Suppressing the liquid product crossover in electrochemical CO₂ reduction

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Funding information
National Natural Science Foundation of China, Grant/Award Number: 51771132

Abstract
Coupling electrochemical CO₂ reduction (CO₂R) with a renewable energy source to create high-value fuels and chemicals is a promising strategy in moving toward a sustainable global energy economy. CO₂R liquid products, such as formate, acetate, ethanol, and propanol, offer high volumetric energy density and are more easily stored and transported than their gaseous counterparts. However, a significant amount (~30%) of liquid products from electrochemical CO₂R in a flow cell reactor cross the ion exchange membrane, leading to the substantial loss of system-level Faradaic efficiency. This severe crossover of the liquid product has—until now—received limited attention. Here, we review promising methods to suppress liquid product crossover, including the use of bipolar membranes, solid-state electrolytes, and cation-exchange membranes-based acidic CO₂R systems. We then outline the remaining challenges and future prospects for the production of concentrated liquid products from CO₂.

KEYWORDS
bipolar membranes, CO₂ reduction, liquid product crossover, solid-state electrolytes

1 | INTRODUCTION

The electrochemical reduction of CO₂ (CO₂R) into fuels, feedstocks, and commodity chemicals has the potential to transform the petrochemical sector into a sustainable industry and to reduce net greenhouse gas emissions.¹ ²

Liquid products, such as formate, acetate, ethanol, and propanol, are of interest in view of their potential as renewable chemical feedstocks and as renewable fuels.³ For industrial deployment, electrocatalytic systems producing liquid products from CO₂ must offer current densities above 200 mA/cm² and stability over thousands...
of hours. To meet these requirements, an increasing number of CO$_2$R studies now use vapor-phase flow reactors, such as flow cells and membrane electrode assemblies. Within these systems, gaseous reactant CO$_2$ is delivered directly to the cathode, thereby increasing CO$_2$ mass transport and enable high current density.

Current flow reactors have some significant shortcomings, such as susceptibility to flooding in the gas diffusion electrode, salt accumulation, and liquid product crossover. In addition, the rapid and thermodynamically favorable reaction of CO$_2$ with OH$^-$ to form CO$_3^{2-}$ imposes steady-state electrolysis conditions that result in large voltage and CO$_2$ losses. This reaction could significantly reduce the flow rate of gas outlet, and along with liquid product crossover lead to inaccurate estimation of faradaic efficiencies for gas and liquid products. Among these, the inhibition of liquid product crossover is increasingly becoming a focal point of the study.

As shown in Figure 1A, anion exchange membranes (AEMs) are typically used in CO$_2$ electrolysis reactors to reduce the extent to which liquid products migrate to the anode and become oxidized back to CO$_2$. Unfortunately, AEMs are far from impermeable to these molecules (Figure 1B). Negatively charged products, such as formate and acetate, cross the AEM by electromigration, while the electroneutral ethanol and propanol cross via diffusion and electroosmotic drag. When cells operate at high current densities (e.g., >200 mA/cm$^2$), the crossover of liquid products through the AEM becomes more pronounced (-30% of total liquid products) due to the combination of high product concentration and high ion flux through the AEM. Moreover, the liquid products from CO$_2$R may evaporate through the gas diffusion electrodes (see Figure 1B) into CO$_2$ off-gas because of their high volatility. These issues impair the quantitative evaluation of the catalytic performance of the catalyst and lead to a substantial product loss in CO$_2$R devices.

Liquid products migrate with the anionic flux through the AEM, and methods to avoid this crossover route have involved the use of alternative membranes and electrolytes. Several such methods have been proposed recently, as we discuss here. Additionally, we offer some general perspectives on the future outlook for generating valuable, concentrated C$_2$+ liquid products.

2 METHODS TO SUPPRESS LIQUID PRODUCT CROSSOVER

First, we examine the effect of introducing a bipolar membrane (BPM). A BPM consists of a cation exchange membrane (CEM), an AEM, and an interfacial connection layer. The dissociation of water in a BPM drives H$^+$ and OH$^-$ ions toward the cathode and anode, respectively, inhibiting the flow of cathode electrolyte to the anode. Over the past few years, BPMs have been successfully incorporated to prevent liquid product crossover in CO$_2$ electrolysis cells. Mallouk compared the crossover performance of AEMs and BPMs in a system that simulates the conditions of a working CO$_2$ electrolyzer. The results showed that the crossover of formate (a negatively charged product) is significant when AEMs are used, especially at high current densities. The crossover rate of formate was 17 times lower than with BPMs under otherwise similar conditions, while the crossover of neutral products, such as methanol and ethanol, were also suppressed using BPMs due to the lower electroosmotic drag coefficients. Neyerlin incorporated the
BPMs to prevent CO\textsubscript{2}R liquid product crossover and achieved a Faradic efficiency of ~90\% for CO\textsubscript{2} reduction to formate at 500 mA/cm\textsuperscript{2} (Figure 2).\textsuperscript{16}

