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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Outline

- Project Description and Objectives
- Project Update
- Preparing Project for Next Steps
- Concluding Remarks

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 modular air separation technology to achieve the DOE goal to support the oxidant feed of an oxygen-blown REMS gasifier scaled to a range of 1 to 5 MW**

Technology benchmarking

	Cryogenic	Chemical looping
Status	mature	developing
Economic range (sTPD)	>20	Undetermined
Energy consumption (MJ/kg O_2)	0.791	~0.2*
Thermodynamic efficiency (%)	25%	>75%
Oxygen purity (%)	99+	99+
By product capability	Excellent	Poor

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

* Based on a process analysis by Moghtaderi, et al. Energy Fuels, 2010, 24, 190–198.

Status of Project

Status at beginning of project:

- Developed (high temperature) oxygen sorbents (OSs) with high oxygen capacity and reaction kinetics, tested in a thermogravimetric analyzer (TGA)
- Preliminary process analysis.

Current status of project:

- Developed and demonstrated both “high temperature” and “low temperature” OSs
- Scalable production of oxygen sorbents: produced and tested two, 1 kg/batch OSs, with three additional, 1 kg/batches being produced
- Developed a preliminary REM-ASU design with energy consumption of 0.23-0.54 MJ/kg O_2, which is **32-70% less comparing to benchmark cryogenic air separation**
- 10,000 cycles with <3% degradation, and optimized operating conditions to improve oxygen purity >95%
- **Teamed up with Thermosolv, LLC and sought feedback from a leading industrial gas company**

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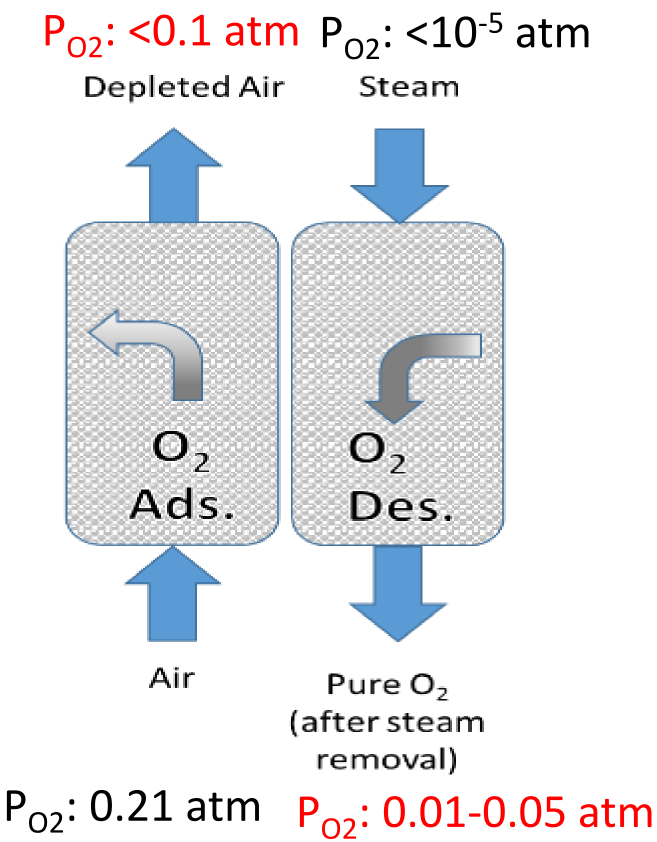
Publication and conference presentations

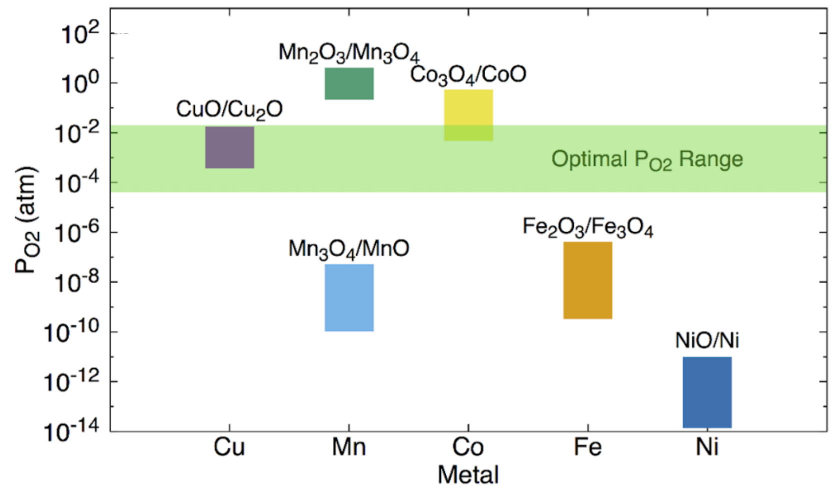
- Jian Dou, Emily Krzystowczyk, Xijun Wang, Thomas Robbins, Liang Ma, Xingbo Liu, and Fanxing Li. *A and B-site Co-Doped $SrFeO_3$ Oxygen Sorbents for Enhanced Chemical Looping Air Separation* ChemSusChem 2020, 13, 385-393.
- Emily Krzystowczyk, Xijun Wang, Jian Dou, Vasudev Haribal, Fanxing Li. *Substituted $SrFeO_3$ as Robust Oxygen Sorbents for Thermochemical Air Separation: Correlating redox performance with compositional and structural properties.* Physical Chemistry Chemical Physics 2020, 22, 8924-8932.
- Jian Dou, Emily Krzystowczyk, Xijun Wang, Anthony R Richard, Thomas Robbins, and Fanxing Li. *$Sr_{1-x}Ca_xFe_{1-y}Co_yO_{3-\delta}$ as facile and tunable oxygen sorbents for Chemical Looping Air Separation* Journal of Physics: Energy 2020, 2, 025007.
- Emily Krzystowczyk, Jian Dou, Xijun Wang, and Fanxing Li*. Perovskite Oxygen Sorbents for "Low Temperature" Thermochemical Air Separation: Correlating Compositions with Redox Performance* AIChE Annual Meeting, Orlando, 2019.

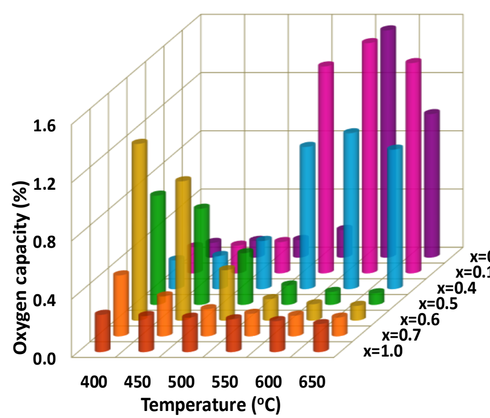
Publication and conference presentations

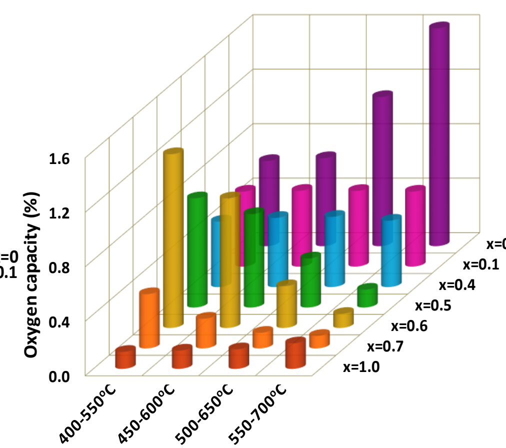
- Jian Dou, Emily Krzystowczyk, Amit Mishra, Xingbo Liu, Fanxing Li*. *Perovskite promoted mixed cobalt-iron oxides for enhanced chemical looping air separation.* ACS Sustainable Chem. Eng. 2018, 6, 15528-15540.
- Amit Mishra, Tianyang Li, Fanxing Li*, and Erik Santiso*. *Oxygen Vacancy Creation Energy in Mn-Containing Perovskites: An Effective Indicator for Chemical Looping with Oxygen Uncoupling*. Chemistry of Materials, 2018, 31, 689-698.
- Jian Dou, Emily Krzystowczyk, Amit Mishra, and Fanxing Li*. *Radically Engineered Modular Air Separation System with Tailored Oxygen Sorbents*. DOE meeting, Washington DC, 2018
- Jian Dou, Emily Krzystowczyk, Amit Mishra, Xingbo Liu, and Fanxing Li*. *Perovskite Promoted Mixed Co-Fe Oxides for Enhanced Chemical Looping Air Separation*. ACS meeting, Orlando, 2019
- Xijun Wang, Emily Krzystowczyk, Jian Dou, Fanxing Li. *Electronic Descriptors for Oxygen Vacancy Formation and Migration in* $SrFeO_3$*-based Perovskites. In preparation.*

Oxygen Sorbent Development: Challenges and Opportunities









Mixed oxides are necessary in order to match P_{O2} of oxygen carriers with air separation conditions. Year 1 and Year 2 have resulted in promising mixed oxide sorbent suitable for different temperature ranges.

Milestone 7.1 (Q9) Scale-up Synthesis of OS

M3.1: Synthesize two 25 kg batch OS

- Sol-gel synthesis performed in-house by Thermosolv in batches up to 1 kg
- Multi-batch approach to produce 25 kg sorbents
- Two different compositions prepared/tested , three more will be made

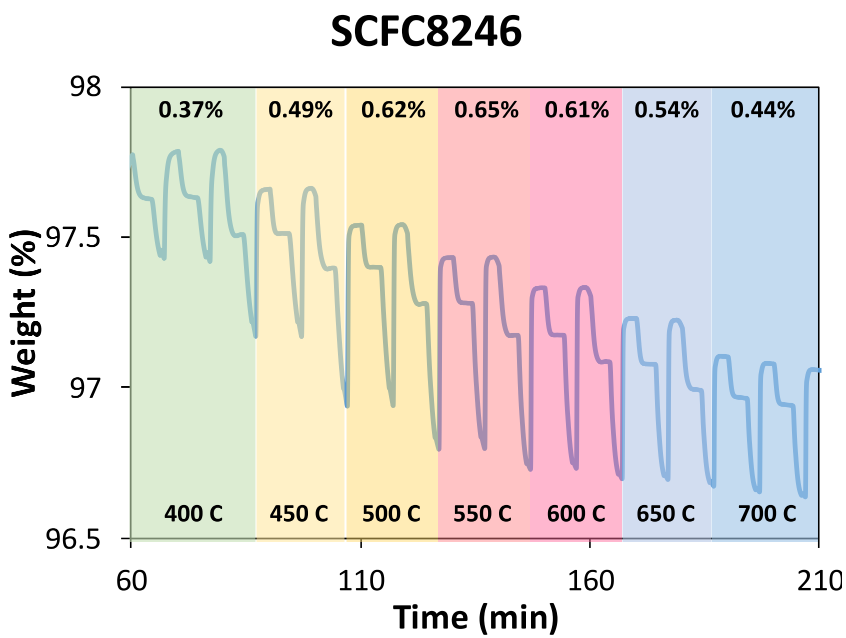
Scale-up Synthesis of OS

List of oxygen sorbents prepared at kg/batch scale:

