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Enriching Surface-Accessible CO₂ in the Zero-Gap Anion-Exchange-Membrane-Based CO₂ Electrolyzer

Qiucheng Xu, Aoni Xu,* Sahil Garg, Asger B. Moss, Ib Chorkendorff, Thomas Bligaard, and Brian Seger

Abstract: Zero-gap anion exchange membrane (AEM)-based CO₂ electrolysis is a promising technology for CO₂ production, however, their performance at elevated current densities still suffers from the low local CO₂ concentration due to heavy CO₂ neutralization. Herein, via modulating the CO₂ feed mode and quantitative analyzing CO₂ utilization with the aid of mass transport modeling, we develop a descriptor denoted as the surface-accessible CO₂ concentration ([CO₂]SA), which enables us to indicate the transient state of the local [CO₂]/[OH⁻] ratio and helps define the limits of CO₂-to-CO conversion. To enrich the [CO₂]SA, we developed three general strategies: (1) increasing catalyst layer thickness, (2) elevating CO₂ pressure, and (3) applying a pulsed electrochemical (PE) method. Notably, an optimized PE method allows to keep the [CO₂]SA at a high level by utilizing the dynamic balance period of CO₂ neutralization. A maximum jCO of 368 ± 28 mA cm⁻² was achieved using a commercial silver catalyst.

Introduction

CO₂ electrolysis to produce value-added fuels or chemicals has emerged as one of the most promising technologies for a sustainable and carbon-neutral future.[1] Among various electrolysis products, CO₂, with a large market demand, is the closest to commercialization.[2] Many recent studies have successfully produced CO₂ at industrial-level current densities (j > 200 mA cm⁻²) by utilizing gas-diffusion-electrodes (GDE) akin to the fuel cell and electrolysis communities.[3] In these cases, the GDE provides a significantly thinner diffusion boundary layer that helps to overcome the CO₂ mass transfer limitations present in aqueous systems.[4] Moreover, the anion-exchange membrane (AEM) based zero-gap electrolyzer approach has attracted much attention due to the advantages of offering an alkaline interface environment that impedes the competing hydrogen evolution reaction (HER) and which possesses less hydrogen resistance loss compared to a flow-cell system.[5] However, the CO₂ utilization in such AEM-based systems has substantial room for improvement due to CO₂ neutralization, during which the CO₂ feed reacts with in situ generated OH⁻ forming CO₃²⁻/HCO₃⁻ at the cathode side. These species crossover to the anode side leading to a ≈50 % loss of CO₂.[6] As an example, Figure 1a exhibits a statistical analysis of CO₂ utilization of recently reported zero-gap AEM-based electrolyzer studies for CO₂-to-CO conversion.[6,7] In detail, a much higher CO₂ inlet feed was required to achieve the maximum partial current density of CO (jCO) when compared to the predicted CO₂ consumption including neutralization, showing a low CO₂ conversion rate (X).[6,7] Such low conversion rates reveals greatly enhanced mass transfer issues that occur in the micro-environments near the catalyst at large current densities. These low conversion rates also will increase downstream separation costs thereby reducing the economic feasibility.

Along with changes in operating conditions, CO₂ neutralization provides diverse micro-environments near the catalyst surface.[7a,8] A few modeling studies have reported that the buffering function of the CO₂ neutralization process stabilizes the local pH at the expense of reducing the local [CO₂].[9] In general, an intertwined reaction mechanism involving the kinetics and mass transfer of both CO₂ and HER needs to be considered. Three modelled linear-polarization curves of CO₂-to-CO reaction at different assumed conditions are displayed in Figure 1b (detailed parameters used for this model are described in the Supporting Information). This figure shows the jCO at three marked overpotential ranges are controlled by the intrinsic catalyst kinetics, the mixed kinetic-diffusion, and CO₂ mass-transfer diffusion, respectively. A high local [CO₂] favors both an increase in the reaction rate and the limiting jCO. In ideal conditions, the maximum limiting jCO (black curve) will be...
achieved when the [CO$_2$] is saturated near the catalyst surface, which is $\approx 34$ mM at room temperature in an aqueous electrolyte. However, when CO$_2$ neutralization occurs, the local [CO$_2$] decreases and reaches a new equilibrium, causing a lower limiting $j_{CO}$ (blue curve). By further considering the competing HER that will reduce FE$_{CO}$ with an increasing overpotential, the $j_{CO}$ will show a volcano type curve behavior and a lower limiting value at a higher overpotential. This volcano effect has actually been seen in the work by Larrazabal et al. where the $j_{CO}$ is maximal at 200 mA cm$^{-2}$ (at $j_{total} = 250$ mA cm$^{-2}$) and then decreases at higher total current densities.$^6$ The above analysis reveals the CO$_2$ neutralization process severely obstructs CO$_2$ mass transfer and is one of the major constraints for better CO$_2$ utilization. Although substantial quantitative analyses have been reported in the ocean acidification field regarding CO$_2$ neutralization,$^10$ little of this knowledge has been transferred to spur the development of CO$_2$ electrolysis. To the best of our knowledge, there is still a lack of investigations related to the neutralization chemistry of local CO$_2$ and OH$^-$ concentrations at large-current density conditions and concomitantly developed strategies to detour such internal limitations.

