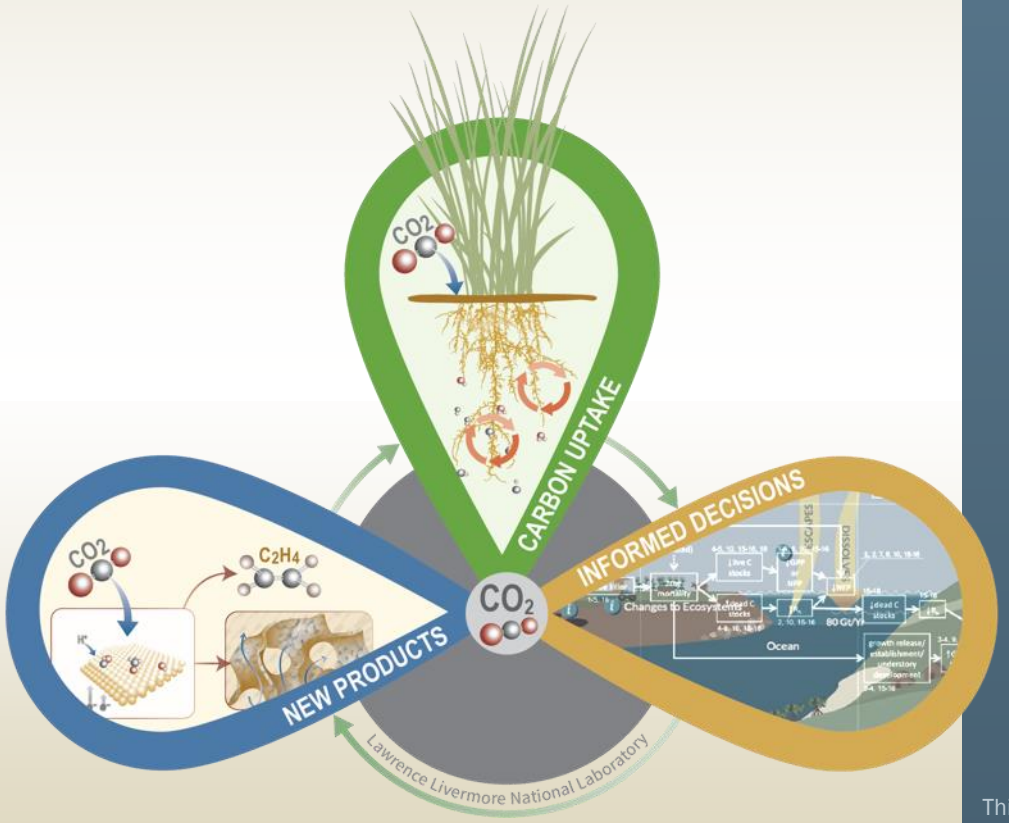
THE LLNL CARBON INITIATIVE

Anticipating the threat and preparing DOE for the next major phase of climate mitigation technology



Understanding Degradation Mechanisms of Aminopolymers Used in Direct Air Capture

LAB 20-2303, SCW1726

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Lawrence Livermore National Laboratory

