ARS Task 5: Oxygen Production for Net-Zero Carbon

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NATIONAL ENERGY TECHNOLOGY LABORATORY

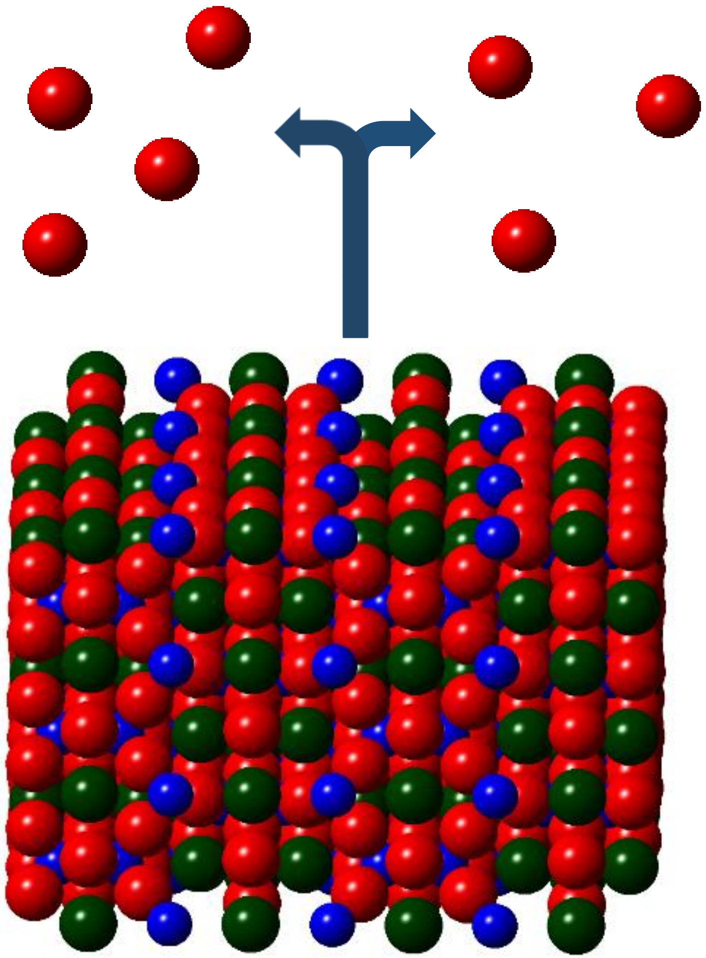
U.S. DEPARTMENT OF ENERGY

Research Objective

Project Objective

The objectives of this task are to design a metal oxide carrier material capable of separating oxygen from air and to develop a reactor based on metal oxide carrier materials

- The carrier will rapidly store and release oxygen
- A knowledge base for the optimization of carrier materials will be created allowing adaptation to different applications
- NETL MFiX Team will collaborate to design an oxygen production reactor



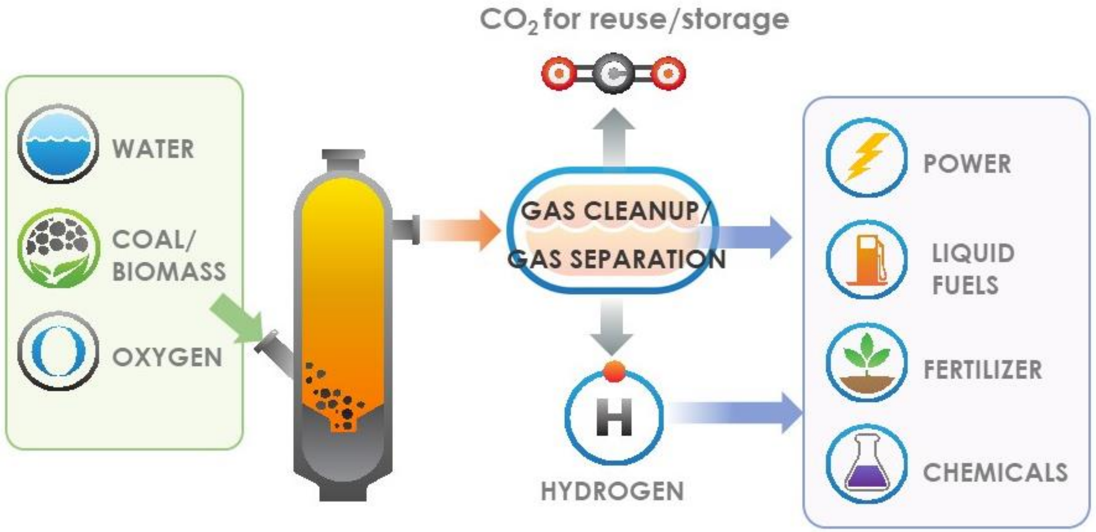
Value Proposition: An oxygen carrier-based air separation unit could provide a scalable oxygen source for an oxygen blown gasification system enabling higher quality syngas, the use of alternate feedstocks, and the production of hydrogen

Research Objective

Alignment with Program & Stakeholder Needs

Development of an improved oxygen carrier material and oxygen production reactor would support the need of the Gasification Program for low-cost oxygen.

- Low-cost oxygen can be used for pre-combustion carbon capture reducing the carbon footprint of a gasification system.
- Alternate fuels such as municipal solid waste and waste plastic perform best in an oxygen blown gasification system.
- An oxygen carrier-based system would support the development of small modular gasification systems by providing an alternative to cryogenic oxygen which can be prohibitively expensive at small scales.



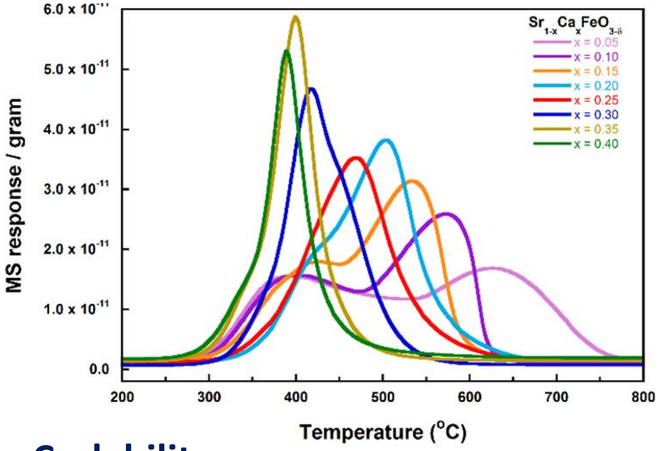
Research Objective

Material Development

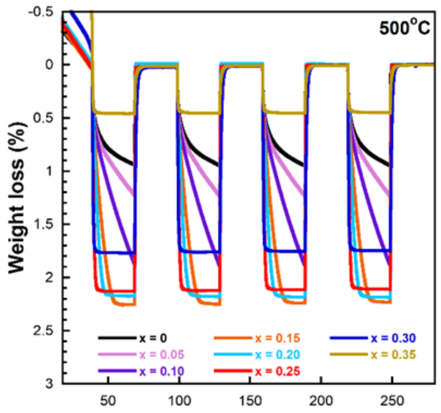
Goals and Metrics

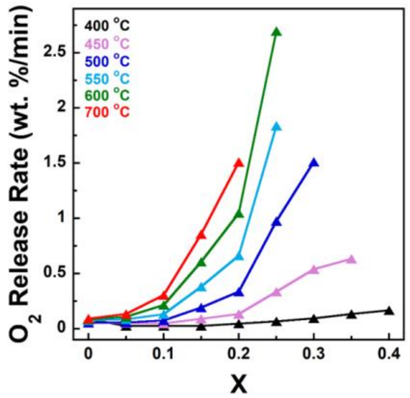
- Design, synthesize, and characterize a metal oxide carrier
- Tuneable Desorption Temperature
    - Ideal operating temperature below 700 °C
    - Tuneability for adaptation into multiple system designs
- Rapid Kinetics
    - Rate should exceed 0.2 wt%/min for complete desorption in less than 10 minutes
- Oxygen Capacity
    - Capacity should exceed 2 wt% oxygen
- Stability
    - The material needs to be cyclable with little to no attrition

