Role of Ion-Selective Membranes in the Carbon Balance for CO\textsubscript{2} Electroreduction via Gas Diffusion Electrode Reactor Designs

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SUMMARY

In this work, the effect of ion-selective membranes on the detailed carbon balance was systematically analyzed for high-rate CO₂ reduction in flow electrolyzers. By using different ion-selective membranes, we show nearly identical catalytic selectivity for CO₂ reduction, which is primarily due to a similar local reaction environment created at the cathode/electrolyte interface via the introduction of a catholyte layer. In addition, based on a systematic exploration of gases released from electrolytes and the dynamical change of electrolyte speciation, we demonstrate the explicit discrepancy in carbon balance paths for the captured CO₂ at the cathode/catholyte interface via reaction with OH⁻ when using different ion-selective membranes: (i) the captured CO₂ could transport through an anion exchange membrane in the form of CO₃²⁻, subsequently releasing CO₂ along with O₂ in the anolyte, (ii) with a cation exchange membrane, the captured CO₂ would be accumulated in the catholyte in the forms of CO₃²⁻, (iii) whereas under the operation of a BPM, the captured CO₂ could be released at the catholyte/membrane interface in the form of gaseous CO₂. The unique carbon balance path for each type of membrane is linked to ion species transported through membranes.
INTRODUCTION

The electrochemical reduction of CO$_2$ to valuable chemicals and fuels powered by renewable electricity provides an attractive strategy to close the anthropogenic carbon cycle and store intermittent renewable energy.$^{1-8}$ In the past, great efforts have been devoted to the development of selective, efficient and stable electrocatalysts in CO$_2$-saturated aqueous solutions using H-type cells.$^{9-16}$ Striking progress has been made in exploring catalysts for CO$_2$ reduction in H-type cells. However, CO$_2$ reduction in H-type reactors only allow for relatively low current densities due to mass transport limitations in aqueous solutions.$^{17-19}$ Large-scale utilization of electrochemical conversion of CO$_2$ requires high reaction rates (i.e. high current densities). In this context, flow electrolyzers with gas-diffusion electrodes (GDEs) has gained considerable attention for CO$_2$ reduction, owing to that GDEs allow for a very thin mass-transfer boundary layer ($\sim 50$ nm).$^{18,19}$ By using GDE-type flow electrolyzers, the mass-transport of CO$_2$ and gaseous products on the surface of the catalysts can be accelerated, achieving commercially-relevant current densities (>$100$ mA/cm$^2$) along with high selectivity toward a desired product.$^{20-29}$

To date, most of the high-rate CO$_2$ reduction studies based on GDE-type flow electrolyzers have been performed using anion exchange membranes (AEM) to avoid product crossover.$^{20-29}$ However, our recent work demonstrated a substantial crossover of anionic CO$_2$ reduction products such as acetate and formate through AEM in GDE-type flow electrolyzers.$^{29}$ More importantly, after the electrolytes reach steady state, it was found that about 70% of consumed CO$_2$ is captured at the cathode/electrolyte interface via reaction with OH$^-$, forming CO$_3^{2-}$, which transports to the anolyte via AEM as a charge-carrier.$^{29}$ Subsequently, CO$_3^{2-}$ coming from the catholyte reacts with H$^+$ in the vicinity of the anode, releasing gaseous CO$_2$ from the anolyte along with the O$_2$ stream, which means that most of the consumed CO$_2$ (70%) is captured in catholyte and emitted from the anolyte.
In other words, only 30% of the CO₂ consumption is involved for CO₂ conversion into products. This finding means that many of the current techno-economic analysis for high-rate electroreduction of CO₂ must be reconsidered if the significant CO₂ crossover occurs.

One approach to reduce the CO₂ crossover would be to use a two-step cascade process, which consists of an initial CO₂ reduction to CO and a subsequent CO conversion into highly valuable multi-carbon products that has no carbon source crossover.30,31 However, even in this two-step procedure with 100% CO faradaic efficiency in the first step, 50% of all consumed CO₂ could still be emitted out of the anolyte using an AEM.29 Theoretically, utilization of a cation exchange membrane (CEM) or a bipolar membrane (BPM) can prevent the CO₂ crossover in GDE-type flow electrolyzers. However, only a few works on high-rate CO₂ reduction (> 100 mA/cm²) have been carried out in GDE-type electrolyzers using a CEM32–34 or BPM35,36 to date.

This study describes a systematic exploration of the effect of ion-selective membranes on the detailed carbon balance including CO₂ consumption, products and CO₂ crossover, as well as CO₂ emission in GDE-type flow electrolyzers. Herein, we demonstrate the comparison of catalytic selectivity, CO₂ consumption rate (via the reaction with OH⁻), and the dynamical change of electrolyte speciation among three different types of ion-selective membranes. By a systematic exploration of gases released from catholyte or anolyte, ion species change in electrolyte and ion species transport via membranes, this work provides mechanistic insights into the role of ion-selective membranes in carbon balancing for high-rate CO₂ reduction.

RESULTS AND DISCUSSION

Electrocatalytic CO₂ reduction performance
In this work, Cu electrocatalyst layers (~70 nm) were prepared on top of microporous carbon layers of GDEs by magnetron sputtering at an argon pressure of 2 mTorr (Figure S1). The detailed materials characterization of the Cu catalyst layers on GDEs has been reported in our previous work. We conducted CO$_2$ reduction electrolysis experiments in a three-compartment flow electrolyzer where a Cu catalyst coated on GDE was positioned between the gas and catholyte chambers, as shown in Figure 1a. An ion-selective membrane was used to separate the catholyte and anolyte flow chambers in which electrolytes continuously flow. During CO$_2$ reduction, gaseous CO$_2$ at a constant flow rate (45 ml min) was continuously fed into the gas chamber (Figure 1a), and a fraction of the CO$_2$ diffused to the surface of the catalysts in an electrolyte and then converted into gas products such as C$_2$H$_4$ and liquid products such as ethanol (Figure 1b). Gas products mixed with the unreacted CO$_2$ were directly vented into the gas-sampling loop of a gas chromatograph (GC) for periodic quantification. The liquid products were diluted and circulated in the given catholyte and anolyte reservoirs, and was detected via high-performance liquid chromatography (HPLC) after completion of the CO$_2$ reduction electrolysis experiment.