U.S. Department of Energy
National Energy Technology Laboratory
Direct Air Capture Kickoff Meeting
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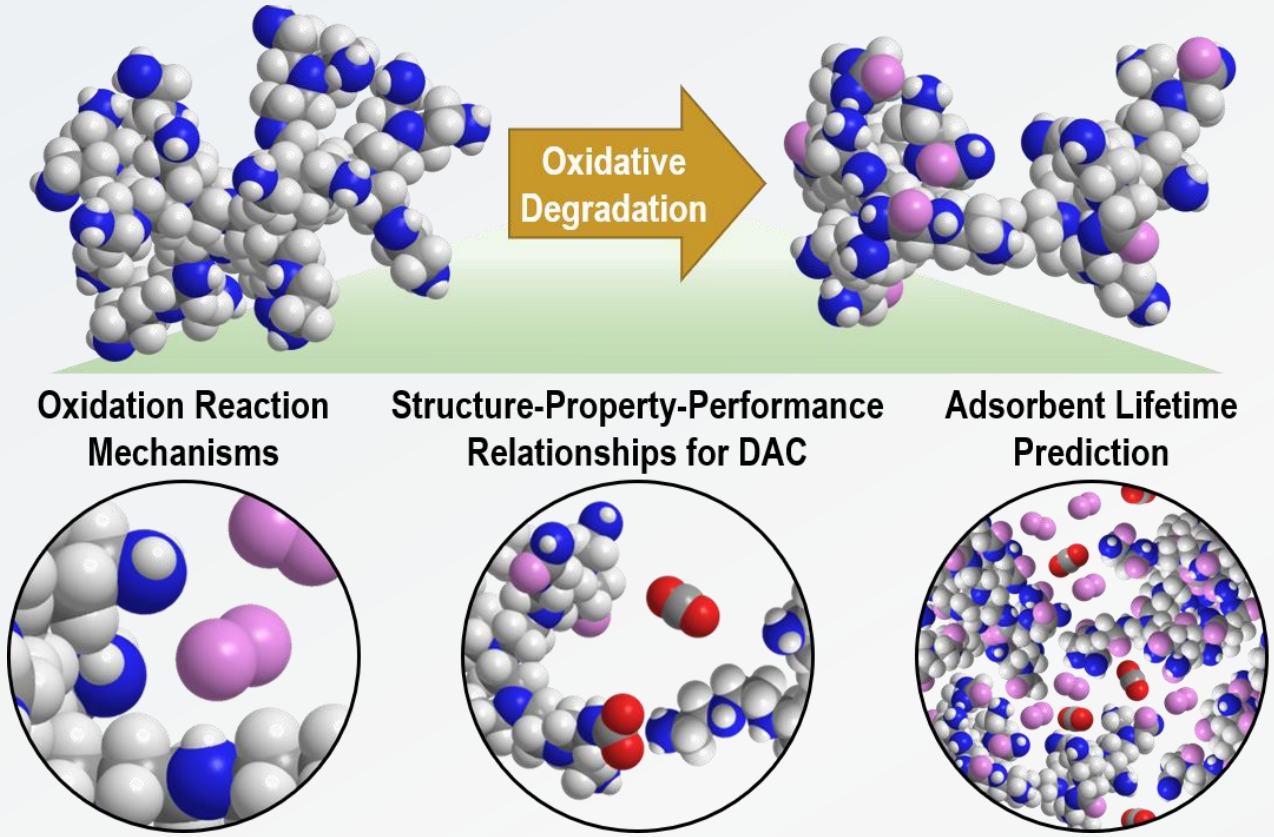
Program Overview

- Overall Project Objective
  - Identify fundamental mechanisms and elucidate key chemical and structural parameters that impact degradation of aminopolymer-based DAC adsorbent materials



- Timeline and Budget
  - Project start date: 10/01/20
  - Project end date: 09/30/23
  - DOE-BES funding: $4.5M

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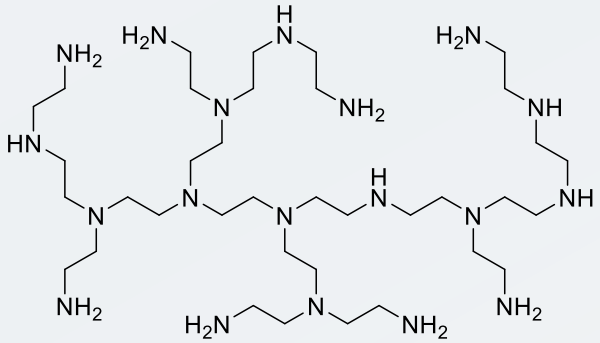
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

