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Oxide materials for thermochemical CO_2 splitting using concentrated solar energy

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Sandia National Laboratories

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Division of Inorganic Chemistry
Environmental and Energy Related Inorganic Chemistry
22 August 2012

Sunshine to Petrol

Vision: Sunshine to Petrol

S2P SUNSHINE PETROL

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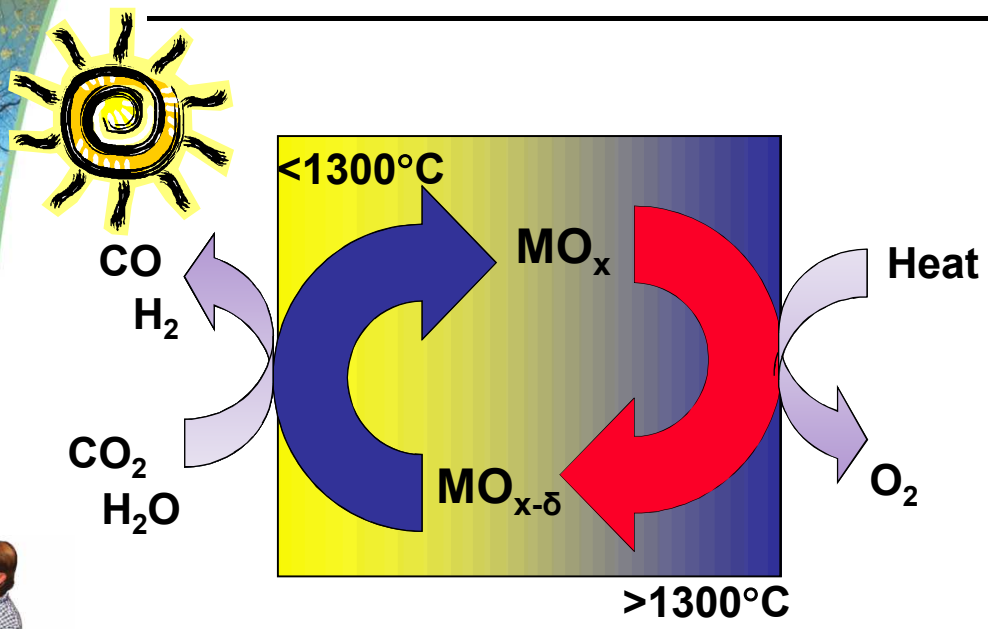

Directly apply a solar energy source to effectively split CO_2 and H_2O into syn gas, utilizing redox-active metal oxides, in a process analogous to, but more efficient than, photochemical or biological processes.

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

$MO_x + Sunlight \rightarrow MO_{x-\delta} + \delta/2O_2$ (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)

$Sunlight + CO_2 + H_2O \rightarrow Fuel + O_2$

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Thermo-Chemical Splitting: The CR5

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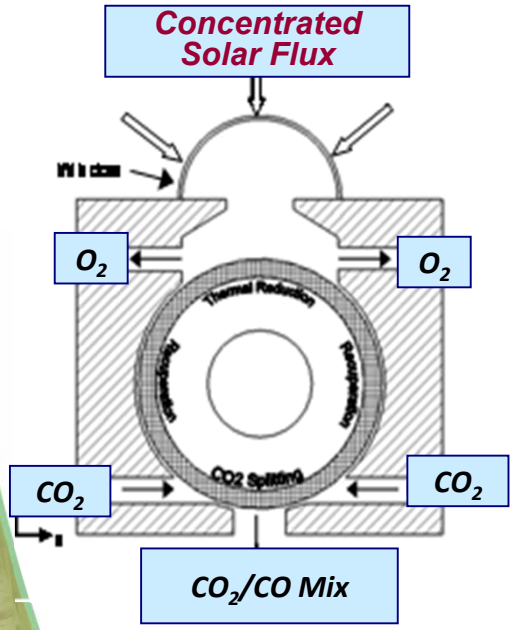
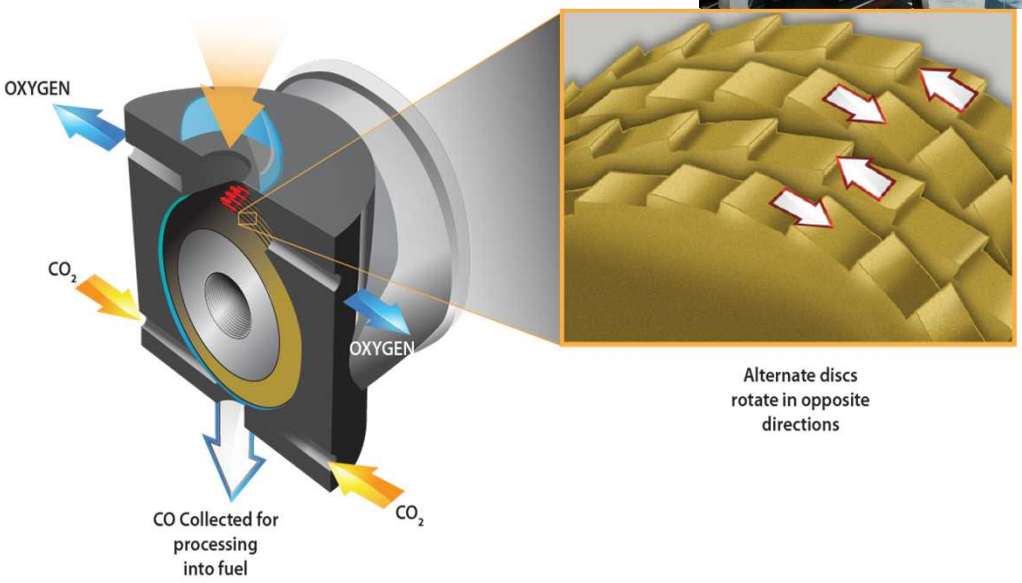
Counter Rotating Ring Receiver Reactor Recuperator

Cross-Section Illustration



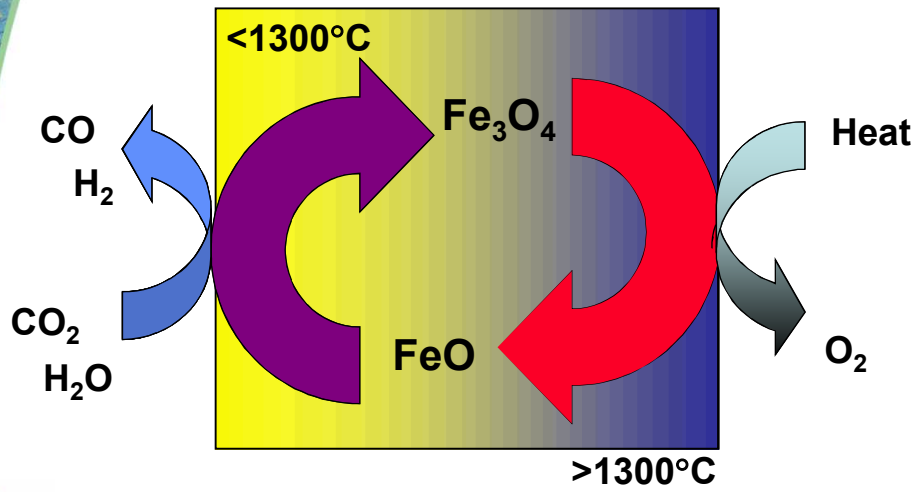
Reaction Separation
Continuous Flow
Recuperation
High Efficiency



