An Advanced Modular Redox Air Separation System for Cost-Effective, Net-Zero Hydrogen Production

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Project Partners: Massachusetts Institute of Technology and GTI Energy
DOE/NETL Project Manager: Sarah (Michalik) Pfeiffer
04/23/2024

NC STATE UNIVERSITY

Presentation Outline

- Project Overview and Background
- Technical Approach
- Key Results
- Summary and Future Work

Project Overview and Background

Period of Performance: 10/16/2023-04/23/2024

Project Partners

	Federal	Cost Share
NCSU	$979,960	$175,548
MIT	$220,000	$55,003
GTI	$100,000	$25,000
Acadian	$50,000	$12,500
Total	$1,249,960	$313,051

Objective: To develop and demonstrate a redox-based, radically engineered modular air separation unit (REM-ASU) for small-scale biomass gasifiers

Key Goals:

i. Advanced steam-resistant oxygen sorbents with > 2 wt.% oxygen capacity

ii. Comprehensive demonstration of the ASU system in a 20 kg O_2/day testbed

iii. Detailed design of the REM-ASU for integration with 5 – 10 MW modular biomass gasifier

Project Overview and Background

Cryogenic vs. CLAS

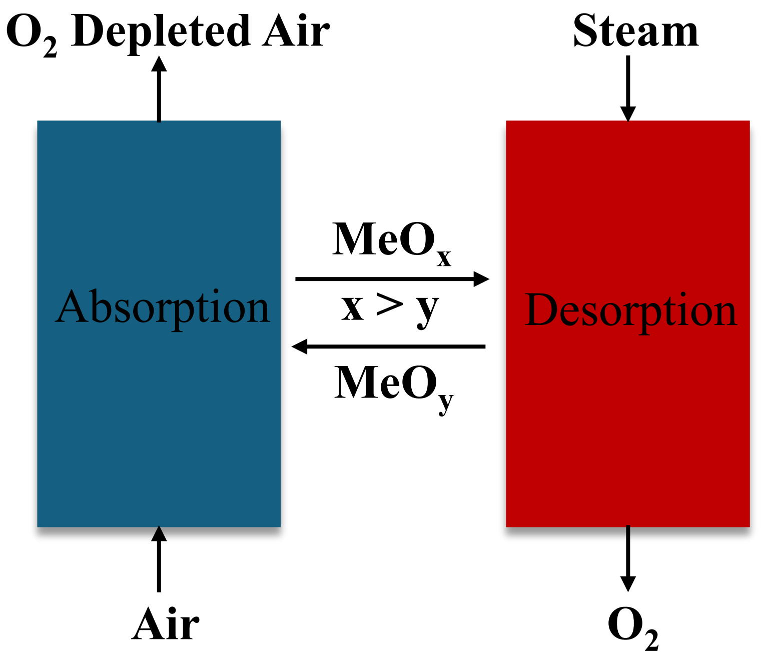
	Cryogenic air separation	Chemical looping air separation
Status	mature	developing
Energy consumption (MJ/kg O_2)	0.79	<0.54
Thermodynamic (second law) efficiency (%)	~25%	>36%
Oxygen purity (%)	99+	99+

Chemical looping air separation (CLAS) has the potential to be highly energy efficient

Source: Krzystowczyk, et al., ACS Sustainable Chem. Eng. 2021,. (2021)

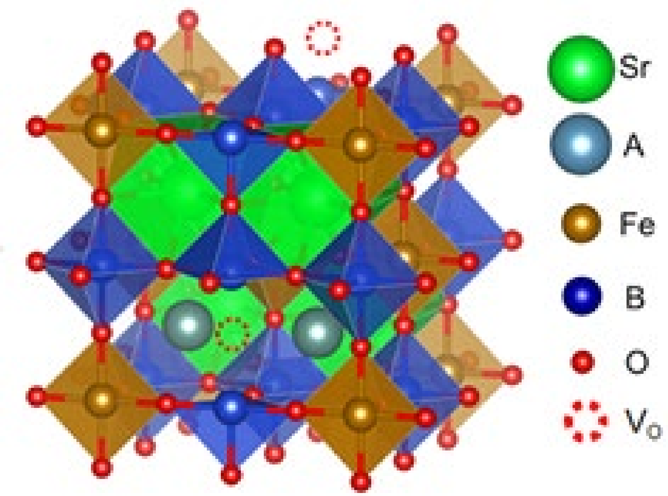
Project Overview and Background

Radically engineered modular air separation unit (REM-ASU)



- 2-step redox loop at 400-600 °C
- Produce concentrated O_2 (up to 99%)
- Steam-resistant oxygen sorbent

Perovskite Oxides ($ABO_{3-\delta}$)



Great sorbent candidates:

- Continuous oxygen exchange
- Flexible thermochemical properties
- Fast kinetics

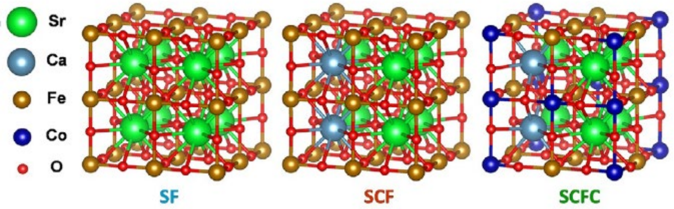
Absorption: $ABO_{3-\delta} + \delta/2O_2(g) \rightarrow ABO_3$ + Heat

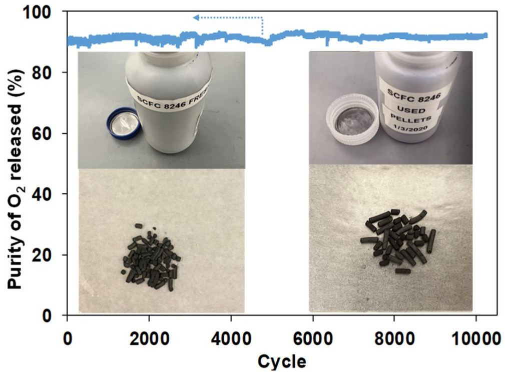
Desorption: ABO_3 + heat $\rightarrow ABO_{3-\delta} + \delta/2O_2(g)$

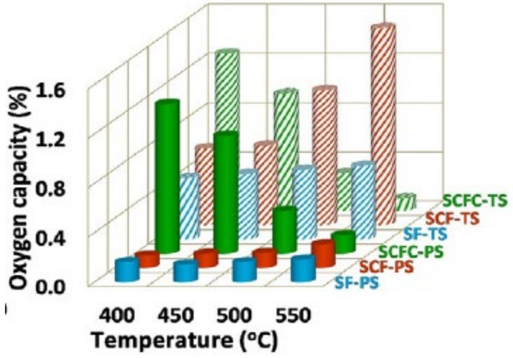
Project Overview and Background

Preliminary Results –Oxygen Sorbent Development

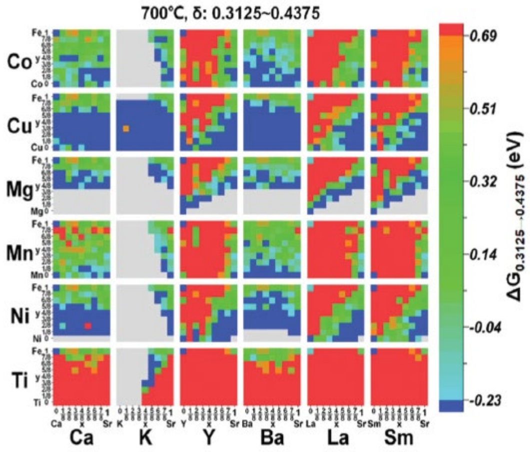
- $Sr_xCa_{1-x}Fe_yCo_{1-y}O_{3-\delta}$ (SCFC) achieved 7-times higher oxygen capacity than $SrFeO_{3-\delta}$ and demonstrated stable performance over 10,000 cycles

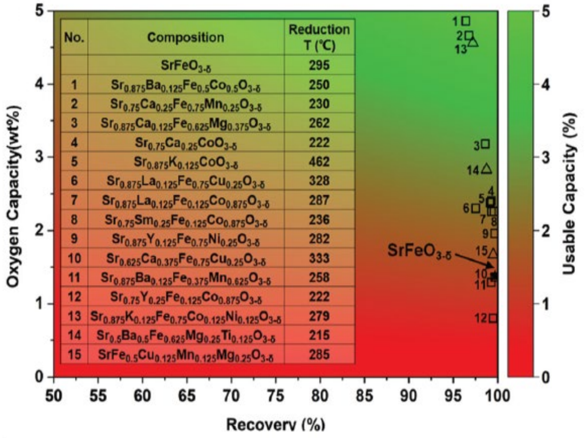






Source: Dou et al., ChemSusChem (2022)





