Electrochemically Mediated Air Separation Modules (EM-ASM)

RTRC

RTX Technology
Research Center

Robert Darling (PI)
RTX Technology Research Center (RTRC)
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FE0032348

U.S. Department of Energy
FECM/NETL Spring R&D Project Meeting
April 23-25, 2024

RTX

Project Overview

Timeline

Project Start:	Oct 1, 2023
Contract End:	Sep 30, 2025
Duration:	24 months

One budget period.

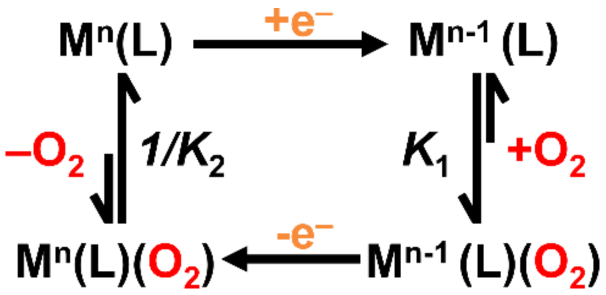
Budget

Project Budget:	\$1,619,431
Federal Share:	\$1,250,000
Cost Share:	\$369,431*
Funds Spent:	\$59,109**

* 22.8% cost share

** as of April 1, 2024

Objectives



This project targets advancing the technology readiness of a novel, scalable, efficient, cost-effective, and durable electrochemically mediated O_2 separation technology that generates O_2 of sufficient purity to enable high-quality syngas production and efficient pre-combustion carbon capture for H_2 production from gasification of biomass and wastes.

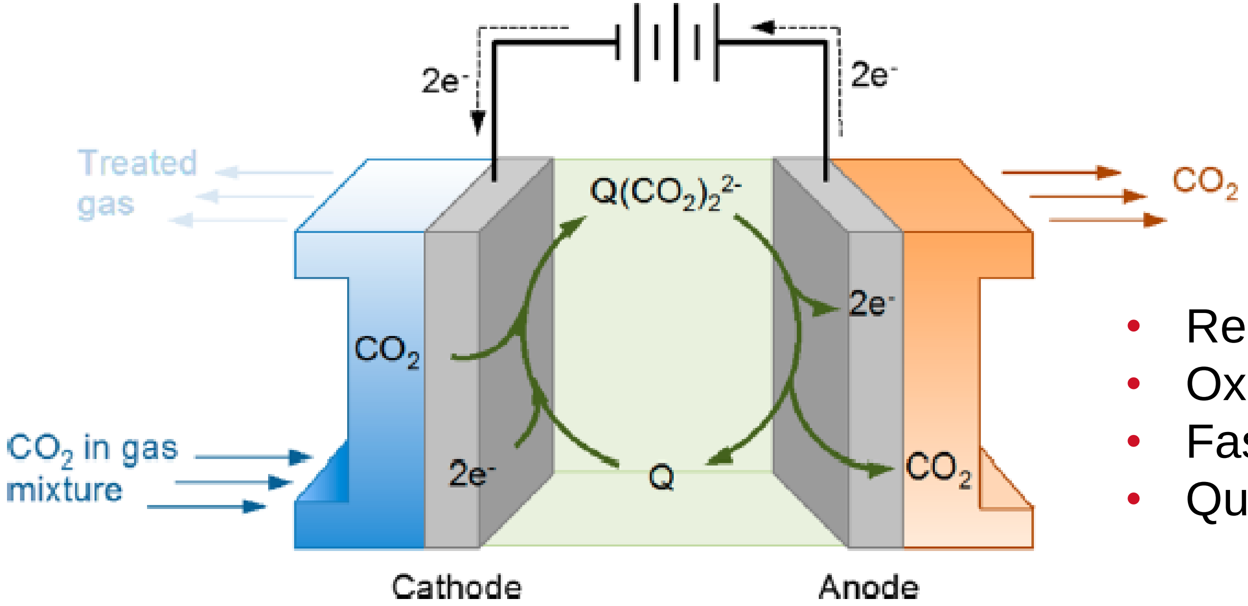
Partners

RTRC RTX Technology Research Center	UCDAVIS UNIVERSITY OF CALIFORNIA	UCI	MIT
Robert Darling **PI**	**Ambar Kulkarni** **Modeling**	**Jenny Yang** **Synthesis**	**Fikile Brushett** **Test**

Technology Background

Electrochemically Mediated Carbon Dioxide Separation

- Recent work by team members and others has demonstrated that CO_2 can be removed from air and flue gas by an electrochemically mediated process called electro-swing sorption (Hatton 2021)
- Quinones can be rapidly electrochemically reduced to hydroquinone
- Carbonyl groups on quinones become nucleophilic and capture CO_2 when reduced
- Oxidizing the adducts causes CO_2 to be released
- This process generates a gas stream that is concentrated in CO_2

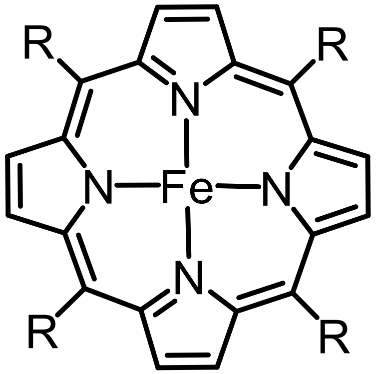


- Reduced quinone must bind CO_2
- Oxidized quinone must release CO_2
- Fast quinone redox kinetics for low power input
- Quinone must tolerate electrolyte environment

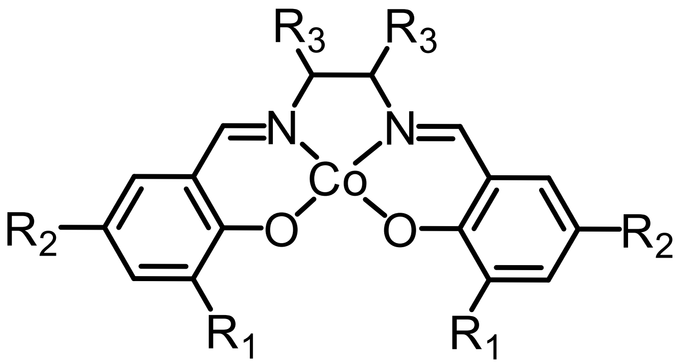
Technology Background

Oxygen Capture Molecules

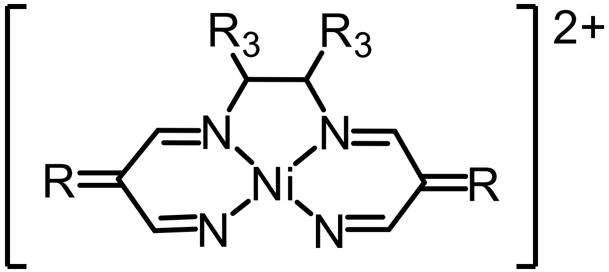
- Several reduced transition metal complexes reversibly bind O_2 with equilibrium constants ranging from 10-100. These values allow O_2 capture from air (preliminary analysis).
- The oxidized versions of these complexes are not known to bind O_2, making them good candidates for reversible O_2 binding and release.
- These macrocycles are easily functionalized to modify electronic properties which will impact their reduction potentials, oxygen binding capabilities, and solubilities