Tuneable



Cyclability



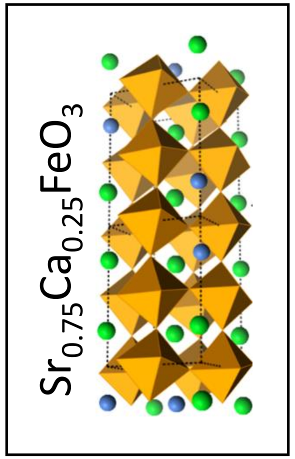


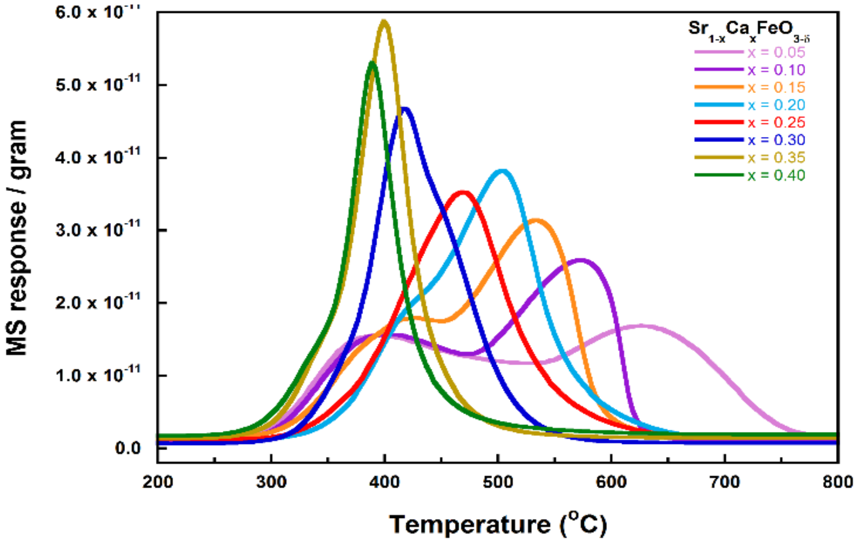
Rapid Kinetics

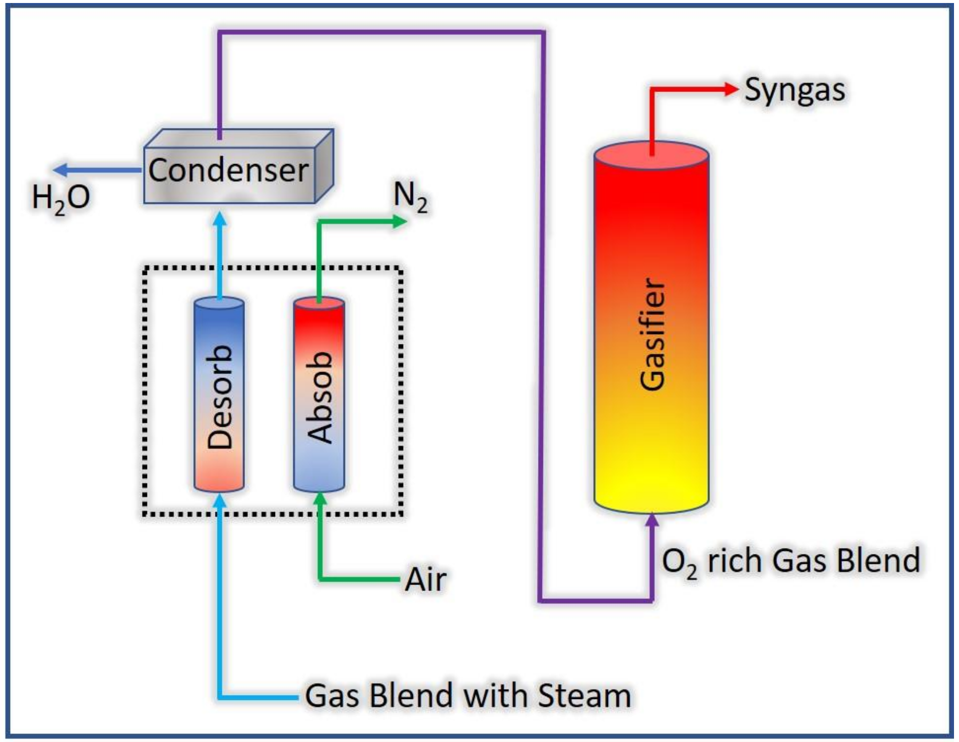
Research Objective

Reactor Design

Project Goal:
To develop a computational model that captures the oxygen storage/release potential of NETL's material, $Sr_{0.75}Ca_{0.25}FeO_3$; to leverage simulation to design a pilot-scale fixed bed, perovskite sorbent oxygen separation unit.





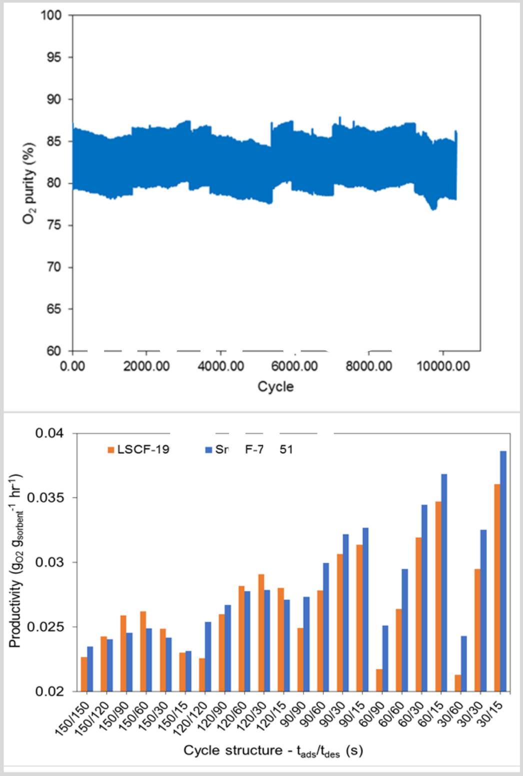


$$Sr_{0.75}Ca_{0.25}FeO_3 \xleftrightarrow{\delta(T,P_{O_2})} Sr_{0.75}Ca_{0.25}FeO_{3-\delta} + \frac{\delta}{2}O_2$$

