Advanced Sorbents for Modular Oxygen Production for REMS Gasifiers

Project DE-FE0031528
U. S. Department of Energy
National Energy Technology Laboratory
PO: Steven Markovich

Prime Contractor:
Thermosolv LLC
Partners:
Western Research Institute

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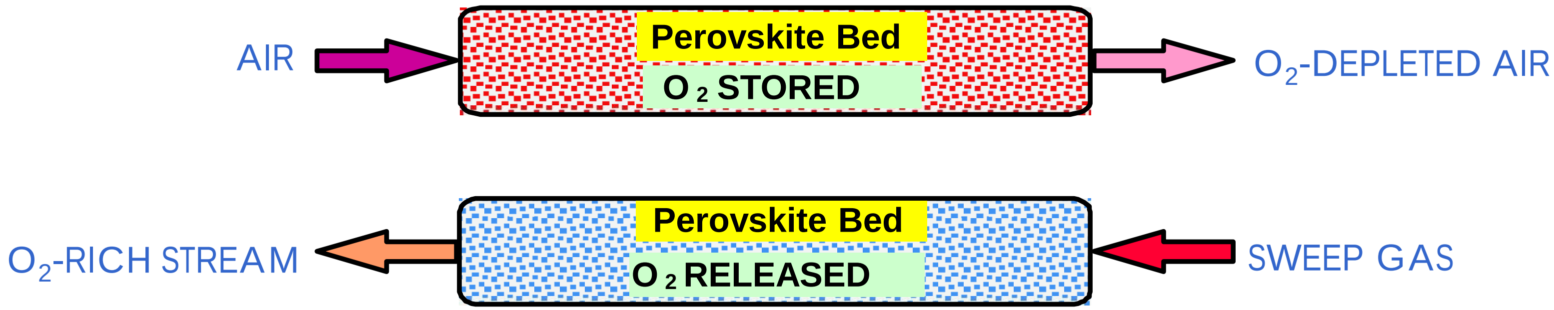
Low-Cost Oxygen…

Background

LCO Process (Perovskite Sorbent-based Oxygen)



- Adsorb O_2 from air in a solid sorbent
- Use of CO_2-rich flue gas as sweep gas allows optimization of the O_2 concentration for oxy-combustion
- Use of vacuum or condensing steam sweep to produce oxygen
- Elevated-temperature process driven by partial pressure of oxygen

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Background

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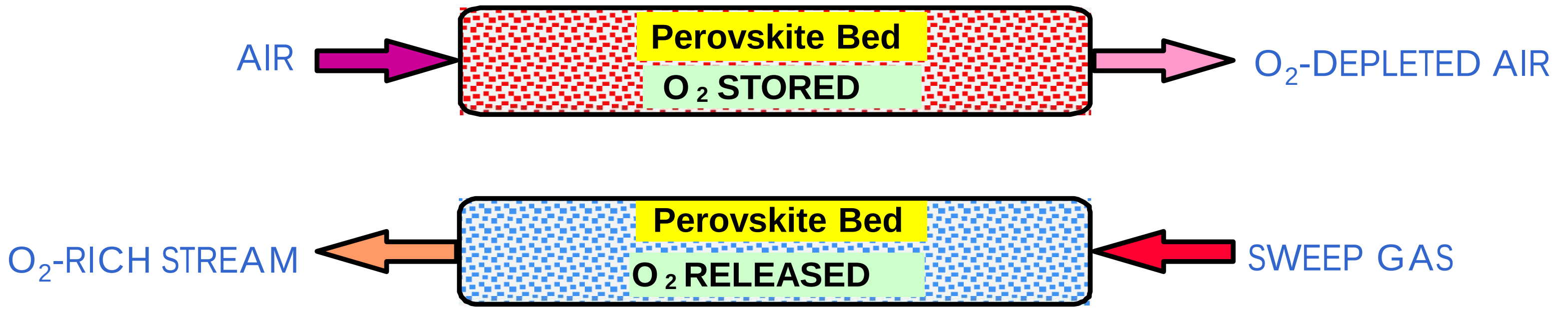

Between 2005 and 2008, under two separate Cooperative Agreements, a two-bed, 60-pph unit was developed by BOC/Linde and tested at EP&G/WRI (Thermosolv LLC). The unit was integrated with an existing 250,000 Btu/h Combustion Test Facility to demonstrate oxy-fuel combustion concepts.

Conclusions:

- Improve sorbent oxygen uptake capacity
- Lower operating temperature from 850° C
- Improve desorption kinetics

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Background

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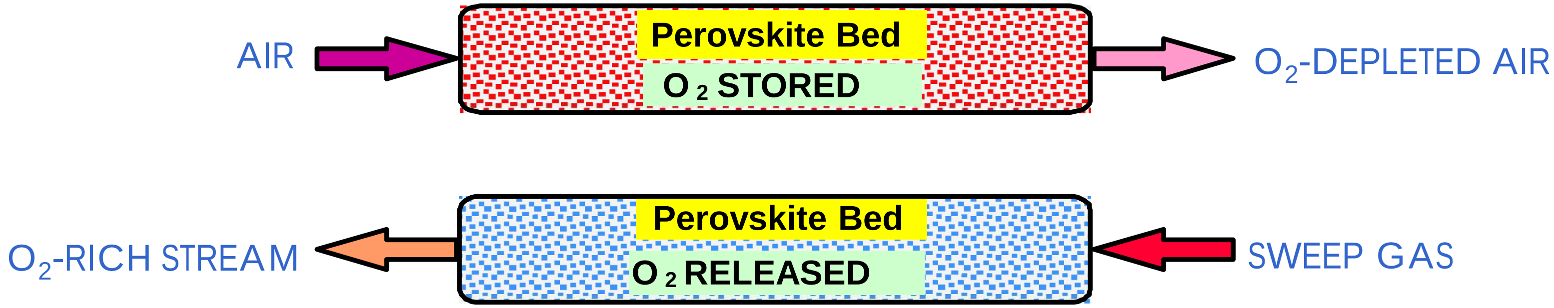

Project DE-FE0024075 (Completed in Late 2016)

Perovskite(s) with order-disorder transition ($La_{0.1}Sr_{0.9}Co_{0.9}Fe_{0.1}O_{3-\delta}$, LSCF1991)

- Lower heat of oxygen sorption
- Improved oxygen uptake capacity
- Lower operating temperature (about 500° C)
- Improved desorption kinetics
- CO_2 sweep can provide oxygen for oxy-fuel combustion
- Using air sweep enriched air can be provided for commercial applications
- VPSA cycle optimized to demonstrate 95% pure oxygen