Herein, using a commercial silver catalyst, we systematically explored the effect of changing the CO$_2$ feed mode (e.g., flow rate, partial pressure, etc.) in a zero-gap AEM-based electrolyzer on CO$_2$ neutralization and the micro-environment. By combining a series of quantitatively analyzed experimental results with theoretical calculations, we found that surface accessible CO$_2$ concentrations ([CO$_2$]$_{SA}$), which is a function of the local [CO$_2$]/[OH$^-$] ratio, is a good descriptor for CO$_2$R performance at high current densities where mass transfer issues often dominate.

To enrich the [CO$_2$]$_{SA}$ in the vicinity of the catalyst, we developed three general strategies: (1) increasing catalyst layer thickness, (2) elevating CO$_2$ pressure, and (3) applying a pulsed electrochemical method. Consequently, a $j_{CO}$ of 368 $\pm$ 28 mA cm$^{-2}$ was achieved through an optimized pulsed-electrochemical method. Under these conditions, the cell can maintain a FE$_{CO}$ of $> 70\%$ for 13 h at 500 mA cm$^{-2}$.

Results and Discussion

To explore how CO$_2$ neutralization affects the local CO$_2$ and OH$^-$ concentration, experiments were performed by controlling the partial pressure ($P_{CO2}$), flow rate ($v_{CO2}$) and applied current densities ($j_{total}$), as illustrated in Figure 2a. The $P_{CO2}$ will regulate the extent of CO$_2$ neutralization in the catalyst vicinity and the CO$_2$ coverage on the catalyst...
surface; the $v_{\text{CO}_2}$ as a dependent parameter, will show a combined effect of the physical transport behavior of $\text{CO}_2$ and the $P_{\text{CO}_2}$, depending on $\text{CO}_2$ supply and consumption; the $j_{\text{total}}$ will affect the local \( \text{OH}^- \) concentration due to the in situ $\text{CO}_2^2-$/HCO$^-_3$ formation. In the experiments, we implemented five different $\text{CO}_2$ feed conditions (Table 1) at $j_{\text{total}}$ ranging from 100 to 300 mA cm$^{-2}$. They can be further classified into three groups according to the total $\text{CO}_2$ supplied. For example, by matching the flow rate and partial pressure, \( \text{II} \) (100% $P_{\text{CO}_2}$ and 10 mL min$^{-1}$ cm$^{-2}$) and \( \text{III} \) (50% $P_{\text{CO}_2}$ and 20 mL min$^{-1}$ cm$^{-2}$) conditions have the same total $\text{CO}_2$ supply of $\approx 7 \times 10^{-6}$ mol s$^{-1}$. A silver membrane (Ag-M, purity $>99.97\%$) with a hydrophilic surface was chosen as the baseline cathode catalyst since it is commercial (i.e., reproducible) and has uniform pore sizes (Figure S1). These features allow both gas and ions to easily access or leave the catalyst surface.

Figure 2b shows the electrochemical $\text{CO}_2$ to $\text{CO}$ performance ($j_{\text{CO}}$) at different operating conditions. Detailed information is provided in Figure S2 and S3 including cell voltage and faradic efficiency (FE). Figure 2b shows that decreasing the $P_{\text{CO}_2}$ dramatically drops the $j_{\text{CO}}$. As it is known that the rate limiting step of $\text{CO}_2$ to $\text{CO}$ is the first electron transfer,[10] it would reason that the activity would scale linearly with $\text{CO}_2$ concentration. At beyond 200 mA cm$^{-2}$, it appears the $j_{\text{CO}}$ has been reached for this experimental design, and the $j_{\text{CO}}$ of \( \text{III} \) is approximately half that of \( \text{II} \) as one would expect.