In order to get reliable catalytic selectivity for gas products in high-rate CO$_2$ reduction, gas flow out of the reactor was monitored via a volumetric flowmeter according to our previous work (Figure S2). Figure 1c shows nearly identical gas flowrates were observed out of the electrolyzer when using AEM, CEM and BPM in 1 M KHCO$_3$ at 200 mA/cm$^2$, indicating a similar CO$_2$ consumption rate. This observation is primarily due to that the same OH$^-$ generation rate via cathodic reactions (i.e. similar local pH created at the cathode/electrolyte interface). The faradaic efficiencies of gas products calculated using these corrected gas flowrates were plotted for different ion-selective membranes (Figure 1c). As shown in Figure 1c, C$_2$H$_4$ is the primary gas product for all the different ion-selective membranes, along with small amounts of CO and H$_2$ and only trace amounts of CH$_4$. 
Notably, the faradaic efficiencies for gaseous products had no obvious variation when different types of membranes were utilized (at nearly identical potentials, as shown in Figure 1c). This result indicates that catalytic selectivity of gaseous products is independent of the type of ion-selective membrane for high-rate CO$_2$ reduction in the three-compartment electrolyzers.

![Figure 1.](image)

**Figure 1.** (a) Schematic illustration of three-compartment flow electrolyzers. (b) Schematic illustration of cathode/electrolyte interface for CO$_2$ conversion. (c) Gas flowrates out of gas chamber after CO$_2$ reduction (left axis) and faradaic efficiencies for gas products (right axis) using different ion-selective membranes in 1 M KHCO$_3$ at 200 mA/cm$^2$. The iR-corrected potentials are labeled with purple color in (c). 45 ml/min CO$_2$ inlet flow was used in all the experiments.
Figure 2. (a) Faradaic efficiencies for detected liquid products in anolyte and (b) faradaic efficiencies for liquid products evaporated from GDEs into the gas chamber. (c) Faradaic efficiencies for all detected gas and liquid products in 1 M KHCO$_3$ at 200 mA/cm$^2$ for various membranes. Total liquid products were counted via analysis of both catholyte and anolyte as well as liquid products evaporated from GDEs into the gas chamber.

In addition to the detected gas products, liquid-phase products in both catholyte and anolyte were all analyzed due to the potential crossover of liquid products from the catholyte to anolyte via membranes. As noted in Figure 2a, substantial anionic CO$_2$ reduction products (such as formate and acetate) crossed over from the catholyte to the anolyte via the AEM by electromigration, with only minimal crossover for uncharged liquid products. In contrast, the CEM and BPM exhibited negligible crossover for both anionic liquid products and uncharged products (Figure 2a). This observation entails both CEM and BPM are capable of inhibiting the crossover of anionic and neutral products.

For determining the total amounts of liquid products, liquid products evaporated from GDEs into the gas chamber of the reactor were also collected for analysis (using a setup shown in Figure S3). No matter which type of ion-selective membrane was used, alcohol products such as n-propanol and ethanol experienced considerable evaporation through the gas diffusion layer of GDE (Figure 2b), which is due to their high volatility. In addition, we found that acetaldehyde had the highest evaporation ratio among the evaporated liquid products (Figure S4). This finding may be
attributed to two reasons, (i) its relatively high vapor pressure and (ii) its further reduction to ethanol on the cathode where a substantial amount of acetaldehyde was produced initially and subsequently converted into ethanol. Based on the quantification of liquid products in both catholyte and anolyte as well as liquid products evaporated from GDEs into the gas chamber (Equation S10), faradaic efficiencies of all liquid products were evaluated for all the different types of membranes (Figure 2c). As shown in Figure 2c, ethanol was the dominant liquid product along with n-propanol, acetate and formate as minor products. There appears to be no significant variation in liquid product formation across all types of membranes. All the above results imply that the role of ion-selective membrane is almost negligible in affecting catalytic selectivity of high-rate CO₂ reduction in the three-compartment electrolyzers, owing to the similar local reaction environment created on the cathode via the introduction of a catholyte layer.

**Capture and emission of CO₂ throughout the electrolyte**

According to our recent carbon balance study, the gases released from the anolyte were systematically explored for CO₂ reduction via an AEM with 1 M KHCO₃, elucidating a two-step procedure of CO₂ capture at the cathode/electrolyte interface via reaction with OH⁻ and subsequent CO₂ degassing from anolyte due to H⁺ in the vicinity of the anode (Scheme 1a). With the nearly identical catalytic selectivity (Figure 2c) and similar total CO₂ consumption rate (similar gas outlet shown in Figure 1c), the same OH⁻ generation rate via cathodic reactions means that the capability of capturing CO₂ for carbonate formation at the cathode/electrolyte interface using CEM and BPM should be similar to that of AEM. Thus, for a CEM and BPM, substantial additional carbonate anions produced in the reaction of CO₂ and OH⁻ generated via the cathodic reactions must be balanced with extra cation species (total anion charge equals to total cation charge) or emitted from
electrolyte as gaseous CO\(_2\). To uncover the role of different membrane types in the carbon balance for flow electrolyzers, gases released from the electrolyte were detected for CEM and BPM, respectively (using a closed-cycle anolyte with a vent for gases shown in Figure S5).

Theoretically, the composition ratio of CO\(_2\)/O\(_2\) in the gas stream from the anolyte will be 4, 2 or 0 if the only anion species for neutralizing H\(^+\) generated on the anode is HCO\(_3\)^\(-\), CO\(_3\)^\(2-\) or OH\(^-\).\(^{28,29}\) In addition, under the consideration of that HCO\(_3\)^\(-\), CO\(_3\)^\(2-\) or OH\(^-\) is the only anion species of neutralization reaction with H\(^+\), the theoretically calculated CO\(_2\) flowrate will be 6.0, 3.0 or 0 ml/min at 200 mA/cm\(^2\) with the geometric active area of 2 cm\(^2\) (Table S2).

Figure 3. Comparison of flow of CO\(_2\) and O\(_2\) released from anolyte (left axis), and corresponding ratio of CO\(_2\) to O\(_2\) (right axis) when using AEM (a), CEM (b) and BPM (c) over the course of CO\(_2\) reduction electrolysis at 200 mA/cm\(^2\). Variation in related electrolyte pH during of CO\(_2\) reduction electrolysis for AEM (d), CEM (e) and BPM (f), respectively. In all the experiments, 1 M KHCO\(_3\) was used as initial catholyte (50 ml) and anolyte (50 ml). Figure (a) and (d) for AEM were adapted based on reference 29.
Scheme 1. Proposed carbon balance paths via CO$_2$ capture at cathode/catholyte interface and CO$_2$ evolution from anolyte or catholyte in flow electrolyzers combined with AEM (a), CEM (b) and BPM (c), respectively, while using KHCO$_3$ as initial catholyte and anolyte. Red dash line with arrows indicate the possible charge-carrying ionic species for membranes. Carbon balance paths for AEM was adapted from ref 29.

