System-Level Approaches for Intensifying the CO_2 Electrolysis Process: From Reaction Chemistry to Process Development

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Link Foundation Energy Fellowship Report

1. Introduction – Electrochemical reduction of CO_2 (CO_2RR) is a promising alternative for producing carbon-based value-added chemicals such as carbon monoxide, ethylene, and ethanol that are currently produced using thermochemical fossil fuel-based production methods.[1] Despite research breakthroughs, significant improvements are still needed in terms of activities (partial current densities – pCDs), selectivities (Faradaic efficiencies – FEs), and full cell energy efficiencies (EEs) before the CO_2 electrolysis process can be employed at industrial scales in an economically feasible and carbon-neutral manner.[2]

2. Objectives – My thesis research pursues aspects of heterogeneous electrocatalysis, electrolyte and reactor engineering, process modeling, and electrochemical spectroscopy to advance CO_2 electrolysis technology. Using a combination of mechanistic insights and engineering techniques, I intend to develop experimental and theoretical approaches for intensifying the CO_2 electrolysis process. These system-level approaches can then be used for establishing design rules for a rational and efficient system design that is economically viable and carbon-neutral at industrially relevant scales.

(i) Rationally designing and engineering the electrolyte to manipulate the electrode-electrolyte interface and the catalyst microenvironment for high rate, selective, and energy-efficient CO_2RR to desired products; **(ii)** Use electrocatalysis and reactor engineering principles to guide batch and flow reactor design and influence kinetics and mass transfer to optimize and intensify the electrochemical performance of CO_2RR; **(iii)** Use process modeling principles to develop kinetic models and system models to bridge the gap between theory and experiments as well as evaluate the techno-economic feasibility for operation in a carbon-neutral manner for CO_2RR; **(iv)** Use *in situ*/*in operando* electrochemical spectroscopic techniques to determine the mechanistically relevant steps and key reaction intermediates in the mechanism of CO_2RR under industrially relevant conditions.

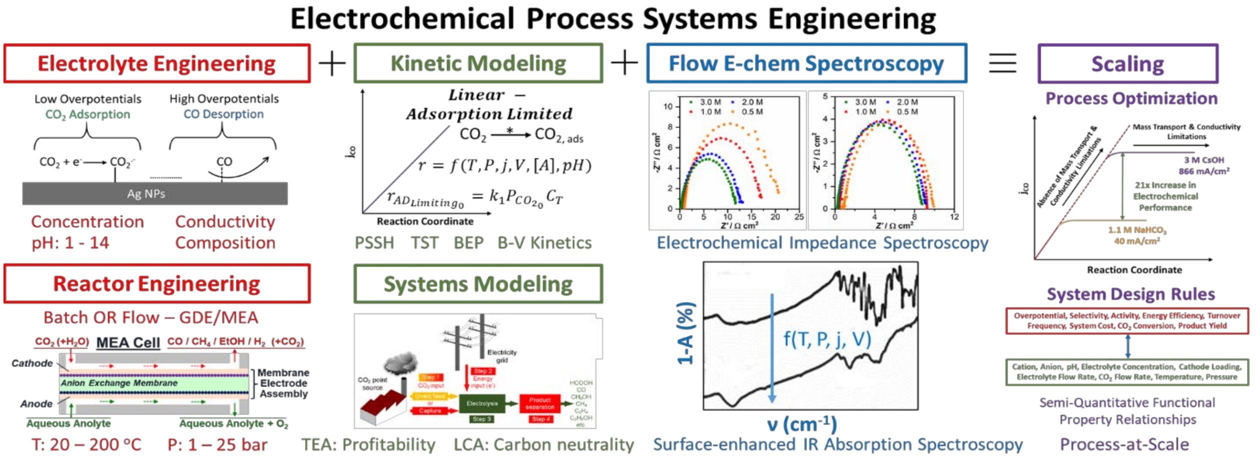


Figure 1. My thesis research combines aspects of electrolyte and reactor engineering, process modeling, and electrochemical spectroscopy to provide necessary fundamental understanding that will enable scaling of CO_2 electrolysis technology.

