

Oxygen-Resistant CO₂ Reduction Enabled by Electrolysis of Liquid Feedstocks

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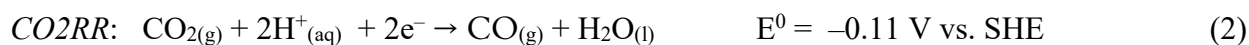
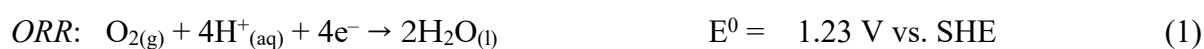
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Abstract:

Electrolytic CO₂ reduction fails in the presence of O₂. This failure occurs because the reduction of O₂ is thermodynamically favored over the reduction of CO₂. Consequently, O₂ must be removed from the CO₂ feed prior to entering an electrolyzer, which is an expensive process. Here, we show the use of liquid bicarbonate feedstocks (e.g., aqueous 3.0 M KHCO₃), rather than gaseous CO₂ feedstocks, enables efficient and selective CO₂ reduction without additional procedures for removing O₂. This advance is made possible because liquid bicarbonate solutions deliver high concentrations of captured CO₂ to the cathode, while the low solubility of O₂ in aqueous media maintains a low O₂ concentration at the same cathode surface. Consequently, electrolyzers fed with liquid bicarbonate feedstocks create an environment at the cathode that favors the reduction of CO₂ over O₂. We validate this claim by electrochemically converting CO₂ into CO with reaction selectivities of ~65% at 100 mA cm⁻² using 3.0 M KHCO₃ solution bubbled with 100% CO₂ or 100% O₂. Similar experiments performed with a gaseous CO₂ feedstock showed that merely 1% of O₂ in the feedstock reduced CO selectivity to 11 ± 3.7%. Our findings demonstrate that a liquid bicarbonate feedstock enables efficient CO₂ reduction without the need for expensive O₂ removal steps.

The electrolytic reduction of CO₂ can reduce greenhouse gas emissions by converting waste CO₂ into valuable products (e.g., CO, formate, methanol, ethylene, alcohols).¹⁻³ However, practical sources of CO₂ contain high concentrations of O₂; for example, air and flue gasses contain 21% and 5-15% O₂, respectively.⁴⁻⁸ Concentrations of O₂ need to be managed because the O₂ reduction reaction (ORR, Eq. 1) occurs at a less negative reduction potential than the CO₂ reduction reaction (CO₂RR, Eq. 2).^{4,9,10} Electrochemical reactors therefore do not efficiently convert CO₂ into valuable products in the presence of O₂.^{4,10,11}



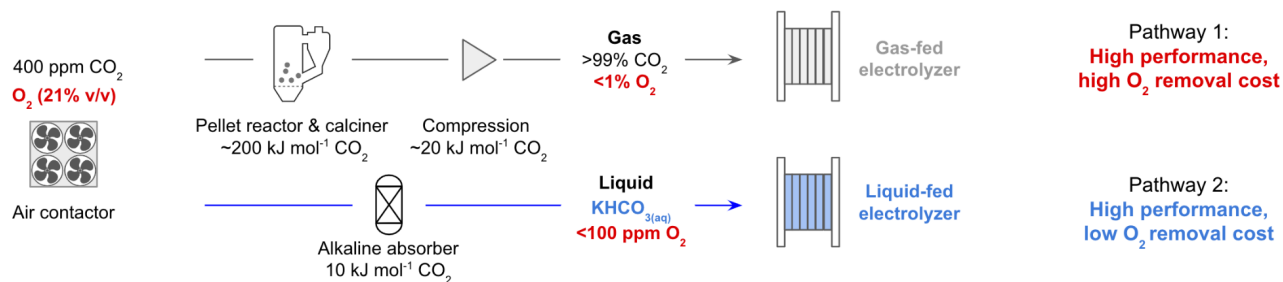
Any electrolyzer fed with gaseous CO₂ (“gas-fed electrolyzer”) must contain a high concentration of CO₂ and low concentration of O₂.⁷ Direct air capture (DAC) can generate concentrated streams of CO₂ containing <1% O₂ through successive drying and calcination steps.^{5,6} These steps require 200 kJ of thermal energy input per mol of CO₂ generated (Figure 1).¹² Amine-based sorbents can generate pure streams of CO₂ from flue gasses, but this process also requires thermal energy to desorb captured CO₂ (Figure 1).^{13,14}

