

# UC Irvine

## UC Irvine Previously Published Works

### Title

Membrane electrode assembly design to prevent CO<sub>2</sub> crossover in CO<sub>2</sub> reduction reaction electrolysis.

### Permalink

<https://escholarship.org/uc/item/8q77b1rw>

### Journal

Communications Chemistry, 6(1)

### Authors

Chang, Hung-Ming

Zenyuk, Iryna

### Publication Date



2023-01-03

### DOI

10.1038/s42004-022-00806-0

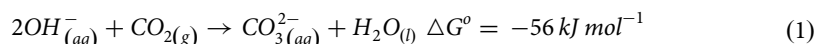
Peer reviewed

## Membrane electrode assembly design to prevent CO<sub>2</sub> crossover in CO<sub>2</sub> reduction reaction electrolysis

Hung-Ming Chang <sup>1,2</sup> & Iryna V. Zenyuk <sup>1,2</sup>✉

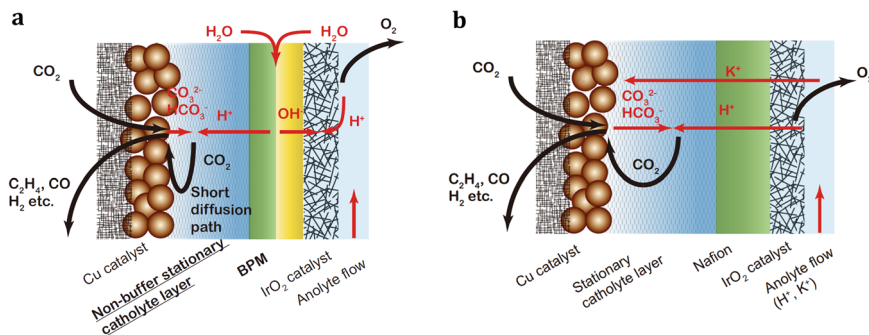
To reach a net-zero energy economy by 2050, it is critical to develop negative emission technologies, such as CO<sub>2</sub> reduction electrolyzers, but these devices still suffer from various issues including low utilization of CO<sub>2</sub> because of its cross-over from the cathode to the anode. This comment highlights the recent innovative design of membrane electrode assembly, utilizing a bipolar membrane and catholyte layer that blocks CO<sub>2</sub> cross-over and enables high CO<sub>2</sub> single-pass utilization.

Low temperature (below 100 °C) CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) electrolyzers are promising negative emission technologies that convert CO<sub>2</sub> to various value-added products<sup>1,2</sup>. These electrolyzers can be easily integrated with renewable power generation (solar and wind) to operate on renewable electricity. For CO<sub>2</sub>RR technologies to be commercially viable they must operate at high: (i) Faradaic efficiency (FE), (ii) conversion rate, (iii) selectivity and (iv) conversion efficiency<sup>3</sup>. It is challenging to achieve all of these four conditions in a single cell experiment, but it is even more difficult to translate the findings to a scaled-up electrolyzer stack system. Specific interest for low temperature electrolysis is its ability to generate multicarbon (C<sub>2+</sub>) products, such as ethylene, ethanol, and propanol because of their commercial value. Recently, significant advances were made to reach competitive product selective current densities (>100 mA cm<sup>-2</sup>) in CO<sub>2</sub>RR to C<sub>2+</sub> products, with overall good stability. This was achieved with careful catalyst nanoparticles design, their integration within the gas diffusion layers to make gas diffusion electrodes, and with tailoring local environments by using ionomers or liquid electrolytes to achieve neutral or alkaline environments. This alkaline/neutral environment is essential for CO<sub>2</sub>RR cathodes because of the preferential formation of H<sub>2</sub> over C<sub>2+</sub> products in an acidic environment. Only very recently<sup>4</sup> researchers realized that basic chemistry is a big issue for CO<sub>2</sub>RR technology in alkaline environments: The rapid reaction of CO<sub>2</sub> with OH<sup>-</sup> in alkaline media to form CO<sub>3</sub><sup>2-</sup> is a thermodynamically favored reaction that results in a loss of CO<sub>2</sub>, consumption of OH<sup>-</sup> and non-steady-state operating conditions, where electrolyte is consumed:



Interestingly, it requires much larger energy to regenerate CO<sub>2</sub> and OH<sup>-</sup> from aqueous CO<sub>3</sub><sup>2-</sup>, and some studies suggest this value to be >230 kJ mol<sup>-1</sup><sup>5</sup>. Overall, the energy stored in CO<sub>2</sub>RR electrolyzer is around 100–130 kJ/mol of electrons. Therefore, if one needs to regenerate electrolyte after the operation, it will be more energy intensive to do so than the energy stored in C<sub>2+</sub> products achieved through electrolysis. This is an inherent issue in alkaline/neutral media that many earlier studies have overlooked and only in the course of the last 2 years, or so, studies have started incorporating single-pass utilization (SPU) of CO<sub>2</sub> as one of the major metrics for the efficiency of the CO<sub>2</sub>RR electrolysis. This metric is defined as the fraction of CO<sub>2</sub> converted

