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A Comprehensive Approach to Investigate CO₂ Reduction Electrocatalysts at High Current Densities

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CONSPECTUS

As electrochemical CO$_2$ reduction studies progress from beaker or H-cell devices operating at low current densities to gas diffusion electrode (GDE)-based devices that sustain high reaction rates and provide an avenue toward commercialization, the overall system becomes significantly more complex. While the current densities may vary for the different approaches, it is essential to maintain the same scientific rigor when analyzing these systems. The mass transfer optimizations used in GDE based approaches necessarily add complexity and provides new challenges that need to be analyze and overcome in terms of both engineering as well as analysis techniques. This account puts into perspective our recent works analyzing high current density CO$_2$ electrolysis reactors via a comprehensive investigation of the entire setup.

In particular, we show the importance of monitoring (i) outlet cathode gas flow rates, (ii) the anodic gas composition for CO$_2$/O$_2$ ratio and (iii) pH variations in the electrolyte. A rigorous analysis of these parameters allows us to achieve a complete carbon balance in addition to accounting for a total of 100% faradaic efficiency. By analyzing both the cathode outlet and anodic CO$_2$:O$_2$ ratio, we demonstrate that these methods can be used to self-validate results providing robustness. We show that this analysis approach holds for both a zero-gap membrane electrode assembly device and a flowing catholyte device. In addition, a comprehensive monitoring approach reveals that having an alkaline environment in the vicinity of the cathode can absorb substantial amounts of CO$_2$, which may greatly distort faradaic efficiencies if not accounted for. While monitoring outlet flow rate of a reactor appears a simple task, the mixed gases and small flowrates in lab scale type reactors can add challenges and we discuss various methods to measure these flow rates.
While pH is well known to play a role in the activity and selectivity of CO₂ reduction, we demonstrate that (i) the operational pH is not necessarily the pH on the initial electrolyte, (ii) that there are long transients in pH before steady state is reached (on order of hours), and (iii) the pH of the anolyte and catholyte can be significantly different.

By varying the membrane type in a flowing catholyte reactor (anion exchange, cation exchange, or bi-polar membrane), we can use this monitoring approach to quantitatively identify the major differences in CO₂ reduction performance related to these distinct membrane types. The overall conclusion is that complex engineering processes along with sensitive catalysts entails that a thorough monitoring of a wide variety of parameters are necessary to accurately analyze the performance of high current density electrochemical CO₂ reduction devices.
Introduction

Society’s sluggish response to the fundamental issues relating to climate change entails that we will now most probably need to go beyond just reducing our CO₂ emissions and will actually need to sequester CO₂ in the future.¹ Fortunately, CO₂ electrolysis provides the possibility to not only replace fossil fuel based chemicals but also acts as a method to temporarily sequester CO₂ (i.e. until the produced chemical is degraded back to CO₂).² While Yoshiro Hori trail blazed scientific discoveries in CO₂ electrolysis in the 1980’s and 1990s,³,⁴ until recently this method was always thought of as a technology in the distant future. However, the drastic drop in renewable electricity prices in the past decade has rapidly pushed this technology closer to economic feasibility. This, in turn, has meant that the low current density fundamental studies which focused primarily on the catalysis need to be modified into high current density scalable approaches that have multiple parameters to optimize in addition to catalysis. Operating at commercially relevant current densities not only clearly affects the device engineering,⁵ but also affects the analysis of the catalytic performance, most notably in relation to the product selectivity.

When we review fundamental studies on electrocatalysts,⁶ the primary figures of merits are the overpotential for a given half reaction and product selectivity. The low current densities used in these studies entail a well-defined environment with a constant pH and a constant flow of purging gaseous CO₂. In addition, low currents are typically linked to low CO₂ conversion rate, which entails that variations in gaseous products and CO₂ consumption will not substantially alter the outlet gas flow rate. This allows for a straightforward way to calculate the selectivity toward gaseous products via concentration-based analytical techniques (such as gas chromatography) and a known flow rate, which can be relatively approximated by the incoming CO₂ flow rate as set by a mass flow controller (MFC).
High current density applied approaches on the other hand should operate at high conversion rates and produce significant amounts of either OH⁻ or H⁺. This characteristic creates transient pH modifications as well as substantial steady-state pH changes, which can then lead to significant changes in the catalytic performance as has been demonstrated in detail by fundamental studies. However, the high conversion rates along with the potential to have significant liquid product crossover greatly complicates the understanding of what is occurring. This entails that, while many of the same figure of merit conditions from low current density still are useful, determining faradaic efficiency and overpotential is much more complicated. In addition, new figure of merits arise, such as conversion rate and ensuring a complete mass balance.

In a series of 3 papers, we have investigated how analysis approaches need to be shifted when focusing on high current density CO₂ electrolysis. In these works, we showed how high current density devices can significantly vary the key evaluation conditions, thus resulting in highly misleading catalytic trends if one uses analysis approaches based on low current density research. We also showed high current density results brings out some of the engineering difficulties in developing commercially viable devices. This account will try to summarize and put into perspective the effects that need to be accounted for.