Figure 3a-c shows the comparison of gases released in the anolyte over electrolysis for all the different ion-selective membranes. When an AEM was used, the CO$_2$/O$_2$ ratio decreased from ~3 to ~2 in the initial 4 h and then maintained at ~2 over the rest of electrolysis. This observation is due to that the CO$_2$ evolution via the H$^+$ neutralization reaction changed rapidly from a mixture of HCO$_3^-$ and CO$_3^{2-}$ to nearly pure CO$_3^{2-}$ using an AEM (Figure 3a). In contrast, as noted in Figure 3b, the CEM experienced a consistent CO$_2$/O$_2$ ratio of ~4 and a constant CO$_2$ flowrate with 6 ml/min for the duration of electrolysis at 200 mA/cm$^2$, which implies that the CO$_2$ formation was always derived from HCO$_3^-$ in the anolyte. This finding is ascribed to that the CO$_3^{2-}$ formed via CO$_2$ capture in the catholyte cannot transport to the anolyte via the CEM since the function groups (typically SO$_3^-$ groups) only allows cation species (such as K$^+$) to transport through (Scheme 1b). It should be noted that the CO$_2$ reduction electrolysis via CEM was tested for just ~3 h, since that the anolyte conductivity rapidly decreased from ~70 mS/cm to ~3 mS/cm after ~3 h using the CEM (Figure S8b). All the above results with the CEM entail that almost no anionic species transported to the anolyte via the membrane, but cation species such as K$^+$ served as the main charge carrier via the CEM. Thus, the concentration of KHCO$_3$ in the anolyte was significantly reduced over time as K$^+$
constantly transported to the catholyte and the remaining HCO$_3^-$ in the anolyte was consumed for CO$_2$ evolution (Scheme 1b).

A bipolar membrane is comprised of a cation exchange layer (CEL) and an anion exchange layer (AEL) as well as a catalyst layer that is sandwiched between CEL and AEL. The catalyst layer in a BPM dissociates water (fed from both the catholyte and anolyte) into H$^+$ and OH$^-$, which subsequently transports to the catholyte and anolyte via the CEL and AEL, respectively (Scheme 1c).$^{39}$ Under operation of a BPM (Figure 3c), the flowrate of CO$_2$ released from the anolyte rapidly decreased from 1.4 ml/min to 0.5 ml/min in the initial 4 h, corresponding to a decline in the CO$_2$/O$_2$ ratio from $\sim$1 to $\sim$0.3. This observation indicates that OH$^-$ served as the major anion species that neutralizes with H$^+$ produced as a byproduct of O$_2$ evolution. In addition, the almost constant conductivity in both catholyte and anolyte over the 10 h electrolysis (Figure S7c) may imply that neither anionic species (CO$_3^{2-}$ or HCO$_3^-$) nor cationic species (K$^+$) had any apparent crossover. This result reveals that the additional anion species (CO$_3^{2-}$ or HCO$_3^-$) generated by CO$_2$ capture could not be accumulated in the catholyte during CO$_2$ reduction electrolysis due to charge balance issue (the total anion charge must equal to the total cation charge). Thus, the additional CO$_3^{2-}$ or HCO$_3^-$ should be emitted from the catholyte as gaseous CO$_2$. As expected, gas bubbles released from the catholyte were observed when a BPM was used (no gas evolution was observed in the catholyte using AEM or CEM), and this gas evolution immediately disappeared after stopping the electrolysis.

To verify that CO$_2$ was generated in the catholyte, the gases released from the catholyte during the CO$_2$ reduction electrolysis were analyzed by a setup shown in Figure 4a. Figure 4b shows CO$_2$ degassing from the catholyte when using a BPM, owing to the neutralization reaction of CO$_3^{2-}$ or HCO$_3^-$ with H$^+$ near the CEL of BPM (Scheme 1c), which is in line with previous BPM work.$^{36}$ In addition, the related flowrate of CO$_2$ released from the catholyte slightly decreased from $\sim$ 3.5
ml/min to ~ 2.6 ml/min, and was maintained at ~ 2.6 ml/min over the electrolysis experiment (Figure 4b). This observation can be attributed to that the carbon source (anion species) for CO2 evolution abruptly transformed from a mixture of HCO3− and CO32− to almost pure CO32−. In addition, a fraction of CO2 released from catholyte chamber can transport back to the cathode surface to be reused for both CO2 reduction36 and the buffering reaction with OH− at the cathode/electrolyte interface. This back-diffusion effect leads to the slightly lower CO2 flow (~ 2.6 ml/min) compared to theoretical value (3.0 ml/min). Furthermore, with nearly identical catalytic selectivity (Figure 2c) and the same OH− generation rate on the cathode (due to the same current density) among all the different membranes, the utilization of a fraction of CO2 released from a catholyte with a BPM results in a slightly lower CO2 consumption rate in the gas chamber. This result is in line with the slightly higher gas outlet flowrate for BPM in comparison with those of AEM and CEM (Figure 1c).

Figure 4. (a) Schematic illustration of the flow cell setup for detecting gases released from the catholyte over the course of CO2 reduction under the use of BPM (a constant N2 flowrate was used as a carrier gas). (b) Flowrate of CO2 released from catholyte under the use of BPM for CO2 reduction at 200 mA/cm2 with negligible amount of H2. 1 M KHCO3 was used as an initial catholyte (50 ml) and anolyte (50 ml).
While each type of ion-selective membrane had a different CO\textsubscript{2} flowrate released from the anolyte, O\textsubscript{2} was detected with a constant flowrate of \(~1.5\) ml/min during the electrolysis irrespective of membrane type (Figure 3a-c). This finding is consistent with the theoretical value of the O\textsubscript{2} flowrate (1.5 ml/min shown in Table S2) at 200 mA/cm\textsuperscript{2} for the geometric active area of 2 cm\textsuperscript{2}.

To further understand the transformation of anionic species in the electrolyte, the pH of the electrolyte was also monitored over the course of the electrolysis for all the membranes. Figure 3e shows that for a CEM the catholyte pH was enhanced from 8.3 to nearly 9.8 after \(~3\) h. The catholyte pH with the AEM increased to 10.2 after \(~3\) h under identical conditions. Thus, the similar increasing trend in catholyte pH between the AEM and CEM over 3 h further confirms that the captured CO\textsubscript{2} at the cathode/electrolyte interface (via reaction with OH\textsuperscript{−}) mainly formed CO\textsubscript{3}\textsuperscript{2−} using the CEM\textsuperscript{,29} leading to CO\textsubscript{3}\textsuperscript{2−} acting as the dominant anion species in the catholyte after 3h. The catholyte pH with the BPM was maintained below 9 over the entire electrolysis experiment (Figure 3f) due to that a constant supply rate of H\textsuperscript{+} from water dissociation in the BPM enables carbonate and bicarbonate concentrations in the catholyte to reach a steady state. However, the observed CO\textsubscript{2} flowrate (2.6 ml/min) from catholyte (after reaching steady state) also reveal that CO\textsubscript{2} was captured and converted to CO\textsubscript{3}\textsuperscript{2−} at the cathode/electrolyte interface, and then combined with the aforementioned H\textsuperscript{+} at the BPM/ catholyte interface to release CO\textsubscript{2}. In addition, it should be noted that the theoretical calculations have shown that the pH near the cathode is \(~13\) in 1 M KHCO\textsubscript{3} at 200 mA/cm\textsuperscript{2}\textsuperscript{,18} which means that the reaction of CO\textsubscript{2} with OH\textsuperscript{−} at the cathode/electrolyte interface forms CO\textsubscript{3}\textsuperscript{2−} instead of HCO\textsubscript{3}− (equation S8 and S9). Thus, all these results reveal that the captured CO\textsubscript{2} by electrolyte near the cathode formed CO\textsubscript{3}\textsuperscript{2−} irrespective of membrane types.