3. Experimental System-Level Approaches –

A. *Electrolyte Engineering*: To understand the role of electrolyte composition on CO_2RR and the rate determining step (RDS) of the mechanism, we pursued continuous flow CO_2RR to CO on Ag nanoparticles (NPs)-based gas diffusion electrodes.[3-5] Cathode onset potentials measured vs. SHE were independent of electrolyte pH and composition indicating that a proton-coupled electron transfer step is not the RDS.[4] Combined with a Tafel slope analysis and electrochemical impedance spectroscopy (EIS) measurements, we also demonstrated that – (i) at low overpotentials, CO_2 adsorption step – a chemical step is rate-determining followed by the formation of the $CO_2^{\cdot-}$ radical – an electron transfer step, and (ii) at high overpotentials, CO desorption step – a chemical step is the RDS.[4] Cell onset potentials decreased as pH increased indicating that operation at higher pH is beneficial for CO_2RR.[4] Studies with electrolytes containing two or more anions or alkali metal cations suggest that the CO pCDs are strongly controlled by the anions in the electrolyte and the CO FEs are strongly controlled by the cations in the electrolyte. This suggests that by manipulating the cations and anions making up the electrolyte composition the CO pCDs and CO FEs can be tuned to the desired performance levels. Systematic process optimization studies resulted in state-of-art performance by achieving key performance benchmarks simultaneously – a CO pCD of 866 mA/cm^2 with a CO FE of 98% was achieved at a cell potential of -3 V with a CO EE of 43% and a conversion per pass of 36%.[4] Furthermore, long-term performance stability studies in different electrolytes combined with EIS and cyclic voltammetry measurements provided insights into the role of electrolyte composition on the durability of electrodes.[6] Currently, we are pursuing the use of artificial neural networks to assist in machine learning-guided rational electrolyte design for CO_2RR.

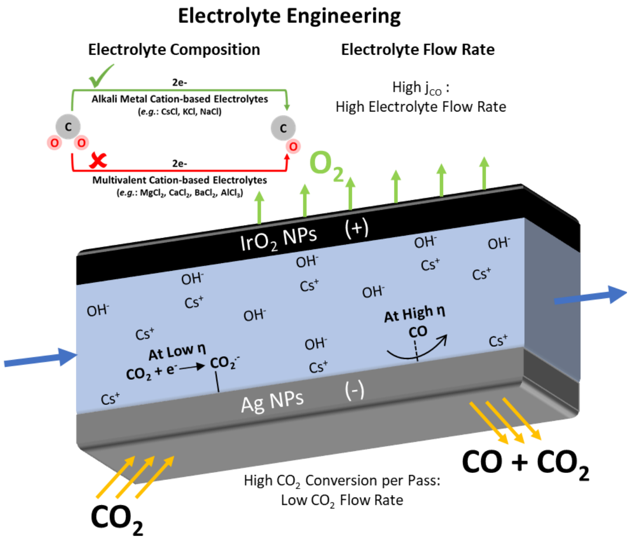


Figure 2. Electrolyte engineering in flow CO_2 electrolysis systems for intensified electrochemical performance.

