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Analysis of Mass Flows and Membrane Crossover in CO₂ Reduction at High Current Densities in a MEA- Type Electrolyzer

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43 **KEYWORDS:** electrocatalysis, CO₂ reduction, silver, anion-exchange membrane, membrane-
44 electrode assembly, electrolyzer
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ABSTRACT

Cell designs that integrate membrane-electrode assemblies (MEAs) with highly selective catalysts are a promising route to reduce ohmic losses and achieve high energy efficiency in CO₂ reduction at industrially relevant current densities. In this work, porous silver filtration membranes are demonstrated as simple and efficient gas-diffusion electrodes for CO₂ reduction to CO at high current densities in a MEA-type device. A partial current density for CO of up to ca. 200 mA cm⁻² was achieved at a cell voltage of ca. 3.3 V, in tandem with minimal H₂ production. However, the analysis of cathodic and anodic outlet streams revealed that CO₂ crossover across the AEM, mostly in the form of CO₃²⁻ but partially as HCOO⁻ generated over the cathode, actually exceeds the amount of CO₂ converted to the target product, resulting in a poor utilization of the reactant and in the early onset of mass transfer limitations. In addition, CO₂ crossover leads to non-stoichiometric decrease of the outlet flow rate from the cathodic compartment that can lead to a substantial overestimation of catalytic performance if the inlet flow rate of CO₂ is used as reference for calculating partial current densities and Faradaic efficiencies. The results of this work highlight the importance of carrying out a carbon balance, in addition to traditional measurements of activity and selectivity, to adequately assess the performance of CO₂ reduction devices at high current densities, and inform future efforts aimed at mitigating membrane crossover in MEA-type electrolyzers for CO₂ reduction.

1. INTRODUCTION

Combining the electrochemical CO₂ reduction reaction (eCO₂RR) with carbon-neutral energy sources offers exciting perspectives for using CO₂ as a sustainable feedstock for the production of fuels and chemicals.¹⁻³ Research efforts over recent years have led to a substantial expansion of the fundamental understanding of CO₂ electroreduction⁴⁻⁶ and, in particular, to the discovery of catalyst compositions and morphologies that show high performance (i.e., low overpotentials and high Faradaic efficiencies) toward CO and HCOO⁻, the simplest eCO₂RR products.⁷ However, recent technoeconomic analyses have emphasized the importance of achieving high current densities (i.e., hundreds of mA cm⁻²) in relation to the practical viability of the eCO₂RR,^{8,9} which demands the adoption of gas diffusion electrodes (GDEs) that allow high local concentrations of CO₂ and support much higher reaction rates than planar electrodes in aqueous electrolytes.¹⁰ In this context, there is a growing awareness of the need to evaluate eCO₂RR catalysts under realistic operating conditions,¹¹ and to investigate the link between different cell configurations and electrocatalytic performance to derive design guidelines for CO₂ reduction devices.

Due to its high selectivity and moderate cost, silver shows interesting properties as a practical catalyst for CO₂ reduction to CO.¹²⁻¹⁴ Bidault and Kucernak investigated the use of porous Ag membranes, commonly used as filtration media in biotechnological applications, as cathodic GDEs in alkaline fuel cells.¹⁵ In contrast to traditional carbon-based GDEs, these porous membranes integrate electrocatalytic functionality, mechanical support, and efficient current conduction (due to the very high electrical conductivity of Ag) within a single, homogeneous structure. Porous Ag membranes have a comparable cost to carbon gas diffusion layers (GDLs),¹⁶ and they might overcome some of the drawbacks associated to the latter, such as the

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3 gradual loss of hydrophobicity¹⁷ and accelerated degradation under alkaline conditions.¹⁸
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5 Consequently, we sought to assess the potential of commercially available porous Ag
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7 membranes as GDEs for CO₂ reduction at high current densities.
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10 Besides having a catalyst that is highly active and selective, achieving high energy efficiency
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12 at elevated current densities requires optimizing the design of the electrolyzer to attain low
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14 ohmic losses.¹⁹ Recent studies have demonstrated the use of highly alkaline catholytes in contact
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16 with the GDE to manipulate the reaction environment and achieve high electrocatalytic
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18 performance.^{17,20,21} However, the practicality of such cell designs is likely limited by the
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20 penetration of CO₂ into the catholyte layer and by high ohmic losses arising from the poor
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22 conductivity of liquid electrolyte solutions.¹¹ By greatly reducing the distance between the
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24 electrodes and eliminating the need of a liquid electrolyte, membrane electrode assemblies
25
26 (MEAs) can decrease significantly the cell ohmic overpotential.^{10,22} It is known that cation-
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28 exchange membrane-based MEAs show poor results in CO₂ reduction because they generate a
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30 highly acidic reaction environment that heavily favors the competing hydrogen evolution
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32 reaction (HER).^{23,24} This fact has led to the exploration of cell designs employing bipolar (BPM)
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34 or anion-exchange membranes (AEM). BPM-based configurations have showed encouraging
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36 results but have also exposed the difficulty of effectively suppressing the HER as well as
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38 stability concerns related to the delamination of the acidic and alkaline layers.^{25–27} In contrast,
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40 AEM-based devices have exhibited outstanding selectivity and stability at high current densities,
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42 particularly in CO₂ reduction to CO.^{28–30} Nevertheless, CO₂ crossover from the cathodic to the
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44 anodic compartment of the cell, caused by the neutralization of CO₂ to HCO₃⁻/CO₃²⁻ and the
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46 transport of these anionic species across the membrane, has been recognized as a significant
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48 limitation of AEM-based devices.^{27,30} This phenomenon has been reported in several CO₂
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3 reduction studies in high-current electrolyzers (usually at a single operating point),^{27,28,31,32} and
4 Xiang et al. recently carried out a study of the impact of crossover on CO₂ utilization in an
5 aqueous (i.e., H-type) cell using different types of ion-selective membranes.³³ Nevertheless, there
6 is currently a lack of systematic analyses of CO₂ crossover at industrially relevant current
7 densities using a zero-gap configuration.³¹ In this context, we herein present a full mass
8 balance—anchored in the analysis of both cathodic and anodic outlet streams—that provides a
9 comprehensive picture of CO₂ crossover in MEA-type electrolyzers, with the aim of informing
10 future efforts geared toward the optimization of this promising class of CO₂ reduction devices.
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24 2. EXPERIMENTAL