We found that the anolyte quickly reached a near neutral pH for both the AEM and the CEM during the electrolysis (Figure 3d and e), which allows for CO\textsubscript{2} degassing in the anolyte.
Specifically, the anolyte pH with the AEM was maintained at ~7.9 after 20 min (Figure 3d), owing to that the constant H\(^+\) generation rate near the anode and continuous carbonate supply derived from the catholyte created a steady state for all the anion species in the anolyte via the neutralization reactions (Scheme 1a). In contrast, with the CEM, the anolyte pH rapidly deceased from 8.3 to 6.7 over 3 h (Figure 3e). This finding is due to that the CO\(_2\) degassing with the continuous consumption of KHCO\(_3\) in the anolyte created a CO\(_2\)-saturated KHCO\(_3\) anolyte and its concentration gradually reduced over time (pH of CO\(_2\)-saturated 0.1 M KHCO\(_3\) is ~6.8). Interestingly, a slow increase in the anolyte pH from 8.3 to 9.6 was observed over 10 h electrolysis under the use of the BPM, as shown in Figure 3f. This observation may be linked to a slow variation in the anionic species concentrations (here, more CO\(_3^{2-}\) was likely created along with less existing HCO\(_3^-\)) in the anolyte during the electrolysis. This alteration in anionic species concentrations is ascribed to that when OH\(^-\) is transported toward the anode as the major anion species being neutralized with H\(^+\) generated near the anode, a fraction of OH\(^-\) may also react with the existing HCO\(_3^-\) in the anolyte to form CO\(_3^{2-}\).

**Carbon balance via different types of membranes**

For high-rate CO\(_2\) reduction in flow electrolyzers, the carbon source for CO\(_2\) fed from the inlet of reactor must be balanced with that of all CO\(_2\) reduction products, captured CO\(_2\) by electrolyte (carbonate formation) and residual CO\(_2\) out of reactor (i.e. unreacted CO\(_2\)). As noted in Figure 5a, (i) the residual unreacted CO\(_2\) flowrate out of the reactor, (ii) the consumed CO\(_2\) flowrate for carbonate formation via the reaction with OH\(^-\) (i.e. captured CO\(_2\) throughout the electrolyte) and (iii) the consumed CO\(_2\) flowrate that was converted into all the gaseous and liquid products add up to a total CO\(_2\) flow of ~ 45 ml/min for each type of the ion-selective membrane. Thus, the carbon
element during the electrolysis is balanced with that of CO$_2$ inlet flowrate (45 ml/min) in this work. In addition, Figure 5b shows the nearly identical CO$_2$ consumption rate for the formation of gaseous and liquid products using different ion-selective membranes, which is in line with the roughly same catalytic selectivity shown in Figure 2b.

It should be noted that there should be nearly the same carbonate formation rate (via CO$_2$ reaction with OH$^-$) near the cathode among all the different membranes due to the identical OH$^-$ generation rate via cathodic reactions at identical current densities. While membrane types should have minimal effect in the total carbonate formation rate near the cathode, the BPM had a slightly lower consumption rate of CO$_2$ from the gas chamber for carbonate formation compared to those of the AEM and CEM, as shown in Figure 5b. This finding is correlated with the discrepancy in carbon balance paths among the three different types of membranes. In other words, while the unavoidable CO$_2$ capture near the cathode forms carbonate in the catholyte, the end results of where the carbonate goes is different in each type of membrane. For the CEM, the captured CO$_2$ was accumulated in the form of carbonate in the catholyte without emission. In contrast, under the use of the AEM, the captured CO$_2$ in the form of carbonate crossed to the anolyte and was emitted as gaseous CO$_2$ with O$_2$ stream in the anolyte. Notably, with the BPM, the captured CO$_2$ could be released from the catholyte as gaseous CO$_2$. Thus, a fraction of the generated CO$_2$ in the catholyte may be involved in the reaction with OH$^-$ for carbonate formation, which corresponds to a relatively low consumption rate of CO$_2$ in the gas chamber for carbonate formation (~65% of total CO$_2$ consumption), as shown in Figure 5b. In addition, the reuse of a fraction of the released CO$_2$ in the catholyte, derived from the captured CO$_2$ in the form of carbonate, also results in a slightly higher CO$_2$ utilization rate of the BPM (ratio of CO$_2$ converted into products versus total CO$_2$ consumption) in Figure 5b.
Figure 5. (a) Carbon balance for high-rate CO₂ reduction in 1 M KHCO₃ using different membranes. The unreacted (i.e., residual) CO₂ flowrate as well as the total consumed CO₂ flowrate for carbonate formation and CO₂ reduction to all liquid and gas products were considered. (b) Ratio of CO₂ converted into products to total CO₂ consumption (right axis).

Implications of the CO₂ degassing

From an economic and environmental perspective, the released CO₂ from the electrolyte in flow electrolyzers would require to be captured and recycled. Under the use of the AEM, the released CO₂ in the anolyte only can be recycled for CO₂ reduction after removing O₂ in the gas mixture (mole ratio of CO₂/O₂ is 2:1). Interestingly, the operation of the BPM could degas CO₂ from the catholyte, which can be directly fed into the gas compartment for CO₂ conversion due to its high purity (~100% CO₂ by mole). Thus, compared to the necessary CO₂ and O₂ separation process for CO₂ recycling with the AEM, the BPM has the potential to reduce the total cost of carbon source. However, it should be noted that using BPM at high-rate CO₂ reduction (current densities > 100 mA/cm²) requires an additional potential (> ~0.8 V) for membranes that may reduce the energy efficiency of CO₂ conversion reactors.\(^{39-41}\) Thereby, how to balance the energy efficiency along with the easy recyclability of the produced CO₂ in the catholyte (from inevitably captured CO₂) under the use of BPMs will need a full techno-economic analysis in the future.
CONCLUSION

In conclusion, our results present that the role of ion-selective membranes is minimal in affecting the catalytic selectivity of high-rate CO₂ reduction, owing to the nearly same local reaction environment created near the catalysts through having a catholyte layer. By rigorously analyzing gases released from electrolytes as well as monitoring electrolyte pH, we found that most of the consumed CO₂ source (≥ ~65%) was captured via reaction with OH⁻ near the cathode to form formed CO₃²⁻, which is almost independent of membrane types.