An alternative way to electrochemically convert CO₂ into fuels is to feed an electrolyzer with a liquid CO₂ carrier such as aqueous KHCO₃.¹⁵⁻²¹ The delivery of KHCO₃ to the cathode compartment of a “liquid-fed electrolyzer” can generate high *in-situ* concentrations of CO₂ (“*i*-CO₂”) at the catalyst surface after reaction with acid delivered by the membrane.^{15,22,23} These liquid-fed electrolyzers can reach electrolyzer performance metrics (e.g., voltage, current densities, carbon efficiencies) that match or exceed those of gas-fed electrolyzers.^{21,24} Importantly, KHCO₃ is an eluent of certain CO₂ capture units, and thus the liquid-fed electrolyzer enables CO₂ capture and conversion (Figure S1).²⁵

Here, we highlight another significant advantage of a liquid-fed electrolyzer: a low concentration of O₂ at the cathode. By delivering CO₂ to the cathode in the form of aqueous bicarbonate solutions, the exceptionally low solubility of O₂ in aqueous medium (0.0012 M @ 1 atm, 298 K)²⁶ naturally maintains a low concentration of O₂ in the reaction environment. Thus, the electrolytic conversion of aqueous bicarbonate solutions can be performed without complications arising from O₂ reduction.

To demonstrate these claims, we tested how varying amounts of O₂ affected the formation of CO from CO₂ in gas- and liquid-fed electrolyzers. The same electrolyzer was used for all experiments in the study, with the only difference being the feedstock for the cathode chamber; the gas-fed electrolyzer was provided CO₂ and the liquid-fed electrolyzer was provided 3.0 M KHCO₃. The volume fraction of O₂ in the CO₂ feed varied from 0-10%, while 0-10% O₂ was bubbled through the liquid feedstock prior to entry into the electrolyzer. The results outlined herein show that even low concentrations of O₂ in the CO₂ stream rendered CO₂RR ineffective, while the performance of the liquid-fed electrolyzer was not affected by bubbling O₂ through the feedstock. This outcome demonstrates how to carry out O₂-resistant CO₂ conversion.