**The importance of measuring the gas outlet flow rate**

When we look towards commercialization of CO₂ electrolysis, an important parameter is increasing CO₂ conversion rate. While the conversion rate of CO₂ in fundamental studies is typically below 1%, industrial practice dictates that this rate should be maximized to reduce the complexity and costs of downstream separation processes. Once we increase to these higher conversions, the reaction stoichiometry can significantly affect gas outlet flow. Looking at a set of
two electron transfer half-reactions below, we can understand this issue much clearer when we relate the reaction to the change in volumetric (i.e. molar) flow, \( \Delta Q \), per electron transferred. While a reaction like CO\(_2\) to CO will not affect gas outlet flow, CO\(_2\) to formate will decrease outlet gas flow, whereas the competing water electrolysis to H\(_2\) will increase outlet gas flow.

\[
\begin{align*}
2e^- + CO_2 + H_2O & \rightarrow CO + 2OH^- & \Delta Q/e^- = 0 & \text{Equation 1} \\
2e^- + CO_2 + H_2O & \rightarrow COO^- + OH^- & \Delta Q/e^- = -\frac{1}{2} & \text{Equation 2} \\
2e^- + 2H_2O & \rightarrow H_2 + 2OH^- & \Delta Q/e^- = \frac{1}{2} & \text{Equation 3}
\end{align*}
\]

Almost all CO\(_2\) product detection techniques are based off measuring the concentration of products in a given volume and then multiplying this by the flow rate to determine the amount of a species produced. In fundamental studies that operate at low current densities we make the assumption that incoming flow rate is a good approximation for outgoing flowrate since the conversion rates are low. However, when operating at high current densities (i.e. hundreds of mA/cm\(^2\)), the conversion rates often become much higher and the effects of the half reaction described in Equation 1-3 start to dominate the gas outlet flow rate for the electroreduction of CO\(_2\) to CO or formate. These issues mean that high current density CO\(_2\) electrolysis (or more accurately high conversion electrolysis) must measure reactor gas outlet flows to achieve an accurate analysis of the catalysis. While these issues do not affect liquid product analysis, the effects on gas product analysis can be much more severe.

Determining outlet gas flows are much more complicated than one would expect, which is largely due to having a gas mixture whose composition is variable and dependent on operating conditions (e.g, current density) and catalyst performance. With an unknown thermal conductivity and viscosity of the outlet gas (i.e., which depend on composition), mass flow meters and ball flow meters cannot be relied upon unless a quite complex multivariable calibration is carried out.\(^7\)
Techniques based on buoyancy, coriolis force or positive displacement are all relatively independent of gas composition and can be used to accurately determine gas flow rates out of the reactors, however, there are currently a limited number of commercial options at the small research scale size. Another approach is to add an inert gas (e.g., nitrogen through a bleed line) to the gas coming out of the reactor. By setting a constant flow rate of the inert gas and determining its post-dilution concentration (e.g., with the GC), the flow rate of the gas coming out of the reactor can be accurately estimated through a simple mass balance (technical note: the inert gas should be quite dilute to ensure it is within a linear calibration regime of the detector). Within our typical operation range (i.e., 0-150 ml/min), we have found that positive displacement-based gas flow calibrators (e.g., Mesa Labs DryCal Defender series) are easy to use and remarkably accurate and precise (i.e., we measured a typical relative standard deviation, RSD, of <0.05% at a fixed flow of 40 ml/min). However, measuring highly humidified gas streams can be problematic since moisture (or worse, dragged electrolyte droplets) entering the instrument’s frictionless piston can result in damage and very costly repairs. A liquid trap upstream of the meter helps avoid this problem.

Figure 1. a) Gas flow rate out from a porous silver cathode operating in a MEA-type configuration at various current densities (the gas inlet was 102.06 ml/min of humidified CO₂) and b) corresponding Faradaic efficiencies. The data is taken from Ref. 7.
Inexpensive soap bubble flowmeters are reasonably accurate and do not have this limitation, but they have the obvious drawback that automated operation and data logging are not possible. This is particularly restrictive for long-term measurements. While not as precise as the primary flow calibrators (i.e., typical RSD of 3% at 40 ml/min, which improves to 0.5% at 5 ml/min), liquid displacement-based meters used for low-flow biogas and fermentation monitoring (e.g., BioProcess Control µFlow) are moisture-resistant, making them good alternatives for volumetric gas flow measurements in high current CO₂ reduction. However, we have found their range to be limited (max. ca. 60 ml/min) and that they should be recalibrated on-site frequently to ensure their accuracy (this is straightforward by feeding directly known gas flows through a MFC). We have also successfully tried the bleed line approach with a wide range of flows. This method has the advantage that the flow measurement is exactly synchronous with the determination of product concentrations, but it is subject to the intrinsic uncertainties of GC quantification (e.g., peak integration, sample loop pressure and temperature) and the time resolution is limited to GC time between runs. In summary, we have found that all of these techniques are functional, with the most suitable choice ultimately depending on the range of flows to be measured, the desired accuracy and precision, the frequency and automation needed for the data acquisition, and the available budget.