Importantly, each type of ion-selective membrane produces a unique carbon balance path for the captured CO₂ source. Specifically, the captured CO₂ in the form of CO₃²⁻ could cross an AEM from the catholyte to the anolyte and then emitted as gaseous CO₂ mixed with O₂ stream. In contrast, the captured CO₂ could not transport to the anolyte when using a CEM or BPM. With a CEM, captured CO₂ in the form of carbonate continuously accumulated in the catholyte, since there was no concomitant H⁺ supply for CO₂ evolution (mainly K⁺ crossed the membrane). With the bipolar membrane, the captured CO₂ was released from the catholyte as gaseous CO₂, owing to the reaction of carbonate with H⁺ transported from its cation exchange layer. In addition, while for an AEM CO₂ was emitted together with O₂, for a BPM the pure CO₂ was released, which can be directly recycled back to the gas compartment for CO₂ conversion, correspondingly decreasing the cost of the CO₂ source. This study shows that while the catalytic selectivity is independent of the types of ion-selective membranes, membrane types play an important role in the corresponding carbon balance path at high-rate CO₂ reduction, thus future work should focus on the membrane exploration for achieving the practical utilization of high-rate CO₂ reduction.
EXPERIMENTAL PROCEDURES

Materials
Potassium bicarbonate (≥99.95%) purchased from Sigma Aldrich was used in this study without further purification. Anion exchange membrane (AEM, Fumasep FAA-3-PK-75), cation exchange membrane (Nafion™ 212), bipolar membrane (BPM, Fumasep FBM) and gas-diffusion electrode (GDE, Sigracet 39 BC) were purchased from Fuel Cell Store. Iridium dioxide (IrO₂) purchased from Dioxide Materials was used as an anode in flow electrolyzers of high-rate CO₂ reduction.

Catalysts preparation
For obtaining high purity Cu catalysts, Cu layers were prepared on top of microporous layer of gas-diffusion electrodes by direct current magnetron sputtering (50 W) from a Cu target at an argon pressure of 2 mTorr. Figure 1S shows a typical schematic illustration for Cu deposition using magnetron sputtering under an argon ambient. The energetic Ar⁺ ions are created in a glow discharge plasma, thus Ar⁺ bombardment occurs on the cathode Cu target, which leads to the removal of Cu atoms. Subsequently, the sputtered Cu atoms condense on a substrate (i.e. GDE) to form a Cu layer. In this work, with ~4 nm/min Cu deposition rate, the thickness of the Cu layers were controlled by the deposition time.

Gas and liquid product analysis
Gas products mixing with unreacted CO₂ flowed out of the electrolyzers, directly injecting into the gas-sampling loop of a gas chromatography (PerkinElmer, Clarus® 590). Ar was used as a carrier gas with a constant flowrate of 10 sccm. The gas chromatography was equipped with a packed Molecular sieve 13x column and a packed Hayesepp Q column to separate the gas products. Thus, exiting the columns, H₂, CO, CH₄ and C₂H₄ could be
identified at different reaction times using a thermal conductivity detector. In addition, the peak area of each gas product was compared to standards (calibration gases) to determine the corresponding concentration of gaseous products. Thus, we can get the faradaic efficiency of a certain gas product as follows:

\[ FE (\%) = \frac{n \times C_{gas \_product} \times \varnothing \times t \times P_o \times F}{I \times t} \times 100\% \]

where \( n \) is the number of electrons required for producing one molecule of the related gas product, and \( C_{product} \) is the concentration of gas product measured by GC. \( \varnothing \) and \( t \) is the gas flowrate out of the electrolyzers and the electrolysis time, respectively. \( P_o \) is the ambient pressure, \( R \) is the ideal gas constant, \( T \) is the absolute temperature, \( F \) is Faraday constant, and \( I \) is the applied current.

The liquid-phase products are analyzed after the electrolysis using a high performance liquid chromatography (HPLC, Agilent 1200 series). Liquid-phase products were separated by an Aminex HPX-87H column (Bio-Rad) that was maintained at 50 °C for the duration of the detection. The HPLC was equipped with a diode array detector (DAD) and a refractive index detector (RID), and the signal response of the DAD and RID was calibrated by known concentration solutions. Thus, we can get the concentration of the detected liquid-phase product. The faradaic efficiency of liquid products can be calculated by equation:

\[ FE (\%) = \frac{n \times C_{liquid \_product} \times V \times F}{I \times t} \times 100\% \]

where \( n \) is the number of electrons required for producing one molecule of the related liquid product, and \( C_{product} \) is the molar concentration of gas product measured by HPLC. \( V \) is the volume of the electrolyte. To obtain accurate selectivity of liquid products, we measured the volume of catholyte and anolyte after electrolysis, respectively.

**Electrolyte pH and conductivity measurements**
pH of the catholyte and the anolyte was monitored by a pH meter (pH 110, VWR) during the electrolysis. In addition, the pH meter was also equipped with a temperature sensor for the temperature-compensation. The pH meter was calibrated by a standard pH 7 buffer and a standard pH 10 buffer before the measurement.

The conductivity of the catholyte and the anolyte was monitored by a conductivity meter (PCE-PHD 1-PH, PCE Instruments) during CO2 reduction electrolysis. Before the measurement, the conductivity meter was calibrated via conductivity standard of 1413 µS / cm (25 °C; 0.01 M KCl) and 111.8 mS / cm (25 °C; 1 M KCl) purchased from VWR. It should be noted that both of the calibration and the measurement were temperature-compensated due to that the solution conductivity is also temperature-dependent at a fixed solution concentration.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online.

ACKNOWLEDGEMENTS
This work was supported by the Villum Foundation V-SUSTAIN grant 9455 to the Villum Center for the Science of Sustainable Fuels and Chemicals. This work was also supported by ECOEthylene project from the Innovation Fund Denmark (Grant# 8057-00018B), SELECTCO2 project from Horizon 2020 of EU (Grant# 851441) and National Research Foundation of Korea (NRF-2019R1A2C2002156). The authors would like to thank Dr. Ezra L. Clark for technical support in the HPLC.

AUTHOR CONTRIBUTIONS
M.M and B.S developed the conceptual idea, designed the experiments and wrote the original manuscript. S. K carried out a part of the electrolyte pH and conductivity measurement. All authors contributed to discussing the results and editing the manuscript.

