Insights into the Carbon Balance for CO₂ Electroreduction on Cu using Gas Diffusion Electrode Reactor Designs

Ming Ma,† Ezra L. Clark,† Kasper T. Therkildsen,‡ Sebastian Dalsgaard,‡ Ib Chorkendorff‡ and Brian Seger†,*

†Surface Physics and Catalysis (Surfcat) Section, Department of Physics, Technical University of Denmark, 2800 Kgs Lyngby, Denmark
‡Siemens A/S, RC-DK SI, Diplomvej 378, 2800 Kgs. Lyngby, Denmark

*Author to whom correspondence should be addressed.

E-mail address: brse@fysik.dtu.dk

Tel.: +45 45253174
**Materials**

Potassium bicarbonate (KHCO$_3$, ≥99.95%) and potassium hydroxide hydrate (NaOH·xH$_2$O, 99.995%, Suprapur®) were purchased from Sigma Aldrich. All chemicals were used in this study without further purification. Anion exchange membrane (AEM, Fumasep FAA-3-PK-75) and gas-diffusion electrode (GDE, Sigracet 39 BC) were purchased from Fuel Cell Store. Iridium dioxide (IrO$_2$) purchased from Dioxide Materials was used as anode in CO$_2$ flow electrolyzers.

**Catalysts fabrication and characterization**

In this work, Cu catalysts were deposited on the top of microporous layer of gas-diffusion electrodes by direct current magnetron sputtering from a Cu target. In order to obtain the accurate deposition rate of Cu, Cu films were deposited on Si substrates, and then the cross-sectional SEM of Cu film/Si was performed. Figure S1 shows the cross-sectional SEM image of Cu film/Si deposited for 50 min, which indicates the fact that ~200 nm thick Cu film was synthesized, corresponding to a Cu deposition rate of ~4 nm/min.

![Figure S1. Cross-sectional SEM image of Cu layer deposited on Si by magnetron sputtering for 50 min.](image-url)
Figure S2. SEM images of microporous carbon layers (a) of gas-diffusion electrodes and Cu catalysts (b) coated on microporous carbon layers of gas-diffusion electrodes.

Figure S3. Digital image of Cu deposited on a gas-diffusion electrode.

Figure S4. XRD patterns of Cu coated on a gas-diffusion electrode (Sigracet 39 BC). XRD measurements were performed using Cu Kα radiation.
**Faradaic efficiency calculation**

The Faradaic efficiency (FE) of product can be calculated according to the below equation:

\[
FE \, (\%) = \frac{Q_{\text{product}}}{Q_{\text{tot}}} \times 100\%  \tag{S1}
\]

where \(Q_{\text{product}}\) and \(Q_{\text{tot}}\) are charge transferred for product formation and charge passed through the working electrode, respectively.

Based on the above equation, the detailed calculation for Faradaic efficiency of gas product could be written as:

\[
FE \, (\%) = \frac{n \times C_{\text{product}} \times \varpi t \times \frac{P_o}{RT} \times F}{I \times t} \times 100\%  \tag{S2}
\]

where \(C_{\text{product}}\) and \(n\) are the concentration of gas product measured by GC and the number of electrons required for producing one molecule of the related gas product, respectively. \(\varpi\) is gas flow rate, \(t\) is the electrolysis time, \(P_o\) is ambient pressure, \(F\) is Faraday constant, \(R\) is ideal gas constant, \(T\) is absolute temperature, and \(I\) is current.
High local pH at cathode/electrolyte interface

In the electrocatalytic CO\textsubscript{2} reduction process, CO\textsubscript{2} can be converted into a variety of gas and liquid products when combined with water on metal surfaces in aqueous solutions according to the reactions\textsuperscript{1-3}:

\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- &\rightarrow \text{CO} + 2\text{OH}^- \quad (-0.11 \text{ V vs. RHE}) \quad (\text{S3}) \\
\text{CO}_2 + 6\text{H}_2\text{O} + 8\text{e}^- &\rightarrow \text{CH}_4 + 8\text{OH}^- \quad (0.17 \text{ V vs. RHE}) \quad (\text{S4}) \\
2\text{CO}_2 + 8\text{H}_2\text{O} + 12\text{e}^- &\rightarrow \text{C}_2\text{H}_4 + 12\text{OH}^- \quad (0.08 \text{ V vs. RHE}) \quad (\text{S5}) \\
\text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- &\rightarrow \text{HCOO}^- + \text{OH}^- \quad (-0.03 \text{ V vs. RHE}) \quad (\text{S6}) \\
\text{CO}_2 + 5\text{H}_2\text{O} + 6\text{e}^- &\rightarrow \text{CH}_3\text{OH} + 6\text{OH}^- \quad (0.03 \text{ V vs. RHE}) \quad (\text{S7}) \\
2\text{CO}_2 + 9\text{H}_2\text{O} + 12\text{e}^- &\rightarrow \text{C}_2\text{H}_5\text{OH} + 12\text{OH}^- \quad (0.09 \text{ V vs. RHE}) \quad (\text{S8})
\end{align*}

The competing H\textsubscript{2} evolution is an unavoidable reaction in CO\textsubscript{2} electroreduction. Thus, water is reduced to H\textsubscript{2} on the surface of catalyst according to the reaction\textsuperscript{1}:

\begin{align*}
2\text{H}_2\text{O} + 2\text{e}^- &\rightarrow \text{H}_2 + 2\text{OH}^- \quad (0 \text{ V vs. RHE}) \quad (\text{S9})
\end{align*}

Thus, OH\textsuperscript{-} ions are produced at the cathode/electrolyte interface in the cathodic reactions (Equation (3-9)), leading to an increased pH near the surface of cathode.\textsuperscript{2,3}

Reaction of CO\textsubscript{2} and OH\textsuperscript{-} near cathode surface

In addition to the electrochemcial CO\textsubscript{2} reduction, CO\textsubscript{2} also can react with OH\textsuperscript{-} created at the electrode/electrolyte interface by cathodic reactions (Equation (S3-S9)) using KHCO\textsubscript{3} electrolye in our three-compartment flow electrolyzer. Of particular note, CO\textsubscript{2} not only reacts with OH\textsuperscript{-} generated by cathodic reactions (Equation (S3-S9)) but also reacts with OH\textsuperscript{-} derived from electrolyte during CO\textsubscript{2} electroreduction in KOH solutions.
CO$_2$ reduction and flowrate measurement of gas outlet after cell

The electroreduction of CO$_2$ was conducted in a three-compartment flow electrolyzer made from Teflon at ambient temperature and pressure. In the cell, catholyte and anolyte flow compartments are separated by an anion exchange membrane, along with continuous flow electrolyte (each bottle is filled with 50 ml electrolyte), as shown in Figure S5. In addition, CO$_2$ was fed into gas chamber at a constant flowrate of 45 ml/min, and then gaseous CO$_2$ could pass through the gas-diffusion layer, diffusing into the surface of the catalyst which was immesed into electrolyte.

During the electroreduction of CO$_2$, the gas mixture (gas outlet) after reactor was directly vented into the gas-sampling loop of a GC for periodic quantification of gas products. In order to get the reliable Faradaic efficiency of gas pruduts, the volumetric flowrate of gas outlet (gas mixture) after reactor was also measured by flow meter during the CO$_2$ reduction, as displayed in Figure S5. Gas outlet flowrate from the gas chamber after CO$_2$ reduction was plotted at various current densities for 1 M KHCO$_3$, 1 M KOH and 5 M KOH electrolyte, respectively (Figure S6). As noted in Figure S6, an obvious decrement in the flowrate of outlet was detected with increasing current densities in the same electrolyte. Here, we calculated the decrease rate of outlet flowrate as a function of current density in 1 M KHCO$_3$, 1 M KOH and 5 M KOH electrolyte, respectively (slope values in Figure S6).

In addition, gas outlet flowrate (or CO$_2$ consumption) should also be correlated with the surface area of Cu coated on GDE. Thus, a fixed geometric surface area (2 cm$^2$) of Cu layer was utilized for all the experiments in this study.
**Figure S5.** The schematic illustration of flow cell setup for reduction of CO$_2$.

