Oxygen Binding Materials and Highly Efficient Modular System for Oxygen Production

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Project Summary

Objective: Develop a process for efficient O_2 separation from air using adsorbents or membranes with oxygen carriers to produce high purity oxygen

- Process can be scaled up in modular form or in large-scale industrial processes
- Process should be competitive with current state-of-the-art processes
- Sorbent bed-factor of less than 600 lb-sorbent/TPD O_2 (tons/day O_2)
- An O_2/N_2 separation factor greater than 20 for membranes

Specific Challenges:

- Develop reversible oxygen binding solid materials with high O_2 capacity and selectivity
- Translate the reversible oxygen adsorption property of cobalt complexes to solid adsorbent or membrane form
- Optimize the chemical kinetics of oxygen adsorption on the sorbent
- Optimize the coordination environment of cobalt on the surface of the sorbent
- Determine oxygen separation process performances
- Consider use of the solid reversible oxygen binding materials on the surface of a membrane for oxygen separation at ambient temperatures

Timeframe: BP1:10/1/16 to 09/30/17, BP2:10/1/17 to 09/30/18

Oxygen Separation Processes

- Vacuum-swing adsorption process can be used with the O_2 sorbents developed as indicated by the adsorption isotherm
- Membrane separation process is a partial pressure driven process and requires high feed-side pressure and low permeate-side pressure. In this case, a vacuum pressure can be used for the permeate side

Our Innovation

- Materials that selectively adsorb/bind oxygen
- Vacuum-pressure-swing adsorption (VPSA) process can be used with the O_2 sorbents developed as indicated by the adsorption isotherm
- Higher purity oxygen product stream
- Higher oxygen recovery rate
- No need to treat the larger stream of nitrogen
- Possible to produce pure N_2 at the same time