In our initial work on this topic we used a membrane electrode assembly (MEA) (i.e., a zero-gap) setup with a Ag catalyst on the cathode, an anion exchange membrane (AEM), and IrO₂ as the anodic catalyst. Anion exchange membranes are typically favored in CO₂ electrolyzers since they allow for an alkaline environment that suppresses the competing hydrogen evolution reaction (HER) and results in enhanced CO₂ reduction selectivity. The relatively straightforward MEA
design, combined with a Ag catalyst with high selectivity toward CO₂ conversion to CO, provided a simple system to analyze our gases and the mass balance of the reactor as a whole.

When we measured the cathodic gas outlet flow rates as a function of operating current (Figure 1a) we could combine this monitored flow rate with gas chromatograph data to get the faradaic efficiencies (Figure 1b). With our CO and H₂ leading to 100% faradaic efficiency, this entailed that we were not producing any formate at current densities from 100 to 200 mA/cm². According to the Equation 1 and 3, an increase in the gas flow rate out of the reactor should be observed. However, we found a decrease in gas flow rate that we needed to account for, and this led us into investigating the missing gases that is linked to the CO₂/carbonate equilibrium.

From Table 1 we can see that all reductive half reactions will produce hydroxyl groups, and when CO₂ interacts with hydroxyl ions it can form either carbonates or bicarbonates via the following two equations:

\[
\begin{align*}
OH^- + CO_2 & \leftrightarrow HCO_3^- + H_2O & pK_a = 6.3 & \text{Equation 4} \\
OH^- + HCO_3^- & \leftrightarrow CO_3^{2-} + H_2O & pK_a = 10.3 & \text{Equation 5}
\end{align*}
\]

The preceding 2 equations demonstrates that we have an alternative mechanism to consume CO₂ that is unrelated to CO₂ actually being converted into a product. (It is our assessment that, because
carbonate/bicarbonate is not a direct faradaic product of CO2 electrolysis, it should not count in terms of CO2 conversion.) The amount of CO2 that is be consumed via the CO2/bicarbonate/carbonate equilibrium can be quite substantial. If we take the situation where only CO is produced in a near neutral pH, this entails that for every CO2 molecule converted, another two CO2 molecules would be lost for bicarbonate formation. Thus, the production of each CO molecule consumes three CO2 molecules, which means that our maximum conversion of CO2 to CO is 1/3 or 33%. Following this logic, we can extend this analysis to the most common CO2 electrolysis products. Table 1 shows the maximum conversion if all produced hydroxides react

\[ \text{Figure 2. a) The actual outlet gas flow rate and the modelled flow rate with various } A \text{ values from Equation 6. b) The CO}_2/O_2 \text{ ratio from the anode and the } A \text{ values derived from the outlet flow rate and Equation 6 both plotted versus current density. The experimental data used for this demonstrative analysis comes from Ref. 7.} \]
with CO₂ to form either bicarbonate or carbonate. For some of the highly reduced species such as methane, ethanol and ethylene, this CO₂ consumption from hydroxide can be quite extreme. From an economic viability standpoint, CO₂ consumption is a serious issue that needs to be considered and mitigated, whereas from an analytical perspective, this effect will greatly reduce the gas flow at the cathode outlet.

It is possible to theoretically calculate our volumetric outlet flow \( Q_{\text{gas, out}} \) as a function of CO₂ inlet flow \( Q_{\text{gas, in}} \) and partial current densities, giving us an understanding to what degree the importance of measuring outlet flow rate is at a given operating condition. With ideal gas law parameters \((P, R, T)\) and Faraday’s constant \((F)\), we can convert currents into gas flow rates. In Equation 6 we break this down into partial current of liquid products \((I_i)\) and gas products \((I_j)\) from water. The CO₂ that gets converted into liquid products will result in a decreased outlet gas flow rate and this quantity is a function of the number of carbons per liquid product \((#C_i)\) and the number of electrons it takes to reduce CO₂ to that product \((#e_i^-)\). For gas products the outlet flow rate will vary as a function of the number of carbons \((#C_j)\) in the product. Note H₂ can and should be considered a gas product in determining outlet flow. We also need to account for CO₂ being consumed by Equation 4 & 5. Using Equation 1-3 as a guide, we can see that the amount of

\[
\text{Table 1. Maximum CO}_2\text{ electrolysis conversion to products if the concomitantly OH}^-\text{ produced also consumes CO}_2\text{ as either HCO}_3^-\text{ or CO}_3^{2-}.}
\]

