La and Yb Incorporated Zr-Doped Ceria for Solar Thermochemical CO$_2$ Splitting:

Thermodynamics and Oxidation Kinetics Study

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2022 AIChE Annual Meeting
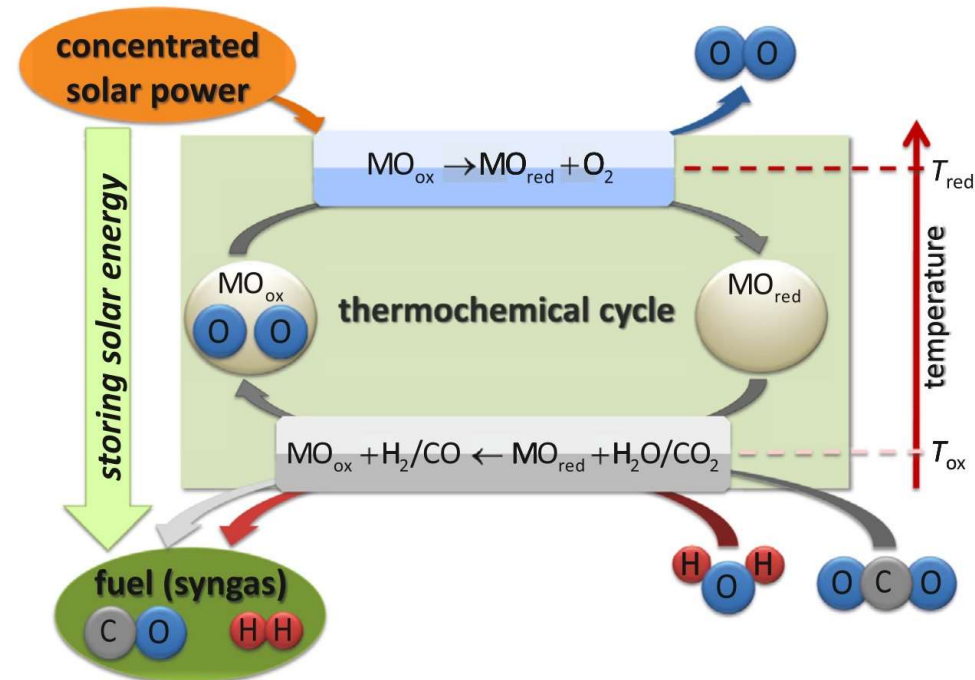**Phoenix, AZ**
November 15, 2022

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INTRODUCTION AND RESEARCH OBJECTIVES

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Introduction

Two-step Thermochemical Redox Cycles

- Step1: Reduction (Q_{solar} input)
  - Operated at 1300 – 1500 °C, lower pO_2
  - Endothermic
  - MO_{ox} becomes MO_{red} (e.g. $CeO_2 \rightarrow CeO_{1.9}$)
  - O_2 released

- Step2: Oxidation (H_2O/CO_2 input)
  - Operated at 800 – 1000 °C
  - Exothermic
  - MO_{red} becomes MO_{ox} (e.g. $CeO_{1.9} \rightarrow CeO_2$)
  - H_2/CO produced (H_2O/CO_2 splitting)

Agrafiotis, C., Roeb, M., and Sattler, C. "A review on solar thermal syngas production via redox pair-based water/carbon dioxide splitting thermochemical cycles." Renewable and Sustainable Energy Reviews 42 (2015): 254-285.
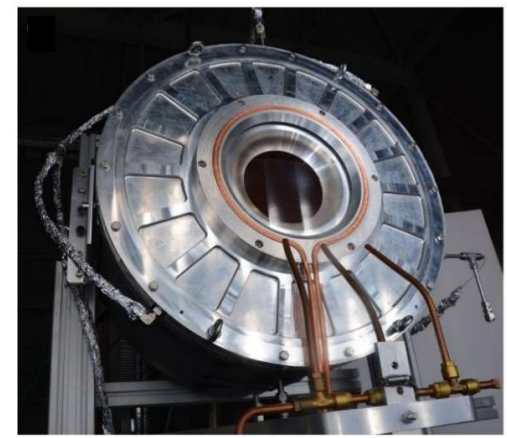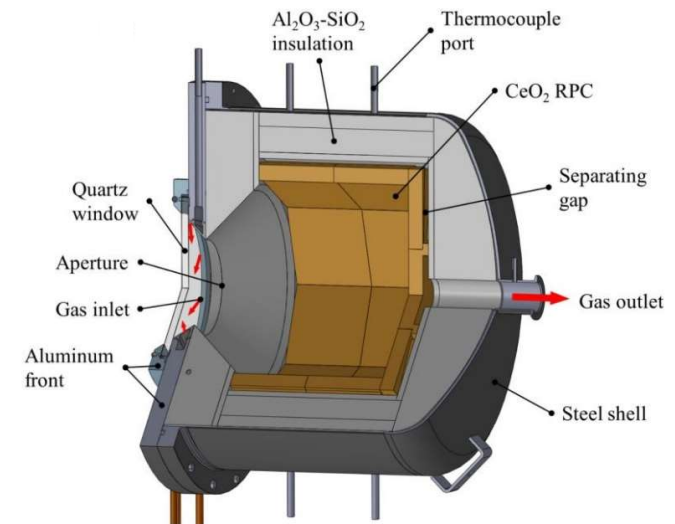
Introduction

Current Status and Potential Outlook

- Current Status
  - CeO_2 as a state-of-the-art redox material
  - Scalability: 50 kW_{th} single-reactor system, 100 kW_{th} dual-reactor system demonstrated
  - Efficiency: Solar-to-fuel efficiency of 5.25 % at a 4 kW_{th} system, 5.6 % at a 50 kW_{th} system (Figure)

- Potential outlook
  - Potential redox materials performing better than CeO_2 suggested
  - 100 MW_{th} scale-up system concepts available
  - 20 % solar-to-fuel efficiency as a potential objective

Zoller, S. *A 50 kW Solar Thermochemical Reactor for Syngas Production Utilizing Porous Ceria Structures*. Dissertation ETH No. 26451, ETH Zurich (2020)
Agrafiotis, C., Roeb, M., and Sattler, C. "A review on solar thermal syngas production via redox pair-based water/carbon dioxide splitting thermochemical cycles." Renewable and Sustainable Energy Reviews 42 (2015): 254-285.
Schäppi et al. "Drop-in fuels from sunlight and air." Nature 601.7891 (2022): 63-68.

Research Objectives

Background and Objectives

- Ceria doped with tetravalent dopants (e.g. Zr^{4+}, Hf^{4+})
  - Enhanced reducibility due to a lower reduction enthalpy compared to pure CeO_2
  - Poor oxidation kinetics being disadvantageous for the CO_2 and H_2O splitting reactions

- The influences of ionic radii or valence on possible structural changes and/or thermodynamic, kinetic properties to establish an associated doping strategy

- Thus, CeO_2-based and $Ce(Zr)O_{2-\delta}$-based materials with additional dopants are suggested.

Research Objectives

Dopant Concentration Selection

Concentration Zr	Concentration M (La/Yb)	Calculated ionic radii [pm] Zr+La	Calculated ionic radii [pm] Zr+Yb
0.0	1.0	116.0	98.5
0.1	0.9	112.8	97.1
0.2	0.8	109.6	95.6
0.3	0.7	106.4	94.2
0.4	0.6	103.2	92.7
0.5	0.5	100.0	91.3
0.547	0.453	98.5	90.6
0.6	0.4	96.8	89.8
0.7	0.3	93.6	88.4
0.8	0.2	90.4	86.9
0.9	0.1	87.2	85.5
1.0	0.0	84.0	84.0

La^{3+}: 116.0 pm
Yb^{3+}: 98.5 pm
Zr^{4+}: 84.0 pm

Ce^{3+}: 114.3 pm
Ce^{4+}: 97.0 pm

Selected samples (Abbreviation)

CeO_2

$Ce_{0.9}Yb_{0.1}O_{1.95}$ (CYO10)

$Ce_{0.9}La_{0.1}O_{1.95}$ (CLO10)

$Ce_{0.9}Zr_{0.1}O_2$ (CZO10)

$Ce_{0.9}Zr_{0.0547}Yb_{0.0453}O_{1.97735}$ (CZYO55)

$Ce_{0.9}Zr_{0.0547}La_{0.0453}O_{1.97735}$ (CZLO55)