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26 **2.1. Cell configuration.** This work was conducted using a commercially available electrolyzer
27 (Liquid-Gas Fuel Cell Test Fixture, Scribner Associates) equipped with gold-plated copper
28 current collectors and graphite and titanium serpentine flow fields for the cathode and anode,
29 respectively (**Figure 1A**). Porous silver membranes with a nominal pore size of 1.2 μm
30 (Sterlitech Inc., purity 99.97%, area 4 cm²) were used as cathodes. Commercially available IrO₂-
31 coated carbon paper electrodes (Dioxide Materials, area 7.3 cm²), previously described by Kutz
32 et al.²⁸ were employed as anodes. A fresh membrane-electrode assembly was constructed for
33 each experiment by intercalating a fresh Sustainion X37-50 grade 60 anion-exchange membrane
34 (Dioxide Materials, 16 cm²) between the electrodes and fastening the bolts of the cell with a
35 torque of 4 N m. Each electrode was surrounded by PTFE gaskets for protection and electrical
36 insulation. The cathodic flow field was fed with CO₂ (AGA, purity 4.5) at a flowrate of
37 100 ml_n min⁻¹, which was humidified upstream of the cell by sparging into a container filled
38 with ultrapure water. Reference conditions for the gas flows in this work are defined as 273.15 K
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3 and 1 bar ($1 \text{ ml}_n \text{ min}^{-1} = 7.434 \times 10^{-7} \text{ mol s}^{-1}$). The anodic flow field was fed with a
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5 0.1 M KHCO_3 solution (Sigma-Aldrich, 99.995% trace metal basis) which was recirculated
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7 continuously at a flowrate of $60 \text{ cm}^3 \text{ min}^{-1}$ using a diaphragm pump. The device was heated
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9 using two cartridge heaters inserted into each end plate and connected to an external temperature
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11 controller, with feedback from a thermocouple inserted into the cathodic end plate.
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15 **2.2. Characterization and electrochemical tests.** Given the large currents involved, the
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17 electrolyses were carried out in galvanostatic mode (range: 200-1600 mA, step size: 200 mA)
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19 using a direct current (DC) power supply (Aim-TTi CPX400DP) connected to the current
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21 collectors of the cell. The cell voltage was measured continuously with a 16-bit analog-to-digital
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23 converter (Microchip Technology MCP3428) interfaced with a Raspberry Pi. A solenoid valve
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25 (SMC Instruments, VQD1151 series) was installed upstream of the cell to switch between
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27 sampling and venting the outlet streams from each compartment (**Figure 1B**). A homemade
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29 Python program controlled the setup and recorded the data at regular intervals. The accuracy of
30
31 the cell voltage measurements under operating conditions was validated with a Bio-Logic VSP-
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33 300 potentiostat with no current passing through the instrument, with the working and reference
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35 electrode terminals connected to the cathodic and anodic current collectors, respectively.
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41 Scanning electron microscopy (SEM) imaging of the porous Ag electrodes at an accelerating
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43 voltage of 15 kV was performed in a FEI Quanta 200 FEG instrument operating in secondary
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45 electron mode. X-ray photoelectron spectroscopy (XPS) analysis was carried out with
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47 monochromated Al $K\alpha$ radiation (1486.7 eV) in a ThetaProbe instrument (Thermo Fisher
48
49 Scientific) equipped with a hemispherical analyzer. Survey scans were acquired in the binding
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51 energy range of 0-1400 eV with an analyzer pass energy of 100 eV.
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3 **2.3. Flow measurement and product analysis.** The molar flow rate of the cathodic and
4 anodic outlet streams of the electrolyzer was measured continuously with either a volumetric
5 flow meter (MesaLabs, Defender 530+) or a mass flow meter (MFM) placed upstream of the gas
6 chromatograph (GC), as shown in **Figure 1B**. For the MFM, a multivariable calibration
7 procedure was carried out to convert the composition-dependent signal of the instrument into the
8 actual molar flow rate and validated with a primary flow calibrator (details provided in the
9 Supporting Information). The composition of the gas streams was determined with a
10 PerkinElmer Clarus 580 instrument equipped with Molecular Sieve 13X and HayeSep Q packed
11 columns, operating with argon as carrier gas at a flow rate of 15 ml min⁻¹. H₂, CO₂ and O₂ were
12 quantified with the thermal conductivity detector (TCD) while CO was passed through a
13 methanizer and quantified with the flame ionization detector (FID). GC runs were initiated every
14 30 min. Post-reaction high performance liquid chromatography (HPLC) analysis of the anolyte
15 was carried out in an Agilent 1200 series system equipped with a Bio-Rad Aminex HPX-87H
16 column heated to 50 °C and refractive index (RID) and diode array (DAD) detectors. An aqueous
17 solution of H₂SO₄ (5 mM, flowing at 0.6 ml min⁻¹) served as the eluent. Additional details on the
18 calculation of the partial current densities and Faradaic efficiencies for each product are provided
19 in the Supporting Information.
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45 **3. RESULTS AND DISCUSSION**