<sup>1</sup>Department of Chemical and Biomolecular Engineering, University of California Irvine, Irvine, CA, USA. <sup>2</sup>National Fuel Cell Research Center, University of California Irvine, Irvine, CA, USA. ✉email: [iryna.zenyuk@uci.edu](mailto:iryna.zenyuk@uci.edu)



**Fig. 1** A schematic of the CO<sub>2</sub>RR electrolyzer and relevant transport processes. The CO<sub>2</sub>RR electrolyzer utilizing (a) a bipolar membrane (BPM) and (b) a cation exchange membrane (CEM). Copyright: Modified from ref. 6, used under CC BY.

electrochemically to the total input CO<sub>2</sub>:

$$SPU = \frac{C_{\text{electrochem}}}{C_{\text{in}}} \quad (2)$$

where the upper limit of SPU was shown to depend on cross-over CO<sub>2</sub> (or loss of CO<sub>2</sub> to electrolyte):

$$SPU_{\text{-max}} = \frac{C_{\text{electrochem}}}{C_{\text{electrochem}} + c_{\text{cross}}} \quad (3)$$

The crossover concentration depends on the ability of CO<sub>2</sub> to react with OH<sup>-</sup> to form carbonate and bicarbonate products that then cross the membrane and form CO<sub>2</sub> on the anode side. The SPU<sub>max</sub> values are currently <25% for C<sub>2+</sub> products, resulting in overall net negative energy balance of the electrolyzer operation.

Recently, Sinton, Sargent and collaborators<sup>6</sup> have reported a novel electrolyzer design based on a bipolar membrane (BPM) that aims to block CO<sub>2</sub> crossover to the anode, achieving a remarkable CO<sub>2</sub> SPU of 78%, a factor of 10× improvement compared to earlier works. The innovative design they propose is based on the requirements that (i) CO<sub>2</sub> must not cross to the anode through the alkaline exchange membrane (AEM) and (ii) CO<sub>2</sub> that is reacted to form carbonates and bicarbonates on the cathodes side must be regenerated internally within the electrolyzer. The first requirement was resolved by incorporation of a BPM, but not in zero-gap configuration, where a cation exchange membrane (CEM) will face the cathode and reduce the FE of the CO<sub>2</sub>RR. The CEM side of the BPM is in contact with a non-buffer stationary catholyte (SC) layer, as shown in Fig. 1a. By allowing this SC-layer, the CEM is sufficiently removed from the cathode catalyst layer to not induce an acidic environment in the catalyst layer. Key to this design that addresses the second requirement is a non-flowing and non-buffer SC-layer, as a flowing catholyte layer would remove CO<sub>2</sub> that was converted to carbonate/bicarbonate, resulting in low SPU. The authors have shown (Fig. 1a) that carbonate and bicarbonate ions recombine with protons to regenerate CO<sub>2</sub> and that the regenerated CO<sub>2</sub> diffuses back to the copper catalyst layer and reacts there. By optimizing feed-in CO<sub>2</sub> concentrations and the thickness of the non-buffer SC-layer to maximize CO<sub>2</sub> regeneration and minimize diffusion losses, while maintaining a high pH at the cathode catalyst layer, one can achieve unprecedented SPU. The team has significant expertise in the design of BPMs and the results suggest that the electrolyzer with the SC BPM membrane electrode assembly at 200 mA cm<sup>-2</sup> has similar cell voltage compared to an AEM electrolyzer but with significantly higher SPU (78%). Furthermore, they have shown >50 h stability operating at 200 mA cm<sup>-2</sup> with restricted CO<sub>2</sub> inlet, being a competitive stability result to the published data.

In the same work, Sinton, Sargent and collaborators<sup>6</sup> have further extended this innovative CO<sub>2</sub>RR electrolyzer concept to a

CEM electrolyzer, as shown in Fig. 1b. The advantage of CEM over BPM is that it eliminates the water dissociation reaction at the bipolar junction and reduces the overall thickness of the membrane. They have shown that the CO<sub>2</sub> crossover with the CEM concept was eliminated too. The CEM electrolyzer had an overall lower cell voltage and comparable SPU. The necessity of the anolyte flow is to provide cations that are needed to shield negative charge in the cathode catalyst layer, the so-called “cation effect”<sup>7</sup>, to enable high FE toward C<sub>2+</sub> products over the hydrogen evolution reaction. As the authors pointed out, without acid and salt addition the steady-state cannot be reached as the pH gradients will be eliminated with co-ion transport and neutralization.