CO₂ sourced from air



CO₂ sourced from flue gas

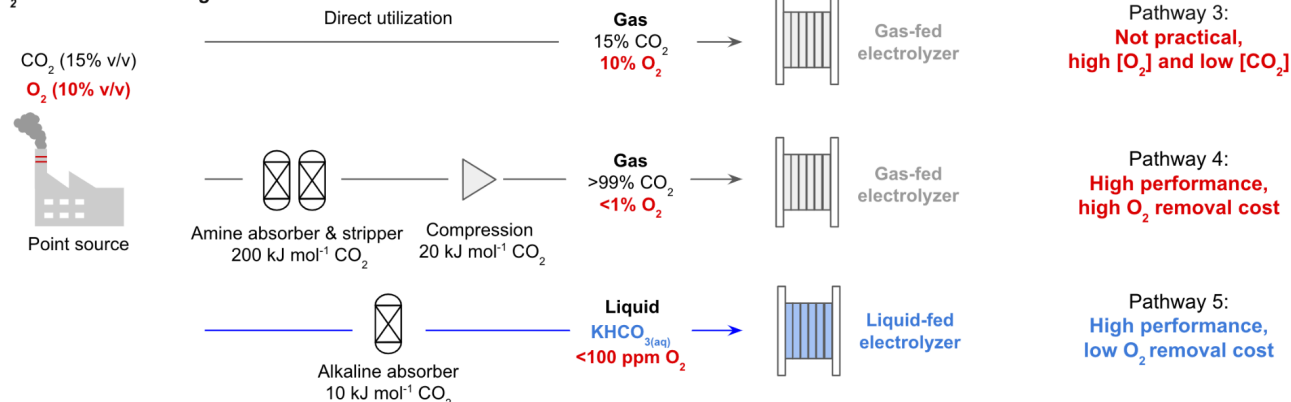


Figure 1: Schematic of various CO₂ capture and conversion pathways from O₂-containing CO₂ streams. Pathways 1 and 2 depict the capture and conversion of CO₂ sourced from the atmosphere using gas- and liquid-fed electrolyzers, respectively. Pathway 3 shows the direct conversion (i.e., no capture steps) of CO₂ sourced from industrial flue gas. Pathways 4 and 5 show the conversion of flue gas CO₂ captured using amine and alkaline sorbents, respectively. Streams of CO₂ purified using amine absorption serve as the feedstock for a gas-fed electrolyzer. Similarly, the KHCO₃ eluent from the alkaline absorber is fed into the liquid-fed electrolyzer.

The liquid-fed electrolyzer used in this study consisted of a composite silver-carbon (Ag/C) cathode and nickel foam anode pressed between cathodic and anodic serpentine flow plates (Figure S2-3). The cathode was prepared by dispersing 8 mg of Ag nanoparticles into an ethanol solution containing 10 μ L of 20 wt% NafionTM. The resulting dispersion was deposited onto carbon paper with a commercial gravity-fed pneumatic spray-coater. The cathode and anode were separated by a hydrated FumasepTM bipolar membrane (BPM), which mediated water dissociation under reverse-bias, transporting H⁺ to the cathode and OH⁻ to the anode. The H⁺ reacted with HCO₃⁻ or CO₃²⁻ to form *i*-CO₂, which was then

reduced at the cathode. The OH^- was oxidized to O_2 and H_2O at the Ni foam anode. Assembly of the gas-fed electrolyzer was the same as for liquid-fed experiments, with the exception of a Sustainion® X37-50 Grade RT anion exchange membrane (AEM) in place of the BPM and a microporous layer on the carbon paper (Figure S3). Gaseous products were detected using in-line gas chromatography in both experimental set-ups.