<table>
<thead>
<tr>
<th>Pure Product</th>
<th>HCO₃⁻</th>
<th>CO₃²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>33 %</td>
<td>50 %</td>
</tr>
<tr>
<td>Formate</td>
<td>50 %</td>
<td>67 %</td>
</tr>
<tr>
<td>Methane</td>
<td>11 %</td>
<td>20 %</td>
</tr>
<tr>
<td>Acetate</td>
<td>22 %</td>
<td>36 %</td>
</tr>
<tr>
<td>Ethanol</td>
<td>14 %</td>
<td>25 %</td>
</tr>
<tr>
<td>Ethylene</td>
<td>14 %</td>
<td>25 %</td>
</tr>
</tbody>
</table>
hydroxyls produced via CO₂ electrolysis will be directly proportional to the number of reductive
electrons (i.e. electrical current) inserted into any product with the exception of anionic species
such as formate and acetate, where the hydroxyls produced will be one less than the reductive
electrons needed per molecule. These hydroxyl groups can either transfer through the membrane
to the anode or equilibrate with CO₂ to form bicarbonate or carbonate. By relating the degree to
which hydroxyl CO₂ equilibration to the electron transfer, we can then account for any CO₂
consumed by this equilibration process. In Equation 6 we account for this by defining a variable
‘A’, which will correspond to a value anywhere between 0 and 1, where $A = 0$ for no CO₂
equilibration, $A = 1$ for equilibration to pure bicarbonate and $A = 1/2$ for CO₂ equilibration to
carbonate. Thus, $A$ is both a function of mass transfer issues relating to CO₂ in an alkaline
electrolyte and the actual pH of that electrolyte (i.e. HCO₃⁻/CO₃²⁻ ratio). It should be noted that $A$
can easily change as a function of current. While Equation 6 does not include variations in
humidity or gaseous products diffusion through the membrane to the anode, it still provides a
reasonably accurate estimation of the outlet flow.

$$Q_{gas, out} = Q_{gas, in} - \frac{RT}{PF} \left[ \sum_{i} I_{i} \frac{#C_{liq,i}}{#e_{liq,i}} + \sum_{j} I_{j} \left( \frac{#C_{gas,j}^{-1}}{#e_{gas,j}} \right) + A(I_{Total} - 1/2 I_{Formate} - 1/8 I_{Acetate}) \right] \quad Equation \ 6$$

Since we used the outlet gas value to determine partial current densities, one of the most direct
uses of Equation 6 is to get an indication of what the $A$ value is. In Figure 2a we use Equation 6 to
plot $A$ of 0, $1/2$, and 1. From this, it is clear that $A = 0.5$ is the most accurate value until there are
CO₂ mass transfer limits and hydrogen starts to dominate at 300 mA/cm². While Equation 6 allows
us to calculate an $A$ value, we can also look at the gas emissions from the anode side as an
alternative method to estimate this value.
While it is clear from Figure 2a that we are consuming carbonate, this must leave the system eventually to maintain a steady state system. Since our initial works used an anion exchange membrane, the \( \text{HCO}_3^- \) and \( \text{CO}_3^{2-} \) competed with \( \text{OH}^- \) to crossover to the cathode. With the anode oxidizing water to oxygen and protons, these protons combined with carbonates to produce gaseous \( \text{CO}_2 \). Table 2 looks at how the aforementioned anions will interact with the oxygen evolution half reaction. Table 2 also relates these half-reactions to both the \( A \) value as well as the \( \text{CO}_2 \) to \( \text{O}_2 \) ratio. Another way to define \( A \) is that it is the number of \( \text{CO}_2 \)’s equilibrated per hydroxyl group. Since \( \text{O}_2 \) evolution is a 4 electron transfer oxidation reaction that effectively consumes 4 hydroxyl groups, the \( \text{CO}_2 \) to \( \text{O}_2 \) ratio will simply be 4, if the \( A \) value is 1. Figure 2b shows the anodic \( \text{CO}_2/\text{O}_2 \) ratio from the experiments in Ref 7 in blue. In this figure we also determine what the \( A \) should be using Equation 3 (since we measured \( Q_{\text{gas}} \), out in our experiments) and plot this in red as well. The very close agreement clearly shows the carbonate produced at the cathode leaves via the anode. From an analysis standpoint, Figure 2a shows that, if one is unable to measure the anodic outlet \( \text{CO}_2/\text{O}_2 \) ratio, one can determine this relatively accurately by using the \( A \) value determined via Equation 6. (This relationship is under the condition that the bicarbonate/carbonate transfer is substantially larger than crossover of \( \text{CO}_2 \) electrolysis products). With this same logic,

**Table 2.** Anodic half reactions for \( \text{O}_2 \) evolution in terms of the anionic species transferring through the anion exchange membrane. This table also relates the \( A \) value from Equation 3 relating to the cathode with \( \text{CO}_2/\text{O}_2 \) ratio of the anode.

<table>
<thead>
<tr>
<th>Anodic half-reaction</th>
<th>( A )</th>
<th>( \text{CO}_2/\text{O}_2 ) ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 4\text{HCO}_3^- \rightarrow 4\text{CO}_2 + \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- )</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>( 2\text{CO}_3^{2-} \rightarrow 2\text{CO}_2 + \text{O}_2 + 4\text{e}^- )</td>
<td>( 1/2 )</td>
<td>2</td>
</tr>
<tr>
<td>( 4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- )</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

if the anode outlet \( \text{CO}_2/\text{O}_2 \) ratio can be measured, then one can use Equation 6 to solve for the
partial current density of products without the need for the cathodic outlet flow provided that the product concentration and total current are known. The most thorough case though is to monitor both anode and cathode outlet flow rates and simply use Equation 6 as a validation test for monitoring the precision of the results. This helps to partially deconvolute one of the trickier issues of the cathodic products being oxidized at the anode.