As mentioned above, operating with a low $v_{\text{CO}_2}$ shows complex effect of mass transfer and $P_{\text{CO}_2}$. The in situ formed gas products would dilute the reactant gas and thus decrease the $P_{\text{CO}_2}$. To verify this, the $v_{\text{CO}_2}$ was reduced from 20 to 5 mL min$^{-1}$ cm$^{-2}$. Figure 2b shows that $j_{\text{CO}}$ was not affected notably when $j_{\text{total}} = 100$ mA cm$^{-2}$. Combining this with the $\text{CO}_2$-to-$\text{CO}$ conversion rate ($X$) in Figure 2c, where $X$ proportionally increases with an increase of $v_{\text{CO}_2}$ (i.e., from 3.1% with \( \text{I} \) to 6.2% with \( \text{II} \) or 11.9% with \( \text{IV} \), $\approx 2$ or 4 times), this suggests that the mass transfer and the $P_{\text{CO}_2}$ are not limited in these conditions. Interestingly, further increasing $j_{\text{total}}$ would amplify the effect of reduced $P_{\text{CO}_2}$ due to an increased consumption of $\text{CO}_2$ as well as an increased formation of $\text{CO}$ and $\text{H}_2$. By using the FE of gas products at different $v_{\text{CO}_2}$, the $\text{CO}_2$ partial pressures at the cathodic outlet ($P_{\text{CO}_2-outlet}$) were estimated (Figure S4). The details are provided in Supporting Information. This shows the $P_{\text{CO}_2}$-outlet drops from $\approx 90\%$ to $\approx 70\%$ when the $v_{\text{CO}_2}$ decreases from 20 to 5 mL min$^{-1}$ cm$^{-2}$ at $j_{\text{total}}$ of 300 mA cm$^{-2}$. This decrease in partial pressure leading to a decrease in limiting $j_{\text{CO}}$ agrees with the trend seen between \( \text{I} \) and \( \text{IV} \). A comparison of \( \text{IV} \) and \( \text{V} \) with each having the same amount of $\text{CO}_2$ supply also clearly shows that $P_{\text{CO}_2}$ seems to be the dominating factor on the $j_{\text{CO}}$ rather than the $v_{\text{CO}_2}$, and this tendency is exacerbated with increasing $j_{\text{total}}$ These results highlight that both $P_{\text{CO}_2}$ and $j_{\text{total}}$ control the micro-environment around the catalyst, thus their quantitative analyses of $\text{CO}_2$ utilization were elaborated as follows.

The $\text{CO}_2$ utilization pathway during electrolysis is illustrated in Figure 3a thus providing a roadmap for analysis. The total $\text{CO}_2$ consumption can be divided into $\text{CO}_2$ reduction (with the generation of $\text{CO}$ and HCOO$^-_3$) and $\text{CO}$ neutralization (forming CO$^2_2$ and HCO$^-_3$). Among these species, anions (HCOO$^-_3$, CO$^2_2$, and HCO$^-_3$) will cross over the AEM under an electric field towards the positively charged anode, and can potentially be further reacted.[13] HCOO$^-_3$ can be oxidized to $\text{CO}_2$ at the anode due to it being thermodynamically favored to oxidize before the oxygen evolution reaction (by $>1.3$ V @ pH = 8).[14] With

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>Total $\text{CO}_2$ supply</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{I} ): 100% $P_{\text{CO}_2}$, 20 mL min$^{-1}$ cm$^{-2}$</td>
<td>$\approx 14 \times 10^{-6}$ mol s$^{-1}$</td>
</tr>
<tr>
<td>( \text{II} ): 100% $P_{\text{CO}<em>2}$, 50% $P</em>{\text{CO}_2}$, 20 mL min$^{-1}$ cm$^{-2}$</td>
<td>$\approx 7 \times 10^{-6}$ mol s$^{-1}$</td>
</tr>
<tr>
<td>( \text{III} ): 100% $P_{\text{CO}_2}$, 10 mL min$^{-1}$ cm$^{-2}$</td>
<td>$\approx 3.5 \times 10^{-6}$ mol s$^{-1}$</td>
</tr>
<tr>
<td>( \text{IV} ): 25% $P_{\text{CO}_2}$, 20 mL min$^{-1}$ cm$^{-2}$</td>
<td>$\approx 3 \times 10^{-6}$ mol s$^{-1}$</td>
</tr>
</tbody>
</table>

