Evaluating the Effects of Membranes, Cell Designs, and Flow Configurations on the Performance of Cu-GDEs in Converting CO₂ to CO

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ABSTRACT: In this study, we evaluate the effect of cell configuration parameters on electrochemical reduction of CO₂ using Cu gas-diffusion electrodes (Cu-GDEs), including the use of proton- or anion-exchange membranes, the CO₂ flow configuration, and the Nafion content used in the ink formulation to prepare the Cu-GDEs. Using a cell configuration (i) containing a Sustainion membrane, (ii) allowing a liquid flow of catholyte and anolyte, and (iii) providing convective supply of CO₂ in a flow-through mode, outstanding faradaic efficiencies toward carbon monoxide (FE CO = ∼85%, at −0.88 V vs RHE, and 50 mA cm⁻²) were obtained. We attribute this performance to an efficient desorption and transport of CO to the exit of the reactor, in agreement with the remarkably low FE toward ethylene at the applied electrochemical potentials. Most importantly, in this configuration and optimizing the Nafion content in the ink formulation to 10 wt %, cell performance could be maintained for at least 10 h of continuous operation at the high FE of CO near 85%.

KEYWORDS: CO₂ gas-diffusion electrode, flow-through configuration, Sustainion, Nafion

1. INTRODUCTION

To decrease carbon dioxide (CO₂) emissions to the atmosphere and to fulfill the Paris climate agreement require the development of sustainable chemical technologies using renewable electricity and CO₂ and H₂O as resources for fuels and base chemicals. Besides improvement of technology for capturing and storing CO₂, the energy efficiency of technology for the electrochemical production of valuable chemicals and fuels, such as carbon monoxide (CO) and ethylene (C₂H₄), needs to be improved. Recently, gas-diffusion electrodes (GDEs) have been demonstrated to operate at unprecedentedly high current densities (>1 A/cm²), as required for industrial-scale operation, with high selectivity toward value-added products. These GDEs are composed of a diffusion layer, a microporous layer, and a catalyst layer (CL), allowing the deposition of different metal-based electrocatalysts. Gold and silver favor CO formation, while copper has the unique ability to produce hydrocarbons and oxygenated compounds, such as ethylene and ethanol with high selectivity. Despite the many benefits of GDE-based systems, some challenges such as flooding of the CL (mainly caused by pressure imbalance across the GDE, gas feed turbulence, and electrowetting effects) and salt (KHCO₃) precipitation due to the reaction of CO₂ with OH⁻ generated at the cathode, remain problematic and are still the subject of investigation.

In terms of electrochemical cells applied for CO₂RR, continuous flow cells have mostly been chosen due to their versatility, while operated with none (zero gap), one (catholyte free), or two electrolyte (catholyte/anolyte) compartments and with or without the addition of membranes. The main differences between these configurations rely on the nature of the reactions occurring in the micro-environment of the CL and the management of aqueous species near the electrode surface. In zero-gap systems, also known as membrane electrode assemblies, an intimate contact between the CL and the solid membrane is achieved. Polymer electrolyte membranes are widely used in fuel cells and water electrolysis, and play an important role in transporting ionic species (and solvation water) to the CL. These membranes are classified into cation exchange membranes (CEMs)—promoting trans-

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port of cations such as $\text{H}^+$, $\text{K}^+$), anion exchange membranes (AEMs—promoting transport of anions ($\text{OH}^-$, $\text{HCO}_3^-$, $\text{CO}_3^{2-}$), and bipolar membranes (BPMs—promoting water dissociation, splitting protons, and anions at different sides).\textsuperscript{25,26} CEMs, such as Nafion-based, present strong acidity and high ionic conductivity.\textsuperscript{27} They can prevent anion crossover to the anode but might promote proton transfer to the catalyst surface, decreasing the pH and favoring the hydrogen evolution reaction.\textsuperscript{28} Anionic exchange membranes can overcome the issues of high acidity near the surface by removing/transferring only anions, boosting efficiency in the CO$_2$RR. Indeed, most of the state-of-the-art CO$_2$ electrolyzers make use of AEMs in their electrode assembly, reaching partial current densities over 1 A/cm$^2$ toward multi-carbon products.\textsuperscript{11,18} Nevertheless, stability issues such as membrane dehydration and carbonation (formation of carbonate crystals due to the reaction of CO$_2$ and OH$^-$) yet need to be resolved.\textsuperscript{29,30}