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47 **3.1. Electrode characterization and cell design.** Commercially available porous Ag
48 membranes provide an interesting platform to develop carbon-free gas diffusion electrodes for
49 CO₂ reduction electrolyzers. In this work, we used membranes with a nominal pore size diameter
50 of 1.2 μm and a thickness of 50 μm,³⁴ although inspection by scanning electron microscopy
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(SEM) revealed that the surface of the Ag membranes is populated by well-connected pore openings of considerably larger size (2-5 μm , **Figure 1A**). The area-based density of the material is ca. 27 mg cm^{-2} , implying a porosity of ca. 55%. Post-reaction SEM analysis showed no changes to the porous structure of the electrode, evidencing its stability during CO_2 reduction at high current densities. The stated purity of the Ag membranes (Sterlitech Corporation) is 99.97%. The XPS survey scan of the Ag membranes revealed the presence of adventitious carbon and oxygen, as well as minor peaks that indicated the presence of chlorine, possibly due to the formation of AgCl during production or handling (**Figure S1**). Nevertheless, no metallic impurities that might interfere with the eCO_2RR were observed within the limit of detection of the XPS analysis.

We prepared each MEA by intercalating a Sustainion anion-exchange membrane between the porous Ag cathode ($A_{\text{cathode}} = 4 \text{ cm}^2$) and an IrO_2/C anode (Dioxide Materials). The cathode was fed with humidified CO_2 , while the anode was fed with a 0.1 M KHCO_3 solution, which was freshly prepared at the beginning of each test, but recycled during the duration of the test. This “exchange-MEA” configuration (i.e., vapor-fed cathode and liquid-fed anode) is expected to afford lower ohmic losses compared to cell designs employing liquid catholyte layers, while avoiding problems due to poor membrane hydration at high current densities with fully gas-fed electrolyzers (i.e., a “full-MEA” configuration).²² The outlet streams both from the cathode and the anode were analyzed by GC and the corresponding molar flow rates were measured with a mass flow meter installed between the outlet of the cell and the gas chromatograph (**Figure 1B**). As will be shown in the following discussion, measuring the non-stoichiometric loss of CO_2 to the anodic compartment is necessary to assess accurately the performance of CO_2 reduction devices at high current densities.