No.	Composition	Reduction T (°C)
	$SrFeO_{3-\delta}$	295
1	$Sr_{0.875}Ba_{0.125}Fe_{0.5}Co_{0.5}O_{3-\delta}$	250
2	$Sr_{0.75}Ca_{0.25}Fe_{0.75}Mn_{0.25}O_{3-\delta}$	230
3	$Sr_{0.875}Ca_{0.125}Fe_{0.625}Mg_{0.375}O_{3-\delta}$	262
4	$Sr_{0.75}Ca_{0.25}CoO_{3-\delta}$	222
5	$Sr_{0.875}K_{0.125}CoO_{3-\delta}$	462
6	$Sr_{0.875}La_{0.125}Fe_{0.75}Cu_{0.25}O_{3-\delta}$	328
7	$Sr_{0.875}La_{0.125}Fe_{0.125}Co_{0.875}O_{3-\delta}$	287
8	$Sr_{0.75}Sm_{0.25}Fe_{0.125}Co_{0.875}O_{3-\delta}$	236
9	$Sr_{0.875}Y_{0.125}Fe_{0.75}Ni_{0.25}O_{3-\delta}$	282
10	$Sr_{0.625}Ca_{0.375}Fe_{0.75}Cu_{0.25}O_{3-\delta}$	333
11	$Sr_{0.875}Ba_{0.125}Fe_{0.375}Mn_{0.625}O_{3-\delta}$	258
12	$Sr_{0.75}Y_{0.25}Fe_{0.125}Co_{0.875}O_{3-\delta}$	222
13	$Sr_{0.875}K_{0.125}Fe_{0.75}Co_{0.125}Ni_{0.125}O_{3-\delta}$	279
14	$Sr_{0.5}Ba_{0.5}Fe_{0.625}Mg_{0.25}Ti_{0.125}O_{3-\delta}$	215
15	$SrFe_{0.5}Cu_{0.125}Mn_{0.125}Mg_{0.25}O_{3-\delta}$	285

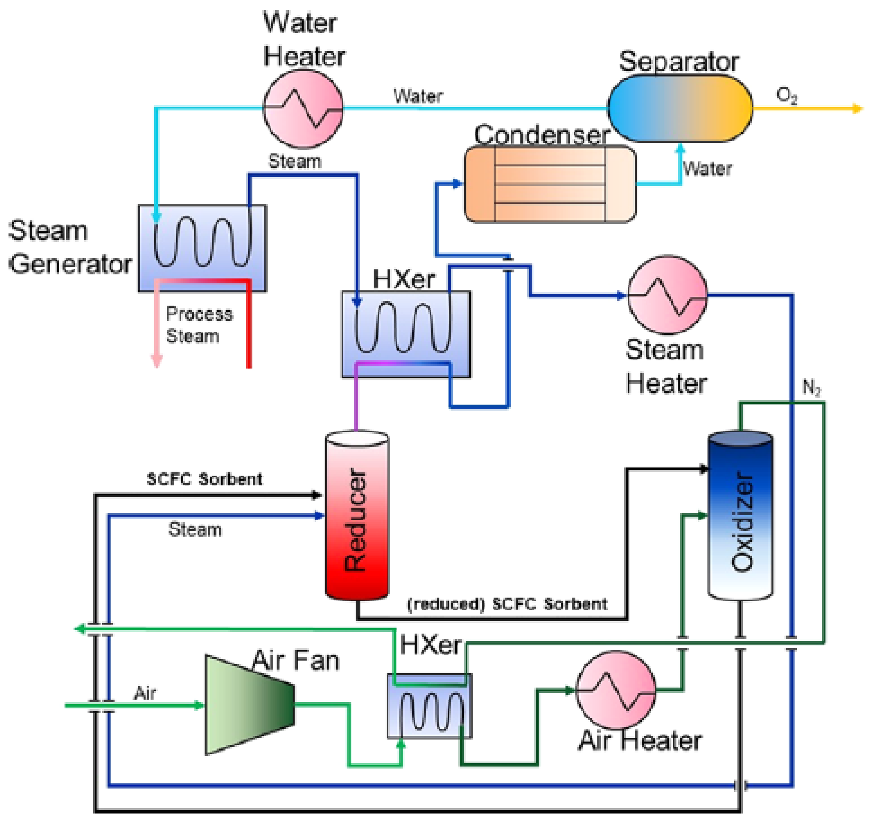
Source: Wang et al., Energy Environ. Sci. (2022)

- Applied a DFT-based machine learning approach to develop alternative sorbents
- 13 out 15 structures showed superior performance to $SrFeO_{3-\delta}$

These results are generated from a recent NETL support (DE-FE0031521)

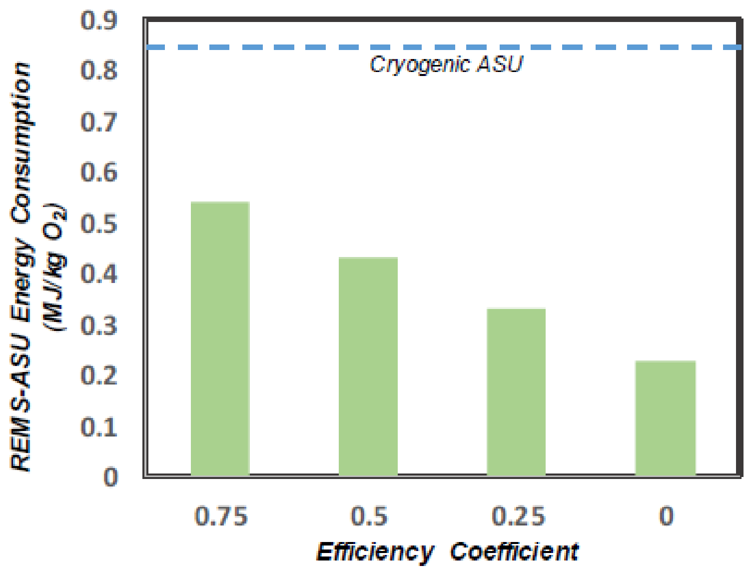
Technical Approach

Preliminary Results –Overall System Performance



Source: Krzystowczyk et al., ACS Sustainable Chem. Eng. (2021)

- REM-ASU process design in the ASPEN Plus
- 30.8% lower energy consumption than cryogenic air separation



These results are generated from a recent NETL support (DE-FE0031521)

Technical Approach

Tasks and Milestones (Year I)

Task 1: Project Management and Planning *(NCSU)*
Task 2: Societal Considerations and Impact

Task 3: Update of the Absorber and Process Models *(NCSU)*

Milestone 3.1: Establish the REM-ASU model compatible with 5 – 10 MW biomass gasifier *(completed)*

Task 4: Optimization of Entropy Stabilized Perovskite Sorbents *(NCSU, and MIT)*

Milestone 4.1: Obtain 4 or more entropy-stabilized perovskite oxygen sorbents with > 1 wt.% oxygen capacity and <5% oxygen capacity decrease over 25 cycles (completed)
Milestone 4.2: Report dopant effects on kinetics (in progress)
Milestone 4.3: Developed an improved DFT model considering the phase stability (in progress)

Task 5: Validation of Advanced Oxygen Sorbents *(NCSU)*

Milestone 5.1: Obtain four or more perovskite OSs with >2 wt.% oxygen storage capacity (in progress)

Technical Approach

Tasks and Milestones (Year II)

Milestone 5.2: Identify two or more advanced steam-resistant OSs with >2 wt.% oxygen capacity, less than 5% deactivation over 250 hours
Milestone 5.3: Determine the operating conditions in fixed bed adsorption/desorption cycles

Task 6: Sub-Pilot System Modification (NCSU)

Milestone 6.1: Operation of the modified sub-pilot system with inert particles for 24 hours

Task 7: Scale-Up of Oxygen Sorbent Synthesis (MIT)

Milestone 7.1 Synthesize two 50 kg batches of advanced oxygen sorbent

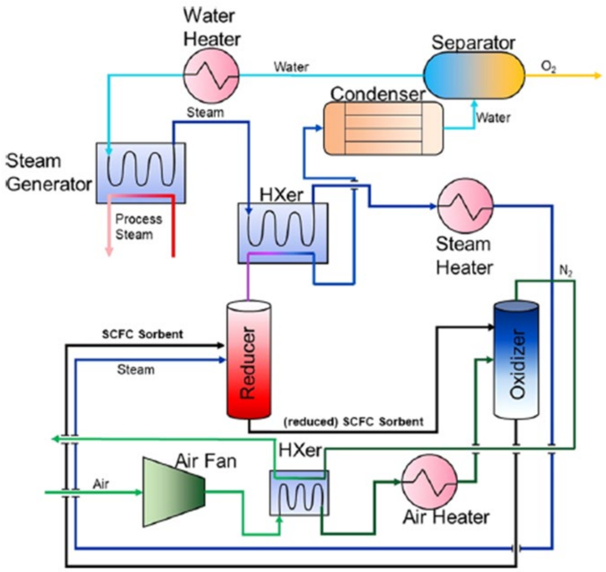
Task 8: Sub-Pilot Scale Testing of REM-ASU (NCSU, Acadian)

Milestone 8.1: Production of >95% pure O_2 for over 500 hours with less than 10% deactivation

Task 9: Performance and Cost Evaluations of the REM-ASU Technology (GTI, NCSU, Acadian)

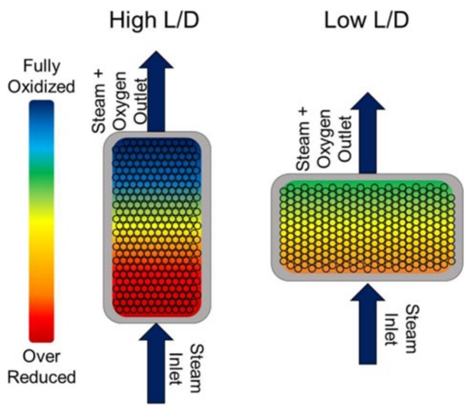
Milestone 9.1: Establish a techno-economic analysis model for REM-ASU (in progress)
Milestone 9.2: Design a 30 TPD REM-ASU unit