Success criteria and overall status- BP2

Success Criteria

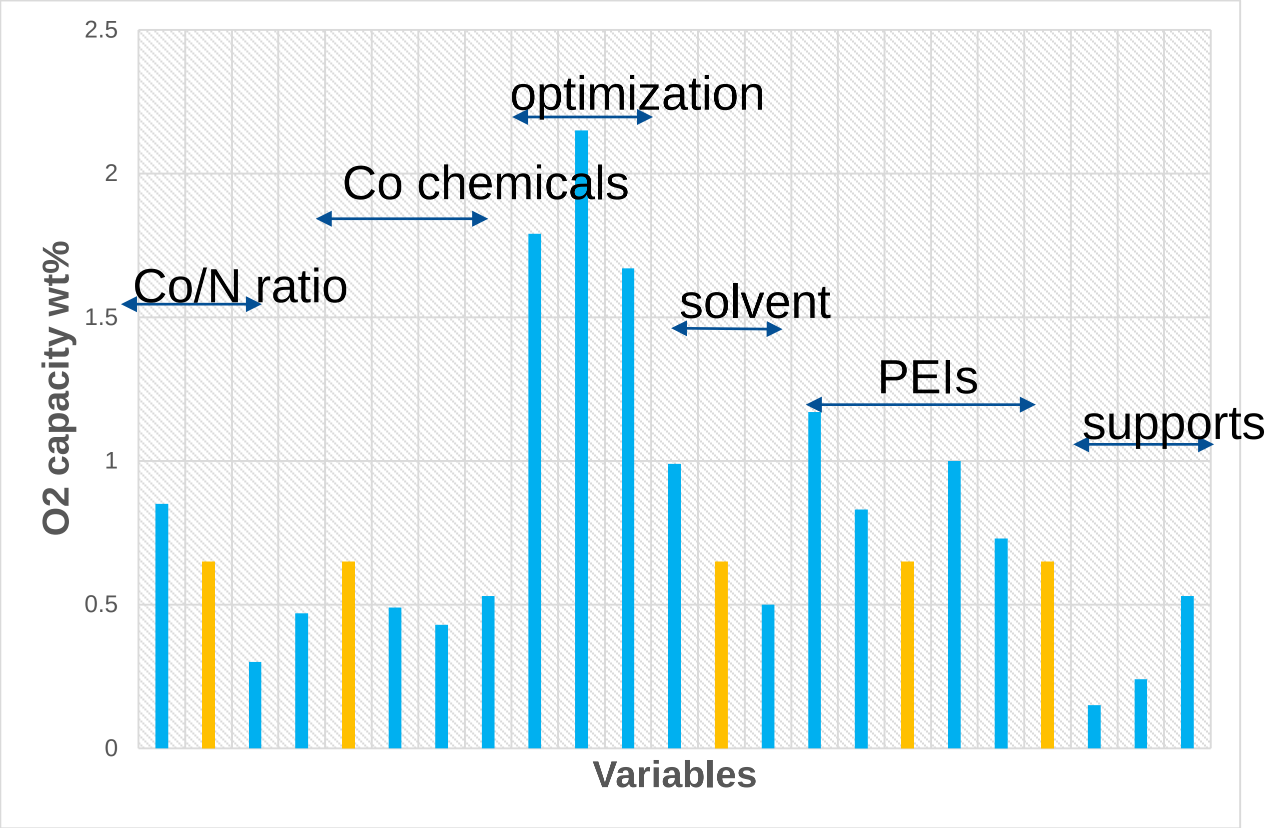
(1) O_2 capacity > 0.5 wt%,

(2) BSF<600,

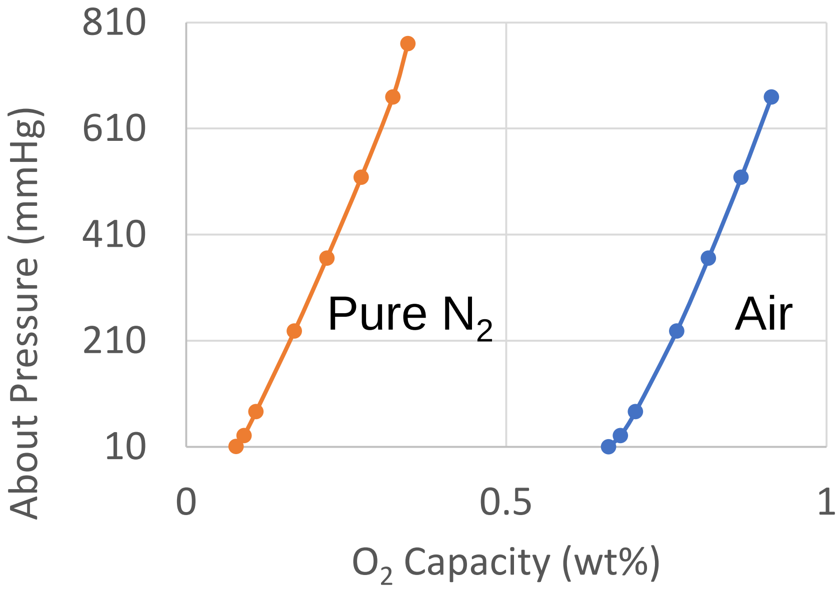
(3) Design and cost of a 5 TPD modular air separation unit ,

(4) A techno-economic analysis conducted for modular systems that produces 5 to 50 TPD O_2.

Influence of Preparation Parameters Oxygen Capacity of Supported Co-PEI Solid Sorbents (50%)