**Figure S6.** Gas outlet flowrates from the gas chamber after CO$_2$ reduction at various current densities in 1 M KHCO$_3$ (pH 8.33), 1 M KOH (pH 13.61) and 5 M KOH electrolyte, respectively (geometric surface area of Gu layer on GDE is 2 cm$^2$).
**CO₂ reduction performance**

Based on the aforementioned flowrate measurement, the volumetric flowrate of gas outlet (gas mixture) after reactor was monitored by flow meter in the course of the CO₂ reduction, and then Faradaic efficiencies of gas products were calculated based on the monitored outlet flowrate. Figure S7 shows the typical catalytic selectivity of gas products over time in 1 M KHCO₃ (a) and 1 M KOH (b) at 200 mA/cm², respectively. The average catalytic selectivity of gas products in Figure 2 was taken during 2.5 h CO₂ reduction electrolysis with the exception of 5 M KOH (fast catalytic deactivation occurred in 5 M KOH due to GDEs lost hydrophobicity during operation in extremely high concentration of KOH⁴).

![Figure S7. Catalytic selectivity of gas products over Cu catalysts in 1 M KHCO₃ (a) and 1 M KOH (b) at 200 mA/cm², respectively. All the tests were performed using 70 nm Cu layer coated on GDEs.](image-url)
Analysis of gas released from anolyte

CO₂ reduction with the competing H₂ evolution takes place on the surface of cathode while O₂ evolution happens on the anode surface. Interestingly, H⁺ created at the anode/electrolyte interface by anodic reaction (Equation 3) could be neutralized by HCO₃⁻ or CO₃²⁻ after using KHCO₃ electrolyte. According to the reactions (Equation 7-8), gaseous CO₂ should be also released from KHCO₃ anolyte, accompanying with O₂. The flow cell setup for reduction of CO₂ in Figure S8 was used to analyse the gases released from anolyte. Specifically, gases released from anolyte were diluted with N₂ carrier gas at a constant flowrate, and then directly went into the gas sampling-loop of the GC to quantify the gases periodically. In addition, the volumetric gas flowrate released from anolyte was also monitored by flow meter over the CO₂ reduction electrolysis (Figure S8).

After using 1 M KHCO₃ as electrolyte for CO₂ reduction, CO₂ released from anolyte was detected via GC, accompanying with O₂ at various current densities (Figure S9). In addition, the related CO₂/O₂ ratio released from anolyte over CO₂ reduction electrolysis at current densities of 150 mA/cm², 250 mA/cm², 300 mA/cm² using 1 M KHCO₃ as the initial catholyte and anolyte was also presented in Figure S9.

In contrast, only O₂ (~1.5 ml/min) was detected from anolyte at 200 mA/cm² over 6 h electrolysis after using 1 M KOH (Figure S11), due to a slow transition of electrolyte caused by the large amount of KOH (each bottle was filled with 50 ml 1 M KOH as initial catholyte and anolyte). For observing a relatively rapid electrolyte transition, each bottle (initial catholyte and anolyte) was filled with 20 ml 1 M KOH, discovering the initial CO₂ generation from anolyte after 2.5 h electrolysis, as shown in Figure 6.
Figure S8. The schematic illustration of flow cell setup for analysing gases released from anolyte during CO$_2$ reduction.
Figure S9. The flowrate of O\(_2\) and CO\(_2\) released from anolyte and the related CO\(_2\)/O\(_2\) ratio over CO\(_2\) reduction electrolysis at current densities of (a) 150 mA/cm\(^2\), (b) 250 mA/cm\(^2\), (c) 300 mA/cm\(^2\) using 1 M KHCO\(_3\) as the initial catholyte and anolyte (each both was filled with 50 ml 1 M KHCO\(_3\) electrolyte).
Figure S10. CO$_2$/O$_2$ flowrate ratio released from anolyte as a function of time at various current densities after using 1 M KHCO$_3$ as the initial catholyte and anolyte (each bottle was filled with 50 ml 1 M KHCO$_3$ electrolyte).

Figure S11. The flowrate of O$_2$ and CO$_2$ released from anolyte over CO$_2$ reduction electrolysis in 1 M KOH (each bottle was filled with 50 ml 1 M KOH as initial catholyte and anolyte).
Theoretical $O_2$ and $CO_2$ flowrate released from anolyte

If charge passed through anode is only used for $O_2$ evolution reaction, $O_2$ flowrate released in anolyte can be expressed as:

$$\phi (O_2) = \frac{Q_{tot}}{nF} \times \frac{RT}{P_o} \quad (S10)$$

where $Q_{tot}$ and $n$ are charge passed through the anode electrode and the number (here is 4) of holes required for producing one $O_2$ molecule, respectively. $F$ is Faradaic constant, $R$ is ideal gas constant, $T$ is absolute temperature, and $P_o$ is ambient pressure.

