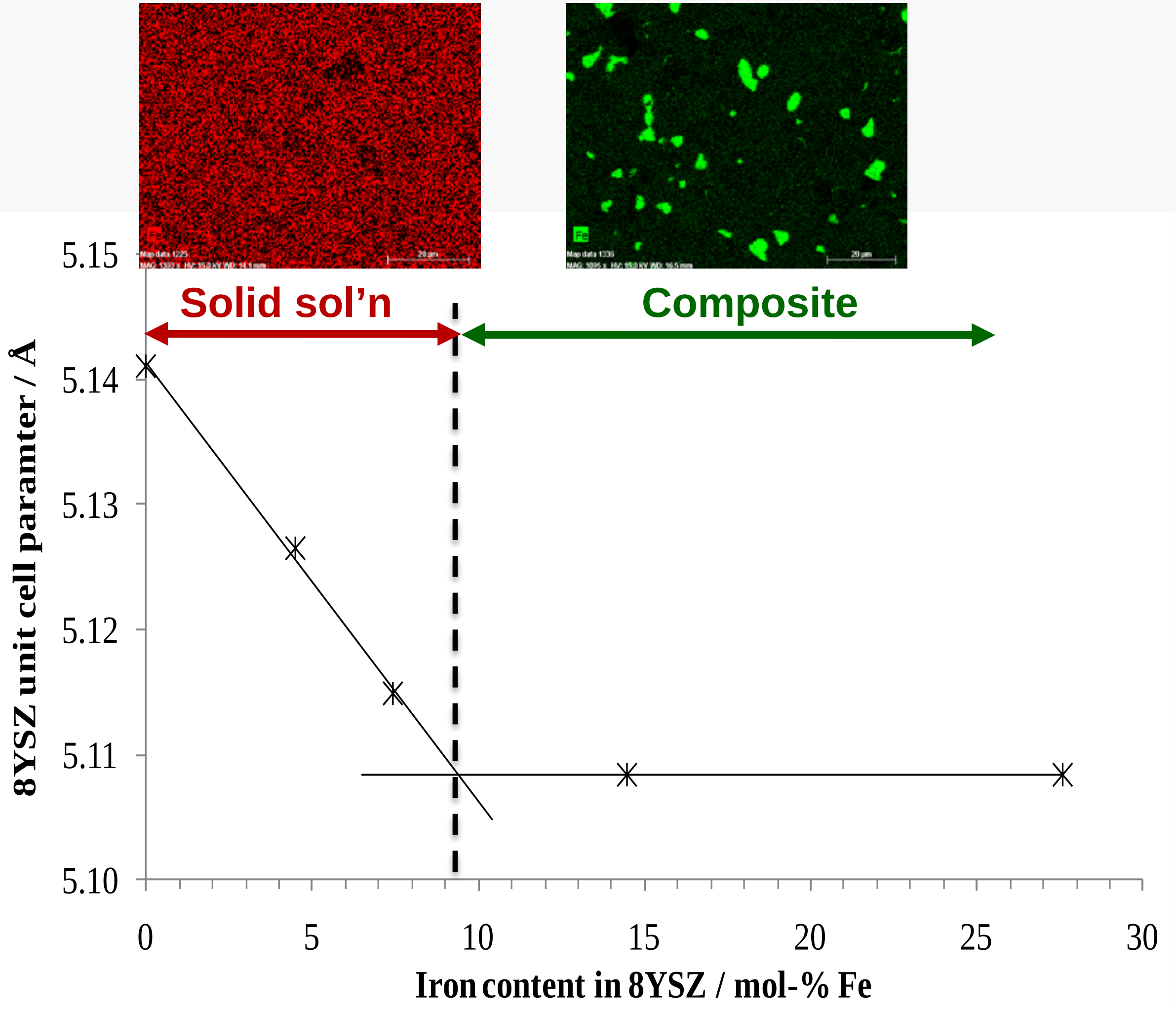
- Such questions include:
  - equilibrium reactions
  - oxygen transport
  - surface chemistry
  - structure-property relationships
  - interaction between support-active material

Room Temperature XRD of Fe_2O_3:8YSZ



Solid Solubility

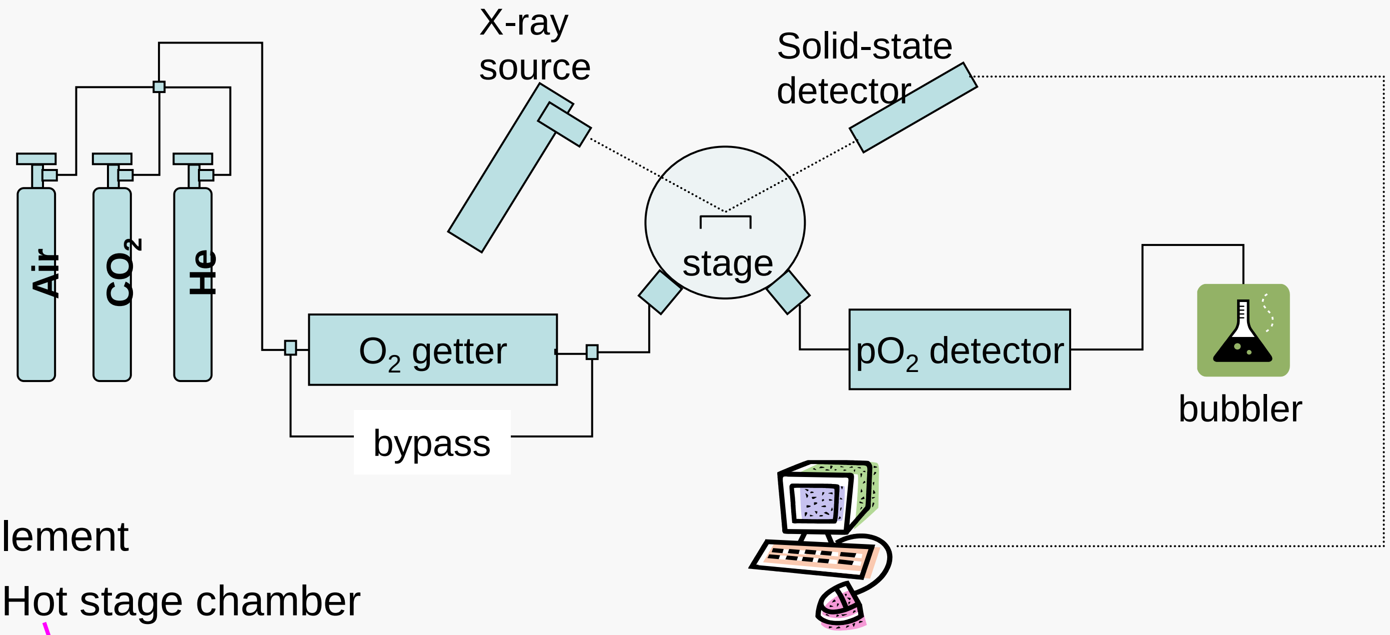
- Following Vegard’s Law, we can estimate a solubility of approx. 6.3 wt% Fe_2O_3 (~ 9.4 mol% Fe) in 8YSZ at room temperature
- At low [Fe_2O_3] can assume complete solid solution, i.e., all Fe is crystallographically substituted in YSZ crystal lattice
- At higher [Fe_2O_3] can assume composite of solid solution + “free” Fe_2O_3