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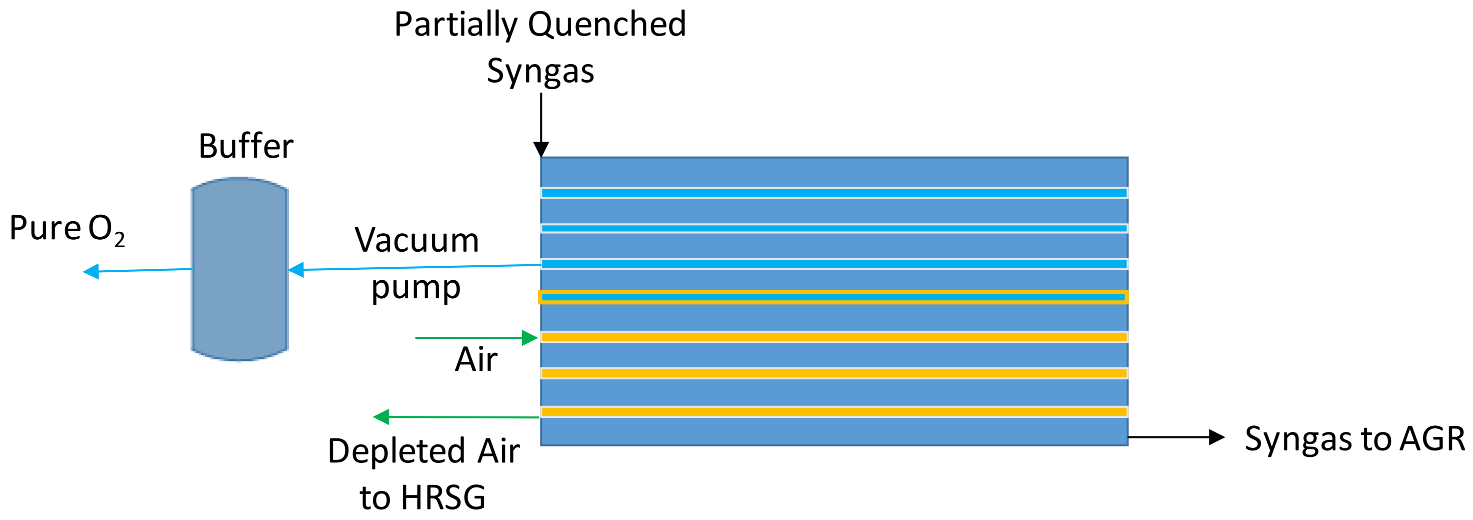
Advanced Sorbents for Modular Oxygen Production….

- LSCF 1991 ($\mathbf{La_{0.1}Sr_{0.9}Co_{0.9}Fe_{0.1}O_{3-\delta}}$) proposed for FE28002 too expensive
- Reduce the cost of sorbent
  - Supported Sorbent (Robust, Light Weight, Inexpensive and Inert Support)
  - Efficient utilization of sorbent and reactor volume
  - Reduce or eliminate Co



Supported Sorbent

Selection criteria:

- Inert
- Low-cost
- Compatible thermal expansion
- Thermal stability
- Mechanical strength
- Acceptable pressure drop

Application Methods:

- In situ precipitation
- Pressed layers
- Dip coating
- Spray coating

Support Materials:

- Zirconia
- Alumina
- Titania
- Magnesia
- Silicon carbide
- Zeolite
- Silica
- Brick chips
- 316 stainless steel (SS)

Additives:

- PVA, PVB, laurel glucoside

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Coating Issues

Issues specific to support shape, surface finish, material

Cobalt segregation

Non-adherence

Inter-pellet adhesion

Insufficient coating thickness

SS Corrosion

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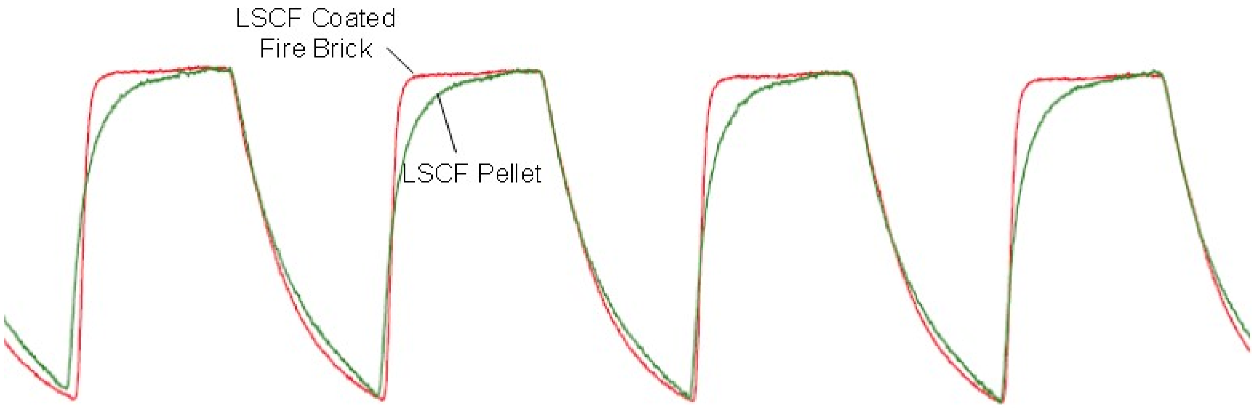
Coating Performance



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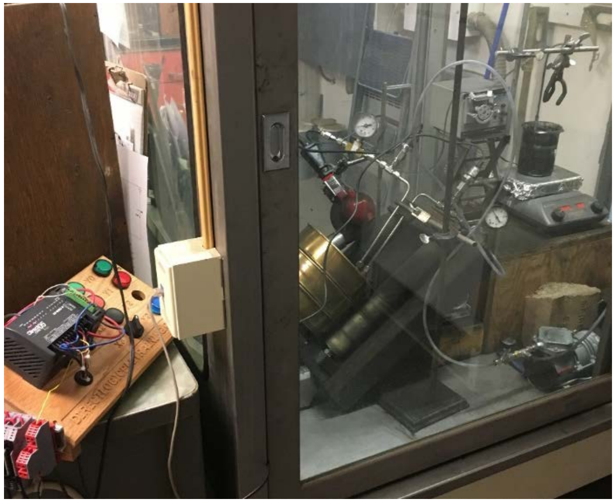
Coating Challenges

Best results found using spray coating on stainless steel

Uncoated and coated stainless steel supports

- Thermally stable
- Good thermal expansion compatibility
- Negligible pressure drop for saddle-like supports
- Cost is too high