[a] The flow rate may have a deviation of $\pm 0.1$ mL min$^{-1}$ cm$^{-2}$ due to the resolution of mass flow controllers; humidified $\text{CO}_2$ is used in all experiments.
regards to HCO$_3^-$ and CO$_2^-$, they can react with protons homogeneously and release CO$_2$ at the anode. Using gas chromatography, the amount of CO formation at the cathode and the amount of CO$_2$ released at the anode can be calculated. Our previous studies show that formate crossover and oxidation at the anode in the MEA-based cell limits the total measurable FE at the cathode to <100%, and we again see that in this work (Figure S3). To quantify the CO$_2$ reduction amount to formate, we assumed that the missing charge in FE calculations at the cathode belongs to the formate. Accordingly, the quantitative results relating to CO$_2$ utilization at different CO$_2$ feed modes are shown in Figure 3b.

The increase of $P_{\text{CO}_2}$ and $j_{\text{f,local}}$ results in both a higher CO$_2$ consumption amount for reduction and neutralization. However, there is no scaling relation between CO$_2$ reduction or neutralization amount with CO$_2$ concentration, indicating that the chemical balance in the micro-environment is changed by the $P_{\text{CO}_2}$. Moreover, the CO$_2$ neutralization degree normalized towards the total CO$_2$ feed is displayed in Figure S5. It shows that a higher ratio of CO$_2$ would participate in the neutralization process when the $P_{\text{CO}_2}$ drops, worsening the [CO$_2^-$]$^{3\text{A}}$.

Furthermore, the local pH near the catalyst surface can be estimated by utilizing the quantitative CO$_2$ neutralization amounts from the experiment (Figure 3b). Both the CO$_2$-to-CO$_2$ half-reaction and HER produce 1 mol of OH" per 1 mol of e" during the electrolysis process. The CO$_2$-to-formate (with the OH"/e" = 0.5) is not considered since an unsubstantial amount of the Faradaic efficiency goes towards this reaction. Applying the chronopotentiometry (CP) method allows for the OH" formation rate (mol s$^{-1}$ cm$^{-2}$) to be calculated to predict the local pH. We assumed a fully saturated GDE and uniform catalytic activity throughout the 50 μm catalyst layer. Figure 3c presents the predicted local pH values at various $j_{\text{f,local}}$ in the absence of any CO$_2$ neutralization. In general, a larger $j_{\text{f,local}}$ allow for a higher alkaline condition at the cathode surface due to the increase of OH" flux, e.g., local pH = 13.3 at 100 mA cm$^{-2}$.[56] By considering the buffer function of CO$_2$ neutralization (CO$_2$ + 2OH" → CO$_3^{2-}$ + H$_2$O), the local pH values at different $P_{\text{CO}_2}$ conditions can be further estimated (Figure 3d). It shows a relatively lower local pH value can be achieved at higher $P_{\text{CO}_2}$ conditions because higher concentrations of CO$_2$ are available to participate in the neutralization process, i.e., pH = 12.9 ± 0.1 at $P_{\text{CO}_2}$ = 100% and pH = 13.1 ± 0.1 at $P_{\text{CO}_2}$ = 25 %. However, the aforementioned simple model ignores the mass-transfer influences of catalyst layer structure, membrane, etc., and thus it can only be used for a qualitative comparison. Nevertheless, the above analysis demonstrates that the CO$_2$ neutralization reaction provides an unwanted feedback effect that reduces [CO$_2^-$]$^{3\text{A}}$.