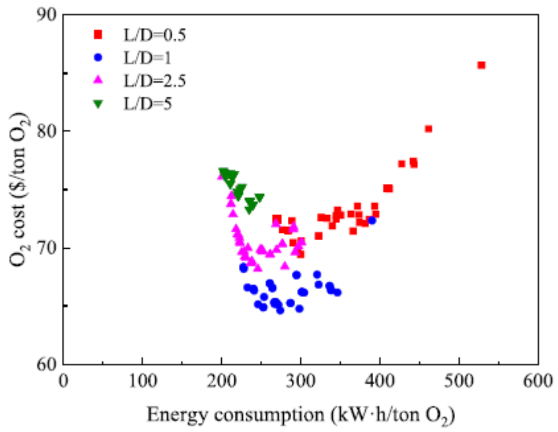
Technical Approach



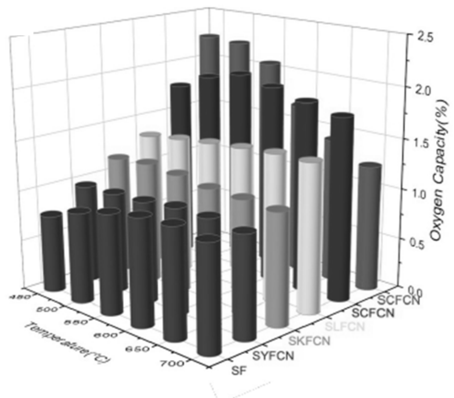
KEY RESULTS

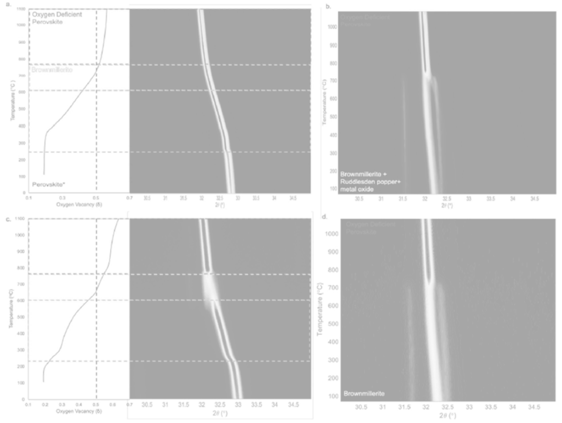
Reactor Modelling and Techno-economic Analyses



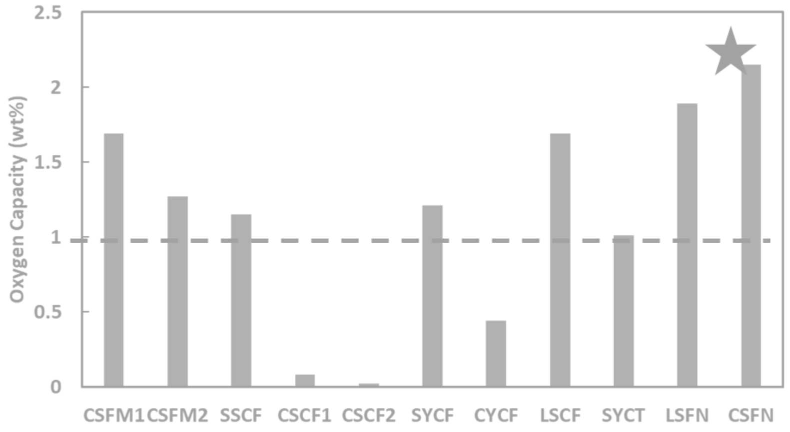


Entropy Stabilized Perovskite Sorbents





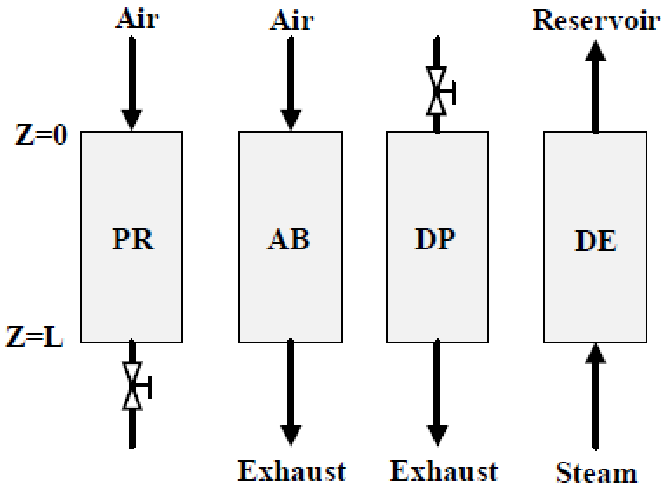
Advancement of Sorbents via an Improved DFT Model



Reactor Modelling and Techno-economic Analyses

Milestone 3.1: Establish the REM-ASU model compatible with 5-10 MW biomass gasifier *(completed)*

- 4-step cyclic configuration was simulated based on SCFC sorbent



PR: pressurization step
AB: absorption step
DP: co-current depressurization step
DE: counter-current desorption step

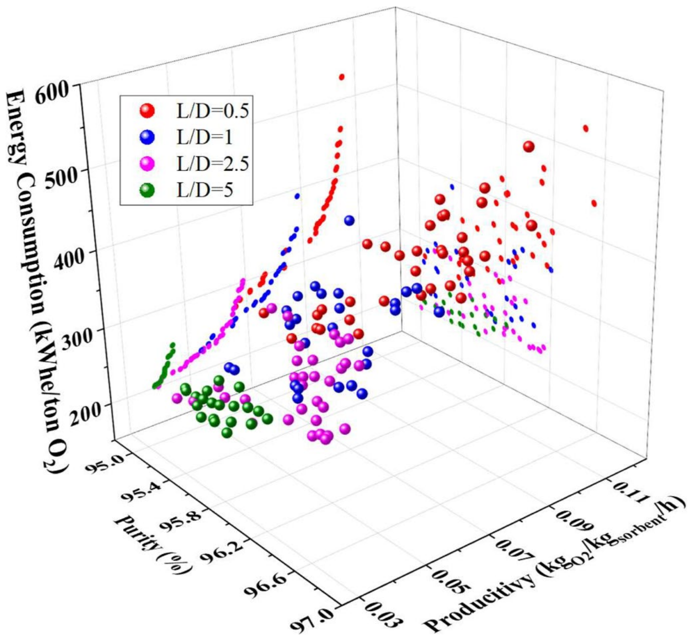
Optimization Parameters:

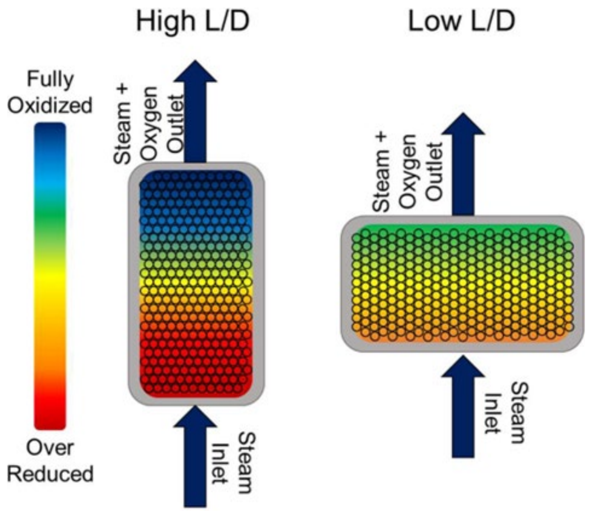
Item	Case1	Case2	Case3	Case4
Absorption time (s)	30-100			
Desorption time (s)	30-100			
Length/Diameter	**5**	**2.5**	**1**	**0.5**
Steam flow rate (mol/min)	778~ 3112	1838~ 7352	3530~ 14118	5577~ 22306
Absorption pressure (bar)	1.6-2			
Air flow rate (SLM)	29630~ 118518	55946~ 223784	88234~ 352942	139412~ 557646
O_2 purity (%)	**>95**			
Optimization Objective	**Max O_2 productivity and min power consumption**			

Source: Cai et al., International Journal of Greenhouse Gas Control (2024)

Reactor Modelling and Techno-economic Analyses

- Decreasing L/D improves oxygen productivity
- At a fixed L/D, higher productivity consumes more energy due to steam consumption