Lab-scale automated spray system

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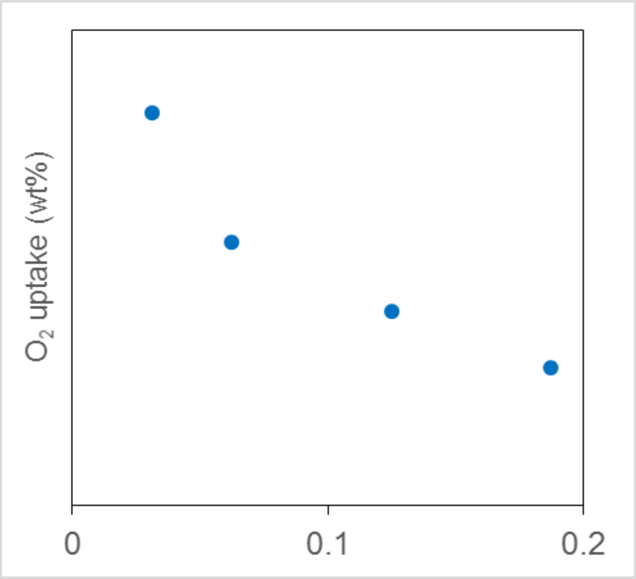
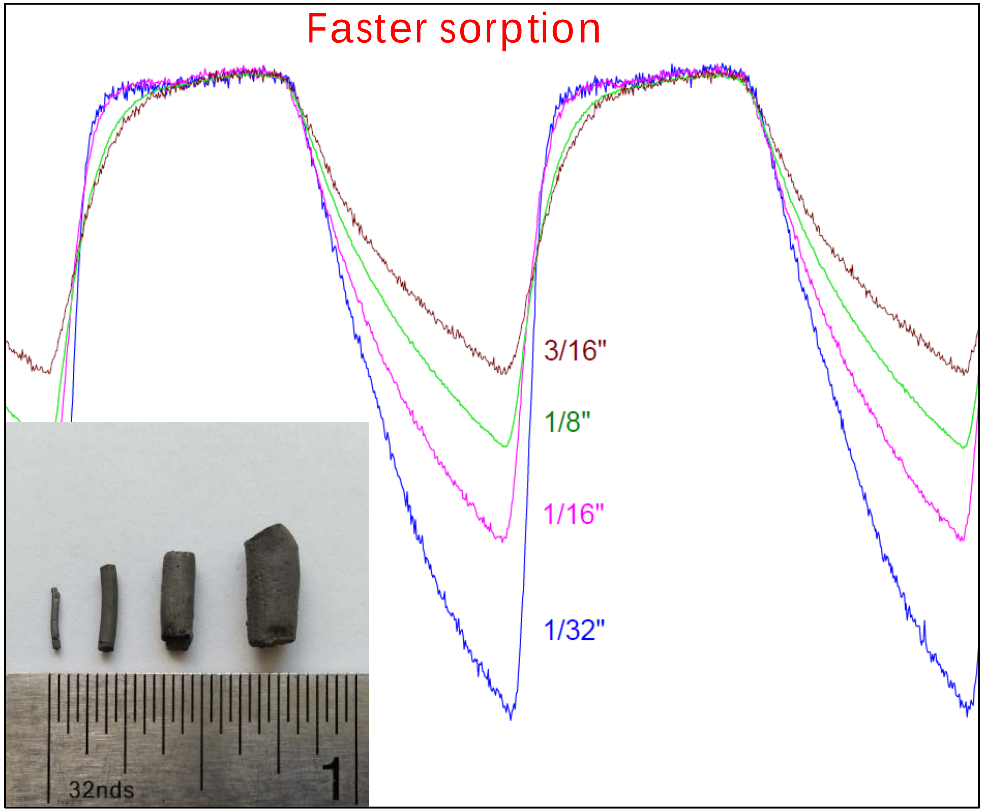
Size Effect

For smaller diameter pellets, TGA shows greater O_2 uptake and faster sorption





Suggests thin coating on inert support and small diameter solid pellet have equivalent performance

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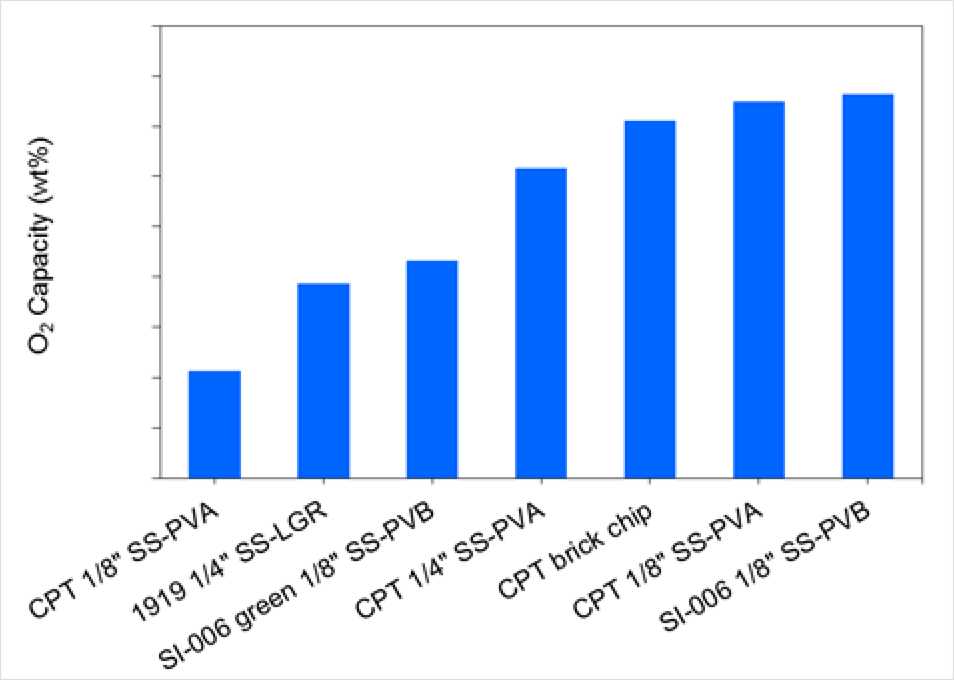
Coating Results Summary

Thermogravimetric (TGA) results: Cycle tests (N_2/Air) at 600 °C



Main findings

- Smaller supports are better (less inert in reactor)
- PVB produced harder coating

