Oxygen Production for Gasification

NATIONAL ENERGY TECHNOLOGY LABORATORY

Jonathan W. Lekse

Gasification Virtual Project Review Meeting, September 2, 2020

Advanced Reaction Systems

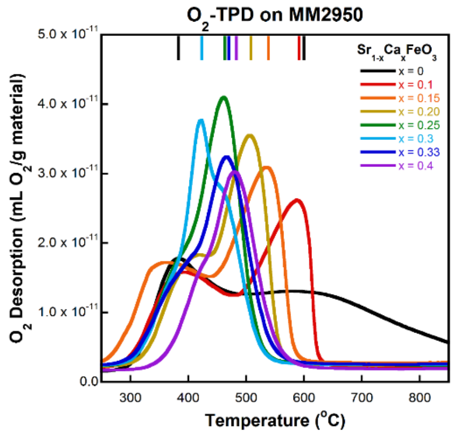
New Approach - Tasks

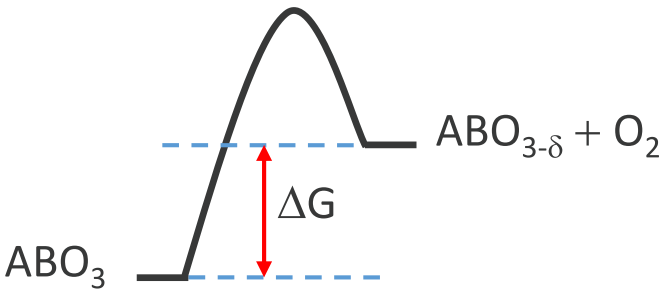
- Task 1 – Project Coordination/Management
- Task 2 – Gasification Test Facility
- Task 3 – Advanced Gasifier Design
- Task 4 – Advanced Manufacturing Technologies for Gasification
- Task 5 – Oxygen Production for Gasification
- Task 6 – Microwave Reactions for Gasification
- Task 11 – Catalytic and Non-Catalytic Processes for Hydrogen Production
- Task 12 – Biomass Gasification Assessment
- Task 13 – Gasification Polygeneration Assessment
- Task 14 – Syngas Conversion to Industrial Chemicals

Oxygen Carrier Studies

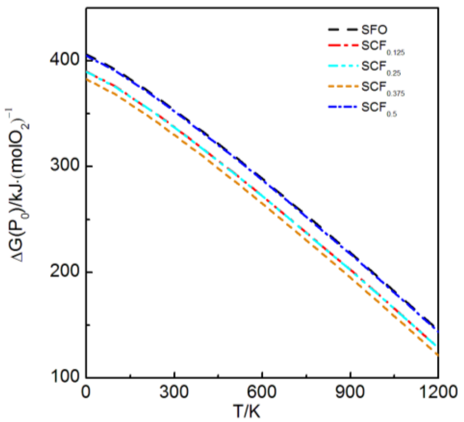
Project Goal: Linking Atomic and Process Scales

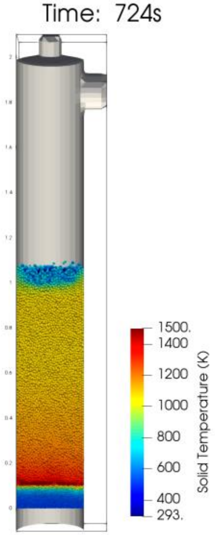
Laboratory Experiments and Atomistic Modelling



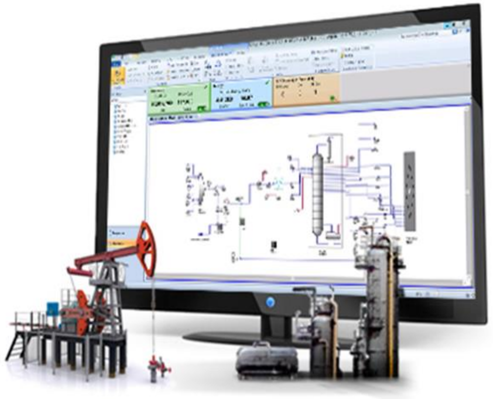


Ellingham Diagrams





Reactor Design and CFD Models

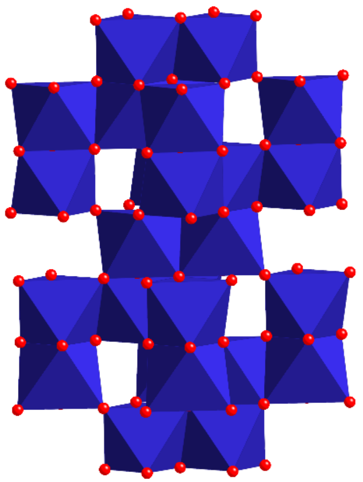


Process Models

Oxygen Carrier Studies

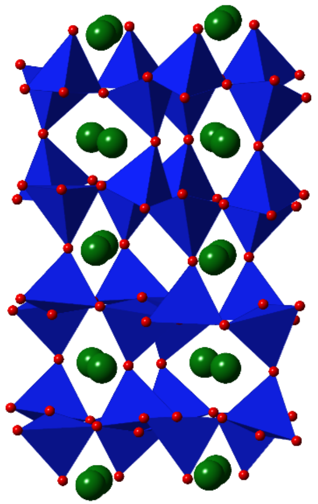
Materials of Interest

Binary Oxides



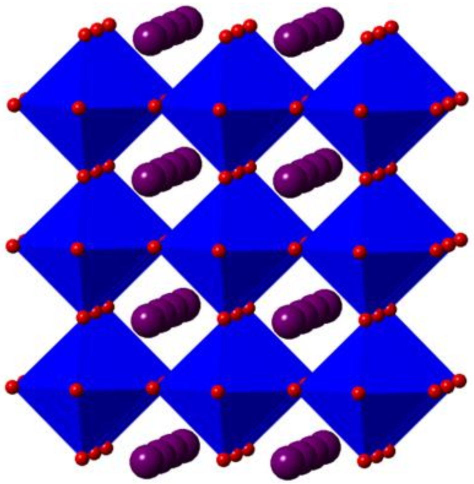
- Inexpensive
- Can have good reactivity
- Limited operating temperature range
- Potential agglomeration

Ferrites



- Can be used for partial oxidation
- Ideal for gasification
- Compositional flexibility
- Stable

Perovskites



- Easily reduced/oxidized
- Compositional flexibility
- Tuneable oxygen capacity and temperature range
- Stable