B. *Electrocatalysis and Reactor Engineering*: The intrinsic activity of the catalysts can be further enhanced by employing reactor engineering techniques. For example, by manipulating the catalyst loadings, we tuned the catalyst mass activities to industrial performance levels – a mass activity of 1843 A/g_{Ag} for CO production was achieved at a CO pCD of 553 mA/cm^2.[4] Temperature (T) and pressure (P) are process levers that have been underexplored in the field of CO_2RR. From a fundamental perspective, operation at higher T and P enhances reaction kinetics, decreases overpotential, and tailors the selectivity for CO_2RR catalysts. During my graduate studies, I have designed and commissioned a continuous flow electrolyzer system that can withstand high temperatures (up to 200 °C) and pressures (up to 25 bar). Data obtained for Ag NPs shows that by

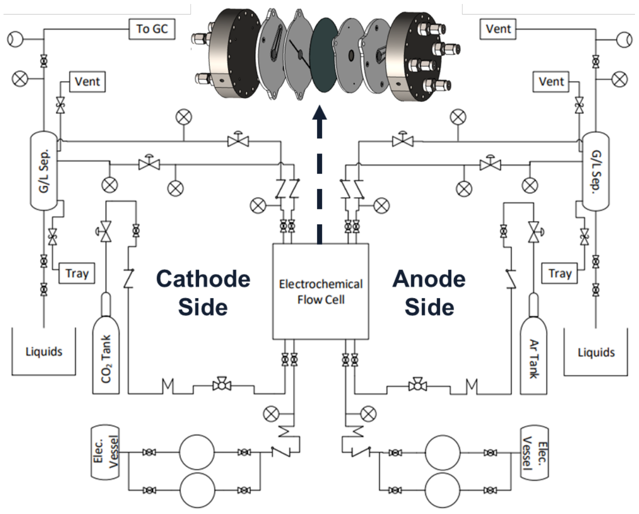


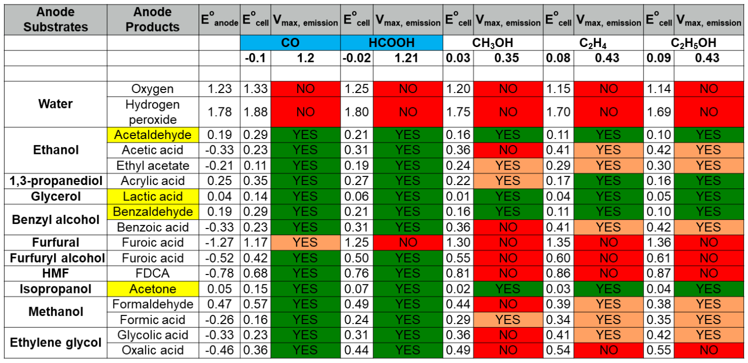
Figure 3. Process flow diagram and schematic of a flow electrolyzer capable of operating at high temperatures and pressures.

increasing the operating temperature, the CO pCDs show a maximum at 40 °C beyond which hydrogen evolution reaction starts to dominate and at 80 °C, liquid products like formate and acetate, not observed at lower temperatures, are also formed. Data obtained for Cu NPs shows that by increasing the operating temperature from 20 °C to 70 °C, a 4-fold improvement in the pCDs and FEs for C_2 products is observed over the pCDs and FEs for C_1 products, suggesting that higher temperatures favor C-C coupling. Furthermore, we have also explored the use of magnetic fields for improving the performance of flow CO_2 electrolyzers by minimizing mass transfer limitations *via* the magnetohydrodynamic effect.[5]

4. <u>Theoretical System-Level Approaches</u> –

A. *<u>Kinetic Modeling</u>*: We have also pursued macrokinetic modeling for CO_2RR systems. By formulating the rate expressions for elementary steps and using the pseudo steady state hypothesis approximation, we derived the concentrations of the surface reaction intermediates and consequently, the overall reaction rate expression and reaction rate parameters – overall rate constant and activation energy. Using experimental data and invoking the transition state theory, the Bronsted-Evans-Polanyi relationships, the Nernst equation, and the Butler-Volmer kinetics, we fitted our model to calculate the model parameters. Such kinetic models have now been used to model the effects of electrolyte composition and concentration, temperature, and pressure. Future work will focus on relating the model parameters to Tafel slopes and refining these models to accurately model the kinetic and mass transport effects.