Best coated support: 1/8" SS – using PVB

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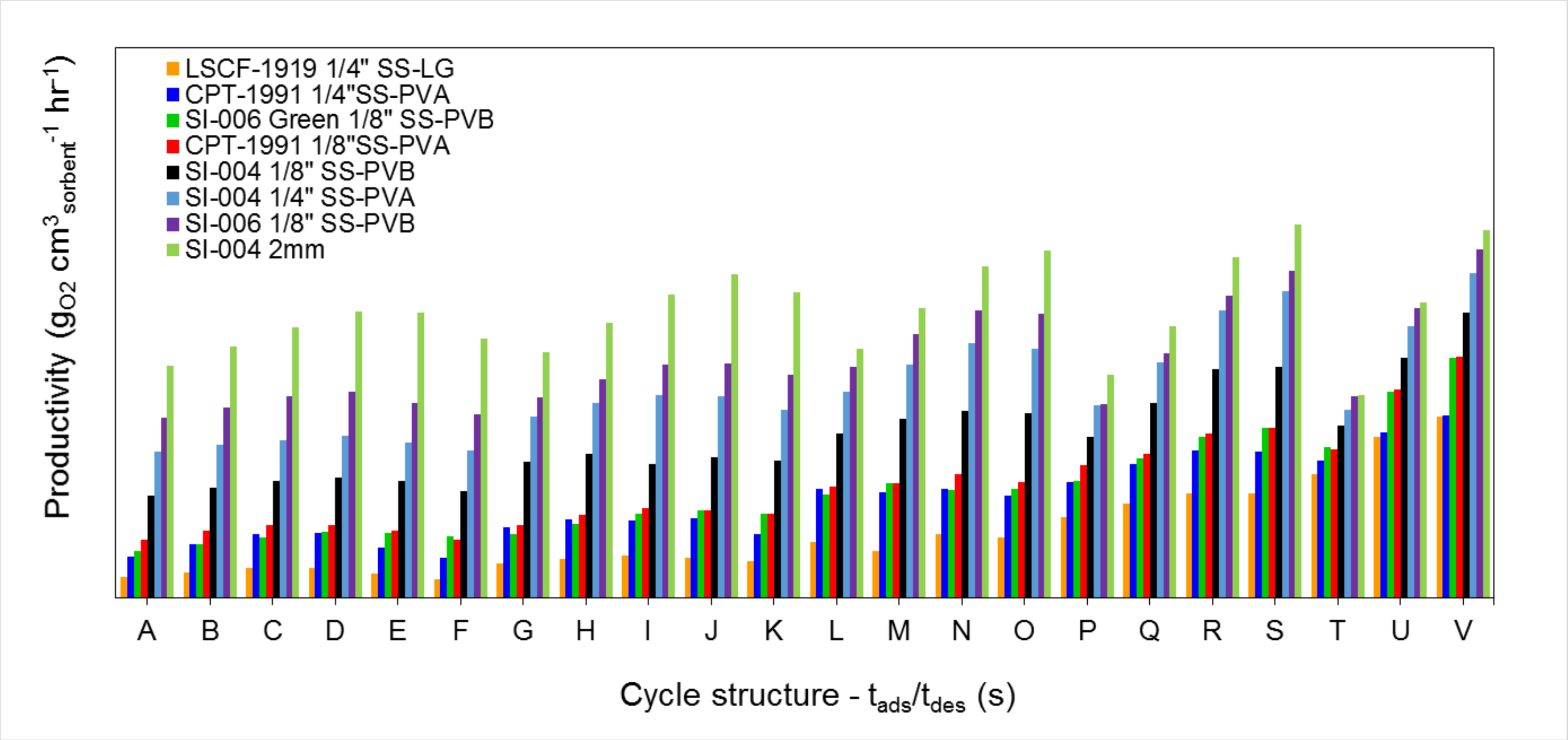
Coating Results Summary

Bench-scale results: Air/vacuum cycles at 600 ºC



Best coated support (1/8” SS – PVB) is outperformed by 2 mm solid pellet

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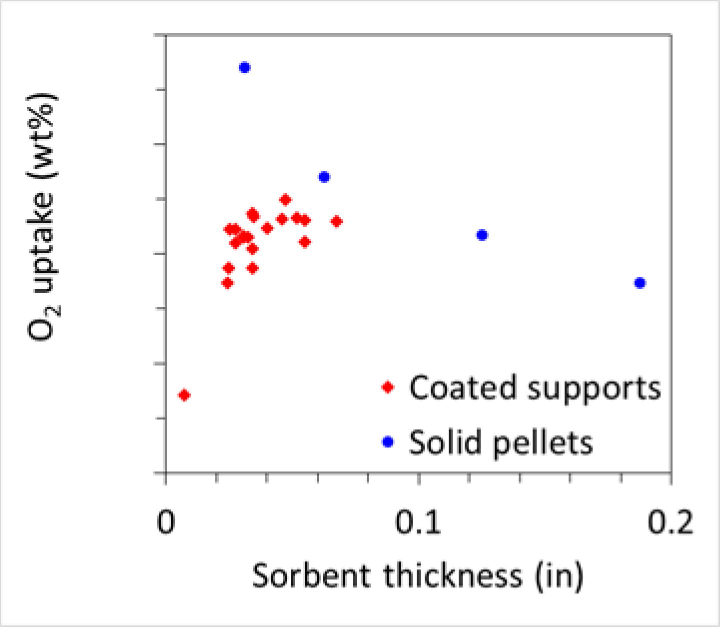
Size Effect

When compared to coated supports, small diameter pellet provides better performance due to several factors:



- Actual coating thickness needed is greater than expected
- Inert support has no activity
- High density pellet / low density coating
- On a volume basis, more accessible sorbent in reactor = more O_2 produced

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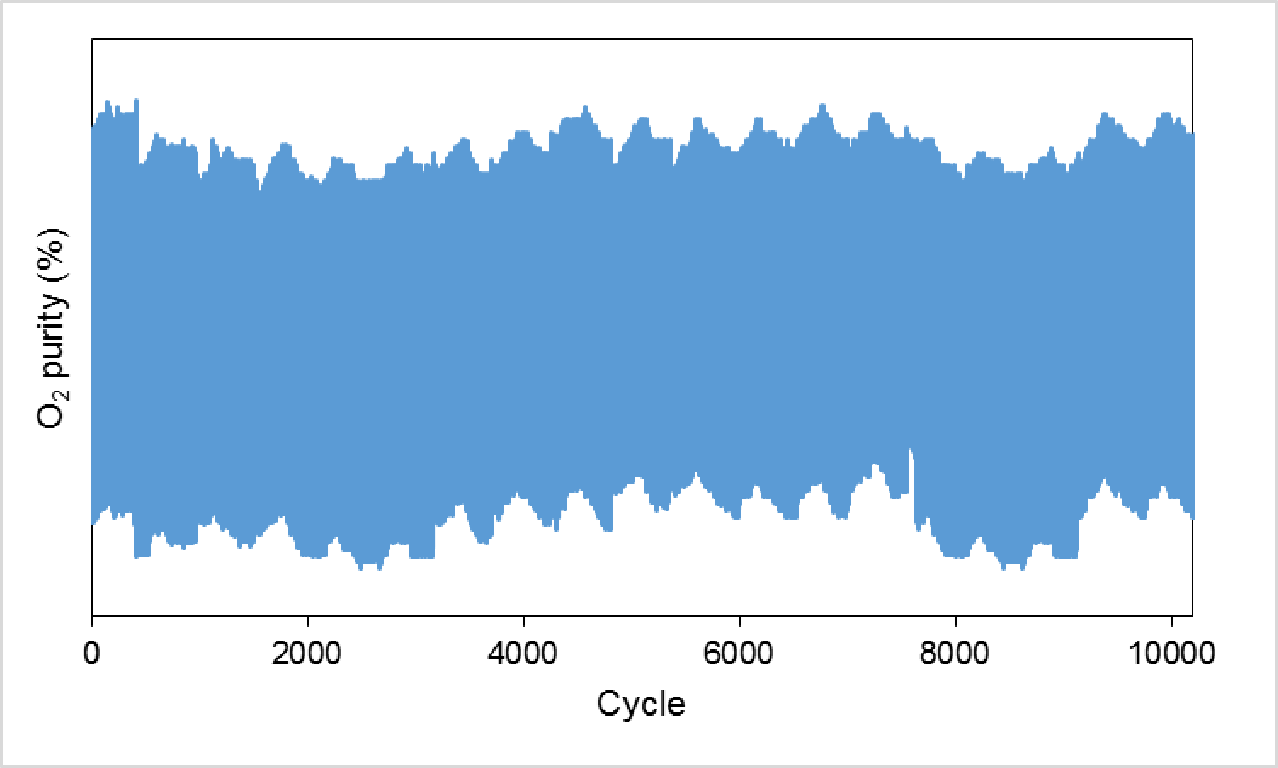
Long-term testing – coated support



