Radically Engineered Modular Air Separation System with Tailored Oxygen Sorbents

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Project Partners:

Thermosolv LLC and West Virginia University

04/09/2019

Project Objectives

- Develop radically engineered modular air separation system (REM-ASU) for small-scale coal gasifiers (1-5 MW)
- Achieve air separation under a cyclic redox scheme using advanced mixed-oxide based oxygen sorbents (OS)
- **Reduce 30% energy consumption** for air separation using REM-ASU compared to state-of-the-art cryogenic air separation process
- Demonstrate the robustness and performance of OS and REM-ASU

Current Status of Project

- Developed LSCF-CF mixed oxides with 2.2-4.2% O_2 capacity, **2-4 times of benchmark** $CaMn_{0.95}Fe_{0.05}O_3$ oxygen sorbent
- Demonstrated high activity of LSCF-CF OS with redox rate of 1.35-2.04 mg O_2/mg sorbent-min, **4-6 times of benchmark** $CaMn_{0.95}Fe_{0.05}O_3$ OS
- Designed low temperature $SrFeO_3$ based OS for chemical looping air separation at 450-600^oC
- Demonstrated steam resistant $SrFeO_3$ based OS for 1000 cycles of air separation with <3% degradation

Publication and conference presentations

- Jian Dou, Emily Krzystowczyk, Amit Mishra, Xingbo Liu, and Fanxing Li*. *Perovskite promoted mixed cobalt-iron oxides for enhanced chemical looping air separation.* **ACS Sustainable Chem. Eng.** 2018, 6, 15528-15540.
- Amit Mishra, Tianyang Li, Fanxing Li*, and Erik Santiso*. *Oxygen Vacancy Creation Energy in Mn-Containing Perovskites: An Effective Indicator for Chemical Looping with Oxygen Uncoupling*. **Chemistry of Materials**, 2018, 31, 689-698.
- Jian Dou, Emily Krzystowczyk, Xijun Wang, Amit Mishra, Thomas Robbins, and Fanxing Li*. *Perovskite Promoted Mixed Co-Fe Oxides for Enhanced Chemical Looping Air Separation*. **ACS National Conference,** Orlando, 2019

Air Separation

Linde Air Separation Plant
(www.linde-engineering.com)

- N_2 and O_2 are the top two widely used industrial gases, > $4.3 billion annual revenue
- Oxygen is widely used for production of steel (~48%), chemicals (~19%), and glass
- Emerging Oxy-fuel combustion for efficient CO_2 capture

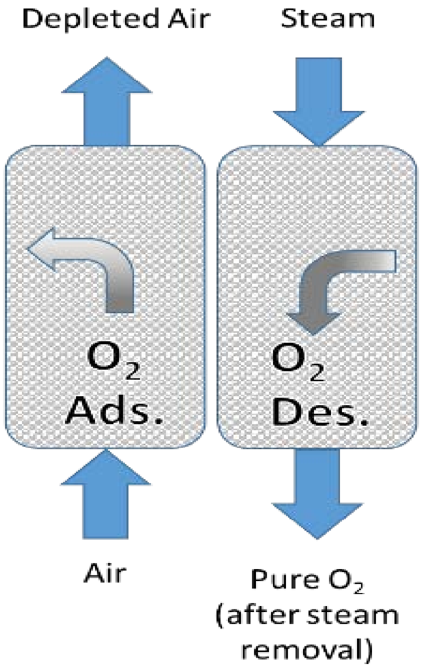
Cryogenic vs Chemical Looping Air Separation

	Cryogenic	Chemical looping
Status	mature	developing
Economic range (sTPD)	>20	Undetermined
Energy consumption (kW/kg O_2)	0.21	0.05-0.07
Thermodynamic efficiency (%)	25%	>75%
Oxygen purity (%)	99+	99+
By product capability	Excellent	Poor

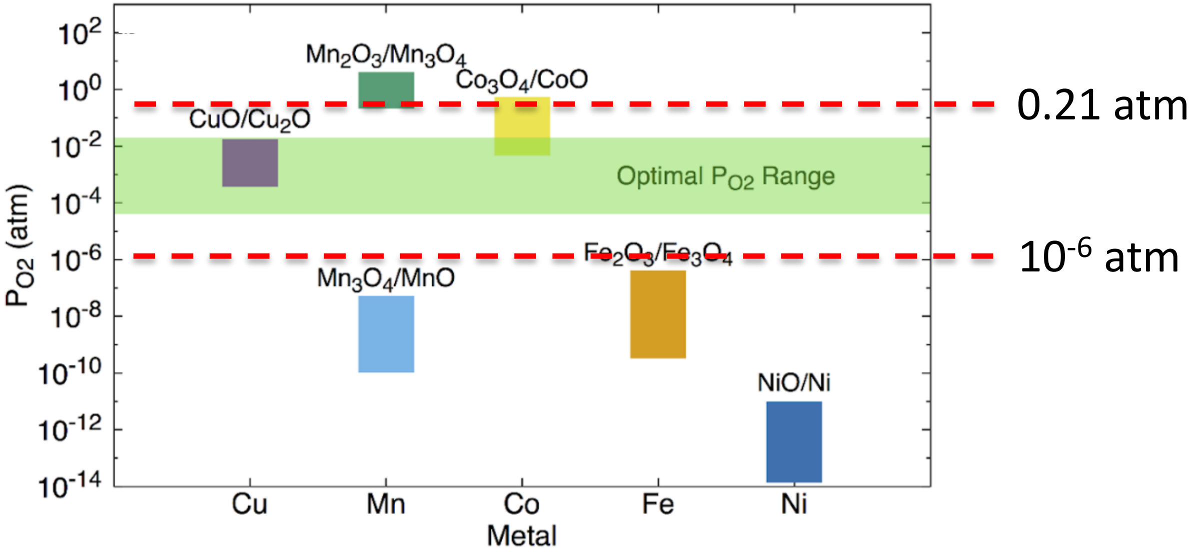
Chemical looping air separation is energy efficient

Oxygen Sorbent Development: Challenges and Opportunities

P_{O2}: <0.1 atm P_{O2}: <10^{-6} atm

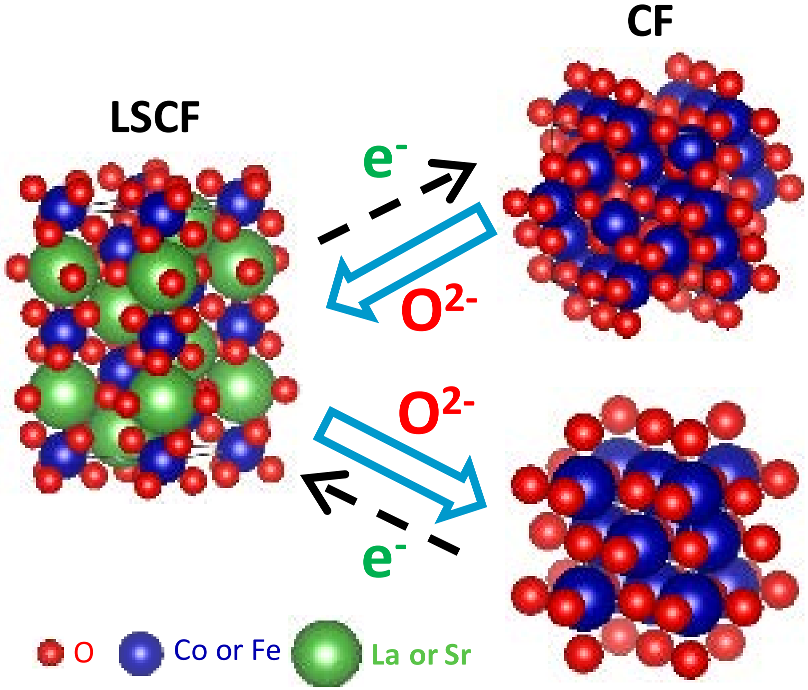


P_{O2}: 0.21 atm P_{O2}: 0.01-0.05 atm



Mixed oxides are necessary in order to match P_{O2} of oxygen carriers with air separation conditions

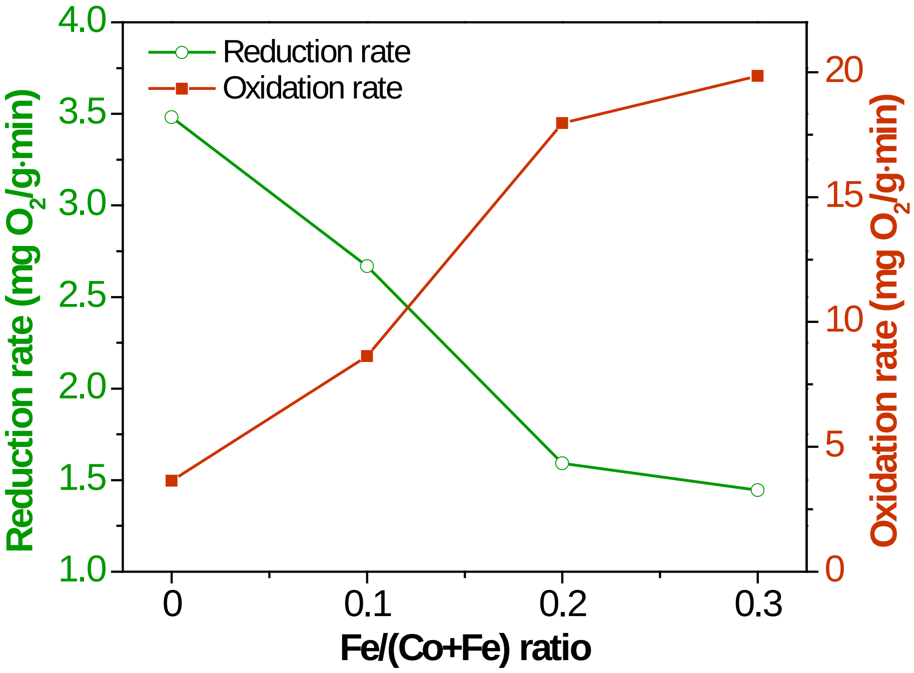
$(La_xSr_{1-x})Co_yFe_{1-y}O_3$ – CoFe (LSCF-CF) Composites