THERMODYNAMICS

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TGA Results: Thermodynamics

TGA Experimental Conditions

- Reduced at T_{red} = 1200, 1250, 1300, 1350 and 1400 °C
  - Under pure Ar for the lowest pO_2
  - Under pure Ar + Ar with O_2 pump at various flow rate ratio at $pO_2 = 10^{-3} - 10^{-3.75}$ atm
  - Under Ar with O_2 pump at various voltage at $pO2$ higher than 10^{-3} atm
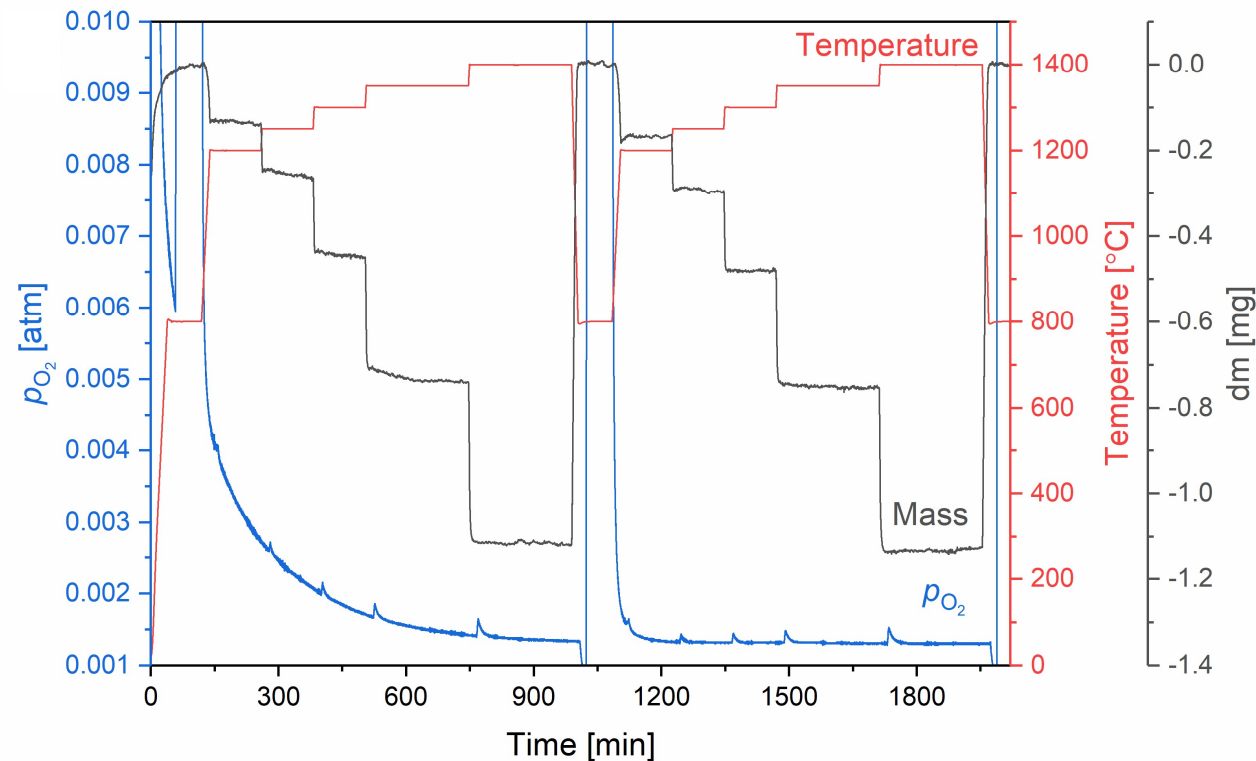
TGA raw data of a CZLO55 pellet during reduction at various temperatures with O_2 pump at maximum voltage (1165 mV)

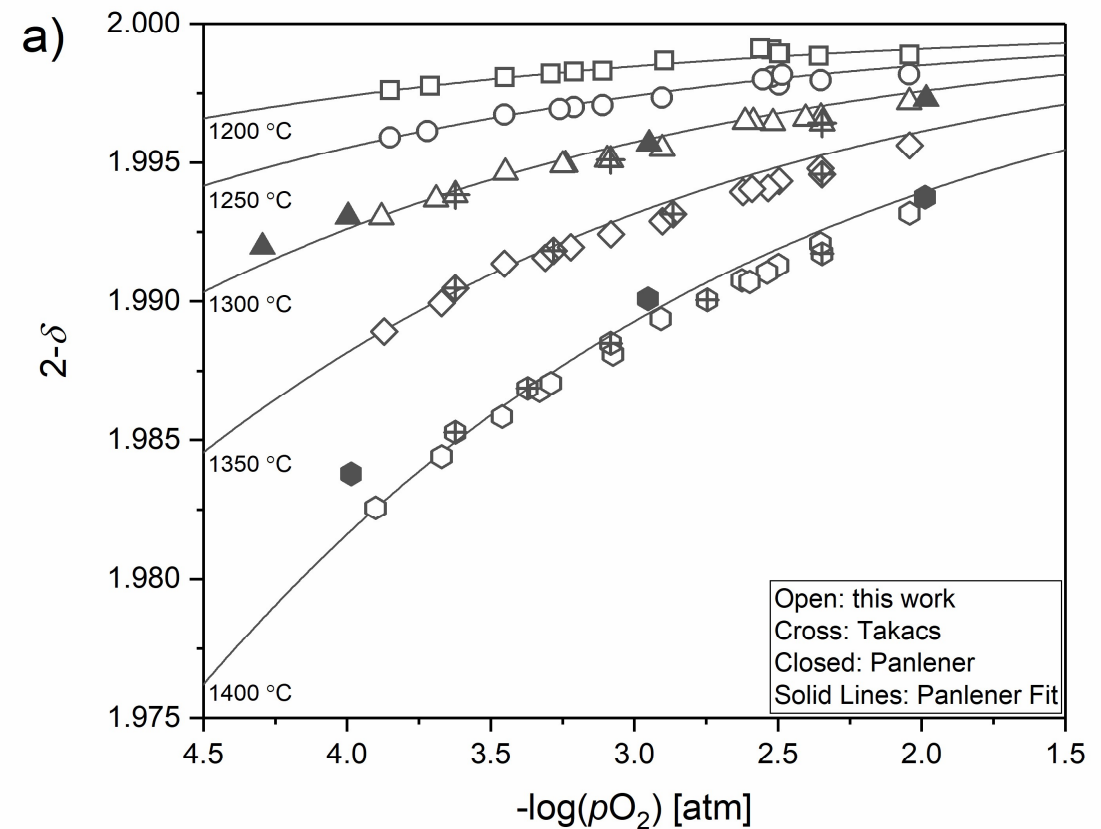# TGA Results: Thermodynamics

Oxygen Nonstoichiometry

- Oxygen nonstoichiometry (δ) of ceria
  - Close to that from literature

- Oxygen nonstoichiometry (δ) of all samples
  - Tetravalent dopants: Higher δ than ceria
  - Trivalent dopants: Lower δ than ceria
  - co-doped: δ between ceria and Zr-doped ceria
  - No significant differences between CZYO55 and CZLO55

a)

Oxygen nonstoichiometry of a) ceria at T_{red} = 1200 – 1400 °C and b) all materials at 1400 °C
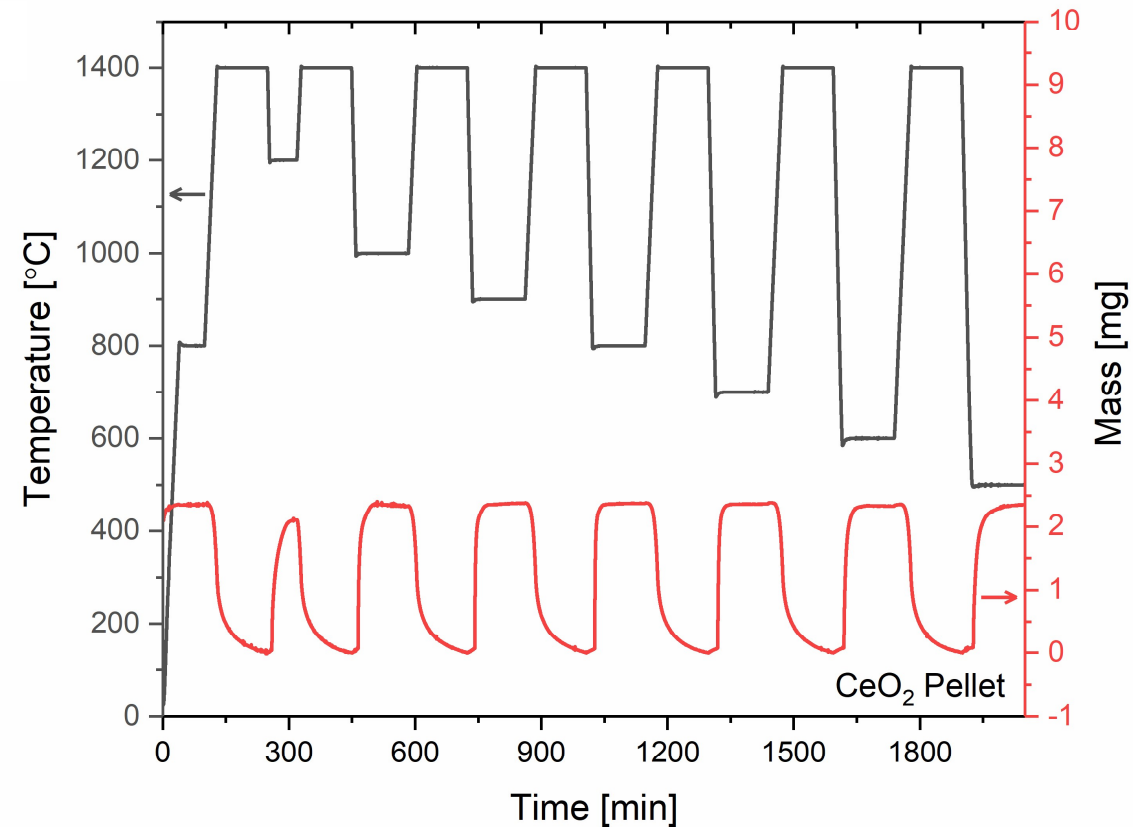
OXIDATION KINETICS