Diver, Miller, et al., **J Solar Ener Eng,** *2008, 130 (4), Art #041001.*

Sunshine to Petrol

The Ferrite System



Fe_3O_4 + Heat → 3FeO + ½ O_2

3FeO + CO_2 → Fe_3O_4 + CO

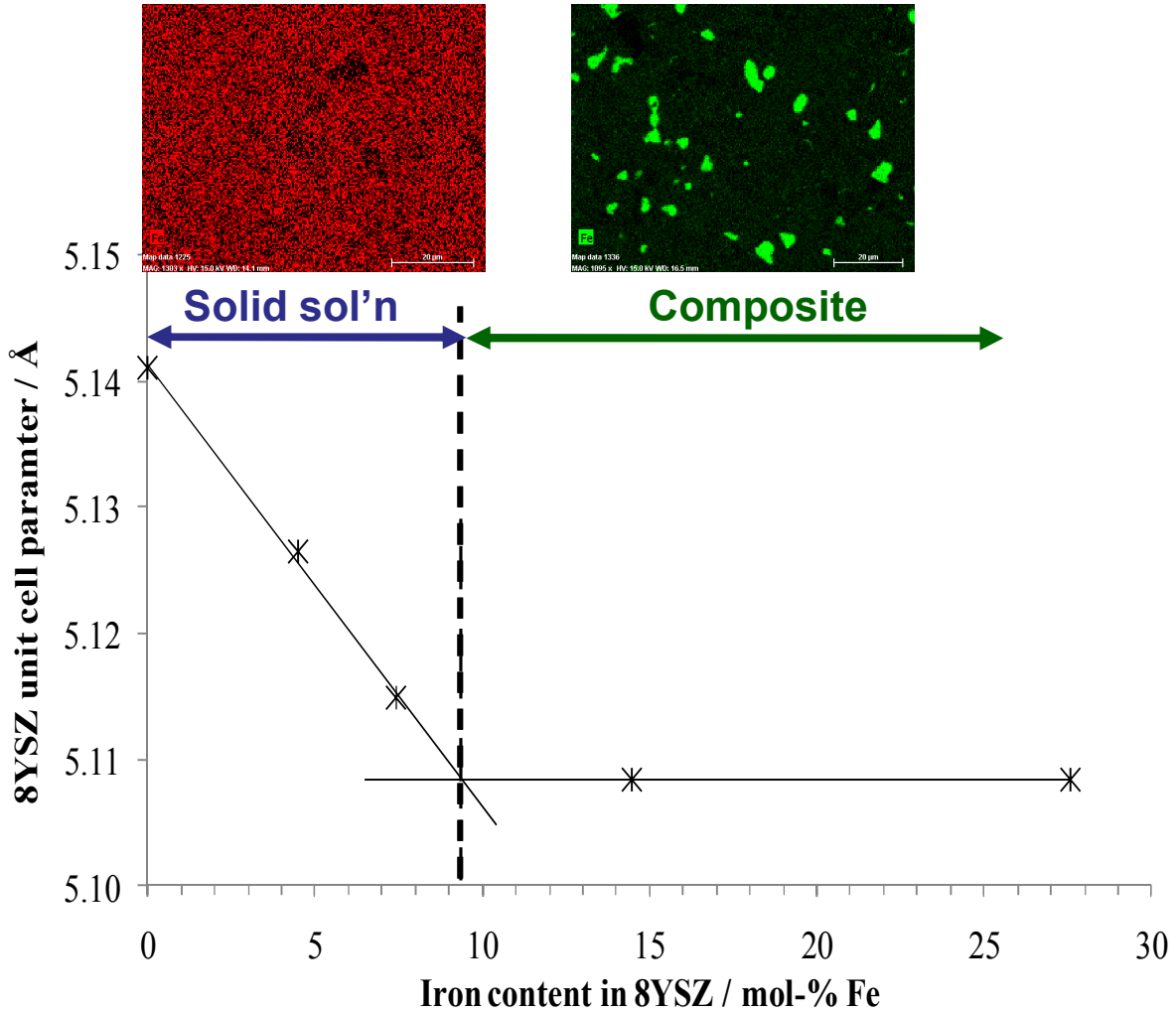
Net: CO_2 → CO + ½O_2

- Ferrites, Fe_3O_4 is redox active
- Require a "support" material, e.g. ZrO_2 or YSZ, for efficient long-term cyclability (Tamaura, Kodama)
- Behavior of the ferrite systems at reactor temperatures and conditions is not well understood
- Such questions include:
  - equilibrium reactions
  - oxygen transport
  - structure-property relationships

A systematic study of the ferrite system has been undertaken to answer these questions. The design of in-situ experiments to investigate the chemistry under operating conditions has been a main focus. The results of these experiments and how they relate to material performance are presented.

Solid Solubility

- Following Vegard's Law, estimate solubility of ~ 9.4 mol% Fe in 8YSZ at rt
- At low [Fe] can assume complete solid solution, i.e., all Fe is crystallographically substituted in YSZ crystal lattice
- At higher [Fe] can assume composite of solid solution + "free" Fe_2O_3



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

AmbrosiniCoker Rodriguez, et al. In *Advances in CO_2 Conversion and Utilization*, American Chemical Society: 2010; Vol. 1056, pp 1.

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In-situ XRD

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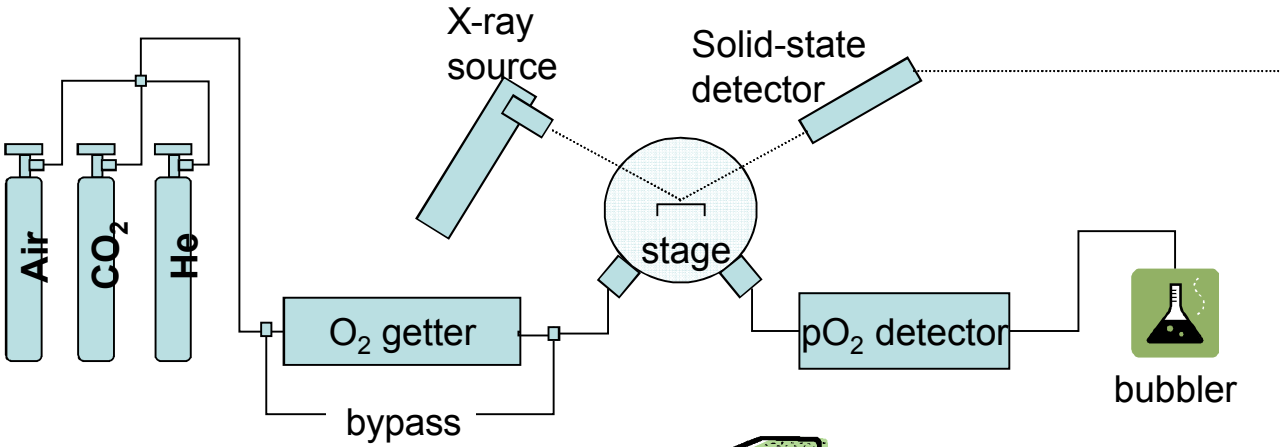
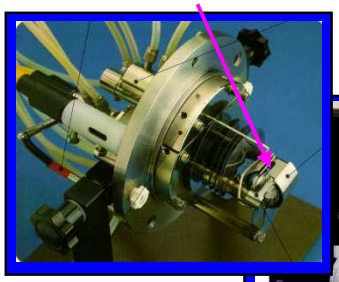
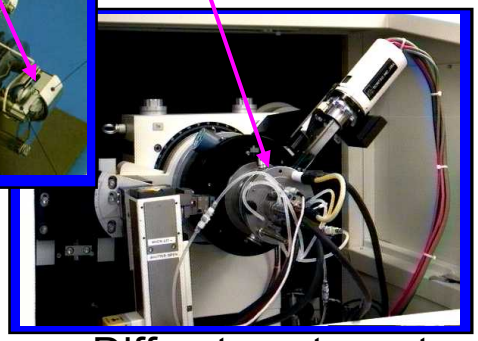
Question: Does solid solubility change with temperature/environment?



XRD output



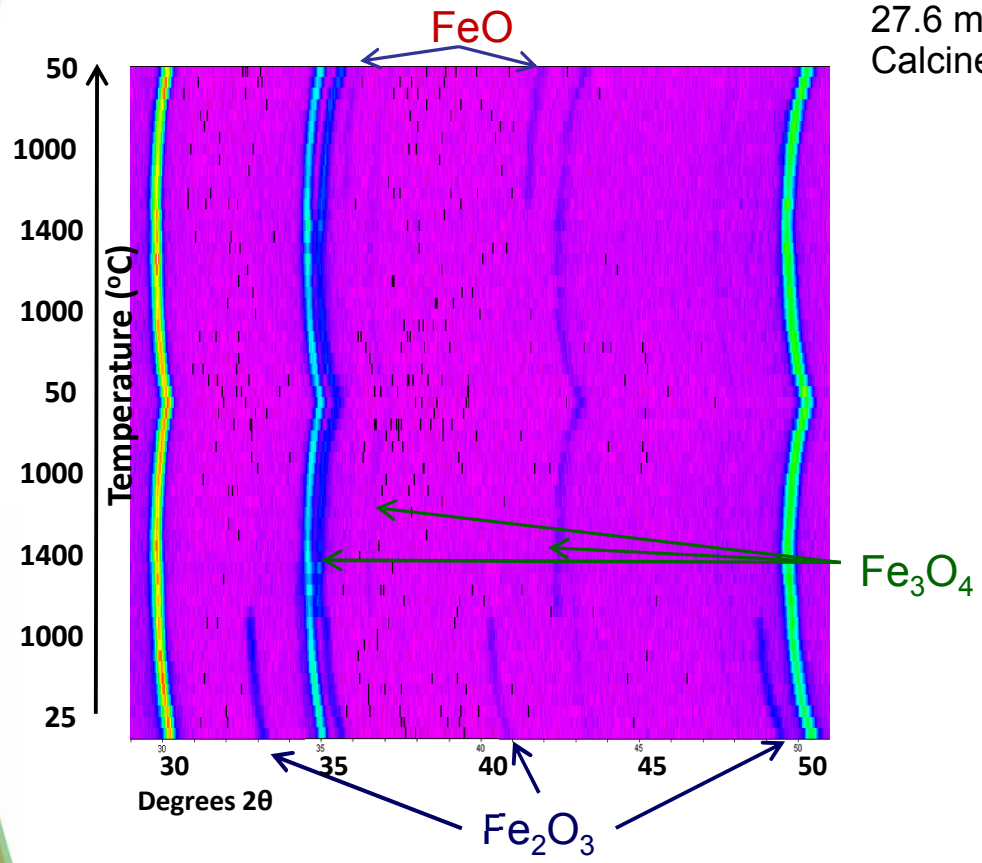
Hot stage



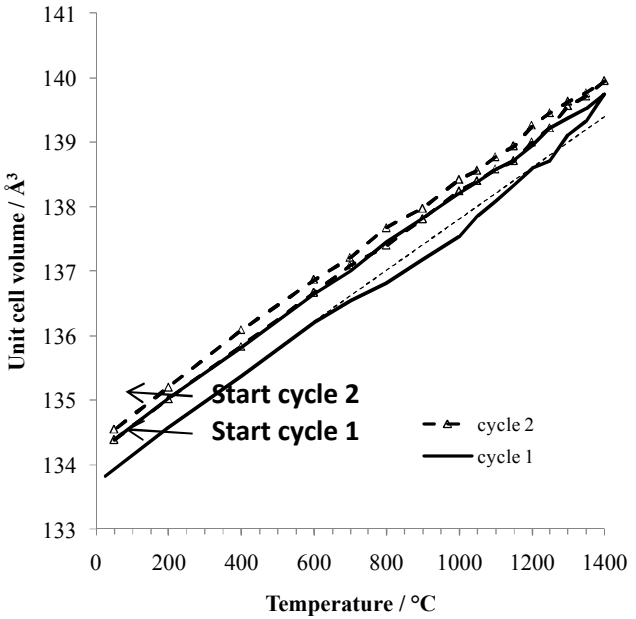
Diffractometer setup

- **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%**

Solubility of Fe in 8YSZ is Dynamic



27.6 mol% Fe:8YSZ
Calcined 1350 ˚C/36hr; 1450 ˚C/4hr



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

Coker, E. N.; Rodriguez, M. A.; Ambrosini, A.; Miller, J. E.; Stechel, E. B., Powd. Diffr., 2012, *27* (02), 117.