It is worth noting that the high preference for carbonate (over bicarbonate) crossover evidenced in Figure 2b is a consequence of the intrinsic properties of the membrane. As a rule of thumb, even in ideal systems ion exchange membranes strongly prefer the counter ion of higher valence, and this preference toward CO$_3^{2-}$ transport has been documented experimentally in several AEMs, so it is expected for Sustainion to behave similarly. In addition, because the HCO$_3^-$/CO$_3^{2-}$ equilibrium has fast kinetics and the reaction environment is highly basic (due to the elevated current density), not even the fact that an additional OH$^-$ is needed for CO$_3^{2-}$ formation can counteract the membrane’s affinity for the divalent anion.

Another useful parameter derived from Equation 6 is the ability to compare the ratio of inlet gas to outlet gas as a function of CO$_2$ conversion, $X$, as shown in Equation 7.

$$X = \frac{CO_2\text{ converted}}{CO_2\text{ in}} = \frac{\sum_i \frac{w_i}{P_i} \frac{\sum_j C_{\text{lq},i,j}}{Q_{\text{lq},i,j}} + \frac{\sum_j C_{\text{gas},j}}{Q_{\text{gas},j}}}{Q_{\text{gas,in}}}$$  \hspace{1cm} \text{Equation 7}

This ratio is useful for two reasons. From a practical standpoint, this gives us information on the relative demands for sizing pipes pre- and post- reactor. From an analytical standpoint, this will tell us our imprecision in measuring selectivity if the inlet flow rate is used instead of the outlet flow rate, which is harder to measure.
To practically analyze this potential imprecision, we can first take the partial current density from Figure 1b at 250 mA/cm$^2$ and then use Equation 3 to determine $A$, which was found to equal 0.54. With this information, we can then see how the inlet/outlet ratio (via Equation 6) varies as a function of CO$_2$ conversion (via Equation 7) as shown in Figure 3. By looking at the right axis, we can see the impact of needing to use the outlet flow when calculating the Faradaic efficiencies of gas products. Figure 3 also shows the cases that would have 100% faradaic efficiency of CO$_2$ to CO with an $A$ value of either 0.5 or 1. The inset zooms in on the low conversion regime typical of fundamental studies carried out at low current densities.

Figure 3. Graph showing the variation in inlet versus outlet ratio of gas flowrates as a function of conversion. This shows this ratio both for the selectivity profile and $A$ value of Ref 7 (at 250 mA cm$^{-2}$) as well as the case of 100% CO$_2$ selectivity to CO for a $A$ values of 0.5 and 1. The inset zooms in on the low conversion regime typical of fundamental studies carried out at low current densities.
used as a relatively accurate approximation (< 5% error) of the flow rate at the outlet. However, as the conversion increases a significant error is added to this estimation purely due to carbonate equilibrium, since pure CO₂ to CO conversion should not vary the volumetric flow rate at all. While not explicitly stated in the figure, 100% selectivity to formate with an $A = 0.5$, would have the exact same profile in Figure 3 as 100% selectivity to CO with an $A = 1$. Since liquid products such as formate are easily oxidizable at the anode, lack of proper formate detection could
significantly distort data analysis for studies on primarily CO-producing catalysts (e.g. Au and Ag).

**Analyzing flowing-catholyte devices**

CO₂ reduction over Ag leads to a straightforward product distribution that simplifies the analysis of mass flows, but using Cu catalyst results in a more challenging picture due to the production of several gaseous and liquid products. Therefore, for studying CO₂ reduction over Cu at high current densities, we employed a gas diffusion layer (GDL)-based cell that features both a flowing catholyte and anolyte, as shown in Figure 4a. This design makes it possible to monitor the electrolyte pH in both compartments, as well as to mitigate the loss of products toward the anode via crossover, along with their possible oxidation over the anode (particularly of formate over IrO₂). Although the relatively thick electrolyte layers significantly increase the cell voltage as a result of ohmic losses, this design allowed for easier liquid product detection with the ability to achieve a more thorough analysis of the complete carbon balance.