- LSCF-1991 coated 1/8" SS supports
- Cycle time of 3-5 min (adsorption/vent/desorption) 600 ºC
- Good stability over 10,000 cycles, but lower O_2 production compared to pellets

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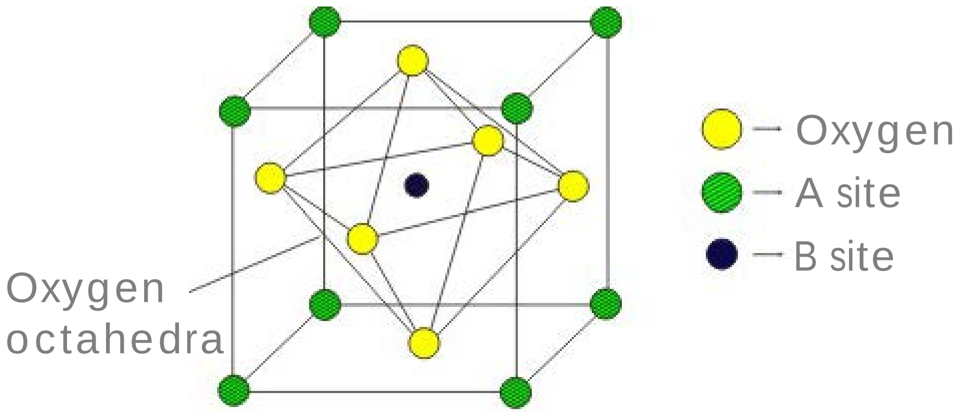
Perovskite Sorbent

Perovskite has ABO_3 structure



Example: LSCF-1991

- A site is Sr with La substitution
- B site is Co with Fe substitution

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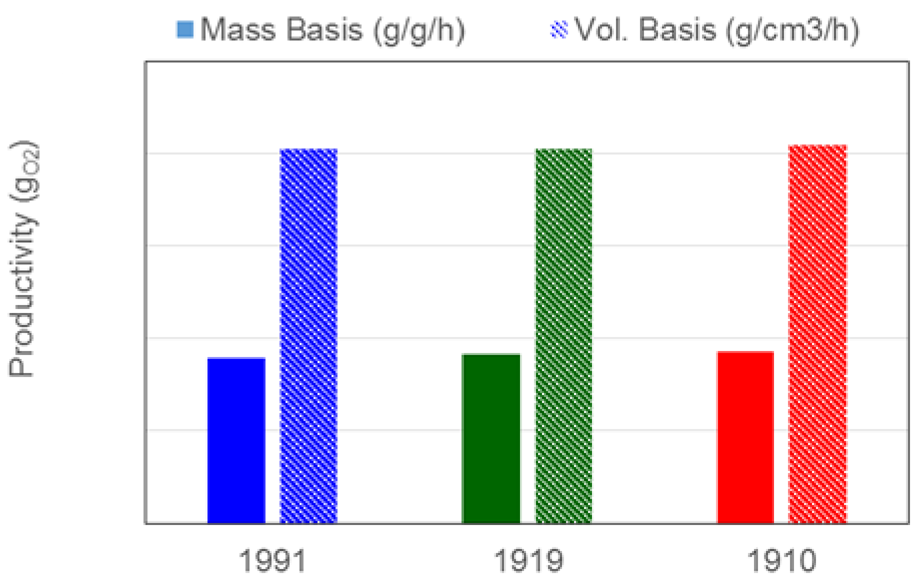
Reducing Material Costs

- The LSCF-1991 formulation was altered to address the high cost of cobalt



- LSCF-1919 dramatically reduces cobalt while increasing iron.
- LSF-1910 eliminates cobalt entirely.
- Results from bench-scale testing show very similar performance.
- Removal of cobalt reduces materials cost by ~27%

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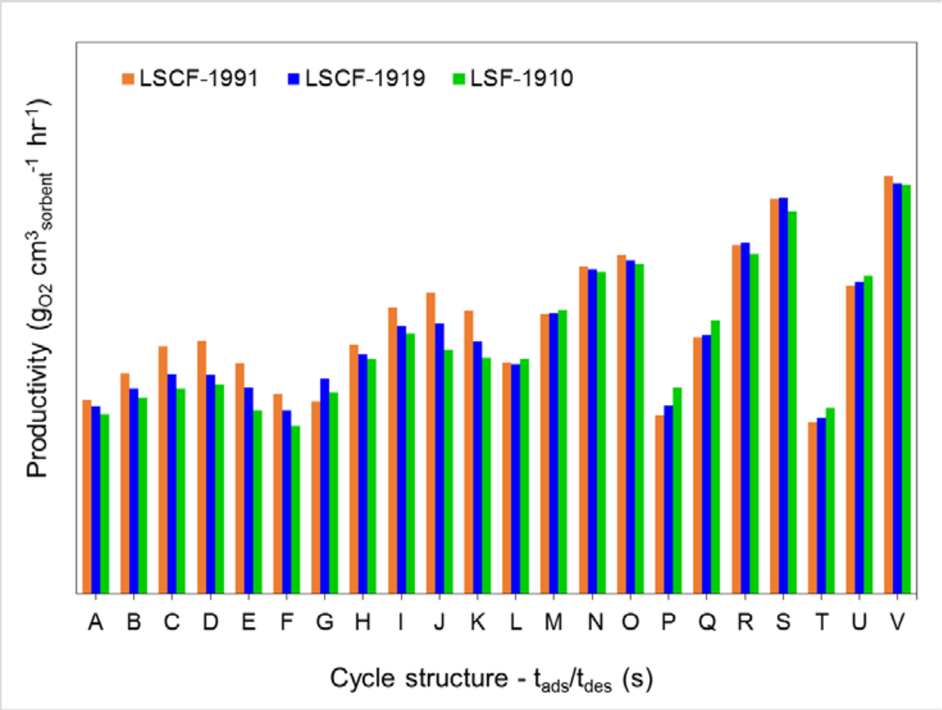