Perovskite Materials

Background

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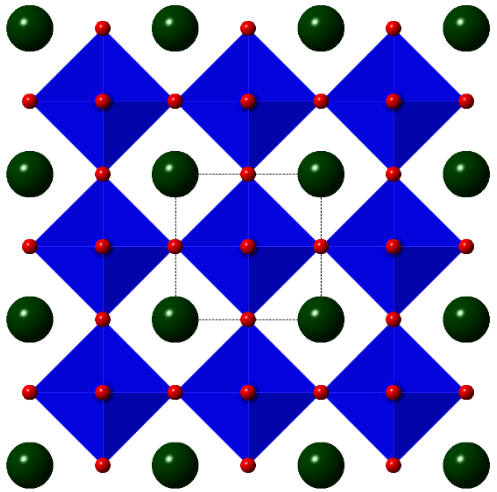
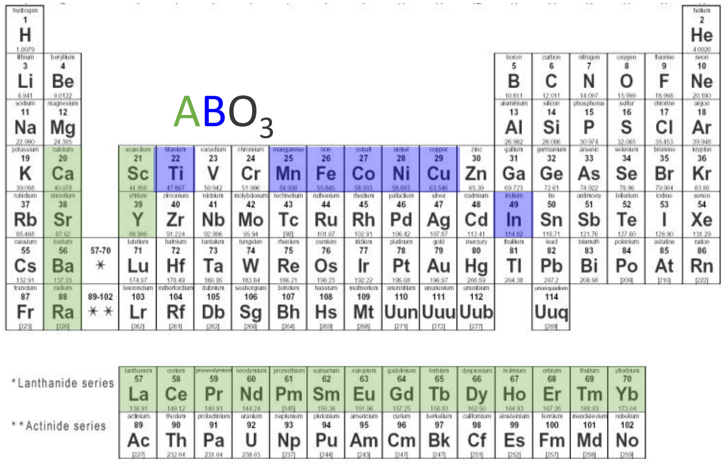
- Perovskites are a well studied type of oxide with the general formula ABO_3
- The first identified Perovskite was $CaTiO_3$
- A-site cation has a dodecahedral coordination
- B-site cation sits in the center of BO_6 octahedra
- "Ideal" structure is cubic though the size of the A-site cation can create distortions

- Applications
    - Chemical looping combustion
        - Potential CLOU candidates, if oxygen is released into the gas phase
    - Pollution remediation
        - NO_x decomposition
    - Replacement of noble metal catalysts in automobiles
    - Syngas production via reforming reactions
    - High Temperature Gas Sensors
    - Solid Oxide Fuel Cells
    - Photovoltaics

- Potentially Interesting Properties
    - Superconductivity
    - Magnetoresistance
    - Ferromagnetism