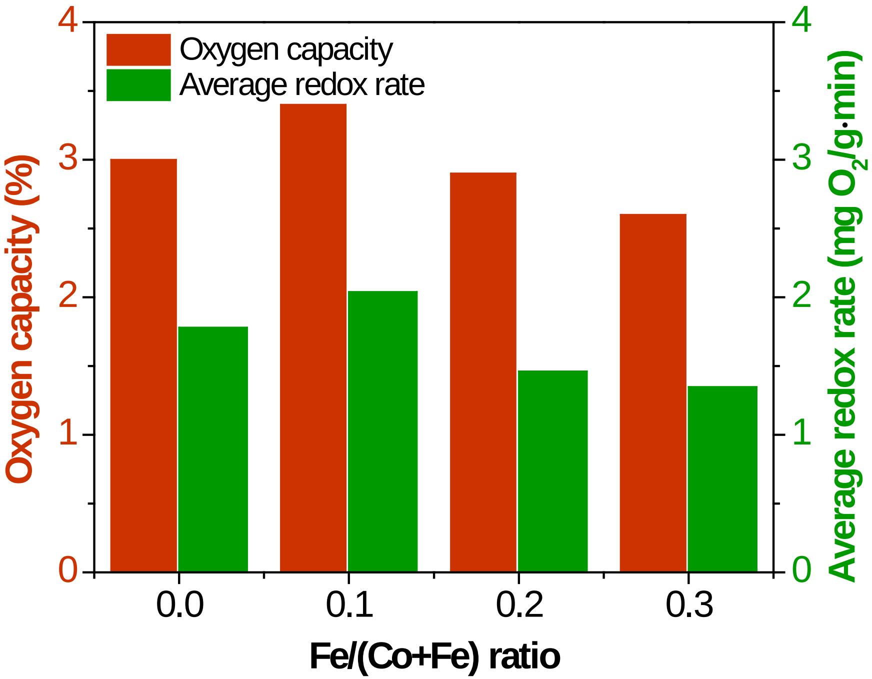


- Co-Fe mixed oxide to tune redox property
- LSCF to promote oxygen diffusion and reduce oxygen diffusion barrier

Dou et al., ACS Sustainable Chem. Eng. 2018, 6, 15528

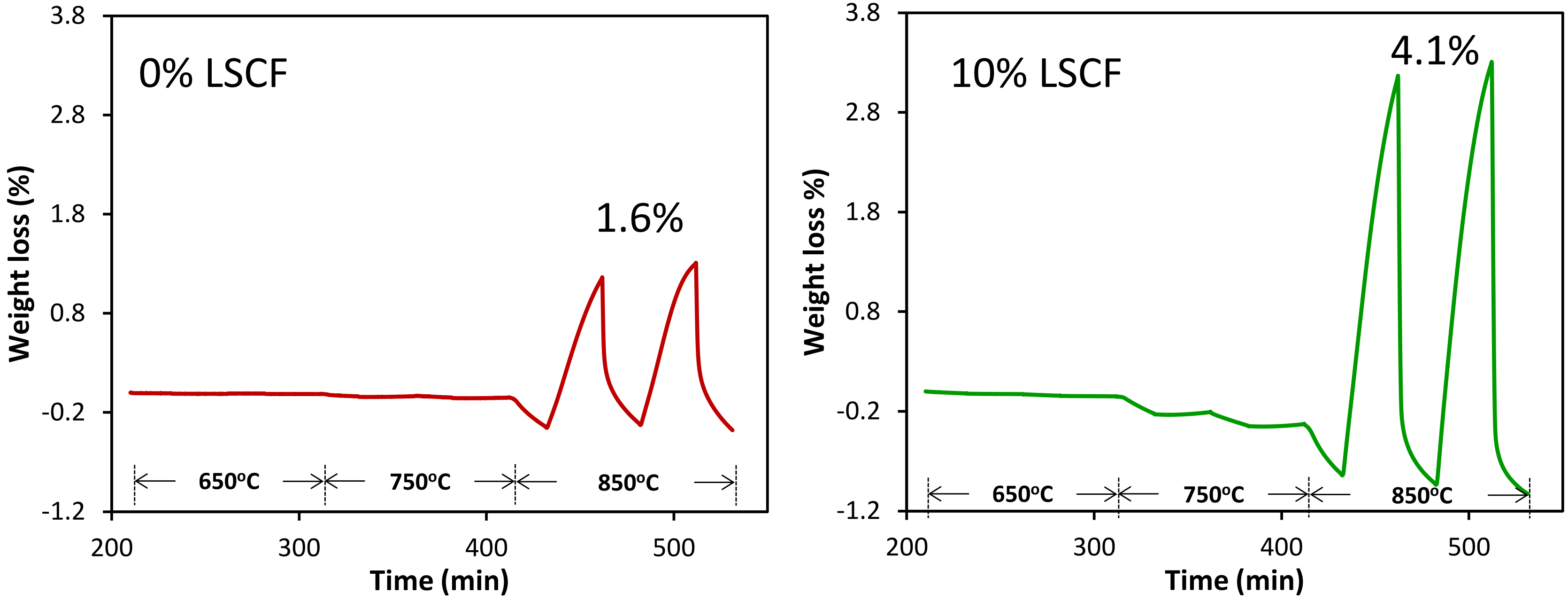
Fe enhances oxidation rate





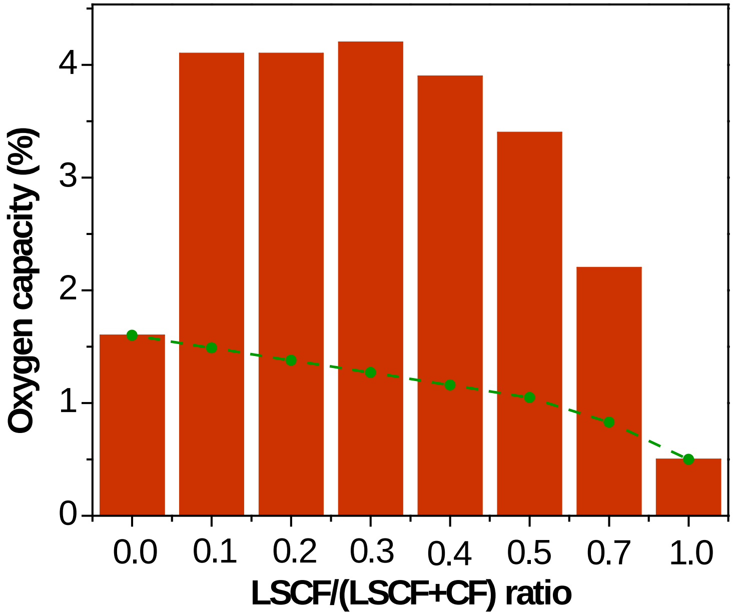
- Fe increases oxidation rate by 2-5 times
- Balanced oxidation and reduction rates maximize O_2 capacity (3.4%)

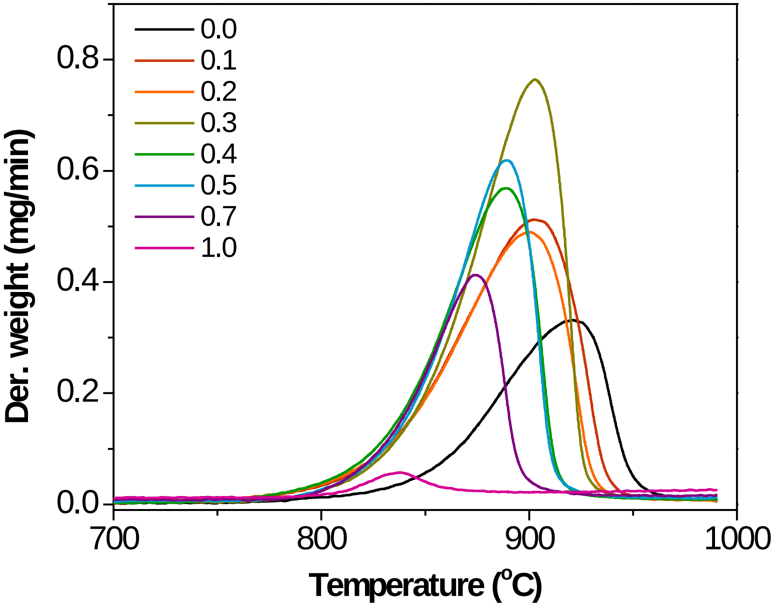
LSCF improves oxygen capacity



- Co:Fe=9:1, Ar-20%O_2, 650-850ºC
- Negligible oxygen capacity at 650-750 ºC
- LSCF increases oxygen capacity by 2.5 times