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3 **3.2. Electrochemical performance.** **Figure 2** shows the typical performance of the
4 electrolyzer toward the main products (CO and H₂) and the overall cell voltage as a function of
5 the total current density. The experiments were carried out in galvanostatic mode by stepping (at
6 the total current density. The experiments were carried out in galvanostatic mode by stepping (at
7 1 hour intervals) successively the total current density from 50 to 400 mA cm⁻². The device was
8 held at 30 °C to maintain a constant temperature throughout testing. The cell voltage was
9 recorded continuously and the gas products were analyzed periodically by gas chromatography
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19 (GC). When argon instead of CO₂ was fed into the electrolyzer, H₂ was the only product formed
20 over the cathode with a Faradaic efficiency of 100% at all current densities (**Figure S2**),
21 excluding the existence of short circuits within the cell (which would lead to a large non-redox
22 current and thus to a FE_{H₂} much lower than 100%) as well as any eCO₂RR activity arising from
23 diffusion of the bicarbonate electrolyte from the anode to the cathode.
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31 The production of CO over porous Ag electrodes in the MEA-type electrolyzer reached a
32 maximum rate of ca. 200 mA cm⁻² (3.74 mmol h⁻¹ cm⁻²) at a cell voltage of 3.3 V. Up to a total
33 current density of 250 mA cm⁻², the HER was negligible and CO was almost exclusively
34 produced in the gas phase (**Figure 2B**). This increase in current without an increase in CO or H₂
35 (or any other gas) production clearly indicates that liquid products must be formed. However,
36 increasing the total current density beyond 250 mA cm⁻² resulted in the light-off of hydrogen
37 evolution accompanied with periodic oscillations of the cell voltage (and conversely, with
38 oscillations of the current when a constant cell voltage was imposed) associated to the
39 appearance of mass transfer limitations (**Figure S3**). These mass transfer limitations are likely a
40 result of flooding of the cathode because of water migration, as predicted by Weber et al. for a
41 MEA-type setup with a liquid-fed anode.²² We remark that we did not observe salt precipitation
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3 at the cathode, although current densities were below the value at which the solubility limit of
4 K_2CO_3 is predicted to be reached (ca. 750 mA cm^{-2}).²²
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8 Overall, the results in **Figure 2** underscore the effectiveness of a MEA approach with an
9 anion-exchange membrane to achieve high rates for CO_2 reduction to CO and highlight the
10 potential of the Ag filtration membranes as simple and robust cathodes for CO_2 reduction.
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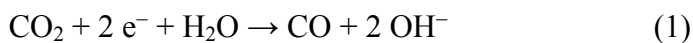
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15 As previously eluded to, at current densities of 250 mA cm^{-2} and above, the sum of the
16 Faradaic efficiencies (FEs) for CO and H_2 was significantly lower than 100% (**Figure 2C**).
17 Besides CO and H_2 in the gas phase, HCOO^- was detected after the reaction by high-
18 performance liquid chromatography (HPLC) both in the anolyte and in droplets condensed from
19 the cathodic compartment of the cell (**Table S1**). Consequently, the Faradaic efficiency that is
20 not accounted for by the gas-phase products (labeled as “Others” in **Figure 2C**) can be
21 reasonably attributed to CO_2 reduction to HCOO^- over the cathode and to its oxidation over the
22 anode (calculation details are provided in the Supporting Information). These results indicate that
23 CO_2 reduction to HCOO^- is a significant side reaction over the porous Ag electrodes in a MEA-
24 type configuration. Previous studies in H-type cells have shown that HCOO^- is a minor eCO_2RR
25 product at highly cathodic potentials over poly-^{13,35} and single-crystalline^{36,37} Ag electrodes,
26 although in most reports Faradaic efficiencies for this product do not typically exceed 10%.
27 Nevertheless, there has been one report that suggests this fraction may be significantly higher at
28 potentials more cathodic than -1.3 V vs. RHE .³⁷ The higher FEs for HCOO^- observed with the
29 MEA-type configuration compared to H-cell studies suggest that a very high local pH at the
30 reaction interface might favor the reduction of CO_2 to HCOO^- at the expense of CO production,
31 particularly at the high cathodic overpotentials needed to achieve high current densities. This
32 observation is consistent with the remarkably high FE toward HCOO^- over Ag GDEs under
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3 extremely alkaline conditions (i.e., up to 38% with a 10 M KOH catholyte) reported by the
4 Sargent and Sinton group.²¹ Nevertheless, we note that modeling studies of Ag GDEs show that,
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6 under buffered conditions, a very large change of local pH occurs between 0 and 50 mA cm⁻²
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8 (up to a pH of ca. 12) while variations thereafter are modest.¹¹ Taking this into account, the
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10 increasing FE for HCOO⁻ we observe with total current density is likely driven by higher
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12 cathodic overpotentials (once the electrode is operating at pH ≥ 12) rather than by further
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14 changes of local pH. Furthermore, as in previous studies,^{21,38} our results indicate that most of the
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16 HCOO⁻ formed over the Ag cathode was transported across the AEM and readily oxidized to
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18 CO₂ over the IrO₂ anode. This is evidenced by (a) the post-reaction concentration of HCOO⁻ in
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20 the anolyte, which is much lower than it would be in the absence of decomposition (**Table S1**),
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22 and by (b) the increasing fraction of the anodic current (at $j_{\text{total}} \geq 250 \text{ mA cm}^{-2}$) that could not be
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24 attributed to the oxygen evolution reaction (OER) (**Figure 2C**). Although corrosion of the carbon
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26 paper substrate of the IrO₂/C anode would likely compromise the performance of the device
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28 under long-term operation, control experiments with an argon-fed cell revealed that the carbon-
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30 based anode is only negligibly oxidized over the short time scales studied in this work, even at
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32 very high cell voltages (**Figure S2**). Furthermore, water oxidation to hydrogen peroxide—
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34 another possible anodic reaction—is very strongly suppressed over IrO₂.^{39,40} In contrast, the
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36 oxidation of formic acid (likely formed in the buffered anolyte from cathodically-generated
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38 HCOO⁻ transported across the AEM) has facile kinetics over IrO₂ electrodes and competes
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40 directly with the OER, as reported by Comninellis and co-workers.^{41,42} We confirmed that
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42 HCOO⁻ is significantly oxidized by the IrO₂/C anode (i.e., FE ca. 20% at 200 mA cm⁻²) even
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44 when it is extrinsically added to the 0.1 M KHCO₃ anolyte (**Figure S4** and the explanation
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46 therein), even though in this scenario this reaction is hindered by HCOO⁻ having to diffuse
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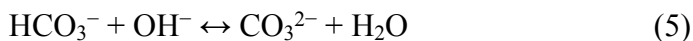
through the thick GDL of the anode to reach the IrO₂ catalyst (a limitation that is absent when HCOO⁻ is transported across the membrane). In this context, CO₂ reduction to HCOO⁻ with AEM-based MEAs is particularly undesirable, because energy is spent to generate (and then decompose) a product that cannot be recovered. This observation motivates further research on the factors that result in higher HCOO⁻ FEs than those typically observed in H-cells, and on devising strategies to limit this side reaction.