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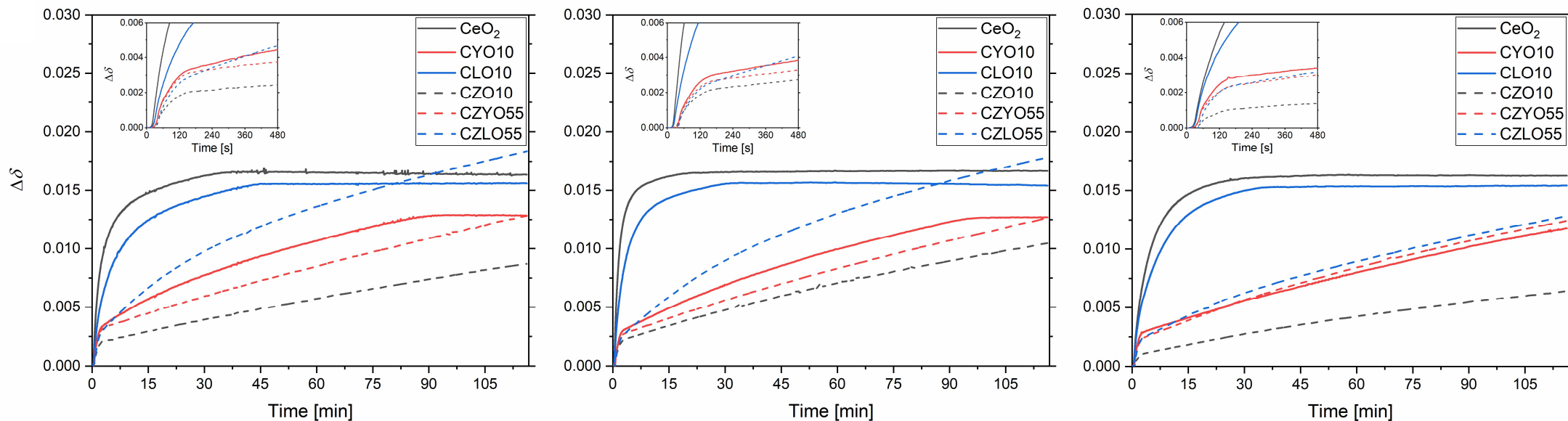
TGA Methods: Oxidation Kinetics

CO$_2$ Splitting of ceria/doped ceria

- Reduced at T_{red} = 1400 °C under Ar atmosphere for 2 hours

- Oxidized
    - at T_{ox} = 1200 – 500 °C under 0.4 atm CO$_2$ balanced with Ar for
        - an hour (1200 °C)
        - 2 hours (1000 – 500 °C)

TGA raw data of a CeO$_2$ pellet during CO$_2$ splitting at pCO$_2$ = 0.4 atm

TGA Results (Δδ): Oxidation Kinetics

Change in nonstoichiometry during CO_2 splitting (Left) at 1000 °C, (Mid) at 800 °C, and (Right) at 600 °C.
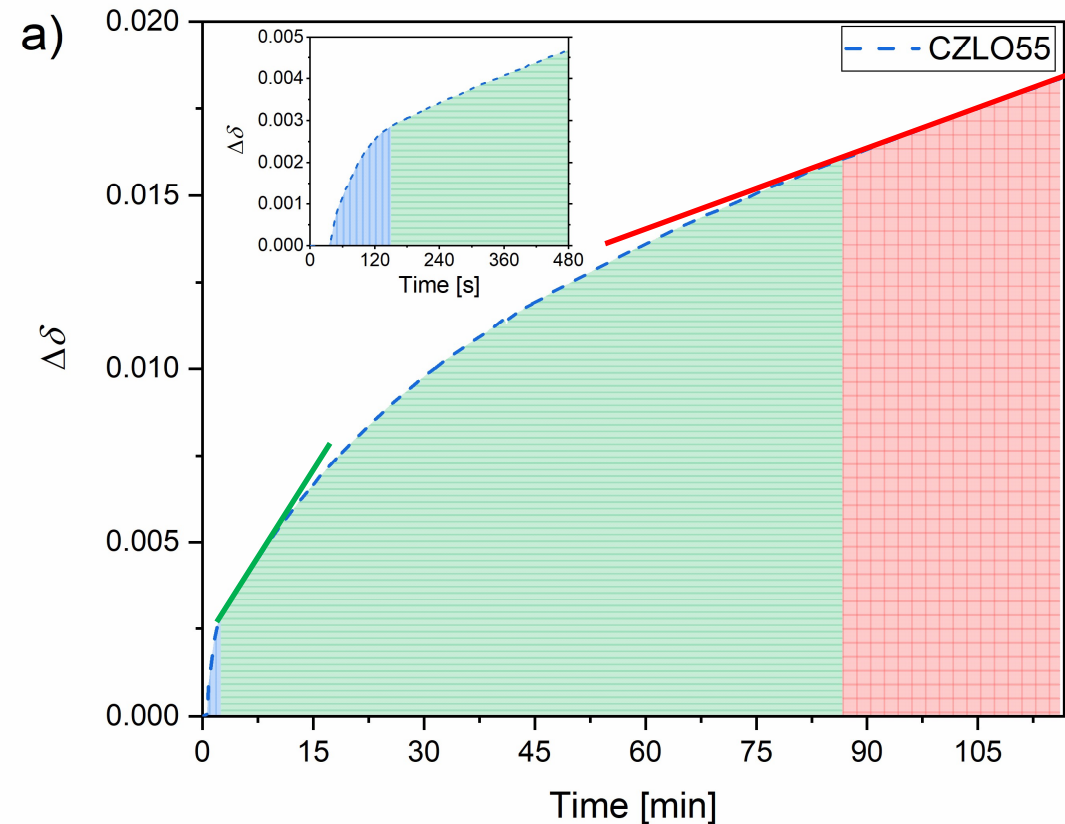Inset: at early reactions (t = 0 – 480 s)

- Reduced at 1400 °C for 2 hours under Ar.
- Oxidized for 2 hours under $p CO_2$ = 0.4 atm, balanced with Ar.

TGA Results: Introducing Reaction Regimes

CO$_2$ Splitting Reaction Regimes

- CO$_2$ splitting consists of multiple reaction regimes with different reaction mechanism.
  - First regime (0 s – about 150 s)
  - Second regime (about 150 s until rate becomes almost linear)
  - Third regime (depending on the material, as soon as rate becomes almost linear)

TGA raw data and reaction regimes of a CZLO55 pellet during CO$_2$ splitting (T_{ox} = 1000 °C)

TGA Results: Introducing Reaction Regimes

CO$_2$ Splitting Reaction Regimes

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  - Second regime (about 150 s until rate becomes almost linear)

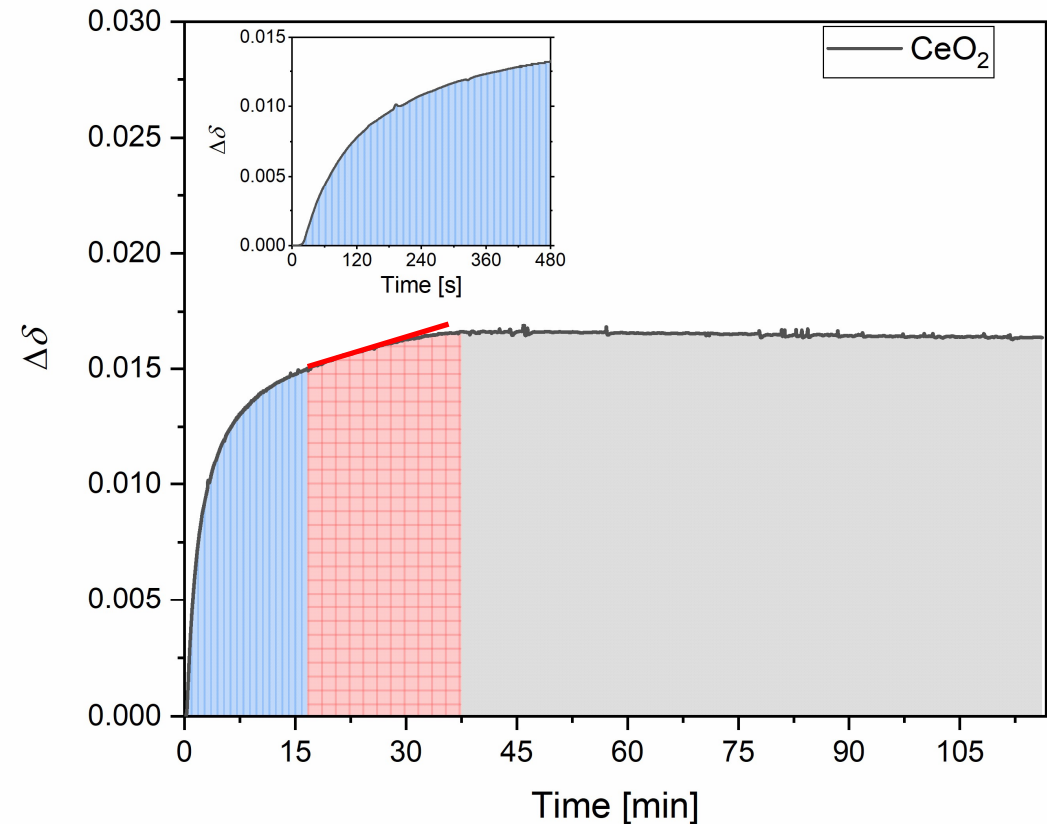 - Third regime (depending on the material, as soon as rate becomes almost linear)