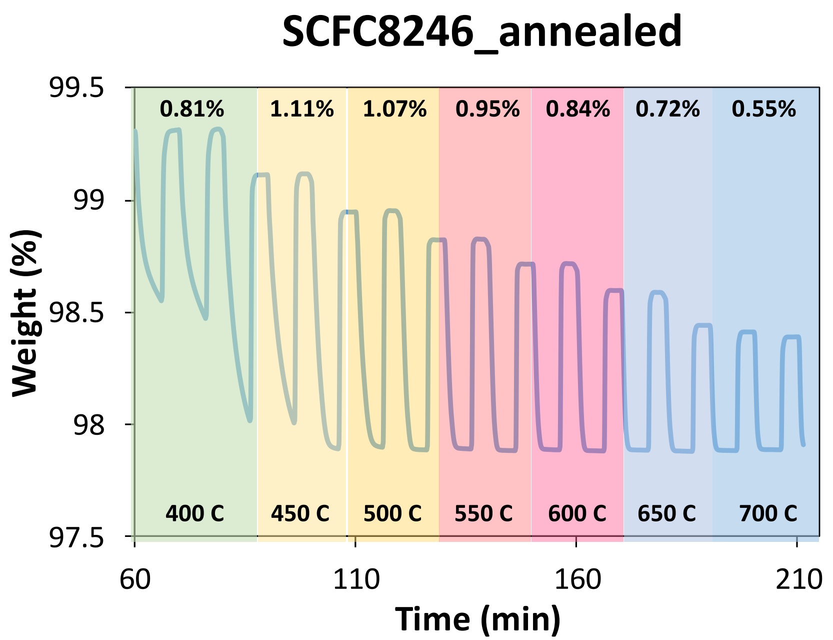
$Sr_{0.8}Ca_{0.2}Fe_{0.4}Co_{0.6}O_{3-\delta}$ (SCFC8246)

$Sr_{0.8}Ca_{0.2}Fe_{0.9}Co_{0.1}O_{3-\delta}$ (SCFC8291)

Evaluation of Large-Scale Synthesized Oxygen Sorbents



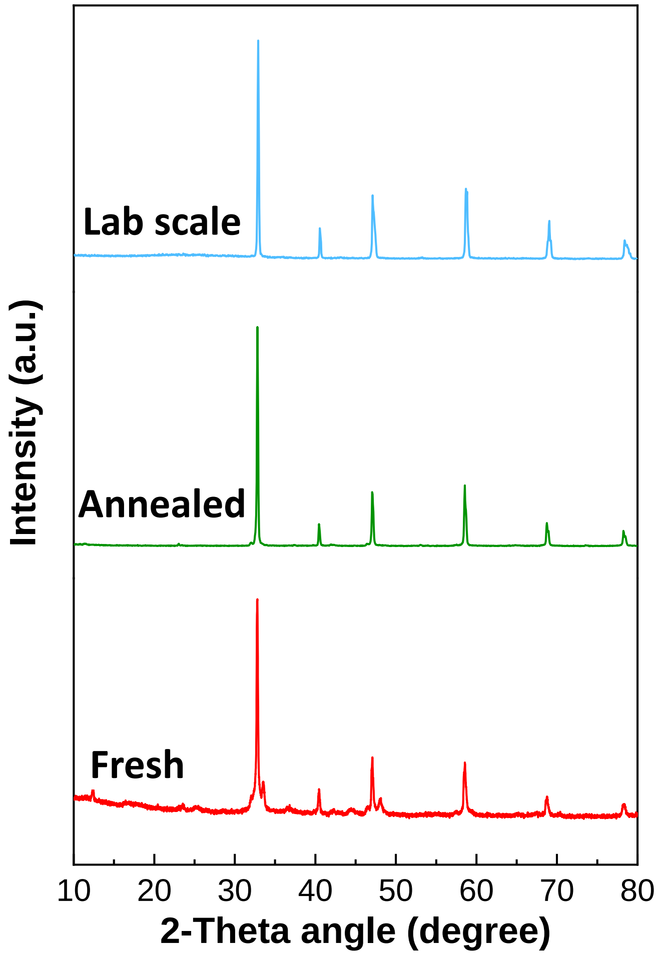
1000°C, 8 h



1000°C, 8 h; followed by 1100°C, 12 h

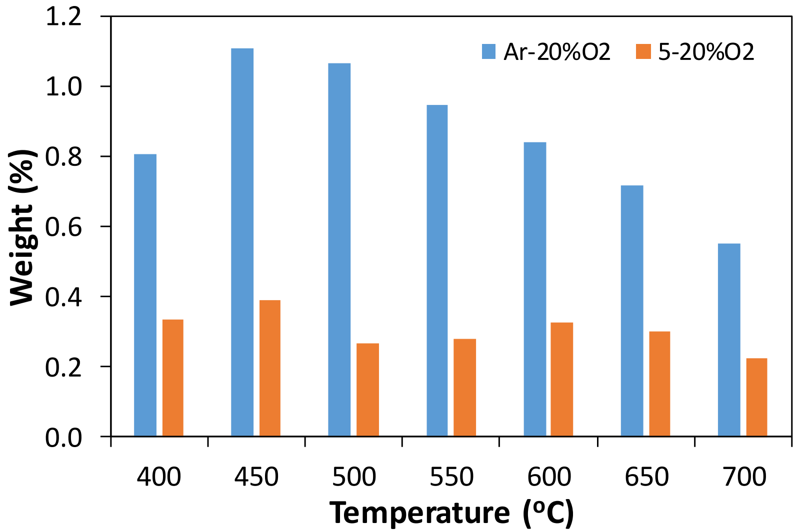
Annealing of large scale synthesized SCFC8246 is critical to obtain high oxygen capacity and fast kinetics

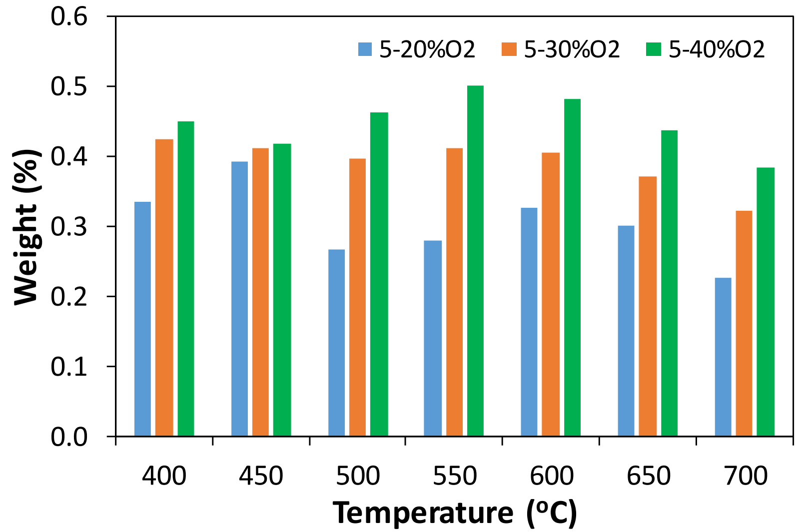
XRD of annealed SCFC8246



Annealing of large scale synthesized SCFC8246 to obtain pure perovskite phase, same as lab scale synthesized sample

Effect of redox condition on oxygen capacity of annealed SCFC8246

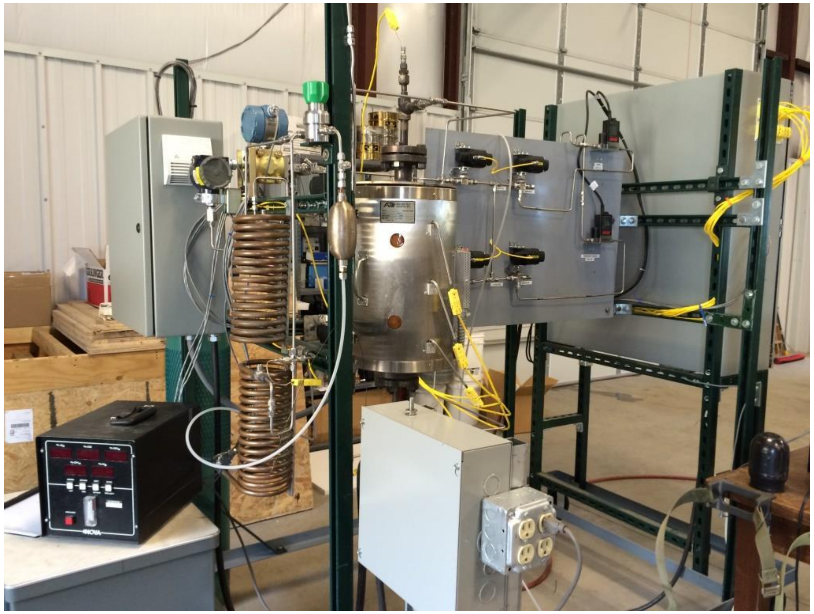


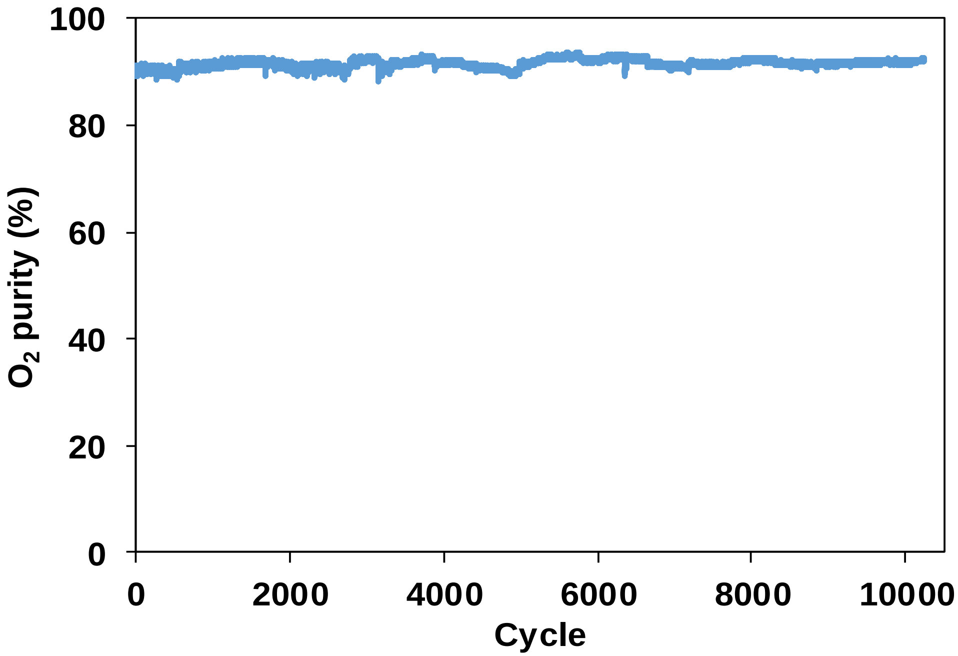


- Annealed SCFC8246 has >1 w.t.% oxygen capacity at 450-500°C
- Oxygen capacity increases with P_{O2} at oxygen absorption stage