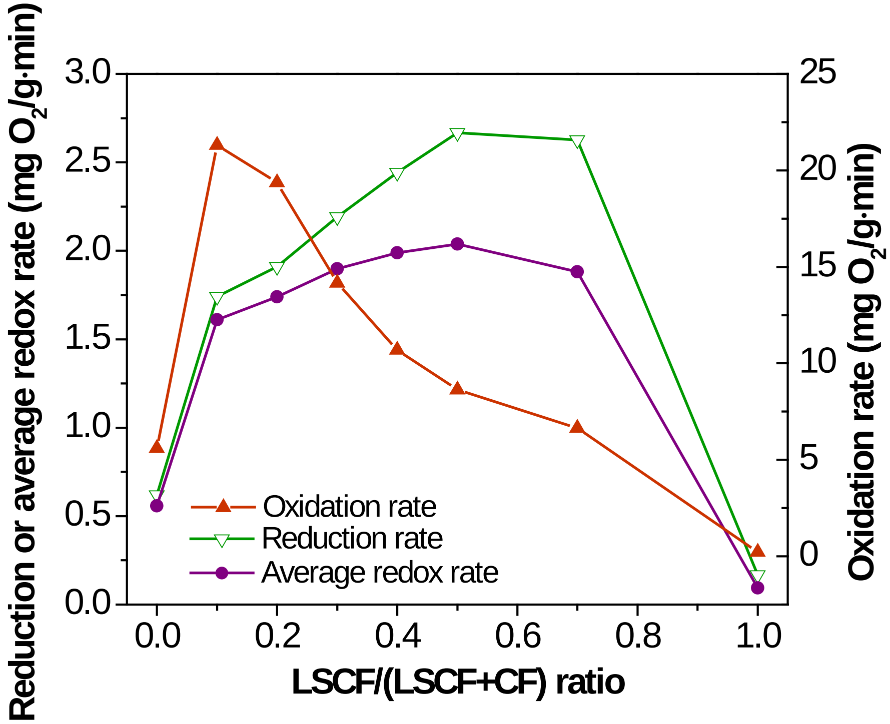
LSCF improves oxygen capacity





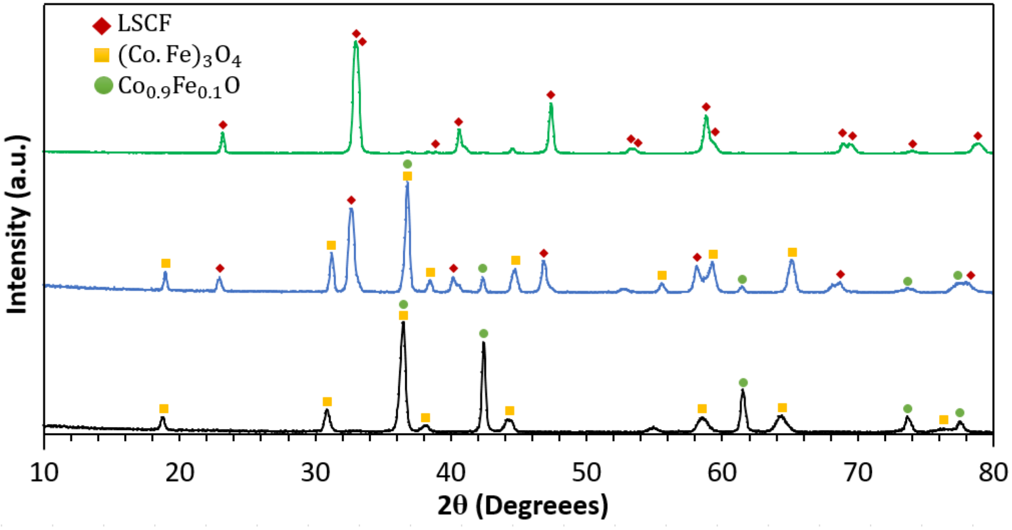
- LSCF increases O_2 capacity by 37-260%
- LSCF decreases reduction temperature by 18-46^{o}C

LSCF increases redox rates



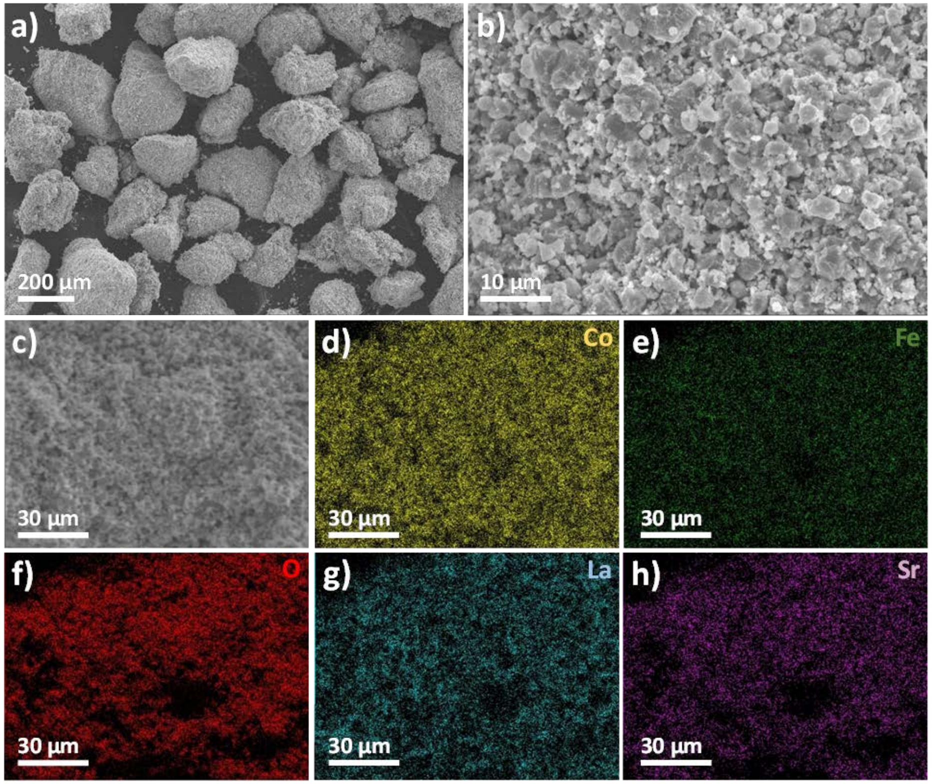
LSCF increases both oxidation and reduction rates by 4-5 times

Structure of LSCF-CF composites



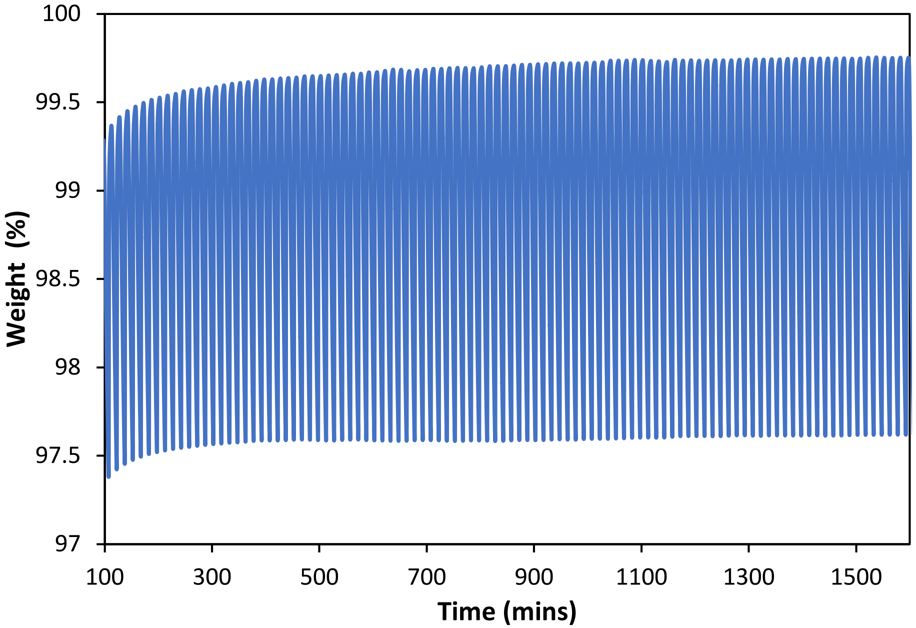
LSCF-CF consists of mixed phases from LSCF and CF

SEM/EDX of LSCF-CF



- Particles are composed of small grains with a size range of 2-3 µm
- Well mixing of LSCF and CF at sub-micrometer level

Stability of LSCF-CF (1:1)



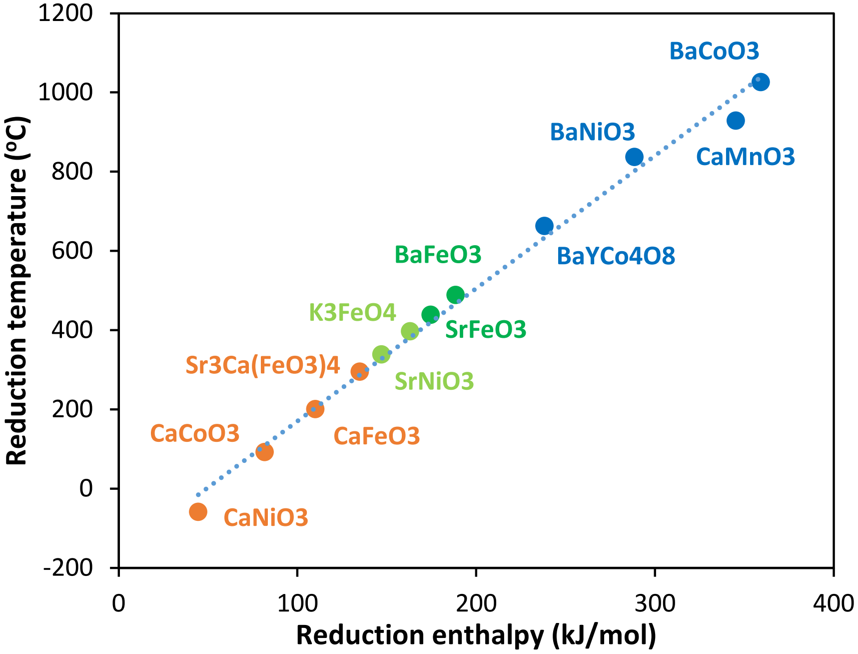
Oxygen capacity (%)