Mass-transport modeling is further employed to verify the above assumptions. A one-dimensional MEA-based model (Figure S6) containing a gas diffusion electrode, silver catalyst layer (CL), AEM, and anolyte was developed by a COMSOL multi-physics field simulation. Dissolved CO$_2$ is considered as the reactant in the modelling based on previous works.[50,51] The local HCO$_3^-$, CO$_3^{2-}$, OH", and CO$_2$ concentrations were based on the average value of CL. Figure S7 presents the local HCO$_3^-$ and CO$_3^{2-}$ concentrations at different operating conditions ($P_{\text{CO}_2}$ and $j_{\text{f,local}}$). Their concentrations have a baseline value of ≈ 100 mM according to the anolyte (100 mM KHCO$_3$). It shows that the [HCO$_3^-$ + CO$_3^{2-}$] increases with both the $P_{\text{CO}_2}$ and current densities, agreeing with the experimental results (Figure 3b). Moreover, the precise CO$_2$/HCO$_3^-$ ratios (calculated from simulations) at different conditions are provided. The CO$_2^-$ are the main carrier ions during the electrolysis and this tendency stands out at larger current densities. This result matches with our previous experiments.[8] Figure 3e further demonstrates the calculated local OH" and CO$_2$ concentration. At 100 mA cm$^{-2}$, all $P_{\text{CO}_2}$ conditions show a similar local [OH"], while a 2.6 times enhancement of local [OH"] is demonstrated when $P_{\text{CO}_2}$ is changed from 100% to 25% at 300 mA cm$^{-2}$. More interestingly, increasing the current density leads to a change of local [CO$_2$] based on partial pressure, which is expected to be 4 times between $P_{\text{CO}_2}$ of 100% and 25%. In fact, a 5-times local [CO$_2$] difference is shown at 300 mA cm$^{-2}$, indicating the additional impact related to CO$_2$ neutralization affects the high current electrolysis and lowers the [CO$_3^{2-}$]$^{3\text{A}}$, which substantially affects the CO$_2$/R activity. Comparing with the values of local [CO$_2$] or local [OH"] alone, this descriptor has the advantage to show the combined effect of the micro-environment, and especially amplifies the dynamic evolution of [CO$_2$] and [OH"] at variable operation conditions. Thus, it is of great significance to maintain the high [CO$_3^{2-}$]$^{3\text{A}}$ by separately regulating the local [CO$_2$] and local [OH"] for overcoming the internal limitation of CO$_2$ neutralization for large current density electrolysis.

Mass-transport modeling has shown that increasing local [CO$_2$] will drop the local [OH"] and thus improve the [CO$_3^{2-}$]$^{3\text{A}}$ on the catalyst for enhancing the $j_{\text{f,local}}$, as displayed in Figure 4a. In principle, the [CO$_2^-$]$^{3\text{A}}$ is closely related to the in situ generated [OH"] per active site and CO$_2$ mass transfer effects ($P_{\text{CO}_2}$, $t_\ell$) during the electrolysis period. In cases where pulsed electrolysis is used, $t_\ell$ is specific to the given time in the absence of CO$_2$/R, thus allowing the CO$_2$ concentration to recover. Accordingly, we utilized three general strategies to enrich [CO$_2^-$]$^{3\text{A}}$ at the catalyst interface: (1) increasing catalyst layer thickness, (2) elevating operating pressure, and (3) applying a pulsed electrochemical technique.

Currently, the main way to compare electrolysis performance under different experimental conditions is using a 2-dimensional electrode area for denoting current density. Although this way is simple and explicit, it neglects the significant function of catalyst structure and loading on the electrolyzer’s performance.[34] For example, by maintaining the catalyst layer volumetric density but increasing its thickness, the cell performance would be substantially modified. This could be enhanced by an increase in the total number of active sites or diminished by lengthening of mass
General strategies to improve the SA-CO$_2$ concentration

- **a)** Relationship between local [CO$_2$], local [OH$^-$] and CO$_2$R performance.
- **b)** Increasing catalyst layer thickness, **c)** elevating CO$_2$ pressure (tested in a cell enabling pressurization), and **d)** applying pulse electrochemical method to enhance the [CO$_2$]$^{3A}$.

Figure 4. General strategies to enrich the [CO$_2$]$^{3A}$. a) Relationship between local [CO$_2$], local [OH$^-$] and CO$_2$R performance. Experimental results of b) increasing catalyst layer thickness, c) elevating CO$_2$ pressure (tested in a cell enabling pressurization), and d) applying pulse electrochemical method to enhance the [CO$_2$]$^{3A}$.