TGA raw data and reaction regimes of a CeO$_2$ pellet during CO$_2$ splitting (T_{ox} = 1000 °C)

TGA Results: Introducing Reaction Regimes

CO$_2$ Splitting Reaction Regimes

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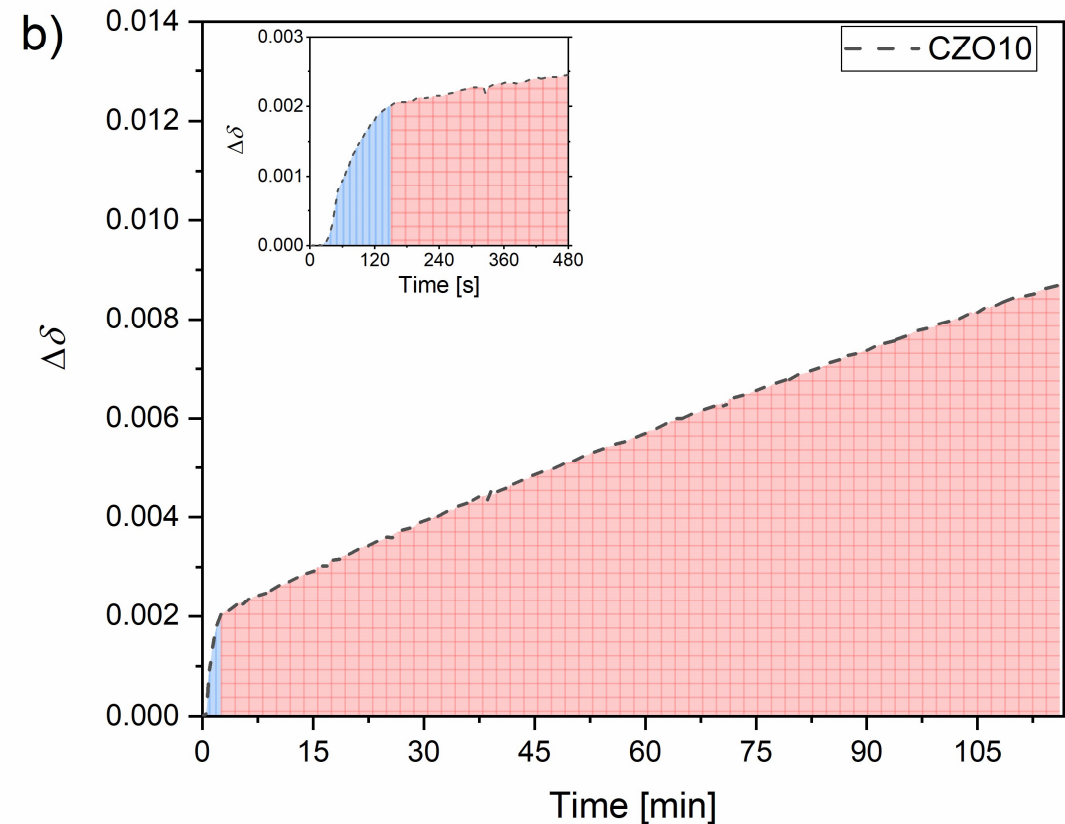 - Third regime (depending on the material, as soon as rate becomes almost linear)

b)

TGA raw data and reaction regimes of a CZO10 pellet during CO$_2$ splitting (T_{ox} = 1000 °C)

TGA Results: Introducing Reaction Regimes

CO$_2$ Splitting Reaction Regimes

- CO$_2$ splitting consists of multiple reaction regimes with different reaction mechanism.
  - Unrestricted regime
    - Solid surface is not occupied
  - Surface exchange limited regime
    - Solid surface is being occupied by adsorbed CO$_2$
    - Slow surface exchange is primarily limiting the reaction
  - Surface exchange limited at equilibrium regime
    - Solid surface is fully occupied by adsorbed CO$_2$
    - Reaction rate is almost linear
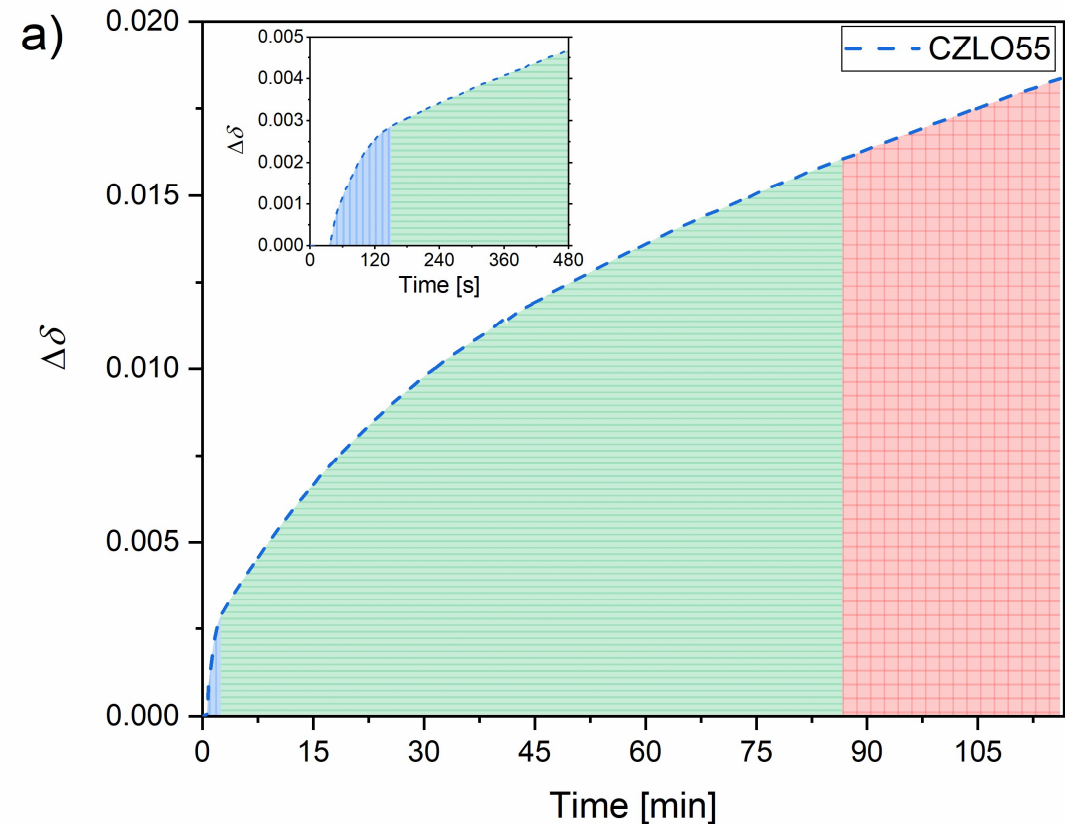
a)

TGA raw data and reaction regimes of a CZLO55 pellet during CO$_2$ splitting (T_{ox} = 1000 °C)

# TGA Results: Modified Exponential Decay Fit/Slope Factor

New ExpDecayMod Fit

- Conventional exponential decay function cannot be used for the activation energy calculation.
  - Near-linear increase in mass at the surface exchange limited regime requires new fitting function.
  - Exponential decay function was modified to compensate for the linearity.

$$y = y_0 + A_1\left(-exp\left((x - x_0)/t_1\right)\right) + A_2(x - x_0)$$

  - Slope factor A_2 represents the slope at the beginning of the second regime.