Project Approach

Accomplishments-to-Date

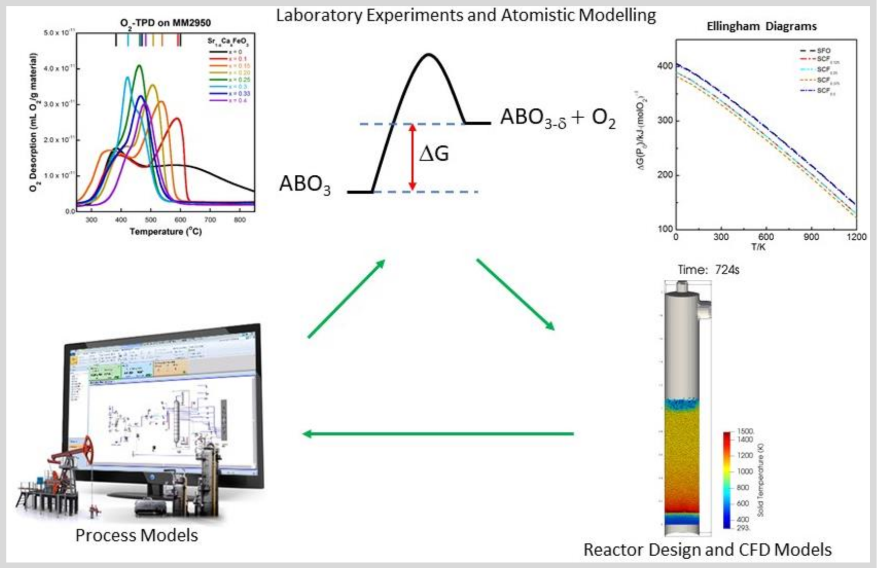
- NETL has demonstrated the ability to control capacity, desorption temperature, and rate through compositional changes in the carrier material
- NETL designed a carrier that meets capacity and rate objectives
  - Carrier demonstrated greater than 2 wt% oxygen capacity
  - NETL carrier achieved rates in excess of 2.0 wt%/min much greater than the desired 0.2 wt%/min
- NETL carrier demonstrated stability over more than 10,000 cycles with no loss in activity or attrition
- NETL designed carrier demonstrated 15% better performance than baseline with a 20% reduction in cost of materials
- Ellingham Diagrams for the perovskite carrier have been calculated and experimentally validated
- Preliminary reactor design using NETL’s MFiX software has initiated



Project Approach

Overall Approach

- NETL uses a multi-disciplinary approach to develop oxygen carrier materials which is enabled by the wide variety of internal capabilities
- NETL has extensive experience in the development of oxide materials including perovskites, delafossites, pyrochlores, and ferrites which is leveraged to design, synthesize, and characterize carrier materials
- Atomistic modelling is used to understand material properties and identify promising candidate materials by creating Ellingham Diagrams
- NETL's MFiX software is used to design and model an oxygen production reactor based on the carrier materials that demonstrate the best performance
- A techno-economic assessment is performed on the MFiX developed design which provides a comparison to currently employed technologies and potentially identifies new carrier needs



Current Research

Overview

- Materials Design, Synthesis, and Characterization

- Reactor Design

- Techno-economic Assessment

Current Research

Overview

- Materials Design, Synthesis, and Characterization
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- Techno-economic Assessment

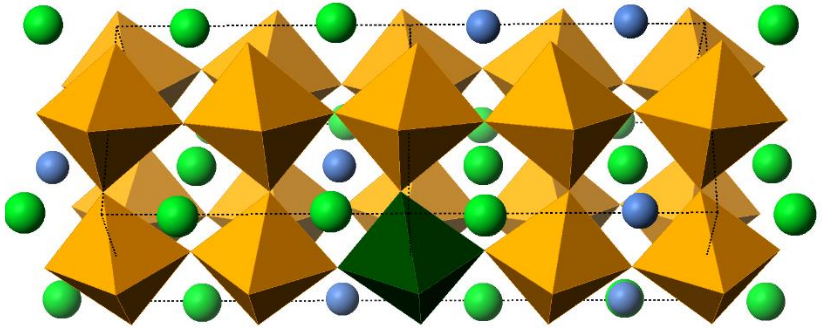
Rapid, Reversible Oxygen Carriers

$Sr_{1-x}Ca_xFeO_3$-based systems for low temperature activity

B-site substitution

May improve kinetics depending on B-site dopant's identity

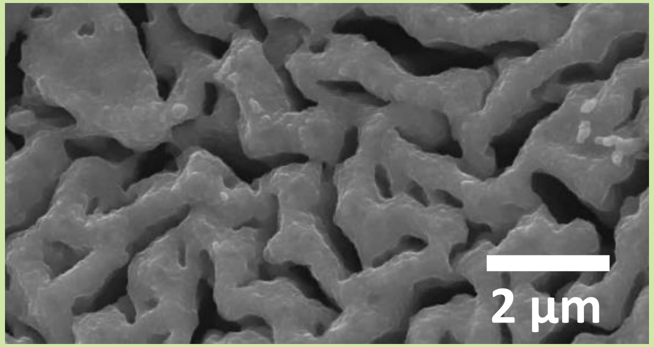
- Cobalt – best dopant to drive oxygen release towards lower temperatures
- Nickel – strong replacement in cobalt-free systems, smaller kinetic effect



Mesopore Introduction

Increased porosity and surface area as synthesis temperature lowered

- Higher surface area – faster kinetics, lower overall storage capacity



Metal (oxide) decoration

Combination of metal B-site substitution/surface decoration on mesoporous materials

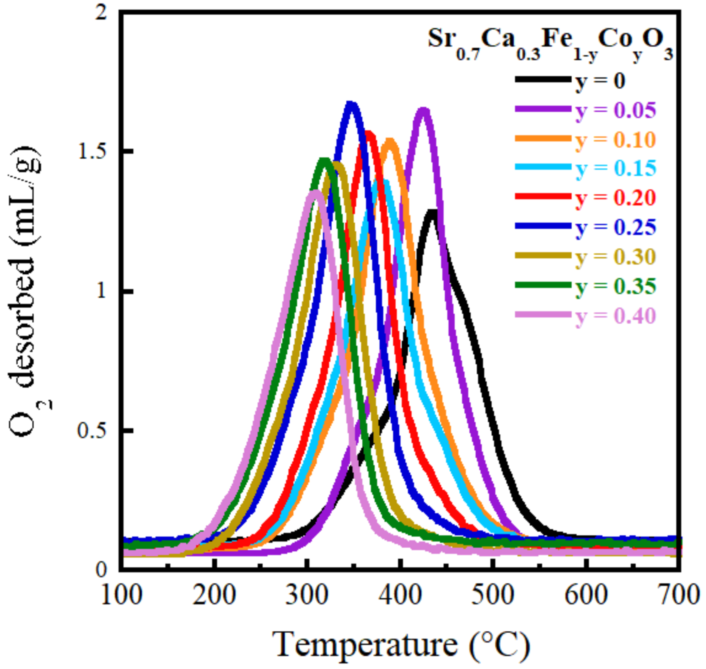
- Stackable improvements to $Sr_{1-x}Ca_xFeO_3$ materials
- Many potential decorations still under study