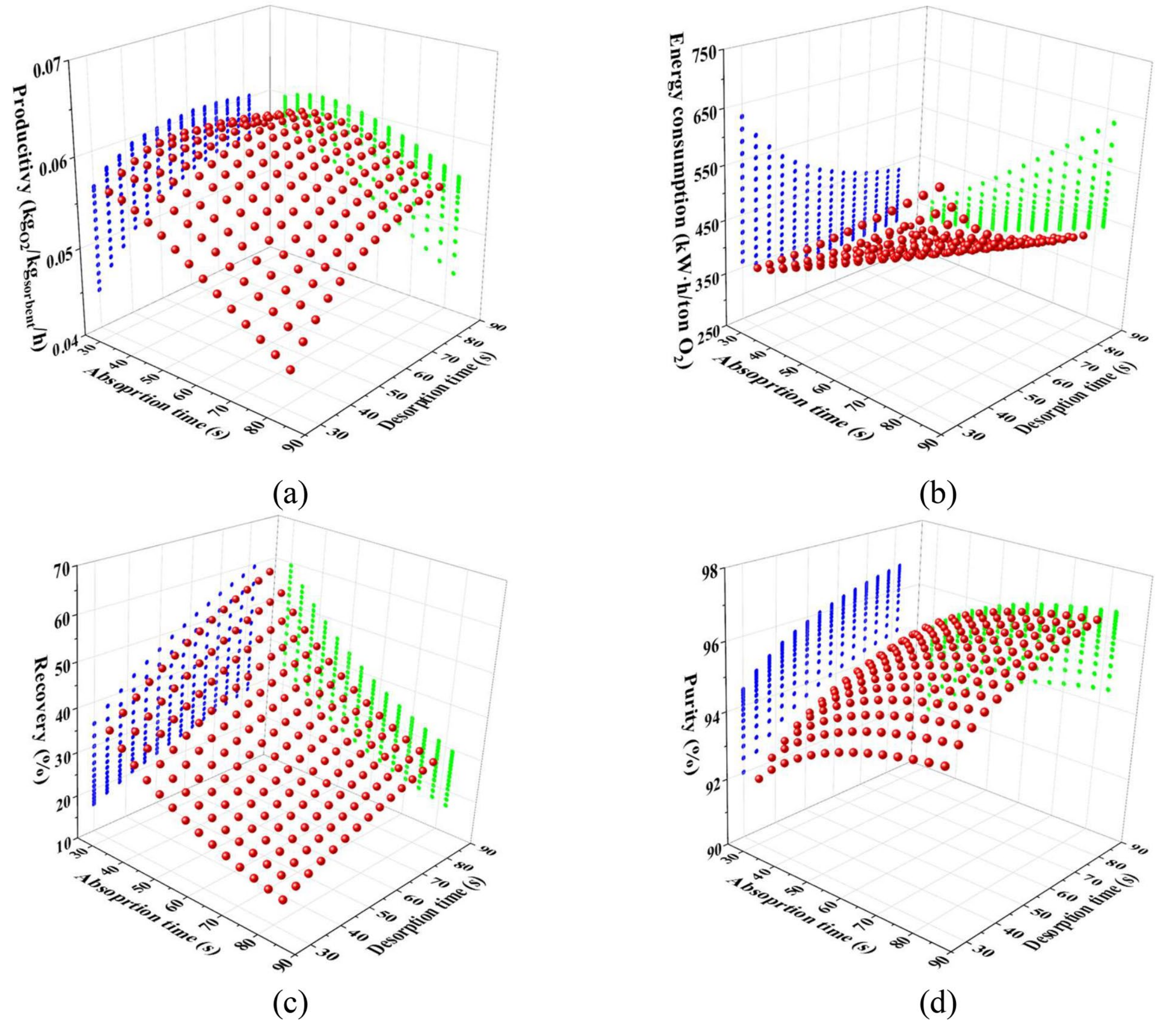




Source: Cai et al., International Journal of Greenhouse Gas Control (2024)

Reactor Modelling and Techno-economic Analyses

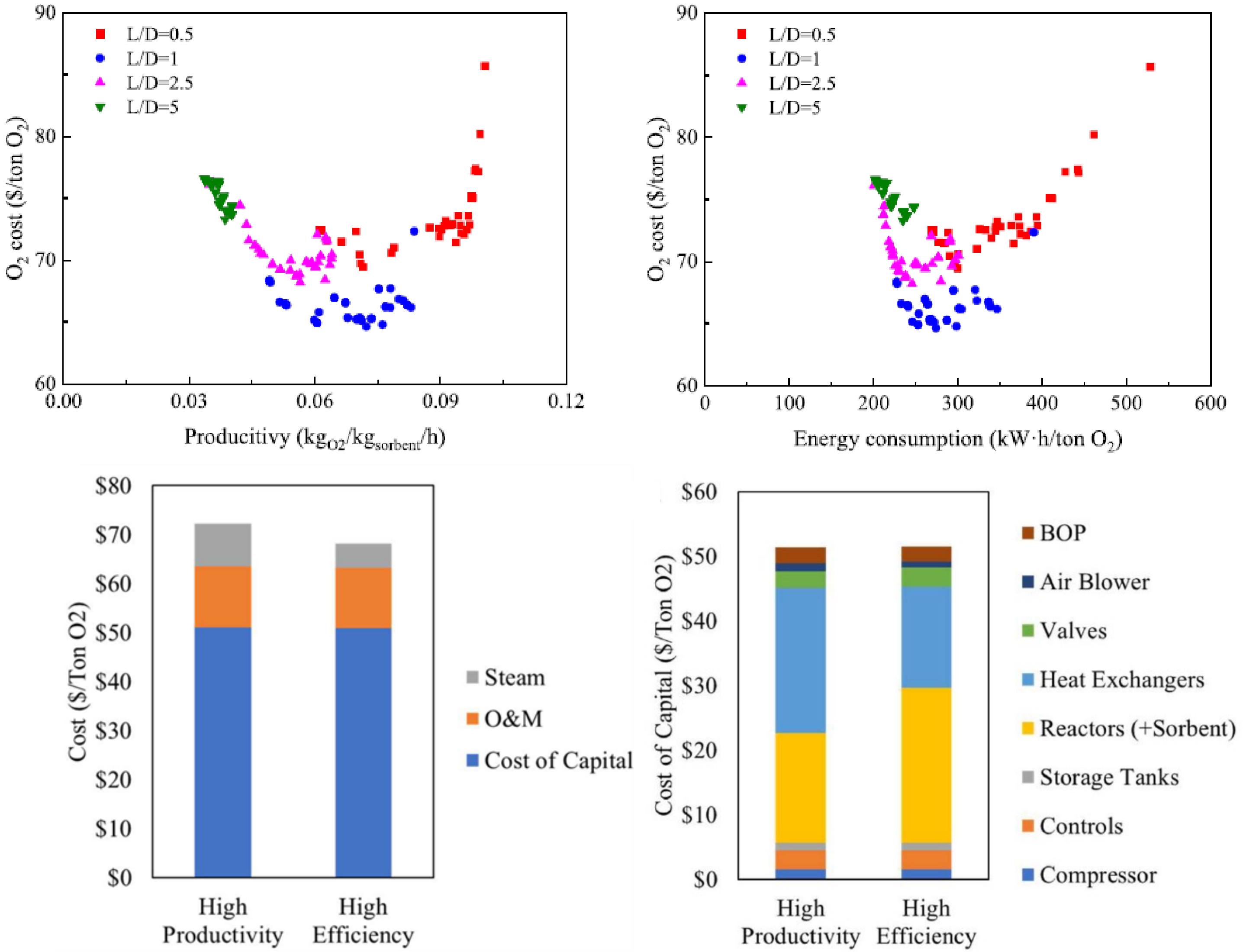
- L/D ratio was set to 1
- Shorter absorption time and longer desorption time lead to better productivity
- Recovery increases with absorption time and decreases with desorption time
- Purity increases with desorption, and absorption time



Source: Cai et al., International Journal of Greenhouse Gas Control (2024)

Reactor Modelling and Techno-economic Analyses

- The cost of oxygen was projected to be as low as **\$65/ton O_2**
- L/D=1 gives the most optimal results
- Reactor size decrease with increased sorbent capacity
- Increased steam demands increase the size of heat exchanger
- **For minimizing capital costs, it is important to optimize sorbent capacity and kinetics**



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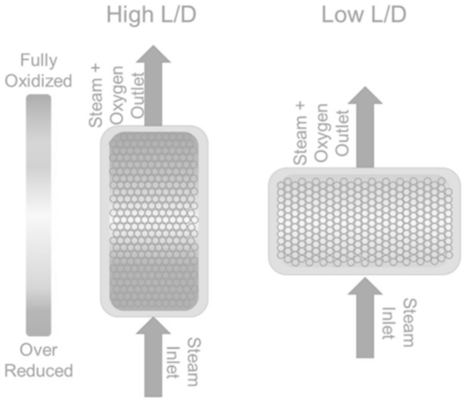
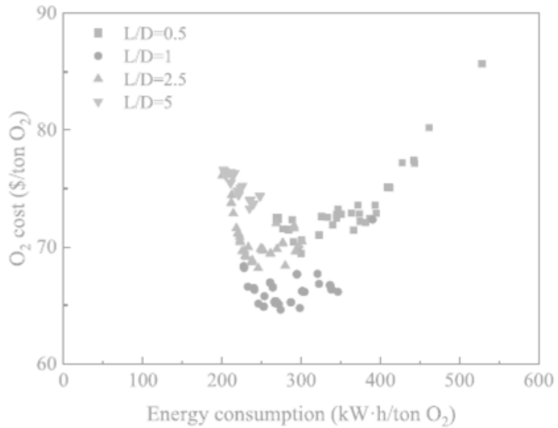
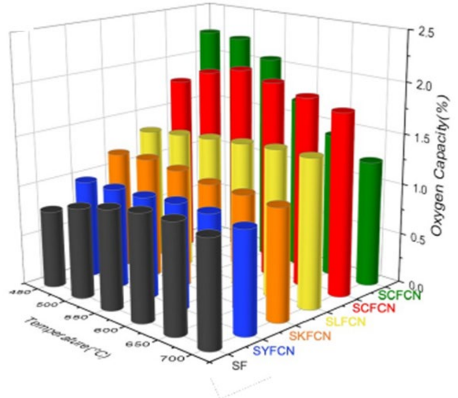
KEY RESULTS

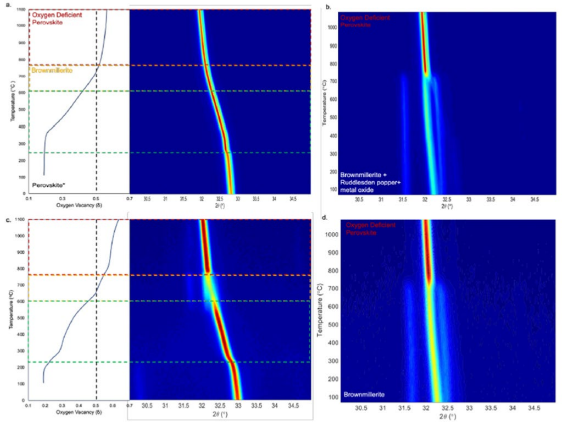
Reactor Modelling and Techno-economic Analyses