	1	2	3	4	5
1st 5 cycles	2.0	2.0	2.0	2.0	2.0
Last 5 cycles	2.1	2.1	2.1	2.1	2.1

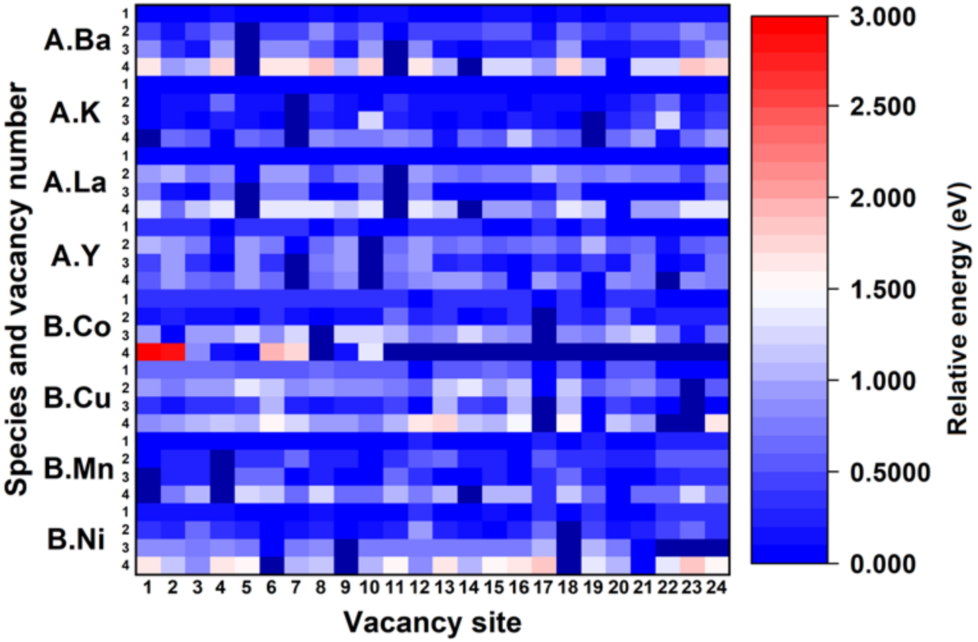
850°C, 100 cycles

LSCF enhances oxygen sorbent stability for extended redox cycling at 850°C for 100 cycles

Screening of low temperature oxygen sorbents



Calculated with data from Materials Project

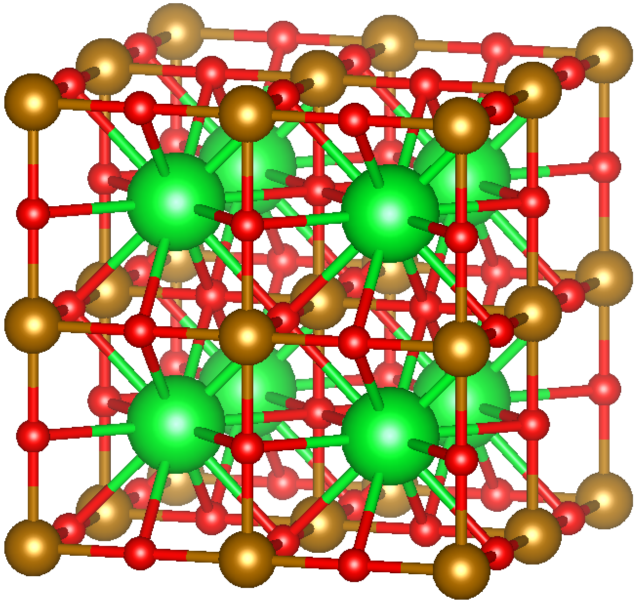


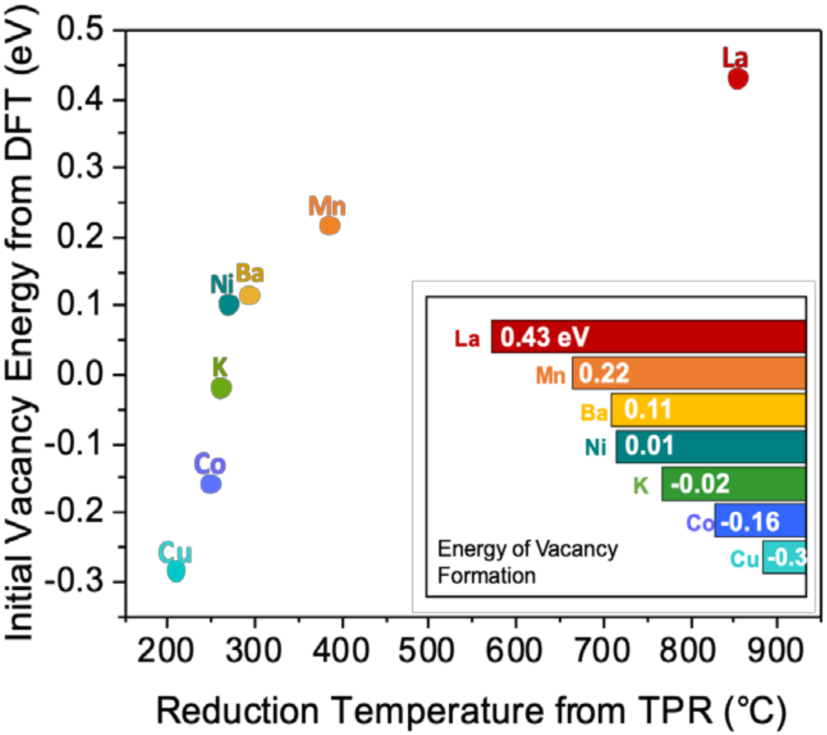
DFT results from NCSU

SrFeO$_3$ is identified as low temperature oxygen sorbents

Effect of A or B site doping on oxygen vacancy formation energy

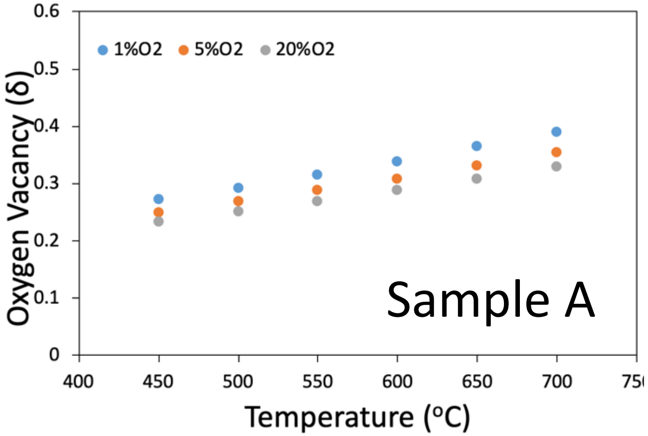
$Sr_8Fe_8O_{24}$

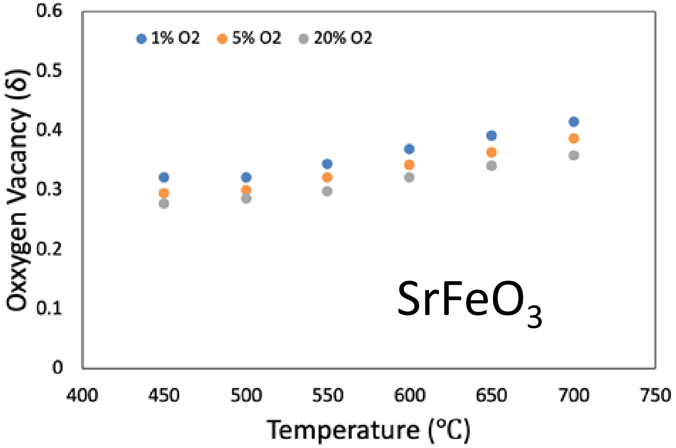




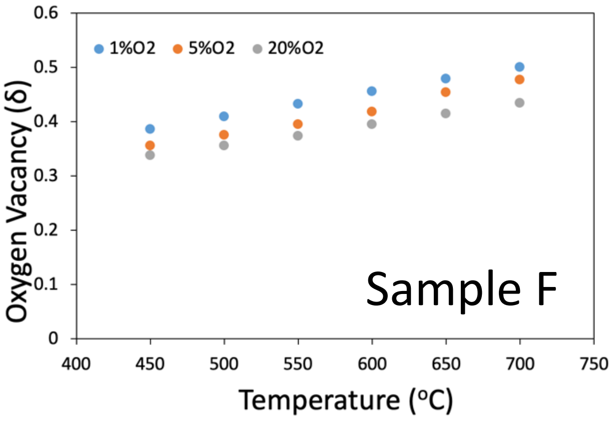
Doping at A or B sites can effectively lower oxygen vacancy formation energy

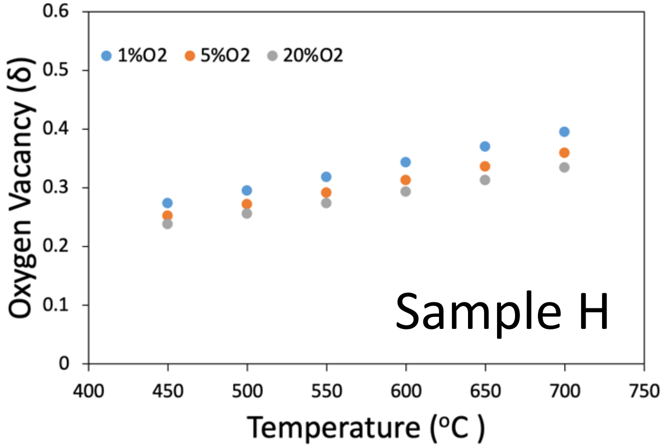
Effect of A site doping on $SrFeO_{3-\delta}$