Milestone 8.1 (Q11) Sorbent Stability

M3.2 Produce >95% pure O_2 over 2000 cycles with less than 10% decrease in oxygen capacity

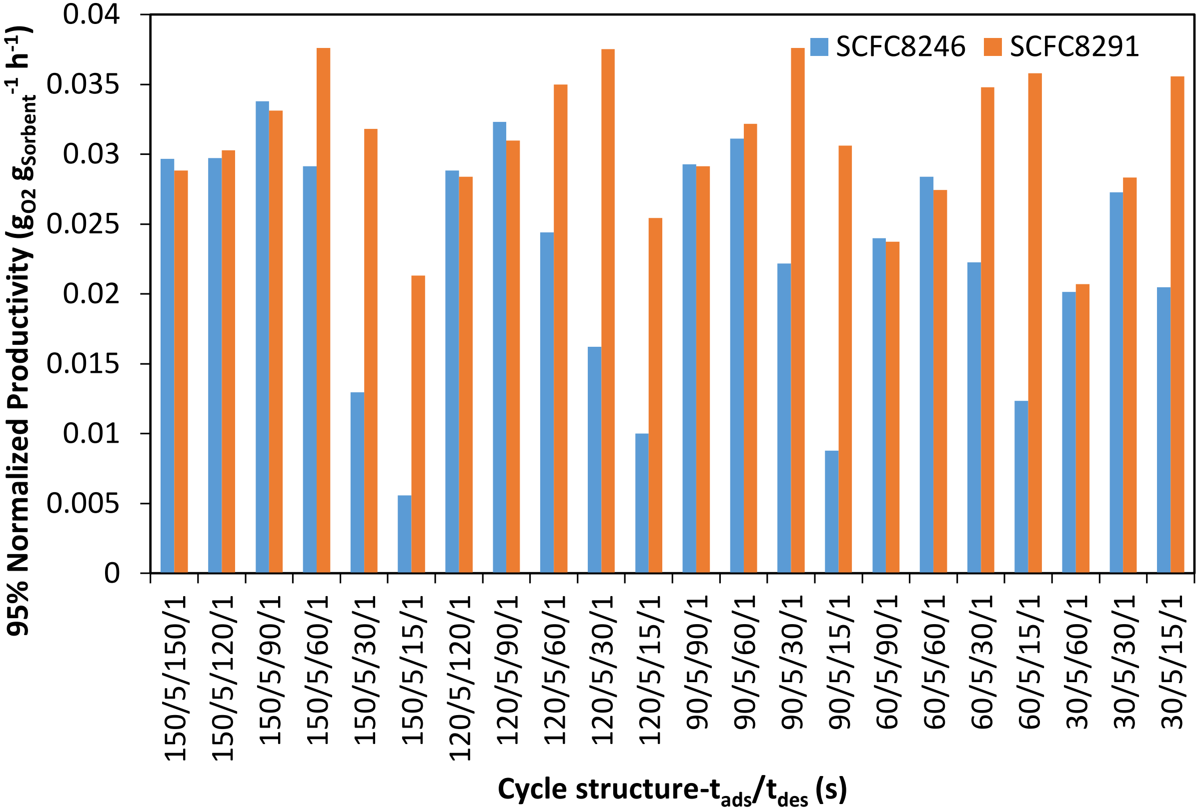




SCFC8246 is stable for 10,000 cycles oxygen production at 25 psig and 600 °C with cycle structure of 90s/5s/60s/1s

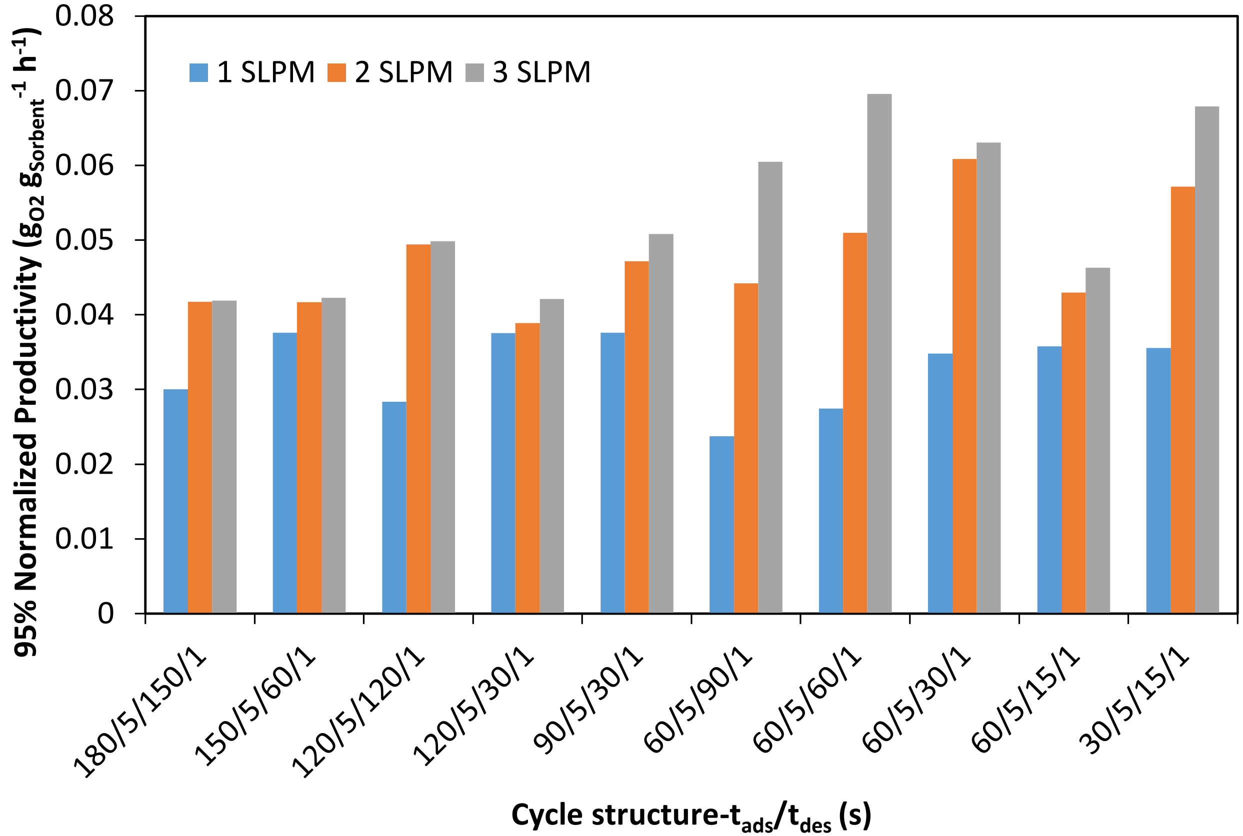
THERMOSOLV LLC

Effect of Cycle Structure on Oxygen Productivity



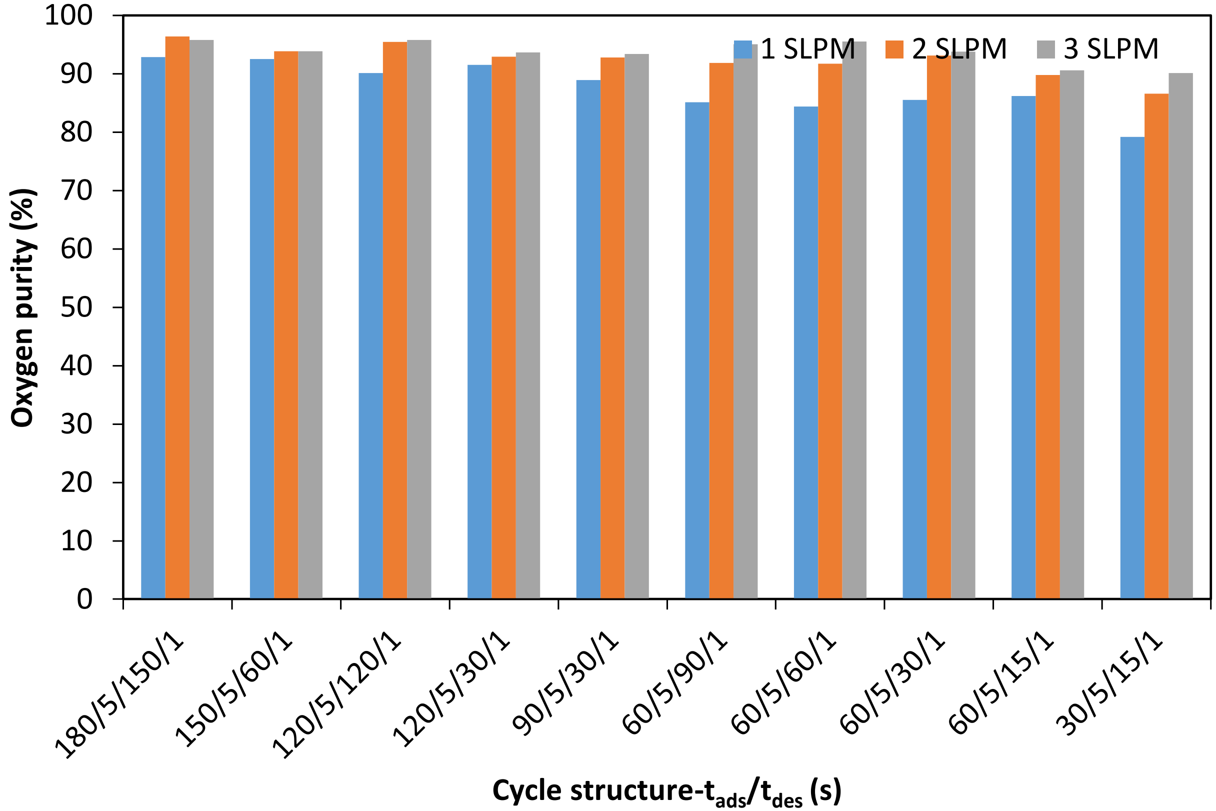
Optimize operating condition to achieve oxygen productivity up to 0.037 $g_{O2}\ g_{sorbent}^{-1}\ h^{-1}$ at 25 psi, 600 ^oC, and 1 SLPM