Iron(II) porphyrin



Co(II)(salen)



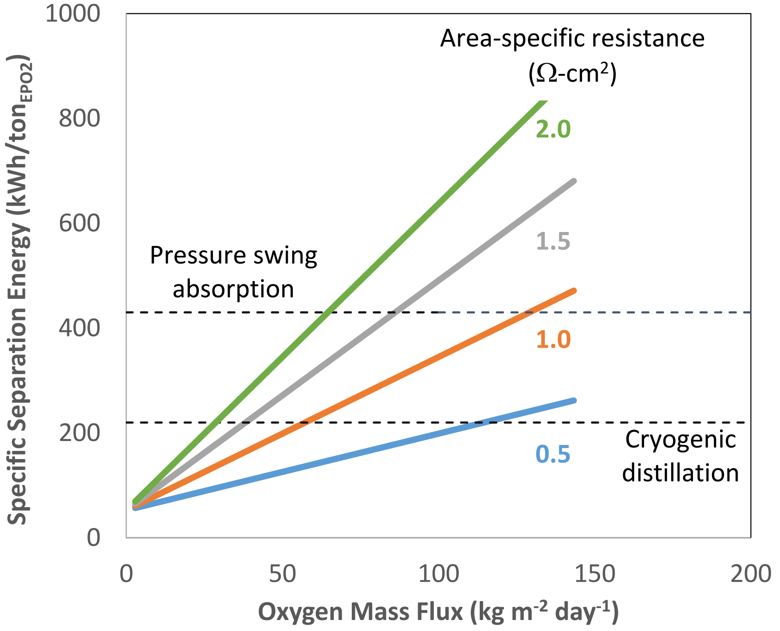
Ni(II)(tetraimine)

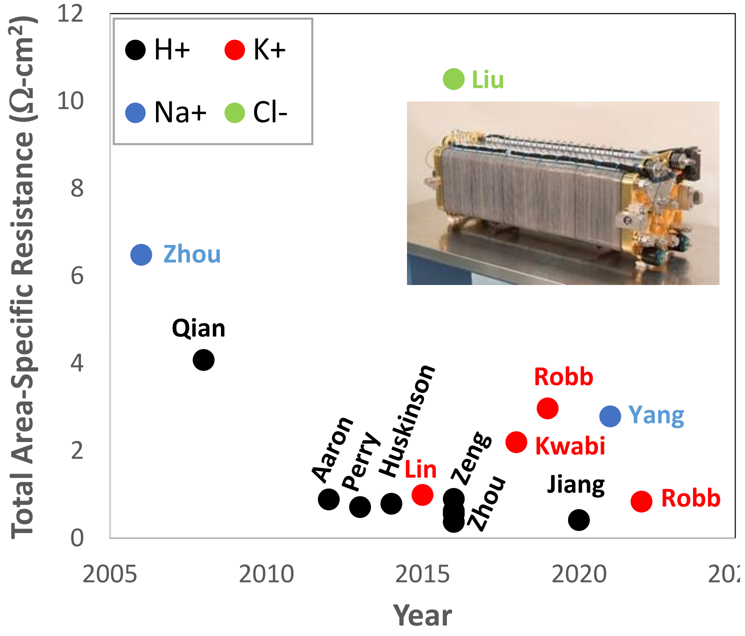
Literature supports oxygen electro-swing sorption concept

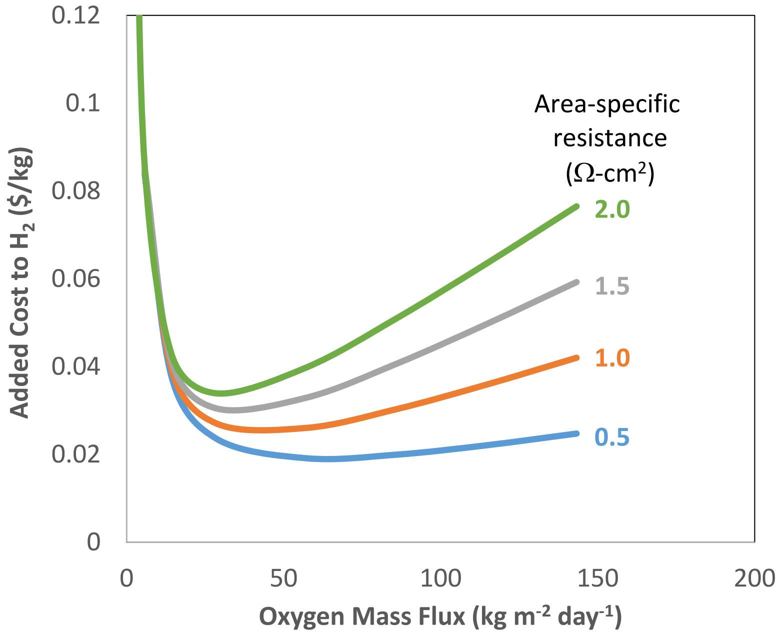
Technical Background

Electrochemical Reactors

- Need reactors with low specific energy (kWh/ton$_{EPO2}$) versus O_2 mass flux (kg m^{-2} day^{-1})
- This corresponds to low over-voltages at high current densities
- A lot of recent work on flow batteries has focused on improving these performance metrics







Need cells with specific impedance levels on par with recent flow batteries.