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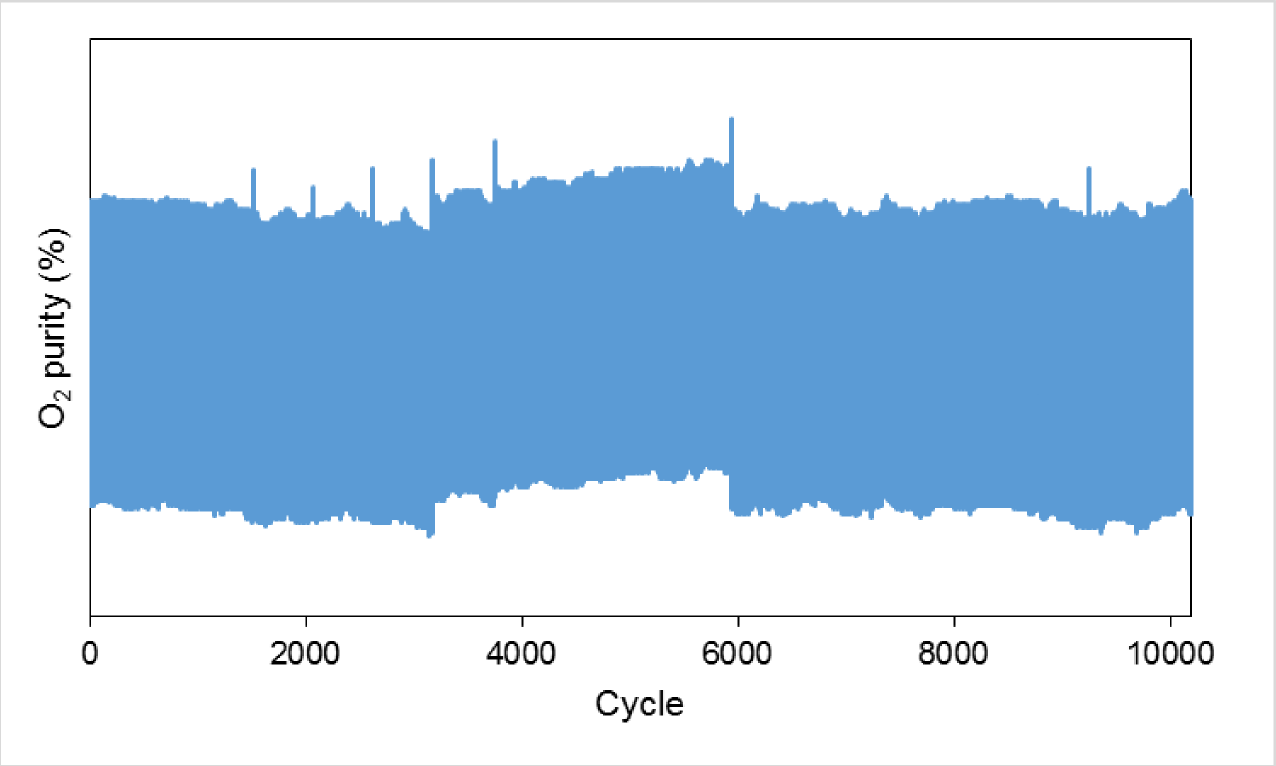
Long-term testing - pellets



- LSCF-1919 pellets produced in-house
- Cycle time of 3-5 min (adsorption/vent/desorption) 600 ºC
- Good stability over 10,000 cycles

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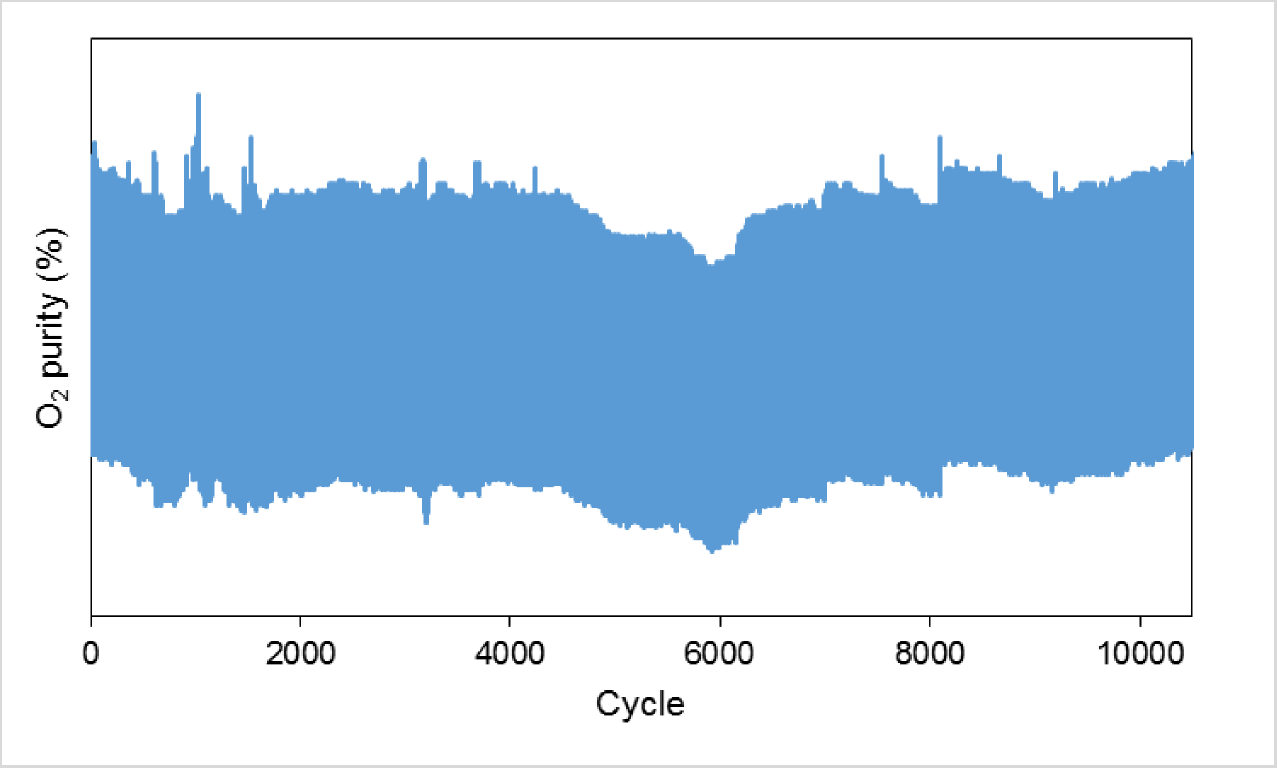
Long-term testing - pellets



- LSCF-1910 pellets produced in-house
- Cycle time of 3-5 min (adsorption/vent/desorption) 600 ºC
- Good stability over 10,000 cycles