Adj. R^2 (ExpDecay) = 0.9447
Adj. R^2 (ExpDecayMod) = 0.9960
Slope Factor = 0.01316
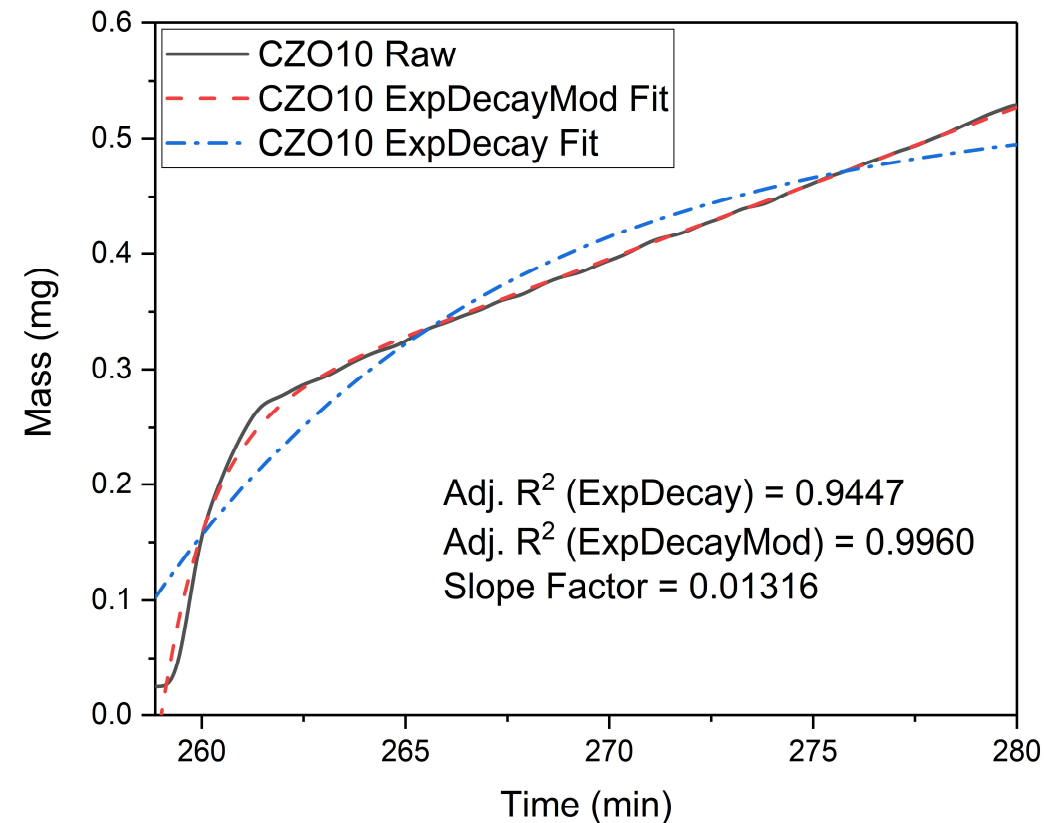
TGA raw data and fits of CZO10/CeO$_2$ pellets during CO$_2$ splitting

TGA Results: Slope Factor Comparison

Oxidation Kinetics and Lattice Constants

- Slope factors vs lattice constants
  - Overall, slope factors are positively proportional to the lattice constant.
  - This trend is possibly due to enhanced surface exchange induced by the stress caused by the larger dopant cations.
  - Exceptions for the CZYO55 at low temperatures (T_{ox} = 600, 700 °C), possibly due to less diffusion limited, or less backward reaction at low temperatures than other materials
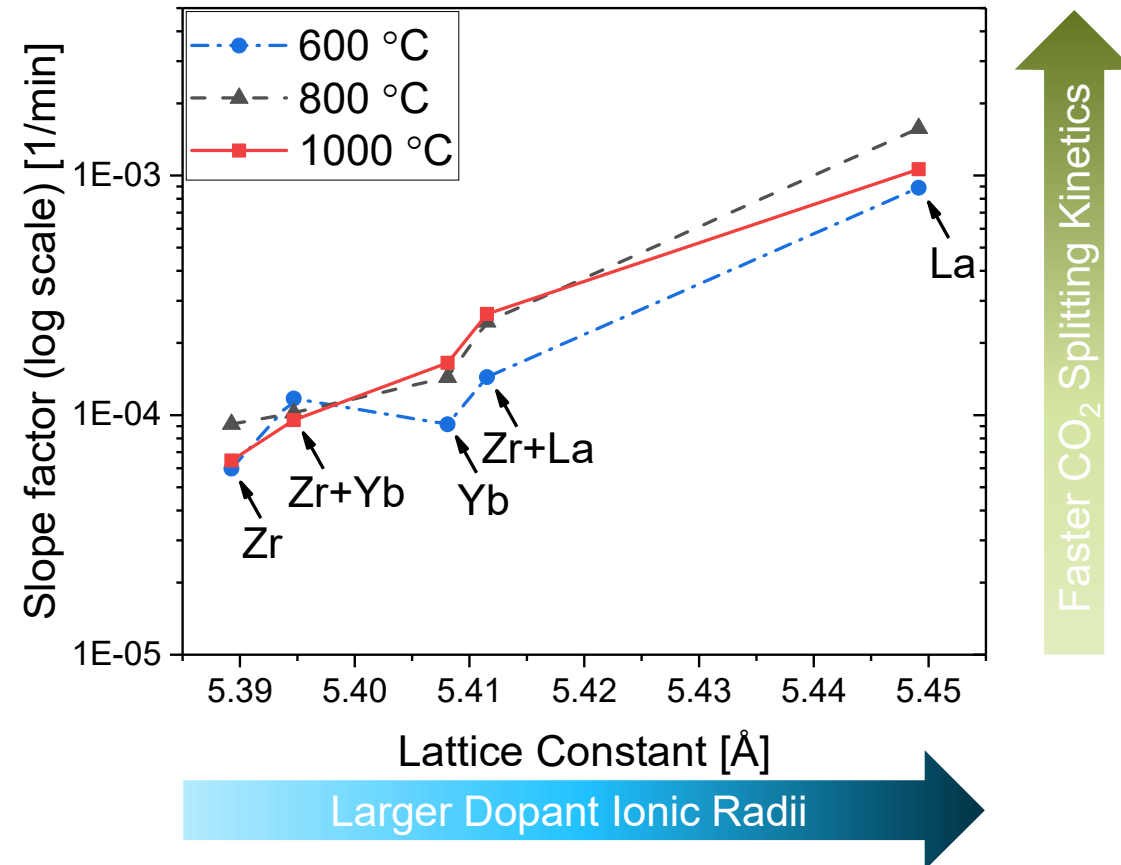
Rate of $\Delta\delta$ vs. Lattice constant of doped ceria at various oxidation temperatures

CONCLUSIONS AND OUTLOOK

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Doping Strategy Based on Thermodynamics/Kinetics

- Some tetravalent dopants such as Zr^{4+} provide excellent reduction capability, but oxidation kinetics is extremely slow due to limited surface exchange capability induced by smaller effective averaged ionic radius.

- Doping larger trivalent cations on the Zr-doped ceria lattice results in larger effective averaged ionic radius and significantly enhances surface exchange during CO_2 splitting. However, thermodynamic properties become less favorable compared to the case when only tetravalent dopant cations are incorporated. The difference in ionic radius of the trivalent dopant does not influence thermodynamics significantly.

- Optimization in dopant concentrations, balancing between more tetravalent dopants for higher reducibility and more trivalent dopants with larger ionic radius for faster oxidation kinetics, is crucial to maximize the fuel productivity.

- Since CO_2 splitting kinetics is rather surface exchange limited, techniques to promote the surface exchange (e.g. introducing micro porosity for larger specific surface area, surface coating with catalysts, etc.) will be even more beneficial.

Acknowledgement

- **DLR Institute of Future Fuels**
  - Discussion

- **DLR Institute of Materials Research**
  - Material Synthesis/Characterization

- **Funding: DFG**
  - Grant No. SCHM 1367/5-1

QUESTIONS?

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Introduction

Economic Analysis and Risk Assessment

- Estimation of fuel production costs for solar thermochemical plant
  - Main assumptions
    - Plant capacity: 1000 bpd of jet fuel and 850 bpd of naphtha
    - Solar plant: Concentration 100 €/m², O&M 2 €/m²,
      Tower: 20 €/kW$_{th}$
      DNI: 2500 kWh/m²
    - Electricity: 0.04 €/kWh$_{el}$ on site
    - CO_2: 108 €/t from air capture (H_2O captured concurrently)
    - Thermochemical energy conversion efficiency: 19 % (without vacuum pumping and gas separation)
    - Fischer-Tropsch: 60 % efficiency, 23000 €/bpd (investment), 4 €/bbl (O&M)
    - Interest rates: 5.7 % (debt nominal, 60 %), 11.8% (equity nominal, 40 %)
    - Value of by-product: Price (naphtha) = 80 % × price (jet fuel)

Falter, Christoph, et al. "An integrated techno-economic, environmental and social assessment of the solar thermochemical fuel pathway." Sustainable Energy & Fuels 4.8 (2020): 3992-4002.