Effect of Flow Rate on Oxygen Productivity



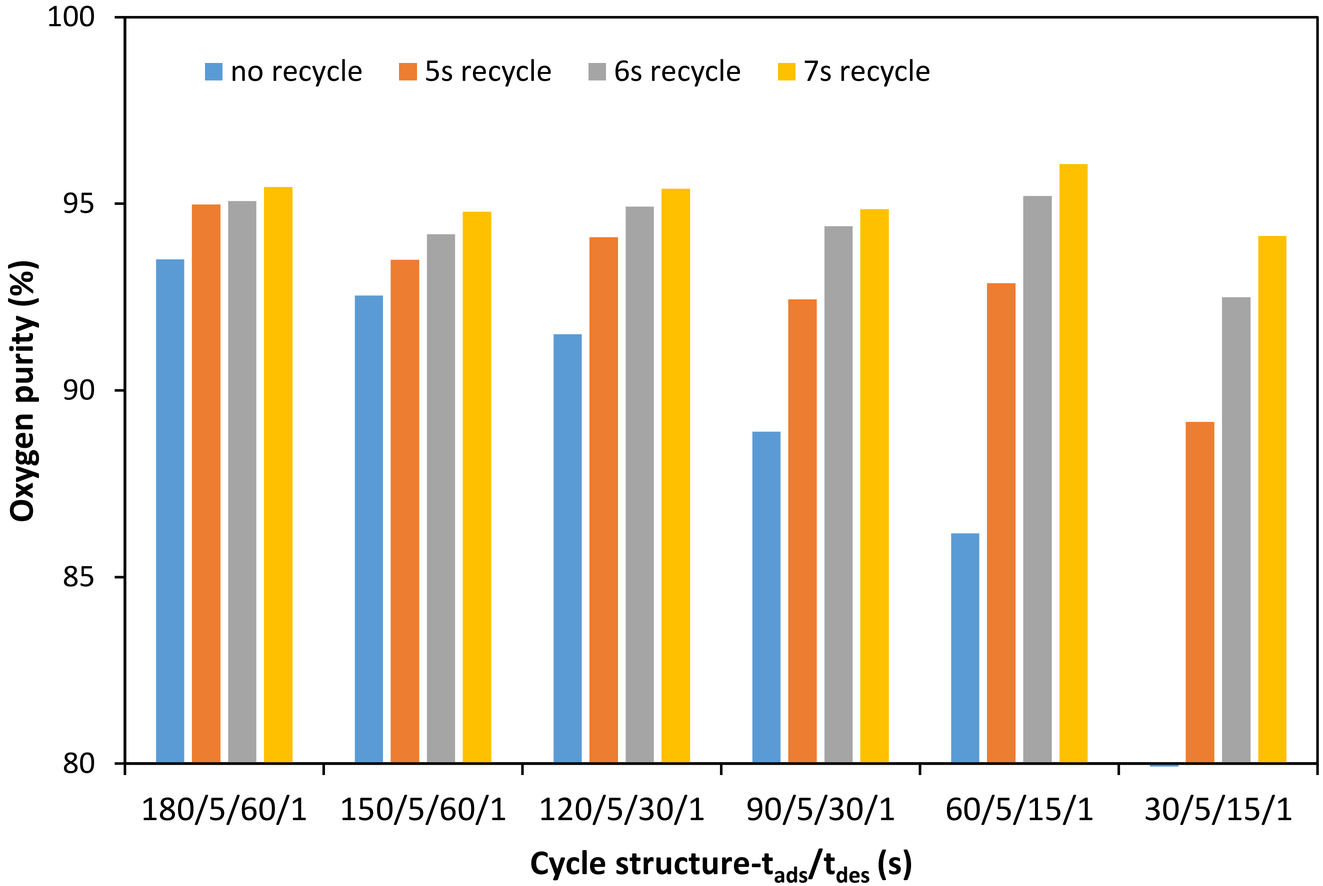
Up to 0.069 g_{O2} $g_{sorbent}^{-1}$ h^{-1} oxygen productivity by increasing air flow rate from 1 to 3 SLPM at 25 psi and 600 ^{o}C for SCFC8291 OS

Effect of Flow Rate on Oxygen Productivity



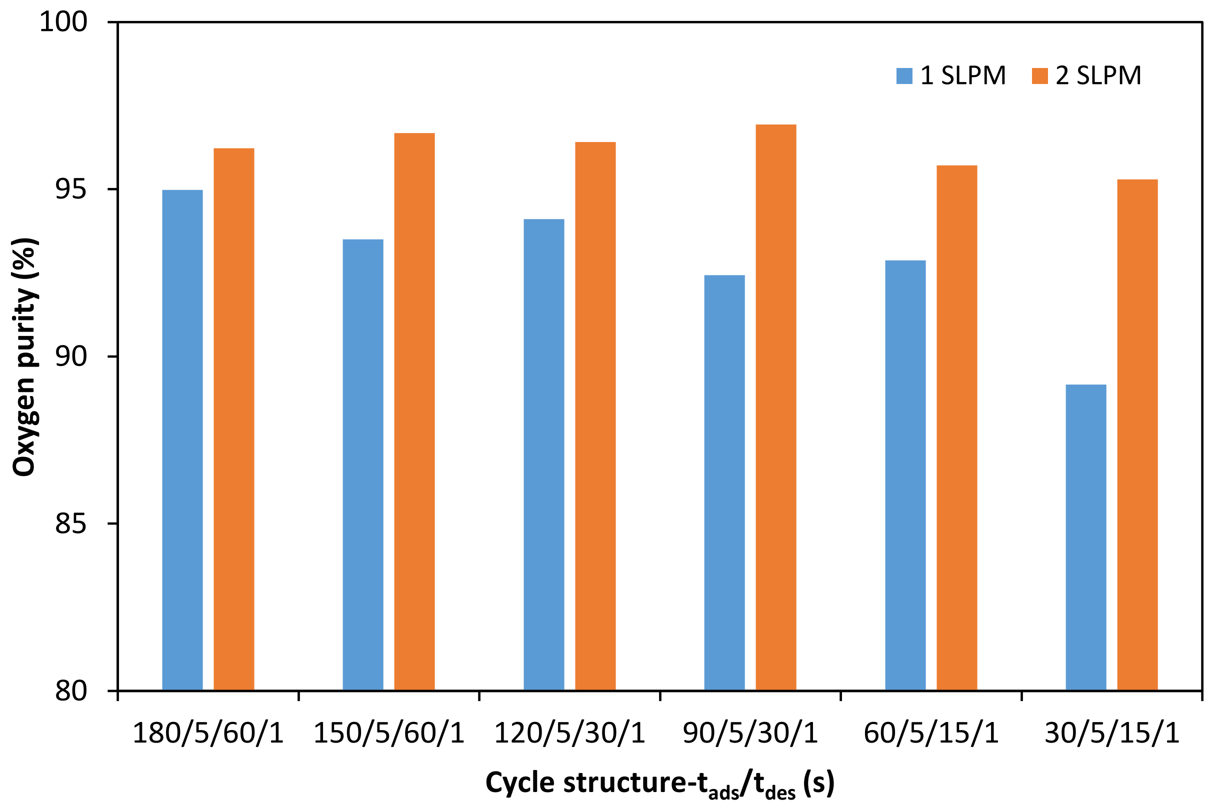
Oxygen purity increased to >95% with 3 SLPM air flow rate at 25 psi and 600 ^{o}C for SCFC8291 OS

Effect of Oxygen Recycle



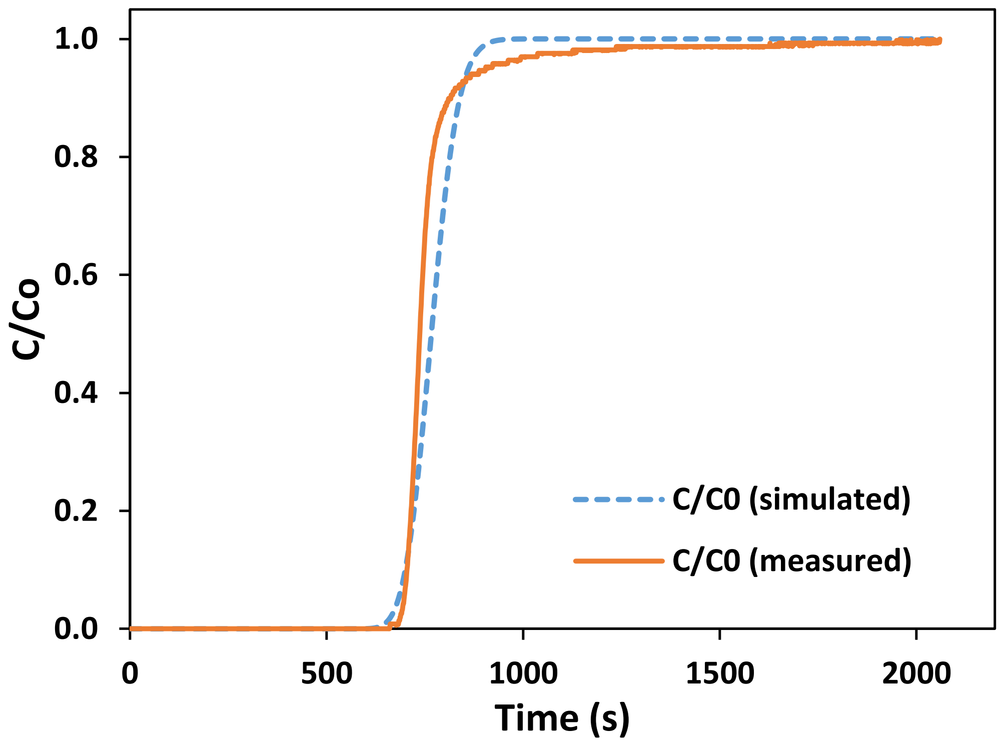
Recycle of oxygen for purging increases purity >95% at 25 psi, 600 ^oC and 1 SLPM for SCFC8291 sorbent