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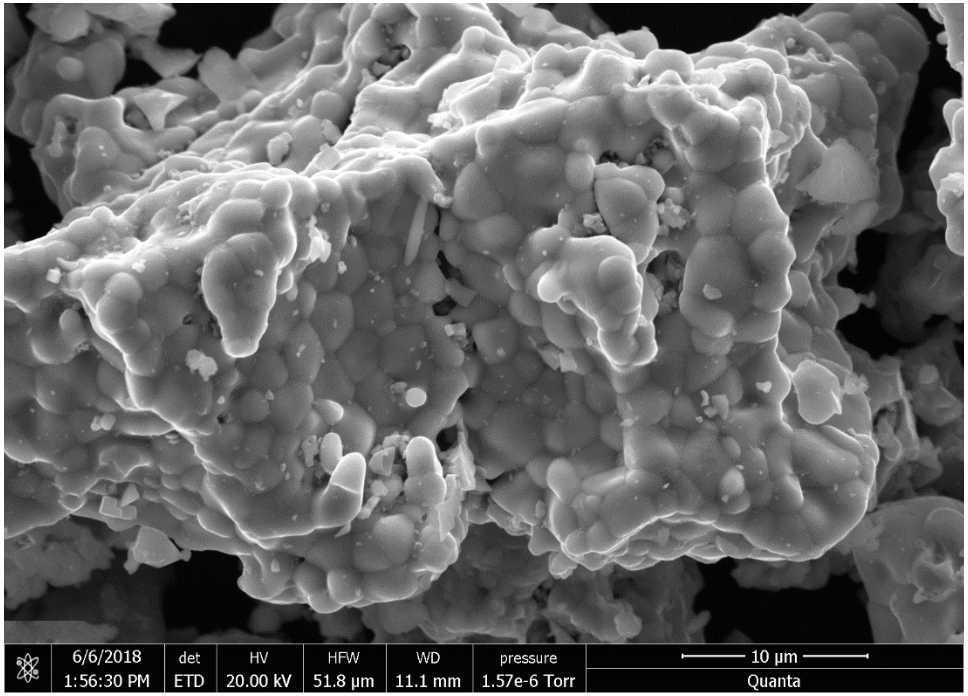
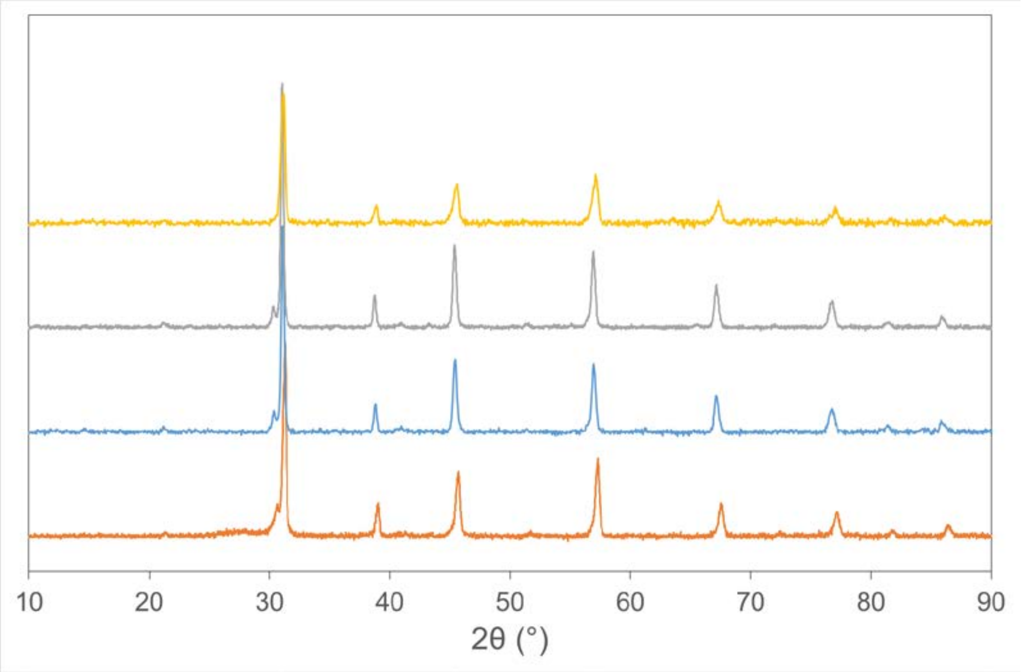
Sorbent Characteristics

- SEM
- Well sintered



Analytical results - XRD

- XRD used to determine phase purity
- 22 different sorbent chemistries examined
- Rules out poor phase purity as cause for poor performance



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Analytical results - TGA

- TGA used to screen performance
- Provides a good indication of VPSA performance