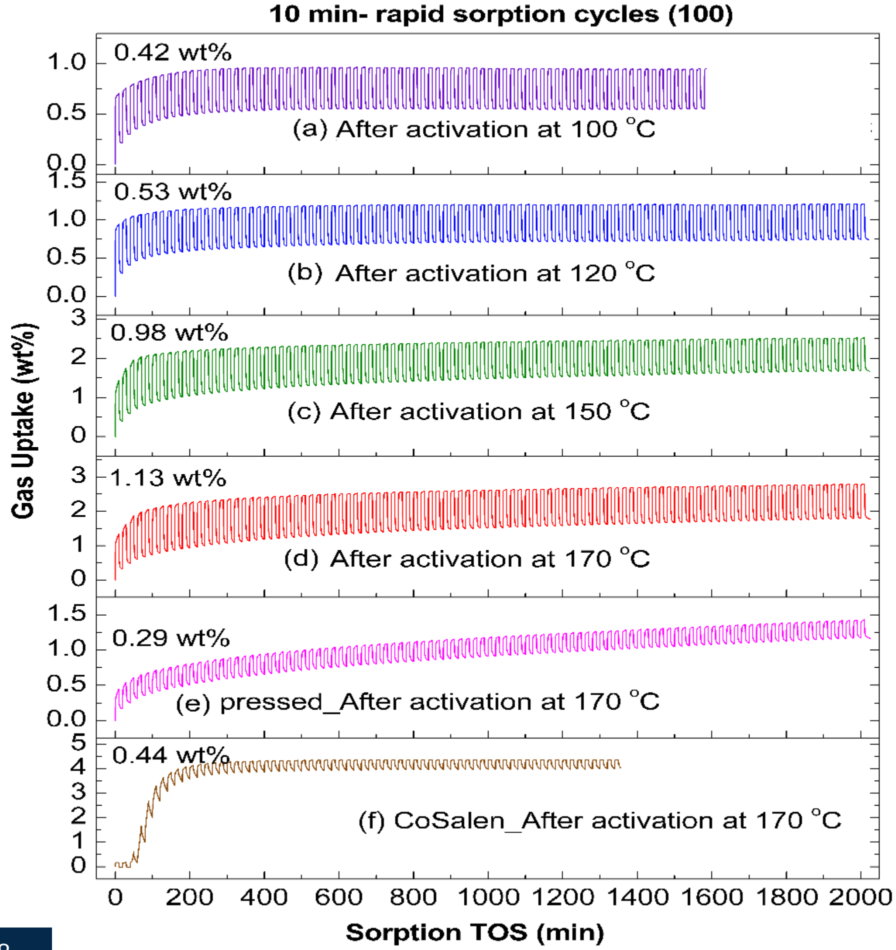


N_2-Air Isothermal Curves of Co-PEI/Support @RT



➢ Co-PEI oxygen capacity remains reasonable oxygen capacity in air

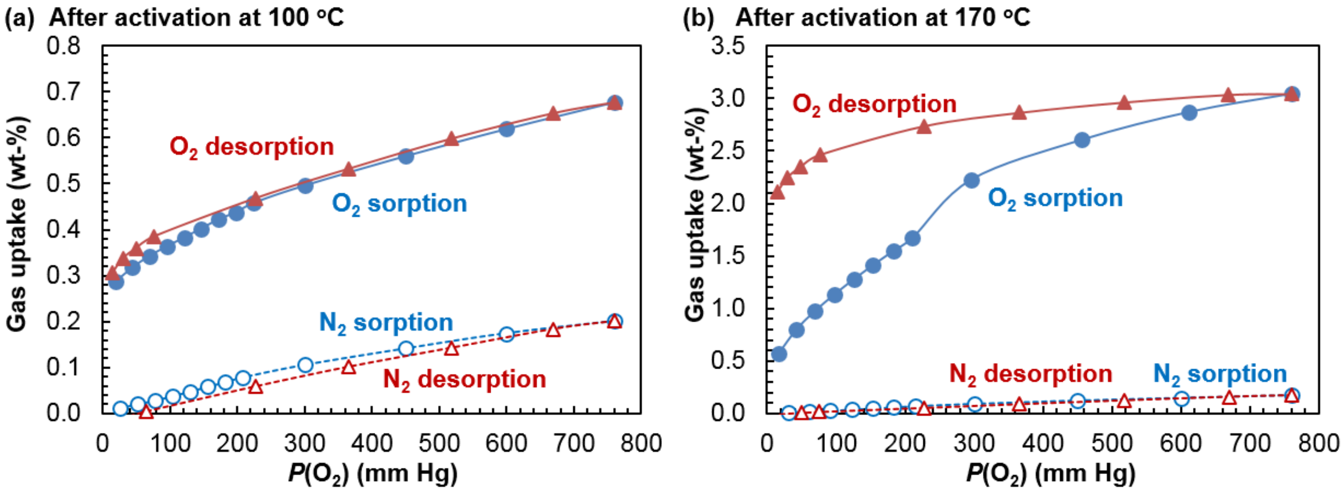
Cyclic capacity of RTI novel Co(II) Schiff compounds



- **O_2 sorption capacity** up to 1.13 wt% (7.91 mL O_2/g sorbent) over 10 min cycle;
- **Improved desorption kinetics** compared to CoSalen;
- **Reversible** O_2 sorption by variation of $p(O_2)$ at room temperature;
- **Stable cyclic** performance (at least 100 cycles).