Solid state synthesis
Calcined 1350 °C/48h, 1500 °C/2hr

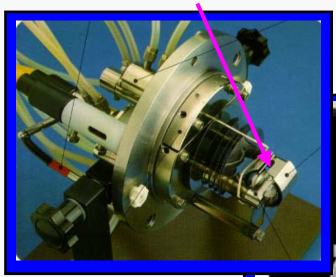
In-situ XRD

Question: Does solid solubility change with temperature/environment?

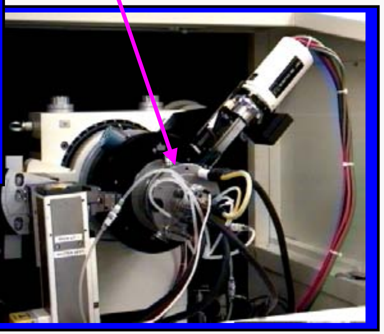


XRD output

Pt/Rh heating element



Hot stage chamber



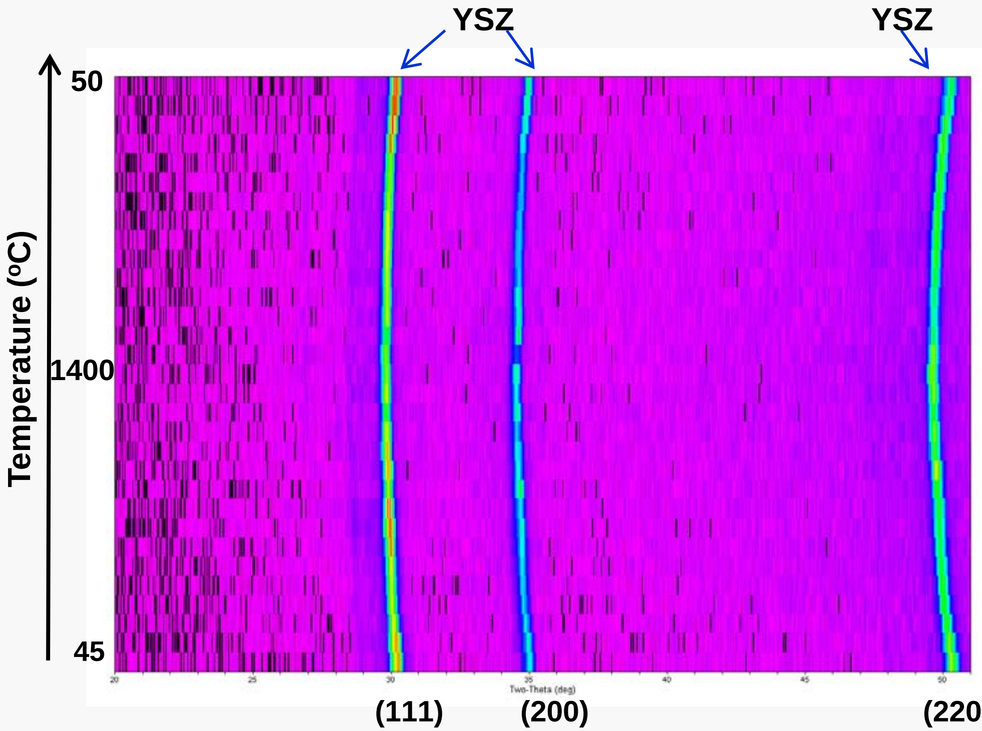
Hot stage

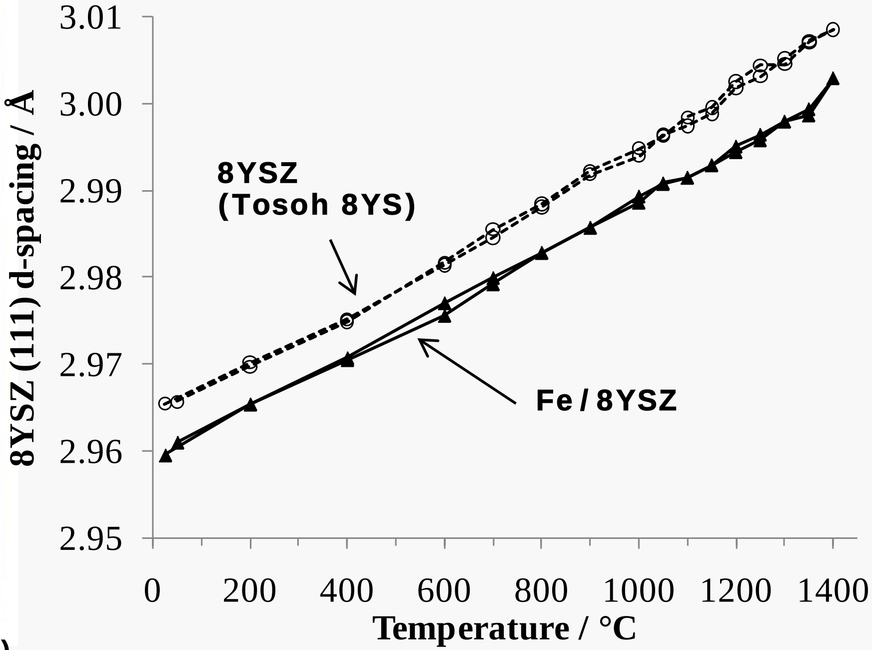
Diffractometer setup

- **Temperature range: 25 to 1450°C**
- **Pressure range: 10^{-9} to 1000 Torr (< 2 bar)**
- **Sample size: ~1 cm^2**
- **Heating rates: 1 to 100 °C/min**
- **Phase fraction detection limit: ~1 w%**