B-site Substitution in $Sr_{1-x}Ca_xFeO_3$

Cobalt Substitution

Thermodynamic Improvements

- Additional calcium/cobalt both lower O_2 desorption temperature
- Combinable

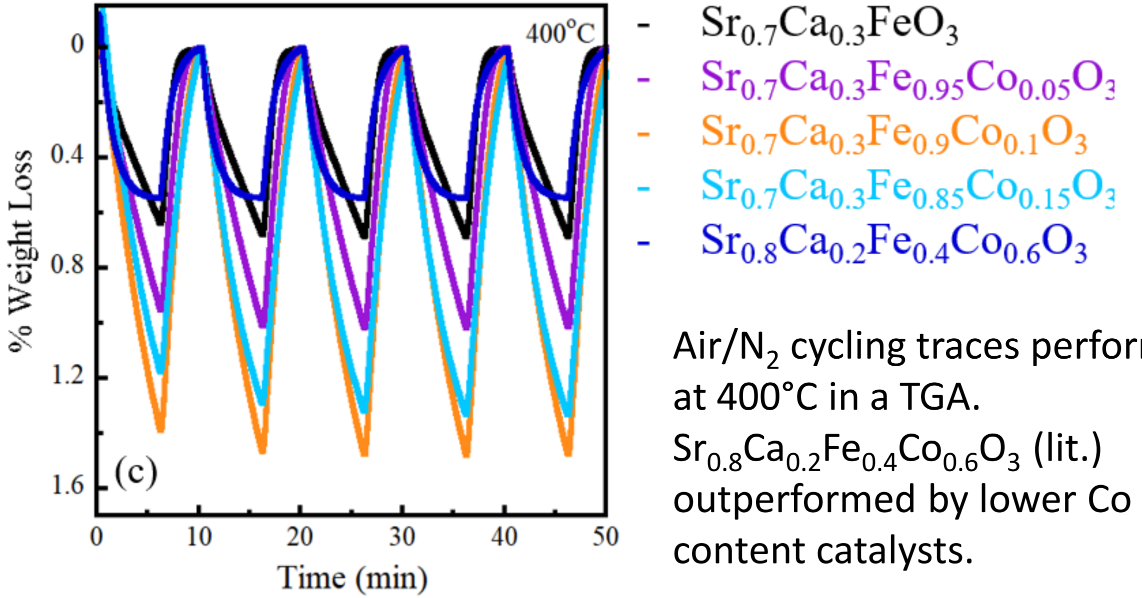


O_2-TPD of $Sr_{0.7}Ca_{0.3}Fe_{1-x}Co_xO_3$ with variable Co contents. Additional cobalt systematically lowers the desorption temperatures.

ChemSusChem **2021**, *14*, 1893.

Kinetic Improvements

- Oxygen release faster, uptake slower as Co content increases
- Top Co-rich catalysts outperformed by lower Co contents in $Sr_{0.7}Ca_{0.3}Fe_{1-x}Co_xO_3$ (x = 0.05-0.15) at most temperatures.



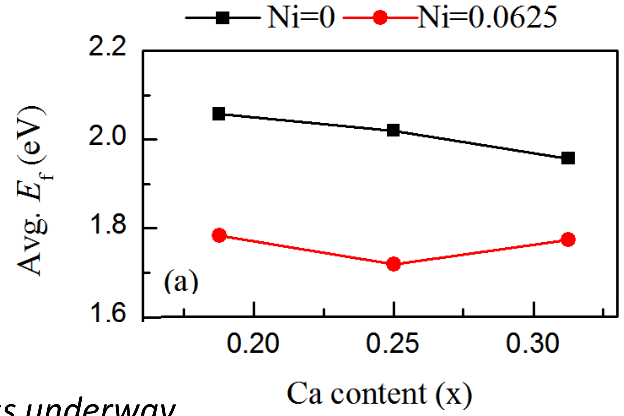
Air/N_2 cycling traces performed at 400°C in a TGA. $Sr_{0.8}Ca_{0.2}Fe_{0.4}Co_{0.6}O_3$ (lit.) outperformed by lower Co content catalysts.

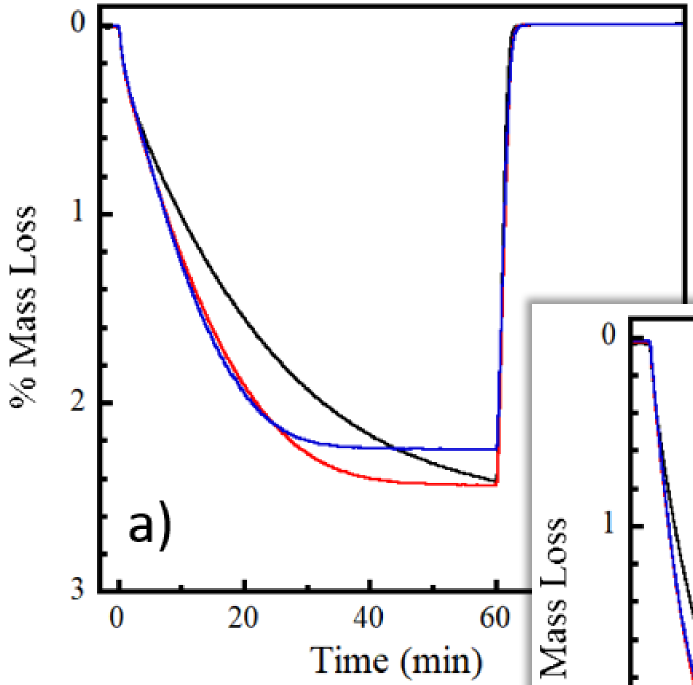
B-site Substitution in $Sr_{1-x}Ca_xFeO_3$

Nickel Substitution

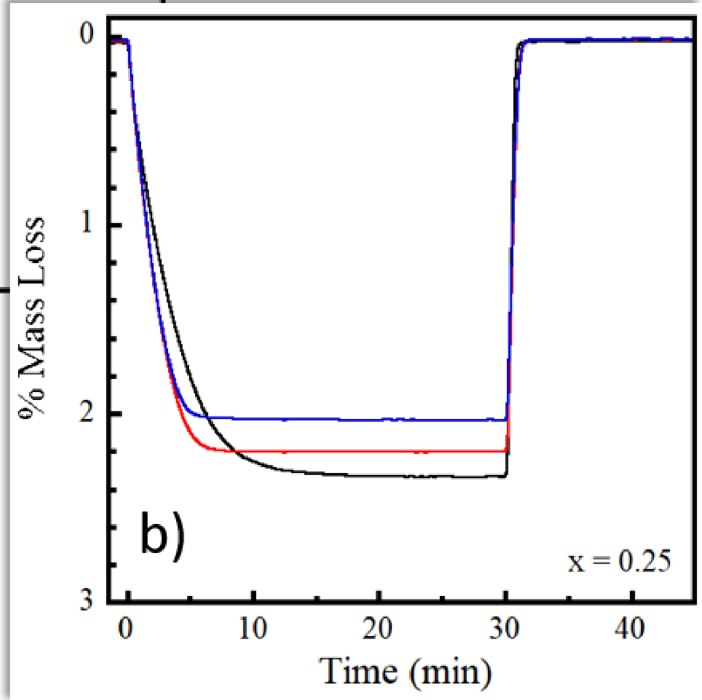
- **Nickel inclusion improves kinetic response**
  - Similar storage capacities (> 2.2 wt.%)
  - <u>≥50%</u> more O_2 over set time y = 0.06 vs. undoped
- **DFT suggests thermodynamic benefits of Ni**
  - Limited maximum Ni doping ~ 0.10 without NiO impurities

Average vacancy formation energies E_f, for $Sr_{1-x}Ca_xFe_{1-y}Ni_yO_3$ from DFT.