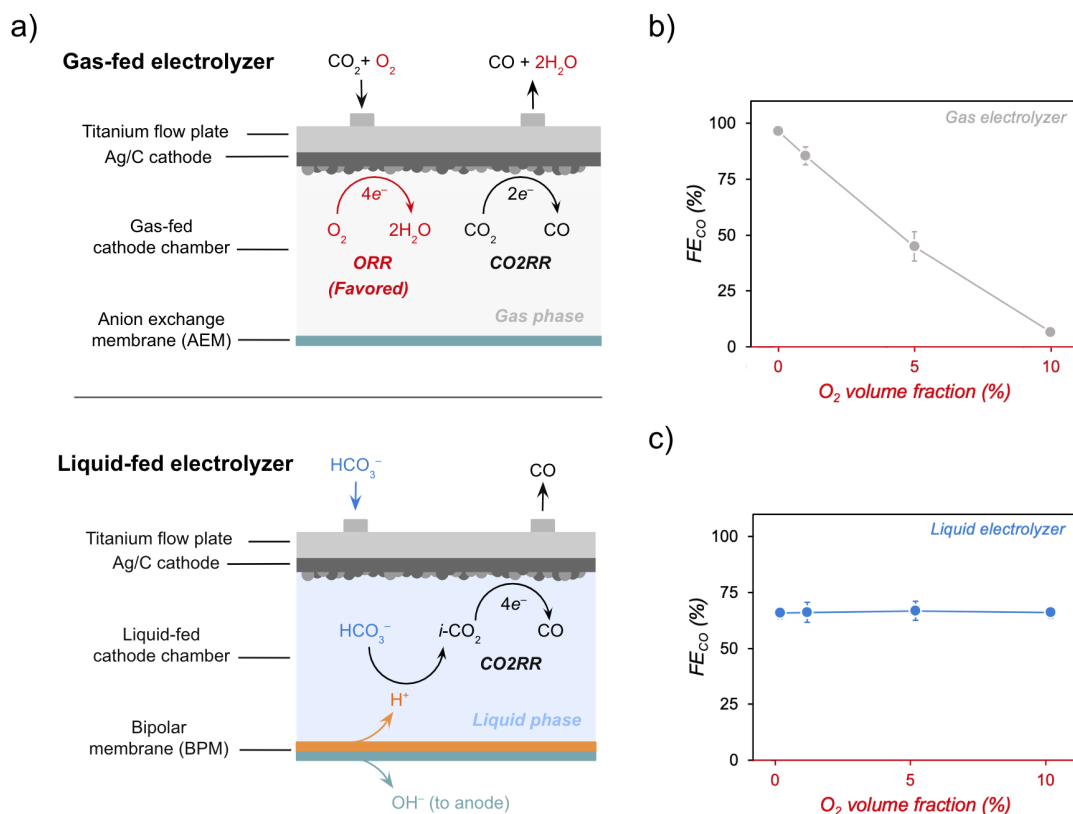


Figure 2: a) Schematic of CO_2 conversion in the cathode compartment of a gas-fed CO_2 electrolyzer (top) and a liquid-fed bicarbonate electrolyzer (bottom). b) CO selectivity following electrolysis of humidified gaseous CO_2 containing 0-10% O_2 at 100 mA cm^{-2} . c) CO selectivity following electrolysis at 100 mA cm^{-2} using 3.0 M KHCO_3 continuously bubbled with CO_2 containing 0-10% O_2 c) CO selectivity following electrolysis of humidified gaseous CO_2 containing 0-10% O_2 at 100 mA cm^{-2} .

We first examined the effects of O_2 on a gas-fed electrolyzer that converted CO_2 into CO (Figure 2b). Control experiments were performed using 100% CO_2 fed to the cathode compartment at a flow rate of 200 sccm . Electrolysis performed at 100 mA cm^{-2} resulted in a faradaic efficiency for CO (FE_{CO}) of $96 \pm 2\%$ (Table S1). When the CO_2 stream contained just 1% O_2 , the FE_{CO} decreased to $85 \pm 4\%$. A volume

fraction of 10% O₂ caused a near-total loss of CO selectivity, which decreased to 6 ± 2%. Over 90% of the total FE was unaccounted (Figure S4), indicating that >90% of the electrons were diverted to the parasitic ORR. These losses in CO formation were consistent with previous studies that showed O₂ suppresses CO₂RR due to the favorable thermodynamics of ORR.^{4,10,11}

Moreover, CO formation in the gas-fed electrolyzer did not fully recover following exposure to O₂ (Figure S5). After restoring a pure CO₂ feedstock following electrolysis at 100 mA cm⁻² using 90% CO₂ and 10% O₂, the *FE_{CO}* did not exceed 10%. The remaining faradaic efficiency is attributed to the formation of H₂ from the parasitic hydrogen evolution reaction (HER). This result is consistent with flooding of the cathode with the H₂O produced from ORR.²⁷⁻²⁹

We then measured *FE_{CO}* losses in the liquid-fed electrolyzer caused by the same volume fractions of O₂. To simulate the steady-state capture of a CO₂ stream contaminated with O₂, we bubbled a mixture of CO₂ containing 0-10% O₂ into a 3.0 M KHCO₃ solution at a flow rate of 200 sccm. This bubbling step was performed for 30 minutes prior to and during electrolysis. The pressure within the catholyte reservoir was maintained at approximately 1 atm. Electrolysis experiments performed at 100 mA cm⁻² using 100% CO₂ resulted in a *FE_{CO}* of 66 ± 3% (Figure 2c, Table S2). We observed no losses in CO selectivity with increasing O₂ volume fraction. For example, *FE_{CO}* remained at 66 ± 2% when the bicarbonate solution was exposed to CO₂ containing 10% O₂.