A sites

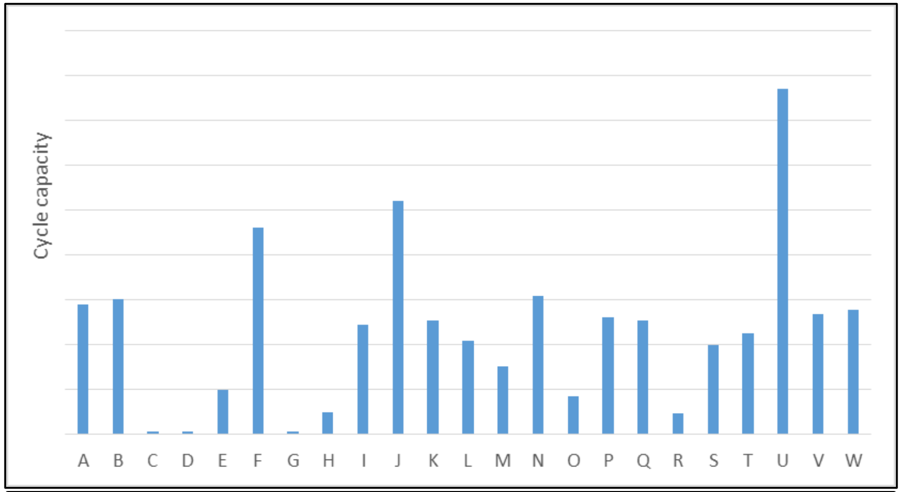
- Ba
- Sr
- Ca
- La
- Pb

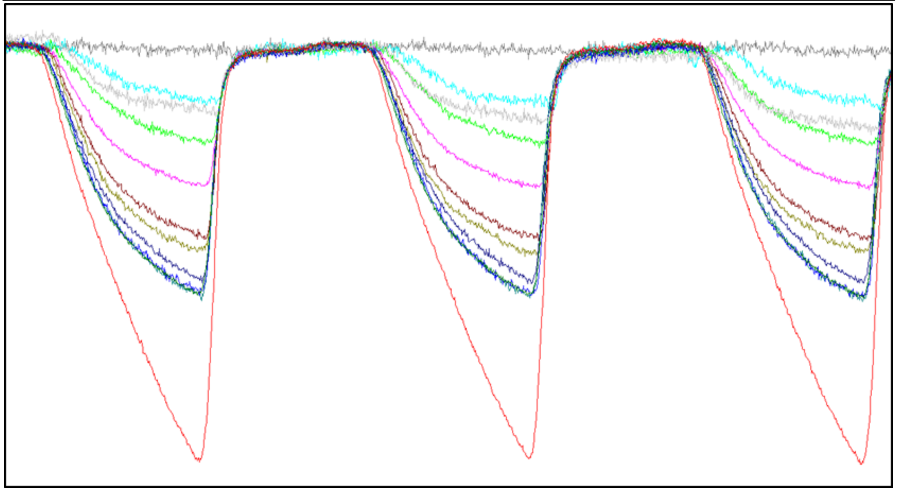
B sites

- Co
- Fe
- Cu
- Ni
- Mn
- Al

Promoters

- Cl
- Ag





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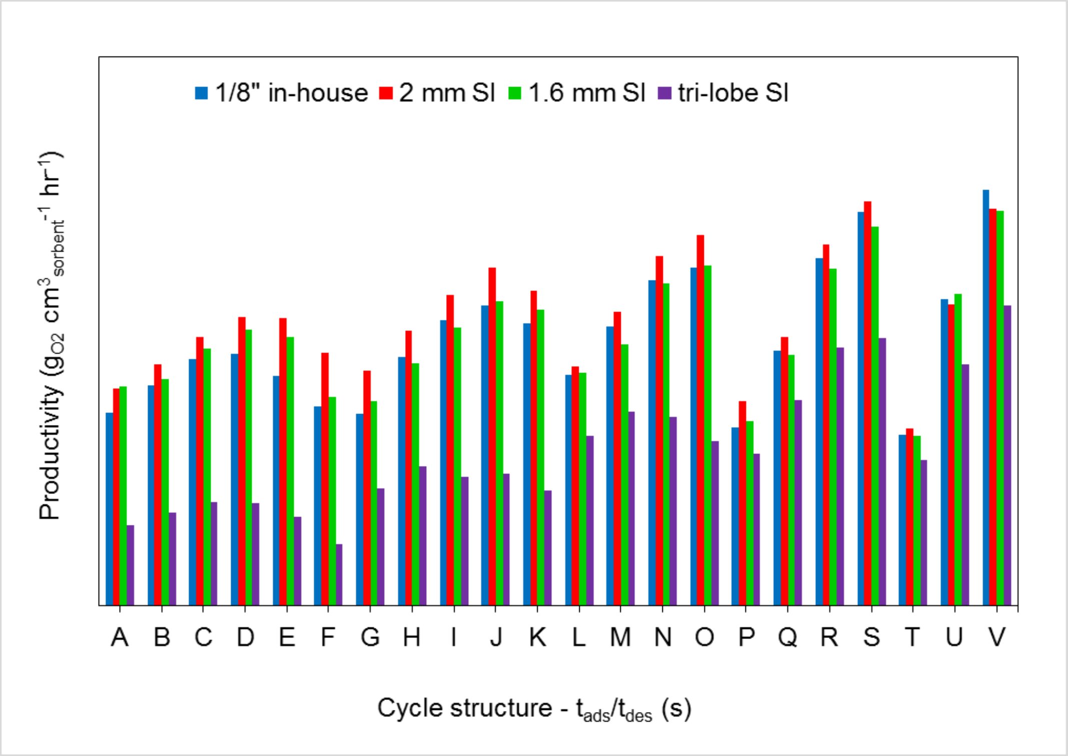
Sorbent Cost

- Newly developed best in class sorbent has reduced cost and superior performance compared to LSCF-1991
- Performance increased by ~15%
- Raw material cost decreased by ~46%

Sorbent Scale-up

Extrudate development



- Scaled-up production yielding top-performing pellets (2 mm)
- Outperforming in-house small-batch best of kind pellets

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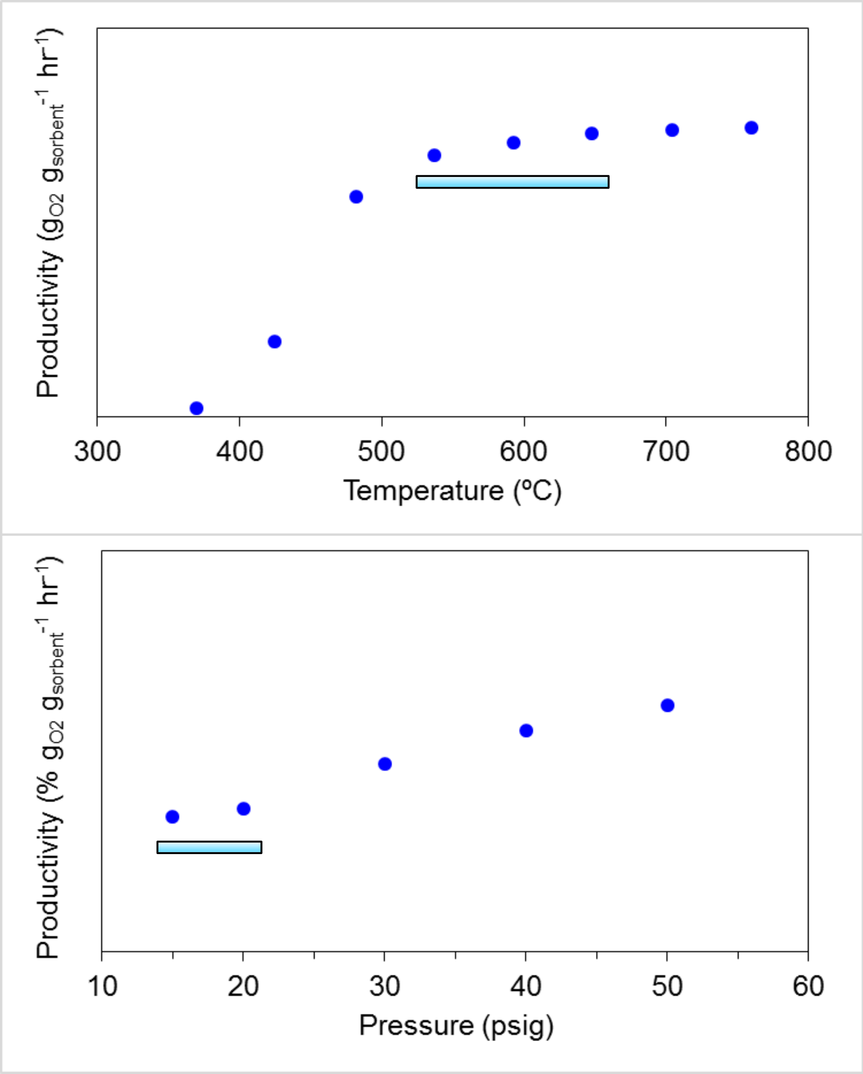
Sorbent Performance



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Acknowledgements

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- **Western Research Institute**

Questions?