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TGA: Redox Ar/CO_2 of Fe_2O_3:8YSZ

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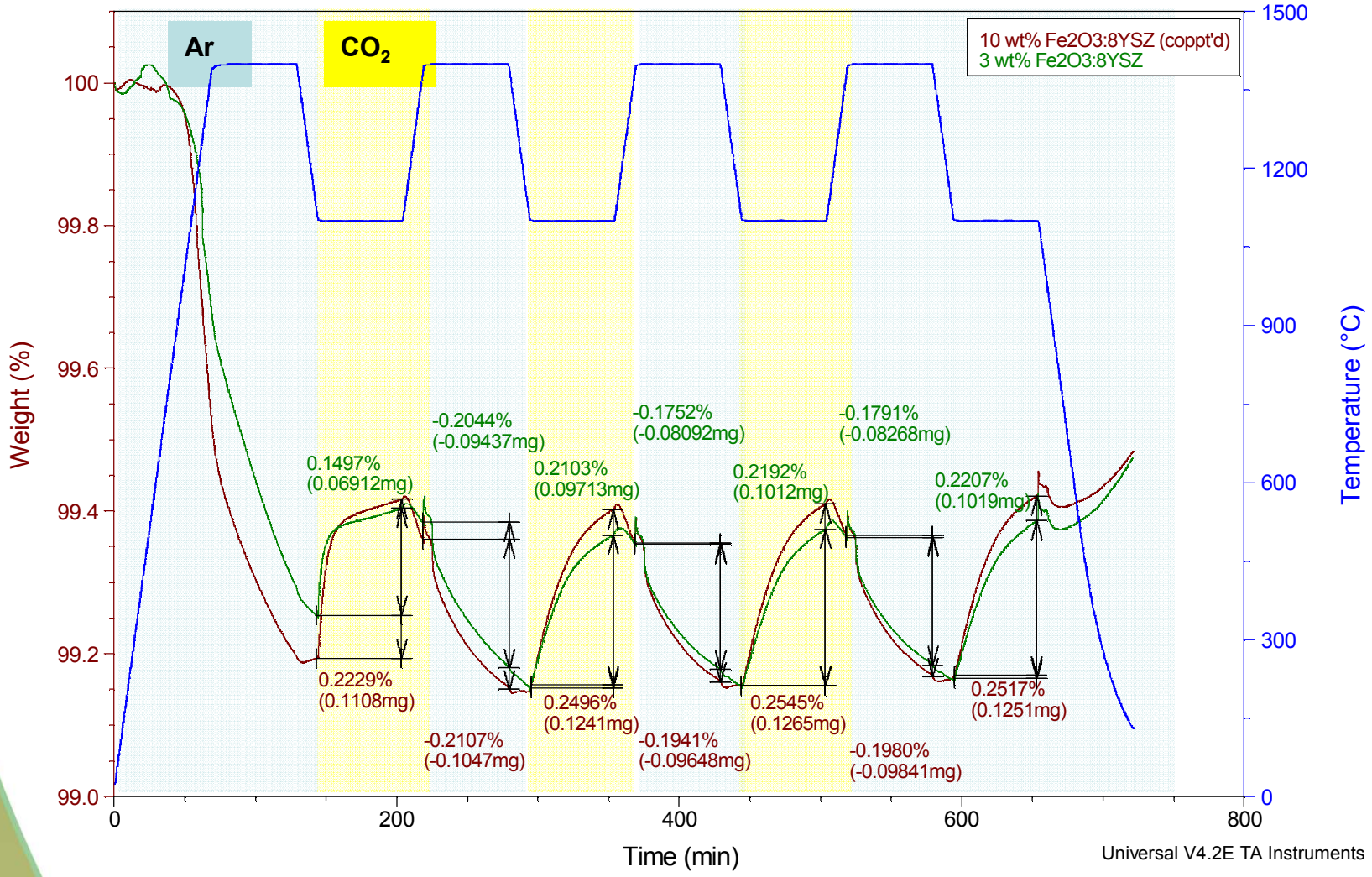

Universal V4.2E TA Instruments

Sunshine to Petrol

Long Redox of Fe_2O_3:8YSZ

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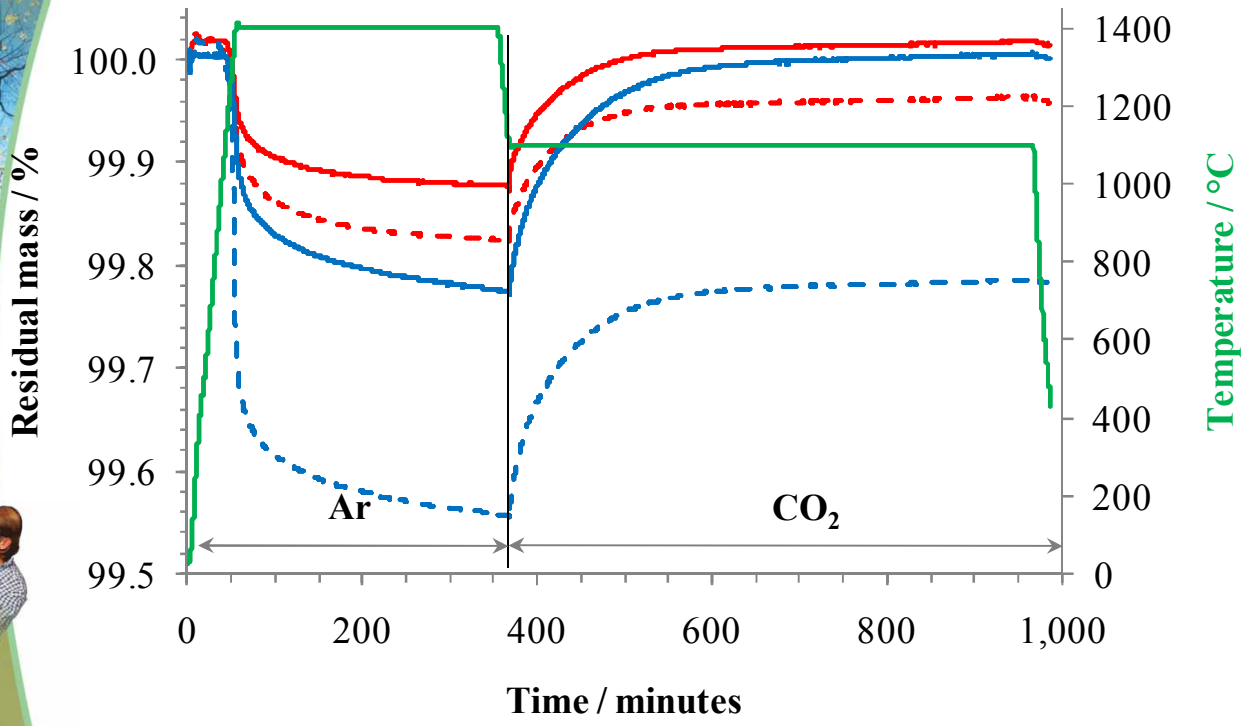


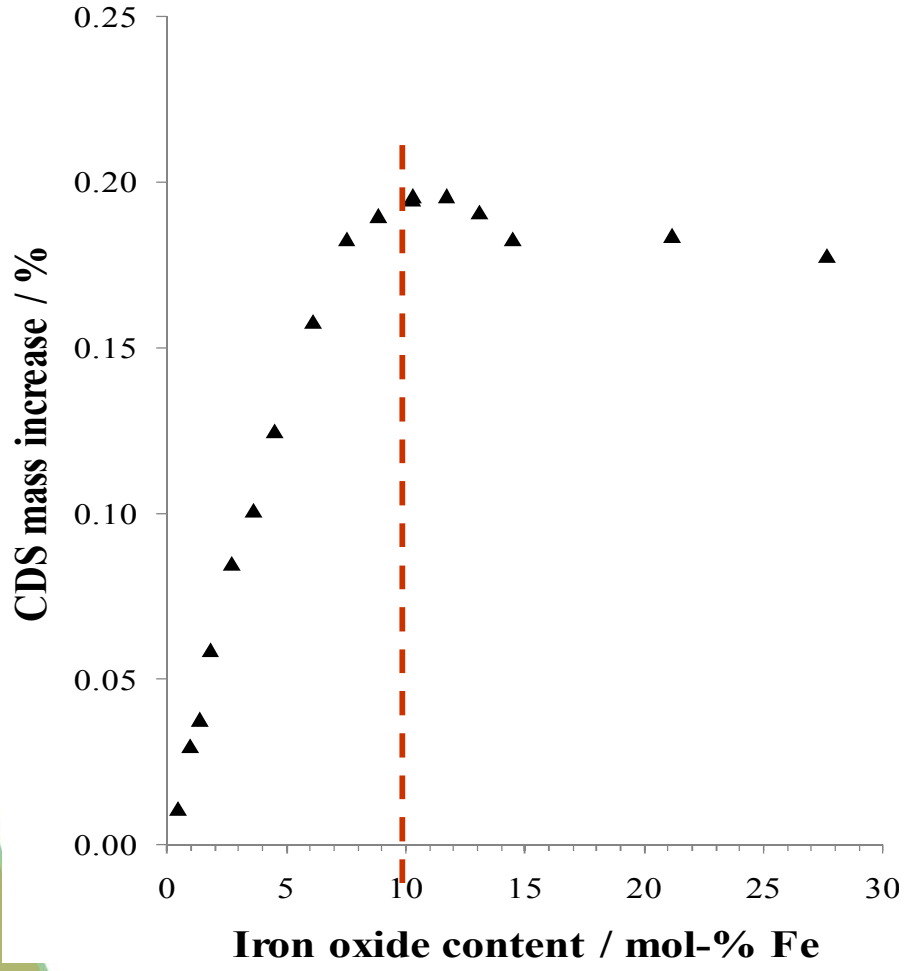
Dashed line – 1st cycle
Solid line – 2nd cycle