The consistent CO selectivities in the liquid-fed electrolyzer even in the presence of O₂ (Figure S6) signals that ORR did not occur. We attribute this result to low concentration of O₂ in solution. Prior to bubbling, the dissolved O₂ concentration in 3.0 M KHCO₃ was consistent with Henry's law at a value of 0.27 ± 0.1 mM in ambient conditions.³⁰ When the bicarbonate feedstocks were bubbled with CO₂ containing 0-10% O₂, the O₂ concentrations in solution decreased (Figure S7). This decrease is likely because CO₂ increased the gas-liquid interface, which caused dissolved O₂ to diffuse into the gas phase.³¹ This degassing effect decreased as the O₂ volume fraction increased. After 30 minutes of bubbling with

100% CO₂, the O₂ concentration measured in solution was 0.04 mM, compared to 0.16 mM when the gas stream contained 10% O₂. These low amounts of O₂ in solution limit mass transport for ORR.

To further assess the O₂ resistance of the liquid-fed electrolyzer, we converted bicarbonate solutions bubbled with more concentrated streams of O₂ (up to 100% O₂). At higher volume fractions, no degassing occurred and dissolution of O₂ into solution was observed (Figure 3a). When 100% O₂ was used, the O₂ concentration in solution reached 0.9 mM, which nears the solubility limit of O₂ under ambient conditions.²⁶ Electrolysis of the bicarbonate solutions at 100 mA cm⁻² following 30 minutes of bubbling prior to and during electrolysis resulted in CO selectivities of ~65% (Figure 3b), which is similar to the *FE*_{CO} values obtained in experiments using 0% O₂. These results indicate that the low solubility of O₂ in solution suppresses ORR in liquid-fed electrolyzers.