Perovskite Materials

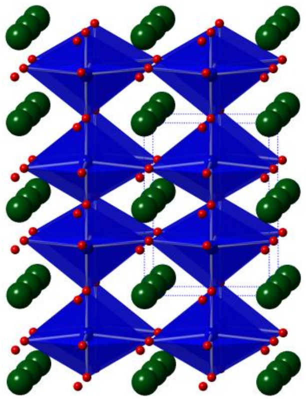
Chemical Substitution

General Perovskite Formula

ABO_3

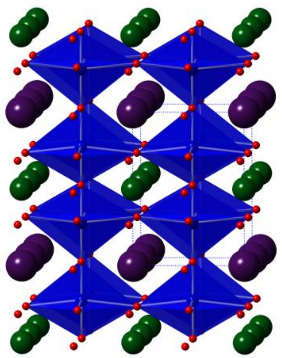
Doubled Perovskite Formula

$A_2B_2O_6$



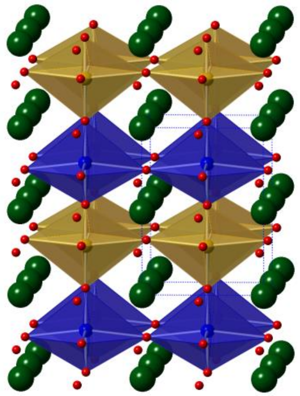
A-Site Substitution

$A^1A^2B_2O_6$



B-Site Substitution

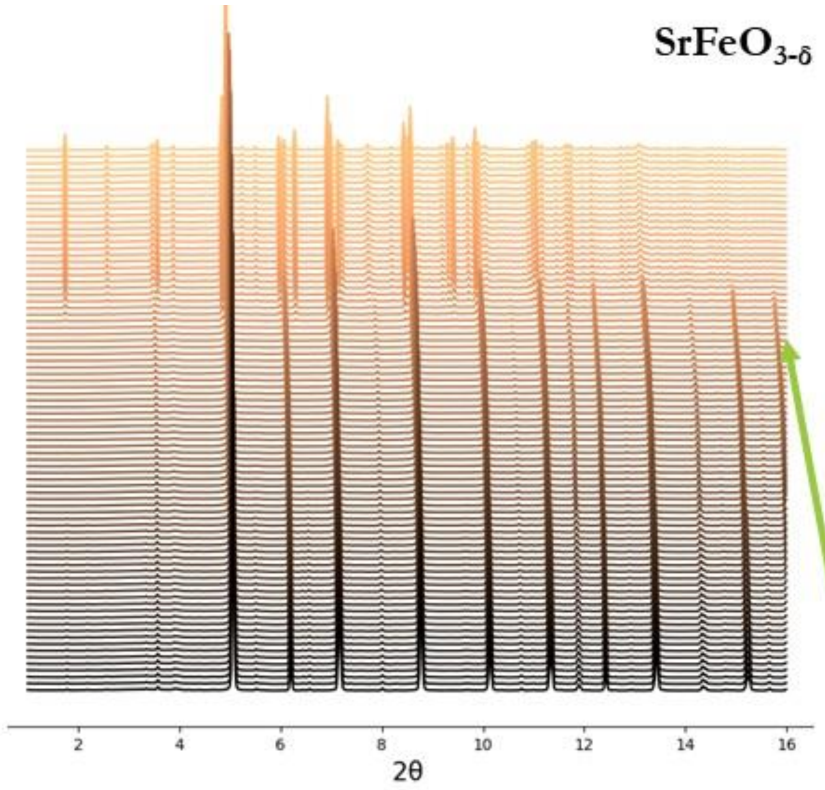
$A_2B^1B^2O_6$

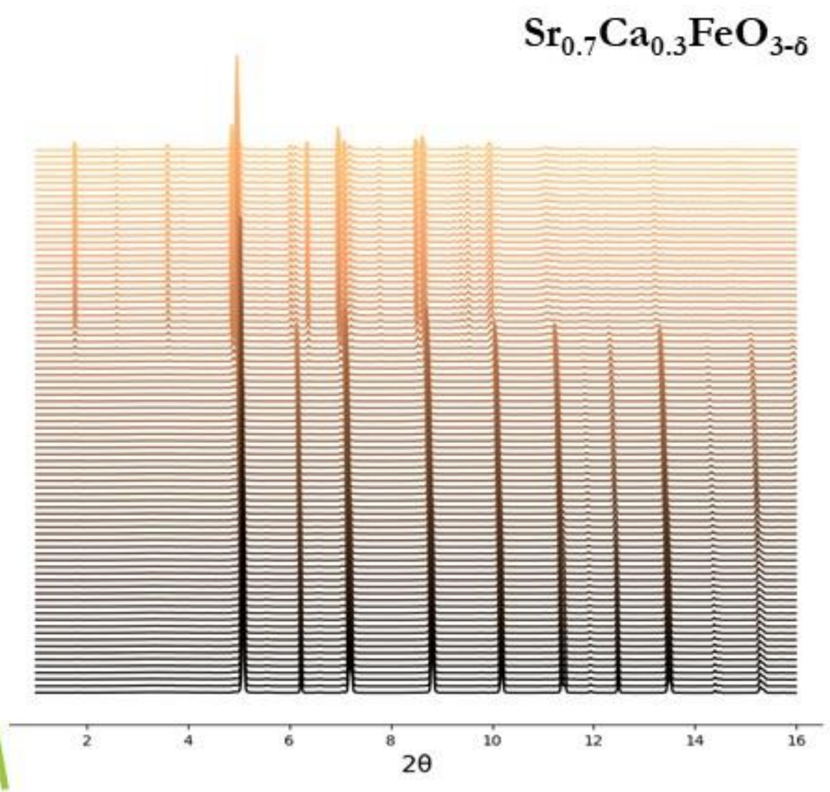


Perovskite Characterization

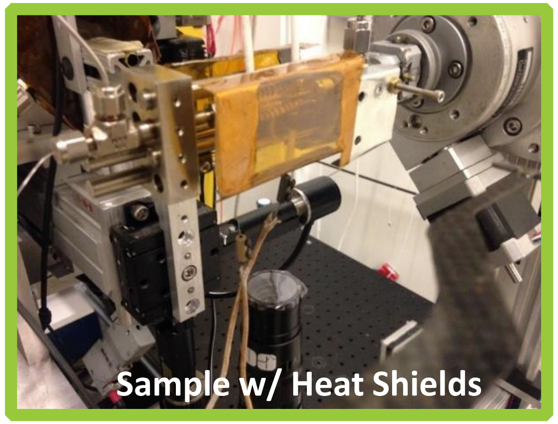
High-resolution, rapid collection synchrotron powder *in situ* XRD

- **Time-resolved *in situ* XRD**
  - Determine structural changes in relation to oxygen release
  - Synchrotron source (APS 17-BM) - high-energy, rapid acquisition





Thermal expansion, possible oxygen release

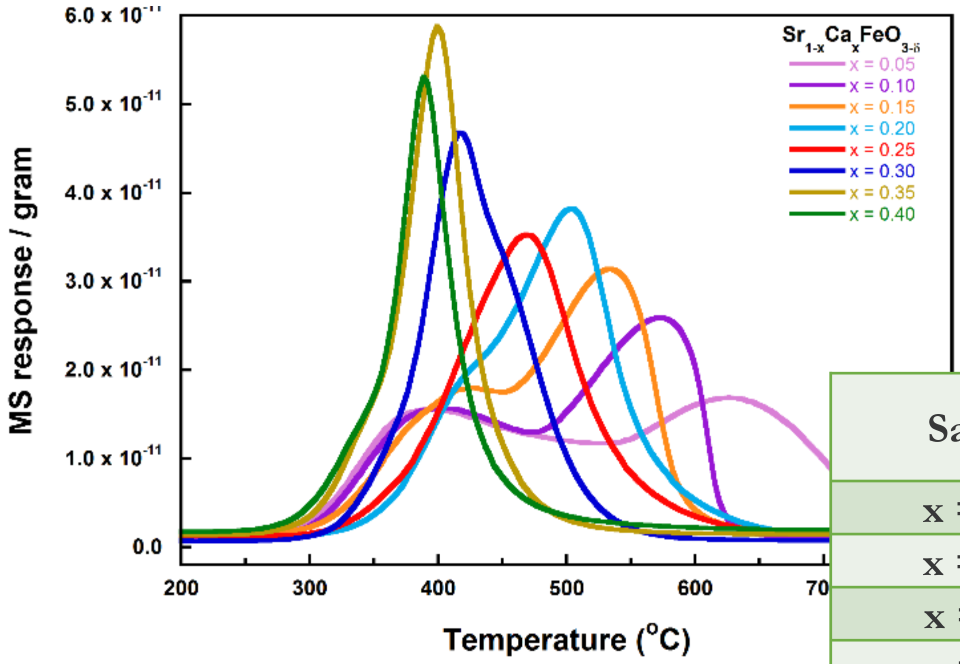


Popczun, E.J.; Tafen D.; Natesakhawat, S.; Marin, C.M.; Nguyen-Phan, T.-D.; Zhou, Y.; Alfonso, D.; Lekse, J.W. *J. Mater. Chem. A*, **2020**, *8*, 2602.

Perovskite Characterization

TPD: Determination of maximum O_2 storage capacities and desorption temperatures

- **Experiment:**
  - Systematic priming at 850°C in air flow for O_2 uptake for 1 hour
  - Cool to RT
  - 10 deg/min ramp to 1050°C in He flow and monitor O_2 release
- **Findings:**
  - As x increases, $T_{des, max}$ decreases
  - As x increases, max O_2 release decreases
  - As x increases, α & β oxygen desorption distinctions merge



Sample	Volume O_2 (mL/g)
x = 0.00	17.134
x = 0.05	16.282
x = 0.10	16.264
x = 0.15	15.292
x = 0.20	15.678
x = 0.25	13.718
x = 0.30	14.388
x = 0.35	13.262
x = 0.40	11.482

