EILERS GRADUATE STUDENT FELLOWSHIP
FINAL REPORT

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FACULTY ADVISOR:	Casey P. O'Brien
REPORT PERIOD:	2022
PROJECT TITLE:	Operando Surface Enhanced Raman Spectroscopy (SERS) Platform for Studying the Structure and Dynamics of Amine-based Membranes in Complex Environments
CONNECTION TO ND ENERGY'S RESEARCH AREAS (CHECK ALL THAT APPLY):	**( ) Energy Conversion and Efficiency ( ) Sustainable and Secure Nuclear** **( ) Smart Storage and Distribution ( ) Transformation Solar** **(x) Sustainable Bio/Fossil Fuels ( ) Transformative Wind**

MAJOR GOALS AND ACCOMPLISHMENTS:

List your major research goals and provide a brief description of your accomplishments (1-2 sentences). Indicate the percentage completed for each goal. Please use a separate sheet to share additional details, technical results, charts, and graphics.

MAJOR RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Design, develop, and test a new experimental *operando* Raman spectroscopic platform that could probe the chemical structure and dynamics of membranes in realistic operating environments.	A new experimental *operando* surface-enhanced Raman spectroscopic (SERS) platform has been established, which can characterize the molecular structure of polymeric membranes and simultaneously measure their gas separation performance under realistic operating conditions. The transport intermediates of CO_2 in PVAm membrane were successfully demonstrated using the new *operando* platform.	100
Model study of Amine-Containing CO_2-Selective Membrane Process for Carbon Capture.	A mathematical model was proposed to describe the transport of CO_2 through the PVAm membrane. The model quantitatively describes the permeability of CO_2 via facilitated transport is an order of magnitude higher than that via solution diffusion. Based on the *operando* SERS platform, the effect of CO_2 partial pressure on CO_2 transport was also studied in molecular scale.	100
Study and address the knowledge gap between different amine-based polymeric membrane structures (PVAm, PMVAm, PDVAm, and P4VP) and performance.	Different amine-based membranes were investigated with the *operando* SERS platform to understand the structure effect on CO_2 transport mechanism, and to understand which amine types and operating conditions exhibit the optimal CO_2 transport performance.	60

RESEARCH OUTPUT:

Please provide detailed information below regarding any output resulting from your research project.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS	National Science Foundation CAREER (CBET-2144362), "Catalytic Membranes for Integrated CO_2 Capture and Conversion," 5 years (June 2022 – May 2027) $537,317.
EXTERNAL AWARDS	N.A.
JOURNAL ARTICLES	1. ACS Applied Materials & Interfaces; *Operando* Surface-Enhanced Raman-Scattering (SERS) for Probing CO_2 Facilitated Transport Mechanisms of Amine-Functionalized Polymeric Membranes; **Hui Xu**, Justin Easa, Sarah G. Pate, Renxi Jin, and Casey P. O'Brien; February 14, 2022; March 22, 2022, 14, 15697-15705. 2. *In Submission,* Mathematical Modeling of CO_2 Facilitated Transport across Polyvinylamine Membranes with Direct *Operando* Observation of Amine Carrier Saturation; **Hui Xu**, Sarah G. Pate, and Casey P. O'Brien.
BOOKS AND CHAPTERS	
PUBLIC PRESENTATIONS, SEMINARS, LECTURES	ND Energy Postdoc and Grad Student Seminar, "*Operando* Surface-Enhanced Raman-

	Scattering (SERS) Platform for Studying the Structure and Dynamics of CO_2 Facilitated Transport in Amine-based Membranes in Complex Environments", November 2022, Notre Dame
AWARDS, PRIZES, RECOGNITIONS	N.A.
INTERNAL COLLABORATIONS FOSTERED	Collaborated with Professor William Philip (Chemical and Biomolecular Engineering) and Professor Jon Camden (Chemistry and Biochemistry).
EXTERNAL COLLABORATIONS FOSTERED	N.A.
WEBSITE(S) FEATURING RESEARCH PROJECT	N.A.
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	N.A.