Black – $Sr_{0.75}Ca_{0.25}FeO_3$
Red – $Sr_{0.75}Ca_{0.25}Fe_{0.94}Ni_{0.06}O_3$
Blue – $Sr_{0.75}Ca_{0.25}Fe_{0.88}Ni_{0.12}O_3$



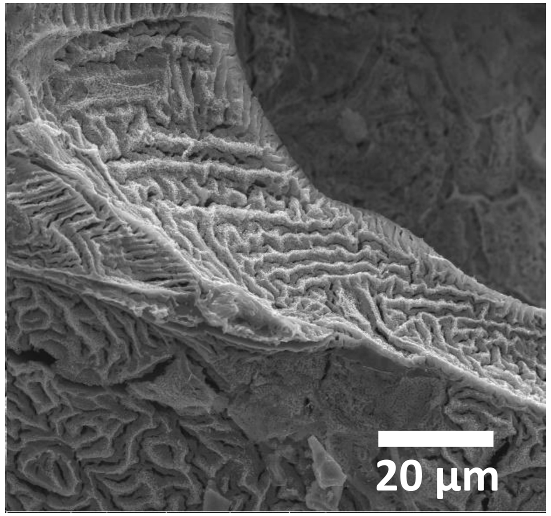
Air/N_2 cycling traces performed on $Sr_{0.75}Ca_{0.25}Fe_{1-y}Ni_yO_3$ at a) 400°C and b) 450°C using TGA.

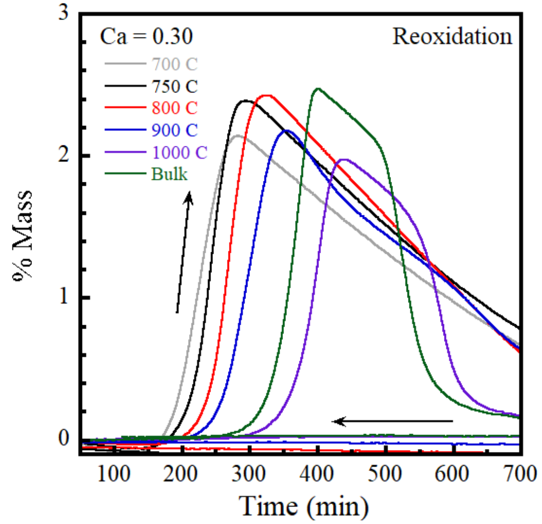
Manuscript in preparation; Patent process underway

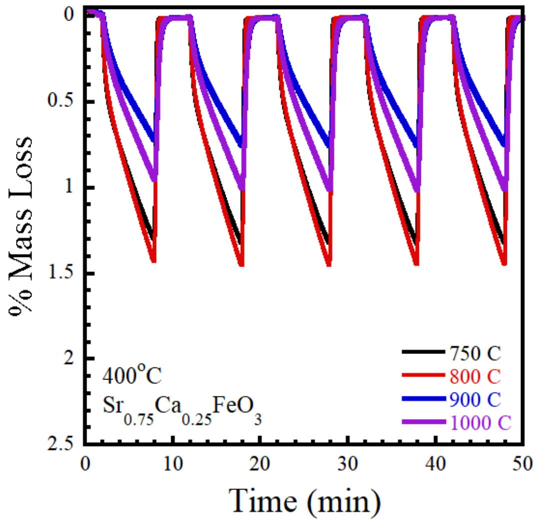
Mesoporous $Sr_{1-x}Ca_xFeO_3$

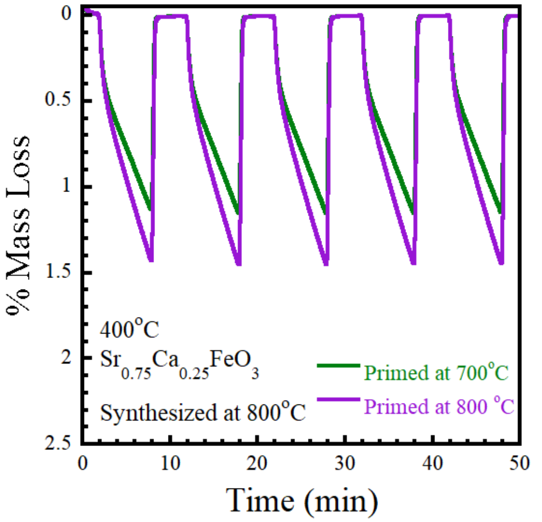
Preliminary Research

- **Surface area increases as synthesis temperature decreases**
  - 700°C – 8.85 m^2/g
  - 750°C – 5.43 m^2/g
  - 800°C – 3.35 m^2/g
  - 900°C – 0.71 m^2/g
  - 1000°C – 0.12 m^2/g
- **Thermodynamic benefits**
  - Highest surface area, lower oxygen uptake/release temperatures
- **Kinetic benefits observed at lower temperatures**
  - >100% more oxygen in 10 min at 400 °C for $Sr_{0.75}Ca_{0.25}FeO_3$ synthesized at 800 °C
    - 750 °C not fastest due to lower priming temperature (750 °C in N_2)
    - Removal of residual carbon necessary before cycling (800°C in N_2 performs best)







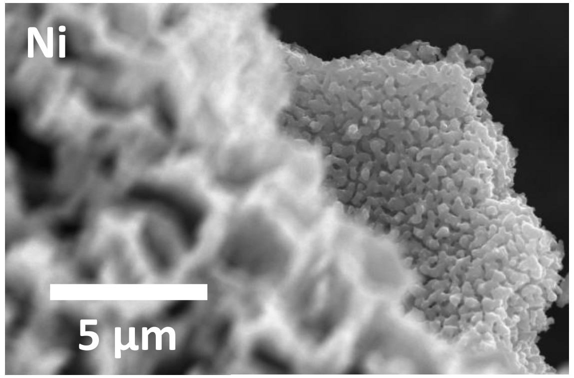


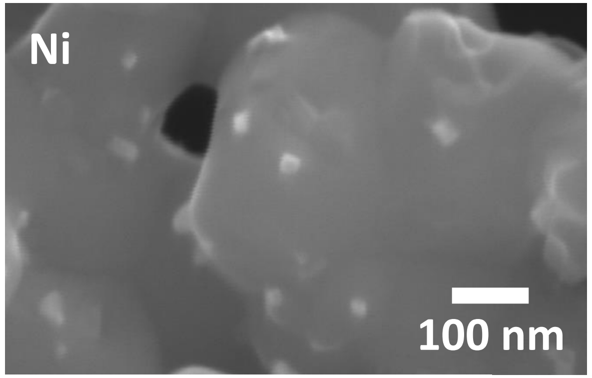
Manuscript in preparation; Patent process underway