If bicarbonate or carbonate is the only charge-carrier via anion exchange membrane, the $CO_2$ flowrate should be $4 \times \phi (O_2)$ and $2 \times \phi (O_2)$ according to the Equation (7) and Equation (8), respectively. Based on these equations, the flowrates for $CO_2$ and $O_2$ were calculated at various current densities (electrode surface area is 2 cm$^2$), as shown in Figure S12.

![Graphs showing the estimated flowrates of $O_2$ and $CO_2$ released from anolyte as a function of current density based on the assumption of that the only charge-carrier via AEM is carbonate (a) or bicarbonate (b).](image)

Figure S12. The estimated flowrates of $O_2$ and $CO_2$ released from anolyte as a function of current density based on the assumption of that the only charge-carrier via AEM is carbonate (a) or bicarbonate (b).
Carbon balance calculation

The unreacted CO₂ (residual CO₂) flowrate in the gas outlet (gas mixture) after reactor can be expressed as:

$$ \Phi_{\text{residual CO}_2} = \Phi_{\text{outlet}} - (\Phi_{\text{CO}} + \Phi_{\text{CH}_4} + \Phi_{\text{C}_2\text{H}_4} + \Phi_{\text{H}_2}) $$  \hspace{1cm} (S11)

where $\Phi_{\text{outlet}}$ is the flowrate of gas outlet from the gas chamber after CO₂ reduction. $\Phi_{\text{CO}}$, $\Phi_{\text{CH}_4}$, $\Phi_{\text{C}_2\text{H}_4}$ and $\Phi_{\text{H}_2}$ are the gas flowrate of CO, CH₄, C₂H₄ and H₂ in the gas outlet from gas chamber during electrolysis, respectively.

The consumed CO₂ flowrate which is electrochemically converted into all gas products (CO, C₂H₄ and CH₄) can be written as:

$$ \Phi_{\text{CO}_2 \text{ to gas}} = \Phi_{\text{CO}} + \Phi_{\text{CH}_4} + 2\Phi_{\text{C}_2\text{H}_4} $$  \hspace{1cm} (S12)

The consumed CO₂ flowrate for electrocatalytic reduction to all liquid products (such as ethanol and formate) can be written as:

$$ \Phi_{\text{CO}_2 \text{ to liquid}} = \Phi_{\text{C}_1} + \Phi_{\text{C}_2} + \Phi_{\text{C}_3} $$  \hspace{1cm} (S13)

where $\Phi_{\text{C}_1}$, $\Phi_{\text{C}_2}$, and $\Phi_{\text{C}_3}$ are the consumed CO₂ flowrate for forming C₁, C₂ and C₃ liquid products, respectively.

CO₂ reduction at high reaction rates, CO₂ conversion into gas products ($> C_1$) and liquid products could reduce the gas outlet flowrate. In addition, the CO₂ consumption at high current via the reaction between OH⁻ and CO₂ could significantly contribute to the decrease of the total gas outlet flowrate (Figure S6). Thus, the carbon element from CO₂ inlet flowrate should be eventually balanced by the below equation:

$$ \Phi_{\text{inlet CO}_2} = \Phi_{\text{residual CO}_2} + \Phi_{\text{CO}_2 \text{ to gas}} + \Phi_{\text{CO}_2 \text{ to liquid}} + \Phi_{\text{OH}^-} $$  \hspace{1cm} (S14)

where $\Phi_{\text{OH}^-}$ is the consumed CO₂ flowrate via the reaction with OH⁻ (Equation 1 or 2).
Table S1. Carbon balance and related CO₂ utilization rate (ratio of CO₂ used in products formation to total CO₂ consumption) in 1 M KHCO₃.