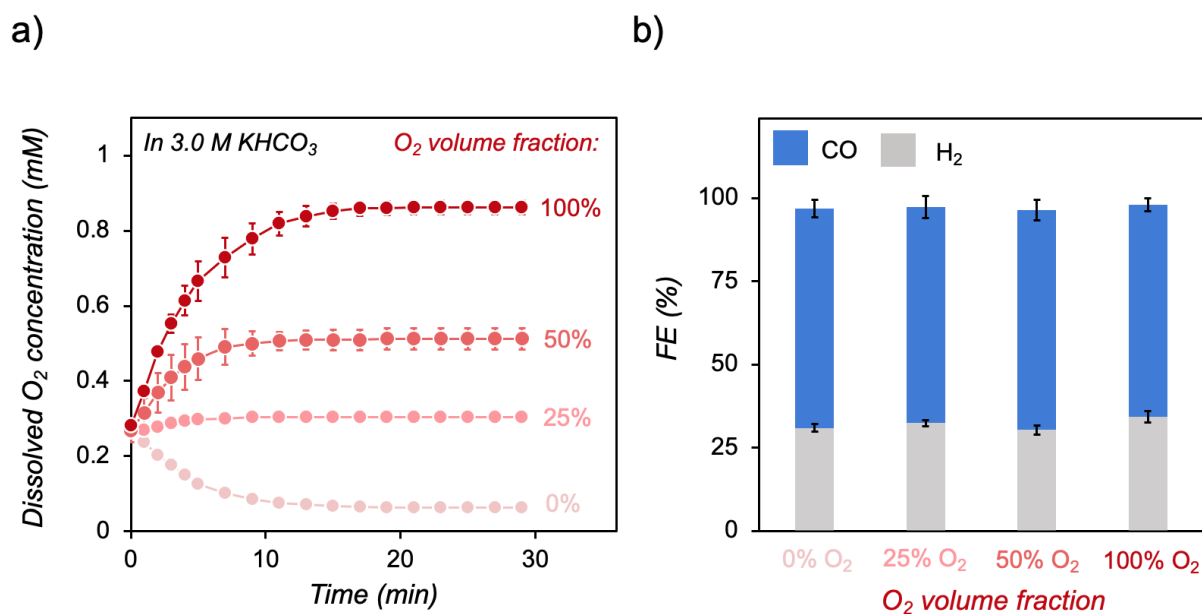


Figure 3: a) Concentration of dissolved O₂ in a 3.0 M KHCO₃ solution prior to electrolysis. Humidified CO₂ (0-100%) and O₂ (0-100%) was bubbled into the solution for 30 minutes prior to and during electrolysis at a contact flow rate of 200 sccm. b) Product distributions from the electrolysis of 3.0 M KHCO₃ bubbled for 30 minutes with CO₂ (0-75%) and O₂ between (0-100%). Electrolysis was performed for 5 minutes at a constant applied current density of 100 mA cm⁻².

In this study, we demonstrate the effects of O₂ on CO formation in an electrolyzer fed with either CO₂ or bicarbonate. When 10% O₂ was present in the CO₂ feed entering the gas-fed electrolyzer, CO selectivity decreased by >90%. The liquid-fed electrolyzer was unaffected by the dissolved O₂ in the bicarbonate solution. The conversion of bicarbonate solutions all resulted in FE_{CO} values of ~65% at 100 mA cm⁻² when bubbled with gas streams containing 0-100% O₂. Our findings indicate that the electrolysis of bicarbonate solutions is an O₂-resistant approach to generating valuable products from waste CO₂.

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Author contributions: D.P. conceived the idea, performed electrolysis experiments and measurements, carried out data analysis, and wrote the manuscript. A.J. supervised gas-fed CO₂ electrolysis experiment. Y.K. supervised liquid-fed bicarbonate electrolysis experiments. C.P.B. conceived the idea and supervised the project. All authors discussed the results and assisted with manuscript preparation.

Competing interests: The authors declare no competing interests.

Data and materials availability: The data supporting the findings of the study are available within the paper and its Supplementary Information.

References:

- (1) Weekes, D. M.; Salvatore, D. A.; Reyes, A.; Huang, A.; Berlinguette, C. P. Electrolytic CO₂ Reduction in a Flow Cell. *Acc. Chem. Res.* **2018**, *51* (4), 910–918.
- (2) Banerjee, S.; Han, X.; Thoi, V. S. Modulating the Electrode–Electrolyte Interface with Cationic Surfactants in Carbon Dioxide Reduction. *ACS Catal.* **2019**, *9* (6), 5631–5637.
- (3) Nitopi, S.; Bertheussen, E.; Scott, S. B.; Liu, X.; Engstfeld, A. K.; Horch, S.; Seger, B.; Stephens, I. E. L.; Chan, K.; Hahn, C.; Nørskov, J. K.; Jaramillo, T. F.; Chorkendorff, I. Progress and Perspectives of Electrochemical CO₂ Reduction on Copper in Aqueous Electrolyte. *Chem. Rev.* **2019**, *119* (12), 7610–7672.
- (4) Xu, Y.; Edwards, J. P.; Zhong, J.; O'Brien, C. P.; Gabardo, C. M.; McCallum, C.; Li, J.; Dinh, C.-T.; Sargent, E. H.; Sinton, D. Oxygen-Tolerant Electroproduction of C₂ Products from Simulated Flue Gas. *Energy Environ. Sci.* **2020**, *13* (2), 554–561.
- (5) Sanz-Pérez, E. S.; Murdock, C. R.; Didas, S. A.; Jones, C. W. Direct Capture of CO₂ from Ambient Air. *Chem. Rev.* **2016**, *116* (19), 11840–11876.
- (6) Keith, D. W.; Holmes, G.; St. Angelo, D.; Heidel, K. A Process for Capturing CO₂ from the Atmosphere. *Joule* **2018**, *2* (8), 1573–1594.
- (7) Harmon, N. J.; Wang, H. Electrochemical CO₂ Reduction in the Presence of Impurities: Influences and Mitigation Strategies. *Angew. Chem. Int. Ed Engl.* **2022**, *61* (52), e202213782.
- (8) Legrand, U.; Apfel, U.-P.; Boffito, D. C.; Tavares, J. R. The Effect of Flue Gas Contaminants on the CO₂ Electroreduction to Formic Acid. *Journal of CO₂ Utilization* **2020**, *42*, 101315.
- (9) Kibria, M. G.; Edwards, J. P.; Gabardo, C. M.; Dinh, C.-T.; Seifitokaldani, A.; Sinton, D.; Sargent, E. H. Electrochemical CO₂ Reduction into Chemical Feedstocks: From Mechanistic Electrocatalysis Models to System Design. *Adv. Mater.* **2019**, *31* (31), e1807166.
- (10) Lu, X.; Jiang, Z.; Yuan, X.; Wu, Y.; Malpass-Evans, R.; Zhong, Y.; Liang, Y.; McKeown, N. B.; Wang, H. A Bio-Inspired O₂-Tolerant Catalytic CO₂ Reduction Electrode. *Sci Bull (Beijing)* **2019**, *64* (24), 1890–1895.
- (11) Li, P.; Lu, X.; Wu, Z.; Wu, Y.; Malpass-Evans, R.; McKeown, N. B.; Sun, X.; Wang, H. Acid-Base Interaction Enhancing Oxygen Tolerance in Electrocatalytic Carbon Dioxide Reduction. *Angew. Chem. Int. Ed Engl.* **2020**, *59* (27), 10918–10923.
- (12) Sharifian, R.; Wagterveld, R. M.; Digdaya, I. A.; Xiang, C.; Vermaas, D. A. Electrochemical Carbon Dioxide Capture to Close the Carbon Cycle. *Energy Environ. Sci.* **2021**, *14* (2), 781–814.
- (13) Aaron, D.; Tsouris, C. Separation of CO₂ from Flue Gas: A Review. *Sep. Sci. Technol.* **2005**, *40* (1-3), 321–348.
- (14) Rochelle, G. T. Amine Scrubbing for CO₂ Capture. *Science* **2009**, *325* (5948), 1652–1654.
- (15) Li, T.; Lees, E. W.; Goldman, M.; Salvatore, D. A.; Weekes, D. M.; Berlinguette, C. P. Electrolytic Conversion of Bicarbonate into CO in a Flow Cell. *Joule* **2019**, *3* (6), 1487–1497.
- (16) Li, T.; Lees, E. W.; Zhang, Z.; Berlinguette, C. P. Conversion of Bicarbonate to Formate in an Electrochemical Flow Reactor. *ACS Energy Lett.* **2020**, *5* (8), 2624–2630.
- (17) Lees, E. W.; Liu, A.; Bui, J. C.; Ren, S.; Weber, A. Z.; Berlinguette, C. P. Electrolytic Methane Production from Reactive Carbon Solutions. *ACS Energy Lett.* **2022**, *7* (5), 1712–1718.
- (18) Pimlott, D. J. D.; Jewlal, A.; Mowbray, B. A. W.; Berlinguette, C. P. Impurity-Resistant CO₂ Reduction Using Reactive Carbon Solutions. *ACS Energy Letters*. 2023, pp 1779–1784.
<https://doi.org/10.1021/acsenerylett.3c00133>.
- (19) Zhang, Z.; Lees, E. W.; Habibzadeh, F.; Salvatore, D. A.; Ren, S.; Simpson, G. L.; Wheeler, D. G.; Liu, A.; Berlinguette, C. P. Porous Metal Electrodes Enable Efficient Electrolysis of Carbon Capture Solutions. *Energy Environ. Sci.* **2022**, *15* (2), 705–713.
- (20) Lees, E. W.; Goldman, M.; Fink, A. G.; Dvorak, D. J.; Salvatore, D. A.; Zhang, Z.; Loo, N. W. X.; Berlinguette, C. P. Electrodes Designed for Converting Bicarbonate into CO. *ACS Energy Lett.* **2020**, *5* (7), 2165–2173.
- (21) Zhang, Z.; Lees, E. W.; Ren, S.; Mowbray, B. A. W.; Huang, A.; Berlinguette, C. P. Conversion of Reactive Carbon Solutions into CO at Low Voltage and High Carbon Efficiency. *ACS Cent Sci* **2022**, *8* (6), 749–755.
- (22) Li, Y. C.; Lee, G.; Yuan, T.; Wang, Y.; Nam, D.-H.; Wang, Z.; García de Arquer, F. P.; Lum, Y.; Dinh, C.-T.; Voznyy, O.; Sargent, E. H. CO₂ Electroreduction from Carbonate Electrolyte. *ACS Energy Lett.* **2019**, *4* (6), 1427–1431.
- (23) Diaz; Gao; Adhikari; Lister; Dufek. Electrochemical Production of Syngas from CO₂ Captured in Switchable Polarity Solvents. *Green*.