**Complete quantification of the Faradaic efficiency**

In our initial work with a flowing-electrolyte configuration (i.e., non-zero gap), we investigated CO₂ reduction over a Cu catalyst layer sputtered onto a commercial carbon-based GDL. Both the anolyte and catholyte consisted of 1 M KHCO₃, and the cell was assembled with an anion exchange membrane and a commercial IrO₂ anode. By monitoring the gas flow rate at the cathodic outlet using a bubble flowmeter, we were able to accurately determine the faradaic efficiencies of the gas-phase products (Figure 4b). While the presence of a catholyte layer allowed us to quantify the liquid-phase products, negatively charged compounds (e.g. formate, acetate) showed a strong
tendency to crossover through the AEM toward the anodic compartment. In fact, ca. 20% of the formate and acetate produced during CO₂ reduction was transported from the catholyte across the AEM (defined here as the crossover ratio), whereas most of the uncharged liquid products exhibited almost negligible crossover (Figure 4c). The latter finding is consistent with previous reports for the very small crossover of ethanol through AEMs by diffusion and electroosmotic drag. However, acetaldehyde showed a high crossover ratio that is comparable to those of anionic compounds, particularly at high current densities. Like most research groups, the catholyte was recirculated continuously during the experiment, allowing the accumulation of liquid-phase products for detectable concentrations by easily accessible analytical techniques (e.g. high-performance liquid chromatography, quantitative nuclear magnetic resonance). Since it is well-known that acetaldehyde can be reduced to ethanol, it is likely that a significant amount of acetaldehyde was produced initially and then further reduced to ethanol during the recirculation of the catholyte. Interestingly, an increase in the crossover ratio of acetaldehyde was observed at higher current densities, which may be ascribed to two reasons, (i) the acetaldehyde that crosses over to the anolyte is preserved from the further reduction, and (ii) the consumption of the acetaldehyde in the catholyte for conversion into ethanol is enhanced at concomitant more reductive potentials (i.e., higher current densities).

Furthermore, the aforementioned results illustrate some of the challenges of using the offline quantification of liquid-phase products to gain insights into the mechanisms and kinetics of CO₂ reduction since these figures can be convoluted by crossover effects and consecutive reduction reactions. While a rapid single-pass catholyte would provide significant clarity to the actual acetaldehyde/ethanol production rates, the resulting liquid product concentrations would probably be too low for quantification. In this context, we highlight the use of mass spectrometry-based
techniques to achieve the online real-time detection of low concentration products,\textsuperscript{16} although their integration into GDE-based setups has not been demonstrated to date. While a detailed mechanistic picture was beyond the scope of this work, after quantifying the liquid-phase products in both the catholyte and the anolyte as well as the gas-phase products, we accounted for a total of more than 95\% faradaic efficiency (Figure 4d). This confirmed the suitability of the proposed methodology and allowed us to achieve a thorough understanding of the product distribution over Cu GDEs at high current densities.

It is worth noting that products such as acetaldehyde and ethanol have relatively high vapor pressures and may be evaporated from GDEs into the gas chamber. Zhang et al. has initially demonstrated this evaporation effect on liquid analysis, revealing that volatile liquid products could evaporate through the GDE into the gas chamber.\textsuperscript{17} In our most recent study,\textsuperscript{9} we defined the evaporation ratio between the amount of certain liquid product evaporated from GDEs and the total amount of corresponding liquid product. We further demonstrated that acetaldehyde, n-propanol and ethanol products had non-negligible evaporation ratios through GDEs owing to their high volatility (e.g. the evaporation ratio of n-propanol > 10\%). Therefore, a comprehensive approach should be considered for quantification of liquid products in the catholyte and anolyte as well as the gas chamber evaporated from GDEs.

**pH variations and CO\textsubscript{2} crossover in flowing-catholyte devices**

The effects of (bi)carbonate formation, crossover and CO\textsubscript{2} evolution were also observed in the flowing-catholyte cell operating with a Cu-coated GDE. As shown in Figure 5a, the CO\textsubscript{2}/O\textsubscript{2} ratio in the anodic outlet gas declined from approximately 3 to 2 during the first couple of hours and subsequently remained constant thereafter.\textsuperscript{5} According to Table 2, this observation was due to that
the source of CO₂ evolved in the vicinity of the anode gradually changed from a mixture of HCO₃⁻ and CO₃²⁻ to nearly pure CO₃²⁻ (Figure 5b). This shift is rationalized by the concomitant change of the charge carrier across the AEM as a consequence of the gradual transformation of the catholyte from the initial KHCO₃ solution to K₂CO₃ over the course of the electrolysis. We further verified this transformation by monitoring the pH of the catholyte during the electrolysis, finding an increase of the pH from ~8.3 to >11.8. Thus to resolve start-up issues one could start with a K₂CO₃ electrolyte or simply add KOH to KHCO₃. For commercial applications this initial start-up time is

**Figure 5.** a) Measured flow of CO₂ and O₂ released from anolyte (left axis), and corresponding ratio of CO₂ to O₂ (right axis) at 200 mA/cm². b) Proposed carbon balance paths for CO₂ capture at the cathode/catholyte interface as well as CO₂ evolution from the anolyte when using AEM. c) The total consumed CO₂ flow for carbonate formation and CO₂ reduction to all liquid and gaseous products as well as residual (i.e. unreacted) CO₂ flow were balanced with CO₂ flow fed into the gas chamber. CO₂ utilization rate (right axis) represents the ratio of CO₂ converted into products versus total CO₂ consumption. 1 M KHCO₃ was used as the initial catholyte (50 ml) and anolyte (50 ml) for all the tests. Figures 5a is adapted from and Figure 5b is reproduced with permission from reference 8. Copyright 2020 Royal Society of Chemistry. Figure 5c is based on data from Ref 8.
likely not very relevant, however for short term research tests, starting with a pH 11 carbonate (with K\(^+\), Cs\(^+\), etc) would resolve transient effects.