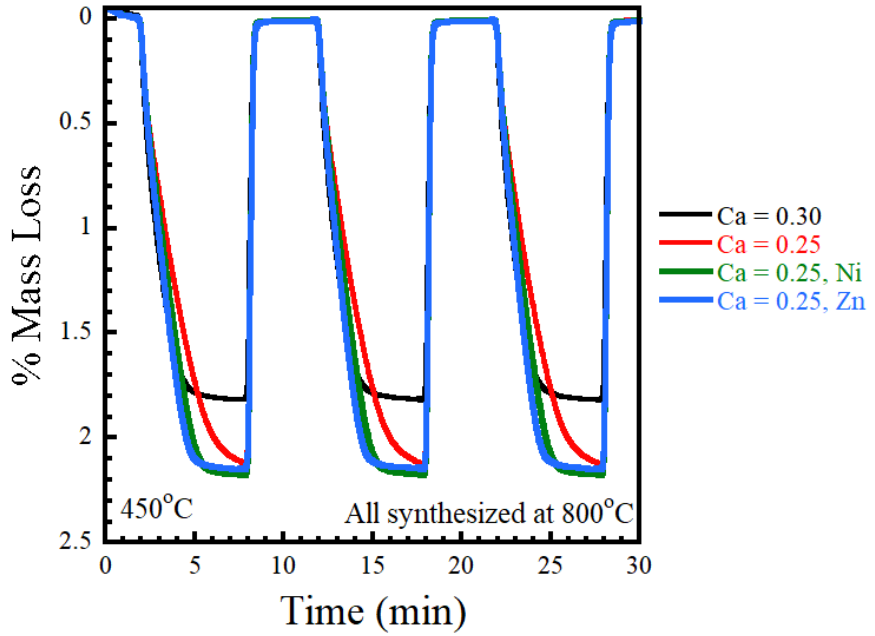
Mesoporous $Sr_{1-x}Ca_xFeO_3$

Improving Mesoporous Materials

- **$Sr_{0.75}Ca_{0.25}FeM_{0.03}O_3$ composition created in one-pot synthesis**
  - Ni – surface decoration
  - Zn – structural substitution
- **Oxygen release faster in select $Sr_{1-x}Ca_xFeO_3$ systems**
  - Up to 2-3x faster (example to right)
  - Further experimentation still needed to confirm benefits
  - Effects only previously observed w/ Pt or Pd in literature
- **To be investigated**
  - Cu, Mn, Mo, Co, etc.
  - One-pot synthesis vs. post-synthesis modification







Manuscript in preparation

Current Research

Overview

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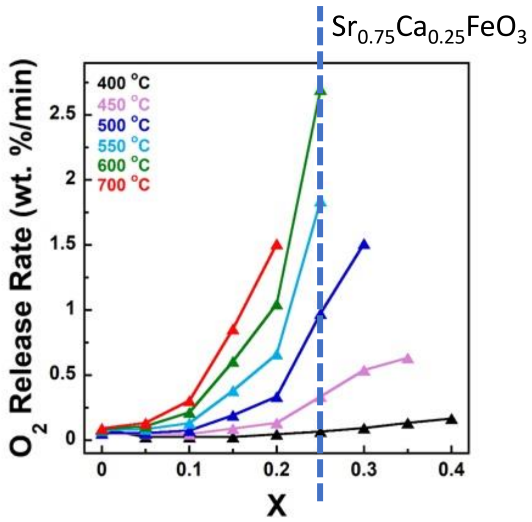
- Reactor Design
- Techno-economic Assessment

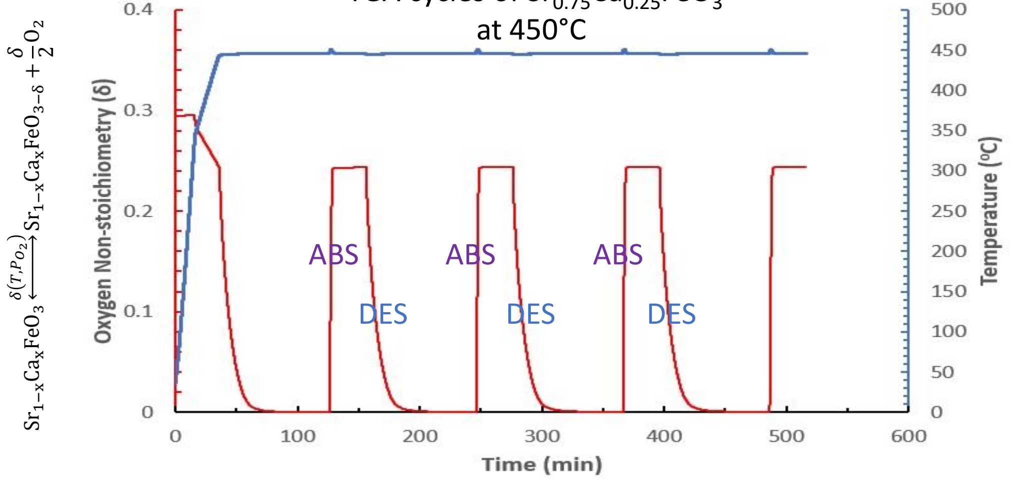
Oxygen Reactor Development

LABORATORY



Experimentation shows that $Sr_{0.75}Ca_{0.25}FeO_3$ has excellent and repeatable O_2 storage and release capability in the temperature range 400 – 600°C

TGA cycles of $Sr_{0.75}Ca_{0.25}FeO_3$ at 450°C



SIMULATION

Kinetic rates are derived to capture absorption and desorption swings across temperature and concentrations of O_2.

He Model [1]

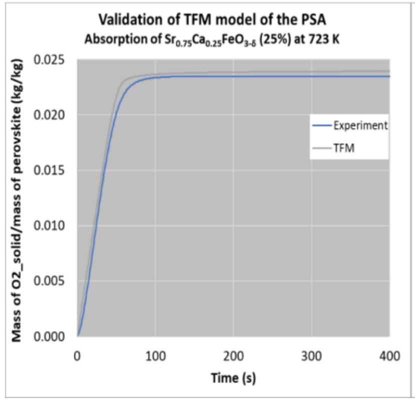
$$q_{abs/des,O_2} = \frac{F_{sweep}}{m} x_{in} t = k_1 t$$

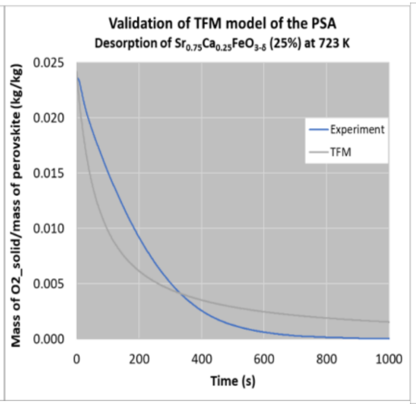
$$\frac{t}{q_{abs/des,O_2}} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}} t$$