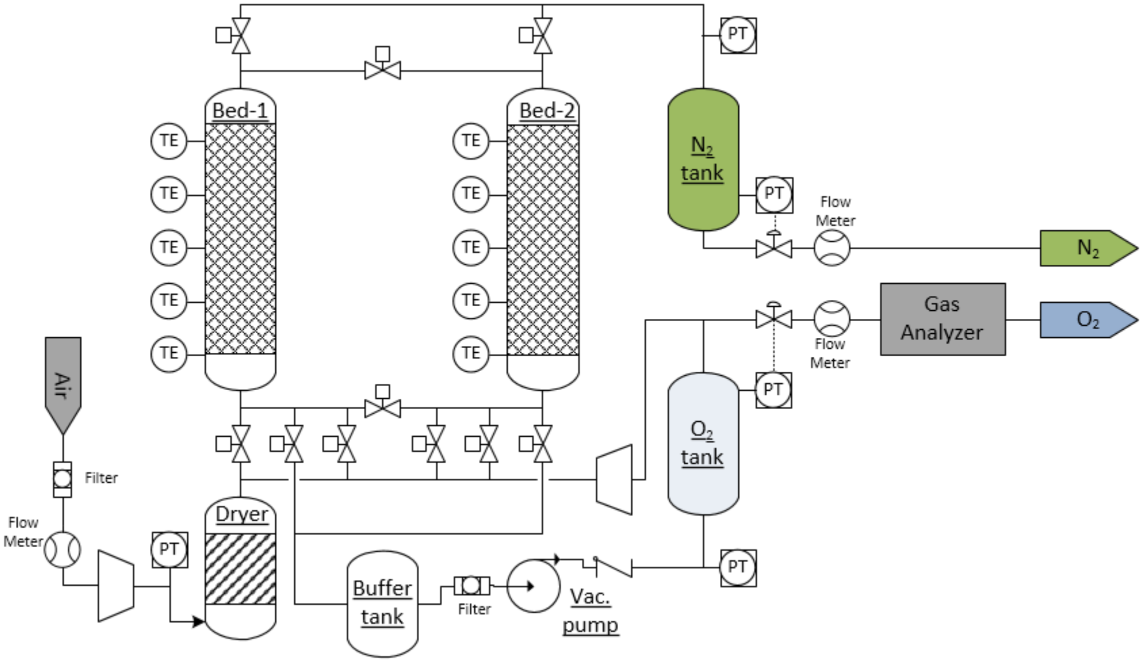
Zheng, Q.; Lail, M.; Zhou, S.; *et al*. Lithiated five-coordinated Cobalt(II) Schiff Compounds for reversible room temperature dioxygen binding. *Manuscript under preparation.*

ASAP isotherms of RTI novel Co(II) Schiff compounds



Zheng, Q.; Lail, M.; Zhou, S.; *et al*. Lithiated five-coordinated Cobalt(II) Schiff Compounds for reversible room temperature dioxygen binding. *Manuscript under preparation.*

Technoeconomic Analysis - Process Layout



- CAPEX estimate does not include the cryogenic storage tanks for O_2 and N_2
- Product O_2 is assumed to be available at atmospheric pressure.

Technoeconomic Analysis - Design Basis

Process Parameter	Value
O_2 Production rate	10 TPD
# adsorber beds	2
Bed working capacity	0.5 wt%
Cycle time	60 sec
% Recovery	60%
O_2 purity	95%
Bed Size Factor (BSF)	600
Adsorption Pressure	4 bar
Desorption Pressure	0.345 bar
Product O_2 pressure	1.013 bar

Financial Analysis Parameter	Value
Financial Basis for reporting	2016 $
Adsorbent cost	$15/kg
Plant Capacity Factor	90%
Capital Charge Factor	0.111
Cost of electricity**	$67.6/MWh
EPC costs (as % of installed costs)	8%
Contingency	15%

Labor costs for operating the plants are assumed to be negligible

**Average price of electricity for industrial users, Annual Energy Outlook 2019
https://www.eia.gov/electricity/monthly/epm_table_grapher.php?t=epmt_5_3

Technoeconomic Analysis - Results

Parameter	Cost
Purchased Equipment Cost (PEC)	$ 313,300
Installation Cost (Matls + Labor)	$ 432,200
Total Installed Costs	$ 745,500
EPC (8% of TIC)	$ 59,640
Contingency (15% of TIC+BEC)	$ 120,770
Total Plant Cost (TPC)	**$ 925,910**
Taxes & Insurance (2% of TPC)	$ 18518
Spare parts (0.5% of TPC)	$ 4630
Financing Costs (2.7% of TPC)	$ 25000
Initial sorbent fill	$ 42,972
Total Owner's Cost	**$1,017,030**
OPEX (Electricity costs) ($8.00/MWh)	**$ 91,250**