Even though zero-gap assemblies present lower cell resistance and allow for broader industrial applicability, the reactor configurations containing two electrolyte channels (catholyte and anolyte) are usually preferred by researchers due to versatility and ease of assembly for testing GDE-based systems at high current densities.\textsuperscript{31} This configuration involves the diffusion of CO$_2$ through the pores of the GDE up to the solid—liquid interface, known as the triple-phase boundary (TPB), where CO$_2$ is suggested to dissolve in the aqueous electrolyte and is further transformed to the desired products.\textsuperscript{21,32} Optimized water management and stability in the pressure balance are essential to maintain the optimized TPB.\textsuperscript{32,33} These are also essential process parameters to prevent electrolyte intrusion into the deeper layers of the GDE, resulting in catalyst flooding and further liquid evaporation and salt formation, blocking the access of CO$_2$ to the catalyst surface.\textsuperscript{34,35}

Conventional metal-coated GDE systems provide CO$_2$ supply via the backside of the GDE (see Figure 1), also known as the flow-by operation, where CO$_2$ diffuses through the porous structure to the boundary layer for reaction. The product once formed enters the gas flow via back-diffusion.\textsuperscript{35} In such a configuration, flooding behavior is often assigned to water intrusion (see the illustration in Figure 1).

An alternative to reduce issues of CO$_2$ depletion at the catalyst surface at high current densities, and to efficiently feed carbon dioxide to the catalyst surface, is via convective CO$_2$ supply, also identified as the flow-through regime (Figure 1).

In this modified-catholyte/anolyte configuration, the outlet gas channel is closed and a positive pressure forces carbon dioxide through the pores to the surface, and after reaction, the products (possibly dissolved) are transported with the electrolyte and separated from the liquid phase in a degassing unit. The main advantages of this cell configuration are (i) convective reactant supply to the catalyst surface preventing CO$_2$ concentration gradients, (ii) improved mixing at the vicinity of catalyst particles due to bubble-induced flow patterns, and (iii) fast product removal. Up to date, only few studies have explored flow-through configurations. For example, Duarte and co-workers compared silver-coated GDEs in both flow-by and flow-through regimes, achieving higher partial current densities toward CO under flow-through conditions (over 200 mA/cm$^2$ at $-2.8$ V vs Ag/AgCl), which was attributed to the enhanced CO$_2$ supply. However, instability issues were still observed, leading to decline in cell performance within the first hour, explained by electrolyte crystallization, inhibiting CO$_2$ flow.\textsuperscript{36} Similar conclusions were drawn by Han and co-workers in their study using copper-gauze in alkaline (10 M KOH) solutions for CO and CO$_2$ reduction. They ascribed the superior performance of flow-through configurations to efficient gas, electron, and ion transfer to the catalyst surface.\textsuperscript{37} These studies point out that further optimization of process parameters can lead to enhanced performance of GDEs,\textsuperscript{38} if, for example, large overpotentials by bubbles generated in turbulent flow regimes can be prevented.\textsuperscript{39–41}

In this work, we compare the performance of several cell configurations in the electrochemical reduction of CO$_2$ including variation of process parameters and composition of the GDE, and highlight the remarkable performance of micrometer-sized copper particles approaching CO selectivity levels, previously only obtained using silver- and gold-coated GDEs.