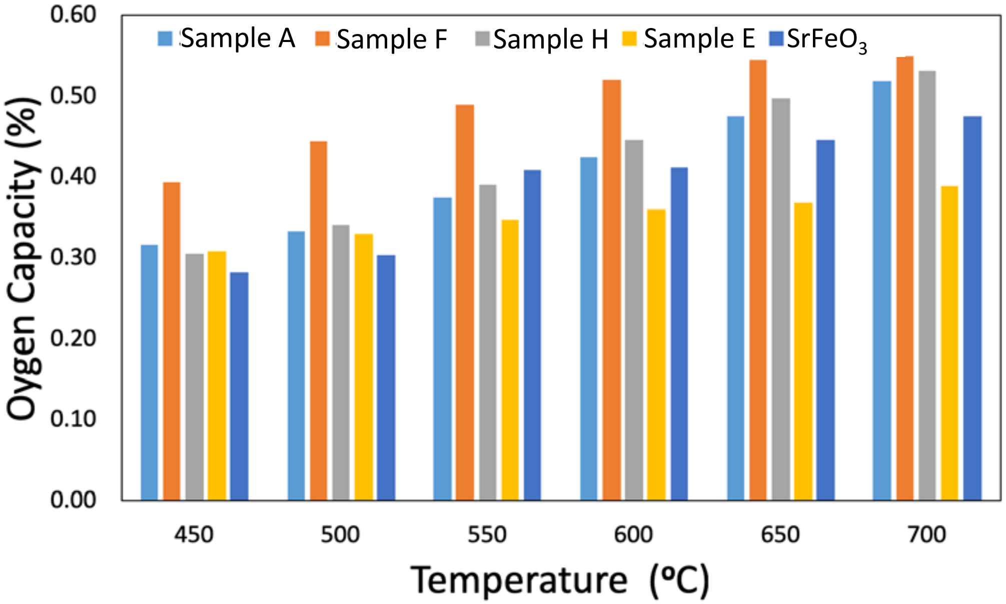


Sample F shows increased oxygen vacancy with doping

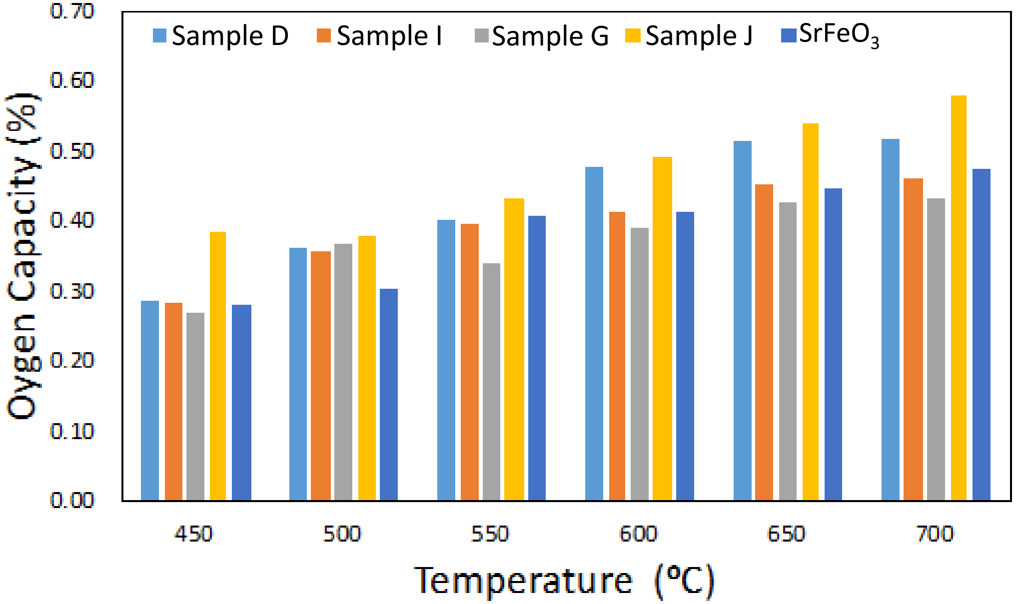




Effect of A/B site doping on O_2 capacity

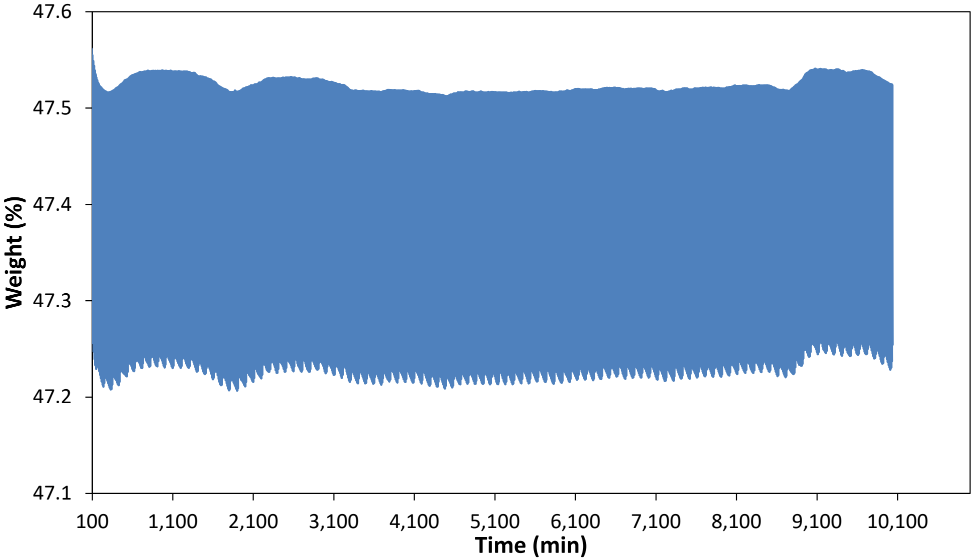


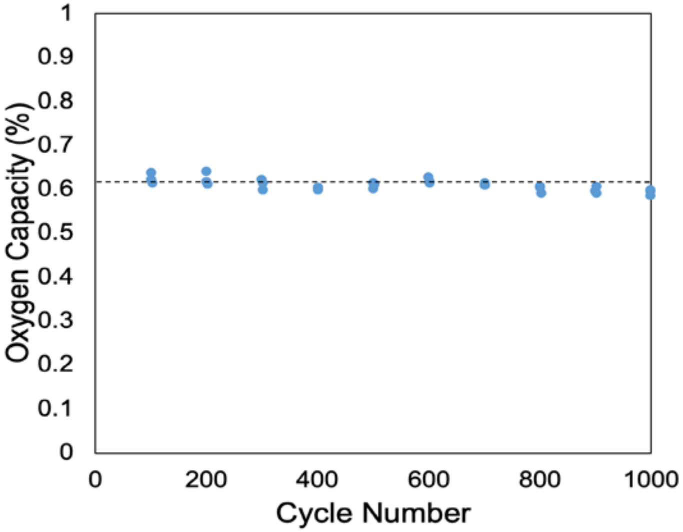
A-site doping indicates Sample F possesses superior oxygen capacity



B-site doping indicates Sample D and sample J possess superior oxygen capacity

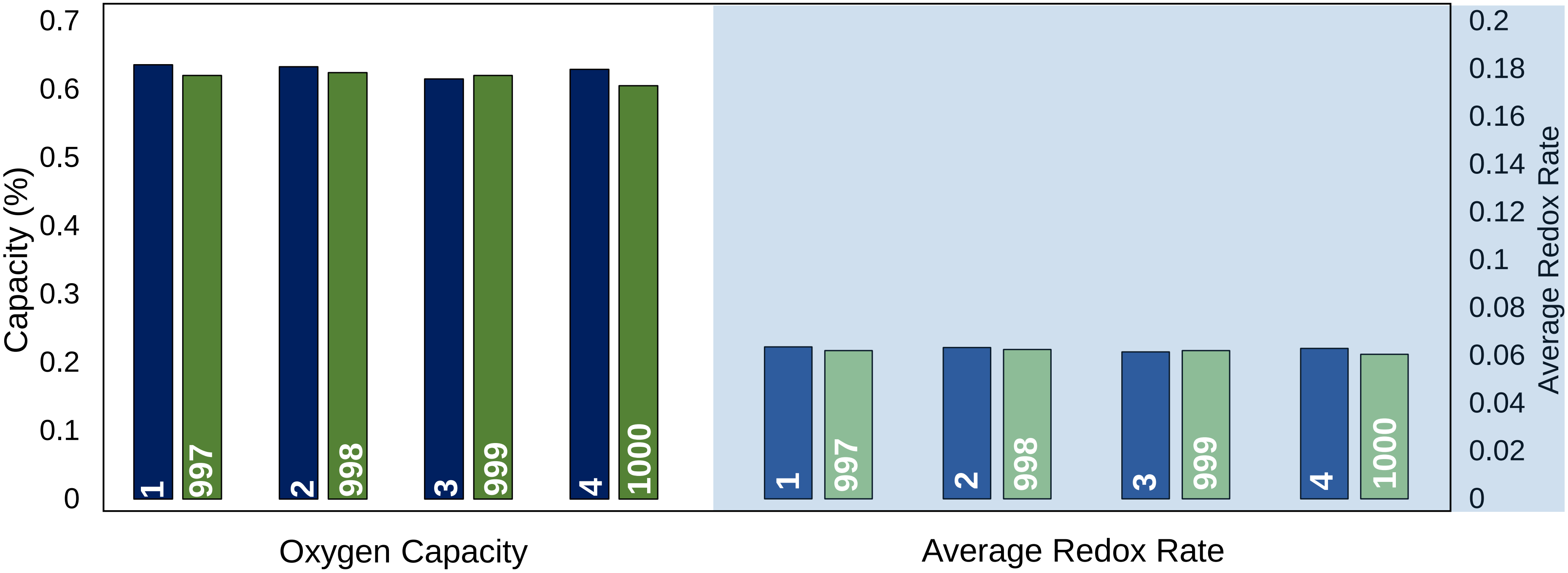
Stability of sample D





- Red: 2.5%H_2O/Ar, 6 min; Oxi: 2.5%H_2O/20%O_2/Ar, 4 min; 600°C
- Sample D is stable for 1000 redox cycles less than 3% degradation