Introduction

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Economic Analysis and Risk Assessment

- Estimation of fuel production costs for solar thermochemical plant
  - Regional variability of production cost
  - Levers to achieve low production costs

Production costs of jet fuel for six countries with favourable solar resource.
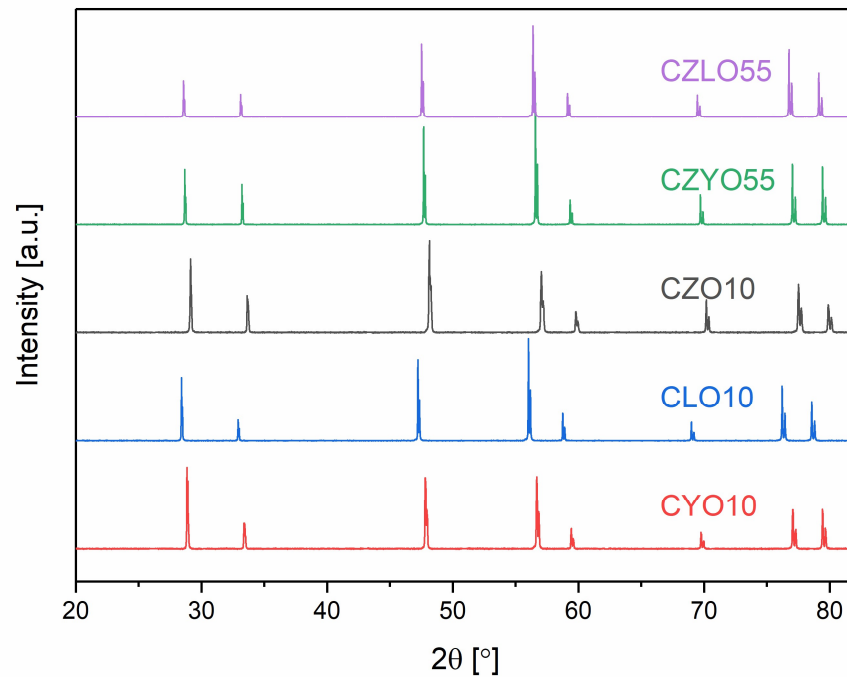
	USA	Australia	Spain	Morocco	Chile	South Africa
DNI [kWh/(m² y)]	2800	2800	2000	2500	3500	3100
Mirror area [10⁶ m²]	8.15	8.15	11.4	9.12	6.52	7.36
Labour costs [10⁶ €]	19.1	19.6	8.71	2.14	3.42	3.46
Investment costs [10⁹ €]	1.53	1.53	1.89	1.64	1.35	1.45
O&M costs [10⁶ €]	82.9	83.4	79.0	67.9	64.4	65.7
WACC [%]	5.7	6.2	4.9	8.1	7.1	13.1
Production costs [€/L jet fuel]	2.17	2.30	2.21	2.37	2.12	3.10

Core assumptions for baseline case and for low-cost scenario.

Subsystem	Baseline case	Low-cost scenario
Heliostat costs [€/m²]	100	75
DNI [kWh/(m² y)]	2500	3500
Thermochemical efficiency	15.1%	20%
Cost of CO_2 capture [€/t]	108	45
Production costs [€/L jet fuel]	2.37	1.60

Falter, Christoph, et al. "An integrated techno-economic, environmental and social assessment of the solar thermochemical fuel pathway." Sustainable Energy & Fuels 4.8 (2020): 3992-4002.

Structural Characterization (XRD)

Abbreviation	Nominal Composition	Actual Composition
CZLO55	$Ce_{0.9}Zr_{0.0547}La_{0.0453}O_{1.97735}$	$Ce_{0.9}Zr_{0.06}La_{0.04}O_{1.98}$
CZYO55	$Ce_{0.9}Zr_{0.0547}Yb_{0.0453}O_{1.97735}$	$Ce_{0.9}Zr_{0.05}Yb_{0.05}O_{1.975}$
CZO10	$Ce_{0.9}Zr_{0.1}O_2$	$Ce_{0.9}Zr_{0.1}O_2$
CLO10	$Ce_{0.9}La_{0.1}O_{1.95}$	$Ce_{0.91}La_{0.09}O_{1.96}$
CYO10	$Ce_{0.9}Yb_{0.1}O_{1.95}$	$Ce_{0.9}Yb_{0.1}O_{1.95}$

- Fig) XRD patterns after heat treatment at 1650 °C
- Table) Nominal and actual composition via EDS

# Structural Characterization (Raman Spectroscopy)

D₁ band
~550 cm⁻¹
Related to
O₂ vacancy

D₂ band
~600 cm⁻¹
Not related to
O₂ vacancy
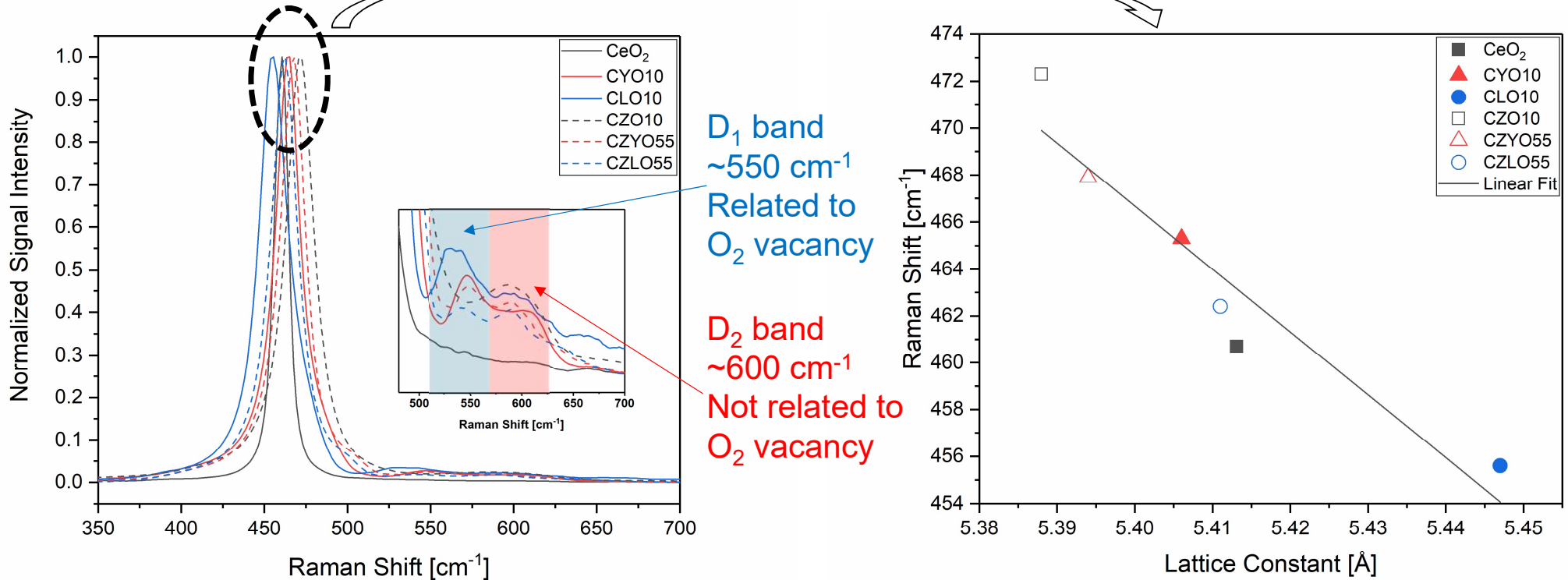
- Fig. Left) Normalized F_{2g} Raman peak of all materials
- Inset) Disorder bands (D_1 and D_2 band)
- Fig. Right) F_{2g} Raman peak position vs. lattice constant of all materials