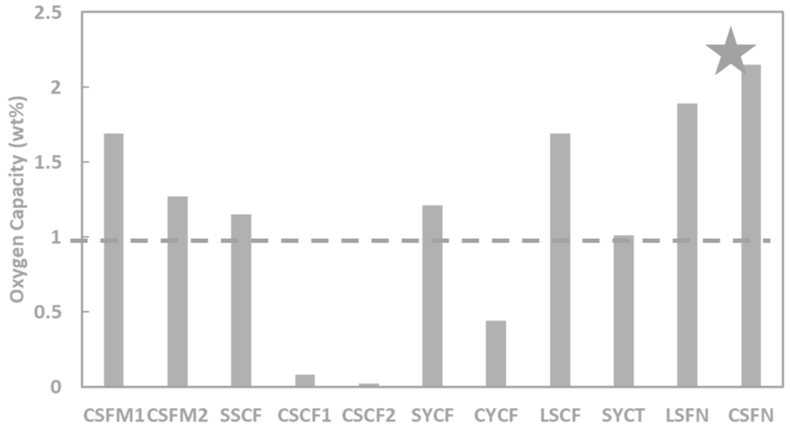


Entropy Stabilized Perovskite Sorbents





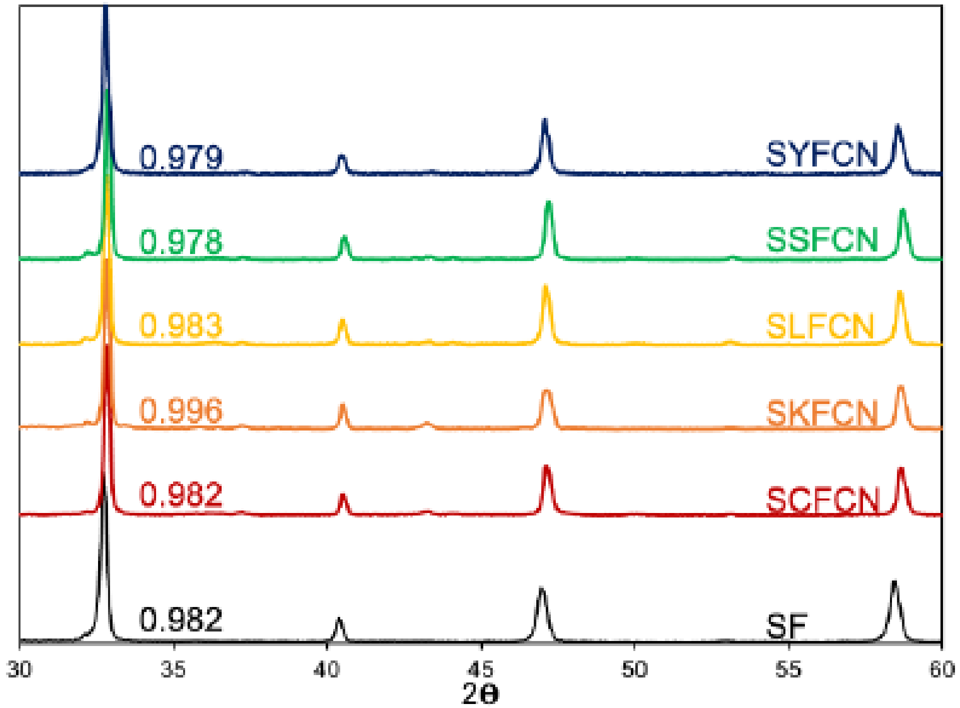
Advancement of Sorbents via an Improved DFT Model



Entropy-Stabilized Perovskite Sorbents

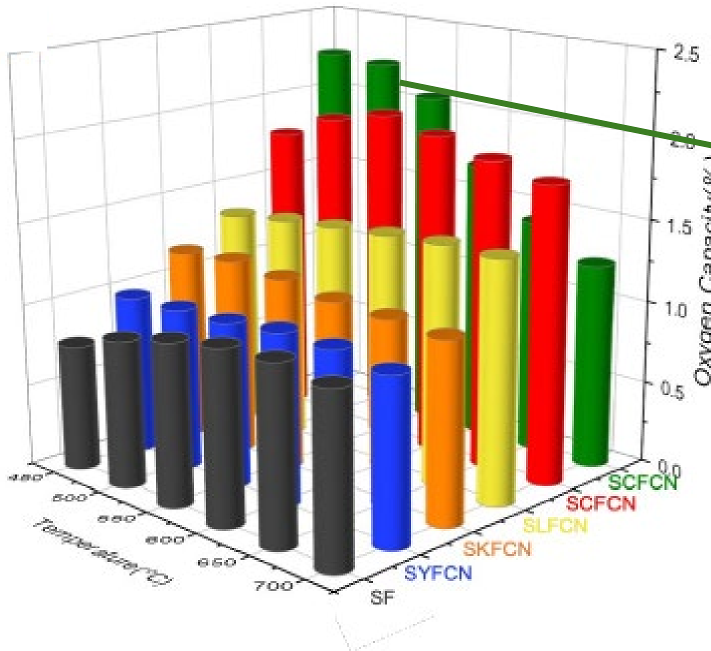
Milestone 4.1: Obtain 4 or more entropy-stabilized perovskite oxygen sorbents with > 1 wt.% oxygen capacity and <5% oxygen capacity decrease over 25 cycles (completed)

- Perovskites with 5 cations have high configurational entropy
- Several compositions were predicted using a ML approach
- Desired phases were obtained using a sol-gel method