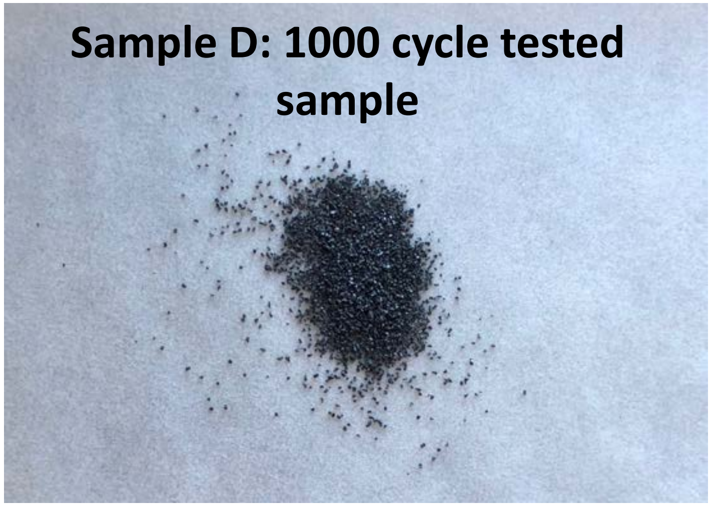
Stability of sample D

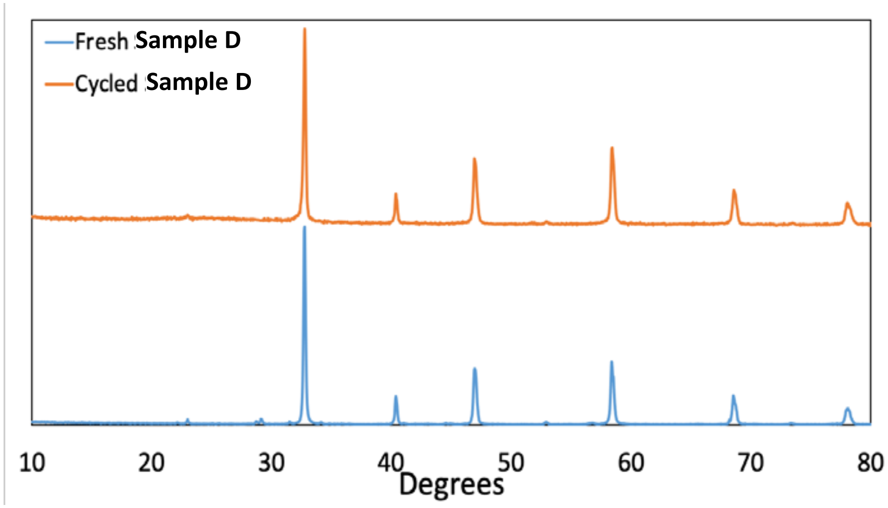


Less than 3% degradation of redox rate and oxygen capacity after 1000 cycles

Physical and Structural Properties


Sample D: Fresh sample

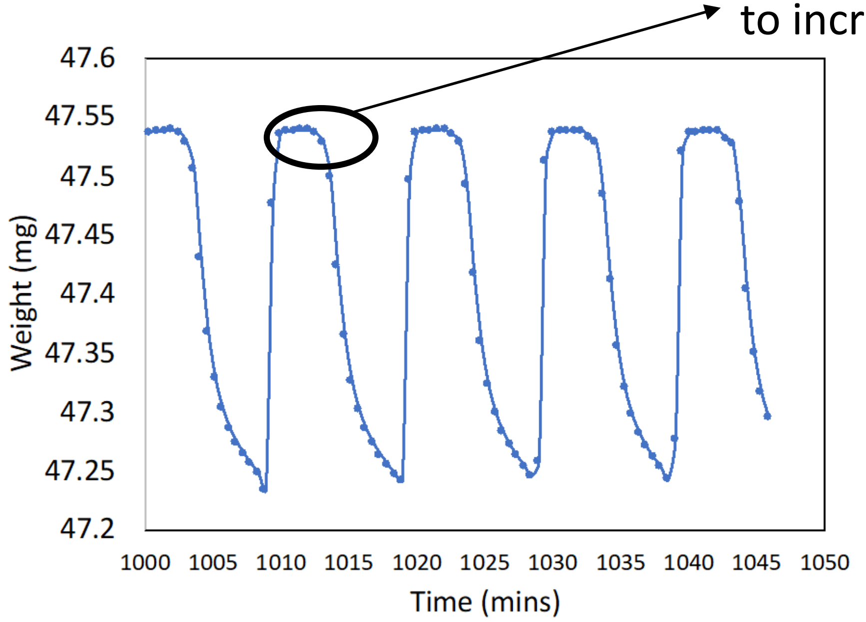

Sample D: 1000 cycle tested sample

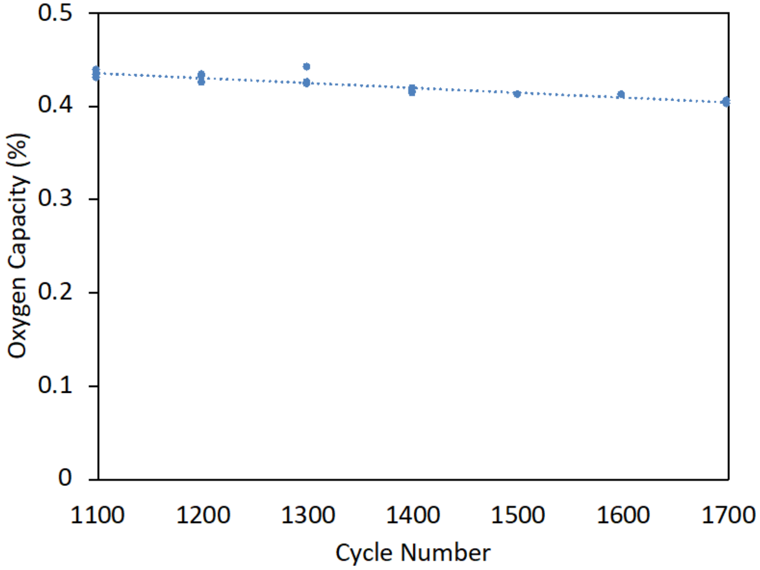


Structure of sample D remains stable after 1000 redox cycles

Cycled 1000-1700

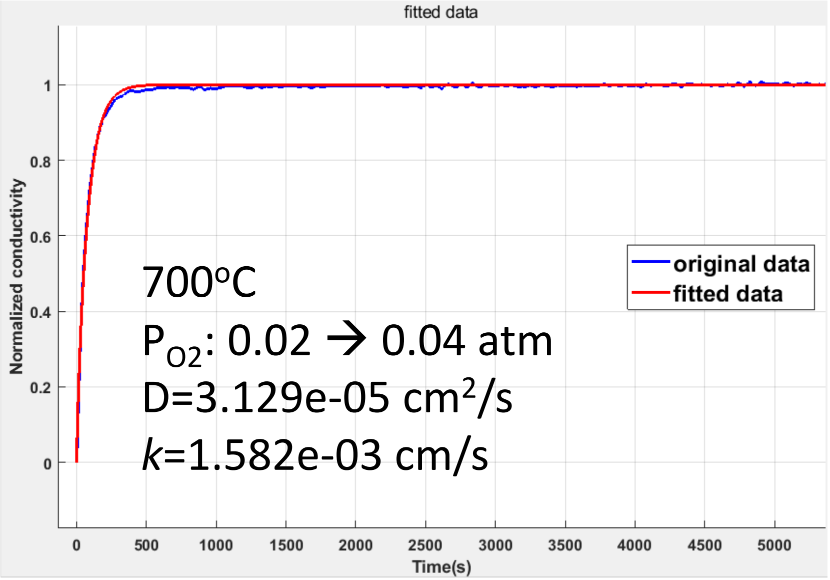
Redundant time for oxidation, so needed to reduce it to increase bed size factor





- Ran next 700 cycles
  - Reduced reduction and oxidation time to optimize cycles
- 5% decrease of oxygen capacity after 1700 cycles

Electrical Conductivity Relaxation (ECR) measurement of sample D

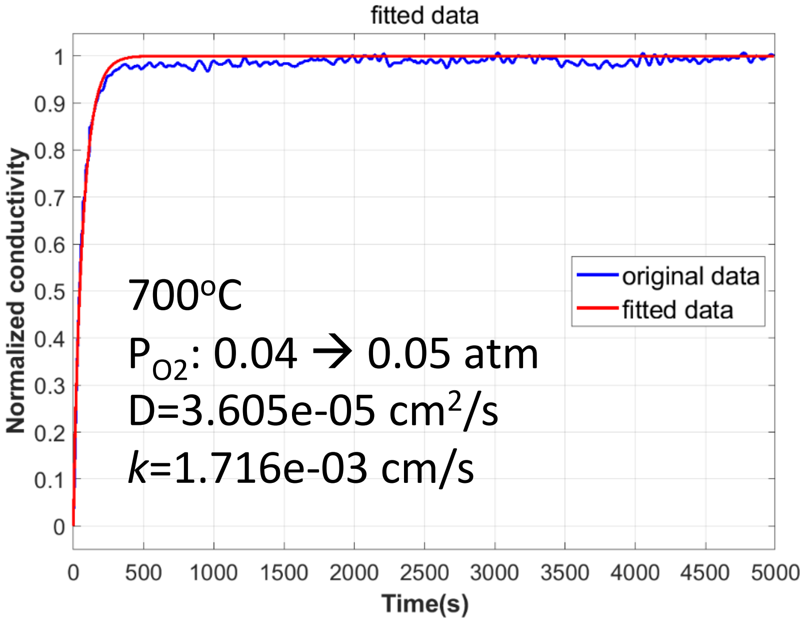


700°C

P_{O2}: 0.02 → 0.04 atm

D=3.129e-05 cm^2/s

k=1.582e-03 cm/s



700°C

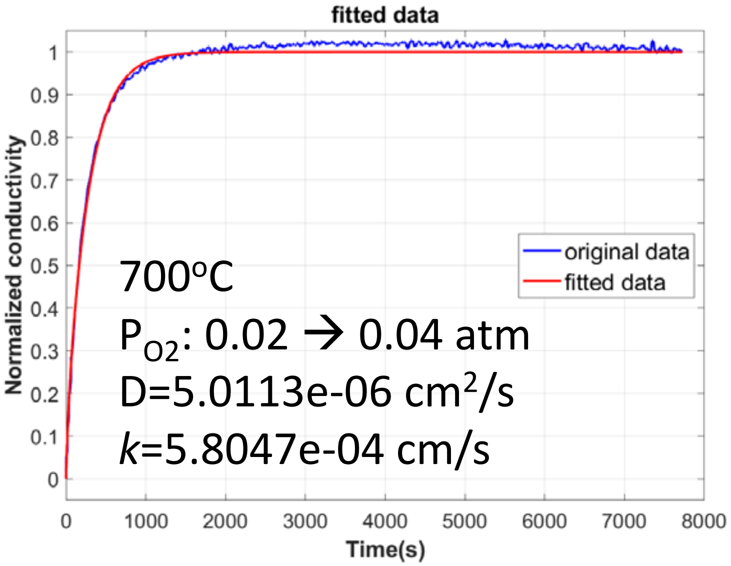
P_{O2}: 0.04 → 0.05 atm

D=3.605e-05 cm^2/s

k=1.716e-03 cm/s

- Characteristic thickness L_c = D/k = ~200 µm, within particle size range of 150-250 µm
- Both oxygen diffusion and surface oxygen exchange determines redox kinetics