TGA Results: Thermodynamics

Partial Molar Enthalpy/Entropy

- Reduced at T_{red} = 1200, 1250, 1300, 1350 and 1400 °C
  - For 2 h at 1200 – 1300 °C and for 4 h at 1350 – 1400 °C
  - Under pure Ar for the lowest pO_2
  - Under pure Ar + Ar with O_2 pump at various flow rate ratio at $pO_2 = 10^{-3} - 10^{-3.75}$ atm
 - Under Ar with O2 pump at various voltage at $pO2$ higher than 10^{-3} atm

a)
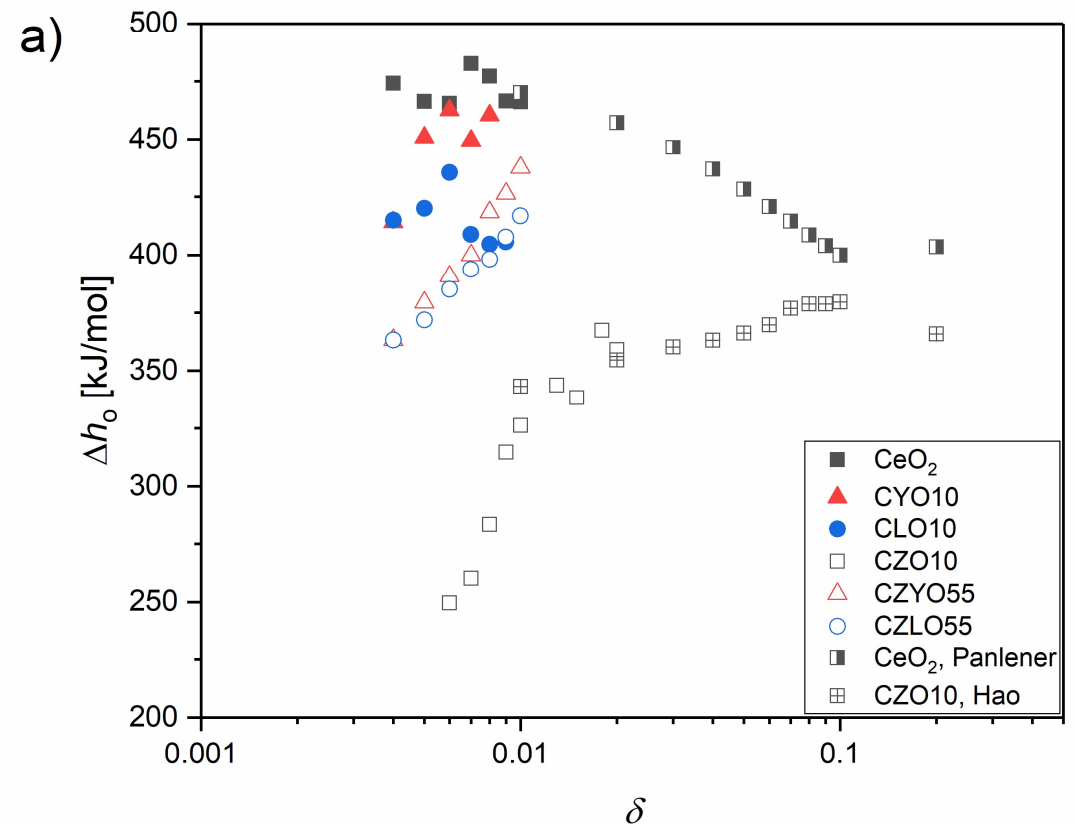
a) Partial molar enthalpy and b) partial molar entropy vs. δ

TGA Results: Thermodynamics

Gibbs Free Energy

- Reduced at T_{red} = 1200, 1250, 1300, 1350 and 1400 °C
  - For 2 h at 1200 – 1300 °C and for 4 h at 1350 – 1400 °C
  - Under pure Ar for the lowest pO_2
  - Under pure Ar + Ar with O_2 pump at various flow rate ratio at $pO_2 = 10^{-3} - 10^{-3.75}$ atm
  - Under Ar with O2 pump at various voltage at $pO2$ higher than 10^{-3} atm
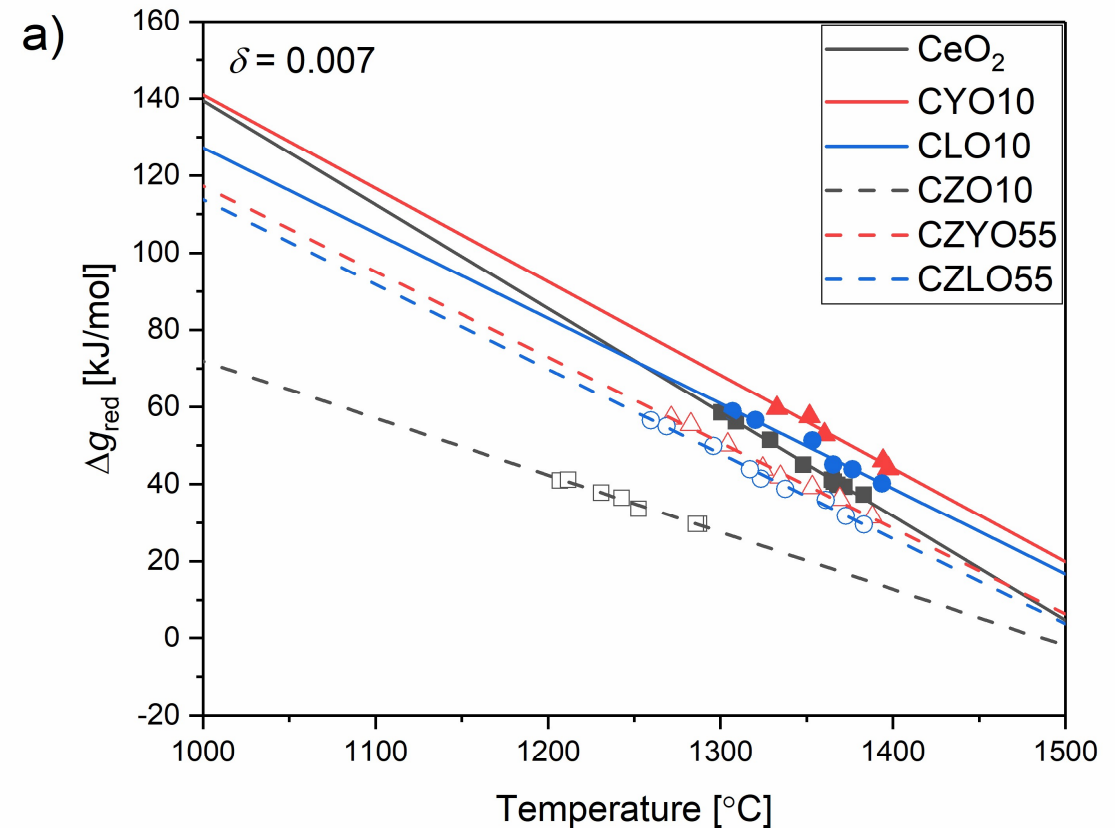
Gibbs free energy for a) reduction and b) oxidation calculated at δ = 0.007.
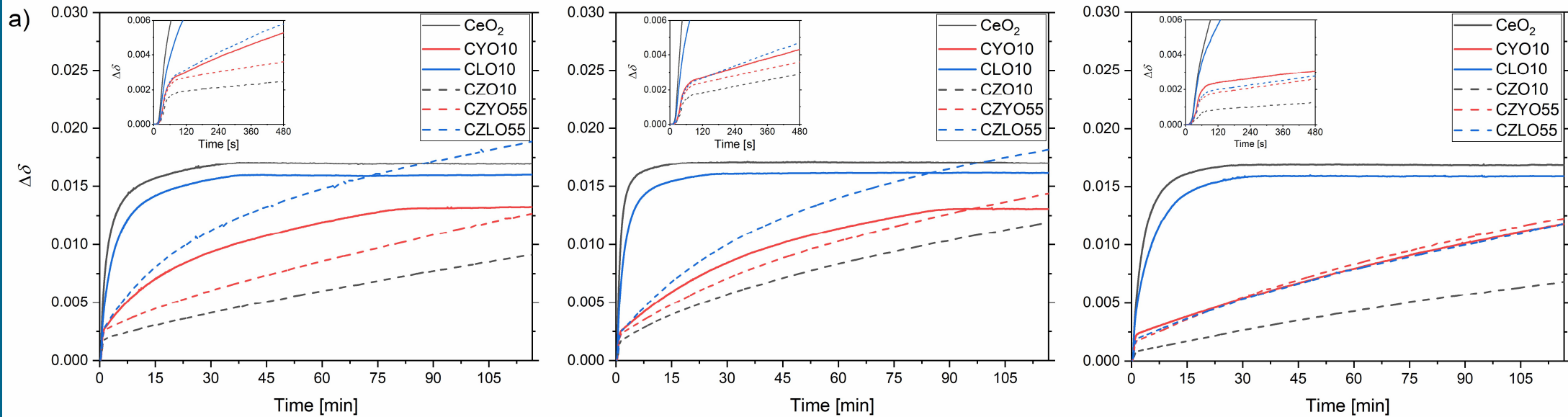
TGA Results (Δδ): Oxidation Kinetics

Change in nonstoichiometry during CO_2 splitting (Left) at 1000 °C, (Mid) at 800 °C, and (Right) at 600 °C.
Inset: at early reactions (t = 0 – 480 s)

- Reduced at 1400 °C for 2 hours under Ar.
- Oxidized for 2 hours under $p CO_2$ = 0.8 atm, balanced with Ar.