Technical Approach

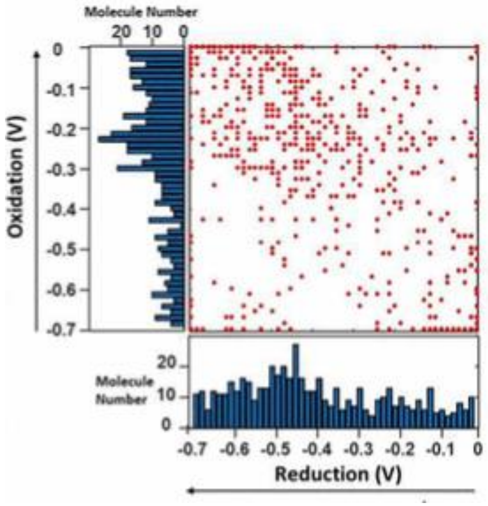
Schematic Illustration of Project Elements and Roles

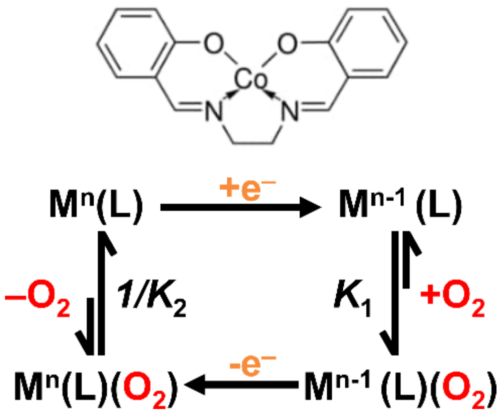
UCDAVIS
UNIVERSITY OF CALIFORNIA

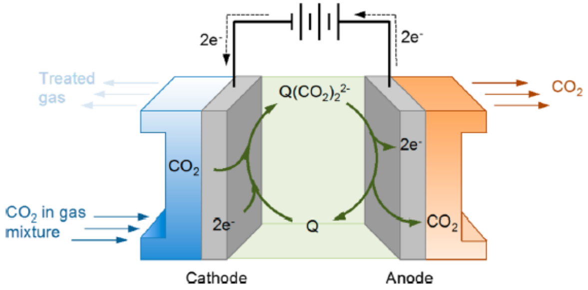
UCI

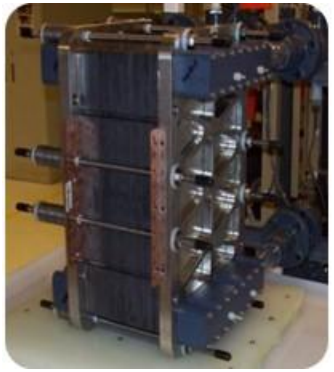
MIT

RTRC









Molecular modeling → Synthesis & screening → Sub-scale reactors → Design, scale-up

Technical Approach

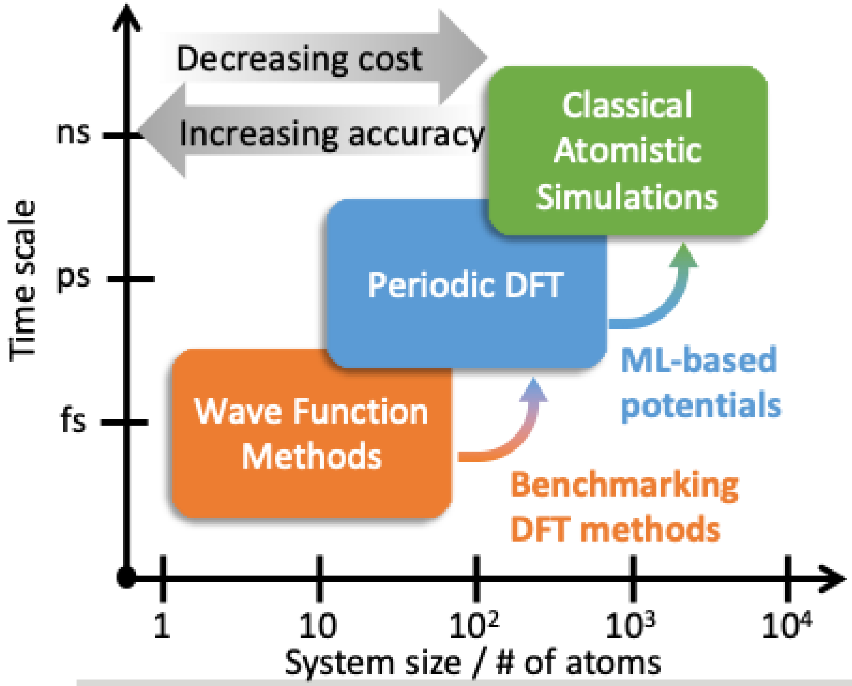
Key Milestones

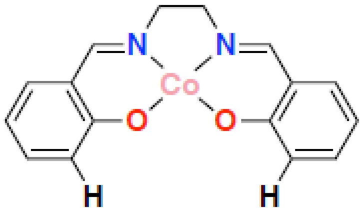
Owner	Milestone	Quarter	Key Milestone Title & Description	Measurable Criteria
UC Davis	2.4	8	Create library of 1 million candidates; estimate performance with machine learning	Candidate molecules can be rapidly screened against target metrics.
UC Irvine	3.4	7	Make 1-3 promising molecules at scale sufficient for reactor testing	Synthesized in sufficient quantity for testing in small reactor. Larger batch meets performance of small batches.
MiT	4.4	8	Derive relationships for electrochemical reactor supporting 10× scale-up at RTRC	Key performance indicators at 10× scale predicted within 20%
RTRC	5.3b	5	Set final sorbent and reactor requirements using all project input to date	Description of key metrics for this approach at the macroscale linked to molecular models and screening experiments and best values achieved.
RTRC	5.6	8	Defensible estimates for sorbent, reactor & system capital and operating costs	Predicted capital and operating costs based on performance measured during project

Progress and Current Status

Molecular Modeling at UC Davis

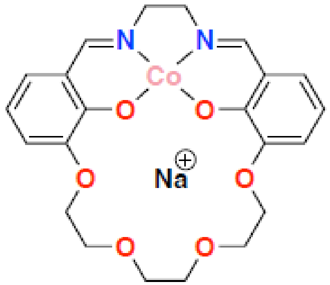
- *Goal:* Use multiscale molecular modeling to accelerate the rational design of selective molecular adsorbents for O_2 capture
  - RBE functional, acetonitrile solvent