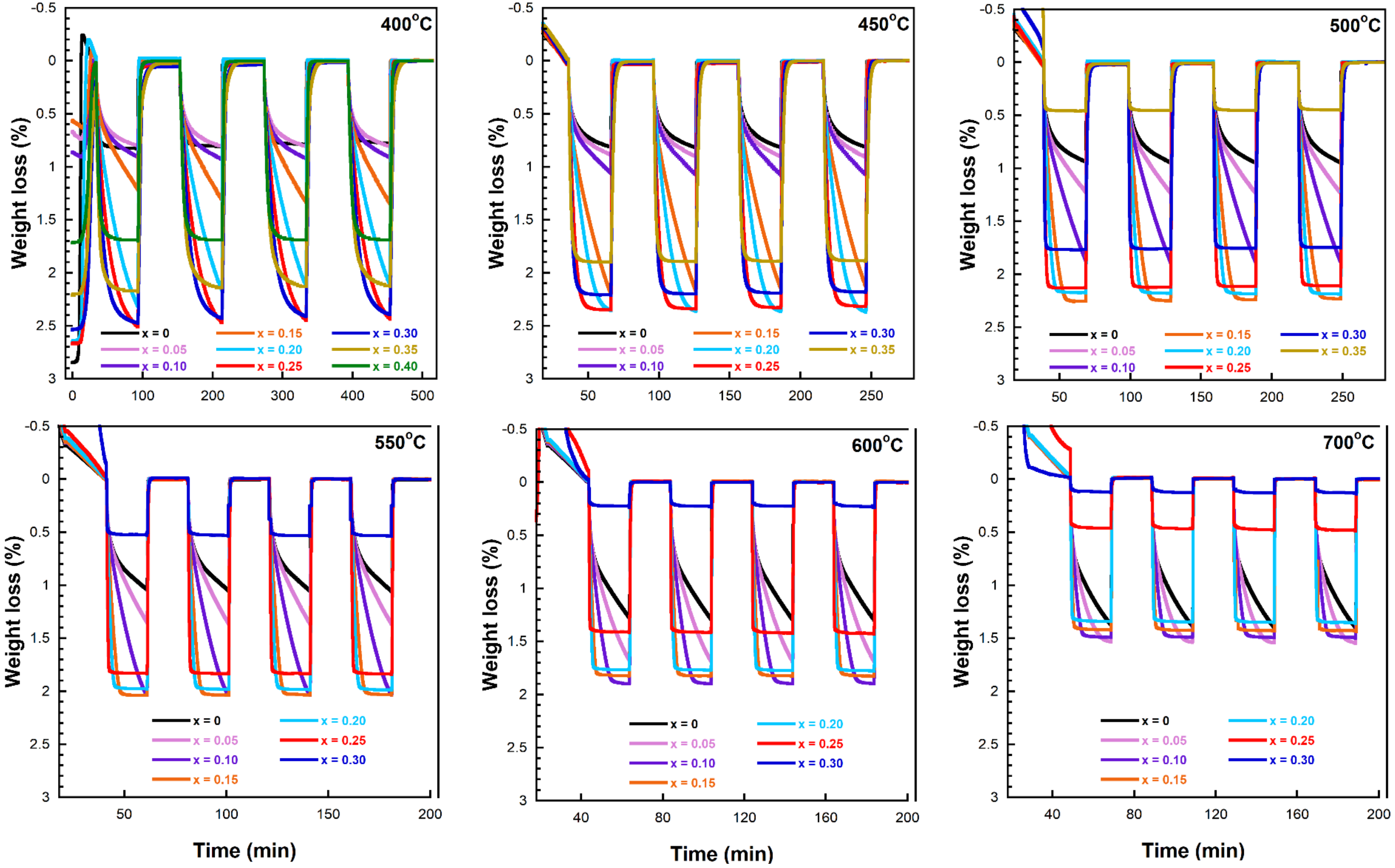
Popczun, E.J.; Tafen D.; Natesakhawat, S.; Marin, C.M.; Nguyen-Phan, T.-D.; Zhou, Y.; Alfonso, D.; Lekse, J.W. *J. Mater. Chem. A*, **2020**, *8*, 2602.

Perovskite Characterization

TGA: All samples show cyclable O_2 uptake and release

- **Samples demonstrate durability and cyclability**
  - 4 uptake/release cycles
    - Shorter cycle timeframe used for higher temperatures
    - Gas flow (75 sccm)
  - Samples aged 6+ mo. in air

- **Findings:**
  - As x increases, max O_2 capacity decreases (agrees with O_2-TPD)
  - As x increases, max uptake temperature increases
  - As x increases, rate of O_2 release at 800°C increases
  - If x ≥ 0.30, sharp decrease in oxygen storage at 450-500°C exists
    - x = 0.20, less abrupt at 550-700°C



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Perovskite Characterization

TGA: Oxygen storage capacities and time to reach 90% released

- As temperature increases, max OSC decreases
  - Instability of oxidized species under air flow
  - Ex: x = 0.30 at 550°C 0.54 wt% O_2

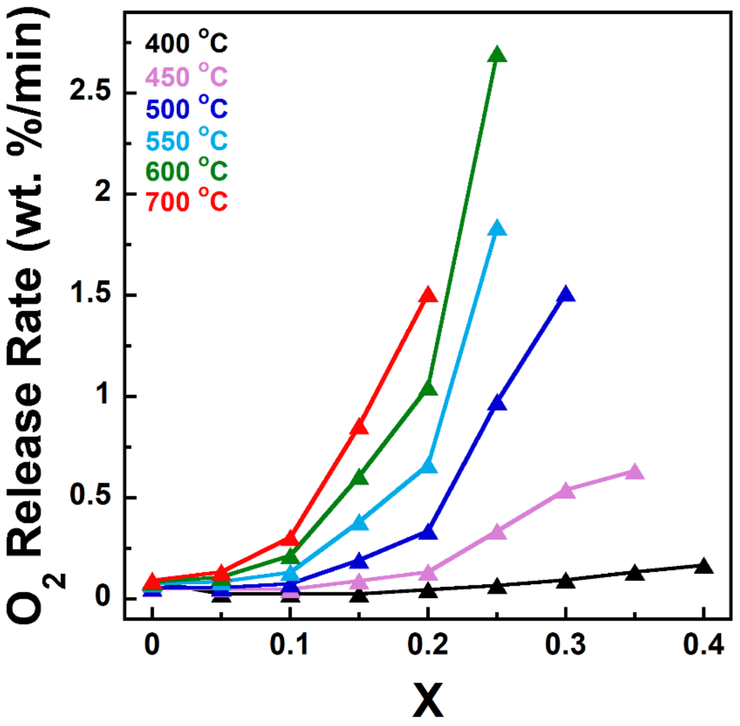
OSCs in wt%

Ca^{2+} ratio (x)	Temperature (°C) 400	450	500	550	600	700
0.00	0.84	0.82	0.95	1.06	1.30	1.40
0.05	0.81	0.91	1.19	1.37	1.69	1.55
0.10	0.93	1.08	1.91	2.04	1.90	1.50
0.15	1.35	2.17	2.26	2.04	1.83	1.44
0.20	2.10	2.37	2.19	1.99	1.78	1.36
0.25	2.41	2.35	2.13	1.84	1.43	0.49
0.30	2.41	2.21	1.77	0.54	0.24	0.14
0.35	2.13	1.90	0.46			
0.40	1.72					