In-situ XRD of 3 wt.% Fe_2O_3:8YSZ

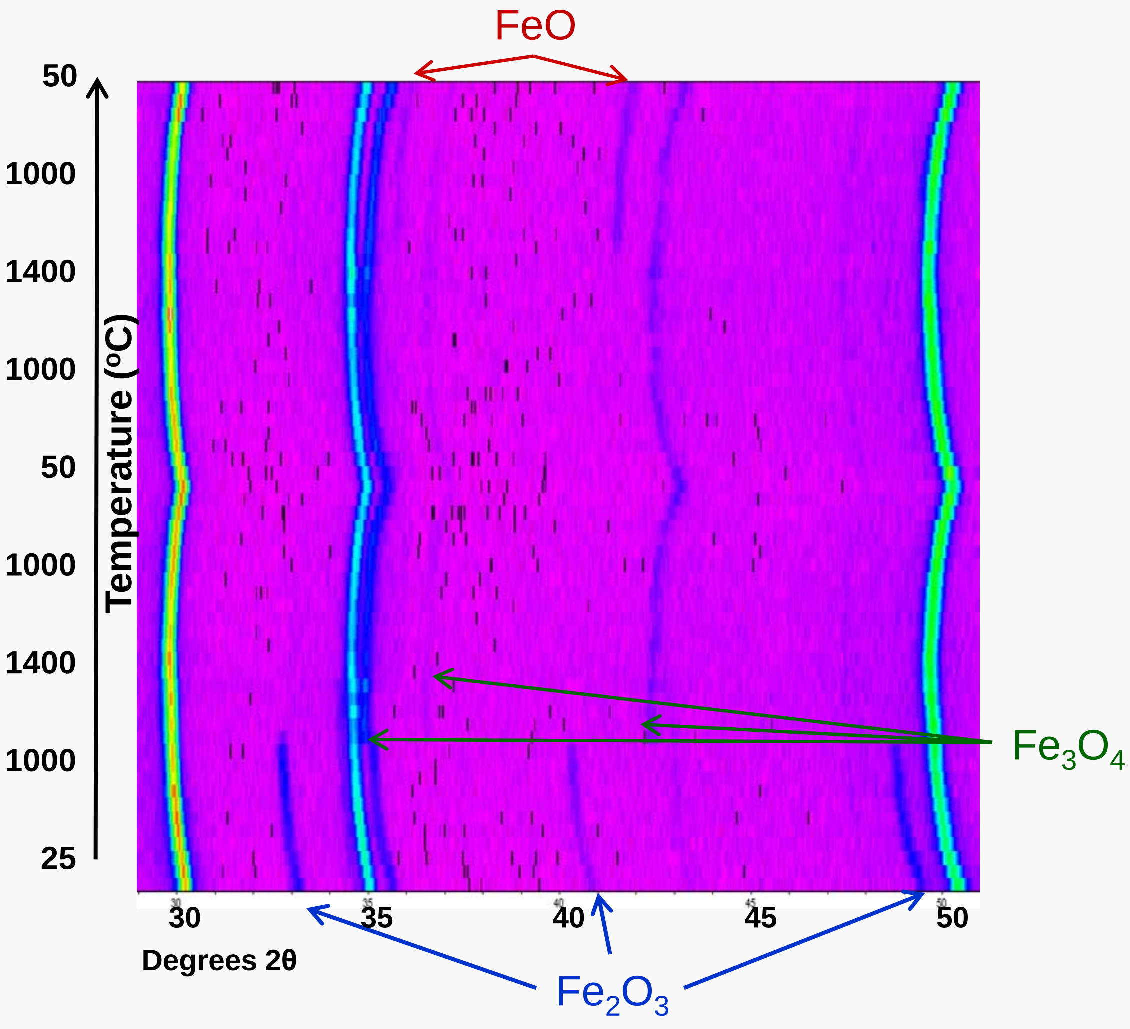
He atmosphere
Sample calcined 1375 °C/48h, 1500 °C/2h

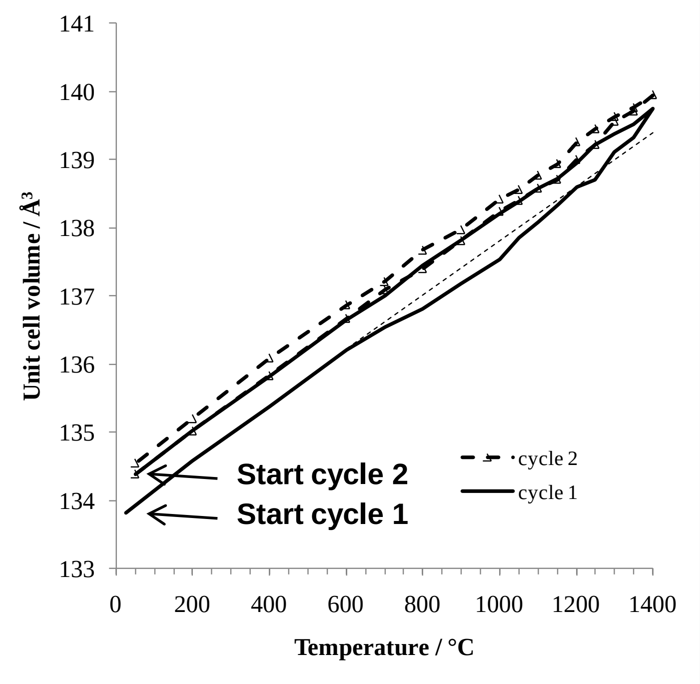




- Fe remains in solid solution during TR cycle
- CO produced during CDS
- Δ Fe oxidation state does not noticeably affect YSZ d-spacing