<table>
<thead>
<tr>
<th>J (mA/cm²)</th>
<th>CO₂ to gas (ml/min)</th>
<th>CO₂ to liquid (ml/min)</th>
<th>OH⁻ (ml/min)</th>
<th>residual CO₂ (ml/min)</th>
<th>CO₂ utilization rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0.749</td>
<td>0.267</td>
<td>2.4898</td>
<td>42.0</td>
<td>29.0</td>
</tr>
<tr>
<td>200</td>
<td>0.922</td>
<td>0.371</td>
<td>3.11156</td>
<td>40.8</td>
<td>29.4</td>
</tr>
<tr>
<td>250</td>
<td>1.169</td>
<td>0.4226</td>
<td>3.80596</td>
<td>39.735</td>
<td>29.5</td>
</tr>
<tr>
<td>300</td>
<td>1.379</td>
<td>0.516</td>
<td>4.50385</td>
<td>38.616</td>
<td>29.6</td>
</tr>
</tbody>
</table>

(∅ CO₂ to gas: the consumed CO₂ flowrate which is electrochemically converted into all gas products (CO, C₂H₄ and CH₄); ∅ CO₂ to liquid: the consumed CO₂ flowrate for electrocatalytic reduction to all liquid products (such as ethanol and formate); ∅ OH⁻: the consumed CO₂ flowrate via the reaction with OH⁻; ∅ residual CO₂: the unreacted CO₂ (residual CO₂) flowrate in the gas outlet (gas mixture) after reactor.)

Table S2. Carbon balance and related CO₂ utilization rate in 1 M KOH.

<table>
<thead>
<tr>
<th>J (mA/cm²)</th>
<th>CO₂ to gas (ml/min)</th>
<th>CO₂ to liquid (ml/min)</th>
<th>OH⁻ (ml/min)</th>
<th>residual CO₂ (ml/min)</th>
<th>CO₂ utilization rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0.776</td>
<td>0.301</td>
<td>3.393</td>
<td>40.53</td>
<td>24.1</td>
</tr>
<tr>
<td>200</td>
<td>0.908</td>
<td>0.357</td>
<td>4.055</td>
<td>39.68</td>
<td>23.8</td>
</tr>
<tr>
<td>250</td>
<td>1.212</td>
<td>0.411</td>
<td>4.767</td>
<td>38.61</td>
<td>25.4</td>
</tr>
<tr>
<td>300</td>
<td>1.399</td>
<td>0.48</td>
<td>5.344</td>
<td>37.777</td>
<td>26.0</td>
</tr>
</tbody>
</table>

(Electrochemical impedance spectroscopy measurement)

To determine the solution resistance (Rs) in this work, potentiostatic electrochemical impedance spectroscopy (PEIS) was performed on Cu deposited GDE in a three-compartment flow electrolyzer at room temperature and atmospheric pressure. During the experiments, the gas flow compartment was continuously fed with CO₂ at a flow rate of 45 ml/min. The impedance spectra were recorded using a potentiostat (Biologic) in the frequency range from 200 kHz to 10 mHz with an amplitude of 10 mV at fixed potentials. It should be noted that the variations in local ion species and concentration near surface of cathode at high-rate cathodic
reactions could make the local reaction environment complicated, and also lead to a distinct conductivity near cathode at high current densities compared to the measured results by PEIS. Even if a very tiny difference in resistance, a very high current could lead to an un-negligible variation in IR-corrected potentials. Thus, while the fixed distance between reference and cathode was less than 2 mm in this work, it is still difficult to get the accurate cathode potentials at relatively high current densities (for instance, the IR-corrected potentials at 300 mA/cm² in Table S3).

Figure S13. Nyquist plots of Cu deposited GDE in 1 M KHCO₃ aqueous solution (a) and 1 M KOH aqueous solution (b) at various potentials.

Figure S14. Current densities as a function of potential in 1 M KHCO₃ aqueous solution (a) and 1 M KOH aqueous solution (b) (The potentials were not IR-corrected).
Figure S15. Applied potentials as a function of time at 200 mA/cm² in 1 M KHCO₃ electrolyte.