- Rates increase as x and temperature increase
  - Disparities due to very low OSCs
  - Only $SrFeO_3$ stays constant

Time (min) to 90% release

Ca^{2+} ratio	Temperature (°C) 400	450	500	550	600	700
0.00	9.56	16.53	17.38	13.93	15.58	15.15
0.05	31.77	18.33	20.70	16.03	15.65	11.67
0.10	36.03	22.08	25.08	15.47	8.85	4.93
0.15	51.35	24.22	11.83	5.35	3.02	1.68
0.20	45.17	17.85	6.53	3.00	1.70	0.90
0.25	36.13	7.00	2.18	1.00	0.53	1.05
0.30	25.83	4.10	1.17	0.70	4.72	17.32
0.35	16.03	3.00	1.07			
0.40	10.30					



Plot estimates the speed of oxygen release:

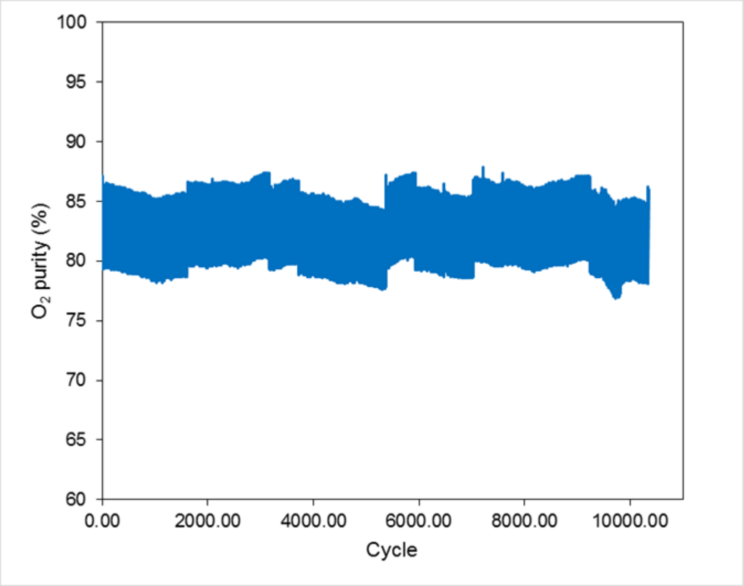
$$rate = OSC_{90\%}/time_{90\%}$$

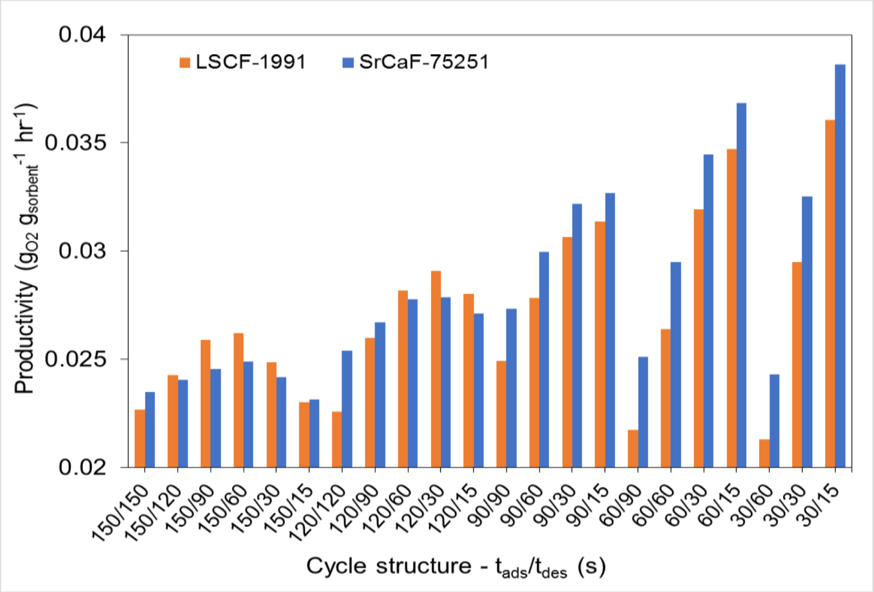
(Larger rates do not specifically suggest use of that material)

Perovskite Characterization

Stability Testing and Comparison to Known Materials

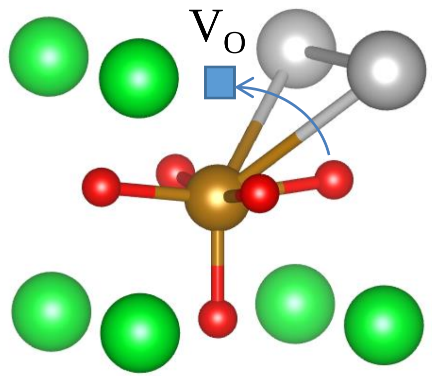
- NETL Perovskite samples were tested in collaboration with ThermoSolv
- NETL sample demonstrated stability over >10,000 cycles
- NETL Perovskite outperformed an LSCF sample in multiple cycle structures