### 2. EXPERIMENTAL SECTION

#### 2.1. Preparation of Electrocatalysts and Membrane Activation

Cu-GDEs were prepared by spray-coating of an ink onto a carbon substrate (Freudenberg H23C6, Freudenberg). The catalyst ink contained 25 mg of 1 $\mu$m sized Cu particles (SkySpring Nanomaterials Inc., 99.8%), 64 $\mu$L (10 wt %) of Nafion 117 ionomer (5 wt % dissolved in isopropanol, Sigma-Aldrich), and 1 mL of Dimethyl sulfoxide (99.5%) as solvent, sufficient to produce two Cu-GDE samples. The ink was mixed in an ultrasonic bath for 30 min until a homogeneous mixture was obtained and then spray-coated onto the carbon substrate using a spray gun (air, 1 bar) and further dried at 160 °C for 16 h, resulting in a catalyst loading of 1.5 ± 0.1 mg/cm$^2$. The anode (an IrO$_2$-GDE) was prepared using iridium black (99%, Thermo Fischer) as a precursor in a similar way as the preparation of the Cu-GDEs, but containing a higher catalyst loading (2.0 ± 0.1 mg/cm$^2$). The preparation of electrocatalysts containing different Nafion concentrations was similar to the procedure described above, maintaining the same copper loading (1.5 ± 0.1 mg/cm$^2$) but changing only the volume of the Nafion solution as follows; 12 $\mu$L for 2 wt %, 64 $\mu$L for 10 wt %, and 143 $\mu$L for 20 wt % Nafion.

Nafion 117 (Fuel cell store) and Sustainion (Dioxide Materials) were tested as cationic and anionic exchange
membrane, respectively. Both membranes were pre-activated before the experiments as previously mentioned.\textsuperscript{42,43} Essentially, Nafion 117 membranes were boiled at 60 °C in solutions of 30% v/v H\textsubscript{2}O\textsubscript{2}, distilled water, 1 M H\textsubscript{2}SO\textsubscript{4}, and distilled water again for 30 min each, while Sustainion membranes were kept in 1 M KOH solutions overnight at room temperature and were then rinsed with MilliQ water.

2.2. Reactor Configurations and Electrochemical Experiments. A homemade PTFE continuous flow reactor was used as an electrochemical cell at room temperature and atmospheric pressure at different configurations for all studies herein presented. CO\textsubscript{2} flow-by experiments were carried out in catholyte-free (Figure 2a) and in conventional catholyte/anolyte (Figure 2b) configurations, while CO\textsubscript{2} flow-through experiments were carried out in a modified catholyte/anolyte-based configuration (Figure 2c), similar to Figure 2b, but with the gas outlet closed, forcing CO\textsubscript{2} to purge through the electrode into the catholyte. A Sustainion membrane was used in those experiments.

In a catholyte-free configuration, the Sustainion membrane was pressed against the cathode, that is, the Cu-GDE, as shown in Figure 2a. The cathode Cu-GDE and membrane were hot-pressed in a FVR FlashVape 20U hot-press machine for 2 min under 2 bar pressure and 40 °C temperature and then assembled into the reactor. This configuration contains only the anolyte, which is located at the back of the membrane and accommodates the reference electrode and recirculates pre-saturated electrolyte 0.3 M KHCO\textsubscript{3} (pH 7.2) at a 1 mL/min rate. A catholyte/anolyte configuration differs from the previous configuration by the addition of a catholyte channel between the cathode and the membrane. This catholyte channel now contains the reference electrode and a flow of 1 mL/min of

![Figure 2. Schematic of the different reactor configurations used in this study: CO\textsubscript{2} flowing by the Cu-GDE with only anolyte flow (catholyte free) (a), CO\textsubscript{2} flowing by the Cu-GDE with both catholyte and anolyte flows (catholyte/anolyte) (b), and CO\textsubscript{2} flowing through the Cu-GDE with both catholyte and anolyte flow (modified catholyte/anolyte) (c).](image)