**Table S3.** IR-corrected potentials in 1 M KOH

<table>
<thead>
<tr>
<th>Current (mA)</th>
<th>R (Ω)</th>
<th>Corrected V vs. SHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.82</td>
<td>-1.61238</td>
</tr>
<tr>
<td>300</td>
<td>0.82</td>
<td>-1.6375</td>
</tr>
<tr>
<td>400</td>
<td>0.82</td>
<td>-1.64313</td>
</tr>
<tr>
<td>500</td>
<td>0.82</td>
<td>-1.6455</td>
</tr>
<tr>
<td>600</td>
<td>0.82</td>
<td>-1.648</td>
</tr>
</tbody>
</table>

**Table S4.** IR-corrected potentials in 1 M KHCO₃.

<table>
<thead>
<tr>
<th>Current (mA)</th>
<th>R (Ω)</th>
<th>Corrected V vs. SHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>1.38</td>
<td>-1.535</td>
</tr>
<tr>
<td>300</td>
<td>1.38</td>
<td>-1.6075</td>
</tr>
<tr>
<td>400</td>
<td>1.38</td>
<td>-1.63</td>
</tr>
<tr>
<td>500</td>
<td>1.38</td>
<td>-1.6425</td>
</tr>
<tr>
<td>600</td>
<td>1.38</td>
<td>-1.595</td>
</tr>
</tbody>
</table>
**Liquid products**

After completion of CO\textsubscript{2} reduction electrolysis, liquid-phase products were analyzed by a high-performance liquid chromatography (not in-situ analysis). In this work, both catholyte and anolyte in the given reservoirs were collected for quantification of liquid products due to that a part of liquid products transported from catholyte to anolyte via AEM (Figure S16). Here, the crossover ratio of one certain liquid product formed on cathode via AEM can be calculated according to the below equation:

\[
\text{Crossover ratio (\%)} = \frac{N_{\text{liquid in anolyte}}}{N_{\text{liquid in anolyte}} + N_{\text{liquid in catholyte}}} \times 100\% \quad (S15)
\]

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. Thus, the above equation can be used to calculate a ratio between the amount of one certain liquid product crossed to anolyte through AEM and the total amount of corresponding liquid product generated on cathode.

It should be noted that the volume of catholyte and anolyte slightly varied after about 2.5 h electrolysis (catholyte volume slightly decreased with increased anolyte), due to the anion species hydrated with water molecules transport from catholyte to anolyte via AEM as charge carriers. Thus, for getting accurate selectivity of liquid products in this study, we also measured volume of catholyte and anolyte after electrolysis, respectively.

![Figure S16. Faradaic efficiencies for all detected liquid products based on catholyte (a) and anolyte (b) in 1 M KHCO\textsubscript{3} at various current densities, respectively.](image)

Figure S16. Faradaic efficiencies for all detected liquid products based on catholyte (a) and anolyte (b) in 1 M KHCO\textsubscript{3} at various current densities, respectively.
Figure S17. Crossover ratio of liquid products via AEM in 1 M KHCO$_3$ (a) and 1 M KOH (b) during about 2.5 h CO$_2$ reduction at various current densities, respectively.

Table S5. Faradaic efficiencies for liquid products in 1 M KHCO$_3$.

<table>
<thead>
<tr>
<th>J (mA/cm$^2$)</th>
<th>Glycolaldehyde (%)</th>
<th>Formate (%)</th>
<th>Acetate (%)</th>
<th>Ethylene Glycol (%)</th>
<th>Acetaldehyde (%)</th>
<th>Allyl Alcohol (%)</th>
<th>Ethanol (%)</th>
<th>n-Propanol (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0.0982</td>
<td>4.321</td>
<td>2.504</td>
<td>0.325</td>
<td>0.335</td>
<td>1.7733</td>
<td>14±0.3</td>
<td>4.511</td>
</tr>
<tr>
<td>200</td>
<td>0.1163</td>
<td>3.023</td>
<td>3.143</td>
<td>0.266</td>
<td>0.3</td>
<td>1.625</td>
<td>17.2±0.86</td>
<td>4.382</td>
</tr>
<tr>
<td>250</td>
<td>0.1322</td>
<td>2.042</td>
<td>3.0953</td>
<td>0.189</td>
<td>0.3</td>
<td>1.206</td>
<td>17.9±0.88</td>
<td>3.756</td>
</tr>
<tr>
<td>300</td>
<td>0.0958</td>
<td>1.906</td>
<td>3.790</td>
<td>0.152</td>
<td>0.21</td>
<td>1.0499</td>
<td>18.74±0.9</td>
<td>3.132</td>
</tr>
</tbody>
</table>

Table S6. Faradaic efficiencies for liquid products in 1 M KOH.

