Radically Engineered Modular Air Separation System with Tailored Oxygen Sorbents

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Project Partners:
Thermosolv LLC and West Virginia University

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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% O₂ capacity, **2-4 times of benchmark** CaMn₀.₉₅Fe₀.₀₅O₃ oxygen sorbent.
- Demonstrated high activity of LSCF-CF OS with redox rate of 1.35-2.04 mg O₂/mg sorbent-min, **4-6 times of benchmark** CaMn₀.₉₅Fe₀.₀₅O₃ OS.
- Designed low temperature SrFeO₃ based OS for chemical looping air separation at 450-600°C.
- Demonstrated steam resistant SrFeO₃ based OS for 1000 cycles of air separation with <3% degradation.
Publication and conference presentations


Air Separation

• N\textsubscript{2} and O\textsubscript{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\textsubscript{2} capture

Linde Air Separation Plant
(www.linde-engineering.com)
## Cryogenic vs Chemical Looping Air Separation

<table>
<thead>
<tr>
<th></th>
<th>Cryogenic</th>
<th>Chemical looping</th>
</tr>
</thead>
<tbody>
<tr>
<td>Status</td>
<td>mature</td>
<td>developing</td>
</tr>
<tr>
<td>Economic range (sTPD)</td>
<td>&gt;20</td>
<td>Undetermined</td>
</tr>
<tr>
<td>Energy consumption (kW/kg O₂)</td>
<td>0.21</td>
<td>0.05-0.07</td>
</tr>
<tr>
<td>Thermodynamic efficiency (%)</td>
<td>25%</td>
<td>&gt;75%</td>
</tr>
<tr>
<td>Oxygen purity (%)</td>
<td>99+</td>
<td>99+</td>
</tr>
<tr>
<td>By product capability</td>
<td>Excellent</td>
<td>Poor</td>
</tr>
</tbody>
</table>

*Chemical looping air separation is energy efficient*
Oxygen Sorbent Development: Challenges and Opportunities

Mixed oxides are necessary in order to match $P_{O_2}$ of oxygen carriers with air separation conditions.
(La$_x$Sr$_{1-x}$)Co$_y$Fe$_{1-y}$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%O₂, 650-850°C
- Negligible oxygen capacity at 650-750 °C
- LSCF increases oxygen capacity by 2.5 times
LSCF improves oxygen capacity

- LSCF increases O₂ capacity by 37-260%
- LSCF decreases reduction temperature by 18-46°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)

LSCF enhances oxygen sorbent stability for extended redox cycling at 850°C for 100 cycles.
Screening of low temperature oxygen sorbents

SrFeO$_3$ is identified as low temperature oxygen sorbents

Calculated with data from Materials Project

DFT results from NCSU
Effect of A or B site doping on oxygen vacancy formation energy

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%H₂O/Ar, 6 min; Oxi: 2.5%H₂O/20%O₂/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

- Characteristic thickness $L_c = D/k = \sim 200 \ \mu m$, within particle size range of 150-250 \ \mu m
- Both oxygen diffusion and surface oxygen exchange determines redox kinetics

700°C

$P_{O2}$: 0.02 → 0.04 atm
$D=3.129e-05 \text{ cm}^2/\text{s}$
$k=1.582e-03 \text{ cm/s}$

700°C

$P_{O2}$: 0.04 → 0.05 atm
$D=3.605e-05 \text{ cm}^2/\text{s}$
$k=1.716e-03 \text{ cm/s}$
Electrical Conductivity Relaxation (ECR) measurement of sample L

- Characteristic thickness $L_c = \frac{D}{k} = 86-116 \ \mu m$, smaller than particle size range of 150-250 $\mu m$

- Surface oxygen exchange limits redox kinetics

$700^\circ C$

$P_{O_2}$: 0.02 $\rightarrow$ 0.04 atm
$D=5.0113e-06 \ cm^2/s$
$k=5.8047e-04 \ cm/s$

$700^\circ C$

$P_{O_2}$: 0.04 $\rightarrow$ 0.05 atm
$D=4.362e-06 \ cm^2/s$
$k=3.741e-04 \ cm/s$
Stability of sample L at 450°C

- Red: Ar, 6 min; Oxi: 20%O₂, 4 min; 450°C, 100 cycles
- Oxygen production rate: 0.082% O₂/min
- Bed size factor: 1693 lbs/TPD O₂
Stability of sample L at 500°C

- Red: Ar, 4 min; Oxi: 20%O₂, 2 min; 500°C, 100 cycles
- Oxygen production rate: 0.156% O₂/min
- Bed size factor: 886 lbs/TPD O₂
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 600$^\circ$C

• 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 SrFeO$_3$ 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 O₂ 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 CO₂ 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
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