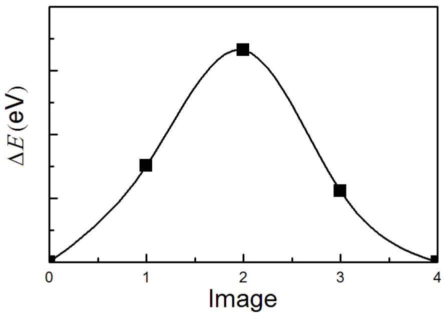




Perovskite Modelling

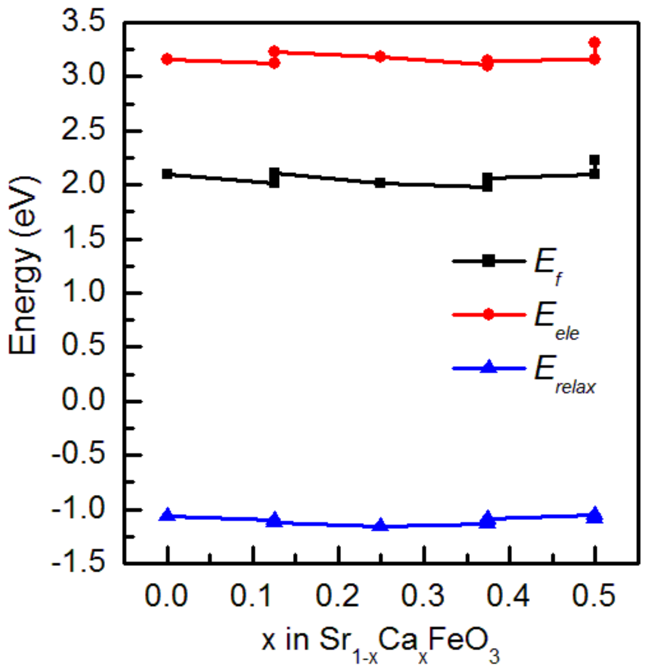
Atomistic Modelling



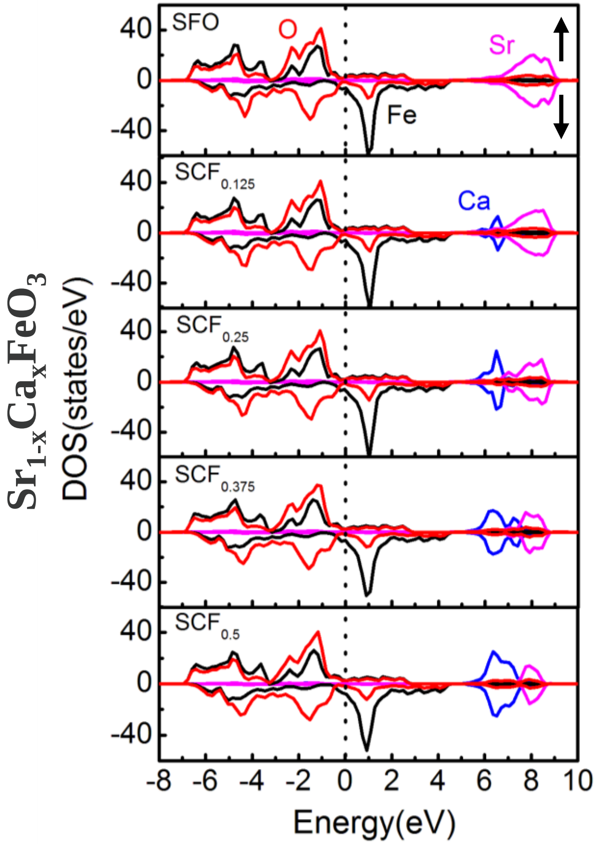


Oxygen Diffusion

Vacancy Formation Energy



Electronic Density of States

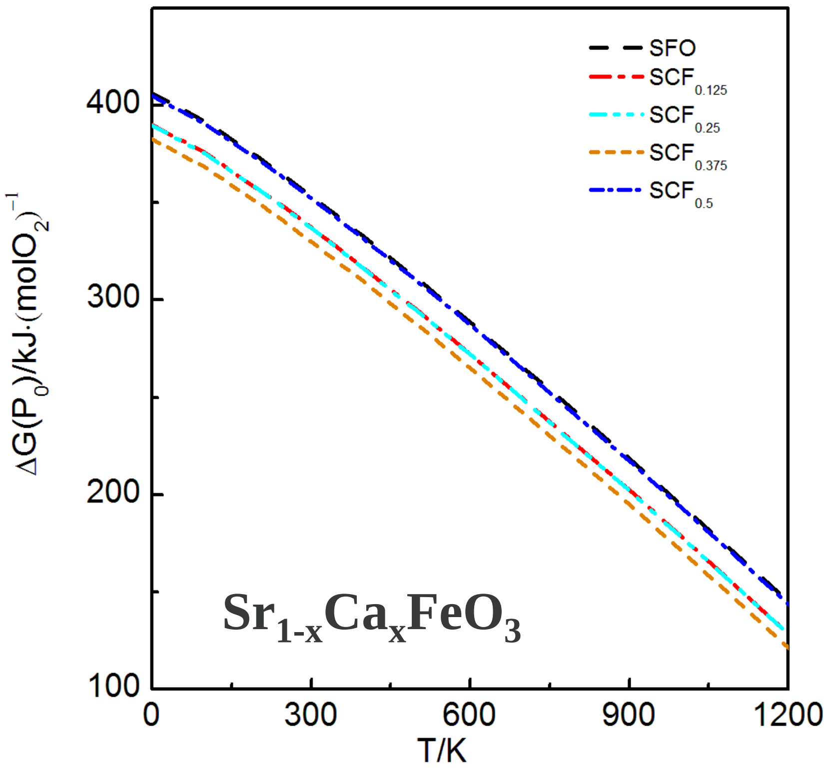


Ting Jia, Eric J. Popczun, Jonathan W. Lekse, Yuhua Duan, *submitted to Appl. Energy.* (2020)

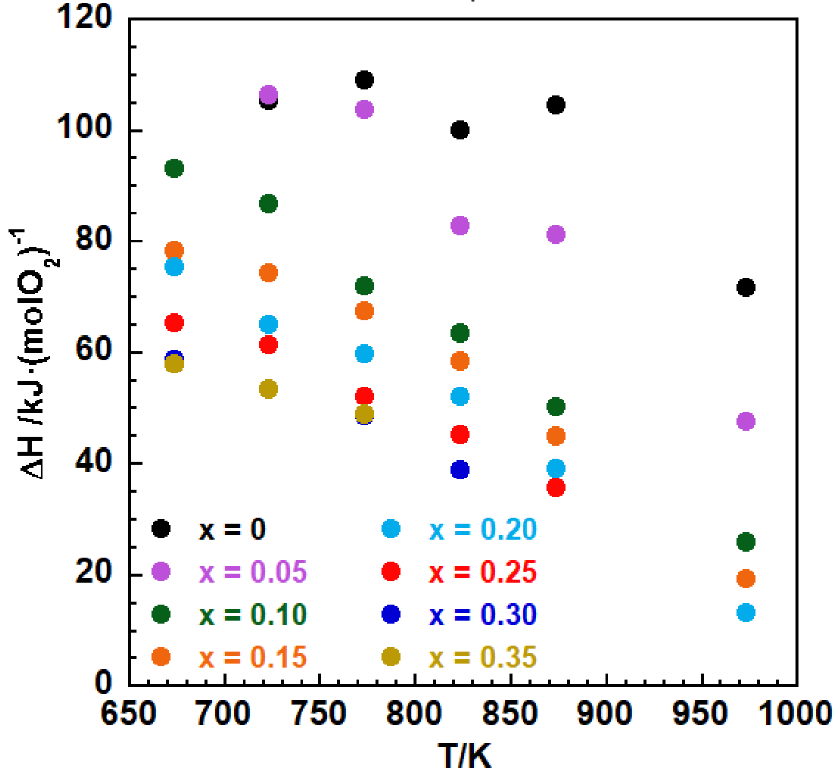
Perovskite Modelling

Ellingham Diagram Calculation

Computational Model



DSC Experiments



- Differential Scanning Calorimetry used to determine enthalpy of oxidation/reduction for each sample at each temperature from cycling experiments
- Decreasing enthalpy as both calcium content and temperature increase
- Agreement between computational models and DSC experiments