DECLARATION OF INTERESTS

There are no conflicts to declare.

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Role of Ion-Selective Membranes in the Carbon Balance for CO$_2$ Electroreduction via Gas Diffusion Electrode Reactor Designs

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Catalysts preparation by magnetron sputtering

Figure S1. Schematic illustration of magnetron sputtering for Cu deposition from a Cu target.

**High local pH near the cathode**

During the process of electrochemical reduction of CO$_2$, CO$_2$ and H$_2$O can be electrochemically converted into a variety of gaseous products such as CO, C$_2$H$_4$ and CH$_4$ on the surface of the catalyst in electrolytes based on the below reactions$^{1-4}$:

\[
\text{CO}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{CO} + 2\text{OH}^- \quad (-0.11 \text{ V vs. RHE}) \quad (S1)
\]

\[
\text{CO}_2 + 6\text{H}_2\text{O} + 8e^- \rightarrow \text{CH}_4 + 8\text{OH}^- \quad (0.17 \text{ V vs. RHE}) \quad (S2)
\]

\[
2\text{CO}_2 + 8\text{H}_2\text{O} + 12e^- \rightarrow \text{C}_2\text{H}_4 + 12\text{OH}^- \quad (0.08 \text{ V vs. RHE}) \quad (S3)
\]

In addition to gaseous products, liquid such as ethanol, formate and acetate also can be produced on the surface of the catalyst in aqueous solutions, as follows:

\[
\text{CO}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{HCOO}^- + \text{OH}^- \quad (-0.03 \text{ V vs. RHE}) \quad (S4)
\]

\[
2\text{CO}_2 + 5\text{H}_2\text{O} + 8e^- \rightarrow \text{CH}_3\text{COO}^- + 7\text{OH}^- \quad (-0.26 \text{ V vs. RHE}) \quad (S5)
\]

\[
2\text{CO}_2 + 9\text{H}_2\text{O} + 12e^- \rightarrow \text{C}_2\text{H}_5\text{OH} + 12\text{OH}^- \quad (0.09 \text{ V vs. RHE}) \quad (S6)
\]
In the electrocatalytic CO\textsubscript{2} reduction process, the competing H\textsubscript{2} evolution is an unavoidable reaction. The electroreduction of H\textsubscript{2}O to H\textsubscript{2} on the surface of catalyst according to the reaction\textsuperscript{1}:

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \] (0 V vs. RHE) \hspace{1cm} (S7)

Due to the above cathodic reactions (Equation (3-9), a large amount of OH\textsuperscript{-} ions can be created at the cathode/electrolyte interface at high current densities, which creates a significantly higher pH near the surface of cathode compared to that of the bulk solutions\textsuperscript{2,3}

**CO\textsubscript{2} capture via high local pH**

During CO\textsubscript{2} reduction in flow electrolysers using 1 M KHCO\textsubscript{3}, CO\textsubscript{2} from the gas chamber of the electrolysers reacts with OH\textsuperscript{-} ions produced at the cathode/electrolyte interface according to the below reactions of CO\textsubscript{2} and OH\textsuperscript{-}:

\[ OH^- + CO_2 \leftrightarrow HCO_3^- \] (pKa=7.8*) \hspace{1cm} (S8)

\[ OH^- + HCO_3^- \leftrightarrow CO_3^{2-} + H_2O \] (pKa=10.3) \hspace{1cm} (S9)

* This is at a CO\textsubscript{2} partial pressure of 1 bar in 1 M HCO\textsubscript{3}\textsuperscript{−}.

**CO\textsubscript{2} reduction performance**

The electrocatalytic reduction of CO\textsubscript{2} was performed in a three-chamber flow electrolyzer made from Teflon at ambient temperature and pressure. At the reactor, an ion-selective membrane was used to separate catholyte and anolyte flow compartments. Catholyte and anolyte bottles were filled with 50 ml 1 M KHCO\textsubscript{3}, respectively (Figure S2). In addition, a fixed geometric surface area (2 cm\textsuperscript{2}) of Cu layer was used for all the tests in this study.

CO\textsubscript{2} was purged into gas compartment at a constant flowrate of 45 ml/min, and then a fraction of gaseous CO\textsubscript{2} diffuses to the surface of the catalyst in electrolyte for CO\textsubscript{2} conversion. In addition, CO\textsubscript{2} also can be captured to form carbonate (equation S8 and S9) via the reaction of CO\textsubscript{2} with OH\textsuperscript{-} generated at the cathode/electrolyte interface.\textsuperscript{5} Thus, the high CO\textsubscript{2} conversion rate to gas (C\textsubscript{2}) and liquid products as well as high local pH can lead to a substantial CO\textsubscript{2} consumption at high current densities, correspondingly varying the gas flow (gas mixture) out of the reactor. The volumetric flowrate of gas outlet (gas mixture) after reactor was monitored.
by flow meter in \( \text{CO}_2 \) reduction (Figure S2), and then faradaic efficiencies of gas products were evaluated under the consideration of gas flow variation between inlet and outlet. It should be noted that the average catalytic selectivity of gas products during 2.5 h \( \text{CO}_2 \) reduction electrolysis was used in this work.

![Figure S2](image)

**Figure S2.** Schematic illustration of flow cell setup for electrocatalytic \( \text{CO}_2 \) reduction.

**Collection of liquid from electrolyte**

It should be noted that the ion species carried with water molecules (hydrated ion) transports via membrane, which means the volume of catholyte and anolyte was varied after electrolysis. For AEM, a decrease in catholyte volume was observed with increased anolyte volume after several hours of \( \text{CO}_2 \) reduction electrolysis, because of the transport of the anion species hydrated with water molecules from catholyte to anolyte via AEM as charge carriers. In contrast, the use of CEM experienced an increased catholyte volume with correspondingly decreased anolyte over the course of electrolysis, due to that the cation species hydrated water molecules transported from anolyte to catholyte via AEM as charge carriers. Notably, no obvious variation in both catholyte and anolyte when BPM was used, which is due to that water supplied almost equally from both catholyte and anolyte was disociated into \( \text{H}^+ \) and \( \text{OH}^- \), transporting to catholyte and anolyte, respectively.
Based on the aforementioned discussion, in order to obtain accurate selectivity of liquid products, volume of catholyte and anolyte was also measured for each test after electrolysis, respectively.