B. *<u>Systems Modeling</u>*: We also utilize system-level modeling to evaluate the techno-economic feasibility for operating the CO_2 electrolysis process at scale in a carbon-neutral or carbon-negative manner over its life cycle.[7-13] This modeling study also extends to the case where CO_2RR at the cathode is coupled with electrooxidation of organic substrates at the anode. Such coupled electrolysis systems produce value-added chemicals at both electrodes as well as reduce the energy requirements for the overall process significantly because organic substrates can be oxidized at much lower potentials than the commonly employed oxygen evolution reaction at the anode. By combining electrochemical engineering principles, process systems analysis and process economics methods, and ISO 14000 standards, we developed a generalized system-level techno-economic and life-cycle assessment framework for evaluating coupled electrolysis systems.



Anode Substrates	Anode Products	E^{o}_{anode}	E^{o}_{cell}	$V_{max, emission}$	E^{o}_{cell}	$V_{max, emission}$	E^{o}_{cell}	$V_{max, emission}$	E^{o}_{cell}	$V_{max, emission}$	E^{o}_{cell}	$V_{max, emission}$
			CO		HCOOH		CH_3OH		C_2H_4		C_2H_5OH	
			-0.1	**1.2**	**-0.02**	**1.21**	**0.03**	**0.35**	**0.08**	**0.43**	**0.09**	**0.43**
Water	Oxygen	1.23	1.33	NO	1.25	NO	1.20	NO	1.15	NO	1.14	NO
	Hydrogen peroxide	1.78	1.88	NO	1.80	NO	1.75	NO	1.70	NO	1.69	NO
Ethanol	Acetaldehyde	0.19	0.29	YES	0.21	YES	0.16	YES	0.11	YES	0.10	YES
	Acetic acid	-0.33	0.23	YES	0.31	YES	0.36	NO	0.41	YES	0.42	YES
	Ethyl acetate	-0.21	0.11	YES	0.19	YES	0.24	YES	0.29	YES	0.30	YES
1,3-propanediol	Acrylic acid	0.25	0.35	YES	0.27	YES	0.22	YES	0.17	YES	0.16	YES
Glycerol	Lactic acid	0.04	0.14	YES	0.06	YES	0.01	YES	0.04	YES	0.05	YES
Benzyl alcohol	Benzaldehyde	0.19	0.29	YES	0.21	YES	0.16	YES	0.11	YES	0.10	YES
	Benzoic acid	-0.33	0.23	YES	0.31	YES	0.36	NO	0.41	YES	0.42	YES
Furfural	Furoic acid	-1.27	1.17	YES	1.25	NO	1.30	NO	1.35	NO	1.36	NO
Furfuryl alcohol	Furoic acid	-0.52	0.42	YES	0.50	YES	0.55	NO	0.60	NO	0.61	NO
HMF	FDCA	-0.78	0.68	YES	0.76	YES	0.81	NO	0.86	NO	0.87	NO
Isopropanol	Acetone	0.05	0.15	YES	0.07	YES	0.02	YES	0.03	YES	0.04	YES
Methanol	Formaldehyde	0.47	0.57	YES	0.49	YES	0.44	NO	0.39	YES	0.38	YES
	Formic acid	-0.26	0.16	YES	0.24	YES	0.29	YES	0.34	YES	0.35	YES
Ethylene glycol	Glycolic acid	-0.33	0.23	YES	0.31	YES	0.36	NO	0.41	YES	0.42	YES
	Oxalic acid	-0.46	0.36	YES	0.44	YES	0.49	NO	0.54	NO	0.55	NO

Figure 4. LCA-based screening of cathode-anode product pairs for a potentially carbon-neutral operation of a CO_2 electrolysis process.