MAJOR GOALS AND ACCOMPLISHMENTS

(Additional Details, Technical Results, Charts and Graphics)

Goal 1: Design, develop, and test a new experimental *operando* Raman spectroscopic platform that could probe the chemical structure and dynamics of membranes in realistic operating environments. This was done. The new experimental *operando* surface-enhanced Raman spectroscopic (SERS) platform has been successfully established (Fig. 1), which can characterize the molecular structure of polymeric membranes and simultaneously measure their gas separation performance under realistic operating conditions. Polyvinylamine (PVAm) membrane was prepared and used to investigate the utility of the new *operando* SERS platform (Fig. 2). The experiments showed that a small amount of plasmonic Ag nanoparticles added to the PVAm solution prior to knife-casting onto PVDF supports selectively enhances the Raman signal intensity associated with CO_2 transport intermediates (carbamate) formed in PVAm during the separation of CO_2/CH_4 (Fig. 2b). The intensity of the Raman bands associated with carbamate species correlates with the CO_2 flux across the membrane (Fig. 2d), indicating that these are the primary intermediates in the CO_2 transport mechanism across PVAm. The new operando spectroscopy platform can be applied to other types of membranes, such as mixed-matrix membranes and ceramic membranes, to provide detailed information under realistic working circumstances, which could help to understand the key factors that determine membrane performance and design new membranes with enhanced performance.

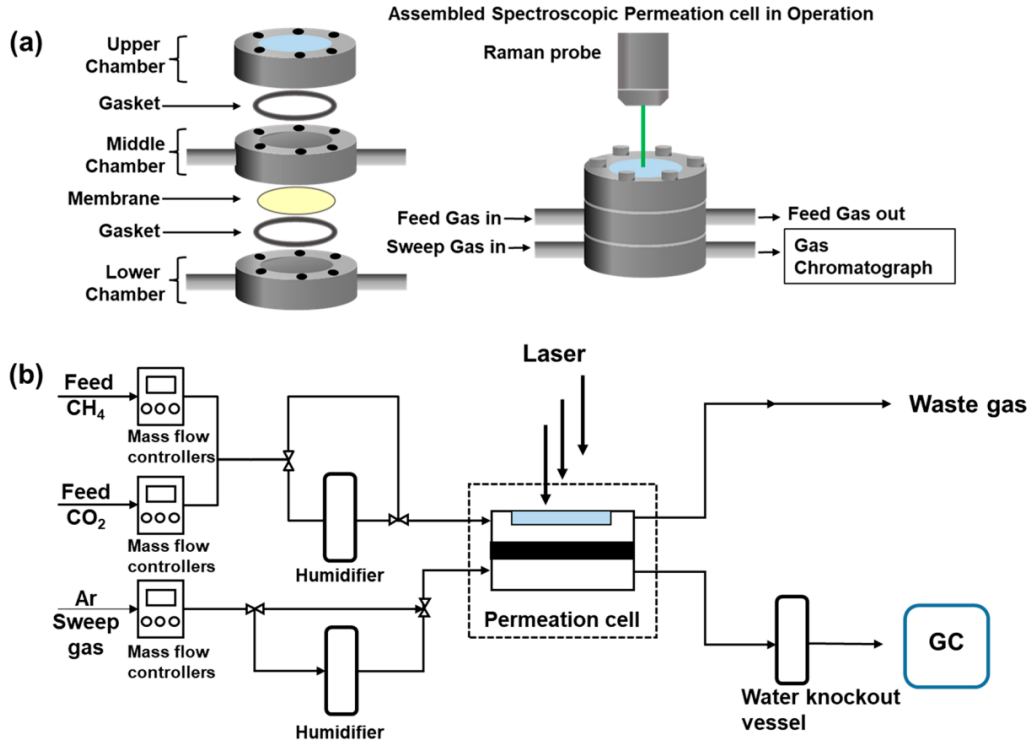

Fig. 1. Schematic illustration of (a) Permeation Cell Exploded (left) and Assembled (right) for Gas Separation Performance Evaluation and (b) the Permeation Apparatus