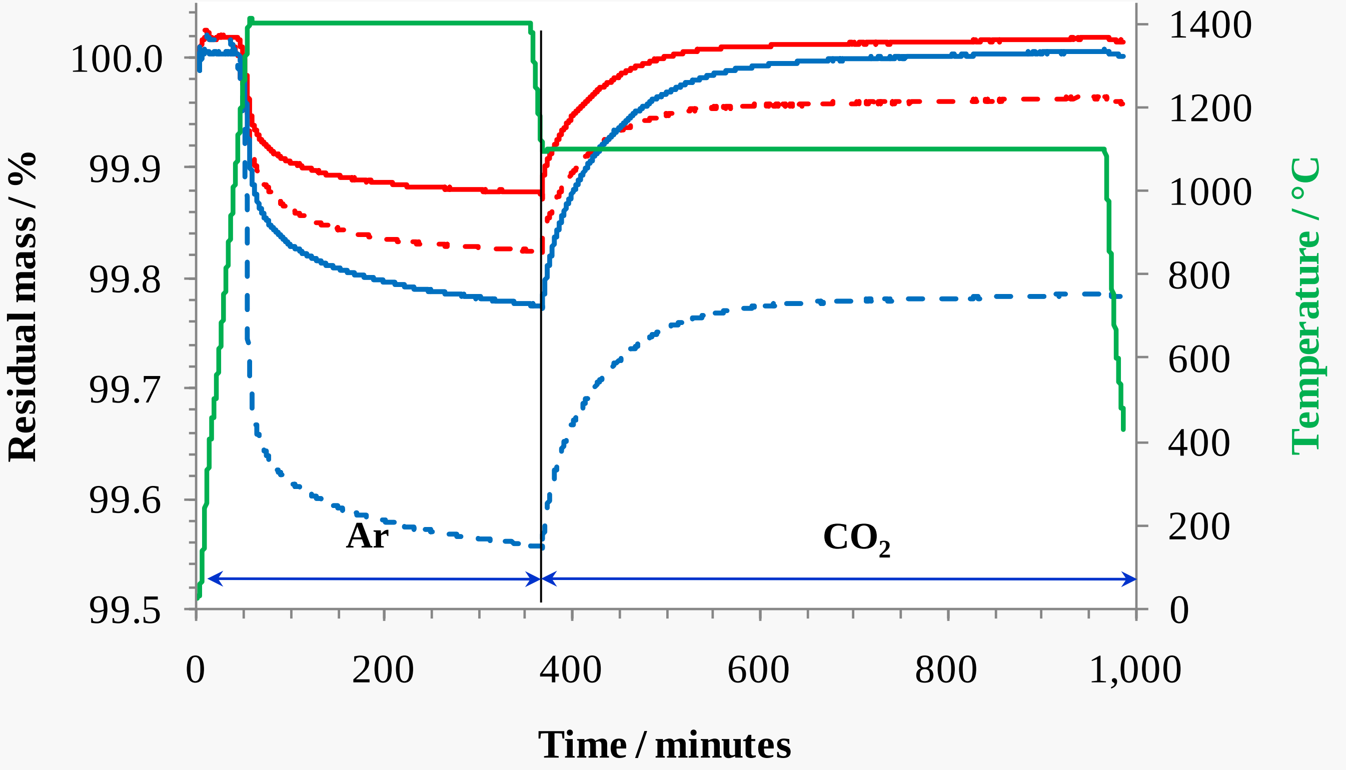
Solubility of Fe in 8YSZ is Dynamic





- As sample is heated under He $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO$
- YSZ lattice expansion occurs due to both thermal expansion and migration of Fe out of lattice
- 1st cycle shows significant migration of Fe out of YSZ
- 2nd cycle shows minor migration of Fe out of YSZ

Long Redox of Fe_2O_3:8YSZ



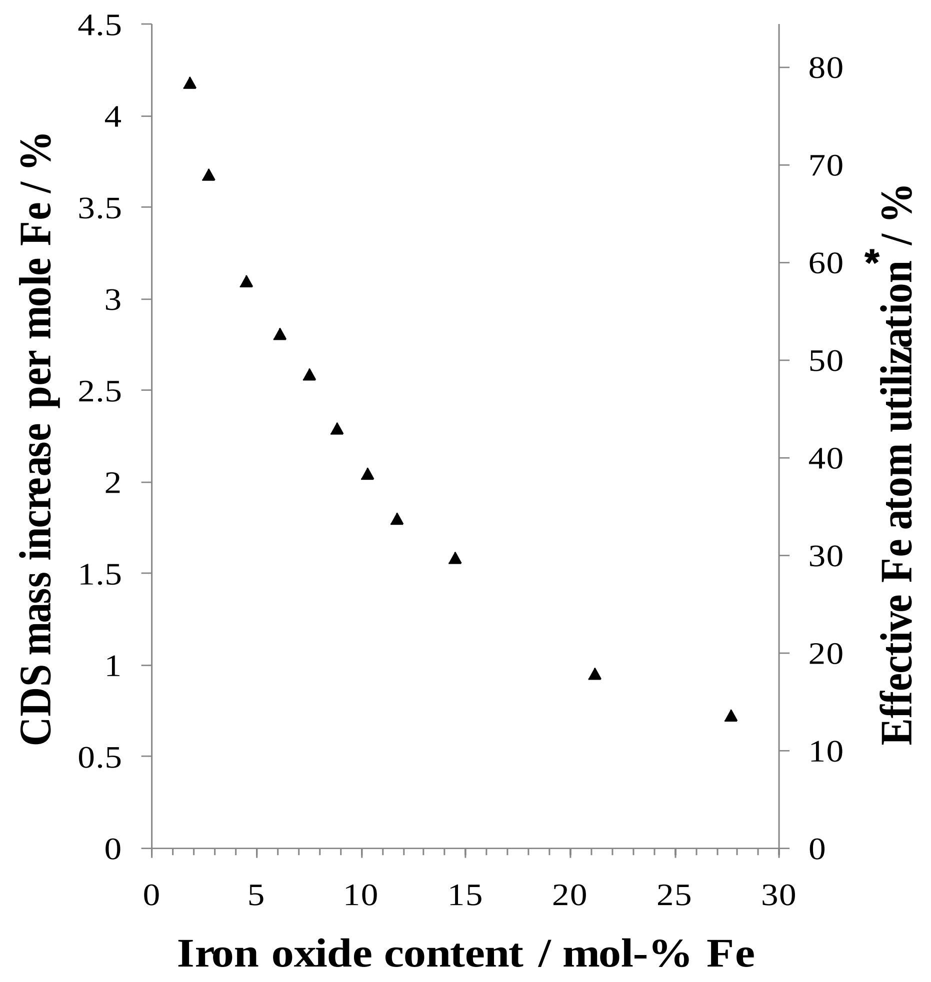
Dashed line – 1st cycle
Solid line – 2nd cycle