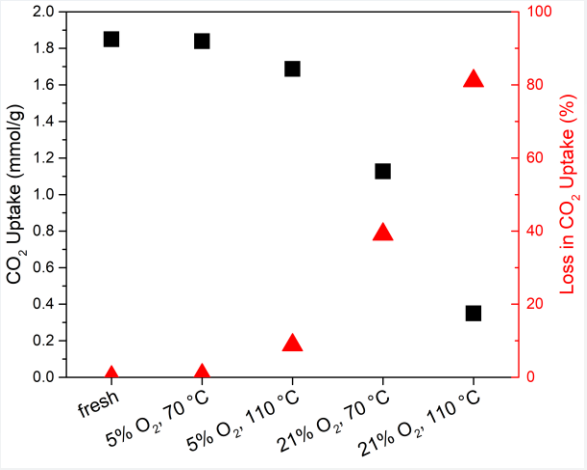
Georgia Tech

Global Thermostat

Technology Background



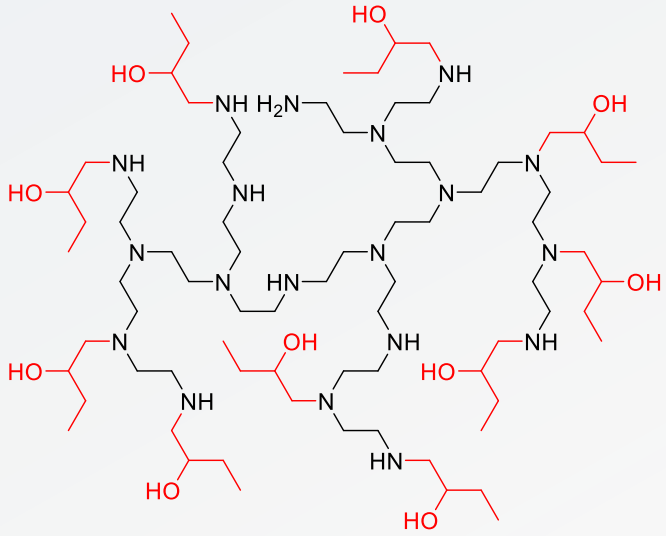
poly(ethylenimine) (PEI)



Bali, et al. *Energy Fuels* 2013

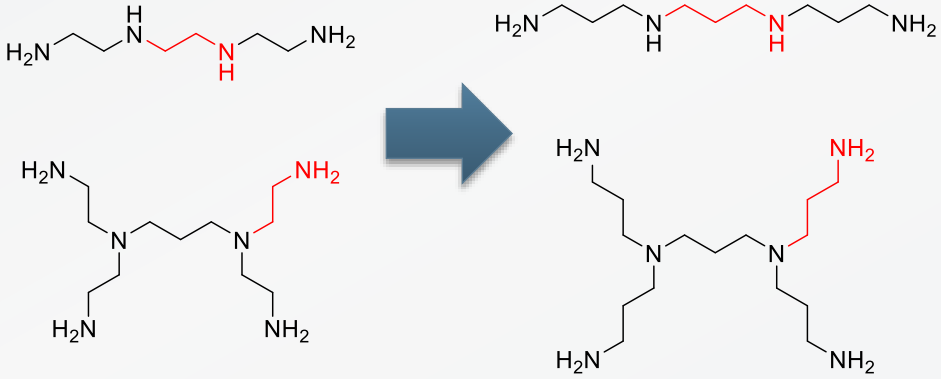
Oxidative degradation of PEI causes **irreversible CO_2 capacity loss**; there is a **critical gap in the fundamental science** about the degradation mechanism and strategies that improve stability are not well understood

Functionalize with hydroxyls



Min, et al. *Nat. Commun.* 2018
Xu, et al. *J. Mater. Chem. A* 2018
Goeppert, et al. *ChemSusChem* 2019

Change polymer backbone

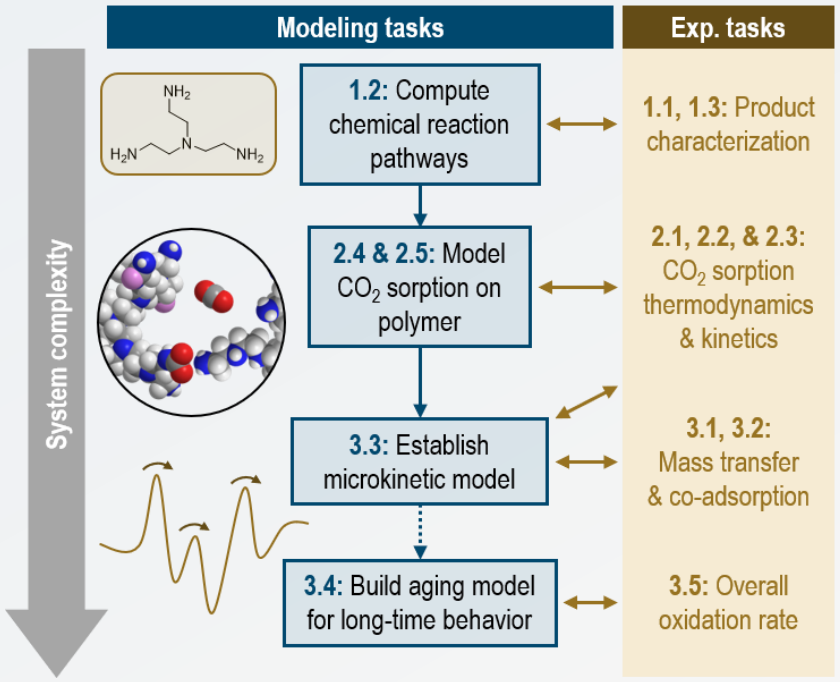


Pang, et al. *JACS* 2017
Sarazen, Jones *Macromolecules* 2017
Pang, et al. *ChemSusChem* 2018
Sarazen, et al. *ACS Sus. Chem. Eng.* 2019
Yoo, et al. *Ind. Eng. Chem. Res.* 2019
Rosu, et al. *ACS AMI* 2020