TGA Results: Introducing Reaction Regimes

## CO$_2$ Splitting Reaction Regimes

- CO$_2$ splitting consists of multiple reaction regimes with different reaction mechanism.
  - **Unrestricted regime** (0 s – about 150 s)
  - **Surface exchange limited regime** (about 150 s until equilibrated)
  - **Surface exchange limited at equilibrium regime** (depending on the material, as soon as it is equilibrated)
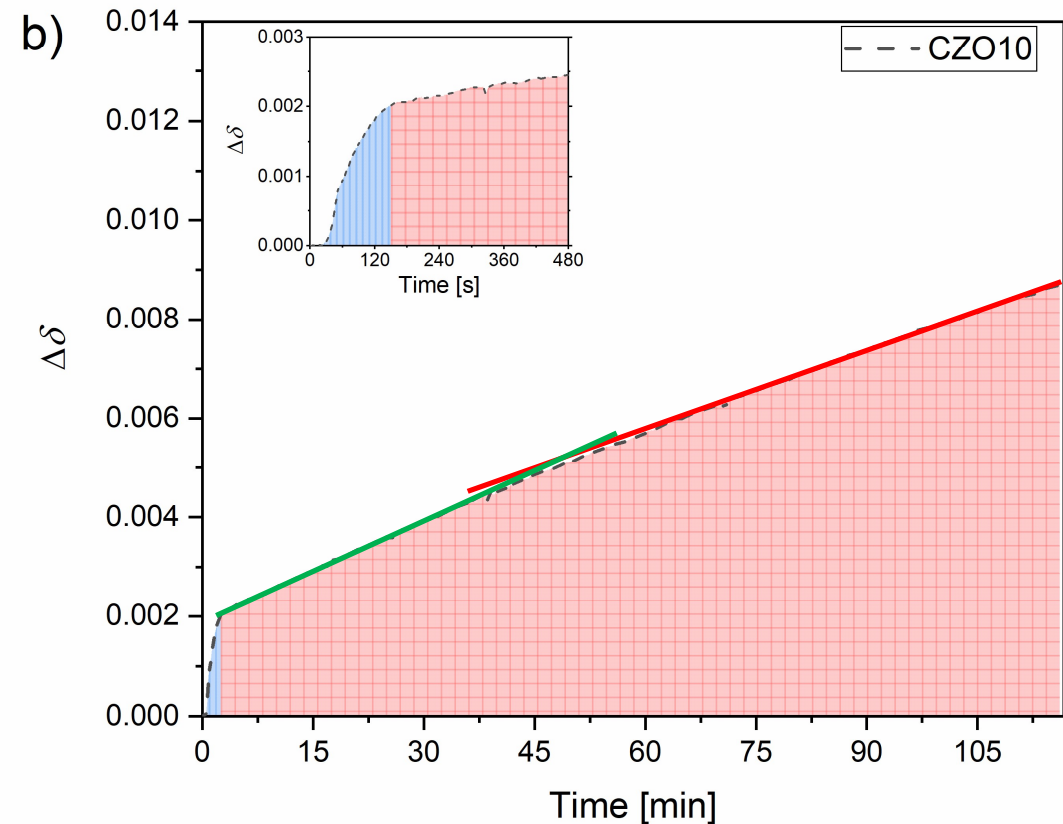
TGA raw data and reaction regimes of a CZO10 pellet during CO$_2$ splitting (T_{ox} = 1000 °C)

TGA Results: Slope Factor Comparison
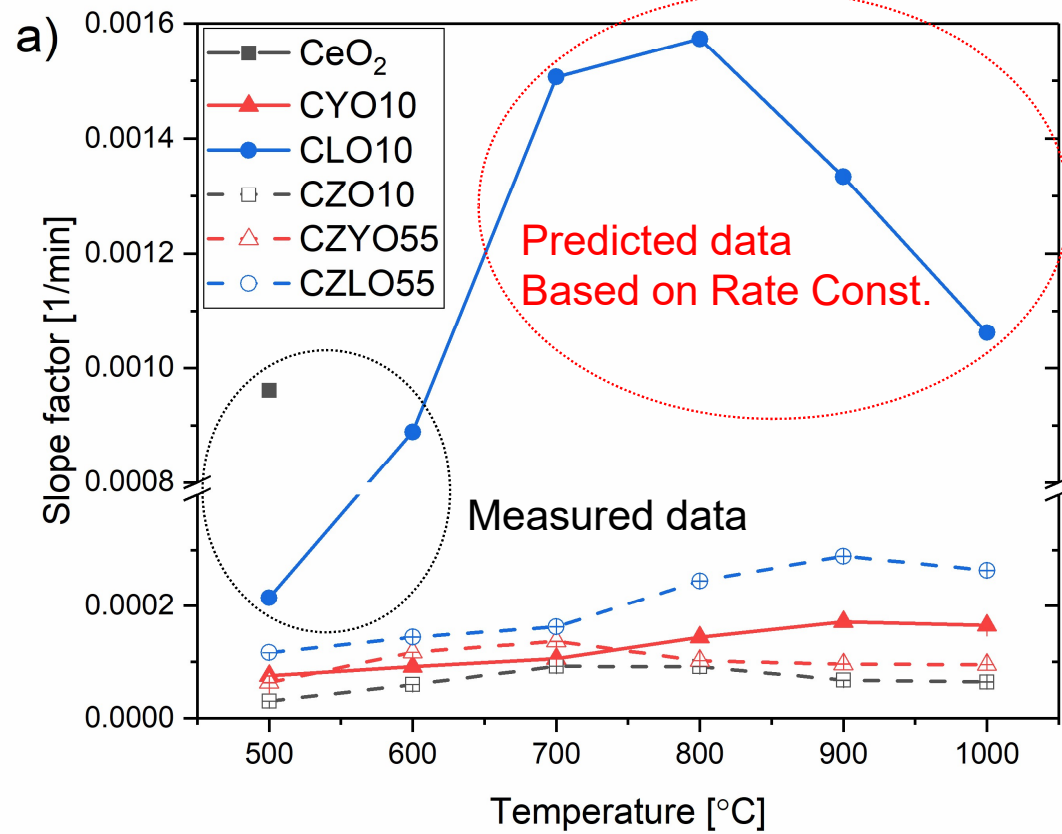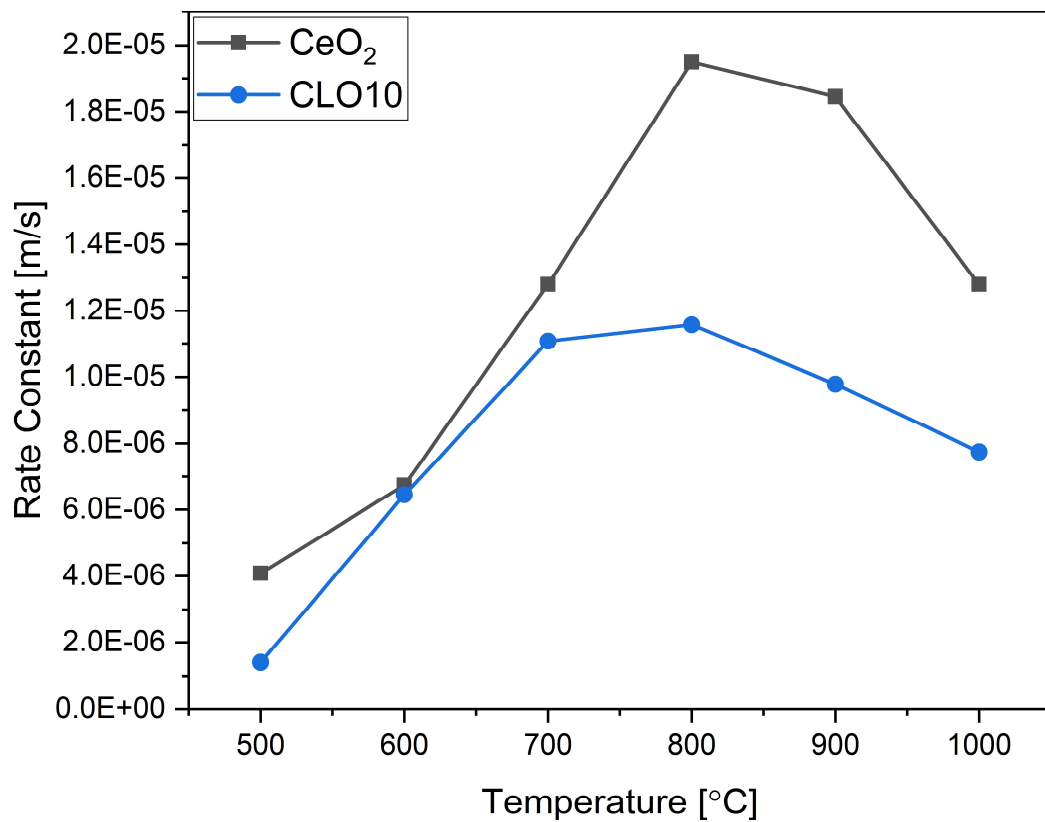
a) Slope factor (Rate of $\Delta\delta$) vs. CO_2 splitting temperatures

Plans For Future Works

- Surface exchange and diffusion coefficients will be determined via Secondary-Ion Mass Spectrometry (SIMS) oxygen isotope experiments, and compared to the TGA results.

- Surface exchange promoting techniques will be tested (developing composites, making foams or other porous samples, etc.).

- Optimized materials with respect to thermodynamics and oxidation kinetics will be proposed and syngas productivity using them will be experimentally demonstrated.