Red:
4.5 mol-% Fe/8YSZ

Blue:
14.5 mol-% Fe/8YSZ

- 1st cycle shows deeper reduction and incomplete reoxidation; more pronounced for 14.5% sample
  - Samples don't reoxidize completely to Fe_2O_3 (or Fe^{3+}) after initial reduction
- However re-oxidation magnitude remains constant between cycles
- Subsequent cycles resemble 2nd cycle (not shown)

Iron utilization



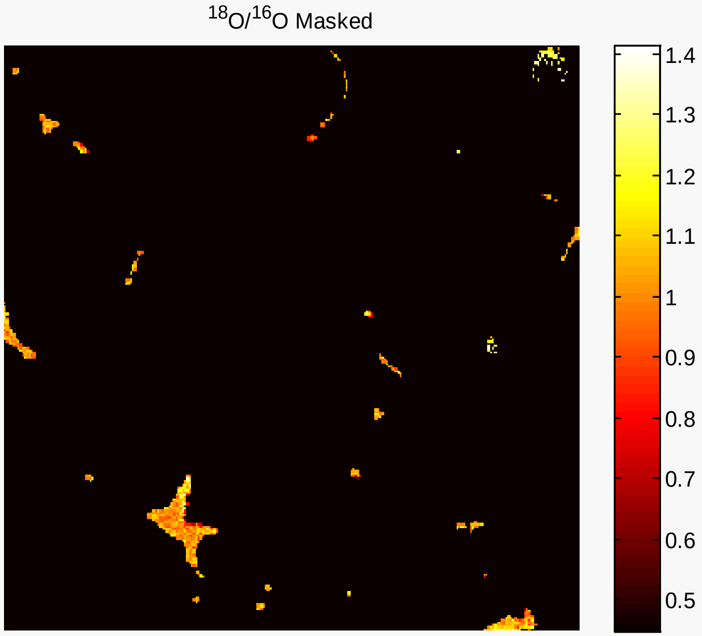
- Lower Fe-loading gives higher utilization
- Even at 1.8 mol-% Fe, still some un-utilized Fe
  - In solid solution, assume redox reaction is between $Fe^{3+} \leftarrow\rightarrow Fe^{2+}$
  - Each Fe is accessible to redox, but there may be an equilibrium state between +3/+2 that prevents full reaction in YSZ
- For "free" iron oxide possible reaction mechanism is: $Fe_2O_3 \rightarrow Fe_3O_4 \leftarrow\rightarrow FeO$
  - After initial reduction to FeO complete reoxidation is unlikely under TGA conditions
  - XRD post-reduction and post-TGA cycle show presence of wüstite and magnetite phases
  - Is the reaction in bulk FeO_x surface limited?

* *Utilization assumes* $Fe_3O_4 \leftrightarrow 3FeO + \frac{1}{2}O_2$

ToF-SIMS

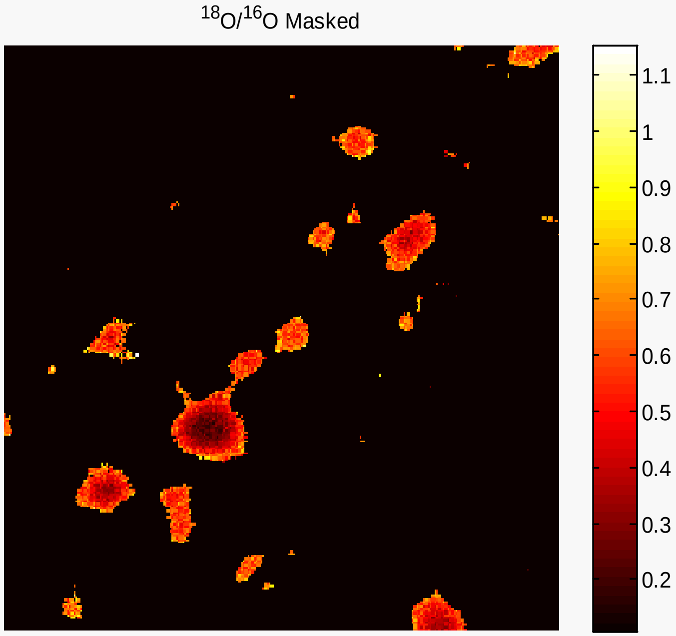
Time-of-Flight Surface Ionization Mass Spectrometry

- Isotopically label sample with ^{18}O; analyze ^{18}O distribution
- TR under Ar; 1400 ° C/16 hr; CDS under $C(^{18}O)_2$; 1100 °C/7 hr
- Disc cross-sectioned, polished
- 8YSZ matrix: uniform 18O & 16O distribution - fast oxygen transport



7.5 mol-% Fe/8YSZ

100 x 100 μm²



14.5 mol-% Fe/8YSZ

^{18}O distribution uniform through small particles (below solubility limit, but still some small FeO)

Fe above solubility limit, and large particles: ^{18}O mostly at surface of FeO_x; interior ^{16}O-rich

Summary and Conclusions

- Iron oxide:8YSZ system shows dynamic behavior during temperature cycling under reducing and oxidizing conditions
  - HT-XRD showed no phase changes in 4.5 mol-% Fe solid solution upon in-situ reduction
  - Phase changes observed in composite material
  - HT-XRD and 8YSZ lattice parameters reflect complex migration of Fe in/out of solid solution
  - 2 – 3 cycles required until steady state composition achieved

- TGA cycling experiments:
  - Illustrate dynamic behavior of composite material
  - 1st cycle reduction greater than subsequent cycles (and not linear)
  - %Fe utilization greater for lower iron-loaded (solid solution) samples

- ToF-SIMS shows limited re-oxidation of bulk iron oxide particles under CO_2
  - ^{18}O permeates YSZ matrix, but concentrates at surface of larger FeO_x particles
  - Smaller (e.g., nano) particles show better O-exchange, implying that composites consisting of nano-Fe particles may show increased activity

Future and Ongoing Work

- Efforts to improve the ferrite materials
  - Increase solid solubility of Fe in YSZ
  - Develop composites that maintain high surface area and/or small ferrite particle size
- Further experiments and collaborative efforts include:
  - Multi-cycle durability experiments (100+ cycles)
  - Atomistic modeling of Fe-Y-Zr oxide system
  - In-situ XPS to define Fe oxidation states
  - Further in-situ XRD and TGA characterization
- Investigation of alternate materials