Electrical Conductivity Relaxation (ECR) measurement of sample L

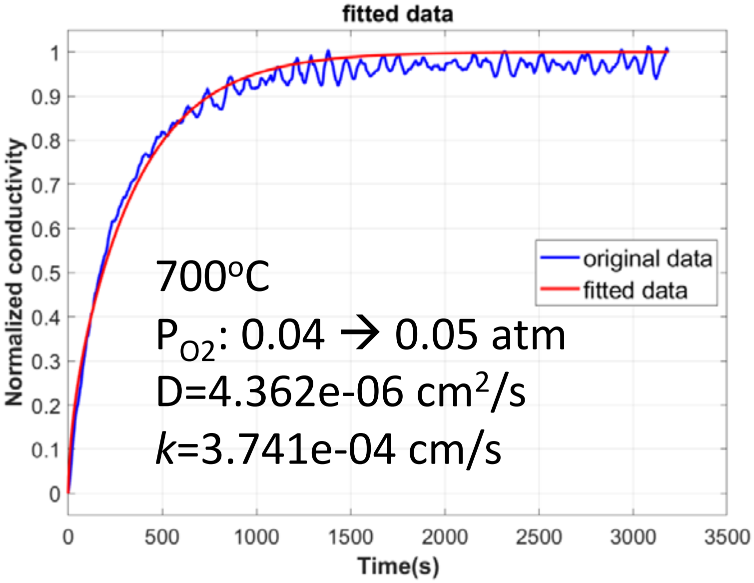


700°C

P_{O2}: 0.02 → 0.04 atm

D=5.0113e-06 cm^2/s

k=5.8047e-04 cm/s



700°C

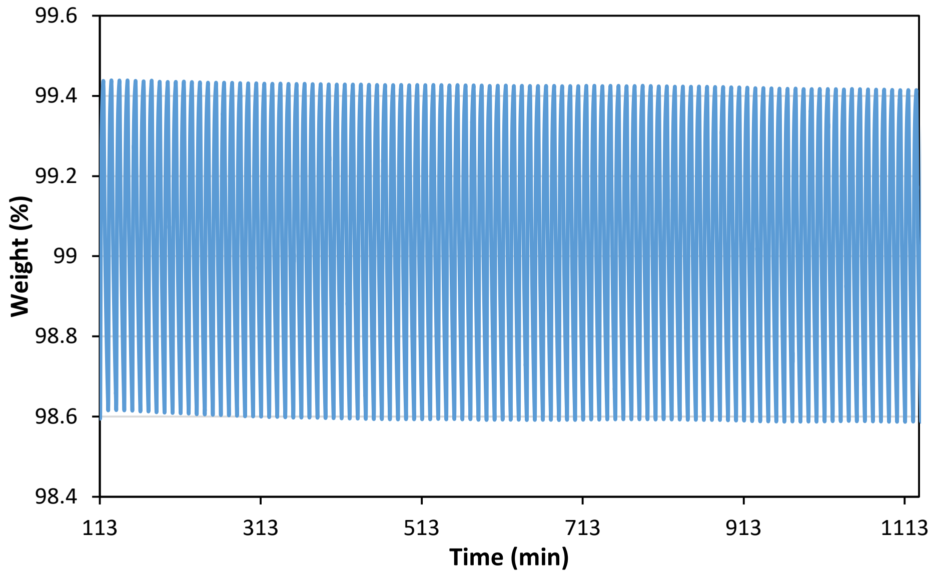
P_{O2}: 0.04 → 0.05 atm

D=4.362e-06 cm^2/s

k=3.741e-04 cm/s

- Characteristic thickness L_c = D/k = 86-116 µm, smaller than particle size range of 150-250 µm
- Surface oxygen exchange limits redox kinetics

Stability of sample L at 450ºC

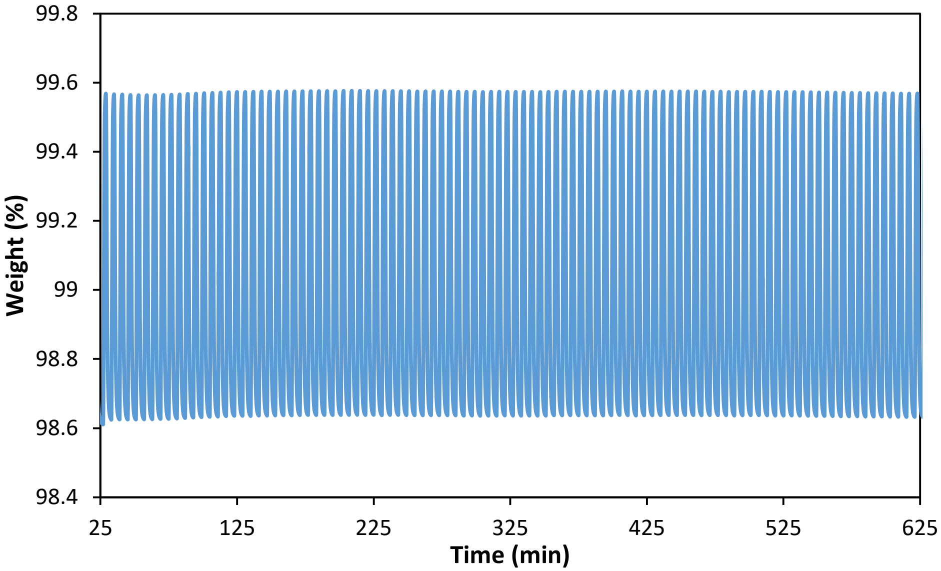


Oxygen capacity (%)

	1	2	3	4	5
1st 5 cycles	0.82	0.82	0.82	0.82	0.82
Last 5 cycles	0.83	0.83	0.83	0.83	0.83

- Red: Ar, 6 min; Oxi: 20%O_2, 4 min; 450ºC, 100 cycles
- Oxygen production rate: 0.082% O_2/min
- Bed size factor: 1693 lbs/TPD O_2

Stability of sample L at 500ºC



Oxygen capacity (%)

	1	2	3	4	5
1st 5 cycles	0.94	0.94	0.94	0.94	0.94
Last 5 cycles	0.94	0.94	0.94	0.94	0.94

- Red: Ar, 4 min; Oxi: 20%O_2, 2 min; 500ºC, 100 cycles
- Oxygen production rate: 0.156% O_2/min
- Bed size factor: 886 lbs/TPD O_2

Summary of “high temperature” oxygen sorbents

- Balanced oxidation and reduction rates improve oxygen capacity
- LSCF promotes metal oxide dispersion and oxygen transport
- LSCF **increases** average redox rates by **4 times** and oxygen capacity by **2.5 times**
- LSCF enhances stability of oxygen sorbents

Summary of “low temperature” oxygen sorbents

- Screening of oxygen sorbents with low reduction temperature by The Materials Project
- Doping at A or B site of $SrFeO_3$ increases oxygen vacancy
- Highly active doped $SrFeO_3$ with **0.5-1.0% O_2 capacity** for air separation at temperature **below 600ºC**
- Steam resistant sample D oxygen sorbent is **stable for 1000 redox cycles**

Future work

NCSU

- **Stability test** (i.e., 2000 cycles) of LSCF-CF and A or B site doped $SrFeO_3$ oxygen sorbents in the presence of steam and obtaining two or more oxygen sorbents with <5% degradation (Subtask 5.1, **04/01/2019-06/30/2019**)
- **Further optimization** in oxygen capacity and redox kinetics of doped SrFeO3 OS (**04/01/2019-12/31/2019)**
- **Fixed bed evaluation** of LSCF-CF and doped $SrFeO_3$ oxygen sorbents (Subtask 5.2, **07/01/2019-09/30/2019**)
- **Testing oxygen sorbents prepared by Thermosolv** using scaled up synthesis (Subtask 7.2, **10/01/2019-03/31/2020**)

Future work

NCSU

- **Process analysis** of REM-ASU for modular coal gasification (Subtask 9.1, **04/01/2020-12/31/2020**)

Thermosolv

- **Develop a preliminary REM-ASU design** with > 30% reduction in energy consumption based on the adsorber/desorber model developed by WVU under subtask 6.1 (Subtask 6.2, **04/01/2019-12/31/2019**)
- **Scaled-up production** of batches (25 kg/batch) of oxygen sorbents with air separation performance to achieve >30% reduction in energy consumption comparing to cryogenic ASU (Subtask 7.1, **10/01/2019-03/31/2020**)