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
- Re-oxidation magnitude remains constant between cycles
- Subsequent cycles resemble 2nd cycle (not shown)

Iron utilization

Dissolved vs. Bulk Fe



Fe in solid solution:

- $Fe^{3+} \leftrightarrow Fe^{2+}$
- Each Fe theoretically accessible, though we don't see 100% utilization

Fe in composite (bulk):

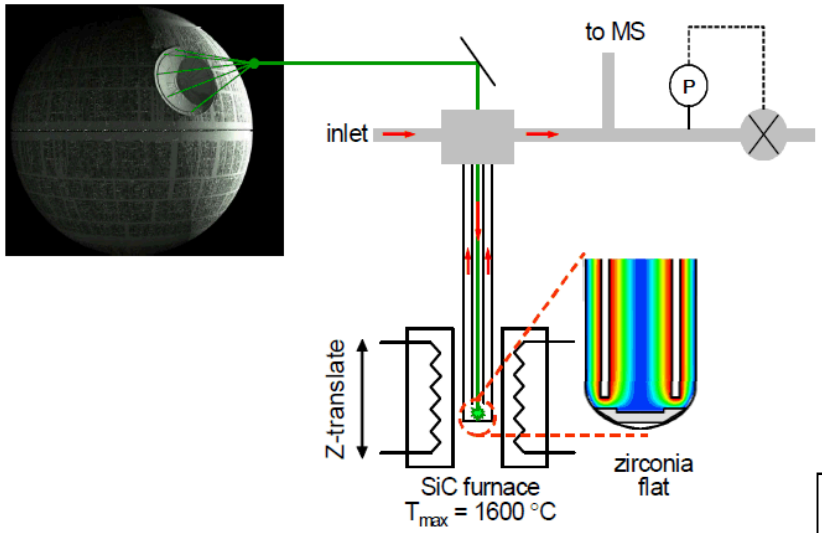
- $Fe_3O_4 \leftrightarrow FeO$
- 2/3 Fe theoretically accessible
- See much less utilization at higher loadings

Why?

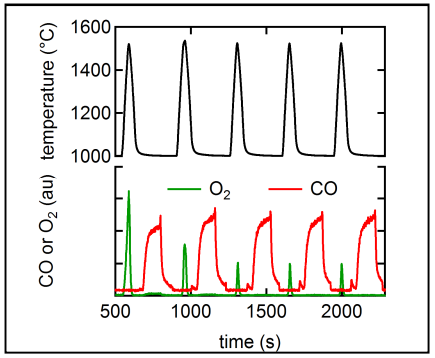
Hypothesis: Surface limitations in bulk redox reaction

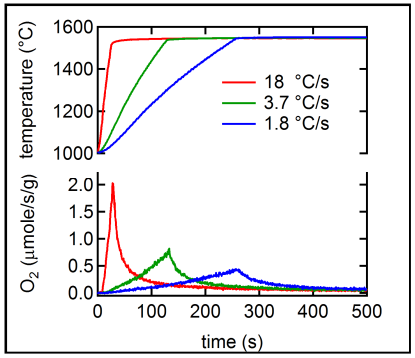
Stagnation Flow Reactor

500 W CW near IR laser (SNL-CA)
- Uniform flux at sample surface
- Investigate thermal reduction
- Investigate cycle variability



- Screen for O_2 uptake and release
  - System viability
- Resolve thermal reduction behavior
  - Variable heating rates
- Resolve gas splitting behavior
  - Variable T, P, [OX]
- Analysis
  - Rate limiting mechanisms
  - Kinetic models
  - Material stability
  - Cycle performance



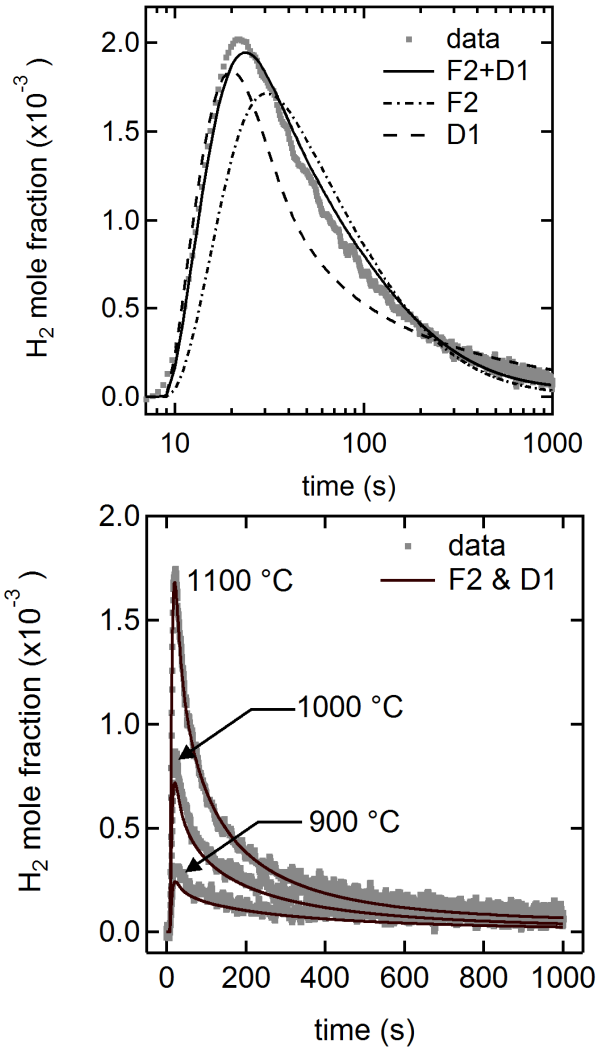


Chem. Mater. 2011, 23, 2030–2038

Modeling Kinetic Data from Stagnation Flow

Validated water oxidation model for ferrite/ZrO_2 composites reveals multiple kinetic mechanisms

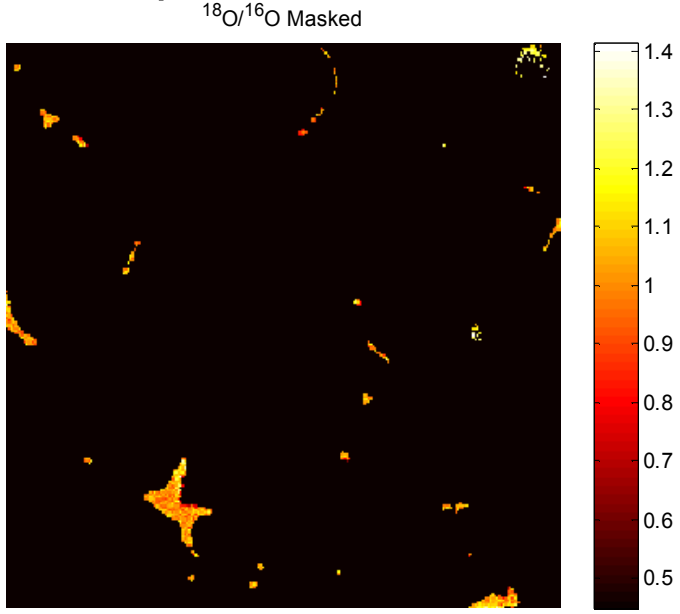
- Least-squares optimization fit to H_2 production rate curves
- Model the entire time domain.
  - Approach is new to this field of research
- Tested 14 individual kinetic models and 9 model pairs.
  - H_2 evolution best described by 1-D diffusion (D1) at early times and 2nd order reaction (F2) at later times
  - D1 is a simple parabolic rate law that describes the thickness of a growing oxide layer in 1-dimension (e.g. surface diffusion)
  - F2 is a second-order based "homogeneous-like" reaction where the rate decelerates parabolically as the extent of reaction increases (e.g. heterogeneous bulk reaction)
  - Results consistent with findings of Coker, *et. al.,* paper
- Model can be used to evaluate material performance in a simulation of a dynamic, reacting environment



J.R. Scheffe, A.H. McDaniel, M.D. Allendorf, A.W. Weimer, submitted to *Energy & Environ. Sci.*, May 2012.

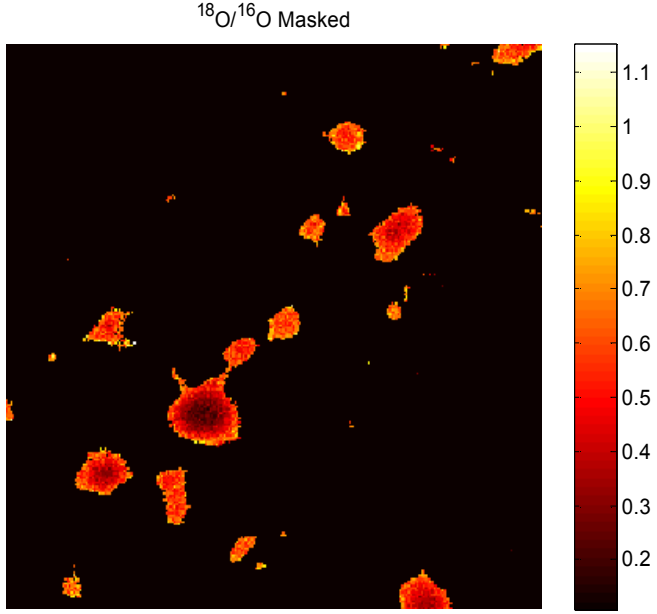
SIMS: Tie Between Structure (Scale) and Performance

- FeO_x particles in YSZ thermally reduced
- Short oxidation with $C(^{18}O)_2$ gives "eggshell" appearance in ^{18}O imaging
- Gradual penetration into interior of particles on extended CDS



7.5 mol-% Fe/8YSZ

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



14.5 mol-% Fe/8YSZ

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

Ohlhausen, Coker, Ambrosini, Miller, *Surf. Interface Anal.* (2012), in press.

