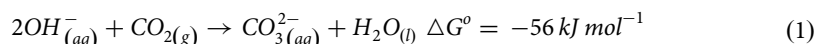COMMENT

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Membrane electrode assembly design to prevent CO_2 crossover in CO_2 reduction reaction electrolysis

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To reach a net-zero energy economy by 2050, it is critical to develop negative emission technologies, such as CO_2 reduction electrolyzers, but these devices still suffer from various issues including low utilization of CO_2 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_2 cross-over and enables high CO_2 single-pass utilization.

Low temperature (below 100 °C) CO_2 reduction reaction (CO_2RR) electrolyzers are promising negative emission technologies that convert CO_2 to various value-added products[1,2]. These electrolyzers can be easily integrated with renewable power generation (solar and wind) to operate on renewable electricity. For CO_2RR technologies to be commercially viable they must operate at high: (i) Faradaic efficiency (FE), (ii) conversion rate, (iii) selectivity and (iv) conversion efficiency[3]. 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_{2+}) 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^{-2}) in CO_2RR to C_{2+} 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_2RR cathodes because of the preferential formation of H_2 over C_{2+} products in an acidic environment. Only very recently[4] researchers realized that basic chemistry is a big issue for CO_2RR technology in alkaline environments: The rapid reaction of CO_2 with OH$^-$ in alkaline media to form CO_3^{2-} is a thermodynamically favored reaction that results in a loss of CO_2, consumption of OH^- and non-steady-state operating conditions, where electrolyte is consumed:

$$2OH^-_{(aq)} + CO_{2(g)} \rightarrow CO^{2-}_{3(aq)} + H_2O_{(l)} \quad \triangle G^o = -56 \, kJ \, mol^{-1} \tag{1}$$

Interestingly, it requires much larger energy to regenerate CO_2 and OH^- from aqueous CO_3^{2-}, and some studies suggest this value to be >230 kJ mol^{-1} [5]. Overall, the energy stored in CO_2RR 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_{2+} 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_2 as one of the major metrics for the efficiency of the CO_2RR electrolysis. This metric is defined as the fraction of CO_2 converted

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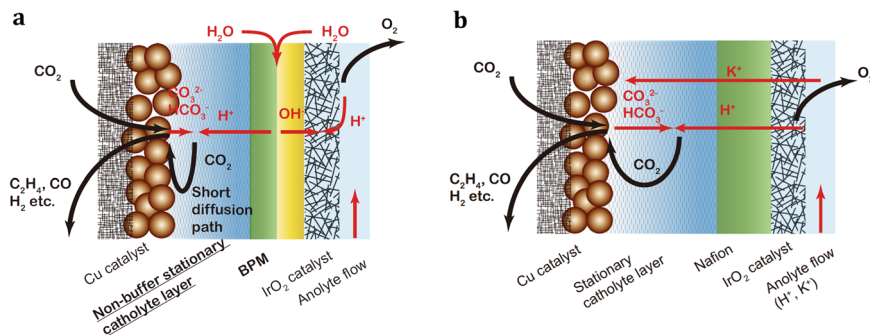
Fig. 1 A schematic of the CO₂RR electrolyzer and relevant transport processes. The CO_2RR electrolyzer utilizing (**a**) a bipolar membrane (BPM) and (**b**) a cation exchange membrane (CEM). Copyright: Modified from ref. [6]., used under CC BY.

electrochemically to the total input CO_2:

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

where the upper limit of SPU was shown to depend on cross-over CO_2 (or loss of CO_2 to electrolyte):

$$SPU\_max = \frac{C_{electrochem}}{C_{electrochem} + c_{cross}} \qquad (3)$$

The crossover concentration depends on the ability of CO_2 to react with OH^- to form carbonate and bicarbonate products that then cross the membrane and form CO_2 on the anode side. The SPUmax values are currently <25% for C_{2+} products, resulting in overall net negative energy balance of the electrolyzer operation.

Recently, Sinton, Sargent and collaborators[6] have reported a novel electrolyzer design based on a bipolar membrane (BPM) that aims to block CO_2 crossover to the anode side, achieving a remarkable CO_2 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_2 must not cross to the anode through the alkaline exchange membrane (AEM) and (ii) CO_2 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_2RR. 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_2 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_2 and that the regenerated CO_2 diffuses back to the copper catalyst layer and reacts there. By optimizing feed-in CO_2 concentrations and the thickness of the non-buffer SC-layer to maximize CO_2 regeneration and minimize diffusion losses, while maintaining a high pH at the cathode catalyst layer, one can achieve unprecedented SPU. The team has significant expertize in the design of BPMs and the results suggest that the electrolyzer with the SC BPM membrane electrode assembly at 200 mA cm⁻² 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⁻² with restricted CO_2 inlet, being a competitive stability result to the published data.

In the same work, Sinton, Sargent and collaborators[6] have further extended this innovative CO_2RR 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_2 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"[7], to enable high FE toward C_{2+} 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[6] has opened a new research area in methods to improve SPU of CO_2RR electrolyzers by enabling CO_2 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_2 SPU has been apparently improved, the cell voltage still has room for improvement. Recent work by Vass at el[8]. suggested coupling CO_2RR 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_2 reaction with OH^-. However, in acidic environments, hydrogen evolution reaction (HER) is kinetically favorable compared to CO_2RR because adsorbed H competes with the adsorption of CO. Wang, Sargent and collaborators[9] 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_2 to C_{2+} SPU of 60% at 500 mA cm⁻² and will serve as a new direction to suppress CO_2 crossover.

A third direction is to modify the anode stream to enable efficient CO_2 separation, as for an AEM a typical mixture is 20–40% O_2 with 60–80% CO_2, which cannot be fed directly into

the cathode, as the oxygen reduction reaction would dominate over the CO_2RR. Recent work by Sinton, Sargent and collaborators[10] reported an all liquid anode to enable easy separation of gaseous CO_2 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_2 recovery and also to generate value-added products on the anode.

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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