While some time is required for reaching equilibrium (Figure 5a), we still can employ the same analysis in Figure 2b to compare the anodic CO\(_2\)/O\(_2\) ratio with the \( A \) value determined from gas flow rates and product selectivities. Figure 5c shows this analysis using the selectivity data in Figure 4d along with their accompanying gas flow rates (data in Ref\(^8\)). As expected, our \( A \) values correspond to the proper CO\(_2\)/O\(_2\) ratio (\(~ 2\) as well as being aligned with our catholyte pH measurements. Having the \( A \) value, CO\(_2\)/O\(_2\) ratio, and electrolyte pH all match helps us to validate our data, and gives us an understanding of what is the accuracy of our measurements.

It should be noted that when using KOH as the initial electrolyte, the final catholyte is also transformed to K\(_2\)CO\(_3\) after reaching steady state.\(^8\) This transformation is due to carbonate formation via Equation 5 even at open circuit. (As a useful sidenote, this is how K\(_2\)CO\(_3\) is made commercially\(^{18}\)). In this case, the non-faradaic consumption of CO\(_2\) can greatly exacerbate issues relating to outlet gas flow rates. It can be tantalizing to try to operate in highly alkaline conditions due to increased conductivity and favorable conditions for C-C coupling, however, the rapid equilibration of CO\(_2\) with OH\(^-\) leads to the concomitant decrease in both the electrolyte pH and the outlet gas flow, which complicates the accurate analysis of these systems.

Another significant point with regards to pH is that in a system with a non-equilibrated pH (both in KOH or KHCO\(_3\)), describing applied potentials in terms of the reversible hydrogen electrode (RHE) is ill defined, and a much more precise way to describe applied potentials for high-rate CO\(_2\) reduction work is to use a non-pH dependent reference (i.e., expressing potentials in the standard hydrogen electrode (SHE) scale).
A carbon balance and overall analysis of CO$_2$ consumption

As previously alluded to, closing the carbon balance is essential for the proper analysis of CO$_2$ electrolyzers operating at high current density. In Figure 6a, we converted all our outlet streams to CO$_2$-equivalent flows (e.g. 1 mole ethanol would have the carbon equivalent of 2 moles of CO$_2$). In the Ag case we operated at an inlet flow rate of 100 mL/min, whereas in the Cu case we operated

Figure 6. (a) This figure shows that all the CO$_2$ going into the reactor can be accounted for both the Ag work and the Cu work (Refs. 7 and 8). This figure is equivalent to a mass balance of the inlet carbon source (i.e., it is normalized to utilized CO$_2$ gas flow rather than moles of carbon). (b) CO$_2$ consumption distribution as a function of current density for the MEA cell with Ag and for the flowing-catholyte cell with Cu.
at 45 mL/min, however in both cases our precision was within ~2% with respect to our mass balance of the inlet carbon (in the form of CO₂).

With the verified carbon balance, we also wanted to break down the CO₂ consumption at the cathode into two parts, (i) consumed CO₂ for conversion into products and (ii) consumed CO₂ for neutralizing the hydroxyl groups. Figure 6b shows this breakdown for both the Ag study and the Cu study. Given that the $A$ value was approximately 0.5 (i.e. hydroxyls converted to carbonate) for both cases, we can use Table 1 as a guide to estimate CO₂ consumption. Since we know the selectivity for the Ag work was primarily CO in Figure 1b, we would expect that 50% of our CO₂ consumption was converted and 50% of that was neutralized with OH⁻. Experimentally this holds true as shown in Figure 6b. The Cu work has a much more complicated selectivity (Figure 4d), however a significant amount of ethanol and ethylene production entails that this conversion ratio of consumed CO₂ would be very low.8 As expected, Figure 6b shows that the 30% of consumed CO₂ for conversion to products and 70% of that for neutralization. From a commercial viability standpoint, losing 70% of the reactants due to neutralization is a serious issue, and this problem has been deemed to be the largest issue facing low temperature CO₂ electrolysis currently.19

**The role of different ion-selective membranes**

More recently, we have explored different cell configurations to avoid CO₂ crossover toward the anode. To this end, we investigated the use of a cation exchange membrane (CEM) and a bipolar membrane (BPM) in flowing-catholyte electrolyzers in 1M KHCO₃.9 We demonstrated that the role of ion-selective membrane itself has a minimal effect on catalytic selectivity in three-compartment flow electrolyzers, owing to a similar local reaction environment created at the cathode/catholyte interface. A systematic exploration of the gases emitted from the electrolytes
and variation of ion species in the electrolytes helped us to uncover the effect of different ion-selective membranes on the detailed carbon balance paths for the CO₂ scavenged by the electrolyte.⁹