Summary and Conclusions

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- The Sunshine to Petrol program at Sandia aims to utilize CSP and redox-active metal oxides to thermochemically split CO_2 and H_2O into syn gas
- The Fe:8YSZ system shows dynamic behavior during temperature cycling under reducing and oxidizing conditions
- In-situ XRD illustrates solubility of Fe in YSZ dependent upon temperature, Fe oxidation state
- TGA cycling experiments show %Fe utilization greater for lower iron-loaded (solid solution) samples
- Stagnation flow experiments and kinetic modeling predict multiple reaction mechanisms
- ToF-SIMS shows limited re-oxidation of bulk iron oxide particles under CO_2
- Techniques developed and lessons learned can aid in the design of improved and more efficient materials for thermochemical water splitting

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Thank You for Your Attention

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This work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, in the form of a Grand Challenge project entitled ‘‘Reimagining Liquid Transportation Fuels: Sunshine to Petrol.’’ 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.

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

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Fossil Fuels – Non Renewable, Buried Sunshine

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- 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.

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CO_2 Splitting Over 5% Fe_2O_3/YSZ

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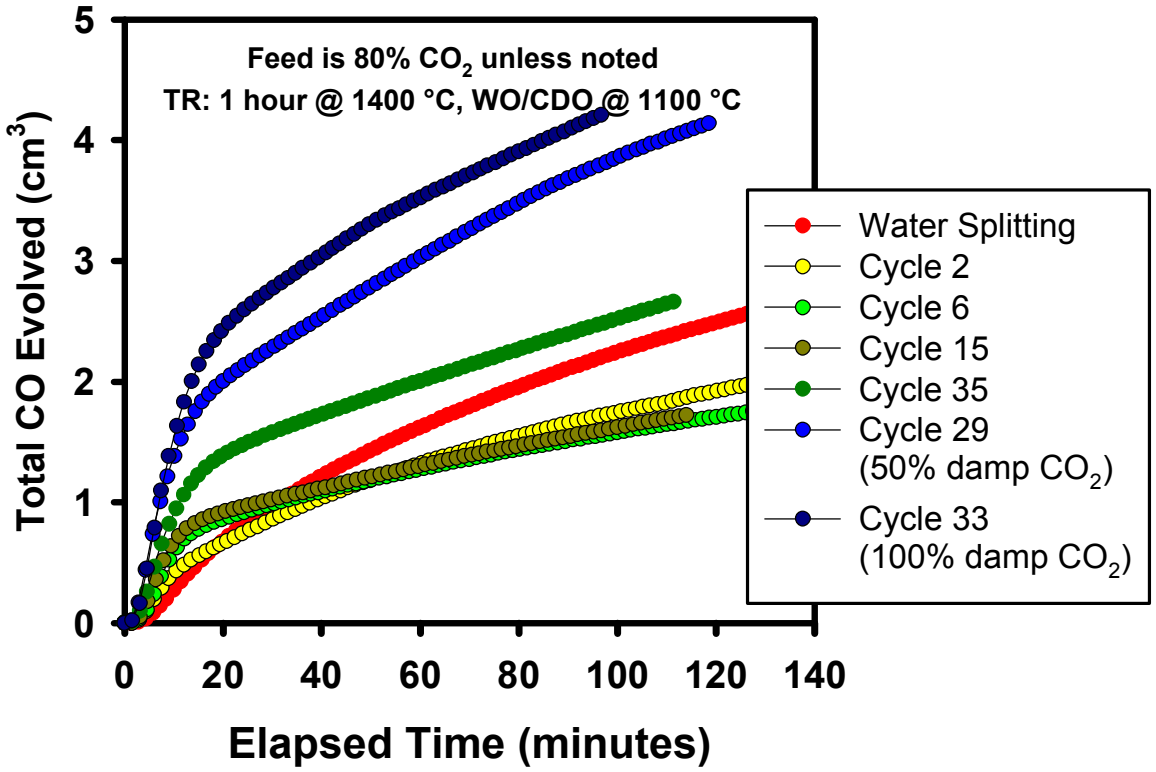

47 cycles laboratory cycles of 2.8 g lattice monolith

- 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)

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Room Temperature XRD of Fe_2O_3:8YSZ

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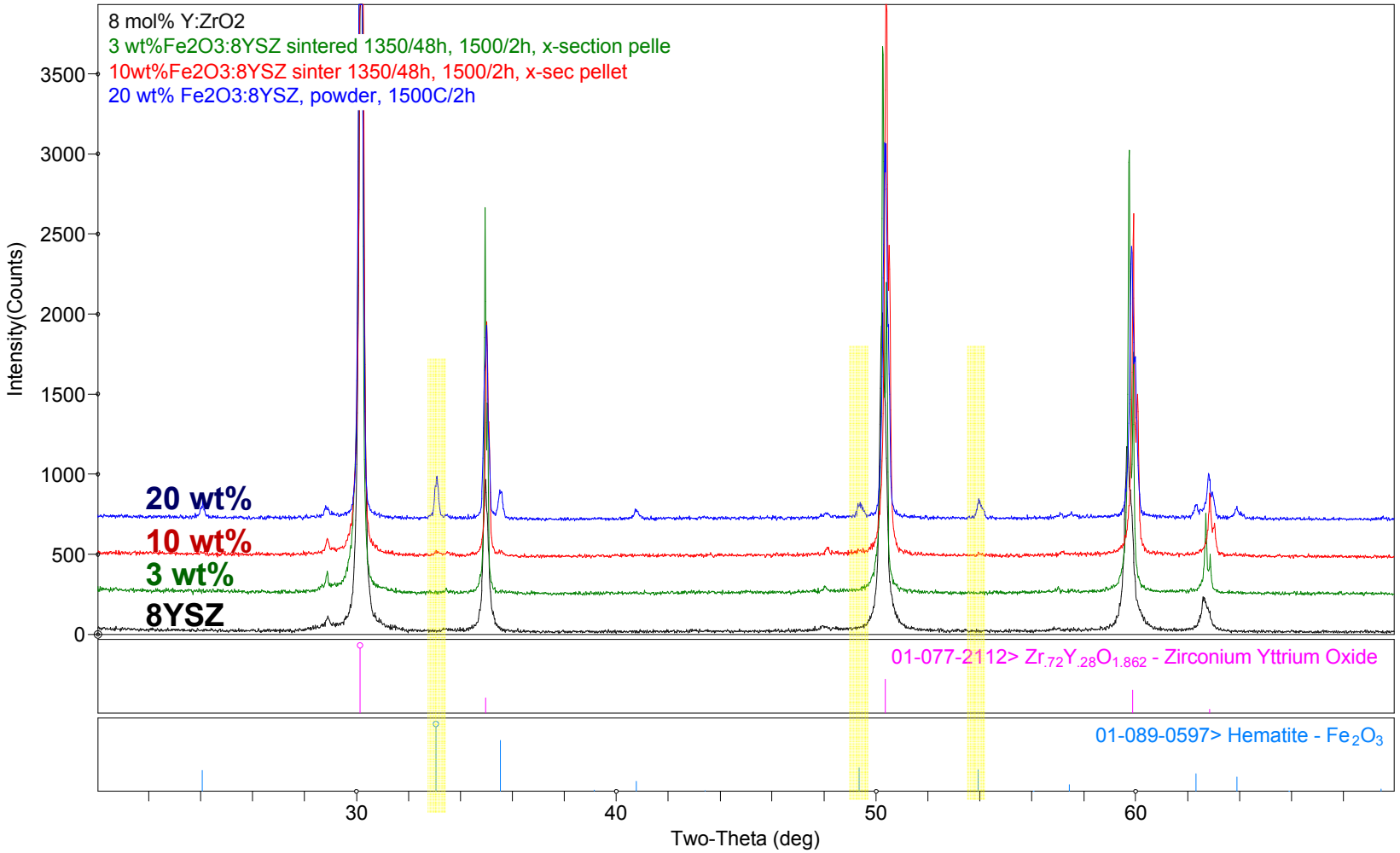

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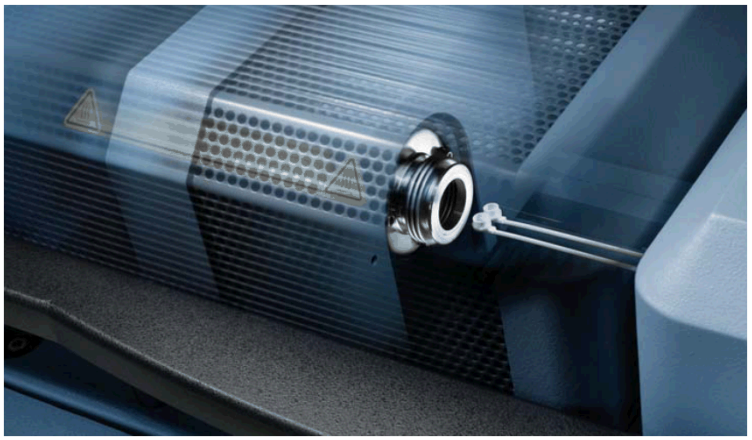
TGA Experiments

- 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)



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XRD of 3 wt% Fe_2O_3 post-redox TGA