Thank You for Your Attention

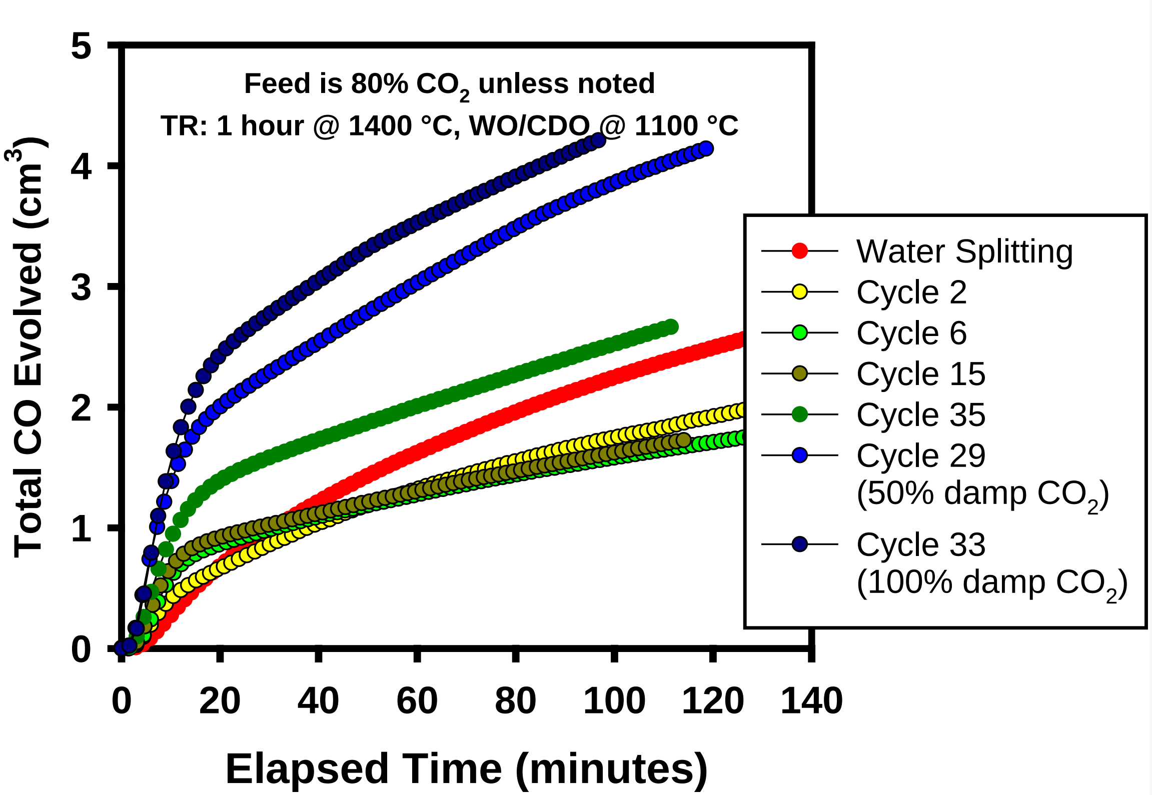
Questions?

Fossil Fuels – Non Renewable, Buried Sunshine

- **Each gallon of gasoline is estimated as equivalent to 100 tons* of prehistoric biomass, processed for millions of years**
  - Ancient stored solar energy
- **Estimate of Conversion Efficiency ~2×10^{-4} %**
  - We don’t have millions of years to make what we are burning in centuries
- **Corn Ethanol Conversion Efficiency ~0.1%**
  - Lot better
- **But can we improve on that efficiency even more by using chemical processes? 10%?**
  - E.g. Solar driven thermo-chemical processes

*Jeffrey S. Dukes, Climatic Change **61:** 31–44, 2003.