Effect of flow rate and oxygen recycle



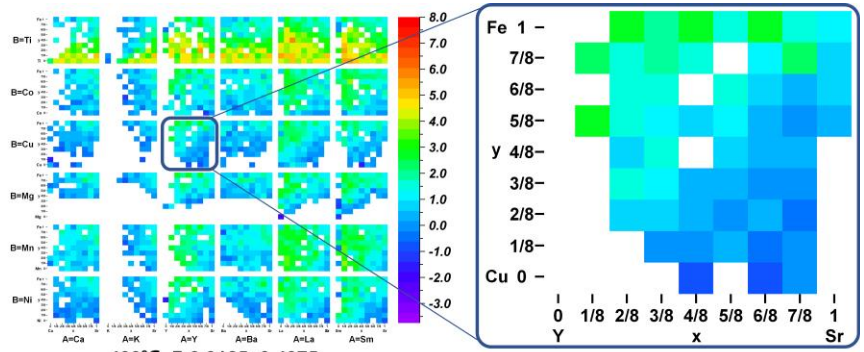
Oxygen with >95% purity obtained with 2 SLPM air flow rate and 5 s cycle of oxygen stream at 25 psi and 600 ^oC for SCFC8291

Breakthrough curve of SCFC8291 and data fitting

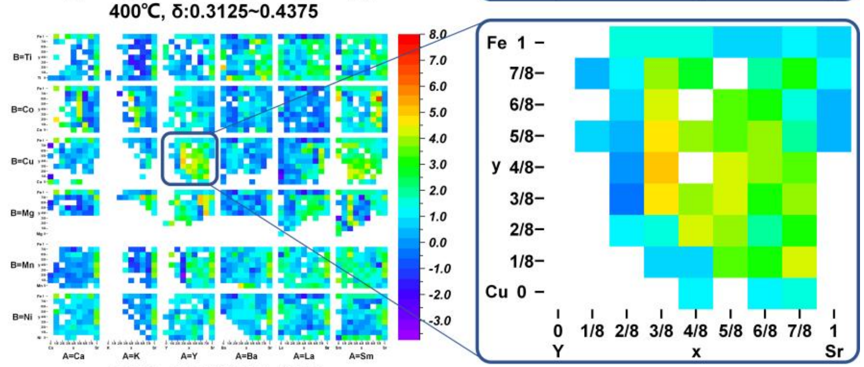


Best fitting of breakthrough curve for SCFC8291 at 20 psi and 600°C with Péclet number of 400

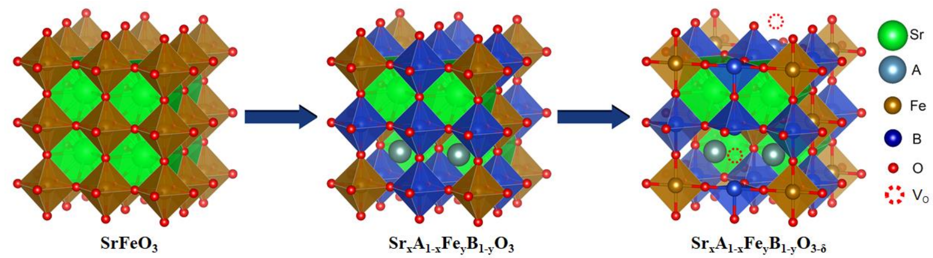
DFT high-throughput screen of $SrFeO_3$-based oxygen sorbents



400℃, δ:0.3125~0.4375



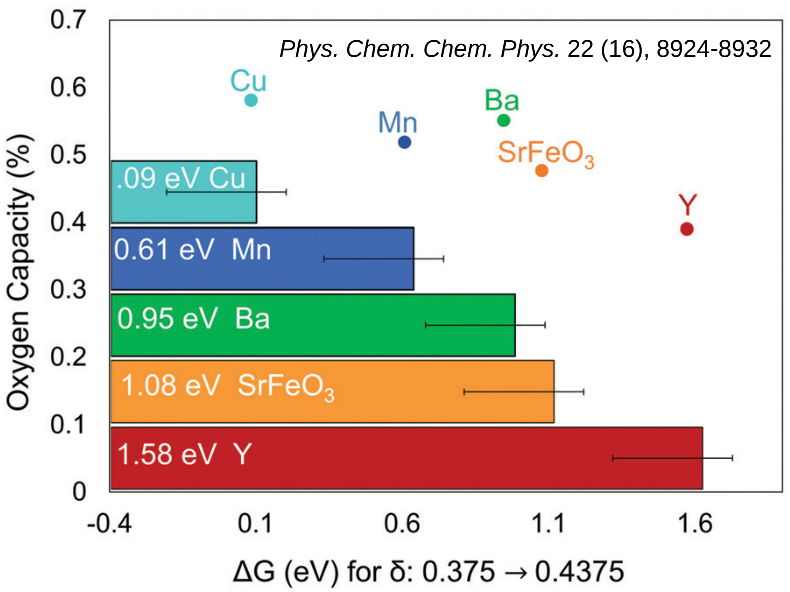
700℃, δ:0.3125~0.4375

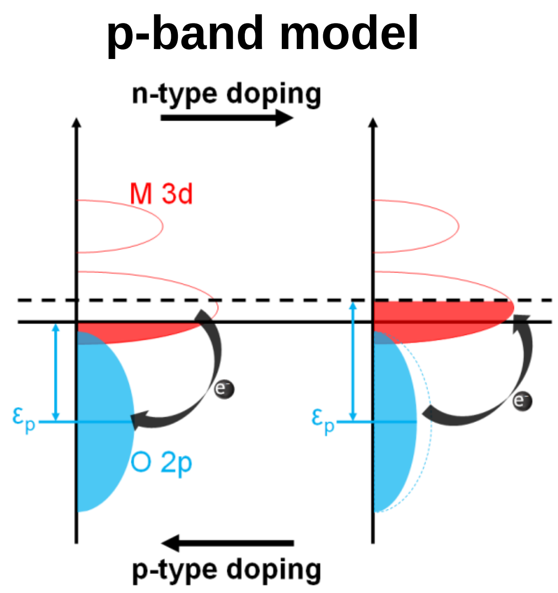


The Gibbs free energies of vacancy formation of 2401 $Sr_xA_{1-x}Fe_yB_{1-y}O_3$ (A=Sr, Ca, K, Y, Ba, La, Sm; B=Fe, Co, Cu, Mn, Mg, Ni, Ti) candidates were computed, and the ones with suitable ΔG were selected for experimental verification.

delta_G	400 ℃			500 ℃			600 ℃			700 ℃		
δ	0.25-0.375	0.375-0.5	0.3125-0.4375	0.25-0.375	0.375-0.5	0.3125-0.4375	0.25-0.375	0.375-0.5	0.3125-0.4375	0.25-0.375	0.375-0.5	0.3125-0.4375
SrBaFeCo-0.625-0.375-0.75-0.25	0.42484	0.40517	0.415	0.3417	0.26436	0.30303	0.26276	0.13155	0.19716	0.18215	0.00103	0.09159
SrBaFeCo-0.875-0.125-0.625-0.375	0.38078	0.32622	0.3535	0.28823	0.21574	0.25198	0.19994	0.10914	0.15454	0.11002	0.00122	0.05562
SrCaCo-0.25-0.75-1	0.34273	0.4499	0.39631	0.25299	0.29854	0.27577	0.16616	0.15183	0.159	0.07696	0.00442	0.04069
SrYNi-0.375-0.625-1	0.62852	0.37872	0.50362	0.50714	0.25408	0.38061	0.38983	0.13334	0.26159	0.27096	0.01126	0.14111
SrSmFeNi-0.625-0.375-0.5-0.5	0.49512	0.3933	0.44421	0.3774	0.27153	0.32447	0.26375	0.15396	0.20885	0.14865	0.03483	0.09174
SrSmFeNi-0.875-0.125-0.75-0.25	0.59237	0.35304	0.47271	0.4741	0.2597	0.3669	0.35992	0.17053	0.26522	0.24446	0.08	0.16223
SrYFeMg-0.875-0.125-0.625-0.375	0.34318	0.44693	0.39506	0.238	0.32281	0.28041	0.13674	0.20284	0.16979	0.03402	0.08138	0.0577
SrSmFeCu-0.5-0.5-0.5-0.5	0.47204	0.44848	0.46026	0.32737	0.3255	0.32644	0.18668	0.20655	0.19661	0.04436	0.08603	0.0652
SrCaFeCo-0.75-0.25-0.875-0.125	0.65947	0.33868	0.49908	0.57603	0.2552	0.41561	0.49547	0.17714	0.3363	0.41277	0.09869	0.25573
SrCaFeMg-0.75-0.25-0.875-0.125	0.49286	0.40975	0.4513	0.38998	0.31142	0.3507	0.29108	0.21697	0.25402	0.19058	0.12117	0.15588
SrCaMn-0.375-0.625-1	0.49732	0.4664	0.48186	0.35827	0.35155	0.35491	0.22289	0.24063	0.23176	0.08607	0.12793	0.107
SrLaFeCo-0.75-0.25-0.125-0.875	0.56898	0.48883	0.52891	0.46068	0.37281	0.41675	0.35617	0.26107	0.30862	0.25008	0.14796	0.19902
SrLaCo-0.75-0.25-1	0.42458	0.41717	0.42087	0.31877	0.33044	0.32461	0.21683	0.2477	0.23227	0.11331	0.1635	0.13841
CaFeCu-1-0.875-0.125	0.66663	0.31811	0.49237	0.55459	0.26356	0.40908	0.44651	0.21423	0.33037	0.33685	0.16451	0.25068
SrLaFeCo-0.625-0.375-0.125-0.875	0.61017	0.47701	0.54359	0.46752	0.37094	0.41923	0.32864	0.26878	0.29871	0.18821	0.16525	0.17673
SrYFeCo-0.75-0.25-0.125-0.875	0.3523	0.54006	0.44618	0.27733	0.41306	0.34519	0.20646	0.28998	0.24822	0.13413	0.16531	0.14972
SrKFeCo-0.875-0.125-0.75-0.25	0.30173	0.4267	0.36422	0.20033	0.33836	0.26934	0.10301	0.25399	0.1785	0.00423	0.16821	0.08622
SrLaFeNi-0.25-0.75-0.125-0.875	0.40379	0.62969	0.51674	0.31558	0.47809	0.39684	0.23126	0.33047	0.28087	0.14554	0.18109	0.16332
SrCaFeCu-0.375-0.625-0.875-0.125	0.516	0.44193	0.47896	0.39883	0.35303	0.37593	0.28552	0.26837	0.27694	0.17088	0.1823	0.17659
SrFeNi-1-0.875-0.125	0.61841	0.49536	0.55688	0.52529	0.39938	0.46234	0.43635	0.3074	0.37187	0.3459	0.21385	0.27987
SrCaFeMn-0.375-0.625-0.75-0.25	0.57099	0.47773	0.52436	0.46552	0.39759	0.43156	0.36442	0.32246	0.34344	0.26176	0.24705	0.25441
SrSmFeCu-0.375-0.625-0.375-0.625	0.51085	0.62004	0.56544	0.36573	0.49743	0.43158	0.2245	0.37866	0.30158	0.08169	0.25818	0.16993
SrCaFeCo-0.5-0.5-0.375-0.625	0.35474	0.60924	0.48199	0.24761	0.50678	0.37719	0.14455	0.40842	0.27649	0.03995	0.30868	0.17432
SrYFeCu-0.875-0.125-0.75-0.25	0.50917	0.6404	0.57478	0.39018	0.54926	0.46972	0.27527	0.46209	0.36868	0.159	0.37339	0.2662
SrCaFeMg-0.875-0.125-0.875-0.125	0.64638	0.65777	0.65208	0.54261	0.56427	0.55344	0.44293	0.47481	0.45887	0.34178	0.3839	0.36284
SrBaFeMg-0.875-0.125-0.875-0.125	0.61191	0.65898	0.63545	0.5174	0.57344	0.54542	0.42686	0.49198	0.45942	0.33498	0.4089	0.37194