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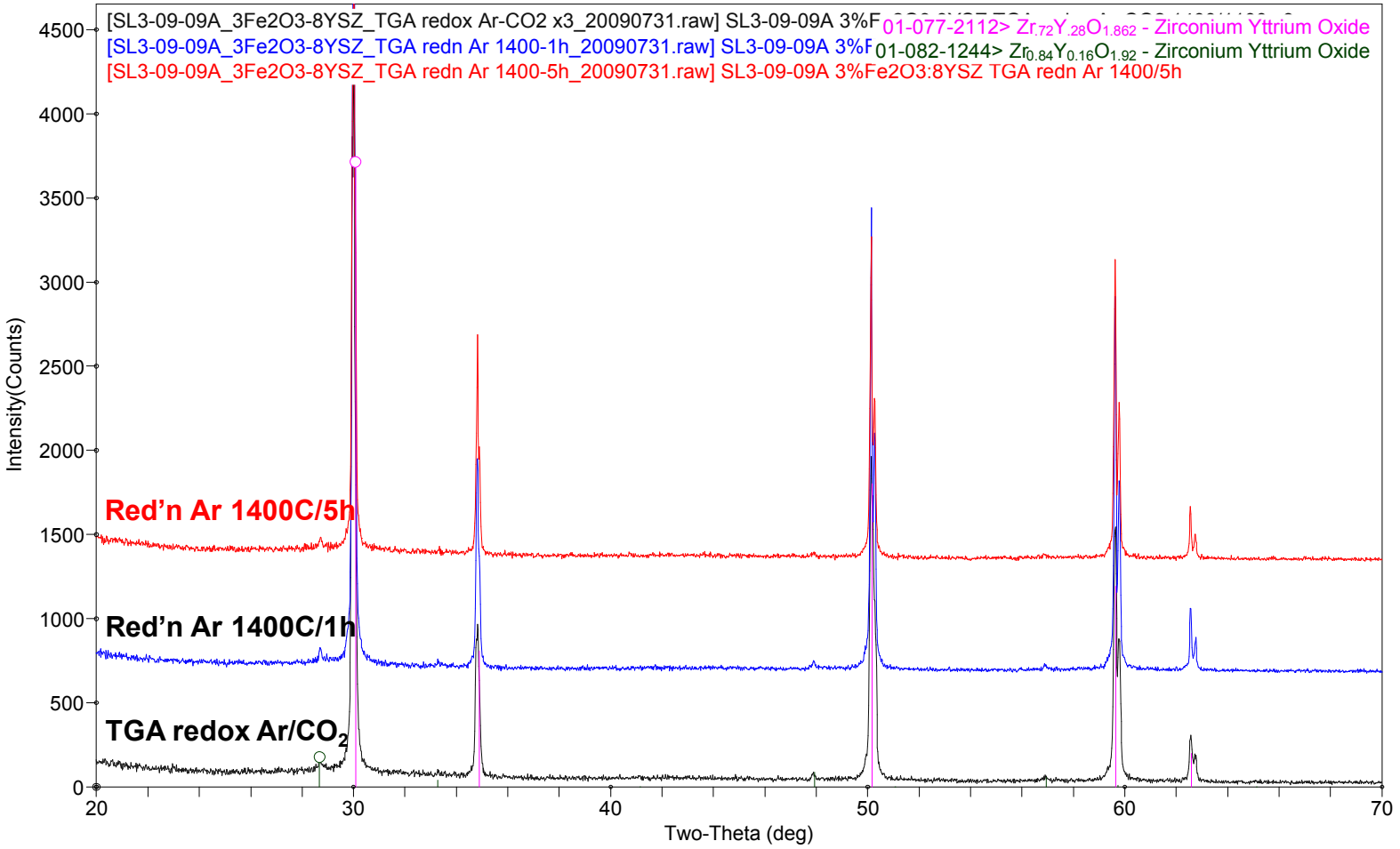

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XRD of 10 wt% Fe_2O_3 post-redox TGA

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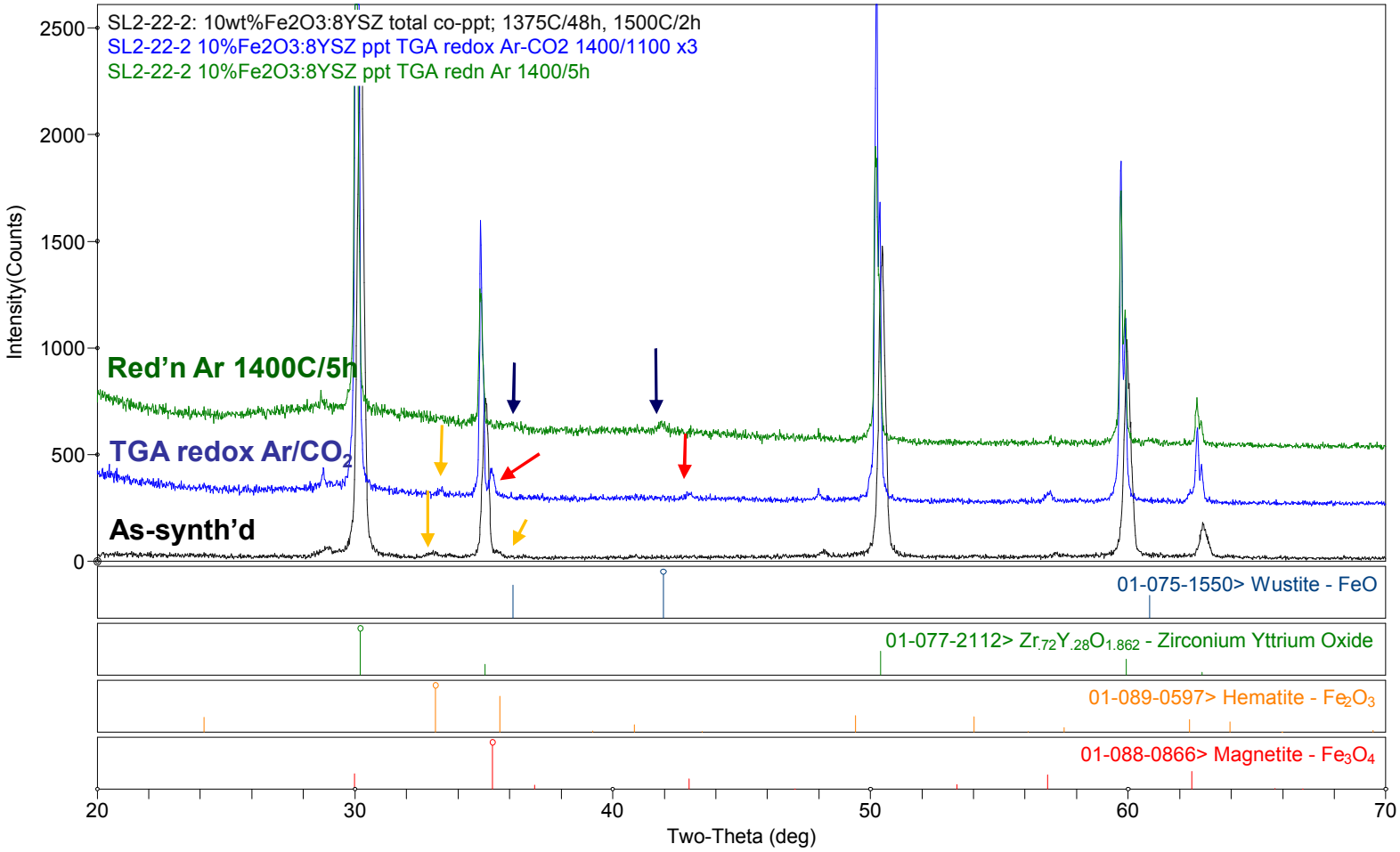
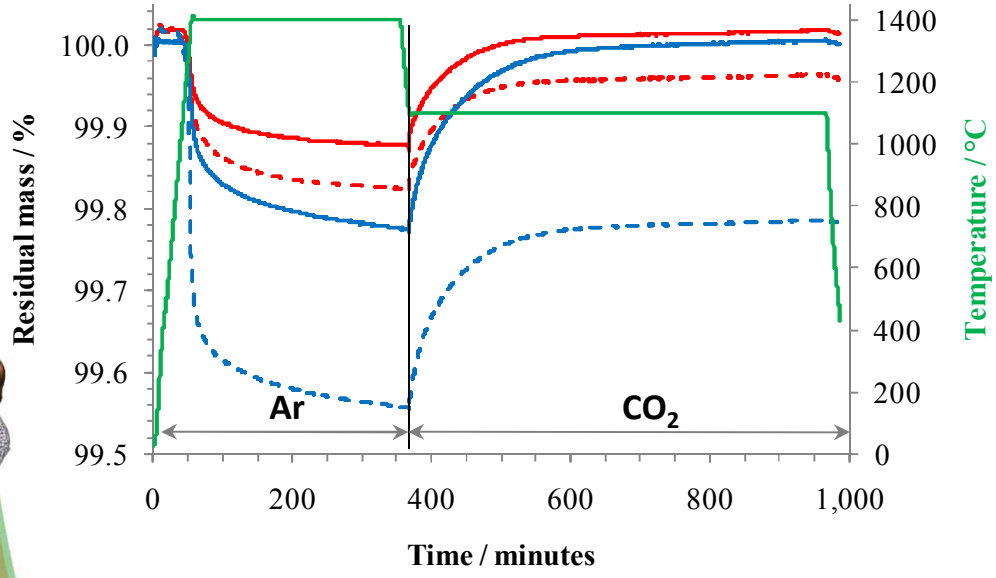
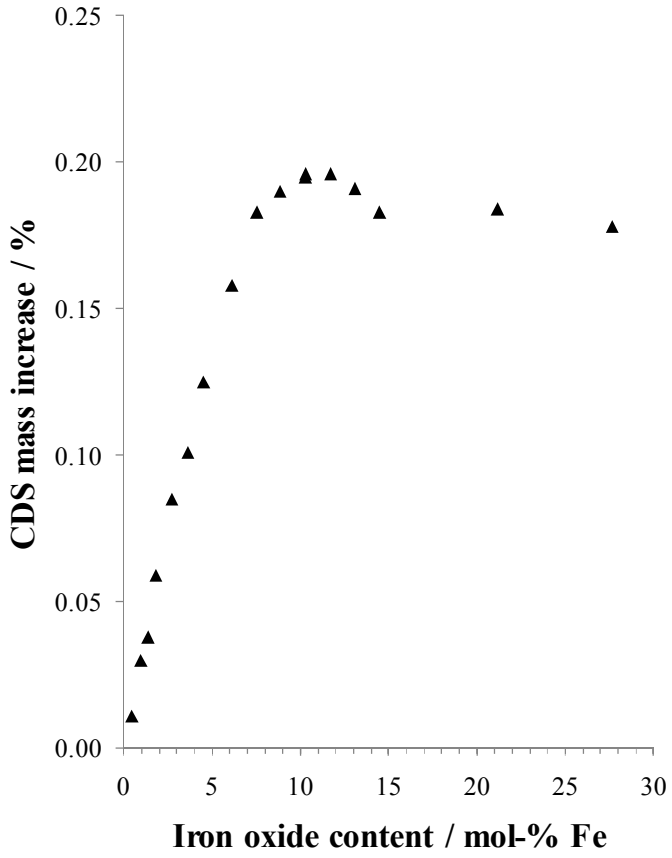