![Figure 3. Influence of the type of ionic membrane on potential-dependent current density (a), FE (b) and partial current density toward CO (c), and C\textsubscript{2}H\textsubscript{4} (d) in a catholyte-free "zero gap" reactor configuration. Chronoamperometry experiments were carried out for 1 h in 0.3 M KHCO\textsubscript{3} (pH 7.2) flowing at 1 mL/min and a CO\textsubscript{2} gas "flow-by" rate of 5 mL/min. Error bars represent the average of at least three measurements.](image)
pre-saturated 0.3 M KHCO$_3$ (99%, Sigma-Aldrich), while the anolyte of 0.3 M KOH (99% Sigma-Aldrich) was made to flow at 1 mL/min. For both flow-by configurations (catholyte-free and catholyte/anolyte), gas products and non-converted CO$_2$/gaseous products were directed inline to a gas chromatograph, while liquid samples were taken every hour and analyzed by ion chromatography. Flow-through experiments were carried out in a modified catholyte/anolyte configuration (Figure 2c), similar to Figure 2b, but with the gas outlet closed, forcing CO$_2$ through the electrode toward the catholyte. Gases were collected as bubbles separated from the liquid in the catholyte compartment and inline directed to a Global Analyser solutions’ gas chromatograph equipped with two channels for detection of hydrocarbons (CH$_4$, C$_2$H$_4$, and C$_2$H$_6$) and light components (H$_2$, CO, and CO$_2$). Hydrocarbons were separated in a Parabond column and detected using a flame ionization detector, while light components were separated in a Mol Sieve column and detected using a thermal conductivity detector. Liquid products were analyzed every hour in the continuously recirculated electrolyte using ion chromatography.

 Unless stated otherwise, all experiments were carried out with a CO$_2$ (99.99%, Linde) flow rate of 5 mL/min (2.5 mL CO$_2$/min·cm$^2$) adjusted by Brooks mass flow controllers and fed into the cathode gas chamber, while the anode side was set to remain open to the air under an atmospheric pressure. Before each experiment, 0.3 M KHCO$_3$ (pH 8.2) electrolyte was pre-saturated with 20 mL/min of CO$_2$ for 30 min, reaching a final pH of 7.2, while 0.3 M KOH (pH 13.4) was used without pre-treatment. Both, the catholyte and anolyte flow rates were fixed at 1 mL/min and recirculated using peristaltic pumps. A leak-free reference electrode (Ag/AgCl, 3.4 M KCl, edaq, miniature leakless) was inserted into the anolyte channel (catholyte-free configuration) or into the catholyte channel (other configurations), allowing individual cathodic potential control. Cathode (Cu-GDE), membranes (Nafion or Sustainion) and anode (IrO$_2$-GDE) were sandwiched between Viton gaskets and assembled into the electrochemical cell using bolts and nuts to guarantee a leak-free reactor. Electrochemical experiments were performed using a Biologic VMP-9 potentiostat, in galvanostatic mode. Chronoamperometry experiments were carried out in a potential range between $-0.4$ and $-1.0$ V versus RHE for 1 h, unless stated otherwise. Stability tests in flow-through experiments were continuously carried out without cell disassembly, until “flooding” was observed. All potentials were automatically corrected for cell resistances, measured prior to the experiments by the current interrupt method.