Theoretical understanding of dopant effects





- n-type doping (larger Δe) → Up-shifting of E_F → More negative ε_p → O anion less active → Higher ΔH (ΔG)
- p-type doping (smaller Δe) → Down-shifting of E_F → More positive ε_p → O anion more active → Lower ΔH (ΔG)

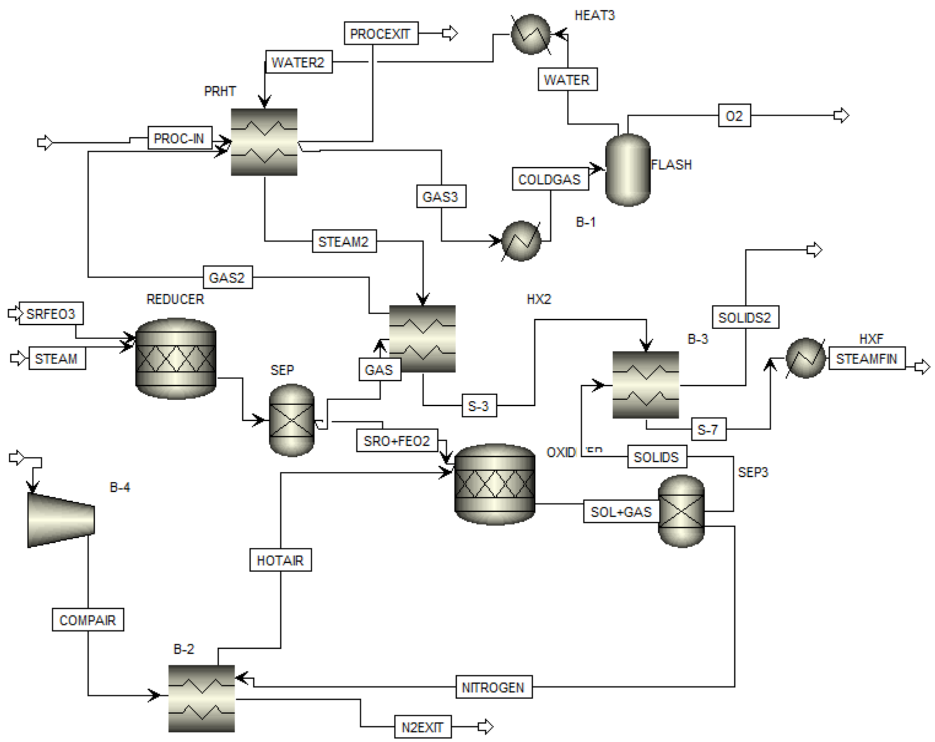
High Throughput Study: Material Screening

T (℃)		
δ		
Likely Candidate (being tested)	Medium Likely Cadidate	Low Likely Candidate
SrBaFeCo-0.875-0.125-0.625-0.375	SrBaFeCo-0.625-0.375-0.75-0.25	SrCaMn-0.375-0.625-1
SrCaCo-0.25-0.75-1	SrYNi-0.375-0.625-1	SrYFeCu-0.875-0.125-0.75-0.25
SrSmFeNi-0.875-0.125-0.75-0.25	SrSmFeNi-0.625-0.375-0.5-0.5	
SrCaFeCo-0.75-0.25-0.875-0.125	SrYFeMg-0.875-0.125-0.625-0.375	
SrCaFeMg-0.75-0.25-0.875-0.125	SrSmFeCu-0.5-0.5-0.5-0.5	
SrLaFeCo-0.75-0.25-0.125-0.875	CaFeCu-1-0.875-0.125	
SrLaCo-0.75-0.25-1	SrLaFeCo-0.625-0.375-0.125-0.875	
SrYFeCo-0.75-0.25-0.125-0.875	SrKFeCo-0.875-0.125-0.75-0.25	
SrCaFeCu-0.375-0.625-0.875-0.125	SrLaFeNi-0.25-0.75-0.125-0.875	
SrCaFeMn-0.375-0.625-0.75-0.25	SrFeNi-1-0.875-0.125	
SrCaFeCo-0.5-0.5-0.375-0.625	SrSmFeCu-0.375-0.625-0.375-0.625	
SrCaFeMg-0.875-0.125-0.875-0.125	SrBaFeMg-0.875-0.125-0.875-0.125	

These additional compositions are being prepared and tested

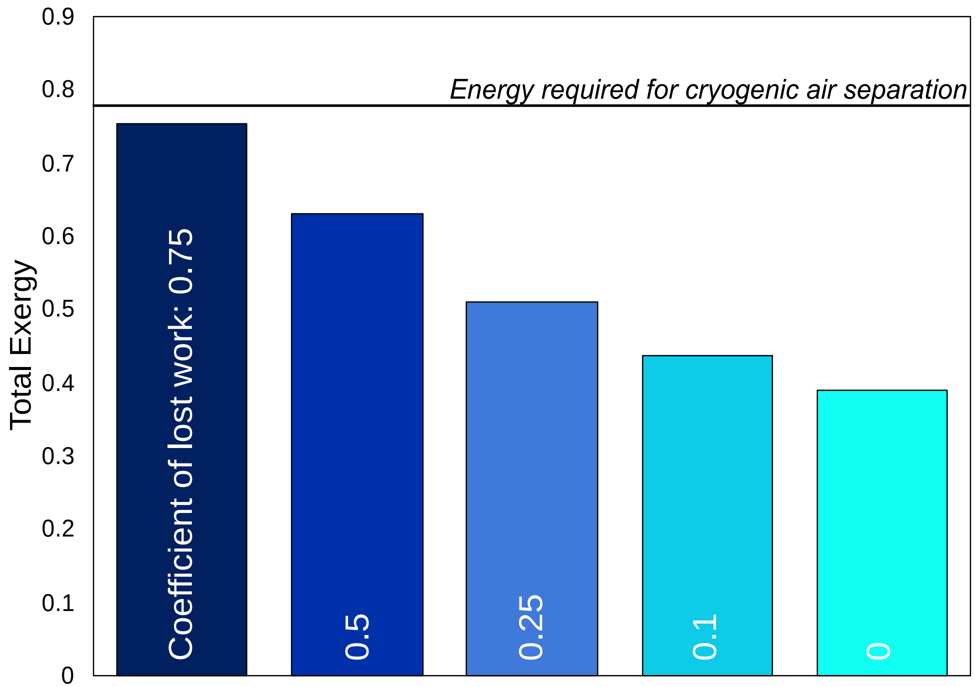
Milestone 6.1 (Q8) Preliminary REM-ASU Design

M6.1: Develop a preliminary REM-ASU design with >30% reduction in energy consumption compared to cryogenic ASU



Aspen Plus flowsheet of the chemical looping air separation (CLAS) system

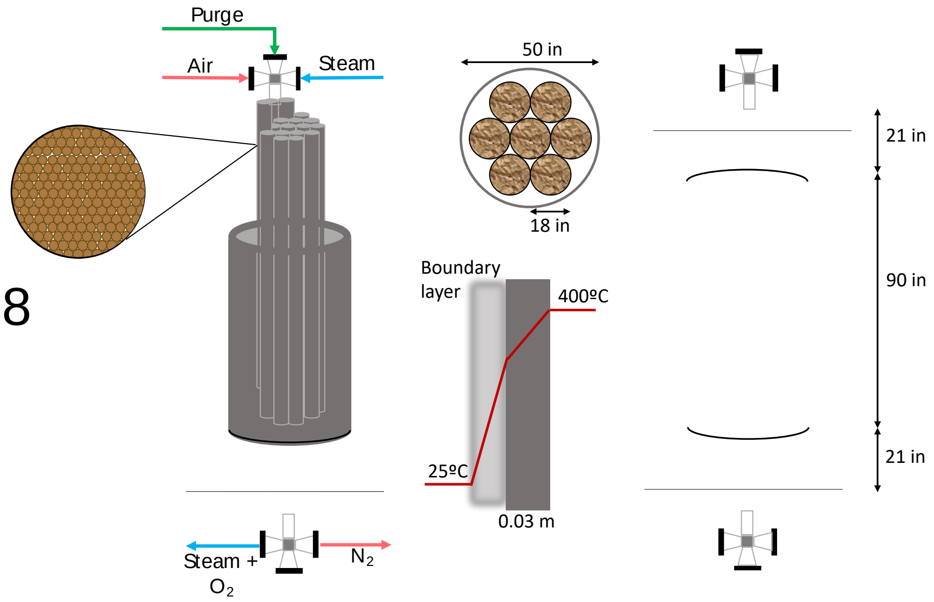
Milestone 6.1 (Q8) Preliminary REM-ASU Design



- Total work for CLAS is estimated to be ~0.75 MJ/kg O_2
- With low grade process heat, energy consumption can be lowered to 0.4 MJ/kg
- REM-ASU can reduce energy consumption by 30-80% comparing to cryogenic air separation