CO_2 Splitting Over 5% Fe_2O_3/YSZ

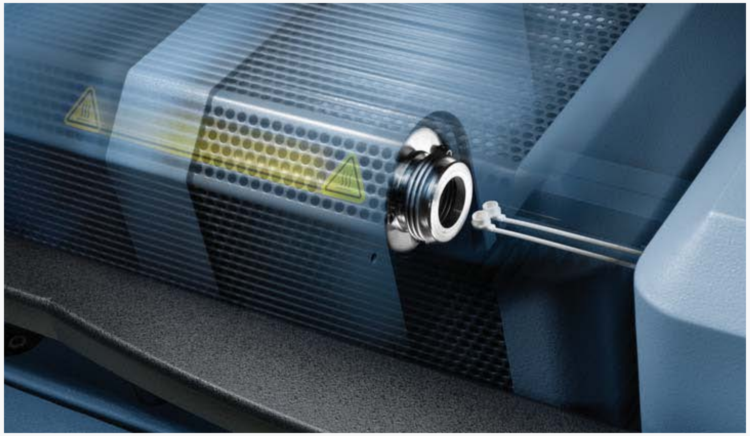


47 cycles laboratory cycles of 2.8 g lattice monolith

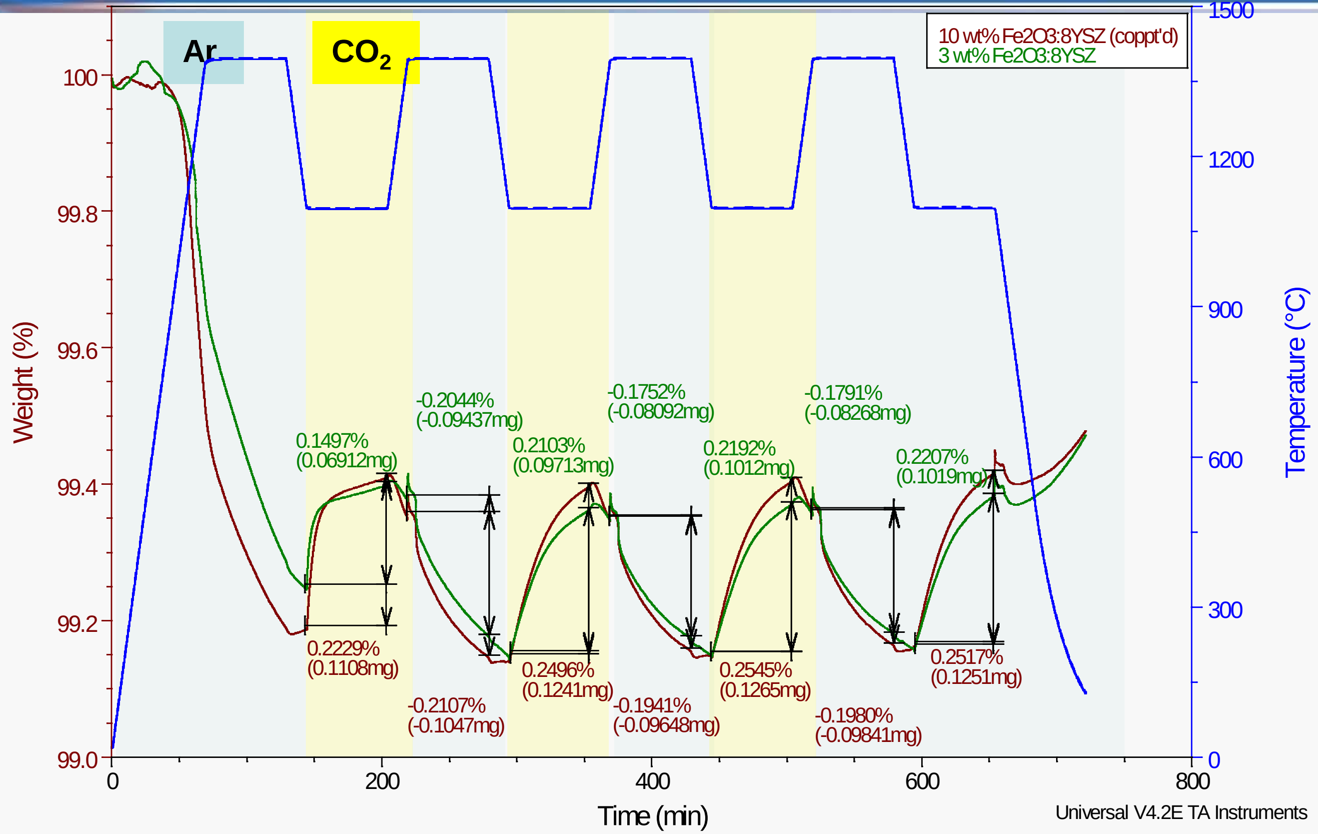
- CO_2 (and H_2O) splitting demonstrated over multiple temperature cycles
- Material does not reach steady state even after multiple cycles
- 10-15% reaction extent in 2-3 minute cycles in On-Sun testing
- Higher % Fe utilization in 5 wt% loaded Fe_2O_3 than 20 wt% (not shown)

TGA Experiments

- Examined both solid solution and composite compositions
- Samples were sintered pellets or bars cut from pellets
- Pt TGA pans used (Al_2O_3 reacts with powders)
- Gas flowed at 100 sccm throughout experiment
- O_2 scrubbers were placed on both Ar and CO_2 gas lines
- Ramp rates were 20 °C/min; gas stream changed when desired temperature reached: 1400 °C for reduction (Ar), 1100 °C for oxidation (Ar/CO_2 or pure CO_2)
- Assumed weight change during isotherm due to O_2 gain/loss in sample; weight change calculated for isotherms (not ramps)