Transfer pathway for ions to reach the anode and CO$_2$ to penetrate the partially hydrated catalyst layer. Figure 4b shows the selectivity improvement of CO (from 52 % ± 3 % to 65 % ± 5 %) with an increase in $j_{CO}$ by ca. 40 mA cm$^{-2}$ when the thickness of the catalyst layer was changed from 50 to 100 μm. The 100 μm sample shows a 2-times larger double-layer capacitance than the 50 μm sample (see Figure S8 for details), indicating a 2-times increase in the number of active sites. In this case, the increase of catalyst layer thickness reduces the amount of charge that flows through per active site, thus reducing the in situ generated OH$^-$ per active site (local pH) helping to maintain a high [CO$_2$]$^{3A}$. The estimated local pH by utilizing the quantitative CO$_2$ neutralization amounts also shows the reduction from 13.5 ± 0.2 to 13.2 ± 0.1, verifying the assumption. Moreover, the mass-transfer modelling result also verifies this assumption, as shown in Figure S9. These features result in a high [CO$_2$]$^{3A}$ allowing for better CO$_2$R performance. This demonstration reveals the immense potential of high-pressure (>10 bar) CO$_2$ electrolysis.$^{[16, 15]}$ Operating at higher pressures does increase capital costs, so other approaches to increase local [CO$_2$] would also be helpful. Thus, another general strategy based on a pulsed electrochemical (EC) method was developed.

Contrary to previous research that utilized the pulsed EC method to regulate the micro-structure and chemical state of the electrocatalyst (e.g., pulsed anodic of the oxidation potential of the metal catalyst),$^{[16]}$ we attempt to regulate the micro-environment near the catalyst via [CO$_2$]$^{3A}$ self-recovery in the MEA-based electrolyzer. The pulsed method denoted below was operated within the metallic regime of Ag, but at a potential that was either just reductive enough to react with CO$_2$ or slightly anodic of this potential, which eliminated Ag oxidation issues and mitigated double-layer capacitance build-up transient effects. As a 2-electrode device was used, the exact cathodic potentials were hard to gauge.

Two operation methods, (1) pulsed potential (PP) and (2) chronopotentiometry (CA), are compared in Figure 4d. CA method utilizes a constant cell voltage of 3.3 V while the
PP method utilizes a pulsed time period ($t_0 = 1$ s) at 3.3 V for the reaction and a recovery time ($t_1 = 0.5$ s) at 2.0 V. During the recovery time, the current of cell equals to zero, indicating no Faradaic reaction. To evaluate the FE of CO and H2, the concentrations of gas products achieved from the GC data were compensated by the deadtime since the gas flow maintains during the whole pulse period, which reflects the average results including the period where there was no reaction. Remarkably, the PP method allows $i_{CO}$ to increase from 164 ± 24 mA cm$^{-2}$ to 191 ± 5 mA cm$^{-2}$ and the FE of CO reduces to <4 % as compared to the CA method. Such improvement comes from the recovery period where no CO$_2$ occurs but the CO$_2$ transfer and neutralization are still continuously happening. This allows [CO$_2$]$^{\text{SA}}$ to increase during the recovery period while simultaneously permitting anions (e.g., CO$_3^{2-}$) to leave the local environment as they should be driven away from the negatively charged cathode since there still is an electric field (2 V) between the cathode and anode.

Literature has demonstrated that a pulsed potential method has shown great promise to regulate the micro-environment.[13] In addition to pulsed potential, the pulsed current (PC) method may provide more value when the mass transfer is the dominating issue being investigated. The PC method enables one to overcome the mass transfer and neutralization are still continuously happening. This allows [CO$_2$]$^{\text{SA}}$ to increase during the recovery period while simultaneously permitting anions (e.g., CO$_3^{2-}$) to leave the local environment as they should be driven away from the negatively charged cathode since there still is an electric field (2 V) between the cathode and anode.