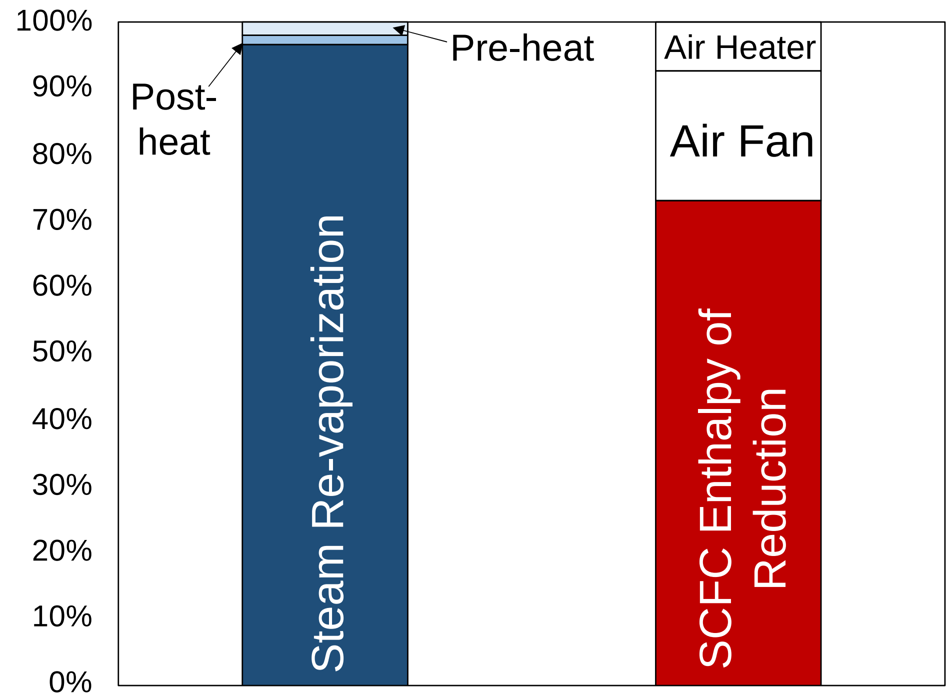
CLAS Aspen Simulation: Reactor Sizing

- Basis: a plant with a 5 MW per day operating capacity
- Kinetics of SCFC 8246 at 600 C, a reduction time of 90 seconds, an oxidation time of 60 seconds, an oxygen capacity of 0.5 wt%
- Oxygen sorbent requirement is 3.88 tons or 2.59 m^3
- Bundled tubes configuration and 7 tubes in a packed formation, the tubes would have a diameter of 18 in and a height to diameter ratio of 5 to 1, the height is 90 in



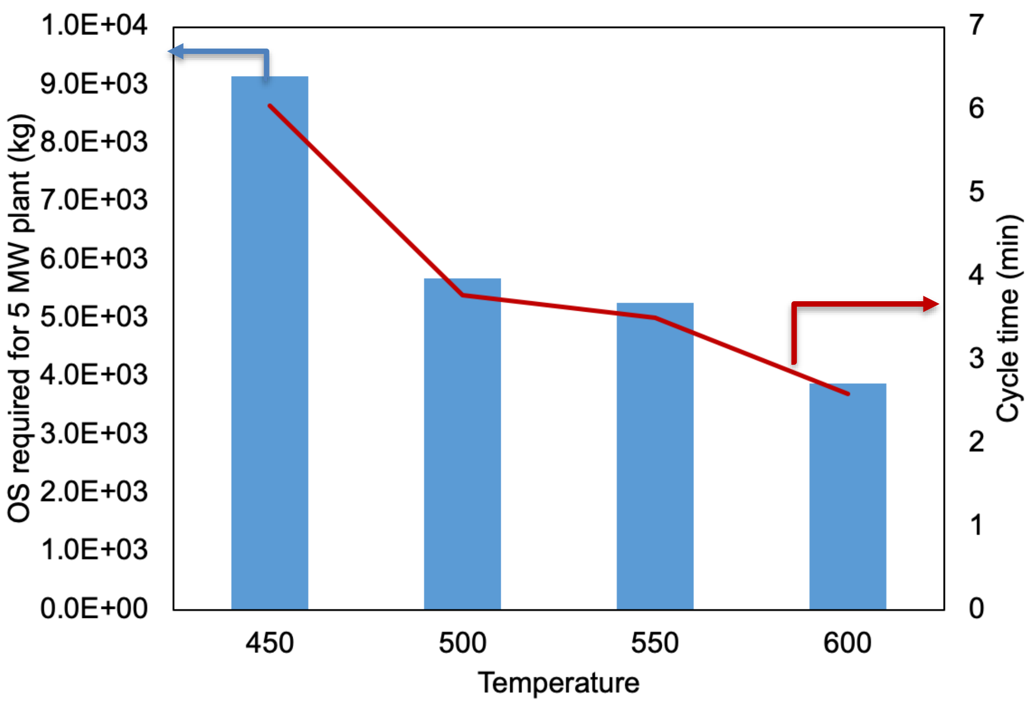
Steam Effects

Total Energy: 0.75 MJ/ kg O_2



Steam vaporization takes up the most energy and accounts for the most lost work

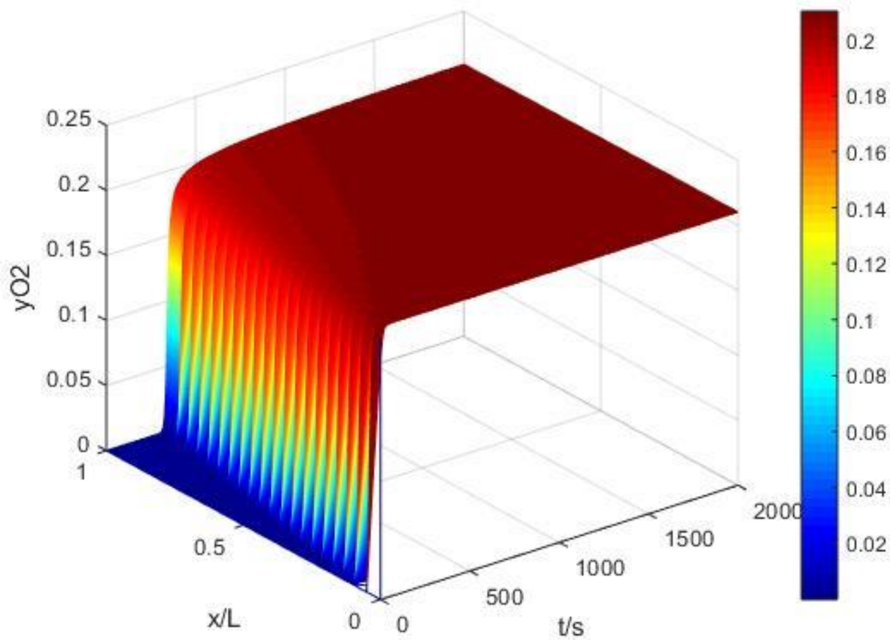
Kinetics for SCFC 8246

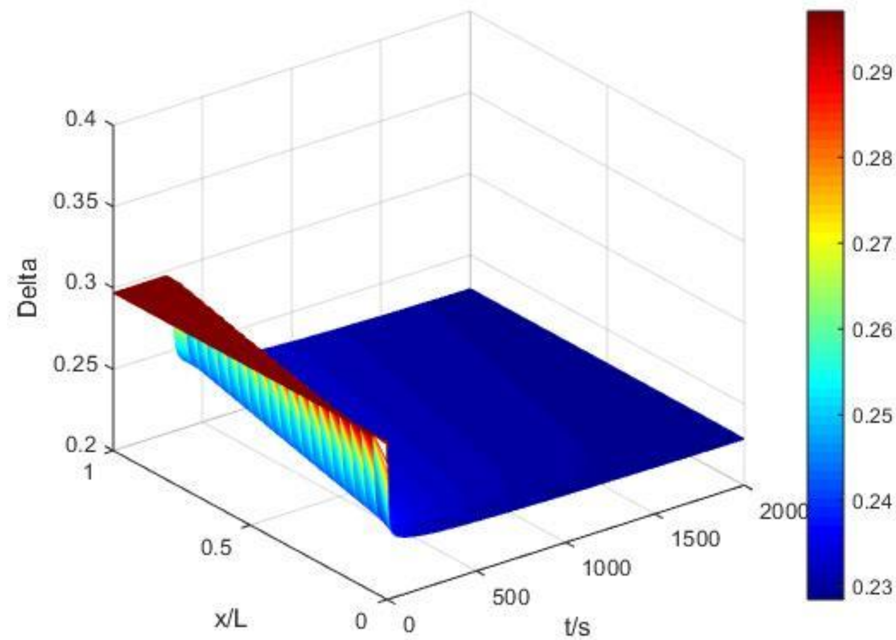


- SCFC shows high oxygen capacity at low temperatures but has relatively poor kinetics
- Higher temperature (600 ℃) allows for significantly less oxygen sorbent and reduces cycle time

Detailed Absorber Modeling (preliminary)