The electrolyte, and the reactor system, may also be adapted to reduce liquid product crossover. Solid-state electrolytes (SSEs), used in solid-state batteries, are alternatives to traditional solution-based electrolytes. In SSEs, ion-conducting solid polymers shuttle ions between anode and cathode for better reliability.\textsuperscript{17} Inspired by this structure, Wang used a SSE to suppress crossover (Figure 3). The SSE is insoluble, and thus reduction products are efficiently collected in the deionized water flowing through the SSE layer. Wang obtained pure formic acid (HCOOH) solutions with concentrations of 12 mol/L, and continuous and stable generation of 0.1 mol/L HCOOH over a period of 100 h with negligible degradation in selectivity and activity.\textsuperscript{18} The authors further improved the system design into an all-solid-state reactor that produced ultrahigh concentrations of pure formic acid solutions.\textsuperscript{19} The production of C\textsubscript{2+} liquid oxygenate solutions, including acetic acid, ethanol, and n-propanol, has been demonstrated on a Cu catalyst. However, obtaining high concentrations of C\textsubscript{2+} liquid products is more challenging due to lower selectivities and will require further work on systems that integrate highly selective catalysts.

A third option is to use a CEM, such as Nafion, which is permeable only to cations. CEMs produce a cation flux opposite to the direction of product crossover and can effectively reduce the electromigration of negatively charged products and the electroosmotic flow of neutral products to the anode.\textsuperscript{20} Currently, CEM-based devices exhibit outstanding performance and stability at high current densities in acidic water-splitting electrolyzers, such as proton exchange membrane electrolyzers.\textsuperscript{21} The extreme pH suppresses the solvation of liquid products and prevents liquid products from diffusing to the anode side.\textsuperscript{22} And the high-concentration proton can be regarded as a reaction intermediate and quickly reacted with the adsorbed *CO to form the hydrocarbon, which may prevent large amounts of *CO intermediates from poisoning the catalyst surface active reaction sites. Thus, an acidic CO\textsubscript{2}R system combined with a CEM has the potential to eliminate crossover. However, the effects of pH on the formation of critical intermediates must be considered. It is well-established that low pH favors H\textsubscript{2} evolution and suppresses selectivity of C\textsubscript{2}H\textsubscript{4} and alcohol formation.\textsuperscript{23} Thus, understanding the competition between hydrogen evolution and CO\textsubscript{2} reduction is of fundamental importance in these systems. Acidic CO\textsubscript{2}R has the potential to eliminate liquid product crossover, provided hydrogen production can be limited. The challenge of suppressing crossover becomes one of suppressing hydrogen.

\section{Conclusion and Recommendation}

Inhibiting crossover is a challenging goal in the hydrogenation of CO\textsubscript{2} into liquid fuels and building-block chemicals. In this review, we introduced three recent...
approaches to suppress or eliminate C₁ and C₂⁺ liquid product crossover in the CO₂R: BPM, SSE, and acidic CO₂R systems. With targeted research and careful implementation, these approaches could lead to the electroproduction of valuable C₂⁺ oxygenate fuels, such as ethanol, acetate, and propanol, at useful concentrations.

The BPM approach promises to inhibit the crossover of both anionic and neutral products of CO₂ electrolysis. Until now, BPM-based systems have suffered from a high rate of hydrogen production, the result of the proton flux toward the cathode, as well as high overpotentials required to drive water dissociation.[24] Furthermore, the crossover of liquid products, while reduced, was not completely eliminated with present-day BPMs. To enable future rational design of membrane materials for this application, further research is warranted to optimize the synthetic parameters of these membranes, such as the prepolymerization solvent content, the cross-linker content, and the length of alkyl spacers between charged functional groups on the liquid crossover performance.

SSEs, possess advantages over liquid-phase electrolytes. The elimination of liquid-phase electrolytes has been found to enable the production of pure formic acid at high concentrations. The application of SSE to C₂⁺ liquid production will require further system optimization and the use of highly selective catalysts to achieve desired product purities under these conditions. The use of multiple electrolyte-membrane layers also introduces additional resistances to the electrolyzer and reduces the overall energy efficiency, especially when operating at high current densities. Other key challenges include the design and integration of new polymer electrolytes that simultaneously provide high ionic conductivity, selectivity, resistance to reactant/product crossover, CO₂ tolerance, cost-effectiveness, and long-term chemical and mechanical stability under high-current operating conditions.