TGA
Soluble vs. bulk iron oxides

Co-precipitation
Calcined 1350 °C/36hr; 1450 °C/4hr



dashed line – 1st cycle
solid line – 2nd cycle
Red: 4.5 mol-% Fe/8YSZ
Blue: 14.5 mol-% Fe/8YSZ



- Always see greater reduction on 1st cycle, even for "fully soluble."
- Mass increase vs. Fe-loading is not linear above 8 mol-% Fe

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SEM of 10 wt% Fe2O3 Before and After TGA

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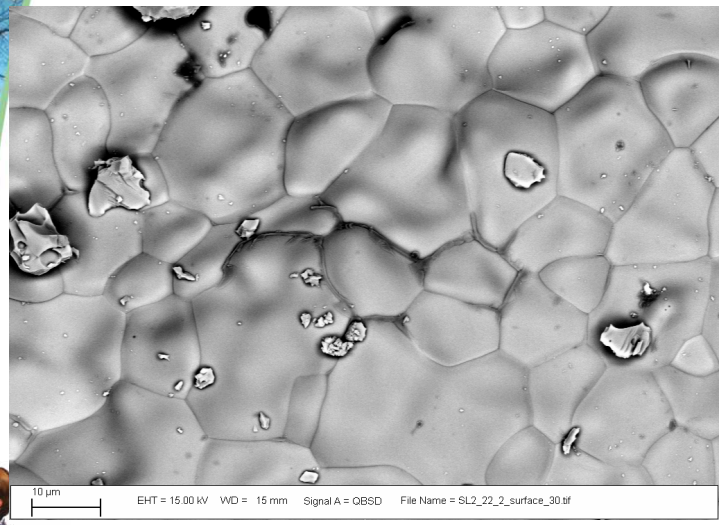
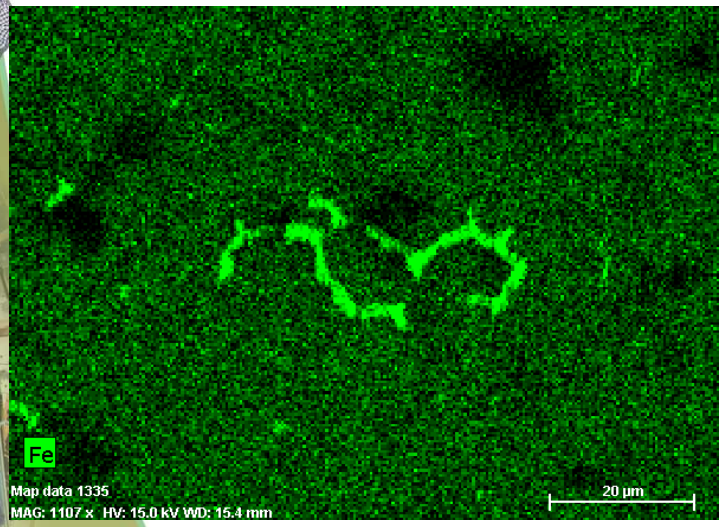
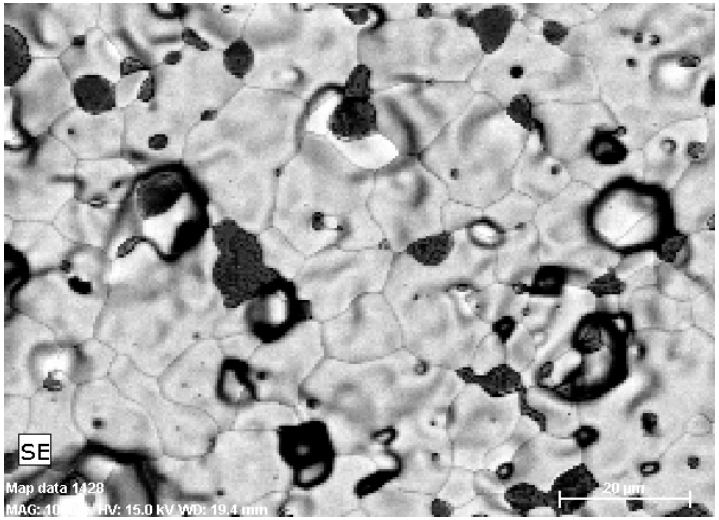
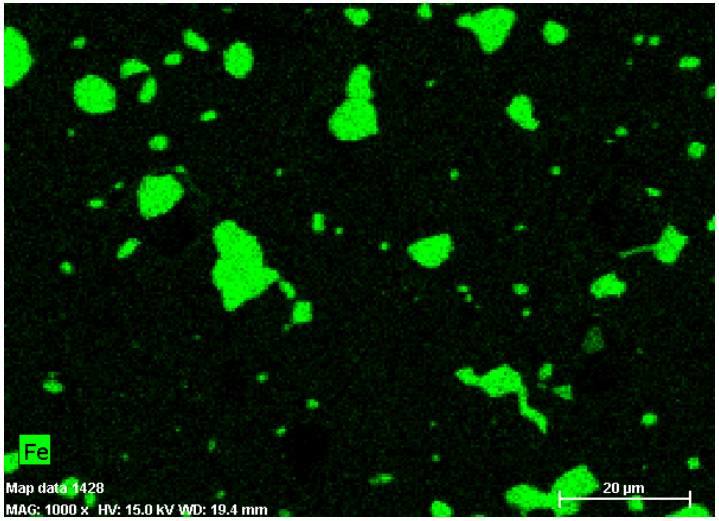
Before





After





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Evaluating oxidation and reduction behavior

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- Screen for O_2 uptake and release
  - System viability
- Resolve thermal reduction behavior
  - Variable heating rates
- Resolve gas splitting behavior
  - Variable T, P, [OX]
- Analysis
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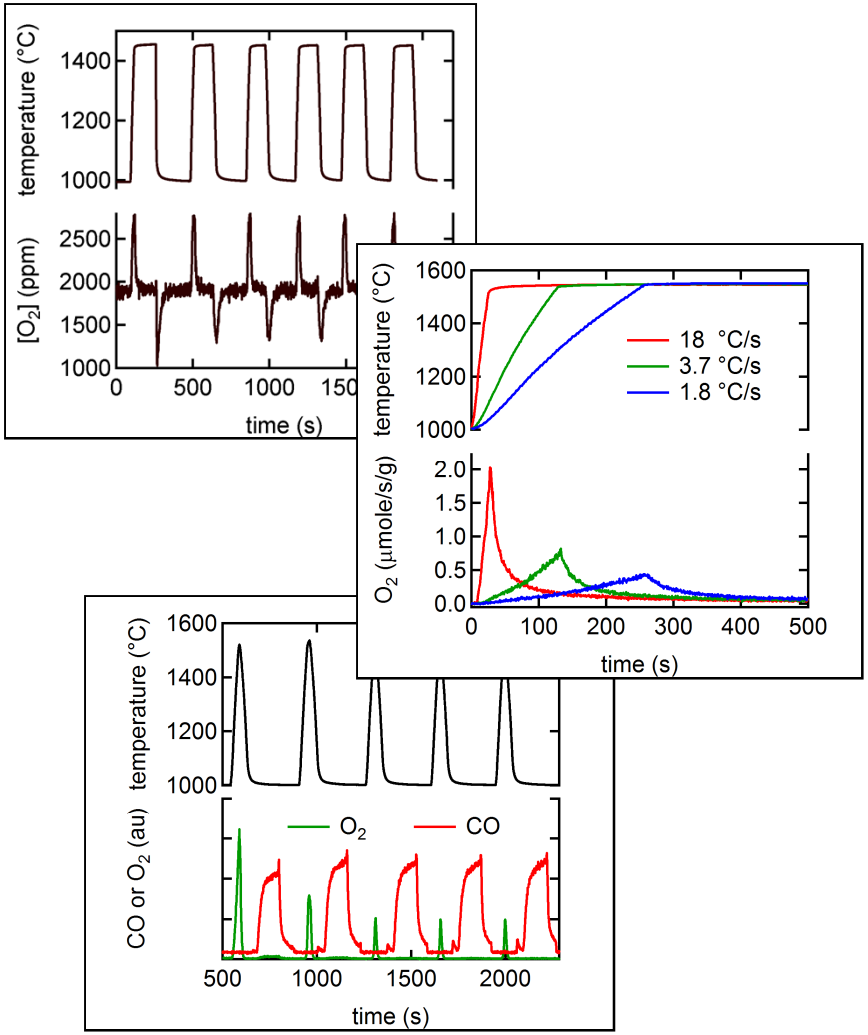