3.3. Analysis of mass flows and CO₂ crossover through the membrane. Under basic and neutral conditions (i.e., with H₂O as the proton donor), the eCO₂RR and the HER generate OH⁻ anions at the cathode (equations 1-3) that react with CO₂ to generate bicarbonate and carbonate anions (equations 4 and 5). The transport of these species as charge carriers through the AEM results in the undesired crossover of CO₂ from the cathodic to the anodic compartment of the device.

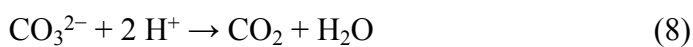
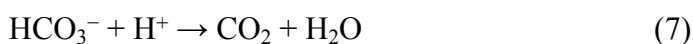
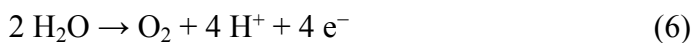
Release of OH⁻ at the cathode

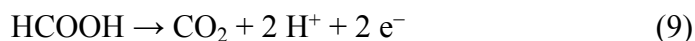


Neutralization of CO₂ at the cathode



Gas evolution (O₂ and CO₂) at the anode





CO₂ crossover will tend to change the molar flow rate coming out of the cathodic compartment in a way that is not necessarily predictable from the reaction stoichiometry. **Figure 3A** shows the molar flow rate measured at the cathodic outlet at different current densities. In principle, the total molar flow rate should be conserved when CO₂ is reduced to CO, but we observed a decrease of the flow of up to ca. 10% in the region of high CO selectivity (50-250 mA cm⁻²). Conversely, at current densities above 250 mA cm⁻², the flow rate tended to increase due to the addition of a component (hydrogen) to the gas phase from a reagent in the liquid phase (water). Gas flows from the anode were significantly higher than expected from oxygen evolution alone, and the decrease of the cathodic outlet flow was accompanied by the detection of an increasing amount of CO₂ at the outlet of the anodic compartment up until the onset of hydrogen evolution (**Figure 3B**). This result evidenced the transport through the AEM of charged species originating from cathodic CO₂ (i.e., HCO₃⁻, CO₃²⁻ and HCOO⁻) and their subsequent release as CO₂ over the anode (equations 6-9). It is interesting to note that both CO₂ crossover and total CO₂ consumption (**Figures 3C** and **4A**, respectively) plateau at high current densities, which suggests the occurrence of mass transfer limitations and the depletion of CO₂ at the reaction interface. **Figure 3C** shows that most of the CO₂ crossover originates from CO₂ neutralization to HCO₃⁻ or CO₃²⁻, although a substantial fraction of CO₂ is “lost” to the anode as HCOO⁻, particularly when $j_{\text{total}} \geq 250 \text{ mA cm}^{-2}$. As argued previously, the oxidation of the carbon substrate of the anode contributes very negligibly to the CO₂ detected in the anodic compartment (**Figure S2**), and the total mass balance of carbon (i.e., practically 100% for all current densities) further supports this observation (**Figure 3C**).

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3 We remark that neglecting the variation of the molar flow rate at the outlet of the cathode can
4 result in an overestimation of the reaction rate of CO₂ reduction to CO and thus in an erroneous
5 assessment of the performance of the device. For example, using the estimated flow rate at the
6 outlet instead of the actual (**Figure 3A**) leads to calculating a maximum j_{CO} that is ca. 6% higher
7 than the actual value. Lowering the flow rate of CO₂ fed into the cathode (e.g., to achieve a
8 higher single-pass conversion) accentuated this issue because the decrease of the flow was
9 proportionally larger (**Figure S5**). Because it results in higher cumulative Faradaic efficiency for
10 gas-phase products, this miscalculation can lead to underestimating the production of liquid-
11 phase products, particularly if they can be transported across the membrane and oxidized over
12 the anode, such as HCOO⁻. Furthermore, using a highly alkaline electrolyte in the cathodic
13 compartment could possibly aggravate this problem due to the neutralization of CO₂ by the
14 electrolyte itself in addition to that by reaction-generated OH⁻ ions.^{20,21} These observations
15 underscore the importance of measuring the actual molar outlet flow from the cathode when
16 characterizing the performance of CO₂ reduction devices operating at high current densities in
17 order to avoid overstated claims of efficiency and selectivity.