Impact: Determining key degradation mechanisms can promote **novel, rationally motivated improvement strategies** for polymer modification, and better predictions of adsorbent lifetime will **reduce uncertainty** about direct air capture cost and economic viability

Technical Approach/Project Scope

Our approach uses a highly integrated combination of **spectroscopic characterization**, **kinetic analysis**, and **advanced quantum simulations** to generate fundamental knowledge about the **mechanisms** and **kinetics** of aminopolymer-based DAC adsorbent degradation



1. Develop oxidative degradation mechanisms using model materials
M1.2–M1.3

- Computed degradation reaction pathways for model compounds
- Validated simulations with spectroscopic and kinetic characterization

- Determined degraded products responsible for CO_2 capacity loss

2. Develop structure-property-performance relationships between aminopolymer oxidation and direct air capture
M2.1–M2.5

- Developed models for sorption on degraded polymer

- Determined O_2 mass transport parameters
- Impact of co-adsorbed CO_2 on degradation
- Validated models with pilot-scale experiments

3. Understand the effect of gas diffusion and presence of co-adsorbates on the rate of oxidative degradation
M3.1–M3.5

A fully successful project will (i) determine **key reaction mechanisms** for oxidative degradation and (ii) develop models that allow better **prediction of short- and long-term degradation** behavior

Team and Facilities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Dr. Roger Aines (LLNL)


Dr. Bryan Pivovar (NREL)


Dr. Wade Braunecker (NREL)


[Dr.] Elwin Sellars (LLNL, Summer 2021)


Hannah Eshelman (LLNL)


Dr. Sichi Li (LLNL)


Dr. Amitesh Maiti (LLNL)


Dr. Maxwell Marple (LLNL)


Dr. Joshuah Stolaroff (LLNL)


Dr. Noemi Leick (NREL)

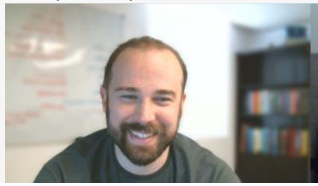

Prof. Christopher Jones (GIT)


Dr. Juliana Carneiro (GIT)


Prof. Carsten Sievers (GIT)

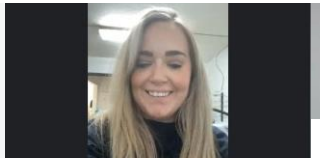

Dr. Giada Innocenti (GIT)

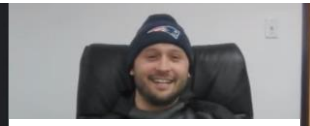

Yoseph Guta (GIT)

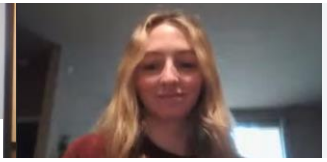

Dr. Eric Ping (GT)


Cassandra Hertz (GT)


Dr. Yanhui Yuan (GT)

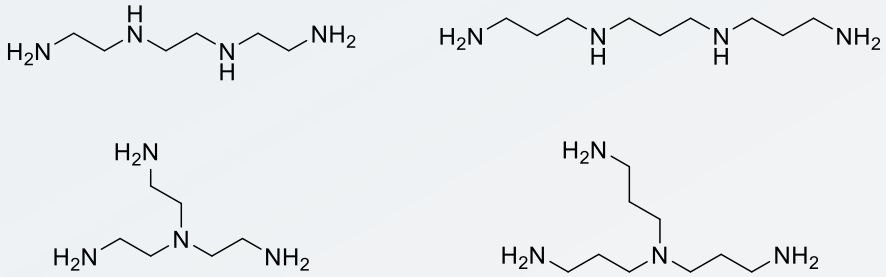

Joanie Racicot (GT)


Dr. Miles Sakwa-Novak (GT)


Abigayle Clabaugh (GT)