An acidic CO₂R system employing extremely low pH electrolytes paired with a CEM could provide a high concentration of protons for CO protonation and prevent the poisoning of the catalyst electrode. Avoiding the use of neutral or alkaline solution liquid electrolytes also interrupts the transport of liquid products to the anode, thereby addressing the liquid crossover issue. However, the competing hydrogen evolution reaction remains a significant issue for CO₂R in acidic systems. While progress has been made in improving CO₂R selectivity by employing mildly acidic electrolytes, major strides are needed to achieve favorable CO₂R selectivity toward C₂⁺. Emerging classes of catalysts, such as transition-metal chalcogenides,[25] metal carbides,[26] and carbon-based metal-free electrocatalysts,[27] may provide the means to break scaling relations between reaction intermediates.

We emphasize that reducing crossover through these methods may have a deleterious effect on the other performance metrics, such as higher cell voltage and product selectivity, toward HER. In Table 1, we provide a direct comparison of the three proposed methods with a flow reactor using an AEM.

While other methods such as increasing the CO₂ and catholyte flow rate have also shown effects on suppressing liquid product crossover into the anolyte, they generally come at the cost of lower product concentration.[12] The high energy requirement associated with downstream separation necessitates the pursuit of increasing liquid product concentration in parallel with suppressing crossover. While not a focus area of this review, we emphasize the importance of achieving high product concentration and note that avoiding liquid product loss via crossover is essential in the pursuit of concentrated liquid products. By reducing the need for postreaction purification and separation, the production of CO₂-derived liquid products is more likely to be economically feasible.

In summary, much progress has been made in recent years to define avenues toward low-crossover reactors for electrosynthesis. The approaches presented here show particular promise in this regard. Each approach requires further innovation to suppress crossover in a manner compatible with the other characteristics essential for ultimate commercial application: high rate, high energy efficiency, and high single-pass CO₂ utilization. The elimination of liquid product crossover is thus a key step to advance the achievement of renewable liquid fuels from CO₂.

### ACKNOWLEDGMENTS

The authors acknowledge funding from the Natural Sciences and Engineering Research Council (NSERC) of Canada and the Ontario Research Fund-Research Excellence program. SciNet is funded by the Canada Foundation for Innovation, the Government of Ontario, Ontario Research Fund Research Excellence Program, and the University of Toronto. Ning Wang and Hongyan Liang acknowledge support from the National Natural Science Foundation of China and the Ontario Research Fund-R Research Excellence Program.

### Table 1: Direct comparison of proposed three methods to stop liquid product crossover

| Methods       | Bipolar membranes | Solid-state electrolyte | Acid CO₂R |
|---------------|-------------------|-------------------------|-----------|
| Cell voltage  | –                 | –                       | ○         |
| Product selectivity | –               | ○                       | –         |

Abbreviations: CO₂R, CO₂ reduction; –, deduction in performance; ○, no effect on performance.
Foundation of China (NSFC No.: 51771132) and the Thousand Youth Talents Plan of China. Alberto Vomiero acknowledges the Kempe Foundation and the Knut & Alice Wallenberg Foundation for financial support.

CONFLICT OF INTERESTS

The authors declare that there are no conflict of interests.