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38 Lastly, comparing the amount of CO₂ (excluding the CO₂ released from formic acid oxidation)
39 and O₂ evolved over the anode provided an indication of the main charge carrier across the AEM
40 (**Figure 3D**). For example, if all the charge is carried by OH⁻, CO₃²⁻ or HCO₃⁻, the CO₂/O₂
41 ratios at the anode would be 0, 2 or 4, respectively.³⁰ We note that the accuracy of this
42 calculation is improved when anodic CO₂ originating from HCOO⁻ oxidation is excluded;
43 therefore, the numerator of the ratio corresponds only to CO₂ that crosses over as HCO₃⁻/CO₃²⁻
44 (i.e., the upper curve in **Figure 3C**). Below 250 mA cm⁻² this ratio is practically constant and
45 equal to ca. 2, indicating that CO₃²⁻ (and not HCO₃⁻) is the main charge carrier across the AEM
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3 in the absence of hydrogen evolution. However, upon the onset of the HER there is a rapid
4 decrease of the anodic CO₂/O₂ ratio, which is most likely a consequence of increased transport
5 across the membrane of OH⁻ produced in the HER. We remark that these results provide
6 experimental validation to the modeling efforts of Weber et al.,²² who predicted that the main
7 charge-carrying species would be carbonate anions in AEM-based MEAs.
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10 While a technoeconomic analysis is beyond the scope of this work, it is clear that CO₂
11 crossover imposes a significant economic penalty on AEM-based eCO₂RR devices, considering
12 that the price of CO₂ would be linked to the (currently elevated) costs of carbon capture
13 schemes.⁴³ Even though our electrolyzer achieves outstanding figures of merit in terms of
14 selectivity, current density and cell voltage, **Figure 4B** shows that, overall, CO₂ utilization is
15 rather poor: even at low total current densities, less than half of the CO₂ consumed by the device
16 (which is shown in **Figure 4A**) is due to its conversion to the target product. In contrast to
17 previous modeling results,²² CO₂ utilization worsens with increasing current density, and at the
18 point of the highest rate of CO production (i.e., at 250 mA cm⁻²), close to 60% of the CO₂
19 consumed is not actually converted to CO. These results illustrate some of the tradeoffs that have
20 to be considered for the development of MEA-based eCO₂RR devices, and encourage the
21 consideration of reactant utilization as a valuable metric to complement the evaluation of CO₂
22 reduction electrolyzers operating at high current densities. In this regard, we note that many
23 different factors (e.g., membrane chemistry, electrolyte composition, mass transfer at the
24 interface) are expected to have an influence on CO₂ crossover.⁴⁴ Consequently, future studies
25 aimed at investigating these aspects are required to tailor the electrode-membrane interface and
26 mitigate this phenomenon.²⁷ Furthermore, future technoeconomic analyses will be valuable to
27 assess the consequences of CO₂ crossover and to establish design parameters, and we highlight
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3 the fact that there is also great potential in investigating process-level solutions (e.g., outlet
4 recirculation, integration with a different anodic reaction) to improve reactant utilization in
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6 eCO₂RR devices.
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10 11 12 **4. CONCLUSIONS** 13

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15 In this work, we demonstrated the potential of porous Ag membranes to act as effective gas
16 diffusion electrodes for CO₂ reduction to CO at high current densities. By using the Ag
17 membranes as gas-fed cathodes (humidified CO₂) in tandem with a liquid-fed IrO₂/C anode
18 (0.1 M KHCO₃) in a membrane-electrode assembly with a Sustainion AEM, a maximum partial
19 current density for CO of ca. 200 mA cm⁻² at a cell voltage of ca. 3.3 V was achieved. Hydrogen
20 evolution was effectively suppressed up to total current density of 250 mA cm⁻²; but operating
21 the cell beyond this point resulted in a rapid increase of H₂ production coupled with the collapse
22 of eCO₂RR activity. Furthermore, we showed large losses of CO₂ to the anode compartment of
23 the cell due to transport of HCOO⁻ and of HCO₃⁻/CO₃²⁻—generated from CO₂ reduction and
24 neutralization, respectively—across the anion-exchange membrane, and CO₃²⁻ was found to be
25 the main charge-carrying species across the AEM. Failure to account for the decrease of the flow
26 rate at the cathodic outlet caused by the non-stoichiometric neutralization and transport of CO₂ to
27 the anode can lead to overstated claims of device performance. Even though the exchange-MEA
28 configuration achieved outstanding results in terms of activity and selectivity, overall CO₂
29 utilization in the AEM-based MEA-type electrolyzer is poor, with less than half of the consumed
30 CO₂ going toward the production of the target product. These results call for the adoption of CO₂
31 utilization as complementary criterion for the evaluation of devices operating at industrially
32 relevant current densities, and encourages further research into strategies to mitigate CO₂
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3 crossover while retaining the favorable features (i.e., high selectivity and low ohmic losses) of
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5 AEM-based membrane-electrode assemblies in CO₂ reduction.
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10 **ASSOCIATED CONTENT**

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12 **Supporting Information.** Multivariable calibration procedure of the mass flow meter.
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14 Calculation of the Faradaic efficiencies and partial current densities. HPLC analysis of liquid
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16 products. Calculation of CO₂ crossover. XPS analysis of a porous Ag electrode. Products and
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18 outlet flows with argon as inlet gas. Cell voltage and gas-phase selectivity versus time in a
19
20 typical galvanostatic electrolysis. Cathodic outlet flow rates for different inlet flow rates.
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41 **Author Contributions**