Future work

Thermosolv

- Preparation of the **Pilot Facility** (Subtask 8.1, **10/01/2019-09/30/2020**)
- **Pilot scale testing** of the REM-ASU technology to achieve >95% pure O2 for over 2000 cycles with less than 10% decrease in oxygen storage/release capacity (Subtask 8.2, **10/01/2019-9/30/2020**)
- Development of **techno-economic models** and commercialization plans. Identify an REM-ASU system design and OS material with >30% reduction in energy consumption comparing to cryogenic ASU (Subtask 9.2, **04/01/2020-12/31/2020**)

Future work

WVU

- Continue characterizing oxygen transport kinetics of LSCF-CF and doped $SrFeO_3$ oxygen sorbents (**04/01/19-12/31/19)**
- Modeling of Adsorption/Desorption Operations using Advanced Sorbents (Subtask 6.1, **04/01/19-12/31/19**)

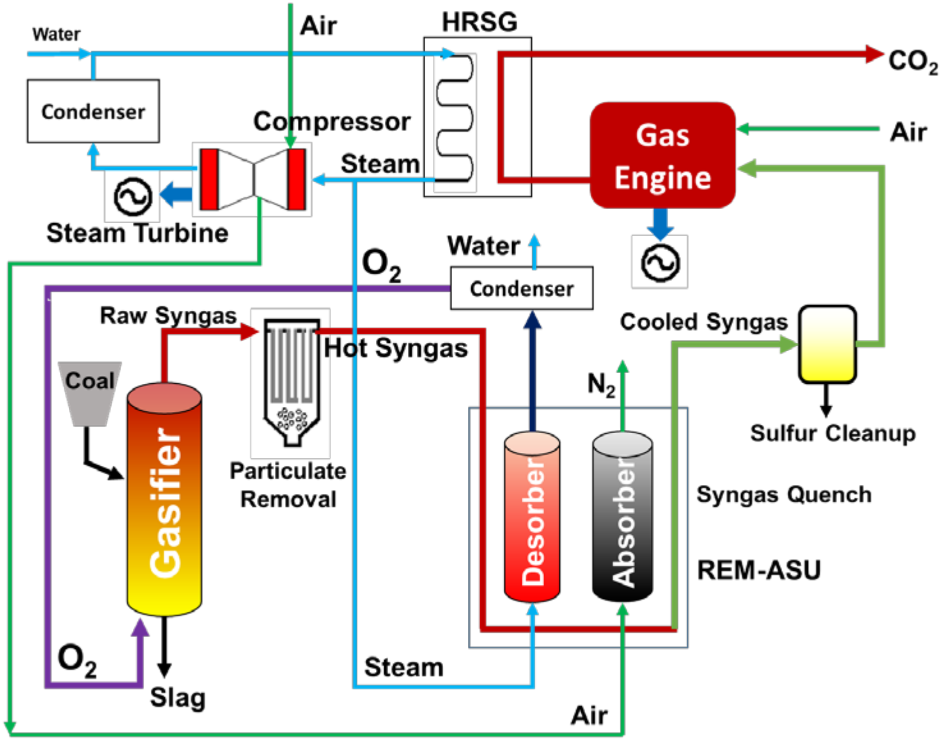
Market Benefits/Assessment

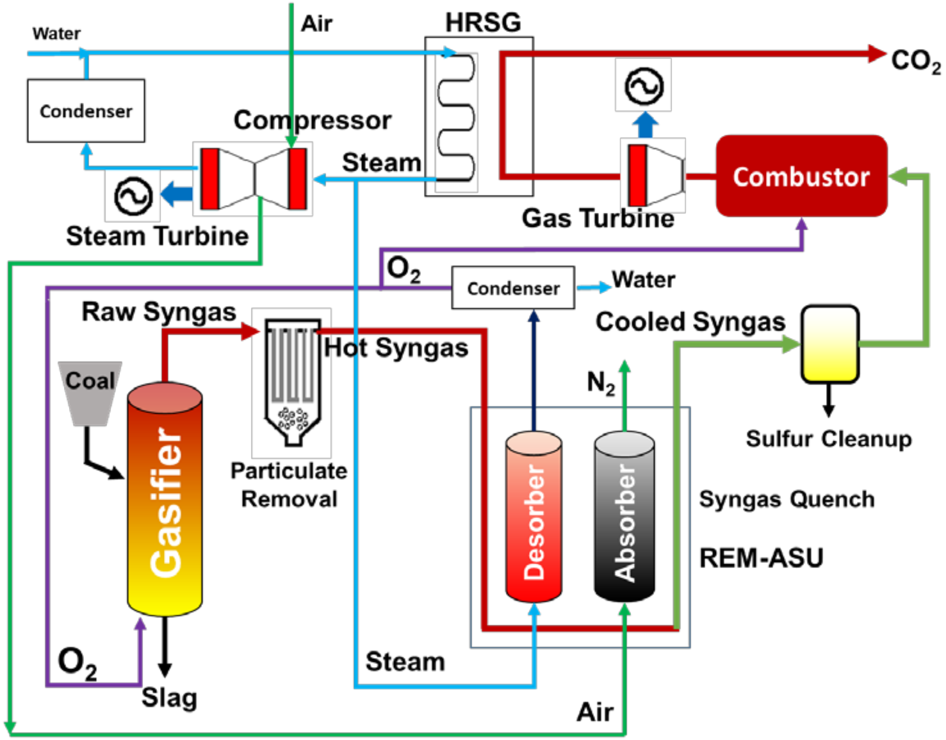
- REM-ASU produces low cost oxygen compatible with modular coal gasification
- REM-ASU can lead to 30% reduction in energy consumption comparing to cryogenic method for air separation
- REM-ASU integrates with gasification system for low-grade heat utilization and O_2 cost reduction
- REM-ASU has lower capital cost and is easy to scale up

Technology-to-Market Path

- Design oxygen sorbents with high O_2 capacity and high activity for efficient air production
- Demonstrate robust and steam resistant oxygen sorbents for long term air separation via pressure swing without using vacuum desorption
- Develop modular ASU for pilot scale testing to produce 95% O_2 over 2000 cycles with less than 10% degradation
- Integrate REM-ASU with 1-5 MW modular coal gasifier with >30% reduction in energy consumption for oxygen generation comparing to conventional ASUs.
- Techno-Economics and commercialization plan development

REM-ASU and Gasifier Integration



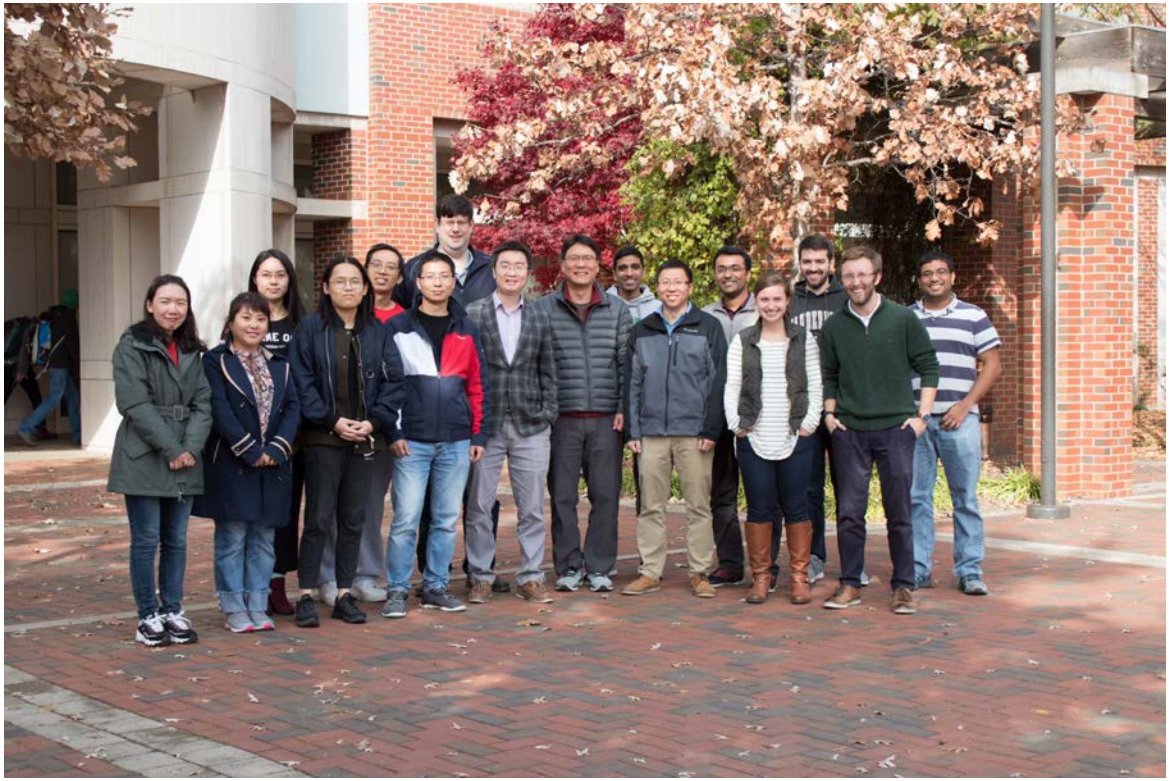


REM-ASU has the potential to be efficient, flexible, and cost-effective

Conclusions

- REM-ASU has the potential to produce low cost oxygen via pressure swing with oxygen sorbent materials
- REM-ASU is tailored to be compatible with 1-5 MW coal gasifier, with the potential for >30% reduction in energy consumption for air separation
- Low cost oxygen reduces cost for coal gasifier deployment, leading to cost effective CO_2 capture and utilization
- Future work include demonstration of robustness and steam resistance of oxygen sorbents for over 2000 cycles with less than 5% degradation, scale up, and demonstration

Acknowledgement



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WVU:
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THERMOSOLV LLC
Drs. Vijay Seith, Beau Braunberger, Anthony Richard

NATIONAL ENERGY TECHNOLOGY LABORATORY

Thank you!