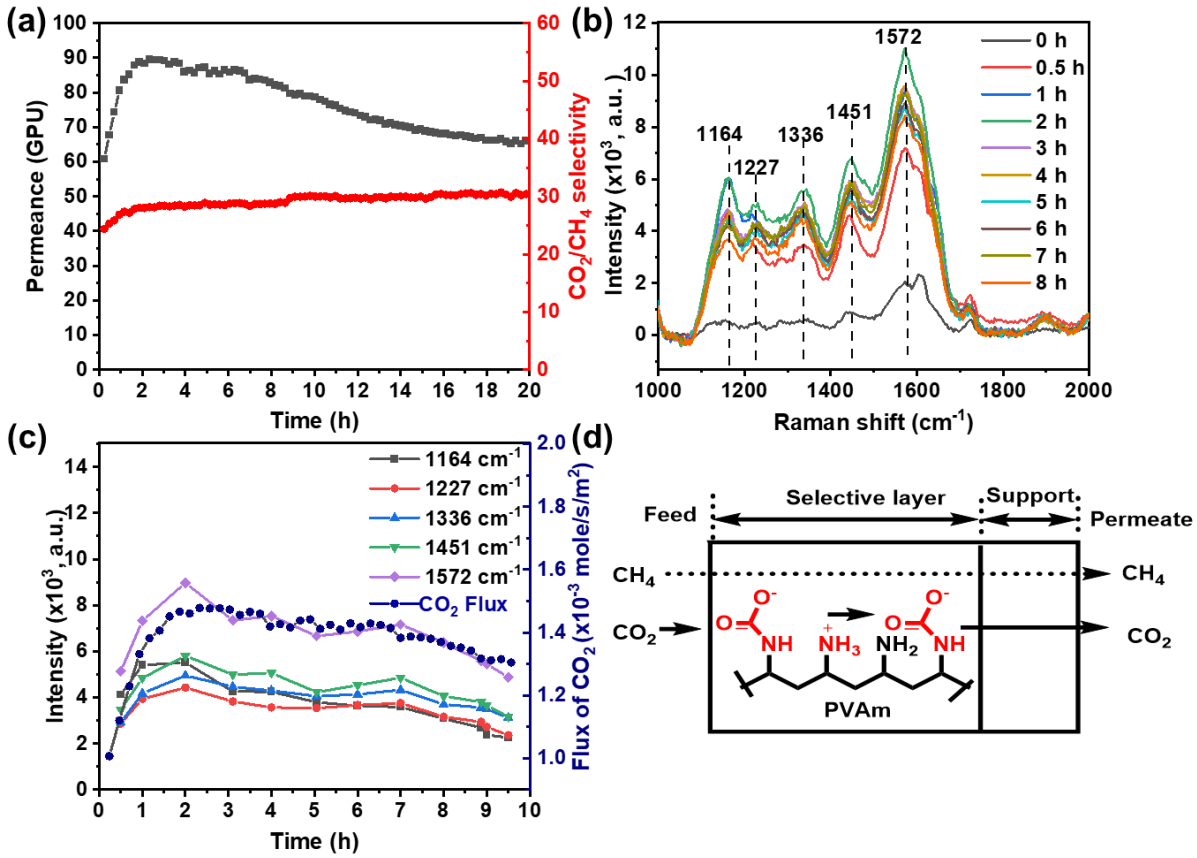

Fig. 2. (a) CO_2 transport performance of PVAm/Ag NPs(20.4mg)-PVDF membrane (PVDF acts as the substrate, while PVAm and Ag nanoparticles form the active separation membrane together); (b) In-situ Raman spectra as a function of exposure time; (c) Chemical structure of PVAm and facilitated CO_2 transport mechanism; (d) Intensity changes of peaks over exposure time and flux of CO_2 over exposure time.

Goal 2: Model study of Amine-containing CO_2-selective Membrane Process for Carbon Capture. This was done. As the CO_2 permeance of facilitated transport membrane is pressure-dependent, the effect of CO_2 partial pressure on CO_2 facilitated transport across PVAm membrane was also studied with our apparatus to study the trend and correlate the phenomenon with molecular- and nano-scale structure. A carrier saturation phenomenon was observed, and a mathematical transport model for CO_2 transport through the amine-containing FTMs was developed with fitting parameters that are verifiable by experiment data (Fig 3). The model quantitatively describes the permeability of CO_2 via facilitated transport is an order of magnitude higher than that via solution diffusion. Based on the operando SERS platform, the effect of CO_2 partial pressure on CO_2 transport was also studied on the molecular scale, which provided direct spectroscopic evidence of the carrier saturation phenomenon (Fig. 4). Our modeling and spectroscopic approaches are not limited to this particular membrane system and may be used to study other amine-based FTMs for CO_2 capture or FTMs for other types of separations such as olefin-paraffin separation, for example.