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43 G.O.L., P.S-H. and J.P.H. and K.Z. developed the experimental setup and carried out
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45 measurements. G.O.L. performed the data analysis, and wrote the manuscript with input from all
46
47 co-authors. K.T.T., I.C. and B.S. conceived the project and oversaw its development.
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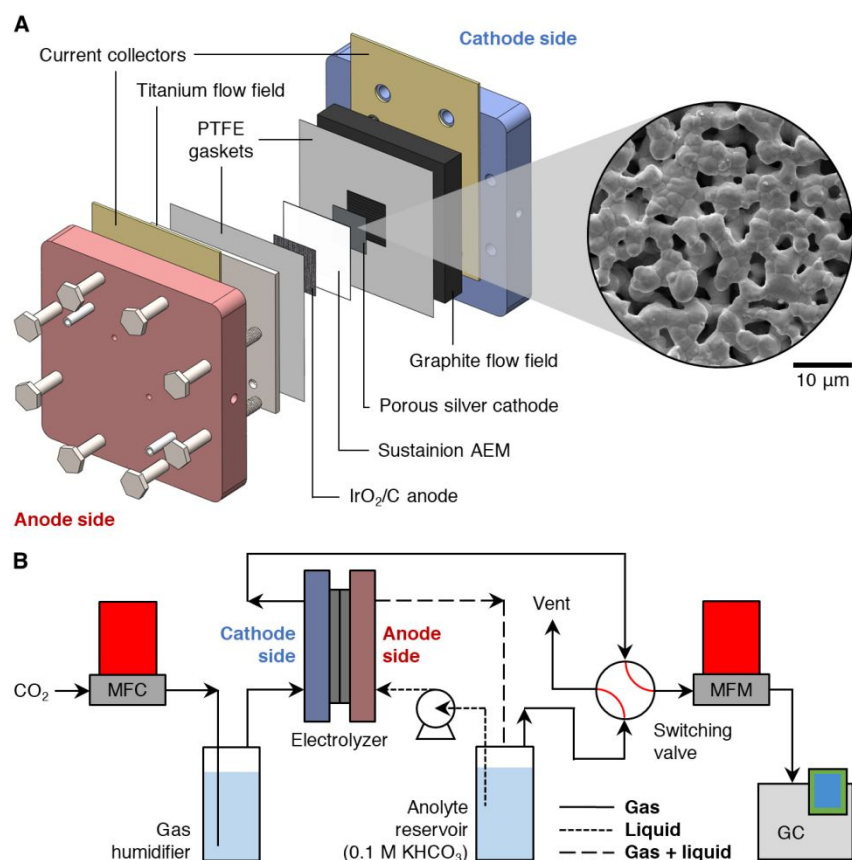


Figure 1. (A) MEA-type electrolytic cell for CO_2 reduction with a gas-fed cathode and a liquid-fed anode. (B) Flow diagram of the electrolysis setup. An automatic switching valve enabled the staggered measurement of the molar flow rate using a mass flow meter (MFM), in tandem with their compositional analysis via GC. A droplet condenser (not shown) was placed downstream of the cathode compartment.

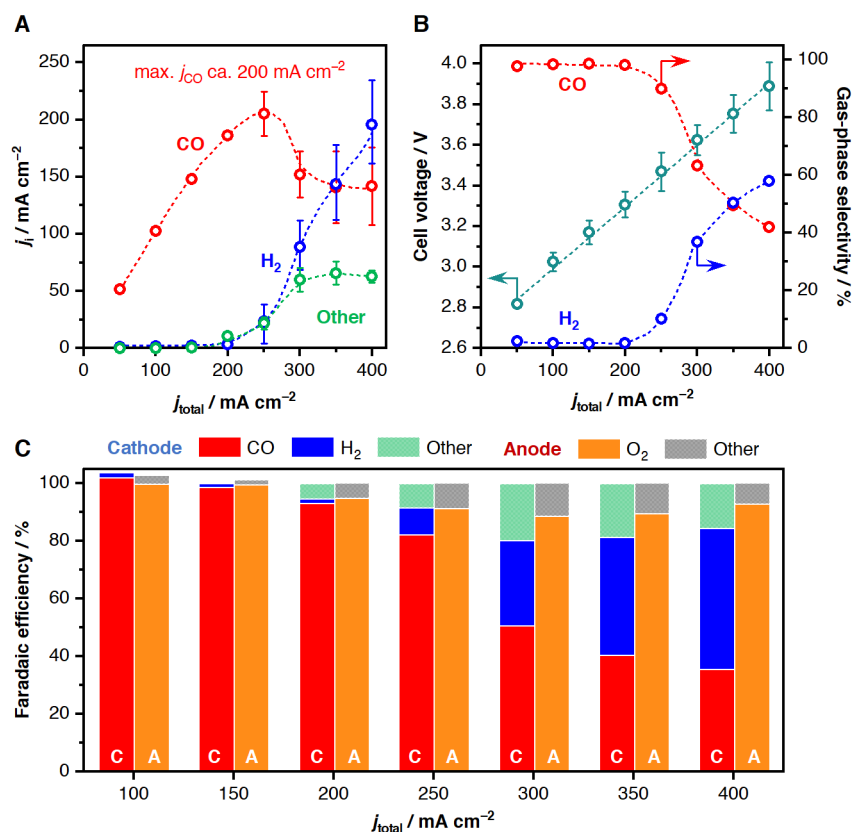


Figure 2. (A) Partial current densities (j_i) for different products as a function of the total current density (j_{total}) over a porous Ag cathode integrated into a MEA with a Sustainion AEM and an IrO₂/C anode. The error bars represent the standard error (SE) of the mean of 4 independent measurements. Error bars smaller than the symbol size are omitted for clarity. Trendlines are provided as a visual aid. (B) Cell voltage and gas-phase selectivity, defined as $j_i / (j_{CO} + j_{H_2})$, as a function of the total current density. Operating the electrolyzer at current densities higher than 250 mA cm⁻² resulted in periodic oscillations likely associated with mass transfer limitations. (C) Faradaic efficiencies over the porous Ag cathode (indicated by C) and the IrO₂/C anode (indicated by A). The values shown correspond to the mean FEs of 4 independent experiments. The fractions of the current that do not correspond to gas-phase products (indicated as “Others”) are most likely attributable to HCOO⁻ formation and decomposition, respectively.