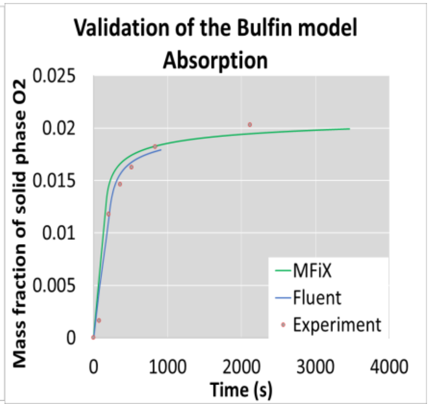
Bulfin Model [2]

$$\frac{dm}{dt} = k_0\, e^{\frac{-E_a}{RT}} (1-X)^m |m_{inf} - m_0| c_{O_2}^n$$

Rates are validated against experimental measure



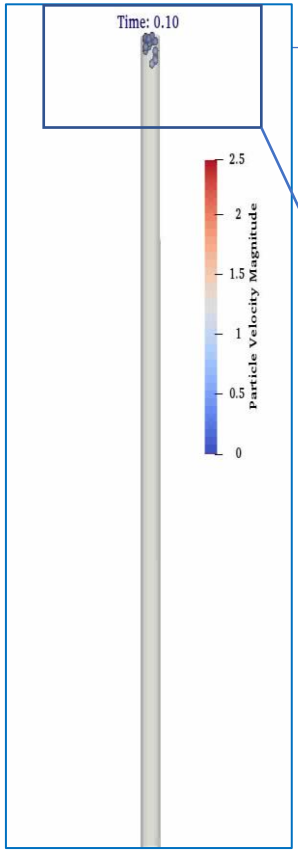




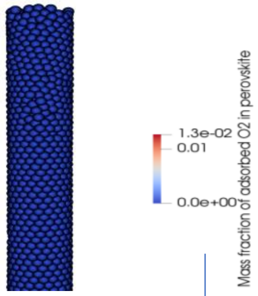
[1] He, Y., Zhu, X., Li, Q., Yang, W., "Perovskite Oxide Absorbents for Oxygen Separation," AIChE Journal, Dec 2009, Vol 55, No 12, pp.3125-3133.
[2] Bulfin, B., Vieten, J., et.al, "Isothermal relaxation kinetics for the reduction and oxidation of SrFeO3 based perovskites," Phys. Chem. Chem.Phys., 2020, Vol 22, pp. 2466-2474.

Oxygen Reactor Development

Changing Simulation Scale



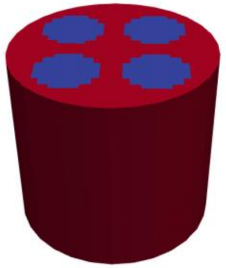
Granular filling used to create an initial condition for perovskite modeling in a 0.021m diameter tube (matching Thermosolv unit).



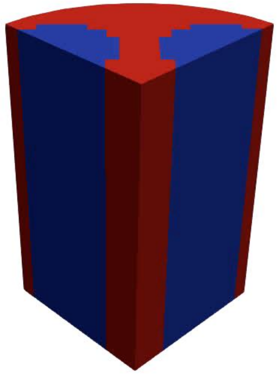
He reaction kinetics (absorption) applied in DEM model at very small scale (300 grams).

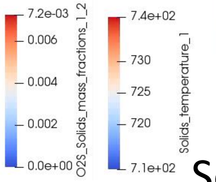
He and Bulfin kinetics applied in MFiX-TFM model at mid-scale (~1 ton) including heat transfer between bed and tubes.

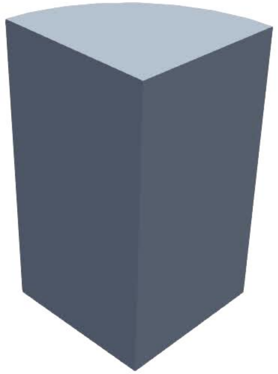
full view



cut view

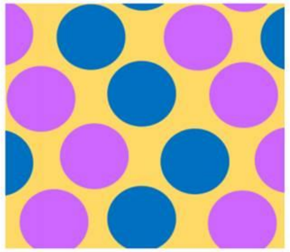






O_2 solids content

Solids Temperature

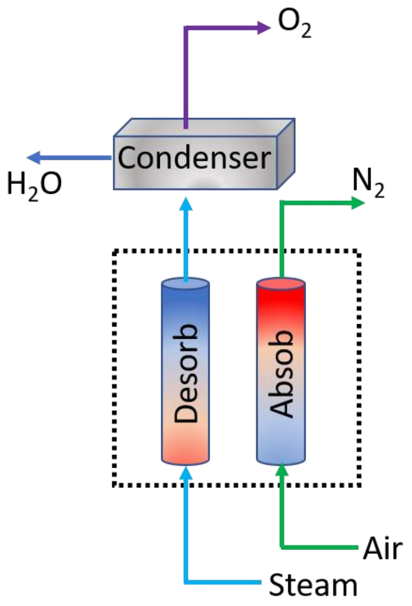


Non-NETL experimentalists suggest concurrent ABS/DES in a circulating solar salt to encourage isothermal operation. [3]

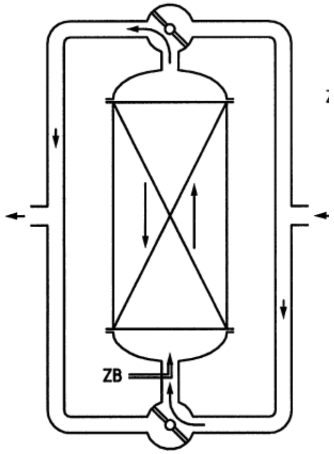
[3] Doris, C., Lu, E., et.al. "High-purity oxygen production using mixed ionic-electronic conducting sorbents," University of Pennsylvania Senior Design Report, 2016, Paper 78.

Future Work

Lab: Understand the effect of steam on desorption mechanism through specialized TGA experimentation

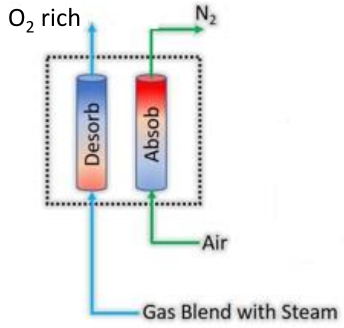


Single tube with periodic flow reversal?



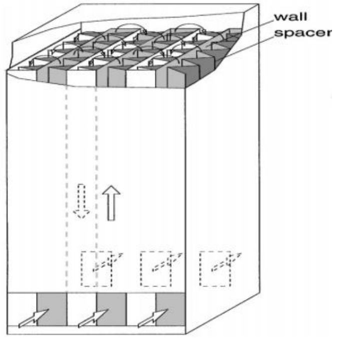
Traditional HT PSA[5]?

Simulation: Answer the question: what design works best in the outlined box?