Ting Jia, Eric J. Popczun, Jonathan W. Lekse, Yuhua Duan, *submitted to Appl. Energy.* (2020)

Perovskite Modeling

MFiX-DEM Verification of TGA Data

Mass in-flow

- Air for adsorb swing
- N_2 for desorb swing

Tube:
Diameter = 0.021 m
Height = 0.559 m

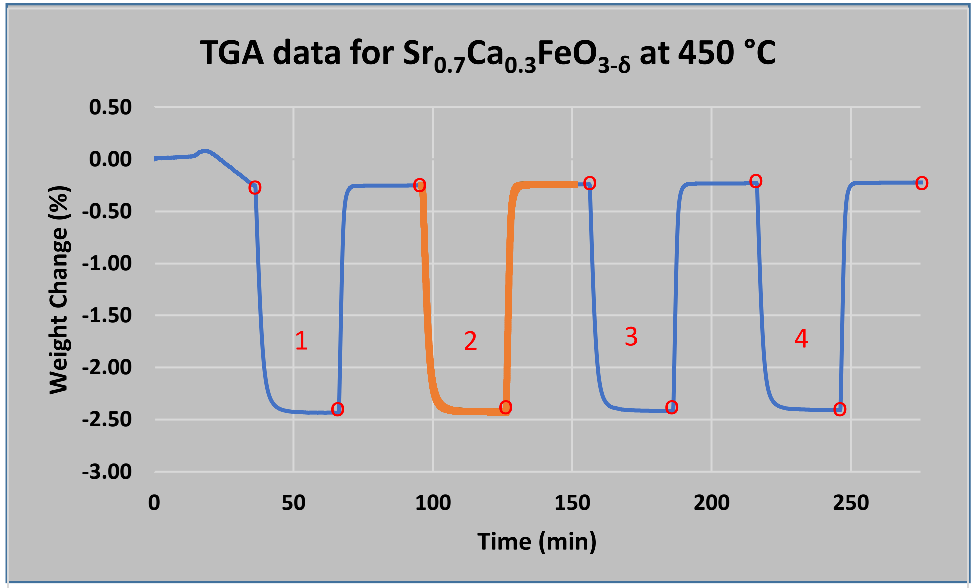
Particles:
Diameter = 0.0031 m
(300 g total)

Mesh: 4 x 60 x 4

Isothermal

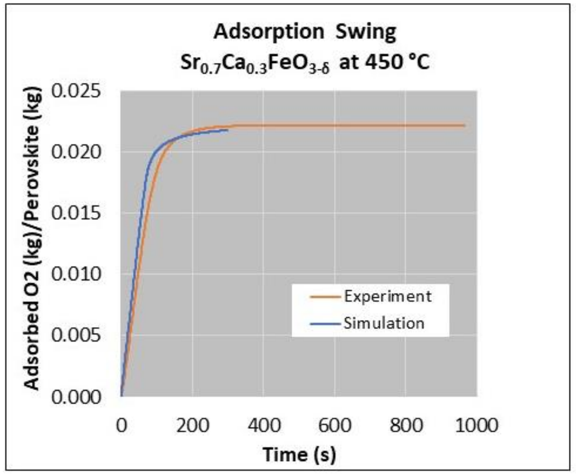
Pressure out-flow

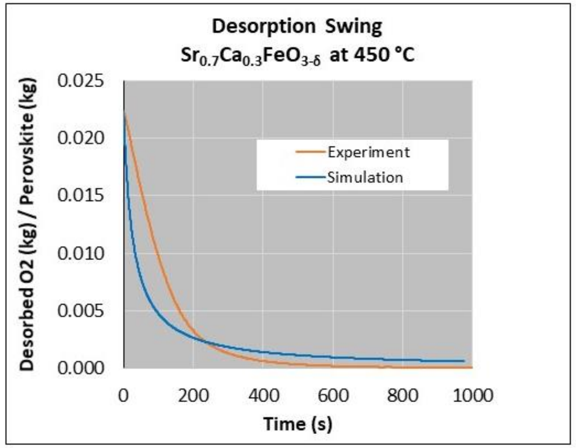
For each case, the 2nd TGA cycle was used to calculate kinetic constants.



Current and Future Work

MFiX Validation and Reactor Design



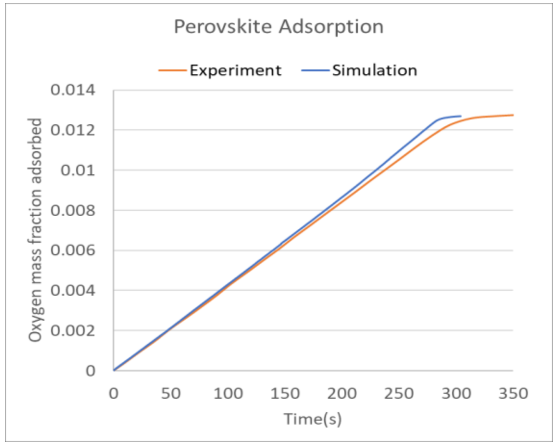


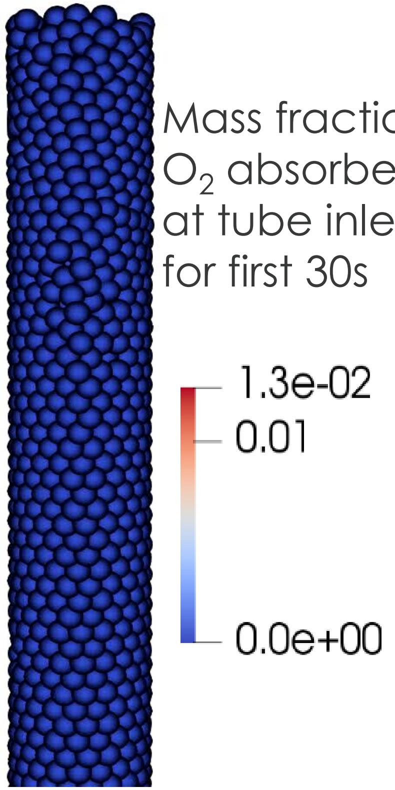
Validated TGA data will contribute to the final MFiX CFD Reactor Design

For each temperature and perovskite composition, a numerical matching of TGA data is necessary.