To simulate the PC method, a pulse period containing a reacting period ($t_0$) of 1 s at an $i_{\text{total}}$ of 100 mA cm$^{-2}$ and a recovery period ($t_1$) of 0.5 s at open circuit conditions was repeatedly applied. This shows that the local CO$_2$ is saturated and local [OH$^-]$ is low when no reaction happens ($t_0$). When applying pulse electrolysis, during the $t_0$ the local [CO$_2$] would gradually drop to a lower degree until reaching steady-state, and then during the $t_1$ (if the time was long enough) it would return to near the initial saturated level; meanwhile the local [OH$^-]$ would vary the opposite way. According to the local CO$_2$ recovery and local [OH$^-]$ mitigation, the PC method allows for a higher [CO$_2$]$^{\text{SA}}$ during the $t_0$ compared to the static CP method. Importantly, the $t_0$ and $t_1$ values can largely regulate the average [CO$_2$]$^{\text{SA}}$ during the $t_0$ period. Experimentally, we operated a $i_{\text{total}}$ of 500 mA cm$^{-2}$ and optimized the $t_0$ by fixing the $t_1 = 1$ s (Figure 5b,c). The total or instantaneous CO$_2$ conversion rate ($X$) is calculated based on the CO$_2$ consumption for the CO$_2$R divided by the CO$_2$ supply during the whole period ($t_0 + t_1$) or only the $t_0$ period, respectively. As expected, the $i_{\text{CO}}$, instantaneous X and FE$_{\text{CO}}$ increase with the $t_0$. An optimized high $i_{\text{CO}}$ of 368 ± 28 mA cm$^{-2}$ with FE$_{\text{CO}}$ of 74 ± 6 % and instantaneous X of 42 ± 4 % can be achieved when $t_0 \geq 0.5$ s, which is 1.8 times higher than that of the CP method. Further increasing the duration of $t_0$ shows no increase of the CO$_2$R performance implying that the local [CO$_2$] is almost recovered when $t_0 \geq 0.5$ s. It is noted that the total $X$ stays at 27 ± 2 % for all $t_1$ conditions. Actually, the total

Figure 5. Pulsed-current (PC) method to optimize the [CO$_2$]$^{\text{SA}}$. a) Modelling results and schematic illustration of the local [CO$_2$], local [OH$^-]$ and [CO$_2$]$^{\text{SA}}$ change at reacting or recovery periods during PC method. b) Partial current density of CO, H$_2$ and CO$_2$ conversion rate (blue straight dot line is $X$ of 50%). c) Faradaic efficiency and cell resistance at different recovery times when applying PC method at 500 mA cm$^{-2}$ with catalyst layer thickness of 100 μm and CO$_2$ flow rates of 10 ml min$^{-1}$ cm$^{-2}$. 

charge passing the electrode as well as the total in situ formed OH\(^-\) amount should decrease if they are normalized to the whole period with lengthening \(t\). In this case, the maintained total \(X\) verifies the continuous process of \(CO\(_2\)\) neutralization during \(t\), which lowers the local \([OH\(^-\)]\) and raises local \([CO\(_3\)^{2-}\]) resulting in the boost of \(j_{CO}\) during the \(t\) period. Moreover, the cell resistance cells in Figure 5c increase with the \(t\), indicating a higher \(CO\(_2\)^{2-}/OH\(^-\)\) ratio in the membrane due to the lower mobility of \(CO\(_2\)^{2-}\) than \(OH\(^-\)\) and also a higher \(CO\(_2\)\) neutralization degree during the whole period.[104]

Furthermore, the long-term stability comparison of the pulse-current (CP) method with \(t=0.5\) s and the normal chronopotentiometry (CP) method at \(j_{total}=500\) mA cm\(^{-2}\) is shown in Figure S11. The \(j_{CO}\) was calculated based on the reacting period of the two methods. During the first 13 h, the PC method shows much better stability in comparison to the CP method. It still shows a \(j_{CO}\) of \(\approx 350\) mA cm\(^{-2}\) with \(FE_{CO}\) of \(\approx 70\%\) at 13 h, which is 2.6 times higher than that of CP method (i.e., a \(j_{CO}\) of \(\approx 135\) mA cm\(^{-2}\) with \(FE_{CO}\) of \(\approx 27\%\)). Considering the whole pulse period, the normalized \(j_{CO}\) is \(\approx 233\) mA cm\(^{-2}\), which is still 1.7 times higher than that of the CP method. Moreover, after 25 h of \(CO\(_2\)\) electrolysis, the PC method can maintain a total \(CO\(_2\)\) conversion rate higher than \(22\%\) (i.e., an instantaneous conversion rate of \(33\%\)) in contrast to the CP method of only \(14\%\). The above results illustrate the bright perspective of the pulse EC method to apply for commercially viable \(CO\(_2\)\) electrolysis designs.