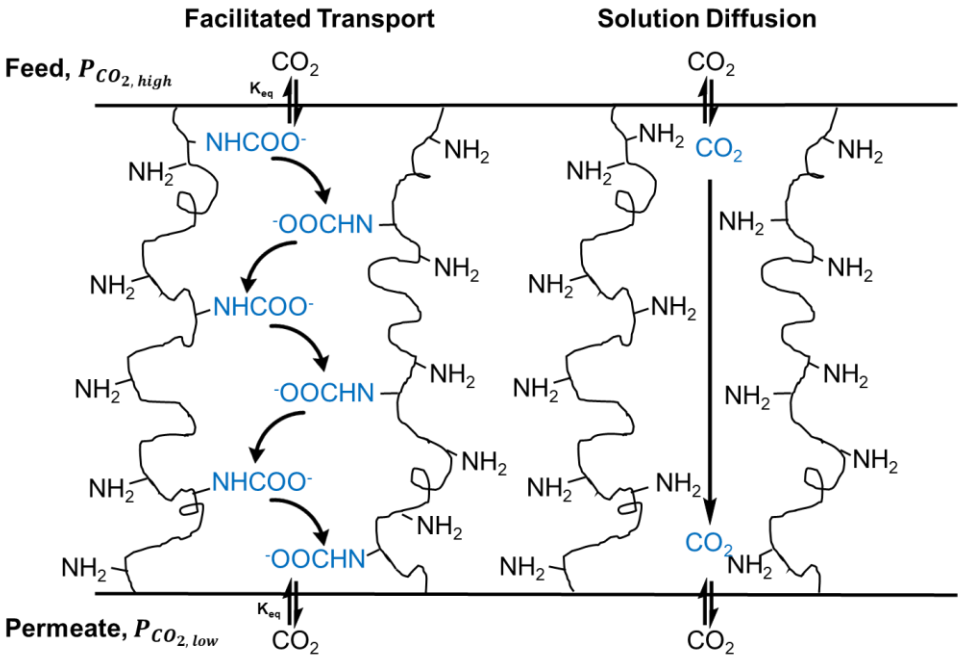

Fig. 3. Schematic representation of CO_2 transport across PVAm via facilitated transport of carbamate and solution-diffusion of CO_2.

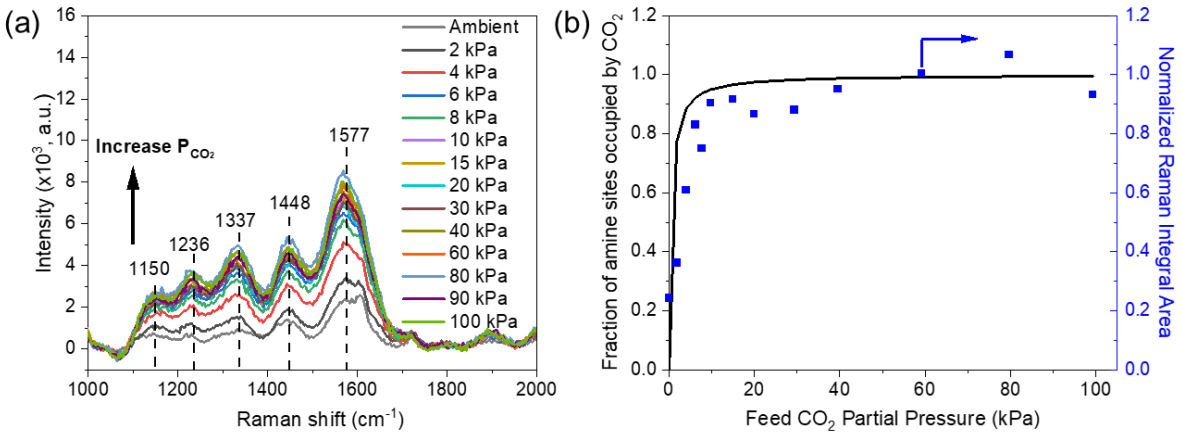

Fig. 4. (a) *Operando* Raman spectra as a function of CO_2 partial pressure during exposure to humidified CO_2/CH_4 with 2-99 kPa CO_2, 2.2 kPa H_2O, and balance CH_4 at atmospheric pressure and room temperature. (b) Fraction of amine sites occupied by CO_2 on the feed side of PVAm from model predictions (black line), and the normalized integral area of the Raman peaks between 1076-1694 cm^{-1} (blue squares), versus feed CO_2 partial pressure.