- Adsorption

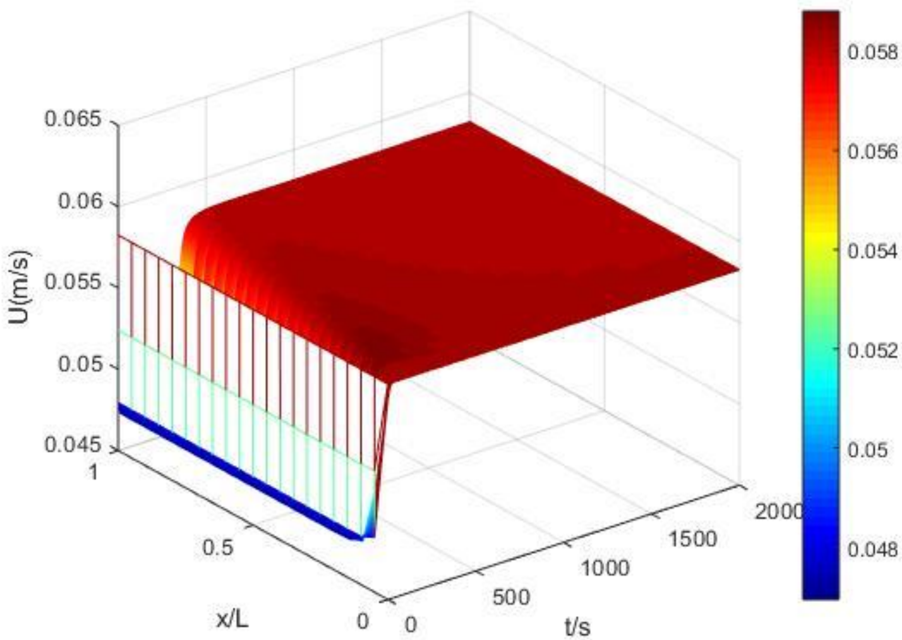


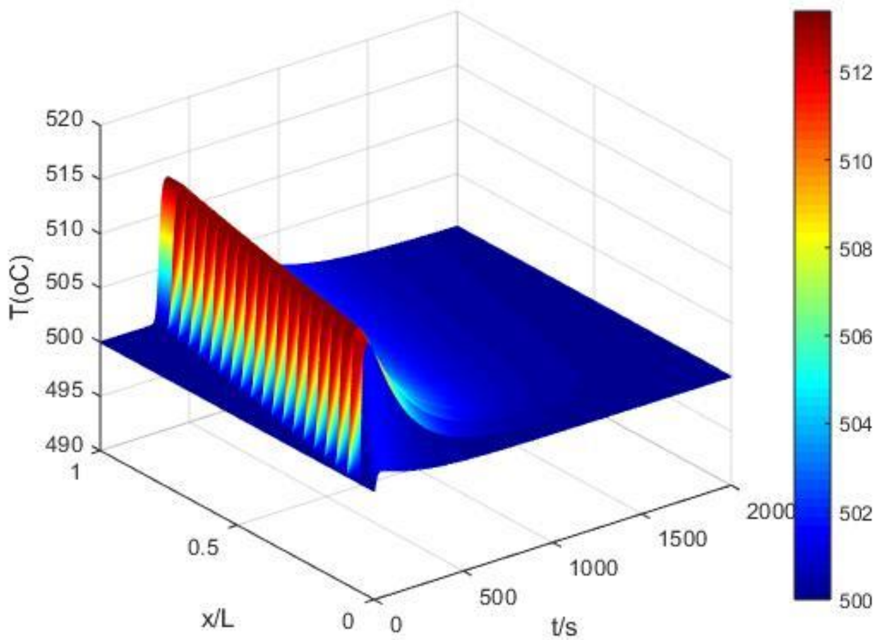


- y_{O2} (Oxygen fraction) *vs* time
- δ (Oxygen vacancy) *vs* time

Detailed Absorber Modeling (preliminary)

- Adsorption





- *U* (Gas velocity) *vs* time

- *T* (temperature) *vs* time

Outline

- Project Description and Objectives
- Project Update
- **Preparing Project for Next Steps**
- Concluding Remarks

Future work

- *M9.1 (Q11) Establish techno-economic analysis model*

Status: preliminary data support the performance target, currently working with Thermosolv to achieve this milestone.

- *M9.2 (Q12) Confirm REM-ASU system with >30% reduction in energy consumption compared to cryogenic ASU*

Status: preliminary data support the performance target, currently working with Thermosolv to achieve this milestone.

Future work

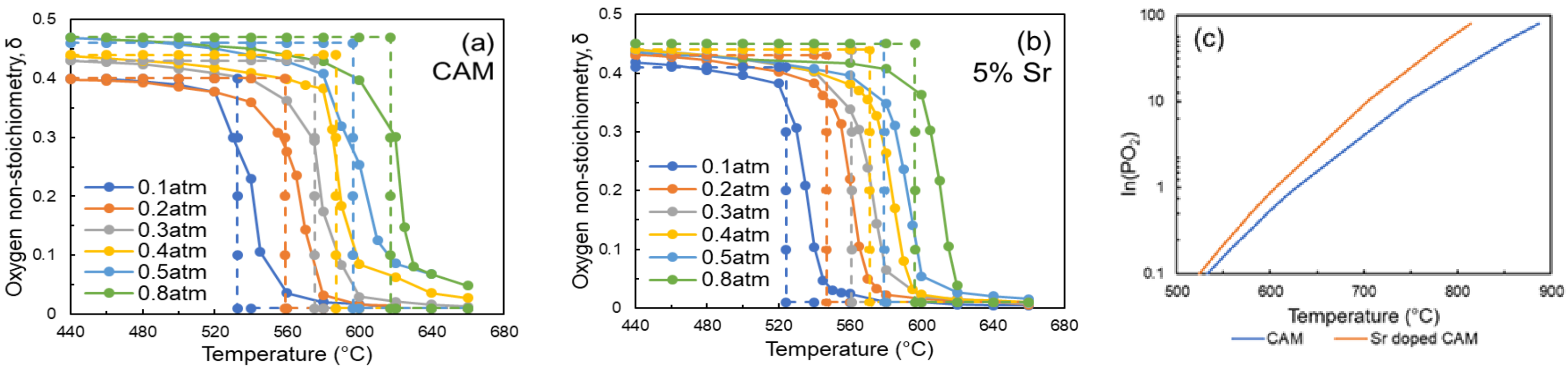
- DFT based high throughput screening on sorbent develop has screened out a few thousand sorbent compositions, experimental preparation/characterization is currently under way;
- We discovered interesting dopant effect, showing that even 0.03 at.% dopant can significantly impact sorbent performance. This phenomena is being further investigated in detail, including Neutron Diffraction studies;
- Novel double perovskite sorbents offer high oxygen capacity and opportunity for integrated O_2 compression have been investigated. It can be particularly suitable for gasification applications;

$CaMnO_3$ Based Double Perovskites for Combined Air Separation and Compression

- Doped material is more sensitive to small variations in temperature.

$$\ln(P_{O_2}) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

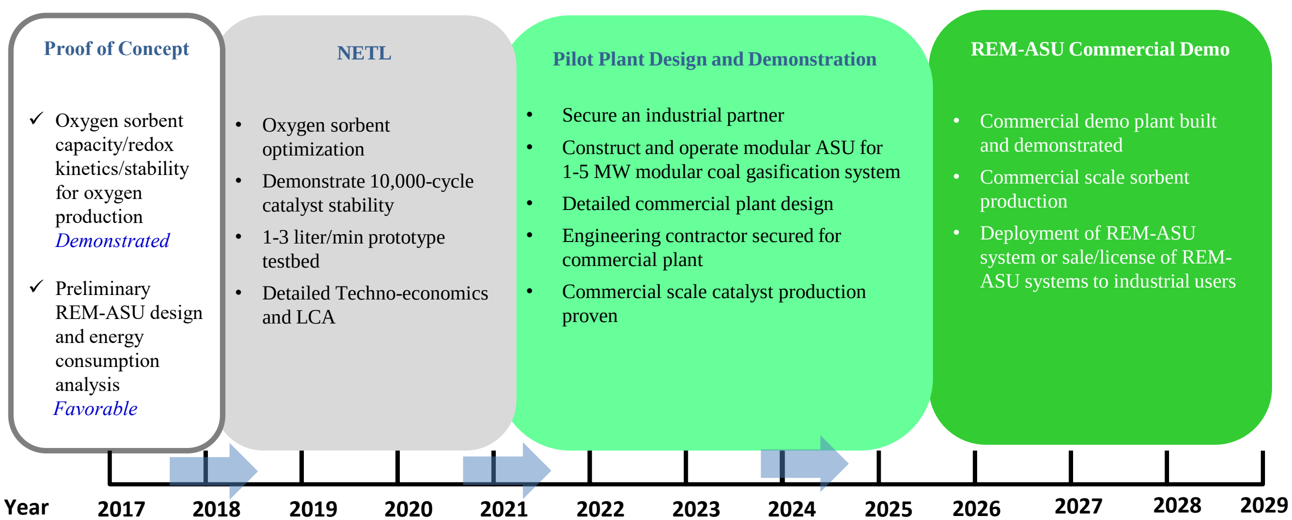
	ΔH° (kJ/mol O_2)	ΔS° (J/mol K)
CAM	146.5 ± 4.7	162.7 ± 5.1
5% Sr CAM	166.2 ± 3.2	189.2 ± 1.3



- The addition of dopants results in the higher reduction extent at lower temperatures.

Market Benefits/Assessment and Tech to Market

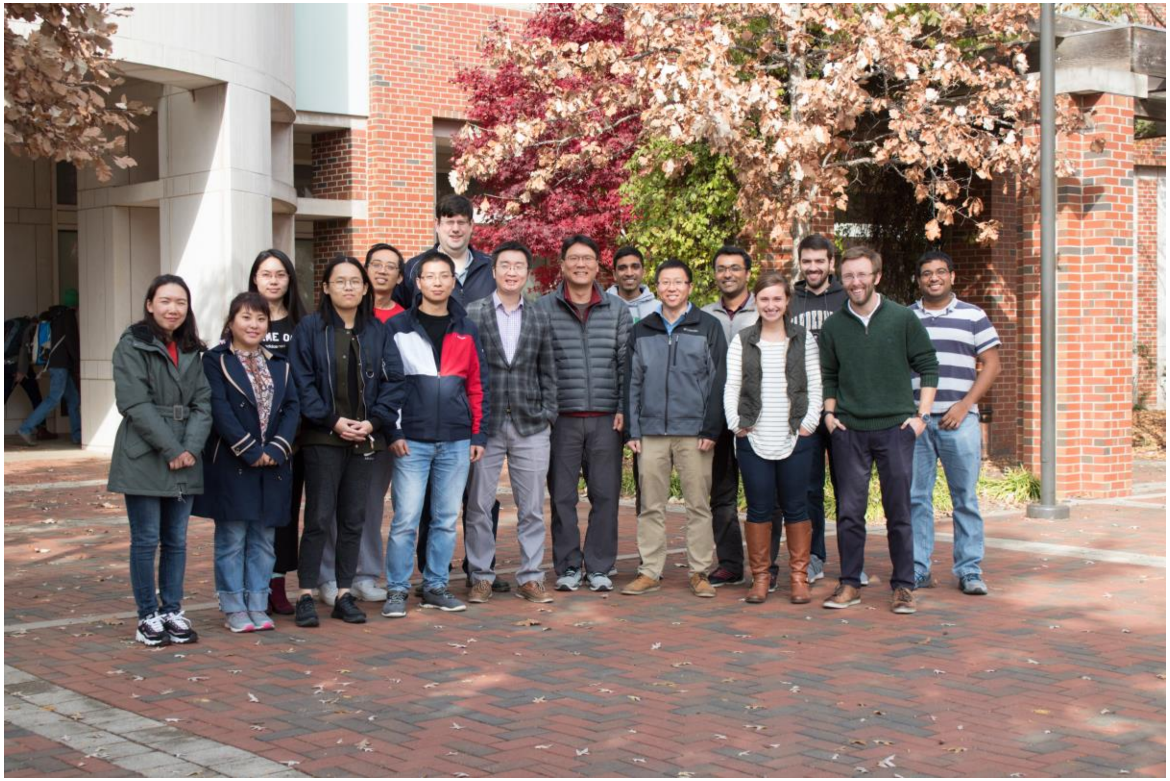
- REM-ASU produces low cost oxygen compatible with modular coal gasification
- REM-ASU can lead to 30% reduction in energy consumption comparing to cryogenic method for air separation
- REM-ASU integrates with gasification system for low-grade heat utilization and O_2 cost reduction
- REM-ASU has lower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



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 TEA analysis, additional stability test, and evaluation of oxygen sorbents selected by high throughput DFT method.

Acknowledgement



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Thank you!