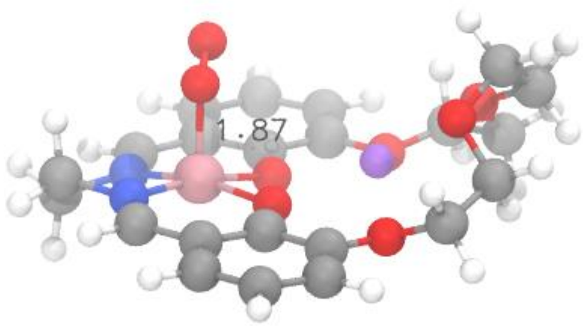
Co-salen

Binding Energy = - 1.42 eV



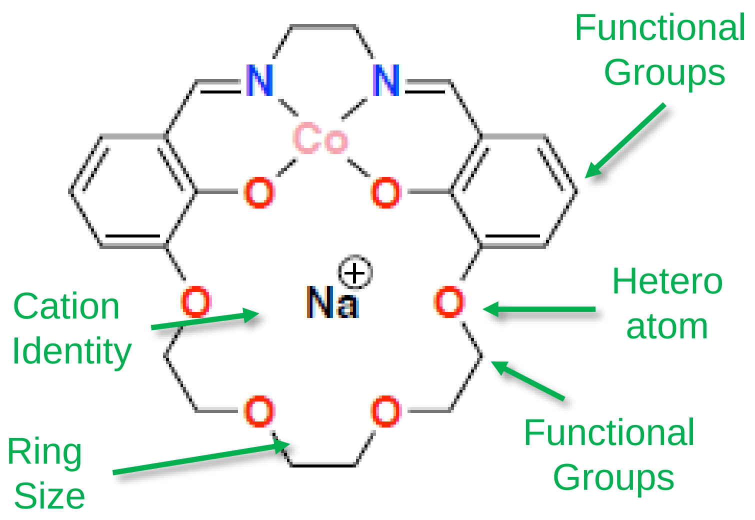
Co-salen/Na-6-crown

Binding Energy = - 1.57 eV



Significant distortion of
the 6-crown ring is observed

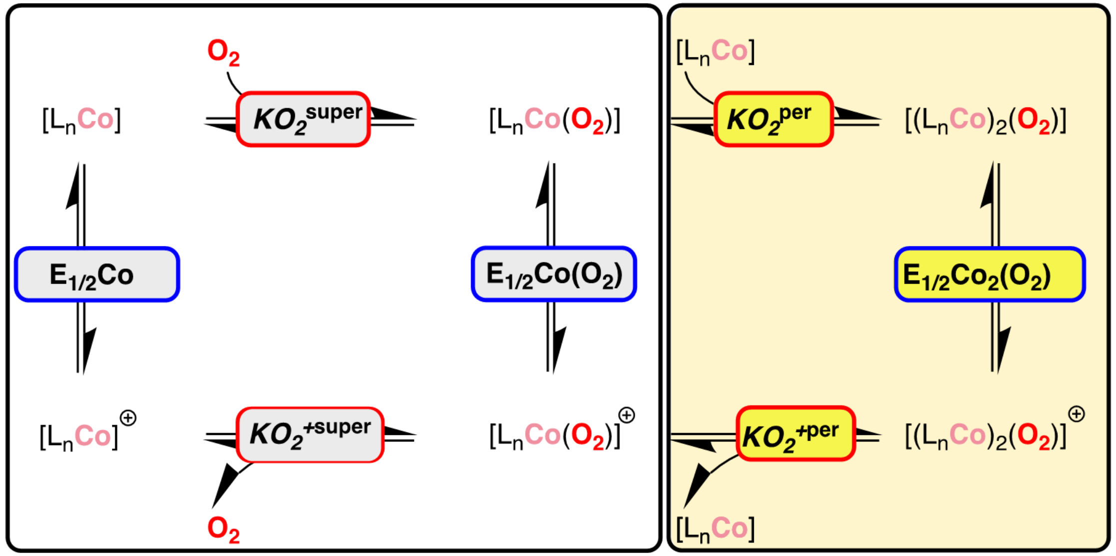
Future Work: Theory-guided Design



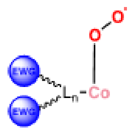
Progress and Current Status

Oxygen Separation Based on a Co(II)-Salen Platform

Big picture: Characterization of System based on Thermodynamics

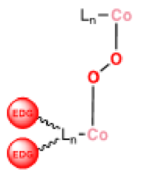


superoxo favored



-1.54 to - 1.59 V vs. $[Fe(C_5H_5)_2]^{0/+}$

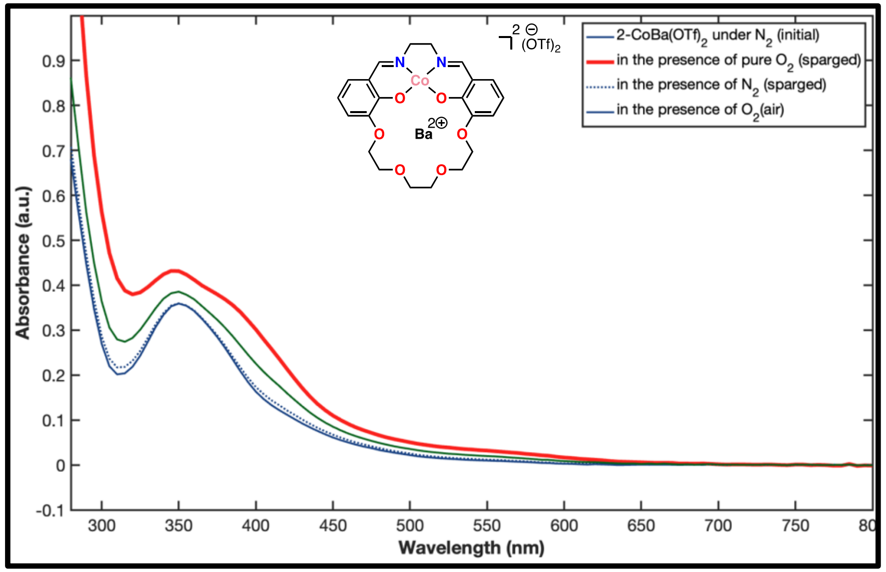
μ-peroxo favored



- 1.72 to - 1.68 V vs. $[Fe(C_5H_5)_2]^{0/+}$

Preliminary KO_2^{per}

@ 25 °C, only the complexes of alkaline earth metals bind O_2 in a reversible manner.