## Outlook

The work by Sinton, Sargent and collaborators<sup>6</sup> has opened a new research area in methods to improve SPU of CO<sub>2</sub>RR electrolyzers by enabling CO<sub>2</sub> regeneration through smart electrolyzer design. The authors suggest area of improvements including use of ionic liquids in the catholyte and tuning the morphology (porosity, pore sizes, tortuosity and wettability) of the SC-layer, which is currently stacked PVDF layers. In terms of larger scale fabrication, SC-layer pretreatment and degassing need to be developed for roll-to-roll fabrication processes. Several issues that might arise include potassium carbonate precipitation, resulting in challenges to long-stability operation. The cation effect might still be important for the system under study and understanding the non-buffering electrolyte selection with various cations can be important.

Although CO<sub>2</sub> SPU has been apparently improved, the cell voltage still has room for improvement. Recent work by Vass et al.<sup>8</sup> suggested coupling CO<sub>2</sub>RR with value-added anode products or with reactions that have lower overpotential on the anode side, enhancing the energy efficiency. As the electrolyzers operate at higher current densities, the challenge of losing liquid products through a BPM will also need to be addressed.

In an alternative approach one can use CEM and local acidic environments to prevent CO<sub>2</sub> reaction with OH<sup>-</sup>. However, in acidic environments, hydrogen evolution reaction (HER) is kinetically favorable compared to CO<sub>2</sub>RR because adsorbed H competes with the adsorption of CO. Wang, Sargent and collaborators<sup>9</sup> have used density functional theory to show that addition of Pd to Cu can help local CO binding and promote C-C coupling, weakening the H-binding energy and therefore suppressing HER. This alternative approach achieved a CO<sub>2</sub> to C<sub>2+</sub> SPU of 60% at 500 mA cm<sup>-2</sup> and will serve as a new direction to suppress CO<sub>2</sub> crossover.

A third direction is to modify the anode stream to enable efficient CO<sub>2</sub> separation, as for an AEM a typical mixture is 20–40% O<sub>2</sub> with 60–80% CO<sub>2</sub>, which cannot be fed directly into

the cathode, as the oxygen reduction reaction would dominate over the CO<sub>2</sub>RR. Recent work by Sinton, Sargent and collaborators<sup>10</sup> reported an all liquid anode to enable easy separation of gaseous CO<sub>2</sub> and liquid products from the anode reactions. They have used organic oxidation reaction (OOR) on the anode side, specifically glucose oxidation reaction, showing high SPU of 48% and lower cell voltage compared to OER. Other OOR could be explored to enable CO<sub>2</sub> recovery and also to generate value-added products on the anode.

Received: 8 December 2022; Accepted: 23 December 2022;

Published online: 03 January 2023

## References

1. Quadrelli, E. A., Centi, G., Duplan, J. L. & Perathoner, S. Carbon dioxide recycling: Emerging large-scale technologies with industrial potential. *ChemSusChem* **4**, 1194–1215 (2011).
2. Hepburn, C. et al. The technological and economic prospects for CO<sub>2</sub> utilization and removal. *Nature* **575**, 87–97 (2019).
3. Grant, P. S. et al. 2022 roadmap on low temperature electrochemical CO<sub>2</sub> reduction. *J. Phys. Energy* **4**, 1–84 (2022).
4. Rabinowitz, J. A. & Kanan, M. W. The future of low-temperature carbon dioxide electrolysis depends on solving one basic problem. *Nat. Commun.* **11**, 10–12 (2020).
5. Keith, D. W., Holmes, G., St. Angelo, D. & Heidele, K. A Process for Capturing CO<sub>2</sub> from the Atmosphere. *Joule* **2**, 1573–1594 (2018).
6. Xie, K. et al. Bipolar membrane electrolyzers enable high single-pass CO<sub>2</sub> electroreduction to multicarbon products. *Nat. Commun.* **13**, 1–12 (2022).
7. Ringe, S. et al. Understanding cation effects in electrochemical CO<sub>2</sub> reduction. *Energy Environ. Sci.* **12**, 3001–3014 (2019).
8. Vass, A., Endrődi, B. & Janáky, C. Coupling electrochemical carbon dioxide conversion with value-added anode processes: An emerging paradigm. *Curr. Opin. Electrochem.* **25**, 1–9 (2021).
9. Xie, Y. et al. High carbon utilization in CO<sub>2</sub> reduction to multi-carbon products in acidic media. *Nat. Catal.* **5**, 564–570 (2022).
10. Xie, K. et al. Eliminating the need for anodic gas separation in CO<sub>2</sub> electroreduction systems via liquid-to-liquid anodic upgrading. *Nat. Commun.* **13**, 1–9 (2022).

## Author contributions

H-M.C. and I.V.Z. all contributed to the conception and writing this comment.

## Competing interests

The authors declare no competing interests.

## Additional information

**Correspondence** and requests for materials should be addressed to Iryna V. Zenyuk.

**Reprints and permission information** is available at <http://www.nature.com/reprints>

**Publisher's note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2023