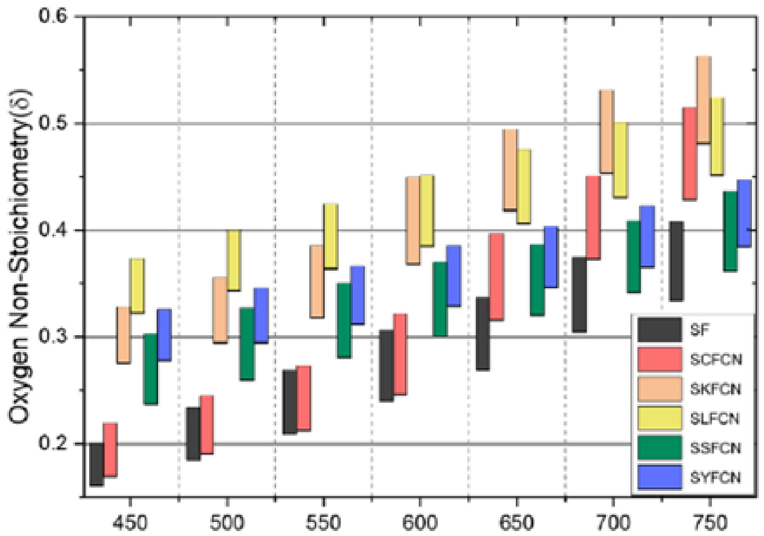
Entropy Stabilized Perovskite Sorbents

oxygen capacities under the conditions of 700ºC- 75% O_2 and 450 ºC-0.5%O_2



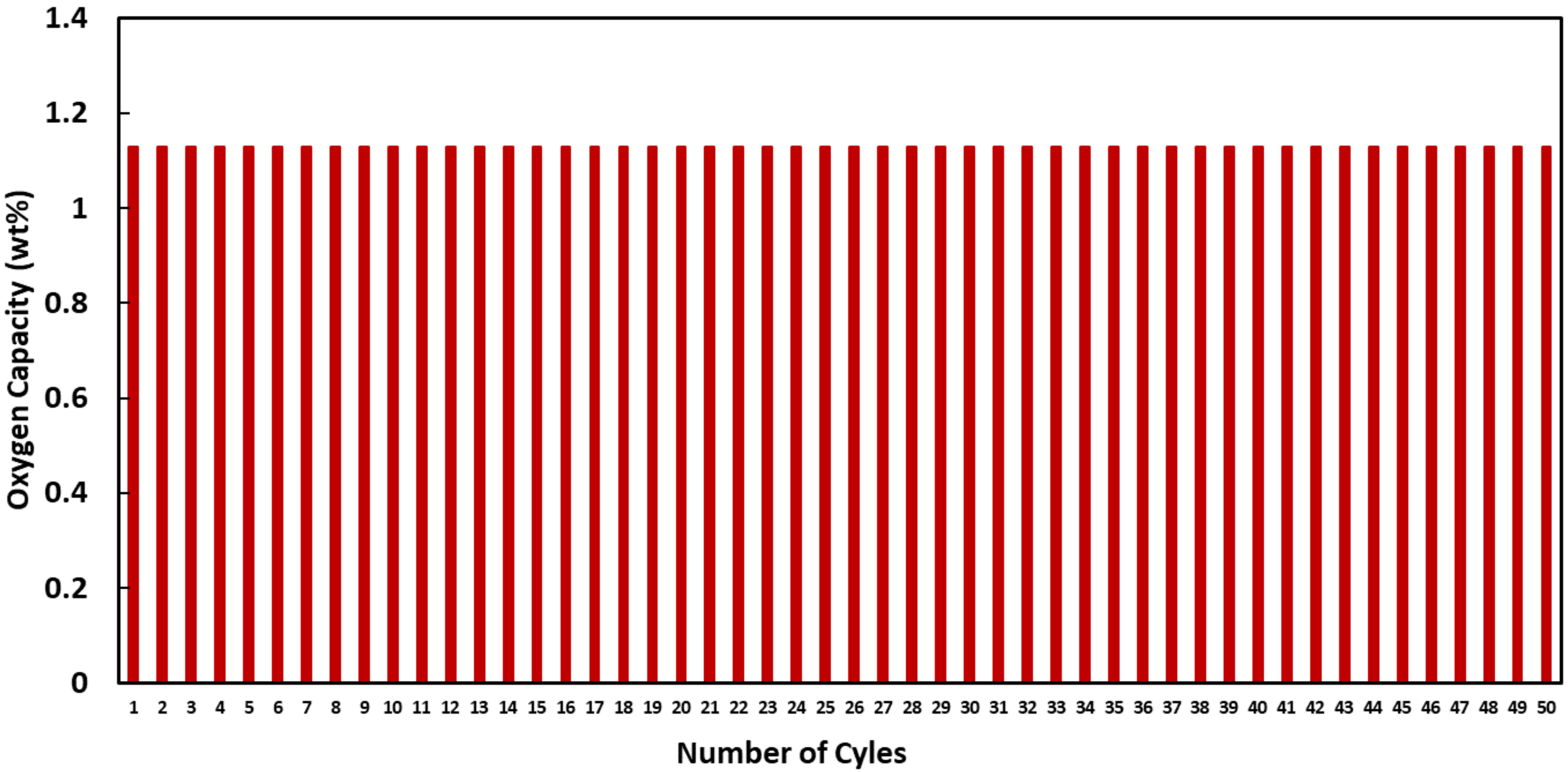
SKFCN achieved >2wt% O_2 capacity

oxygen vacancies under the conditions of 700ºC- 20% O_2 and 450 ºC-Ar



Entropy Stabilized Perovskite Sorbents

- SKFCN maintained its oxygen capacity of **1.13 wt%** under 600 °C /1%O_2 and 400 °C /20%O_2 for 50 cyles



Entropy Stabilized Perovskite Sorbents

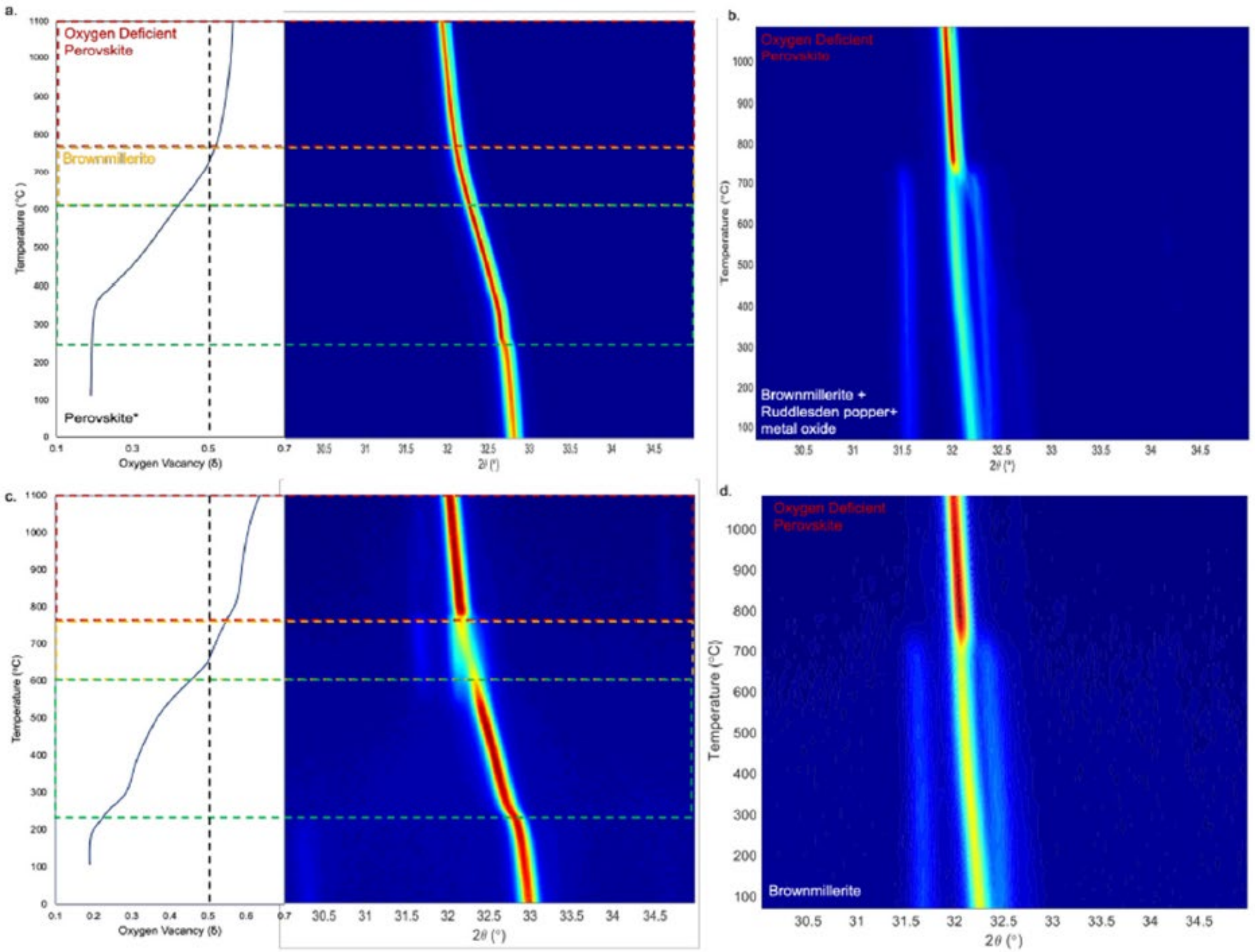
In-situ XRD results with Ar TPD and cooling results

SF:

- Once it reaches a vacancy concentration > 0.5, the material begins to decompose.

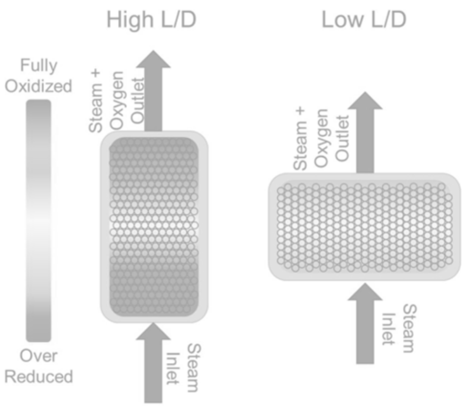
SKFCN:

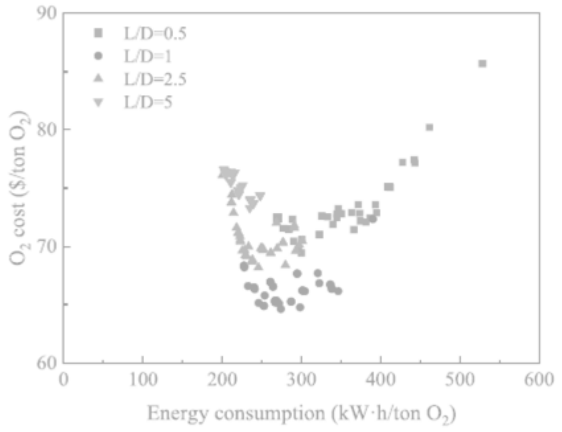
- The material stays stable a vacancy concentration of > 0.5



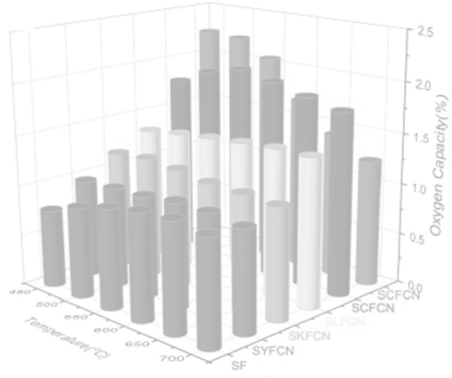
KEY RESULTS

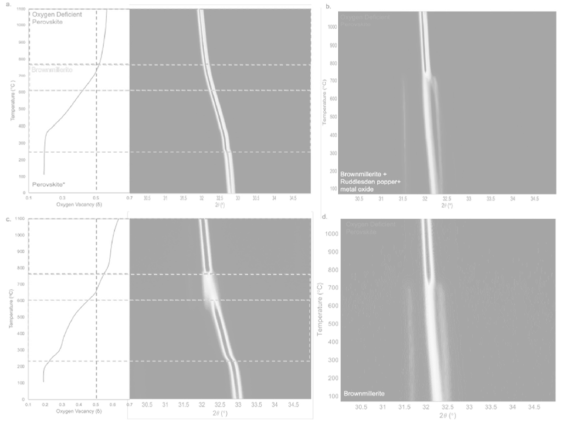
Reactor Modelling and Techno-economic Analyses