3. RESULTS AND DISCUSSION

3.1. Effect of the Membrane in Flow-by Configurations on Cell Performance. The effect of the ionic membrane on CO$_2$RR current density and faradaic efficiency (FE) was first evaluated in a catholyte-free (“zero gap”) reactor configuration (see Figure 2a), operated in flow-by mode (Figure 3a−d). Fresh copper-coated GDE catalysts and electrolytes were used for each experiment.
Figure 3a shows the potential-dependent current density, which was obtained from chronoamperometry experiments at each voltage for 1 h under CO$_2$ flow, for Nafion (black line) and Sustainion (red line) membranes. In general, an increase in the applied cathodic potential resulted in higher current densities, reaching a maximum of $-60$ mA/cm$^2$ at the most negative potential investigated of $-0.87$ V versus RHE for the Nafion 117 membrane. Nafion generally exhibits higher current densities in the range from $-0.6$ to $-0.85$ V compared to Sustainion. In the lower potential region ($> -0.6$ V vs RHE), we observed mainly hydrogen as the product, accounting for over 90% of the FE. In an intermediate potential window ($-0.75$ V $< E_{we} < -0.6$ V vs RHE), carbon dioxide reduction products such as CO and ethylene start to be formed in considerable amounts, accounting for approximately 20% of the FE (see Figure 3b), with consistently higher FE toward CO for the cell configuration with the Sustainion membrane. Finally, in the higher potential range (more negative than $-0.75$ V vs RHE), higher FEs were obtained toward ethylene with Sustainion-based cell configurations. Combining the data of Figure 3a,b, the trends in $J_{CO}$ and $J_{C_2H_4}$ were determined. The $J_{CO}$ is higher for Nafion in the potential range of $-0.5$ to $-0.85$ V (see Figure 3c) and significantly higher partial current density toward ethylene at the highest potential investigated ($-0.88$ V) for Sustainion (see Figure 3d). Previous studies also revealed a superior performance of anionic exchange membranes over cationic ones toward ethylene at high current densities. However, issues such as CO$_2$ crossover to the anode side via carbonate/bicarbonate exchange, resulting in CO$_2$RR efficiency losses, were also reported, revealing the need for further membrane optimization.$^{26,41,44}$

Figure 4a shows the current-potential behavior for both Nafion and Sustainion membranes in a catholyte-anolyte reactor configuration. We can observe slightly higher current densities for Nafion-based systems (similar to catholyte-free conditions) in the intermediate potential range ($-0.8$ to $-0.6$ V vs RHE), while reaching a maximum of $-55$ mA/cm$^2$ at the largest potential investigated of $-0.92$ V versus RHE, similar for both membranes, but somewhat lower than under the catholyte-free conditions (see Figure 3a). In contrast to catholyte-free configurations, where a relatively high ethylene production rate was achieved, the catholyte-anolyte type of reactor exhibited mostly carbon monoxide as the product, as shown in Figure 4b.

The absence of ethylene suggests that the interfacial pH (electrode/electrolyte) is lower than in the catholyte-free configuration, in agreement with the continuous replenishment of the electrolyte and favorable mass transfer properties induced by the liquid flow in the catholyte compartment.$^{45}$ When compared to Nafion-based systems, Sustainion membranes show higher FE$_{CO}$ at potentials more negative than $\sim -0.85$ V (see Figure 4c). A maximum CO$_2$RR efficiency of 75% was obtained at the most negative applied potential ($-0.93$ V vs RHE), in which a FE$_{CO}$ of 65% was achieved, compared to only 40% for Nafion-based systems, which favor the formation of H$_2$. Generally, the partial current density toward ethylene is similar for the two membranes that were
applied (Figure 4d), the slightly higher \(J_{C2H4}\) for Nafion being somewhat counterintuitive, given that a relatively low local pH typically does not favor ethylene formation.

Besides the modulation of the local pH to more neutral or slightly basic environments by the flowing catholyte, the desorption and transport of CO away from the catalyst surface is also promoted, in agreement with the lower FE toward ethylene, which is generally assumed to be formed by the dimerization of CO. To explain the slightly higher \(J_{C2H4}\) for Nafion, we then assume that the availability of CO in close proximity to the catalytic sites might depend on the affinity of CO for the membrane, favored by Nafion in the cell configuration used to accumulate the data presented in Figure 4.

3.2. Flow-by versus Flow-through Configurations. We utilized a catholyte–anolyte reactor configuration using a catholyte containing 0.3 M KHCO\(_3\) flowing at 1 mL/min and the anolyte consisting of 0.3 M KOH flowing at 10 mL/min.