$$2[L_nCo] + O_2 \overset{Ko_2}{\rightleftharpoons} (L_nCo)_2O_2$$

$$K_{O_2} = \left[P_{1/2}[L_nCo]_0\right]^{-1}$$

$P_{1/2}$: half-oxygenation pressure

pO_2 (atm)	Abs @349 nm
0	0.36
1	0.43
0.2	0.38

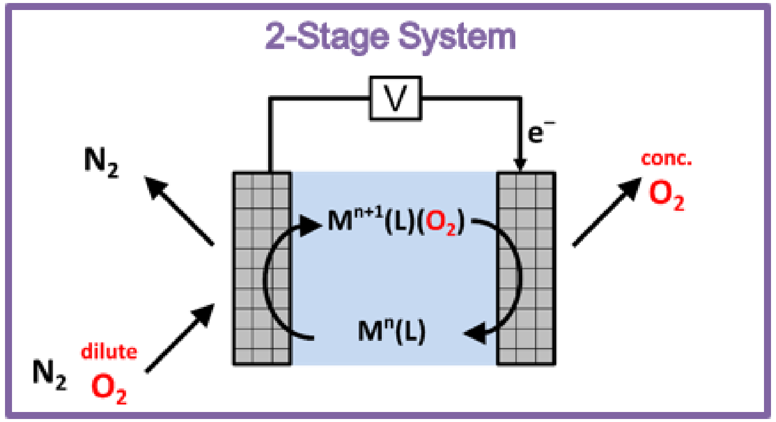
$$P_{1/2} = 0.45 \text{ atm}$$

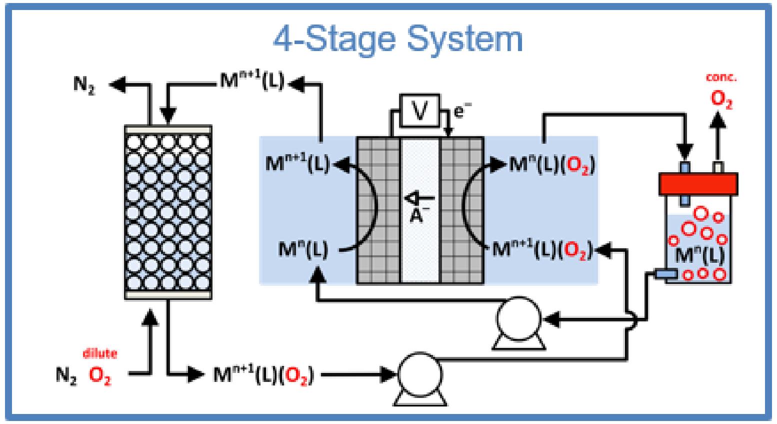
$$K_{O_2} = 4.49 \text{ x } 10^5 \text{ M atm}^{-1}$$

Progress and Current Status

Small Reactor at MIT

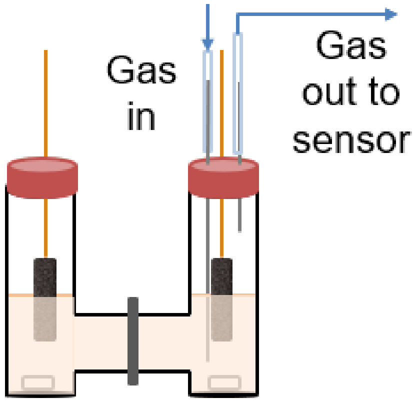
Potential system configurations


2-Stage System

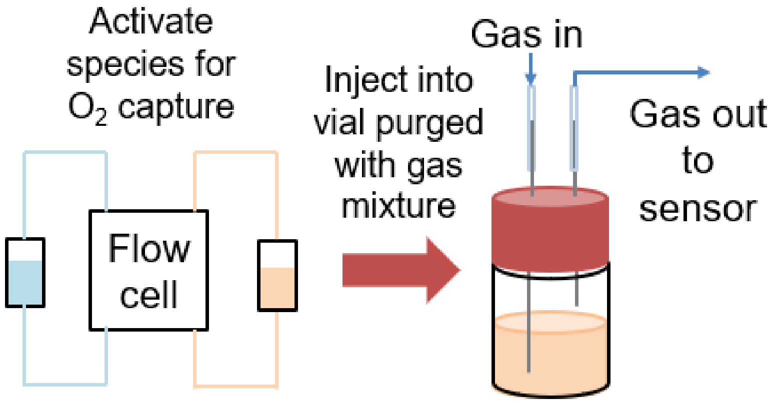

4-Stage System

Initial experimental setups

- Simultaneous activation/deactivation & capture/release of oxygen



- Activation and separate gas contact



Progress and Current Status

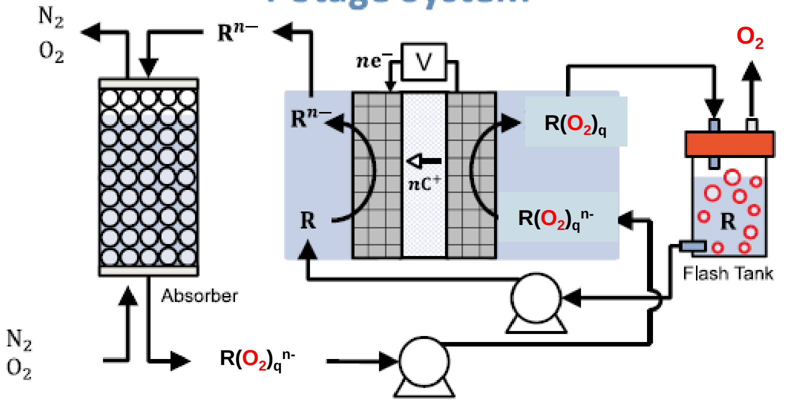
Design for Scale-up at RTRC

RTRC
RTX Technology Research Center

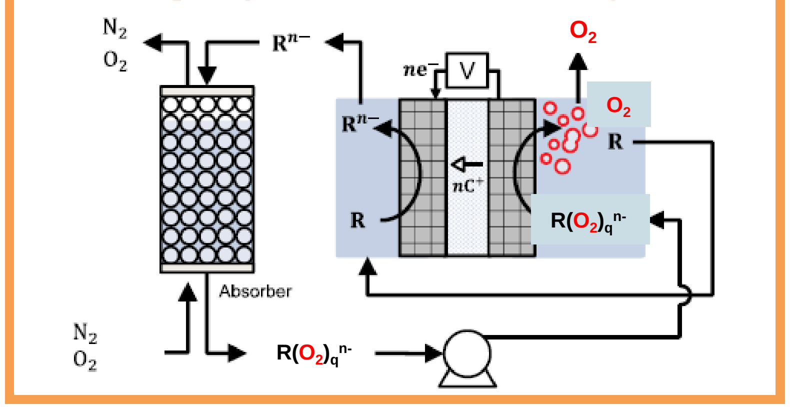
Absorption and desorption outside e-reactor. Reactor like a flow battery, only needs to handle liquids. Need to check for O_2 release on anode.

Probably easiest design to implement.

4-Stage System



3-Stage System (Anodic Desorption)



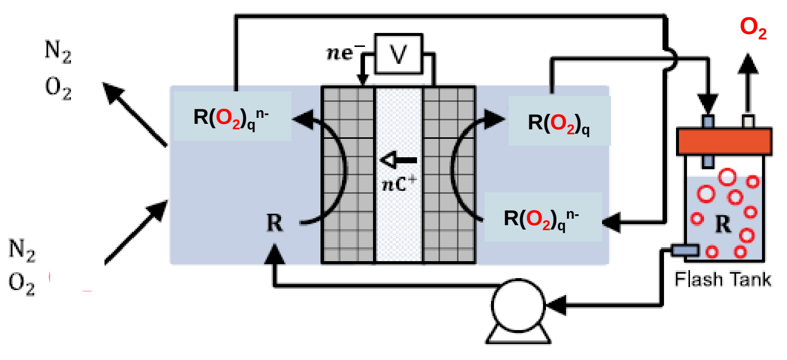
Absorption outside e-reactor. Desorption inside e-reactor. Like a water electrolyzer but need to feed liquid to both sides.

More complicated design.