5. <u>*In situ/in operando* Flow Electrochemical Spectroscopy</u> –

Surface enhanced infrared absorption spectroscopy (SEIRAS) systems can be used to analyze the electrode-electrolyte interface and to track mechanistically relevant surface reaction intermediates.[14-16] However, flow electrochemical SEIRAS systems that can operate under high T & P conditions are relatively rare. I have developed a flow spectro-electrochemical setup that can perform electrochemical SEIRAS measurements under catalytically relevant conditions (*i.e.*, high CDs, high T, high P). We are currently validating the setup and subsequently, we will be investigating CO_2RR on Ag and Cu catalysts under high T & P conditions. Fundamental insights obtained from spectroscopic measurements can help tune the electrochemical performance to industrially relevant levels. Moreover, this setup is generalizable to any electrochemical reaction (reduction or oxidation) of interest.

6. Publications, Patent Application, and Conference Presentations acknowledging Link Fellowship –

S. S. Bhargava, P. J. A. Kenis, *On the Sustainability, Scalability, and Energetics of the CO_2 Electrolysis Process*, In Preparation
S. S. Bhargava, E. R. Cofell, P. Chumble, D. Azmoodeh, S. Someshwar, P. J. A. Kenis, *Exploring Multivalent Cations-Based Electrolytes for CO_2 Electroreduction*, Electrochimica Acta, 2021, 394, 139055
S. S. Bhargava, D. Azmoodeh, X. Chen, E. R. Cofell, A. M. Esposito, S. Verma, A. A. Gewirth, P. J. A. Kenis, *Decreasing the Energy Consumption of the CO_2 Electrolysis Process using a Magnetic Field*, ACS Energy Letters, 2021, 6, 2427-2433

S. S. Bhargava, D. Azmoodeh, P. Chumble, S. Someshwar, P. J. A. Kenis, "System-Level Approaches for Intensifying the CO_2 Electrolysis Process", **Nov 2021**, AIChE Annual Meeting, Boston, Massachusetts, USA ***(Invited Talk – Sustainable Engineering Forum Plenary Session)***
S. S. Bhargava, P. J. A. Kenis, "System-Level Approaches for Intensifying the CO_2 Electrolysis Process: From Reaction Chemistry to Process Development", **Aug 2021**, ACS Fall Meeting, Virtual ***(Invited Talk – Industrial and Engineering Chemistry Division Graduate Student Award Symposium)***
S. S. Bhargava, D. Azmoodeh, P. Chumble, F. Proietto, S. Someshwar, E. R. Cofell, D. A. Henckel, S. Verma, C. J. Brooks, A. A. Gewirth, P. J. A. Kenis, "System Design Rules for Intensified CO_2 Electroreduction", **May 2021**, 239th ECS Meeting, Virtual
S. S. Bhargava, D. Azmoodeh, X. Chen, E. R. Cofell, A. M. Esposito, S. Verma, A. A. Gewirth, P. J. A. Kenis, "Using Magnetic Fields to Intensify the CO_2 Electrolysis Process", **May 2021**, 239th ECS Meeting, Virtual
S. S. Bhargava, D. Azmoodeh, A. A. Gewirth, P. J. A. Kenis, "System-Level Approaches for Intensifying the CO_2 Electrolysis Process", **Oct 2020**, 238th ECS Meeting, Virtual ***(Invited Talk – Industrial Electrochemistry and Electrochemical Engineering Division Student Achievement Award Address)***

P. J. A. Kenis, **S. S. Bhargava**, *Enhancing the CO_2 Electrolysis Process using Magnetic Field Effects*, US Patent Application 63/283667, **2021**

7. How did the Link Fellowship make a difference? –

The support provided by the Link Foundation for my research has allowed me the freedom to pursue several of my own ideas and not be tied to a particular project. The fellowship also allowed me to focus on my research because I did not have to teach anymore for obtaining funding. This extra time combined with the research freedom allowed me to pursue some ambitious and risky projects which were time-consuming but greatly satisfying and rewarding – something I truly could not have done without the support of this fellowship. I once again thank the Link Foundation for this honor and the fellowship.

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