CFD Model Demonstration for 300s O_2 absorption sweep

- 22mm x 559mm tube
- $Ba_{1-x}Sr_xCo_{0.8}Fe_{0.2}O_{3-\delta}$ data from He (2009)

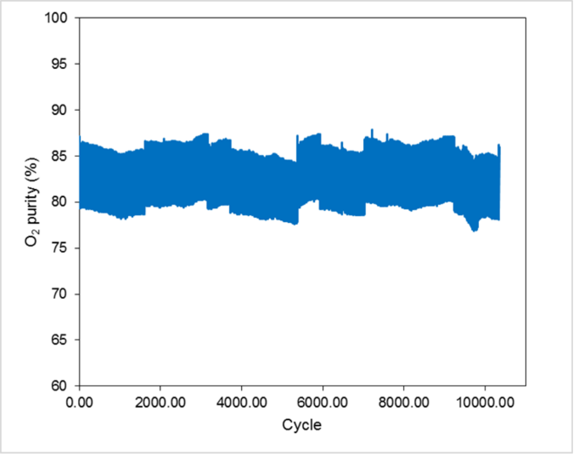


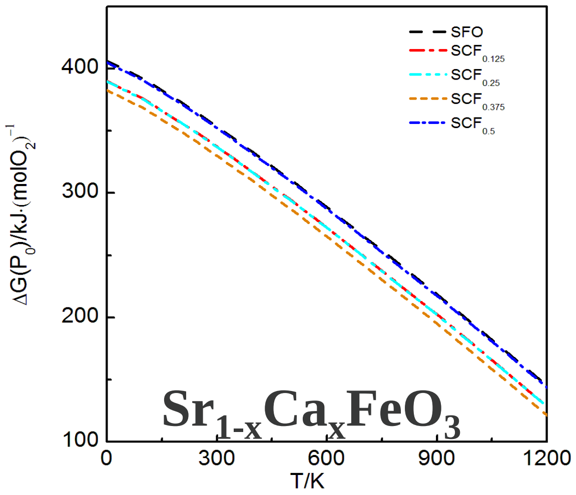


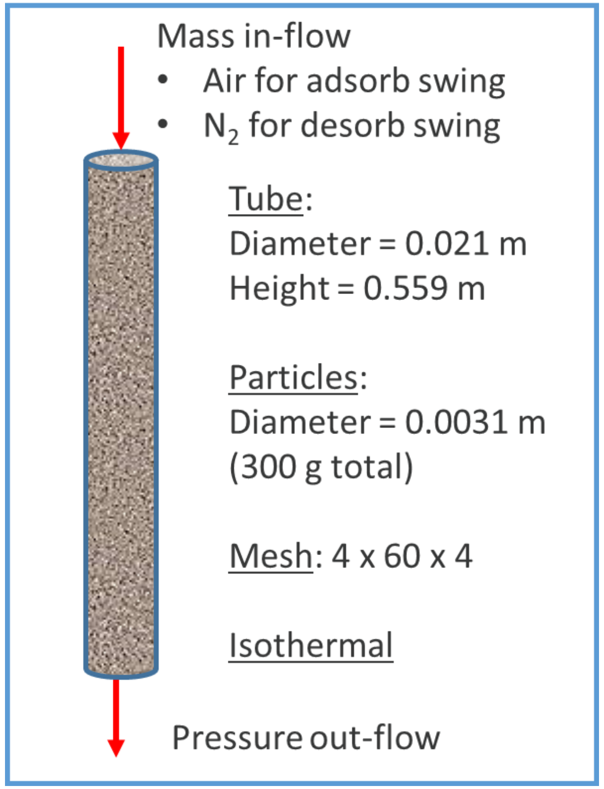
Mass fraction O_2 absorbed at tube inlet for first 30s

Conclusions

- Synthesized more than 24 perovskite materials
- Achieved more than 2.4 wt % O_2 capacity
- Achieved control of desorption temperature
- $Sr_{1-x}Ca_xFeO_{3-d}$ found to outperform LSCF
- $Sr_{1-x}Ca_xFeO_{3-d}$ found to be stable over >10,000 cycles
- Experimentally validated Ellingham Diagrams
- Initiated CFD design and model validation



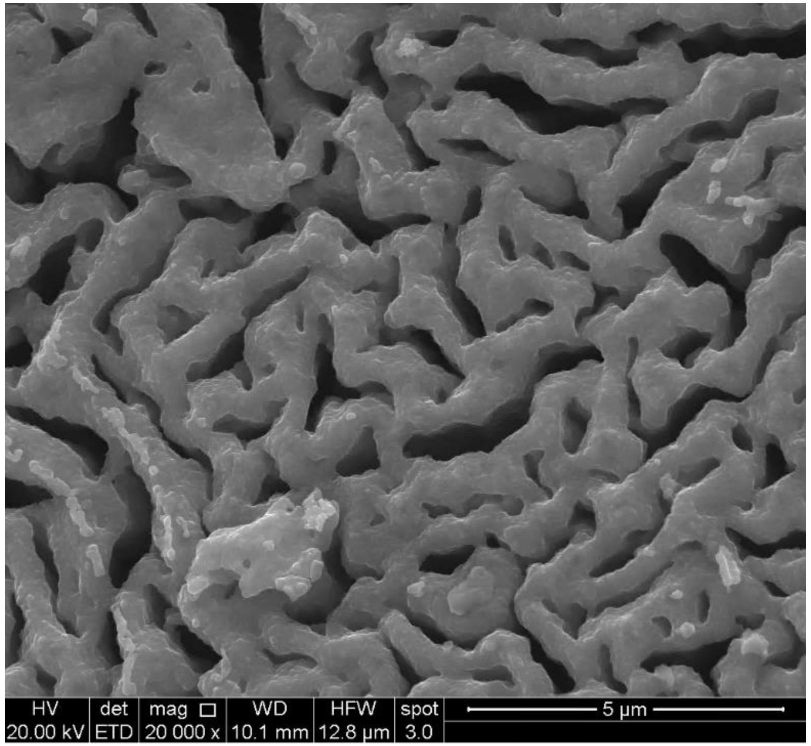




Future Work

Mesoporous $Sr_{1-x}Ca_xFeO_3$

- **Larger surface areas obtained by changing synthesis technique and temperature**
- **Particle synthesis based on literature precedent from Dou**
  - Use of citric acid and ethylene glycol allows lower temperature synthesis (at 1000 °C)
  - Show increased activity versus their solid-state materials
- **Did not alter temperature to synthesize different particle sizes or morphologies**
  - NETL: 700-1000 °C
    - BET surface areas: 8.2-15.0 m^2/g depending on synthesis temperature
    - Mesoporous sample observed at 800 °C



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