We found that, independent of the membrane type, nearly the same amount of carbonate was formed at the cathode/catholyte interface, which can be attributed to identical OH⁻ generation rates at a constant current density.⁹ However, in contrast to the AEM, the captured CO₂ is unable to cross over to the anolyte through the CEM or the BPM. For the CEM, K⁺ serves as the main charge carrier (rather than H⁺) crossing through the membrane (Scheme 1a), thus the absorbed CO₂ continuously accumulates as potassium carbonate in the catholyte. The lack of H⁺ supply in the catholyte entails that the pH will always stay significantly high, which prevents CO₂ evolution and degassing. However, CO₂ degassing still occurs near the anode since H⁺ is produced. With a constant consumption of HCO₃⁻ for CO₂ degassing and transportation of K⁺ to the catholyte through the CEM, the concentration of ions (i.e. KHCO₃ concentration) in the anolyte decreased considerably during the electrolysis, resulting in a significant drop in the anolyte conductivity (i.e. a decrease from 70 mS/cm to 10 mS/cm within just 3 hours, anolyte volume 50 mL) and a concomitant increase of the cell voltage. Interestingly, by using a BPM, we discovered negligible

**Figure 7.** Proposed carbon balance paths for the captured CO₂ at the cathode/catholyte interface when using a CEM (left) and BPM (right) with KHCO₃ as the initial catholyte and anolyte. Reproduced with permission from reference 9. Copyright 2020 Royal Society of Chemistry.
variations in conductivity in both the catholyte and the anolyte even over a 10 h electrolysis. In 
this configuration, CO$_3^{2-}$ formed from CO$_2$ neutralization at the cathode/catholyte interface was 
released as gaseous CO$_2$ at the catholyte/membrane interface due to the reaction with H$^+$ constantly 
being supplied from water dissociation in the BPM (Figure 7).

Several technoeconomic studies have explored the impact of different figures of merit (e.g., 
overvoltage, Faradaic efficiency) on the industrial viability of CO$_2$ reduction,$^{20-22}$ but to date there 
are no works that deal specifically with the technoeconomic impact of collecting and recycling 
CO$_2$ released from the anode when an AEM is used. We expect that such a separation of CO$_2$ and 
O$_2$ would incur significant capital and operating costs. The advantage of the BPM is that CO$_2$ 
released from the catholyte stream is free of O$_2$, thus it can be directly recycled into the cathode 
gas chamber for CO$_2$ electrolysis. Consequently, this direct recyclability could potentially provide 
an easy route to reduce the total cost of the carbon source for CO$_2$ reduction.$^6$ However, the use of 
a BPM requires an additional potential for the membrane to dissociate water into H$^+$ and OH$^-$, 
leading to an increased energy requirement from the whole reactor.$^6,23$ To be able to take advantage 
of the easy recyclability of the released CO$_2$ in BPM’s, significant research focus should be put on 
reducing the overpotential for driving water dissociation within these membranes. It is worth 
noting that there have been some recent breakthroughs with significantly reduced membrane 
potentials,$^{24,25}$ thereby showing signs of promise in reducing these energy losses for high-rate CO$_2$ 
reduction with BPMs. There could also be hope for CEMs if certain conditions are met. CEM 
water electrolysis devices can operate without electrolytes, using hot pressing and ionomers to 
ensure ionic conductivity from catalysts on gas diffusion layers.$^{26}$ If CO$_2$ reduction could use this 
approach and engineer the local CO$_2$ reduction catalyst to operate in an alkaline (or at least non-
acidic) environment, this would allow for only protons to cross over the CEM and would resolve
the CO$_2$ crossover issue. However, there are considerable challenges with this approach, especially in regard to the selectivity of CO$_2$ reduction over water electrolysis to H$_2$.

**Conclusions**

The major point this perspective is trying to portray is that detailed analysis of CO$_2$ electrolysis reactors can not only allow greater insights into the system but also provide multiple checks to validate the accuracy and precision of the catalytic selectivity. Through this analysis, we show the complexities of properly measuring gas product selectivities due to outlet flow issues, and the importance of this issue cannot be understated since improper measurements tend to lead to an overestimation of selectivities. We demonstrate that the cathodic CO$_2$ consumption by the reaction with hydroxyl ions is not only the leading cause of variations in gas outlet flow rate, but also leads to significant loss of the CO$_2$ out the anode when using an anion exchange membrane. While we show that cation exchange and bipolar membranes help alleviate this issue, they have other issues complicating their potential use. Thus, through this comprehensive analysis, we demonstrate that understanding and developing a commercially viable device has many interrelated issues entailing that device engineering will be potentially even more challenging than the electrocatalysis of CO$_2$ reduction itself.

**ASSOCIATED CONTENT**

**Supporting Information.**

There is no supporting information accompanying this work.

**AUTHOR INFORMATION**

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡ These authors contributed equally.

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Gastón O. Larrazábal studied Chemical Engineering at Simón Bolívar University in Venezuela and earned his doctorate from ETH Zurich in 2018 under the supervision of Prof. Javier Pérez-Ramírez. He then moved to the Technical University of Denmark, where he is currently a Marie
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**Brian Seger** obtained his Ph.D. with Prashant Kamat at Notre Dame in 2009. After post-docs in University of Queensland and at the Technical University of Denmark, he became an Assistant Professor at DTU in 2014 and is currently an Associate Professor as of 2018. His early research focused on graphene and photoelectrochemistry, but more recently, his focus has shifted to CO₂ electrolysis and other electrosynthesis reactions.
REFERENCES


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