Levelized Cost of O_2

$$\frac{TOC * CCF + VOPEX * CF}{O_2 \text{ Production} * CF}$$

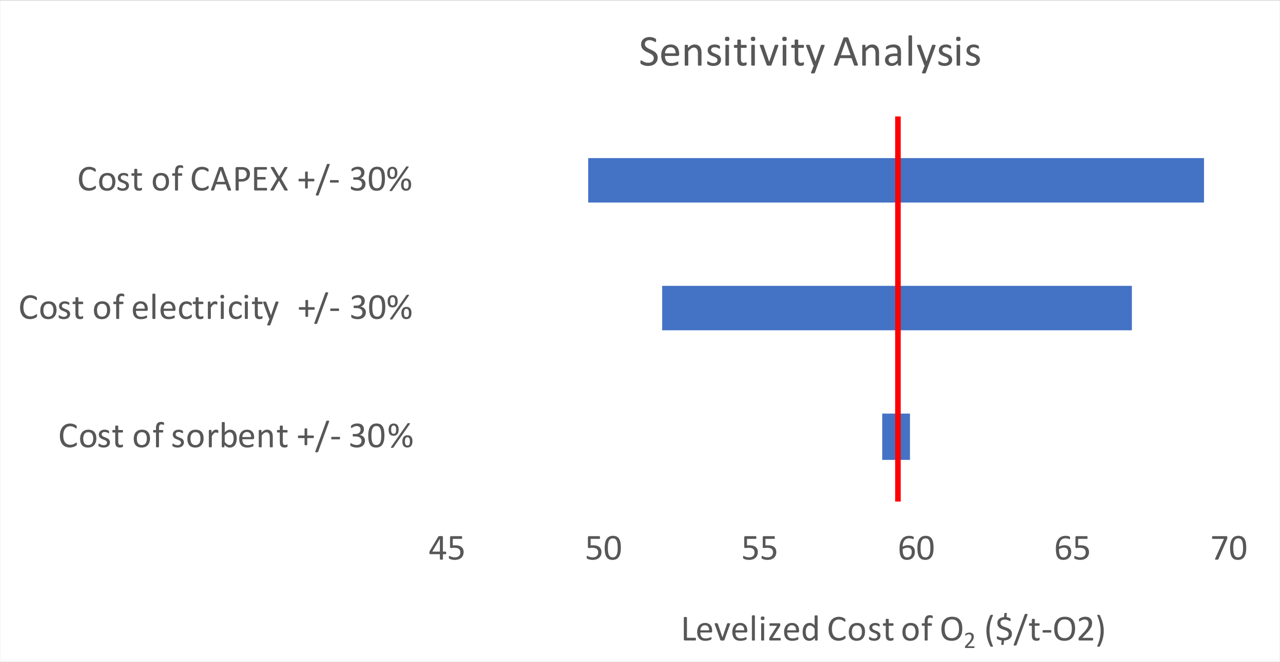
where

TOC = Total Owner's Cost
CCF = Capital Charge Factor
VOPEX = Variable Operating costs
CF = Capacity factor

Levelized Cost of O_2 = $59.4/ton of O_2

- CAPEX estimated using Aspen Process Economics Analyzer
- Cost of electricity takes from DOE's Annual Energy Outlook, 2019 for electricity costs for industrial sector

Technoeconomic Analysis – Sensitivity Analysis



Cost O_2 is most sensitive to the CAPEX and cost of electricity.

Cost of O_2 is relatively insensitive to adsorbent cost

Key Technical Challenges and Solutions

1. **Improvement in O_2 binding/releasing kinetics**

- Optimize O_2 material physical and chemical properties and its morphology for fast O_2 binding and releasing kinetics;
- Use mesoporous/microporous support to anchor the Co complexes on the surface to promote pore/surface/gas-phase diffusion, which is known be much faster than lattice diffusion.

2. **Improvement in O_2 binding reversibility**

- Optimize material composition (less prone to auto-oxidation or moisture poisoning)
- Optimize process condition (temperature, pressure, cycle time, flow rate, etc.)

3. **Improvement in material stability**

- Test promising materials over long test cycles (~100 hours or more) to evaluate their performance stability.

Project Wrap Up - Key Findings to Date

1. **Developed multiple synthesis routes for O_2 binding solid materials**
2. **Synthesis optimization in progress for:**
   - High O_2 adsorption capacity (already reached 0.5 wt% BP1 target)
   - Enhanced O_2 binding reversibility
   - Improved material stability
   - Efficient and economic synthesis routes
3. **Materials selected for further performance evaluation**
   - Co-PEI type solid sorbents
   - Co-Schiff base type solid sorbents
4. **Cost of O_2 production**
   - \$59.4/ton O_2 (2016\$) at 10 ton/day
   - \$61.49 (2016\$) at 4,900 t/day for 550 MW plant ASU production cost

Acknowledgments

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Questions?

Thank you!

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