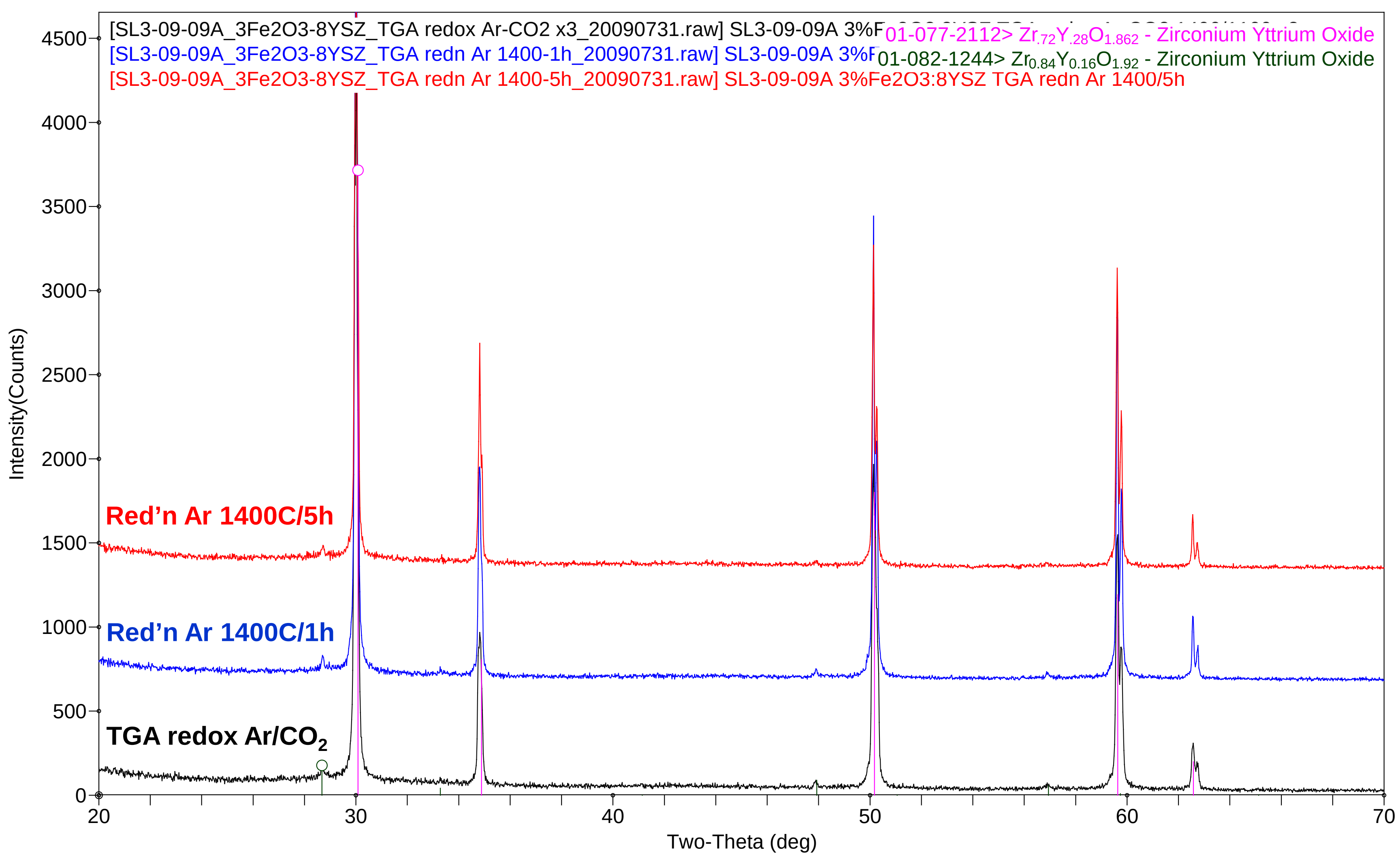


TGA: Redox Ar/CO$_2$ of Fe$_2$O$_3$:8YSZ



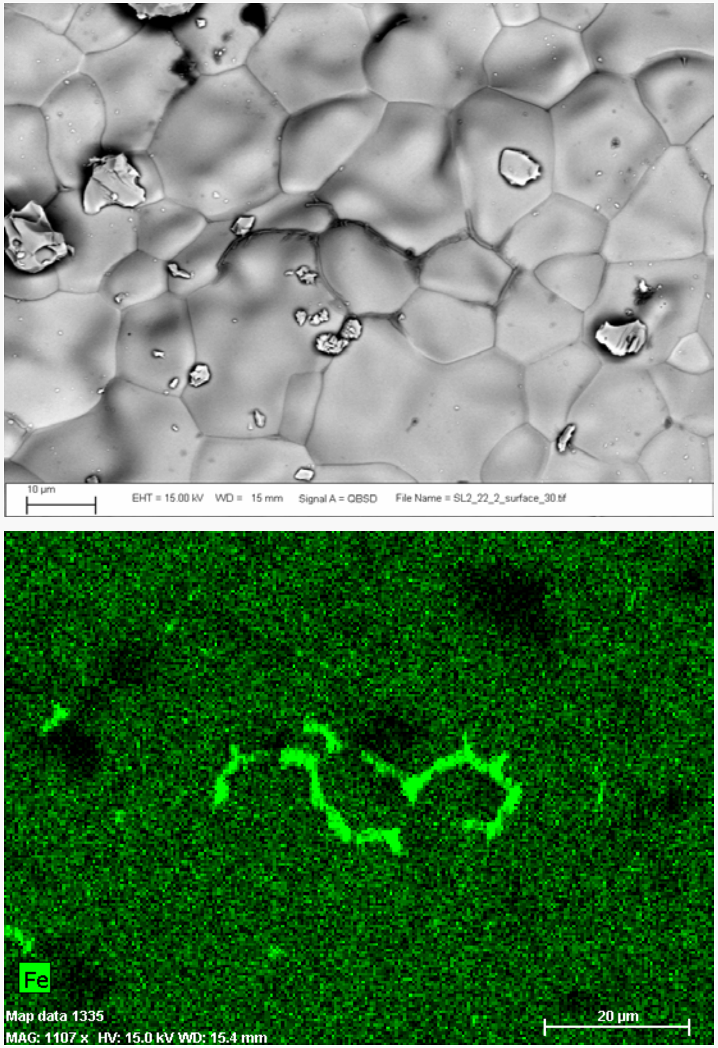
- Deeper reduction on first cycle
- Neither sample reaches equilibrium (1hr) or shows complete reaction compared to theoretical calculations
- Solid solution (3 wt%) and composite (10 wt %) react similarly, despite different loadings

XRD of 3 wt% Fe_2O_3 post-redox TGA

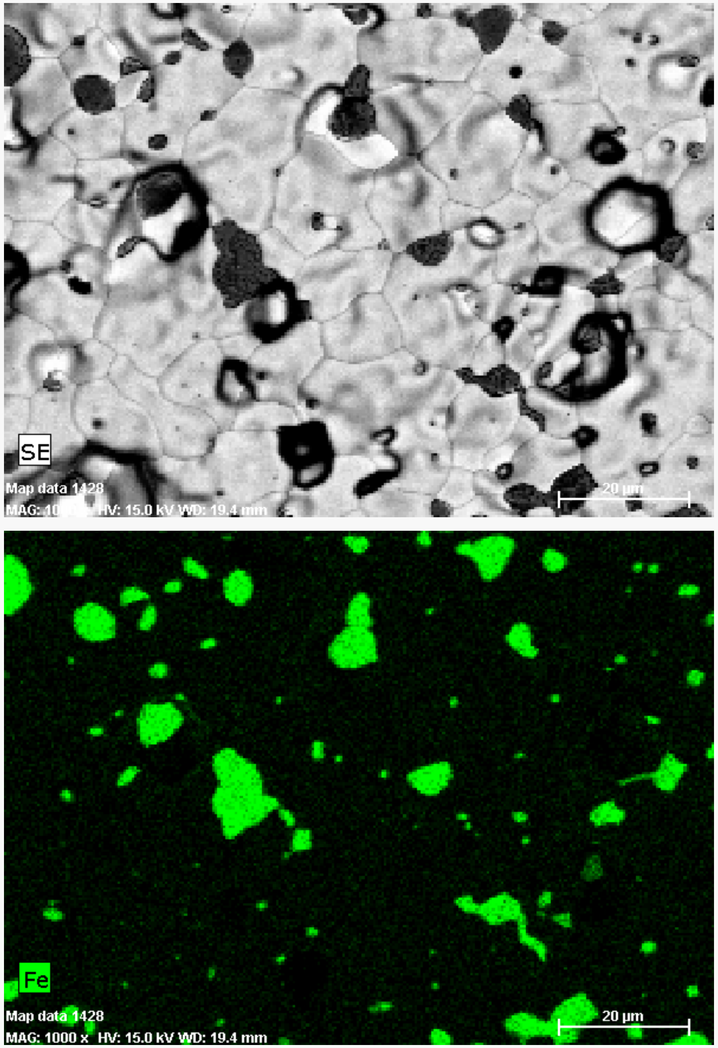


SEM of 10 wt% Fe_2O_3 Before and After TGA

Before



After



XRD of 10 wt% Fe_2O_3 post-redox TGA