- (24) Ozden, A.; García de Arquer, F. P.; Huang, J. E.; Wicks, J.; Sisler, J.; Miao, R. K.; O'Brien, C. P.; Lee, G.; Wang, X.; Ip, A. H.; Sargent, E. H.; Sinton, D. Carbon-Efficient Carbon Dioxide Electrolysers. *Nature Sustainability* **2022**, *5* (7), 563–573.
- (25) Welch, A. J.; Dunn, E.; DuChene, J. S.; Atwater, H. A. Bicarbonate or Carbonate Processes for Coupling Carbon Dioxide Capture and Electrochemical Conversion. *ACS Energy Lett.* **2020**, *5* (3), 940–945.
- (26) Xing, W.; Yin, G.; Zhang, J. *Rotating Electrode Methods and Oxygen Reduction Electrocatalysts*; Elsevier, 2014.
- (27) Bhattacharya, P. K. *Water flooding in the proton exchange membrane fuel cell*. https://www.sciencetheearth.com/uploads/2/4/6/5/24658156/waterflooding_protonexchangemembrane.pdf (accessed 2023-04-02).
- (28) Ge, X.; Sumboja, A.; Wu, D.; An, T.; Li, B.; Goh, F. W. T.; Hor, T. S. A.; Zong, Y.; Liu, Z. Oxygen Reduction in Alkaline Media: From Mechanisms to Recent Advances of Catalysts. *ACS Catal.* **2015**, *5* (8), 4643–4667.
- (29) Yang, K.; Kas, R.; Smith, W. A.; Burdyny, T. Role of the Carbon-Based Gas Diffusion Layer on Flooding in a Gas Diffusion Electrode Cell for Electrochemical CO₂ Reduction. *ACS Energy Lett.* **2021**, *6* (1), 33–40.
- (30) Sander, R. Compilation of Henry's Law Constants (version 4.0) for Water as Solvent. *Atmos. Chem. Phys.* **2015**, *15* (8), 4399–4981.
- (31) Butler, I. B.; Schoonen, M. A.; Rickard, D. T. Removal of Dissolved Oxygen from Water: A Comparison of Four Common Techniques. *Talanta* **1994**, *41* (2), 211–215.