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REFERENCES

1. Song RB, Zhu W, Fu J, et al. Electrocatalytic CO₂ reduction: Electrode materials engineering in electrocatalytic CO₂ reduction: Energy input and conversion efficiency (Adv. Mater. 2020;32:1903796).
2. Shao Q, Wang P, Huang X. Opportunities and challenges of interface engineering in bimetallic nanostructure for enhanced electrocatalysis. Adv Funct Mater. 2019;29:1806419.
3. Li YC, Wang Z, Yuan T, et al. Binding site diversity promotes CO₂ electroreduction to ethanol. J Am Chem Soc. 2019;141:8584-8591.
4. Jouny M, Luc W, Jiao F. General technoeconomic analysis of CO₂ electrolysis systems. Ind Eng Chem Res. 2018;57:2165-2177.
5. Spurgeon JM, Kumar B. A comparative technoeconomic analysis of pathways for commercial electrochemical CO₂ reduction to liquid products. Energy Environ Sci. 2018;11:1536-1551.
6. Gabardo CM, O’Brien CP, Edwards JP, et al. Continuous carbon dioxide electroreduction to concentrated multi-carbon products using a membrane electrode assembly. Joule. 2019;3:2777-2791.
7. Weekes DM, Salvatore DA, Reyes A, Huang A, Berlinguette CP. Electrolytic CO₂ reduction in a flow cell. Acc Chem Res. 2018;51:910-918.
8. Verma S, Hamasaki Y, Kim C, et al. Insights into the low overpotential electroreduction of CO₂ to CO on a supported gold catalyst in an alkaline flow electrolyzer. ACS Energy Lett. 2018;3:193-198.
9. Lv JJ, Jouny M, Luc W, Zhu W, Zhu JJ, Jiao F. A highly porous copper electrocatalyst for carbon dioxide reduction. Adv Mater. 2018;30:1803111.
10. Rabinowitz JA, Kanan MW. The future of low-temperature carbon dioxide electrolysis depends on solving one basic problem. Nat Commun. 2020;11:5231.
11. Ma M, Clark EL, Therkildsen KT, Dalsgaard S, Chorkendorff I, Seger B. Insights into the carbon balance for CO₂ electroreduction on Cu using gas diffusion electrode reactor designs. Energy Environ Sci. 2020;13:977-985.
12. Lin M, Han L, Singh MR, Xiang C. An experimental- and simulation-based evaluation of the CO₂ utilization efficiency of aqueous-based electrochemical CO₂ reduction reactors with ion-selective membranes. ACS Appl Energy Mater. 2019;2:5843-5850.
13. Li YC, Yan Z, Hitt J, Wycisk R, Pintauro PN, Mallouk TE. Bipolar membranes inhibit product crossover in CO₂ electroreduction cells. Adv Sustainable Syst. 2018;2:1700187.
14. Zhang J, Luo W, Züttel A. Crossover of liquid products from electrochemical CO₂ reduction through gas diffusion electrode and anion exchange membrane. J Catal. 2020;385:140-145.
15. Li YC, Lee G, Yuan T, et al. CO₂ electroreduction from carbonate electrolyte. ACS Energy Lett. 2019;4:1427-1431.
16. Chen Y, Vise A, Klein WE, et al. A robust, scalable platform for the electrochemical conversion of CO₂ to formate: identifying pathways to higher energy efficiencies. ACS Energy Lett. 2020;5:1825-1833.
17. Manthiram A, Yu X, Wang S. Lithium battery chemistries enabled by solid-state electrolytes. Nat Rev Mater. 2017;2:16103.
18. Xia C, Zhu P, Jiang Q, et al. Continuous production of pure liquid fuel solutions via electrocatalytic CO₂ reduction using solid-electrolyte devices. Nat Energy. 2019;4:776-785.
19. Fan L, Xia C, Zhu P, Lu Y, Wang H. Electrochemical CO₂ reduction to high-concentration pure formic acid solutions in an all-solid-state reactor. Nat Commun. 2020;11:3633.
20. Ma M, Kim S, Chorkendorff I, Seger B. Role of ion-selective membranes in the carbon balance for CO₂ electroreduction via gas diffusion electrode reactor designs. Chem Sci. 2020;11:8854-8861.
21. de Beer F, van der Merwe JH, Bessarabov D. PEM water electrolysis: preliminary investigations using neutron radiography. Physics Procedia. 2017;88:19-26.
22. Ramdin M, Morrison ART, de Groen M, et al. High-pressure electrochemical reduction of CO₂ to formic acid/formate: effect of pH on the downstream separation process and economics. Ind Eng Chem Res. 2019;58:22718-22740.
23. Hori Y, Murata A, Takahashi R, Suzuki S. Enhanced formation of ethylene and alcohols at ambient temperature and pressure in electrochemical reduction of carbon dioxide at a copper electrode. J Chem Soc Chem Commun. 1988;9:17.
24. Blommaert MA, Verdonk JAH, Blommaert HCB, Smith WA, Vermaas DA. Reduced ion crossover in bipolar membrane electrolysis via increased current density, molecular size, and valence. ACS Appl Energy Mater. 2020;3:5804-5812.
25. Yuhas BD, Prasittichai C, Hupp JT, Kanatzidis MG. Enhanced electrocatalytic reduction of CO₂ with ternary Ni-Fe₄S₄-based biomimetic chalcogels. J Am Chem Soc. 2011;133:15854-15857.
26. Wang J, Kattel S, Hawxhurst CJ, et al. Enhancing activity and reducing cost for electrochemical reduction of CO₂ by supporting palladium on metal carbides. Angew Chem Int Ed. 2019;58:6271-6275.
27. Paul R, Zhu L, Chen H, Qu J, Dai L. Recent advances in carbon-based metal-free electrocatalysts. Adv Mater. 2019;31:1806403.

How to cite this article: Wang N, Miao RK, Lee G, et al. Suppressing the liquid product crossover in electrochemical CO₂ reduction. SmartMat. 2021;2:12-16. https://doi.org/10.1002/smm2.1018