<table>
<thead>
<tr>
<th>J (mA/cm$^2$)</th>
<th>Glycolaldehyde (%)</th>
<th>Formate (%)</th>
<th>Acetate (%)</th>
<th>Ethylene Glycol (%)</th>
<th>Acetaldehyde (%)</th>
<th>Allyl Alcohol (%)</th>
<th>Ethanol (%)</th>
<th>n-Propanol (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0.8</td>
<td>3.705</td>
<td>2.871</td>
<td>0.25</td>
<td>0.56</td>
<td>1.5</td>
<td>16.74±0.87</td>
<td>4.5</td>
</tr>
<tr>
<td>200</td>
<td>0.6</td>
<td>2.1</td>
<td>2.8843</td>
<td>0.1404</td>
<td>0.26</td>
<td>1.105</td>
<td>19.7±0.95</td>
<td>3.61</td>
</tr>
<tr>
<td>250</td>
<td>0.504</td>
<td>2.1</td>
<td>1.7735</td>
<td>0.11</td>
<td>0.25</td>
<td>1.1</td>
<td>18.44±0.88</td>
<td>3.84</td>
</tr>
<tr>
<td>300</td>
<td>0.462</td>
<td>1.9</td>
<td>2.581</td>
<td>0.11</td>
<td>0.7</td>
<td>1</td>
<td>18.4±0.2</td>
<td>3.04</td>
</tr>
</tbody>
</table>
**Effect of CO$_2$ inlet flowrate**

Effect of CO$_2$ inlet flowrate on the evaluation of Faradaic efficiencies for gas products in flow electrolyzers with and without the consideration of CO$_2$ consumption was explored in 1 M KOH electrolyte at 300 mA/cm$^2$. With decreasing the CO$_2$ inlet flowrate, gas products concentration in the gas chamber of the reactor enhanced significantly such as the detected CO concentration in Table S4.

**Table S7.** Detected CO concentration by GC under different CO$_2$ inlet flowrates in 1 M KOH electrolyte at 300 mA/cm$^2$.

<table>
<thead>
<tr>
<th>CO$_2$ inlet flow (ml/min)</th>
<th>CO concentration in the gas compartment of reactor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>1.722336</td>
</tr>
<tr>
<td>30</td>
<td>2.85054</td>
</tr>
<tr>
<td>20</td>
<td>4.219992</td>
</tr>
<tr>
<td>15</td>
<td>5.45034</td>
</tr>
</tbody>
</table>

Without considering the CO$_2$ consumption (using uncorrected flow), the Faradaic efficiencies of gas products can be overestimated. Here, we defined the overestimation ratio of catalytic selectivity (only for gas products) without CO$_2$ consumption consideration by the following equation:

$$\text{Overestimation ratio (})% = \frac{FE_{\text{inlet flow}} - FE_{\text{outlet flow}}}{FE_{\text{outlet flow}}} \times 100\% \quad (S16)$$

where, $FE_{\text{outlet flow}}$ and $FE_{\text{inlet flow}}$ are the Faradaic efficiency of gas product with and without the consideration of CO$_2$ consumption, respectively. After considering the calculation equation S2 for Faradaic efficiency of gas product, the equation S16 can be rewritten as:

$$\text{Overestimation ratio (})% = \frac{\phi_{\text{inlet}} - \phi_{\text{outlet}}}{\phi_{\text{outlet}}} \times 100\% \quad (S17)$$

Where, $\phi_{\text{inlet}}$ and $\phi_{\text{outlet}}$ are the CO$_2$ inlet flowrate before reactor and a gas mixture outlet flowrate after reactor, respectively. Thus, we got the overestimation ratio as a function of CO$_2$ inlet flowrate in 1 M KOH electrolyte at 300 mA/cm$^2$, as shown in Figure S18.
Figure S18. Overestimation ratio of gas product selectivity without CO$_2$ consumption consideration as a function of CO$_2$ inlet flowrate in 1 M KOH electrolyte at 300 mA/cm$^2$.

REFERENCES