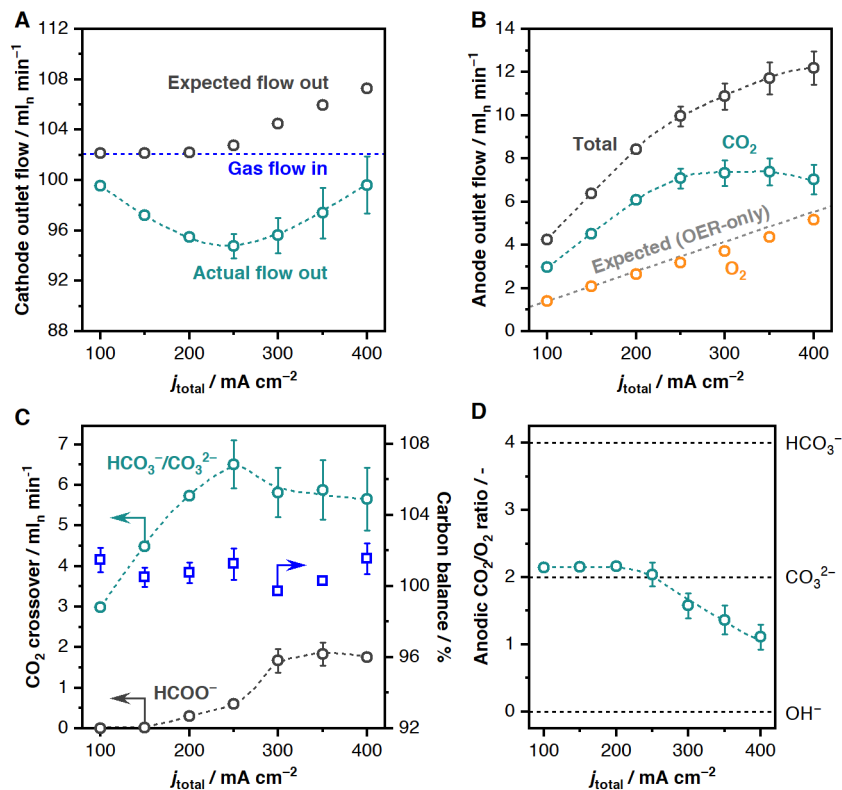


Figure 3. (A) Actual and expected outlet gas flows from the cathodic compartment of the electrolyzer as a function of the total current density (j_{total}). The inlet CO₂ flow (indicated by the horizontal dashed line) was $102.06 \pm 0.07 \text{ ml}_n \text{ min}^{-1}$. The expected outlet flow was calculated from the data in **Figure 2C** based on the FEs for the gas-phase products and the reaction stoichiometry. (B) Total and per-component gas flows evolved over the anode as a function of j_{total} . The expected anodic outlet flow in the absence of CO₂ crossover (dashed line) corresponds to a 100% FE for the OER. (C) CO₂ crossover through the AEM as different anionic species as a function of j_{total} and total mass balance of carbon around the cell. (D) Ratio of CO₂ to O₂ evolved over the anode as a function of j_{total} . The dashed lines indicate the theoretical values of CO₂/O₂ if all the current were carried by a single anionic species.

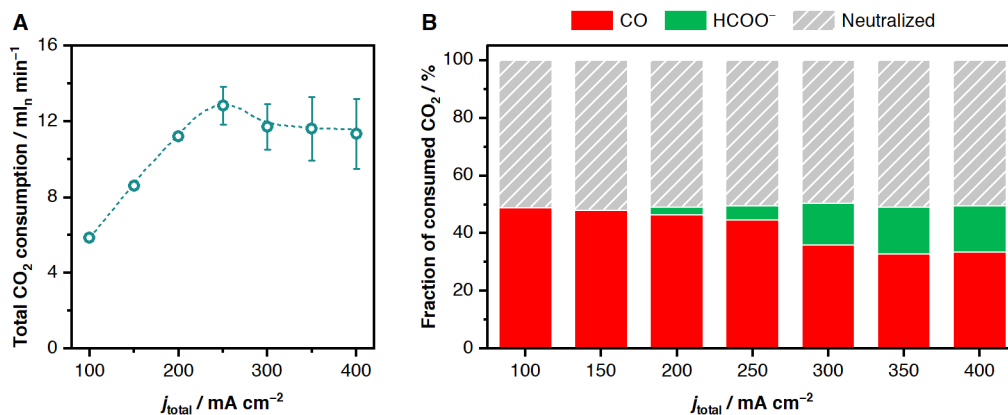


Figure 4. (A) Total consumption of CO₂ in the electrolyzer as a function of the total current density. The plateau that occurs at $j_{total} \geq 250$ mA cm⁻² is indicative of mass transfer-limited operation. (B) Breakdown of CO₂ consumed at different total current densities (j_{total}) due to (1) CO evolution, and lost to the anode through (2) HCOO⁻ evolution and (3) neutralization to HCO₃⁻/CO₃²⁻. The results highlight the overall poor utilization of consumed CO₂ in the AEM-based MEA-type electrolyzer.

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