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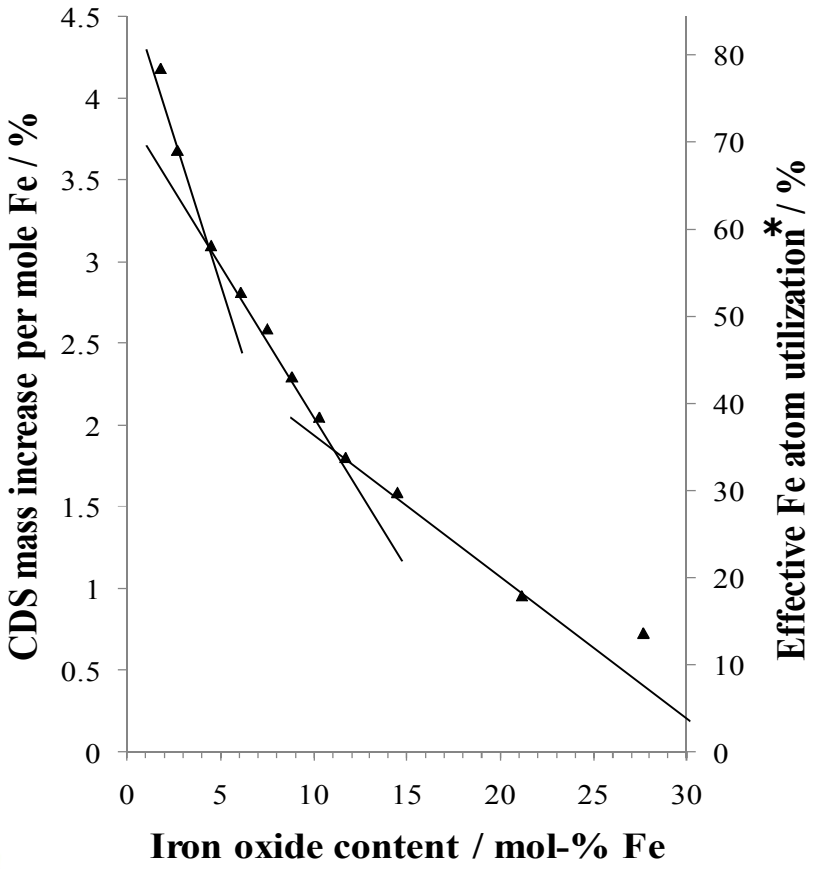
Iron utilization



- Even at 1.8 mol-% Fe, still some un-utilized Fe
- Lower Fe-loading gives higher utilization

- For "free" iron oxide possible reaction mechanism is: $Fe_2O_3 \rightarrow Fe_3O_4 \leftrightarrow FeO$
  - 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* $Fe_3O_4 \leftrightarrow 3FeO + \frac{1}{2}O_2$

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HT-XRD: 10 wt.-% Fe_2O_3/8YSZ, He

S2P SUNSHINE PETROL

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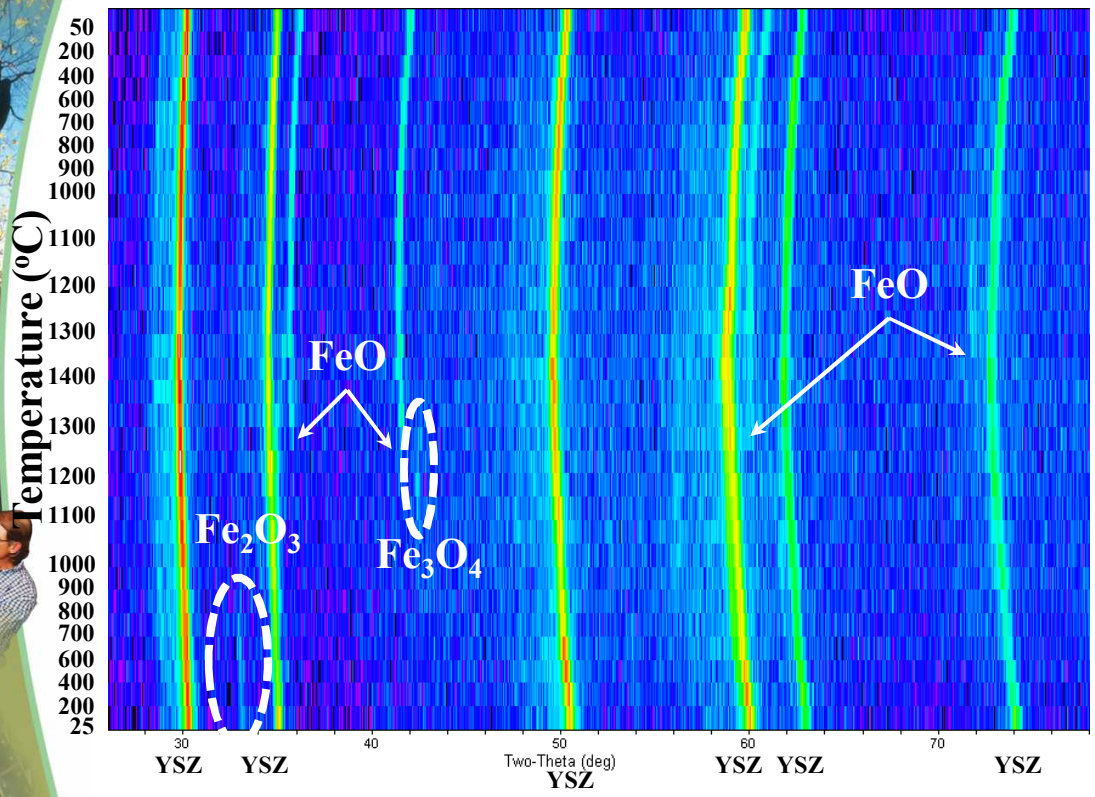

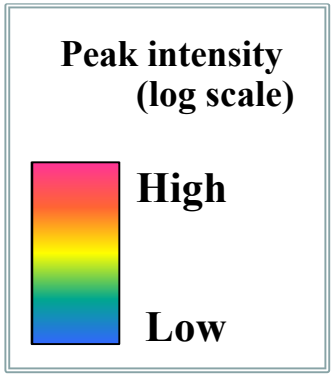

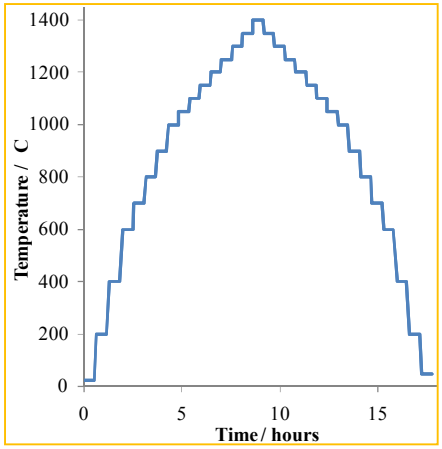

- Fe_2O_3 disappeared by 800 ° C
- Trace of Fe_3O_4 1100 – 1300 ° C
- FeO first observed ~ 1250 ° C
- No other Fe-phases 800 – 1100 ° C; Fe in solid solution with YSZ
- Solubility limit (Fe_2O_3 in 8YSZ) ≥ 9 wt.-% (14 mol.-%) 800 – 1100 ° C
- Once FeO formed, it does not return to solid solution on cooling under He

Sunshine to Petrol

ToF-SIMS

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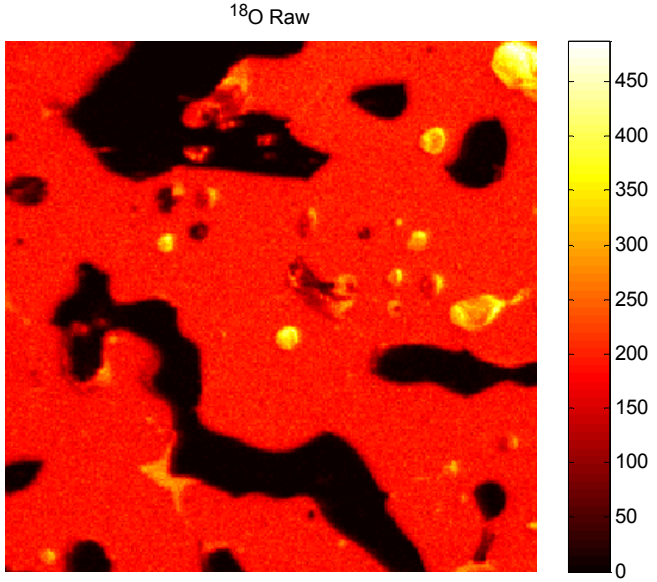
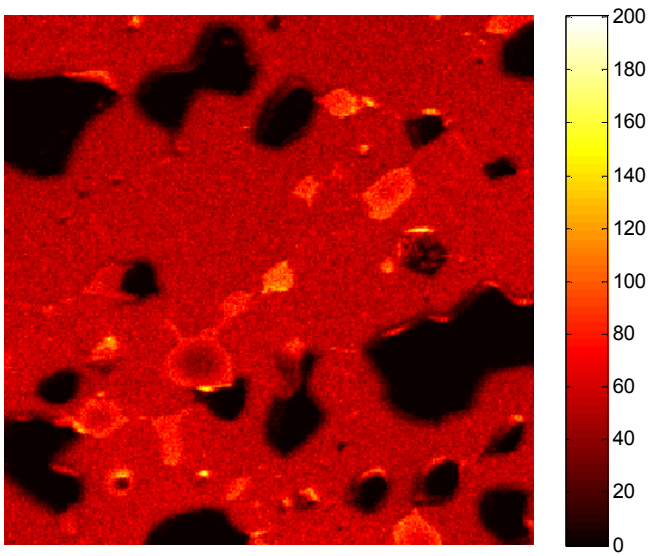
Time-of-Flight Surface Ionization Mass Spectrometry

- 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



7.5 mol-% Fe/8YSZ



14.5 mol-% Fe/8YSZ

8YSZ matrix: uniform ^{18}O & ^{16}O distribution--fast oxygen transport