**Collection of liquid products evaporated from GDEs**

Some liquid products can be evaporated from the gas diffusion layer of GDE and then flow out of the gas compartment of the reactor with unreacted CO$_2$ and gas products. To collect the evaporated liquid products from GDEs (i.e. gas chamber), gas outlet flow after the reactor was directly purged into a sealed bottle filled with 30 ml de-ionized water (the outlet flow tube was immersed into de-ionized water), as shown in Figure S3. After completion of CO$_2$ reduction, the liquid products diluted with de-ionized water in that sealed bottle were analysed via high-performance liquid chromatography (HPLC). Figure 2b presents the faradaic efficiencies of liquid products evaporated from GDEs when using distinct ion-selective membranes, indicating that only alcohols products such as ethanol and propanol evaporate and escape from the cathode/electrolyte interface irrespective of membrane types, which is due to their high volatility.

In addition, both catholyte and anolyte in the given reservoirs were collected for quantification of liquid products, owing to liquid products crossover from catholyte to anolyte via membranes.$^5$ Thus, the total amount of one certain liquid product formed on cathode GEDs can be written as:

$$N_{\text{total liquid}} = N_{\text{liquid in anolyte}} + N_{\text{liquid in catholyte}} + N_{\text{evaporated liquid}}$$  \hspace{1cm} (S10)

where $N_{\text{liquid in anolyte}}$ and $N_{\text{liquid in catholyte}}$ are the amount of one certain liquid product detected in anolyte and catholyte, respectively. $N_{\text{evaporated liquid}}$ is the amount of one certain liquid product evaporated from GEDs. Here, the evaporation ratio of one certain liquid product formed on cathode GEDs can be calculated based on the below equation:

$$\text{Evaporation ratio (\%)} = \frac{N_{\text{evaporated liquid}}}{N_{\text{total liquid}}} \times 100\%$$  \hspace{1cm} (S11)

Thus, the equation (S11) was used to calculate a ratio between the amount of one certain liquid product evaporated from GDEs and the total amount of corresponding liquid product formed on the cathode, as shown in Figure S4.
Figure S3. The schematic illustration of flow cell setup for collecting liquid products evaporated from GDEs during CO$_2$ reduction.

Figure S4. Evaporation ratio of related liquid products escaped from GDEs (i.e. gas chamber) at 200 mA/cm$^2$ when using AEM, CEM and BPM, respectively.
Analysis of gas released from the anolyte

When the electrocatalytic CO₂ reduction occurs on the surface of the cathode, water oxidation reaction (i.e. O₂ evolution) takes place on the anode surface. By the water oxidation reaction, a large amount of H⁺ can be created at the anode/electrolyte interface, which leads to a decrease of pH locally near the anode. Subsequently, H⁺ produced at the anode/electrolyte interface can be neutralized with HCO₃⁻, CO₃²⁻ or OH⁻ in anolyte. The H⁺ neutralization with HCO₃⁻ or CO₃²⁻ forms CO₂, leading to CO₂ degassing from anolyte with the stream of O₂. For analysing the gases released from anolyte over the course of CO₂ reduction, the flow electrolyser setup in Figure S5 was utilized. In that setup, N₂ at a constant flowrate was used as a carrier, thus gases released from anolyte were diluted with N₂, directly venting into the gas sampling-loop of the GC for periodical quantification. The volumetric gas flow released from anolyte was also monitored by in situ flow meter over the electrolysis, as shown in Figure S5.

Figure S5. The schematic illustration of flow cell setup for detection of gases released from the anolyte over the course of CO₂ reduction.
Analysis of gas released from the catholyte using BPMs

No any gas evolution in catholyte was observed when AEM or CEM was used. However, under the use of bipolar membrane in flow electrolyzers, we found that gas bubbles released from the catholyte, which is unique in comparison with the other two membranes. To analyze the gas released from catholyte over the course of CO$_2$ reduction using BPM, a test setup in Figure S6 was utilized. Similar to gas analysis from anolyte, a constant N$_2$ flow was also used as a carrier gas, which mixed with gases released from catholyte, venting into the gas sampling-loop of the GC for periodical quantification, followed with an in situ volumetric flow meter (Figure S6). We found CO$_2$ gas release from the catholyte, along with only trace amount of H$_2$ in Figure 4. It should be noted that the mole ratio of CO$_2$/H$_2$ released from the catholyte is 5000, which means that the purity of released CO$_2$ is about 99.98%.

Figure S6. The schematic illustration of flow cell setup for detection of gases released from the catholyte over the course of CO$_2$ reduction under the use of BPM. 1 M KHCO$_3$ was used as initial catholyte (50 ml) and anolyte (50 ml).
**Applied potentials on the cathode**

Potentiostatic electrochemical impedance spectroscopy (PEIS) was conducted on Cu deposited GDE in the flow electrolyzer to determine the solution resistance (Rs). A detailed procedure was described in a previous work.\(^5\) It should be noted that the distance between reference and cathode was less than 2 mm in order to reduce Rs in this work. Table S1 shows the solution resistance for the different ion-selective membranes. However, the cathodic reactions at high current densities can lead to a significant change of ion species and related concentration in the vicinity of the cathode, which indicates a difference in solution resistance near the cathode at high current densities compared to that of PEIS which was performed at relative low current densities. Thus, this difference in the solution resistance is closely correlated with the accuracy in IR-corrected potentials at a high current.

![Figure S7. Applied potentials under the use of the different ion-selective membranes in 1 M KHCO\(_3\) aqueous solutions. (The potentials were not iR-corrected).](image)

| Membrane type | Rs (Ω) | Corrected V vs. SHE |
|---------------|--------|---------------------|
| AEM           | 1.375  | -1.63               |
| CEM           | 1.25   | -1.60               |
| BPM           | 1.38   | -1.50               |

**Table S1.** IR-corrected potentials for CO\(_2\) reduction at 200 mA/cm\(^2\) in 1 M KHCO\(_3\) under the use of the different ion-selective membranes.
Theoretical estimation of \( \text{O}_2 \) and \( \text{CO}_2 \) flowrate generated from electrolyte

Assuming that all charge passed through the anode is just employed for oxidation of water into \( \text{O}_2 \), thus theoretical \( \text{O}_2 \) flowrate released from anolyte can be expressed as:

\[
\Phi (\text{O}_2) = \frac{Q_{\text{tot}}}{nF} \times \frac{RT}{P_o}
\]  

(S12)

where \( n \) and \( Q_{\text{tot}} \) are the number (here is 4) of electrons lost from 2 \( \text{H}_2\text{O} \) for forming one \( \text{O}_2 \) molecule and total charge passed through the anode, respectively. \( F \) is the faradaic constant, \( R \) is ideal gas constant, \( T \) is absolute temperature, and \( P_o \) is ambient pressure.