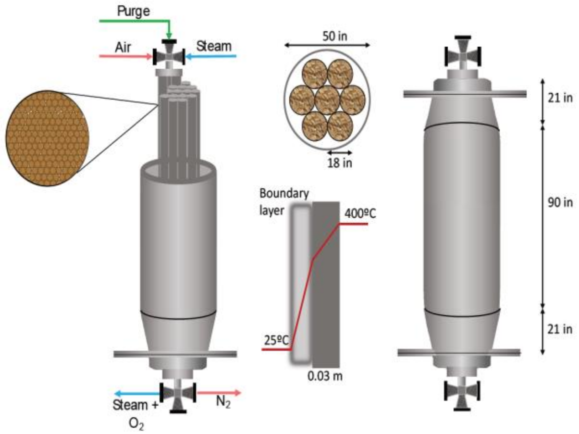


- Maximize O_2 production
- Minimize pressure drop
- Quantify efficiency
- Suggest operating conditions for pilot scale device

Folded plates?



Bundle tubes to advantage heat transfer [4]?



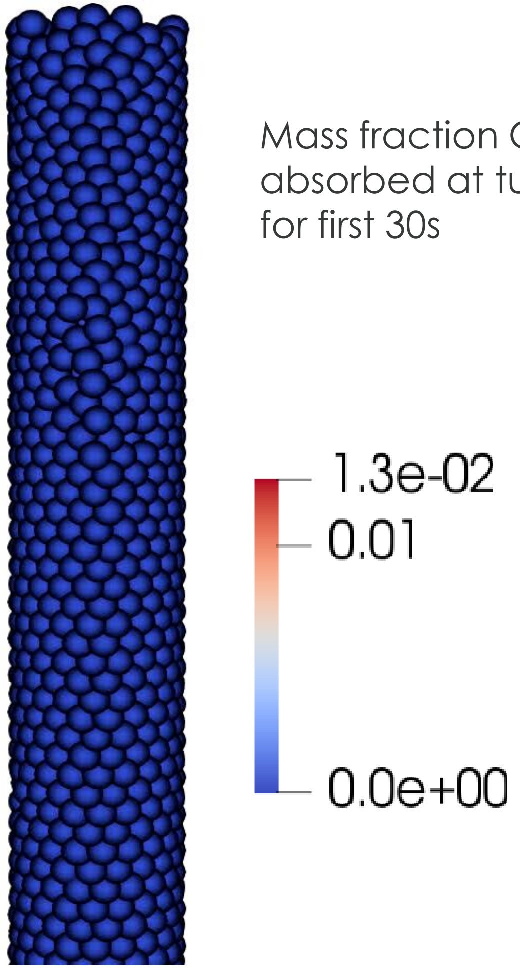
[4] Li, F., "Radicaly Engineering Modular Air Separation System with Tailored Oxygen Sorbent," Report to NETL, 9/20/2020.

[5] Tokyo Power High Temperature PSA Unit, Sales Literature, 2016.

Future Work

Research Plan through Completion

- Carrier development will continue
  - Investigation of surface modification
  - Investigation of preparation methods that result in mesoporous samples
- Continue model design and validation
  - The completed model will provide information on oxygen purity, ideal operating temperature, and adsorption/desorption cycling times
- Perform a Techno-Economic Assessment of the Oxygen Production Reactor Design ending with a Go/No Go decision
  - A Go decision will lead to the pursuit of an industrial partner to continue reactor development
  - A No Go decision will potentially lead to a need for additional experimental or modelling research



Mass fraction O_2 absorbed at tube inlet for first 30s

Engagements & Technology Maturation

Engagement Activities

Partners

THERMOSOLV LLC

NEXCERIS where energy meets environment

Argonne NATIONAL LABORATORY

CARNEGIE MELLON UNIVERSITY PITTSBURGH PENNSYLVANIA 1900

Outreach & Engagement Activities

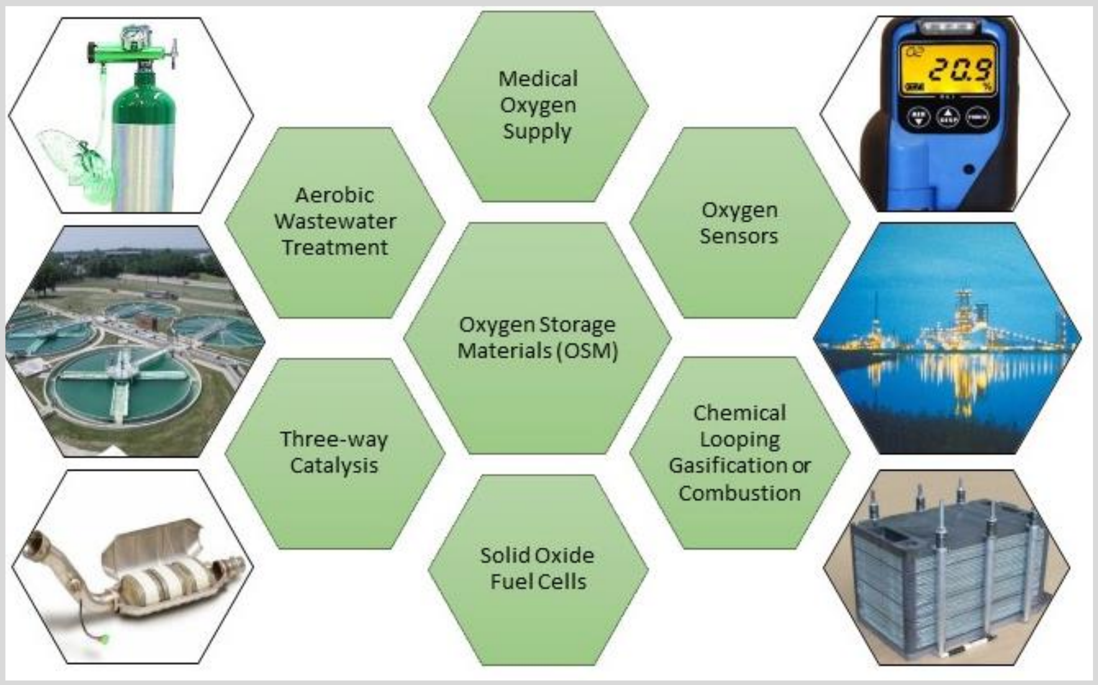
- ThermoSolv – ThermoSolv and NETL have an NDA in place to facilitate discussions of carrier composition and perform complementary carrier testing
- Nexceris – Nexceris and NETL have been working together to scale up synthesis of carrier material for additional testing
- Argonne National Laboratory – NETL has been awarded time on the 17BM beamline for structural characterization
- CMU – CMU and NETL have worked together to develop a material development tool that combines Numerical Modelling and Density Functional Theory to predict ideal carrier composition

Acknowledgments

- Acknowledgment
  - This material is based upon work supported by the Department of Energy research under the Gasification Research Program. The research was executed through the NETL Research and Innovation Center's Advanced Reaction Systems field work proposal. Research performed by Leidos Research Support Team staff was conducted under the RSS contract 89243318CFE000003.

Conclusion

- Metal oxide carrier materials provide an alternative approach to produce oxygen for a wide variety of applications
- In the Gasification program pure oxygen provided by a reactor based on a metal oxide carrier could enable systems capable of producing power, chemicals, or mixtures of the two from a wide variety of feedstocks and with neutral to net-negative CO_2 emissions



?Questions?