Due to the higher \(FE_{CO}\) in flow-by experiments obtained for Sustainion than for Nafion, Sustainion membranes were selected to evaluate the transport mechanism and effects of flow rate on CO selectivity. The \(CO_2\) gas flow was fixed at 5 mL/min in the flow-by mode as well as in the flow-through mode. Figure 5a shows only small differences in current density between flow-by mode and flow-through mode in the entire potential window investigated, being favorable only by a few mA cm\(^{-2}\) for the flow-through configuration. This indicates that the range of flow rates tested was high enough to surpass transport limitations, while maintaining an optimized triple phase boundary. A too high flow rate of \(CO_2\) in the flow-through mode will likely push the triple phase boundary toward the membrane, decreasing the degree of active catalyst surface and leading to higher charge-transfer cell resistances. The main effect of the flow-through mode of operation on the performance of our micro-sized Cu particles can be found in the increase of \(FE_{CO}\) from 60 to 80% (Figure 5b). This is also reflected by the higher partial current density toward CO (Figure 5c).

Both observations suggest that desorption and transport of CO away from the reactive electrode is favored by the gas flow exiting the pores of the GDE into the catholyte.

![Figure 6](https://example.com/figure6.png) **Figure 6.** Current density (a) and FE (b) results for different \(CO_2\) flow rates on flow-through experiments. Chronoamperometry experiments carried out for 1 h in 0.3 M KHCO\(_3\) (pH 7.2) flowing at 1 mL/min and \(CO_2\) flow rate of 5 mL/min. Error bars represent the average of at least three measurements.

![Figure 7](https://example.com/figure7.png) **Figure 7.** Stability test for Cu-GDE catalysts prepared using 10 wt % Nafion (a) and 20 wt % Nafion (b) within the ink composition, operated in a flow-through regime. The blow-out in (b) shows the current behavior when flooding occurs, which drops, and is restored by adjusting the potential. The experiments were conducted under the same conditions as in Section 3.2 (i.e., fixed \(CO_2\) flow rate of 5 mL/min, catholyte 0.3 M KHCO\(_3\), and anolyte 0.3 M KOH flowing at 1 mL/min and Sustainion membranes separating the electrolyte compartments).
Figure 8. Schematic of the effect of ionomer concentration on carbon dioxide supply and mixing for 2, 10, and 20 wt % Nafion samples.

A more dramatic increase in current density than shown in Figure 5a was found by Duarte and co-workers for Ag-GDEs. *Flow-through* regimes were reported to lead to improvement in partial current densities from $J_{CO-FlowBy} = -120 \text{ mA/cm}^2$ to $J_{CO-FlowThrough} = -200 \text{ mA/cm}^2$, although stability issues associated to crystallization of electrolyte salts inside the GDE pores caused a drop in $FE_{CO}$ after just 1 h.36 This larger effect is likely due to the higher intrinsic activity of the Ag particles, in comparison to our micro-sized Cu particles.

To further investigate the transport phenomena induced by convective $CO_2$ supply, we varied the $CO_2$ flow-through rate. Figure 6a,b shows the results. We observed a small increase in current density increasing the $CO_2$ flow rate from 5 to 20 mL/min $^{-1}$, slightly larger than the error margin (error bars correspond to small deviations in current and IR-corrected potential, respectively). This suggests that the transport phenomena are not largely improved at higher flow rates or that we have reached the kinetic limit in performance of our Cu particles. This is also apparent from the FE values toward $CO$ for which are hardly flow rate-dependent. Still, a maximum $FE_{CO}$ of 85% under 20 mL/min of $CO_2$ at $-0.88 \text{ V versus RHE}$ was achieved at $\sim 50 \text{ mA/cm}^2$, being one of the highest values reported in the literature for copper-based electrodes.48

3.3. Effect of Nafion Content and Stability Evaluation. Figure 7 shows the potential-dependent FEs toward $CO$ for two GDEs, one prepared with a Nafion concentration of 10 wt % (a) and another with a concentration of 20 wt % (b), respectively. A GDE was also prepared with only 2 wt % loading, but the data for this electrode could not be included in Figure 7, since flooding was apparent already after less than 1 h of flow-by operation.