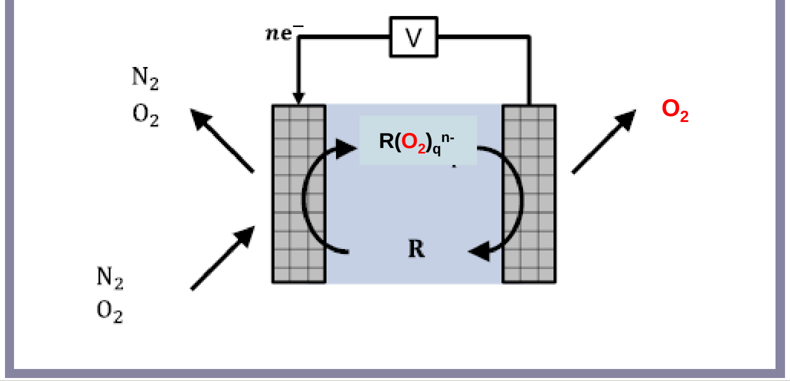
Absorption inside e-reactor. Desorption outside e-reactor. Need to simultaneously deliver liquid and gas cathode.

More complicated design.

3-Stage System (Cathodic Absorption)



2-Stage System



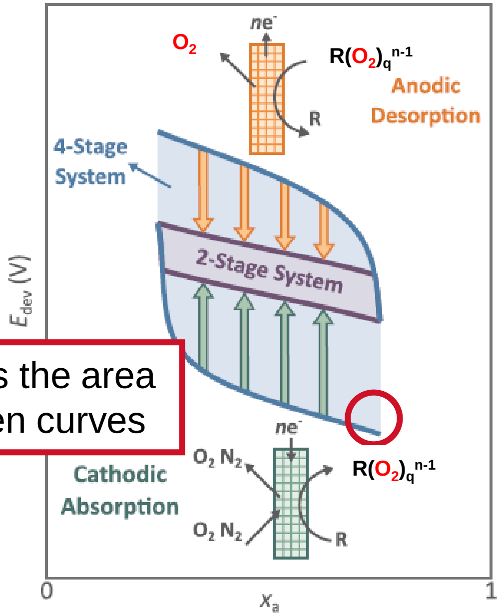
<u>Flowing</u> electrolyte is complicated. Need to deliver liquid while delivering & removing gas.

<u>Stagnant</u> looks simpler but may be limited to low rates and prone to electrolyte evaporation.

Four Process Diagrams Considered

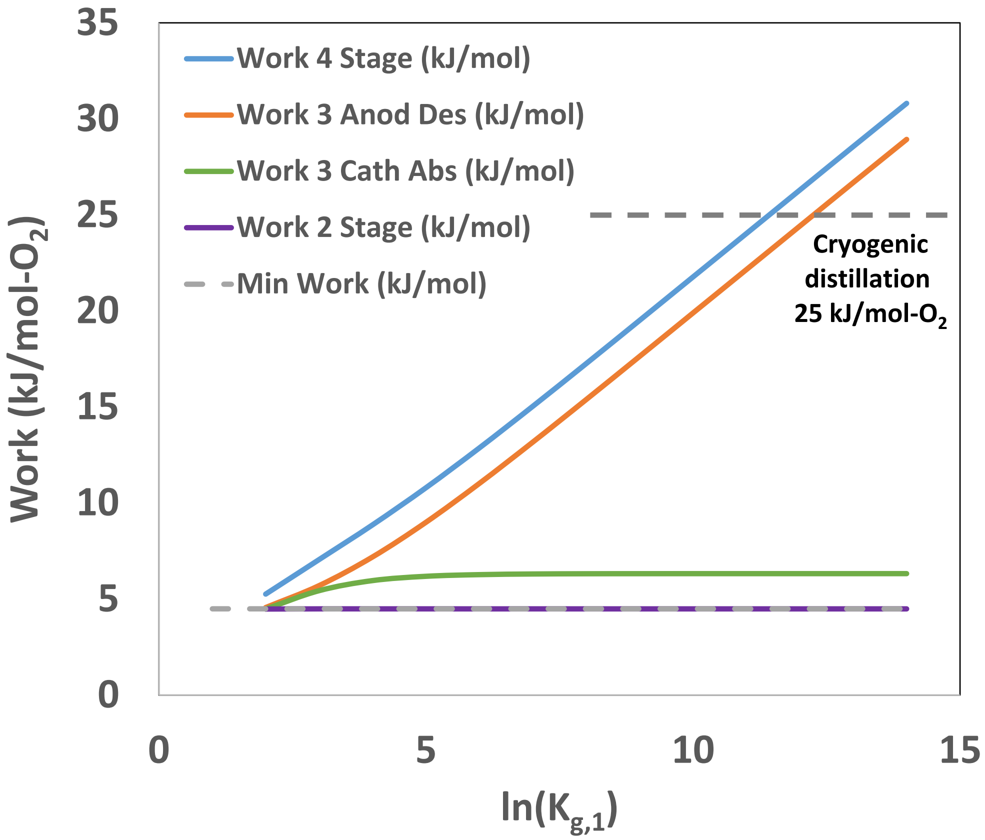
Progress and Current Status

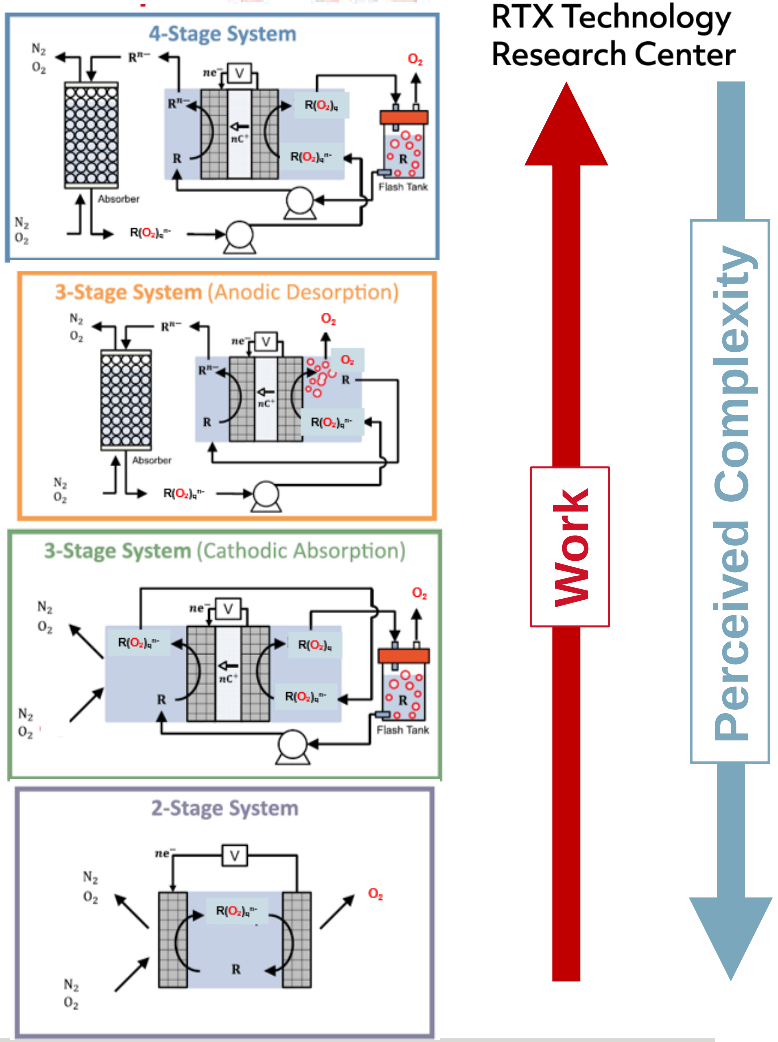
Sample Thermodynamic Work (J/mol-O_2)