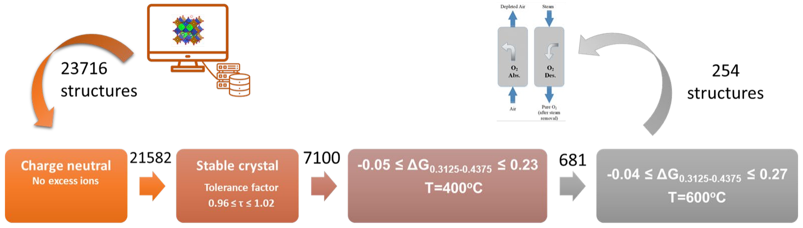


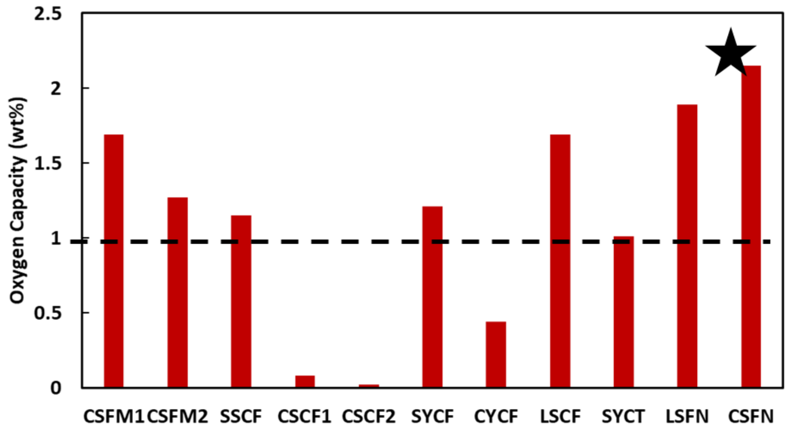
Entropy Stabilized Perovskite Sorbents



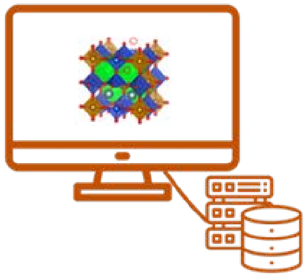


Advancement of Sorbents via an Improved DFT Model



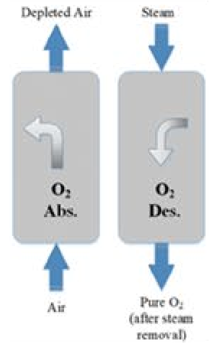


Advancement of Sorbents via an Improved DFT Model



23716 structures

$(A_xA'_{1-x}B_yB'_{1-y}O_{3-\delta})$



254 structures

Charge neutral
No excess ions

→ 21582

Stable crystal
Tolerance factor
$0.96 \le \tau \le 1.02$

→ 7100

$-0.05 \le \Delta G_{0.3125\text{-}0.4375} \le 0.23$
T=400°C

→ 681

$-0.04 \le \Delta G_{0.3125\text{-}0.4375} \le 0.27$
T=600°C

Sufficient oxygen capacity was aimed at both T=400°C and 600°C.

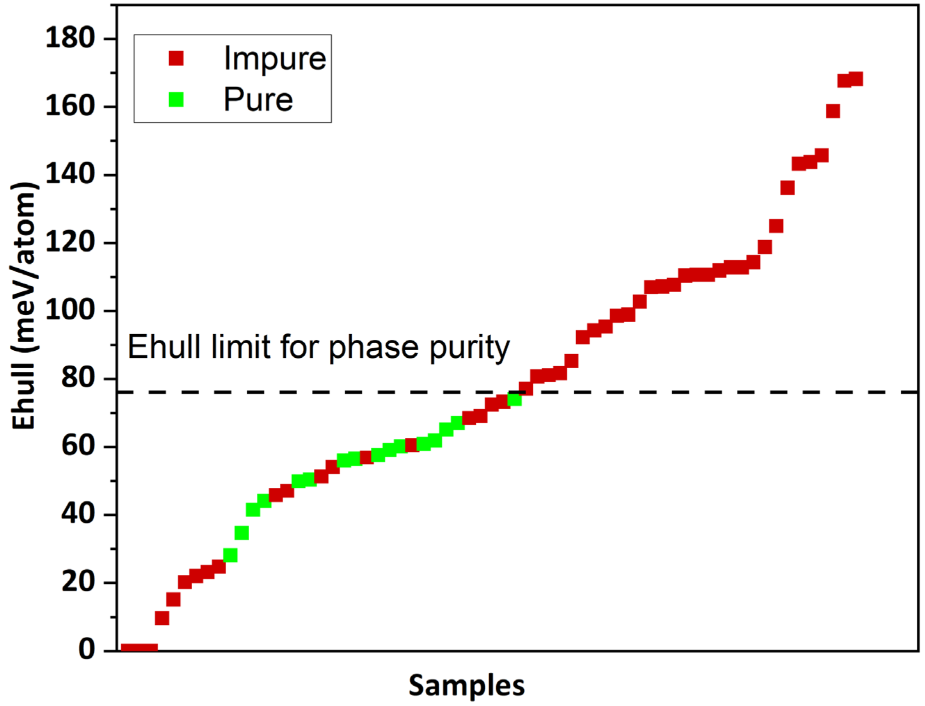
Absorption: $ABO_{3-\delta}+\delta/2O_2(g) \rightarrow ABO_3+\Delta H$, $p_{O2=0.01}$ bar

Desorption: $ABO_3+\Delta H \rightarrow ABO_{3-\delta}+\delta/2O_2(g)$ $p_{O2=0.02}$ bar

$$\Delta G_{\exp} = -\frac{1}{2}RT\ \ln\frac{P_{O_2}}{P^0}$$

Advancement of Sorbents via an Improved DFT Model

Milestone 4.3: Developed an improved DFT model considering the phase stability (in progress)



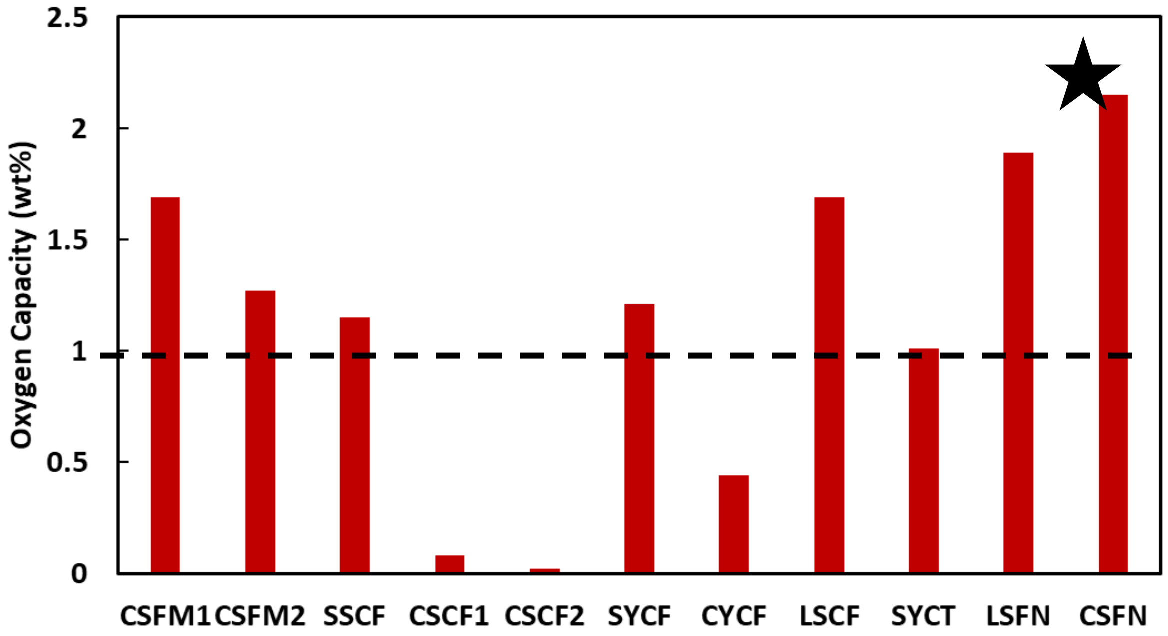
The calculation method for Ehull was taken from the study below:
Source: Morgan et al., Computational Materials Science (2018)

- We predicted thermodynamic stability of 254 structures by calculating energy above convex hull (Ehull)
- All the synthesized samples with pure phases was found to be below an Ehull limit of **75 meV/atom**
- **85** samples below the Ehull limit is currently considered for synthesis and testing
- **Limitation:** Ehull calculations are done using the ground state formation energies, which does not reflect the temperature effects

Advancement of Sorbents via an Improved DFT Model

Milestone 5.1: Obtain four or more perovskite OSs with >2 wt.% oxygen storage capacity (in progress)

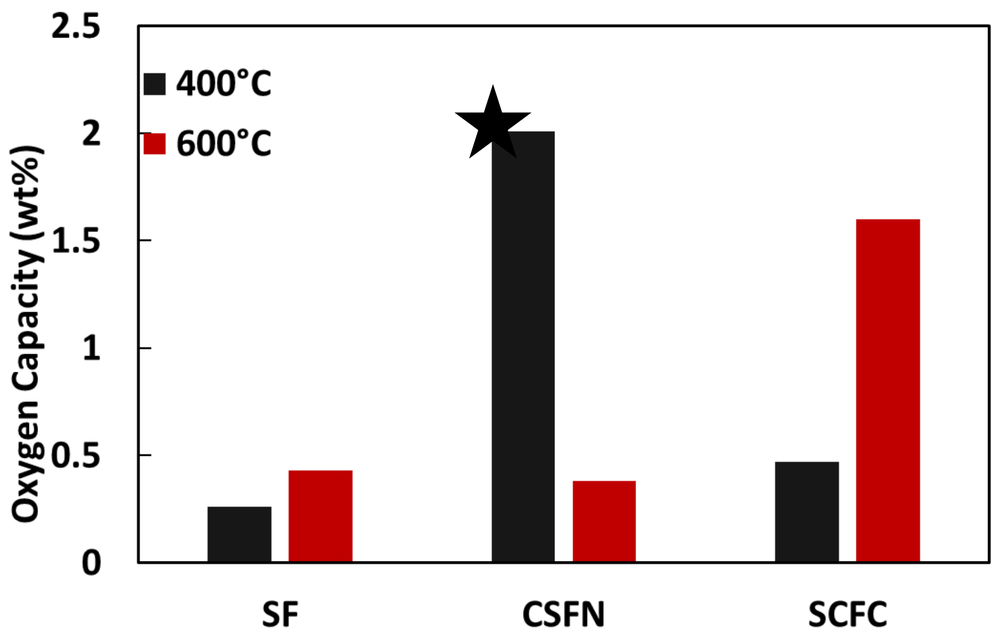
oxygen capacities under the conditions of 600°C- 20% O_2 and 400 °C-Ar