In order to confirm long-term stability of flow-through operation, we performed multiple chronoamperometry experiments using the same Cu-GDE electrode, without disassembling the electrochemical flow cell.49-53

We can observe a stable current for the 10 wt % Nafion sample in the whole cathodic potential range, including a $3 \text{ h}$ stability at $-0.92 \text{ V versus RHE}$, maintaining the excellent FE of $\sim 80\%$ at an $\sim 50 \text{ mA/cm}^2$ current density. Increasing the Nafion loading to 20 wt % decreases the FE toward $CO$ (more hydrogen is formed), while also the stability is lowered. Loss in $FE_{CO}$ and current instability occurred after 6.5 h of operation. We also observe an increase in the variation (“noise”) in current density at more negative potential values, suggesting gas accumulation at the solid–liquid interface, leading to poor catalyst wettability and a higher interfacial resistance, thus requiring higher overpotentials.39,40

A schematic overview of interfacial phenomena occurring in gas flow-through operation, in combination with the Nafion coverage of the GDE, is shown in Figure 8. We assume that gas can exit the pores of the GDE from the backside into the flowing catholyte effectively up to Nafion ionomer concentrations of $\sim 10 \text{ wt %}$ in the ink formulation. This leads to effective mixing and favors the formation of CO. If only 2 wt % Nafion is applied, this exposes quite some of the Cu surface to the electrolyte, possibly affecting the interfacial pH (more basic), and most importantly limiting the mechanical stability of the Cu particles. Detachment of particles from the surface due to the low adhesion to the GDE might also occur, resulting in loss of catalyst activity and explaining the fast degradation of cell performance. Similar particle detachment was also observed previously for GDEs prepared with only 3 wt % Nafion.50

The excellent performance of the 10 wt % Nafion containing GDE derives from the synergistic benefits of an optimum CL composition, providing sufficient catalyst adhesion, sufficient supply of protons, and efficient wettability due to the hydrophilicity of Nafion, in combination with effective $CO_2$ purge—inducing high $CO_2$ and $CO$ mass transfer rates. The literature demonstrates similar ionomer concentrations as optimum (PTFE was the ionomer), attributed to optimized hydrophobicity and $CO_2$ diffusion to the catalyst surface.54 Finally, at high ionomer concentrations (20 wt % Nafion), a significant fraction of the pores are likely blocked, leading to a less equal distribution of exiting gas (higher gas flow rate to a smaller amount of pores), lowering the advantages of *flow-through* operation in achieving a high FE toward CO and enhancement in stability by favorable mass transfer phenomena. The lower quantity of effective pores and the higher hydrophilicity at 20 wt % Nafion likely result in flooding after short periods of operation, as experimentally observed in Figure 7b.

4. CONCLUSIONS

In this work, we evaluated cell design and the effect of process parameters and GDE composition on electrochemical reduction of $CO_2$. In the *catholyte-free* configuration, we observed an improvement from a $FE_{CH_4}$ of 25% for the Nafion membrane to a $FE_{CH_4}$ of 40% for the Sustainion membrane. We attribute the difference between Nafion and Sustainion to differences in local pH, particularly lowered by the acidic nature of the Nafion membrane in close contact with the Cu-GDE. In the *flowing catholyte* configuration, a $FE_{CO}$ of 65% was obtained using Sustainion, in comparison to a $FE_{CO}$ of 45% achieved with a Nafion membrane. The fast transport of
protons through the Nafion membrane likely lowers the pH of the catholyte compartment, favoring the formation of H⁺.

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The authors declare no competing financial interest.

L.de S. performed all experiments and wrote the article. G.M. co-supervised the work and provided suggestions for experiments. Finally, very stable currents and CO production rates were achieved in long-term operations in flow-through regimes, running over 10 h without deactivation at an optimized Nafion ionomer concentration in the ink formulation of 10%. Therefore, by using a flow-through-based Cu-GDE cell configuration, we were able to achieve, to the best of our knowledge, one of the most stable cell performances reported, with an exceptionally high FEₐCO₂ of 85%.

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L.de S. performed all experiments and wrote the article. G.M. supervised the work and read and corrected the article. N.E.B. co-supervised the work and provided suggestions for experiments.

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