Goal 3: Use the new operando Raman spectroscopic platform to study and address the knowledge gap between different amine-based polymeric membrane structures (PVAm, PMVAm, PDVAm, and P4VP) and performance. Other amine-based membranes were investigated further to understand the structural effect of membrane materials on the CO_2 transport mechanism and which amine types and operating conditions exhibit optimal CO_2 transport performance. The SERS-active polymeric membranes were prepared and tested with our operando SERS technique. According to the result, new peaks appeared during their separation process. Comparing the CO_2 separation performances, we found that involving Ag NPs doesn't have much effect on the selectivity of the membranes, although there are changes in their CO_2 permeance. The Raman peaks assignment and study of the role of water in CO_2 transport through the membranes still need to be finished.

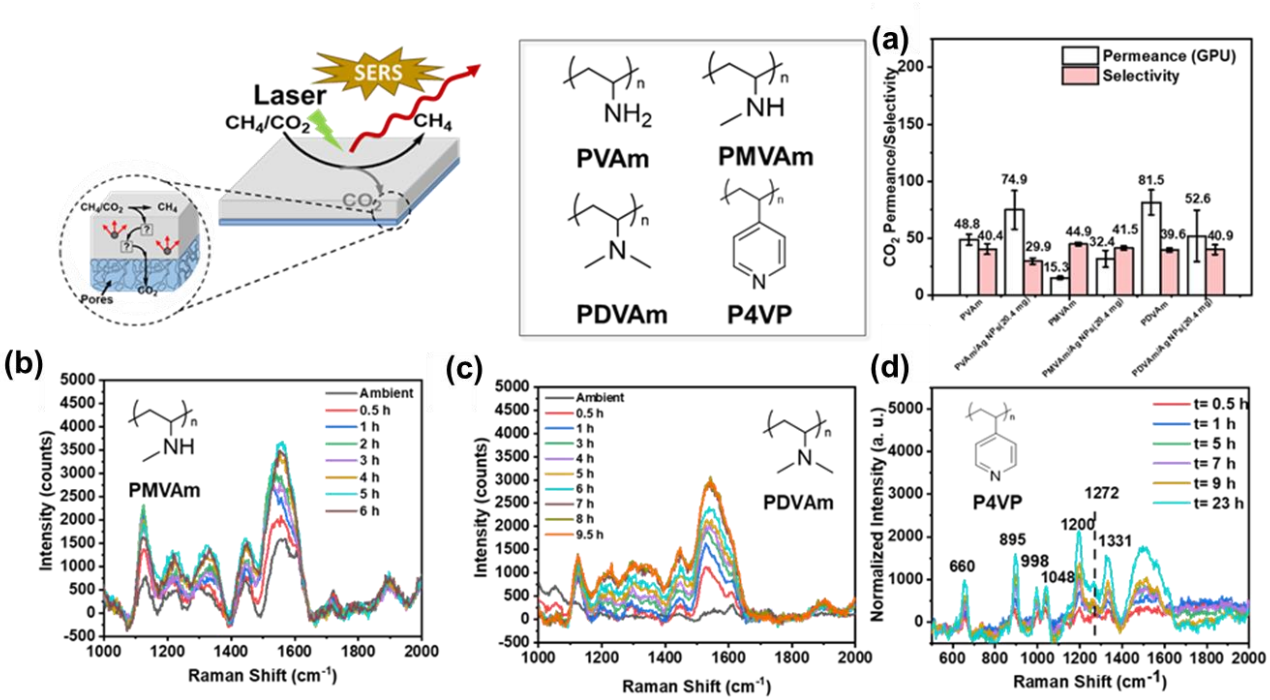

Fig. 5. (a) Comparison of gas separation performance of the membranes with and without Ag NPs involving when separate the simulated biogas. (b) In-situ Raman spectra of PMVAm membrane. (c) In-situ Raman spectra of PDVAm membrane. (d) *In-situ* Raman spectra of P4VP membrane (feed side: 49 mol% CH_4, 49 mol% CO_2, 2 mol% H_2O, 1atm; sweep side: 98 mol% Ar, 2 mol% H_2O, 1 atm; Temperature: 19 ^oC).