Single-pass \(CO\(_2\)\) conversion (SPC) as a factor to reflect the \(CO\(_2\)\) utilization has attracted great attention recently.[109] In our work, we mainly discussed the internal limitations of \(CO\(_2\)\) neutralization and provide three strategies to enrich \([CO\(_2\)]^A\). These strategies have one general feature: they decrease the \([OH\(^-\)]\) as well as improve the \([CO\(_2\)]^A\) by utilizing \(CO\(_2\)\) neutralization. Therefore, they are not suitable for pursuing high SPC. On the other hand, some advanced cell configurations regarding the electrolyte and membrane designs have been reported to increase the SPC of \(CO\(_2\)\). Their design principle is to create an acidic environment (e.g., acidic electrolytes) or a flow of protons by utilizing a cation-exchange membrane (CEM) to either directly suppress the \(CO\(_2\)\) neutralization or in situ release the consumed \(CO\(_2\)\).[104] Accordingly, a high SPC of \(>75\%\) can be achieved in those configurations, however, they struggle with large ohmic loss in their setups.

Another important research area for \(CO\(_2\)\) reduction is to precisely measure the local \(pH\) and \(CO\(_2\)\) concentration near the catalyst surface (within micro- or nano-meters).[19] Significant progress have been made. For example, Monteiro et al. reported a time-resolved local \(pH\) measurements during \(CO\(_2\)\) reduction by using scanning electrochemical microscopy.[183] They detected a plateau region of \(pH\) nearby the catalyst surface during \(CO\(_2\)R\) due to the formation of \(HCO\(_3\)\) buffering the reaction interface. This kind of experimental results are useful to estimate the real local \(pH\) values across the diffusion layer, thus further helping to develop the model and improve the modelling parameters. However, until recently, it is still a challenge to in situ characterize the local \(pH/CO\(_2\)\) concentration in MEA-based setups due to the complex interfacial structure. Thus, mass-transfer modelling and calculations play an important role in supporting the experimental results.[21] We advocate to further develop operand spectroscopy and microscopy for the MEA-based cell and extract knowledge from these techniques to optimize the theoretical models, achieving a better understanding on the \(CO\(_2\)\) electrolysis.

### Conclusion

In this work, we systematically explored the change of \(CO\(_2\)\) neutralization in terms of local \([CO\(_2\)]\) and local \([OH\(^-\)]\) near the catalyst layer by regulating the \(CO\(_2\)\) feed mode (e.g., flow rate, partial pressure, \(etc\.)\) and applied current densities in a zero-gap AEM-based electrolyzer. The quantitative analyses and theoretical calculation results together reveal that the \([CO\(_2\)]^A\) (i.e., local \([CO\(_2\)]/[OH\(^-\)]\)), which has the advantage of amplifying the dynamic evolution of local \([CO\(_2\)]\) and local \([OH\(^-\)]\) in the micro-environment at different operation conditions, is a good descriptor for \(CO\(_2\)R\) performance. A higher \([CO\(_2\)]^A\) is favorable for electrochemical \(CO\(_2\)\) to \(CO\) conversion.

In principle, \(P_{CO2}\) and \(j_{total}\) help set the initial local \([CO\(_2\)]\) and local \([OH\(^-\)]\) respectively, whereas once electrolysis proceeds, they would chemically balance with each other until reaching steady state. Increasing the initial \(P_{CO2}\) and decreasing the \(j_{total}\) will both render a lower ratio of \(CO\(_2\)\) to participate in the neutralization process, leading to a high local \([CO\(_2\)]\) and a low local \([OH\(^-\)]\), i.e., improving the \([CO\(_2\)]^A\). Moreover, \(CO\(_2\)\) neutralization is a dynamic process requiring some period of time to reach equilibrium. This phenomenon creates a possibility to utilize the dynamic evolution of the local \([CO\(_2\)]\) and \([OH\(^-\)]\) to keep the \([CO\(_2\)]^A\) at a high level, such that one may overcome the internal limitations of \(CO\(_2\)\) neutralization. Based on these understandings, three general strategies were developed to enrich \([CO\(_2\)]^A\) for high current electrolysis: (1) increasing the catalyst layer thickness to reduce the \(j_{total}\) per active sites, (2) elevating \(CO\(_2\)\) pressure (e.g., \(P_{CO2}>1\) bar), and (3) employing pulse electrochemical method to keep the \([CO\(_2\)]^A\) at a high level. Consequently, a commercial silver baseline catalyst achieved a \(j_{CO}\) of \(368\pm28\) mA cm\(^{-2}\) with \(FE_{CO}=74\pm6\%\) via an optimized pulsed-electrochemical method.

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### Conflict of Interest

The authors declare no conflict of interest.
Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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