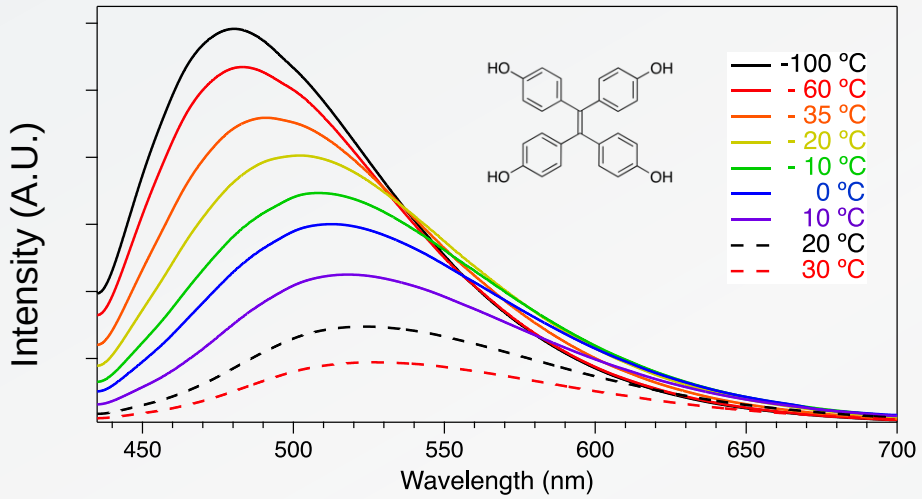
Progress and Current Status of Project

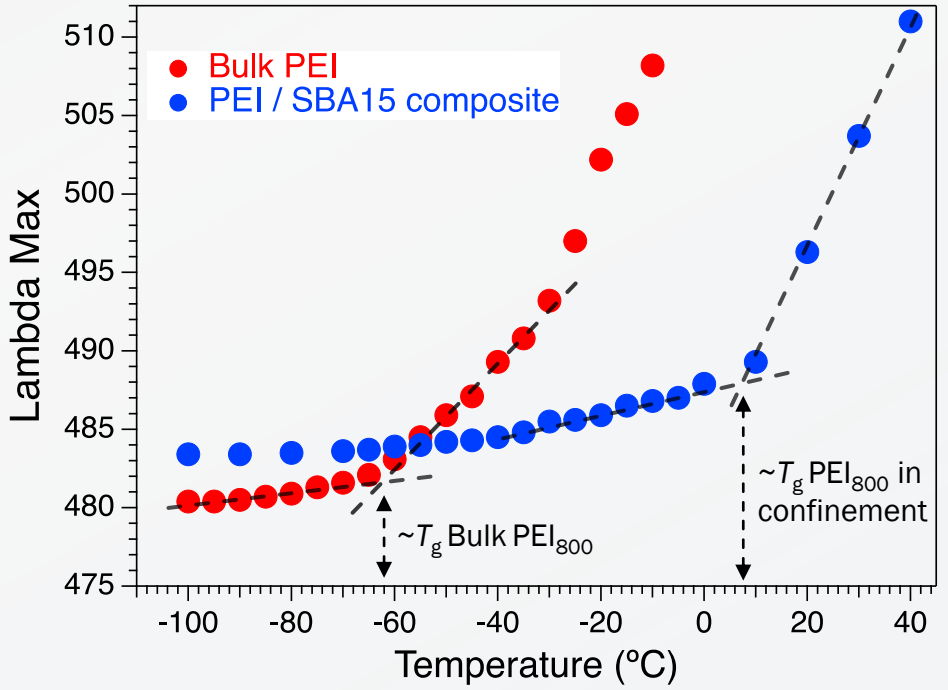
- Model material studies



  - Multi-analytical spectroscopic approach (NMR, FTIR, mass spectrometry) to investigate oxidation product distribution and formation kinetics
  - Developing methods to sample the reaction space of O_2 interaction with model compounds; compute reaction free energies, activation barriers, and NMR spectra
- Polymer mobility in model supports
  - Fluorescence measurements of PEI under pore confinement indicate dramatic change in mobility (right)
  - Examining polymer-support interactions with SSNMR to identify chemical environments for degraded materials

Fluorescence Spectra of PEI_{800} doped with 1 wt.% Fluorophore





Opportunities for Collaboration

- Integration of project components
  - Synthesis and characterization with advanced quantum simulation and multiscale modeling
  - Characterization methods across team members coupled to simulation of spectroscopic fingerprints
  - Kinetic analysis connecting short-term accelerated behavior with long-term consequences
- Collaboration with industry provides context and model validation
  - Global Thermostat a leading practitioner of amine-based DAC
  - Project will develop models for predicting adsorbent lifetime, to be validated against quasi-accelerated aging experiments
- Looking forward…
  - Development and scale-up of next generation adsorbent materials and other degradation mitigation strategies