From our previous work, the ratio of \( \text{CO}_2 \) and \( \text{O}_2 \) released from the anolyte will be 4, 2 and 0 if the only anion species for neutralization reaction with \( \text{H}^+ \) is \( \text{HCO}_3^- \), \( \text{CO}_3^{2-} \) or \( \text{OH}^- \). Thus, after getting the \( \text{O}_2 \) flowrate at 200 mA/cm\(^2\) (the cathode with 2 cm\(^2\) geometric active area was used for all the tests) based on equation S12, we can easily get the related flow of \( \text{CO}_2 \), as shown in Table S1.

**Table S2.** The theoretically calculated flowrates of \( \text{O}_2 \) and \( \text{CO}_2 \) released from electrolyte if the only anion species for neutralization reaction with \( \text{H}^+ \) is \( \text{HCO}_3^- \), \( \text{CO}_3^{2-} \) or \( \text{OH}^- \) at 200 mA/cm\(^2\).  

| Anion species for neutralization with \( \text{H}^+ \) | \( \text{CO}_2 \) flow (ml/min) | \( \text{O}_2 \) flow (ml/min) |
|-----------------------------------------------|-------------------------------|-----------------------------|
| \( \text{HCO}_3^- \)                        | 5.970                         | 1.492                       |
| \( \text{CO}_3^{2-} \)                      | 2.985                         | 1.492                       |
| \( \text{OH}^- \)                          | 0                             | 1.492                       |
Electrolyte conductivity

Figure S8. Conductivity of catholyte and anolyte as a function of time when using AEM (a), CEM (b) and BPM (c) over the course of CO₂ reduction electrolysis at 200 mA/cm². 1 M KHCO₃ was used for both catholyte (50 ml) and anolyte (50 ml).
Calculation of the carbon balance

The residual unreacted CO$_2$ flowrate in the gas outlet (gas mixture) out of gas compartment of flow electrolyzers can be written as:

$$\phi_{\text{residual CO}_2} = \phi_{\text{outlet}} - (\phi_{\text{CO}} + \phi_{\text{CH}_4} + \phi_{\text{C}_2\text{H}_4} + \phi_{\text{H}_2}) \quad (S13)$$

where $\phi_{\text{outlet}}$ is the monitored gas flowrate out of the reactor during CO$_2$ reduction electrolysis using the setup shown in Figure 2S. Here, $\phi_{\text{CO}}$, $\phi_{\text{CH}_4}$, $\phi_{\text{C}_2\text{H}_4}$ and $\phi_{\text{H}_2}$ are the gas flowrate of CO, CH$_4$, C$_2$H$_4$ and H$_2$ produced from electrochemical CO$_2$ conversion in the gas outlet, respectively. Based on the equation S1-3, each molecule of CO, CH$_4$ and C$_2$H$_4$ formation requires 1, 1 and 2 CO$_2$ molecule. Thus, the consumed CO$_2$ flowrate that is converted into all gas products (CO, C$_2$H$_4$ and CH$_4$) in CO$_2$ reduction can be expressed as below:

$$\phi_{\text{CO}_2 \to \text{gas}} = \phi_{\text{CO}} + \phi_{\text{CH}_4} + 2\phi_{\text{C}_2\text{H}_4} \quad (S14)$$

Depending on the number of carbon atoms in liquid molecule produced in CO$_2$ reduction, the consumed CO$_2$ flowrate involved in all liquid products formation can be written as:

$$\phi_{\text{CO}_2 \to \text{liquid}} = \phi_{C_1} + \phi_{C_2} + \phi_{C_3} \quad (S15)$$

where $\phi_{C_1}$, $\phi_{C_2}$, and $\phi_{C_3}$ are the consumed CO$_2$ flowrate for forming C$_1$, C$_2$ and C$_3$ liquid products, respectively. For high-rate CO$_2$ reduction, the inevitably captured CO$_2$ in forms of carbonate via reaction with OH$^-$ could consume substantial CO$_2$ flow, significantly reducing the total gas flow out of the reactor (Figure 1c). It is known that the carbon element from CO$_2$ inlet flowrate should be eventually balanced with those of residual unreacted CO$_2$, all products and carbonate formed via reaction between OH$^-$ and CO$_2$. Thus, the consumed CO$_2$ flowrate via the reaction with OH$^-$ generated on the cathode surface can be expressed as:

$$\phi_{\text{OH}^-} = \phi_{\text{inlet CO}_2} - (\phi_{\text{residual CO}_2} + \phi_{\text{CO}_2 \to \text{gas}} + \phi_{\text{CO}_2 \to \text{liquid}}) \quad (S16)$$

where $\phi_{\text{inlet CO}_2}$ is CO$_2$ flowrate fed into the gas chamber of the reactor. In this work, a constant CO$_2$ flow was used. It should be noted that mass flow controller used in this work was calibrated for CO$_2$ flow by volumetric flow meter before and after each CO$_2$ reduction test for high accuracy. Thus, we got the below carbon balance in Table S2.
Table S3. Carbon balance and related CO\textsubscript{2} utilization rate (ratio of CO\textsubscript{2} used in products formation versus total CO\textsubscript{2} consumption) for different ion-selective membranes in 1 M KHCO\textsubscript{3}.

| Membrane type | $\bar{\varnothing}_{\text{CO}_2 \text{ to gas}}$ (ml/min) | $\bar{\varnothing}_{\text{CO}_2 \text{ to liquid}}$ (ml/min) | $\bar{\varnothing}_{\text{OH}^-}$ (ml/min) | $\bar{\varnothing}_{\text{residual CO}_2}$ (ml/min) | CO\textsubscript{2} utilization rate (%) |
|---------------|---------------------------------|-------------------------------|-------------------------------|---------------------------------|---------------------------------|
| AEM           | 0.922                           | 0.3917                        | 2.74                          | 41.02                           | $\sim$32.4                     |
| CEM           | 0.91885                         | 0.391                         | 2.75                          | 40.99                           | $\sim$32.3                     |
| BPM           | 0.966                           | 0.385                        | 2.499                         | 41.15                           | $\sim$35.1                     |

($\bar{\varnothing}_{\text{CO}_2 \text{ to gas}}$: the consumed CO\textsubscript{2} flowrate that is converted into all gas products (CO, C\textsubscript{2}H\textsubscript{4} and CH\textsubscript{4}) in CO\textsubscript{2} reduction; $\bar{\varnothing}_{\text{CO}_2 \text{ to liquid}}$: the consumed CO\textsubscript{2} flowrate for all liquid products in CO\textsubscript{2} reduction (such as ethanol); $\bar{\varnothing}_{\text{OH}^-}$: the consumed CO\textsubscript{2} flowrate via the reaction with OH\textsuperscript{-} generated in cathodic reactions; $\bar{\varnothing}_{\text{residual CO}_2}$: the residual unreacted CO\textsubscript{2} flowrate in the gas outlet (gas mixture) out of gas compartment of flow electrolzyers)
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