Work is the area between curves

The 4 processes follow different paths and have different end points





All 4 approaches probably give high enough thermodynamic efficiency

Future Plans

Testing, Development, and Commercialization

- **UCI**
  - Use IR and EPR to understand how cation and ligand affect speciation
  - Use UV-vis to see what factors favor 1:1 Co-O_2 (temperature, ligand, cation, solvent, etc.)
  - Probe O_2 release from Co-Salen O_2 adducts with cyclic voltammetry
- **UC Davis**
  - Working to speed up computations to increase throughput (Generalized Gradient Approximation)
  - Investigating possibility of hybridizing models with AI/ML
- **MiT**
  - Investigating cell designs appropriate for simultaneous reduction/oxidation while bubbling gas
  - Identifying sensors for quantifying oxygen levels in gas streams
- **RTRC**
  - Modeling rate capabilities, polarizations of 2, 3, and 4-stage reactors and incorporating into techno-economics
  - Quantifying suitable targets for thermodynamic and kinetic properties of capture compounds

Outreach and Workforce Development Efforts

- Project supporting graduate students at UC Davis, UC Irvine, and MIT
- Project plan includes a paid summer internship at RTRC

Summary

- **Key findings** – binding constants for Co-Salen adequate, efficacy of electro-swing being tested (CV), preliminary thermodynamic and kinetic analyses promising
- **Future plans** – molecular modeling, synthesis and bench-scale evaluation of molecules, reactor development, and process modeling

Key take aways

- Electroswing approach to air separation analogous to CO_2 separation
- Theoretically suited to smaller process units with low work of separation
- Working to find molecules that perform all necessary functions

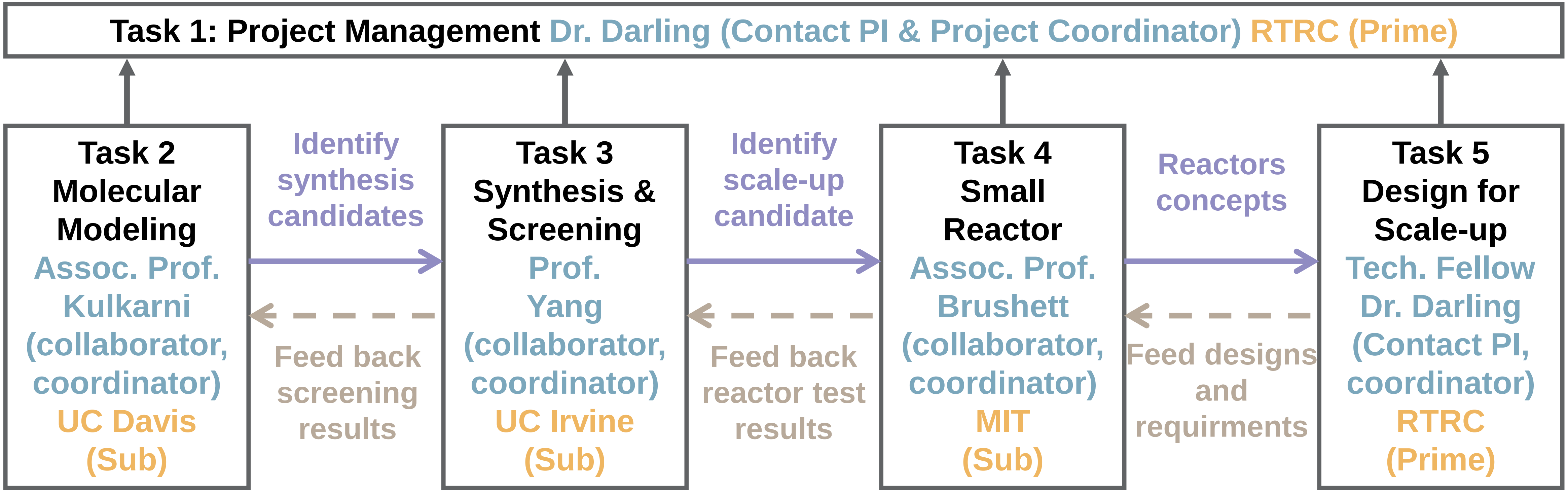
Acknowledgement and Disclaimer

- **Acknowledgment:** "This material is based upon work supported by the Department of Energy Office of Fossil Energy under Award Number(s) DE-FE003248."

Appendix

Organization Chart

Electrochemically Mediated Air Separation Modules (EM-ASM)



Task 1: Project Management Dr. Darling (Contact PI & Project Coordinator) RTRC (Prime)

Task 2
Molecular Modeling
Assoc. Prof. Kulkarni (collaborator, coordinator)
UC Davis (Sub)

Identify synthesis candidates

Feed back screening results

Task 3
Synthesis & Screening
Prof. Yang (collaborator, coordinator)
UC Irvine (Sub)

Identify scale-up candidate

Feed back reactor test results

Task 4
Small Reactor
Assoc. Prof. Brushett (collaborator, coordinator)
MIT (Sub)