- Candidates with phase purity are tested for their oxygen capacity
- 8 of the tested sorbent candidates showed capacities of ≥1 wt% under temperature and pressures swing conditions
- Particularly, CSFN achieved as high as **2.15 wt%**
- **These results establish the effectiveness of the improved DFT model**

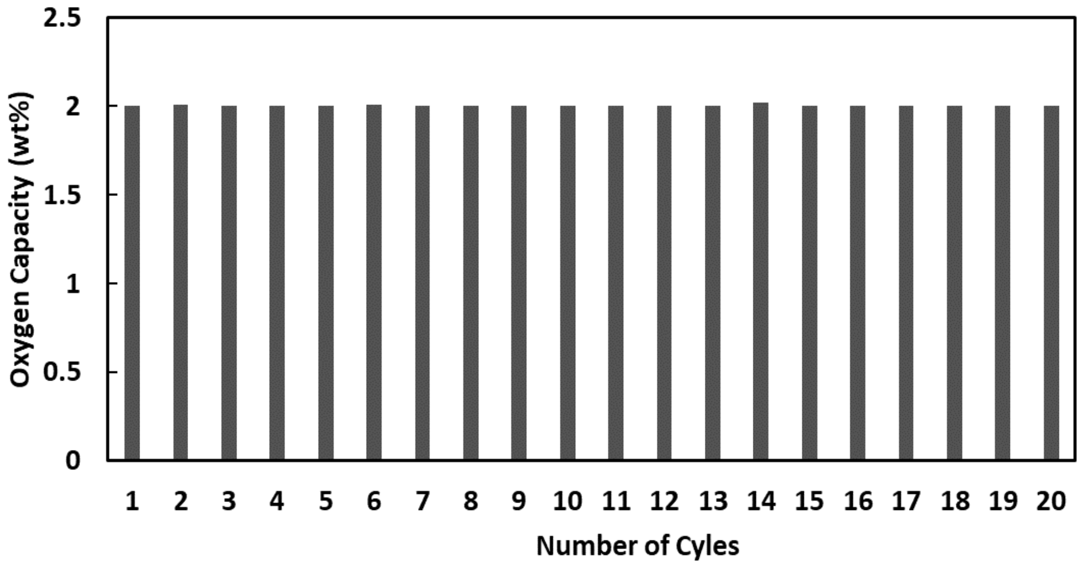
Advancement of Sorbents via an Improved DFT Model

Isothermal oxygen capacities under a pressure swing between 20% O_2 and 1% O_2



- CSFN , which was predicted through DFT model, exhibited superior oxygen capacity to SCFC8291 at lower temperatures (400°C)
- CSFN maintained an isothermal oxygen capacity of 2 wt% over 20 cycles

Limitation: At such low temperatures, kinetics is limited which require longer desorption time



Summary

Reactor Modelling and Techno-economic Analyses:

- A reactor modeling was conducted to optimize L/D ratio and other performance parameters
- A techno-economic analysis to achivee the cost of oxygen production as low as \$65/ton O_2

Entropy Stabilized Perovskite Sorbents :

- Entropy stabilized perovskite sorbents were synthesized, tested and characterized
- The stability of SKFCN was demonstrated over 50 cycles

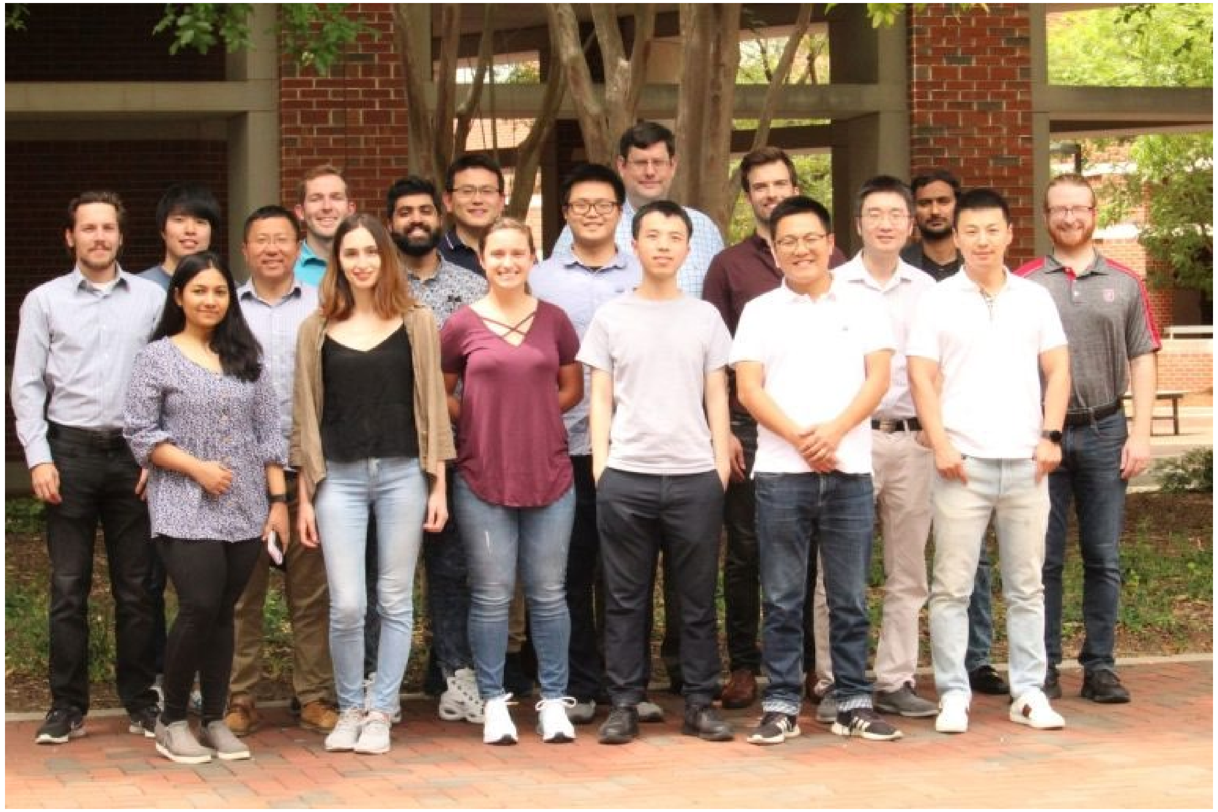
Advancement of Sorbents via an Improved DFT Model:

- An improved DFT model that considers phase purity was developed
- The oxygen capacities of the materials with phase purity were tested
- CSFN was found as a promising sorbent for low temperature operations of REM-ASU

Future Work

- Phase purity prediction of DFT model will be further supported via additional calculations that can reflect the structures at high temperatures
- Additional characterization and optimization will be conducted for CSFN to optimize operating temperature and kinetics for sake of the efficiency
- Alternative candidates will be searched by continuing the experimental evaluation based on the results of DFT model
- Long-term performance of the promising sorbents will be evaluated for pilot testing

Acknowledgments



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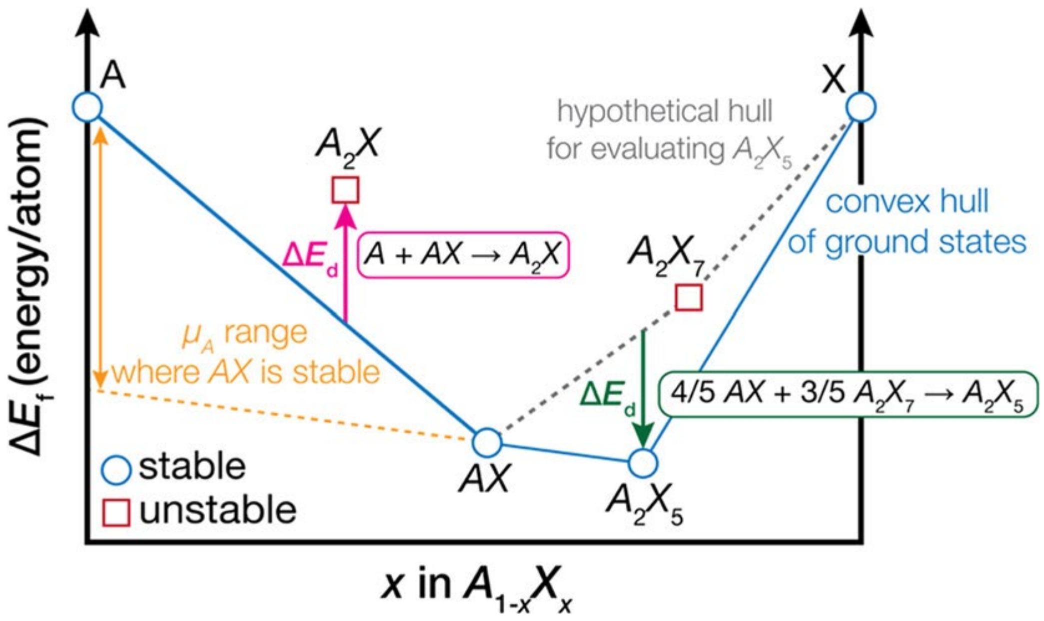

Source: Bartel et al., Computational Materials Design(2022)