Reactors concepts

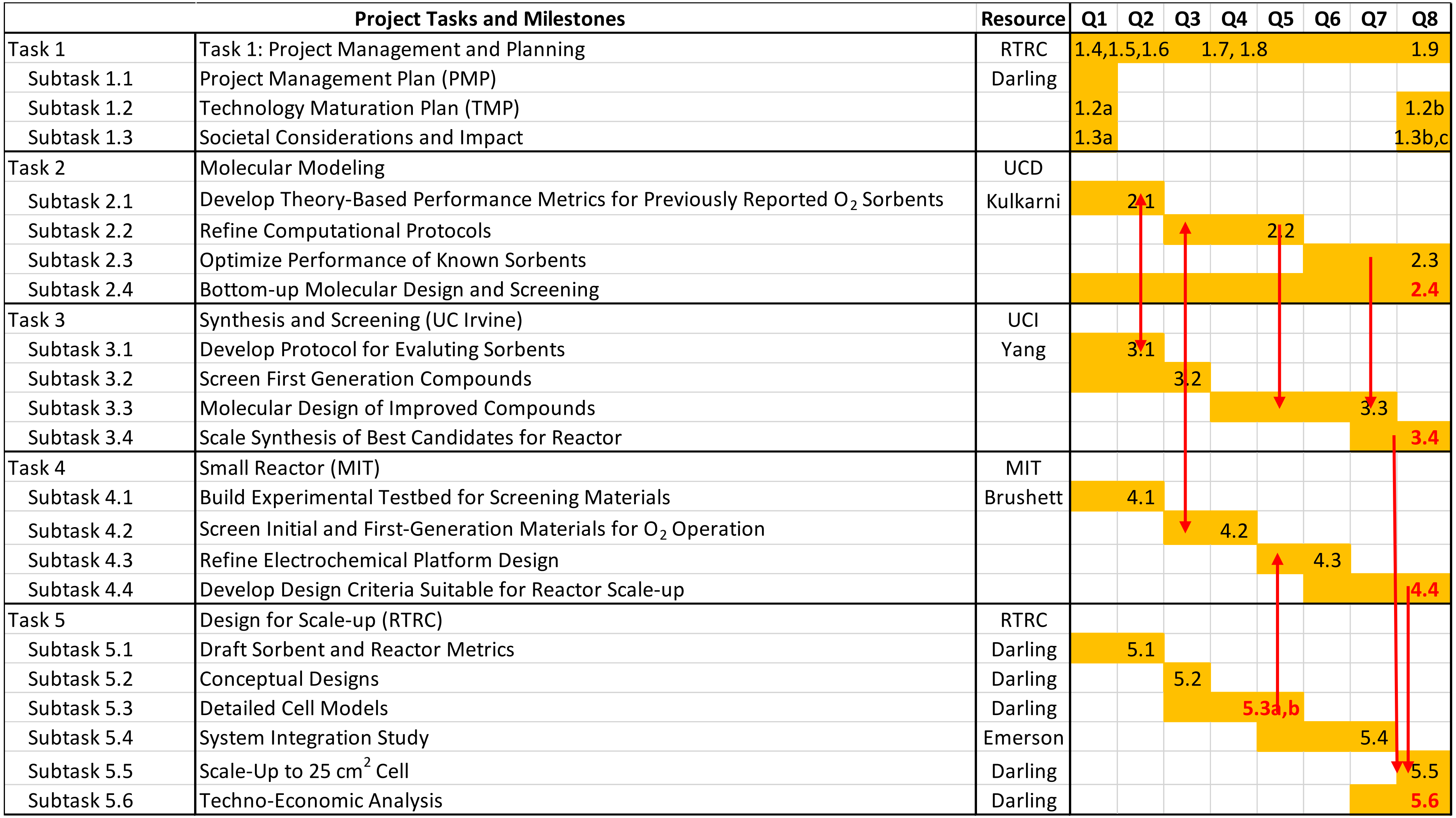
Feed designs and requirments

Task 5
Design for Scale-up
Tech. Fellow Dr. Darling (Contact PI, coordinator)
RTRC (Prime)

Gantt Chart

At least one technical milestone per quarter

One 24-month budget period



Project Tasks and Milestones		Resource	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8
Task 1	Task 1: Project Management and Planning	RTRC	1.4,1.5,1.6	🟨	🟨	1.7, 1.8	🟨	🟨	🟨	1.9
Subtask 1.1	Project Management Plan (PMP)	Darling	🟨							
Subtask 1.2	Technology Maturation Plan (TMP)		1.2a							1.2b
Subtask 1.3	Societal Considerations and Impact		1.3a							1.3b,c
Task 2	Molecular Modeling	UCD								
Subtask 2.1	Develop Theory-Based Performance Metrics for Previously Reported O_2 Sorbents	Kulkarni	🟨	2.1						
Subtask 2.2	Refine Computational Protocols				🟨	🟨	2.2			
Subtask 2.3	Optimize Performance of Known Sorbents							🟨	🟨	2.3
Subtask 2.4	Bottom-up Molecular Design and Screening		🟨	🟨	🟨	🟨	🟨	🟨	🟨	**2.4**
Task 3	Synthesis and Screening (UC Irvine)	UCI								
Subtask 3.1	Develop Protocol for Evaluting Sorbents	Yang	🟨	3.1						
Subtask 3.2	Screen First Generation Compounds		🟨	🟨	3.2					
Subtask 3.3	Molecular Design of Improved Compounds					🟨	🟨	🟨	3.3	
Subtask 3.4	Scale Synthesis of Best Candidates for Reactor								🟨	**3.4**
Task 4	Small Reactor (MIT)	MIT								
Subtask 4.1	Build Experimental Testbed for Screening Materials	Brushett	🟨	4.1						
Subtask 4.2	Screen Initial and First-Generation Materials for O_2 Operation				🟨	4.2				
Subtask 4.3	Refine Electrochemical Platform Design						🟨	4.3		
Subtask 4.4	Develop Design Criteria Suitable for Reactor Scale-up							🟨	🟨	**4.4**
Task 5	Design for Scale-up (RTRC)	RTRC								
Subtask 5.1	Draft Sorbent and Reactor Metrics	Darling	🟨	5.1						
Subtask 5.2	Conceptual Designs	Darling			5.2					
Subtask 5.3	Detailed Cell Models	Darling			🟨	🟨	**5.3a,b**			
Subtask 5.4	System Integration Study	Emerson					🟨	🟨	5.4	
Subtask 5.5	Scale-Up to 25 cm^2 Cell	Darling								5.5
Subtask 5.6	Techno-Economic Analysis	Darling							🟨	**5.6**

Background

Air Separation Technologies

- Pure oxygen supports low-cost hydrogen production via modular gasification
- Air separation is energy intensive, and the most efficient methods do not scale down to rates that support modular gasifiers

Process	**Energy (kWh/ton$_{EPO2}$)**	**Production (ton/day)**	**O_2 Purity (%)**
Theoretical minimum	53	-	100%
Cryogenic distillation	220	> 300	> 99%
Pressure swing absorption	430	< 100	95%
Hollow fiber membrane	275	< 25	< 40%
Hollow fiber membrane OBIGGS	1000	~ 1	28%
High temperature electrochemical, O^{--}	1500	Lab scale	> 99%
Low temperature electrochemical, H^{+}	3200	Lab scale	> 99%

Seek a new method for separating oxygen from air that can be scaled down for modular gasifiers

End of Slides