Electrochemical CO₂ Reduction: Tailoring Catalyst Layers in Gas Diffusion Electrodes

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The electrochemical conversion of CO₂ into commodity chemicals or fuels is an attractive reaction for sustainable CO₂ utilization. In this context, the application of gas diffusion electrodes is promising due to efficient CO₂ mass transport. Herein, a scalable and reproducible method is presented for polytetrafluoroethylene (PTFE)-bound copper gas diffusion electrodes (GDEs) via the dry-pressing method and compositional parameters are emphasized to alter such electrodes. The assembly of the catalytic layer plays a critical role in the electrode performance, as elevated bulk hydrophobicity coupled with good surface wettability is observed to offer highest performance in 0.5 m KHCO₃. With optimized electrodes, formate, CO, and H₂ are obtained at a current density of 25 mA cm⁻² as main products in 1 m KOH in faradaic efficiencies (FEs) of 27%, 30%, and 36%. At 200 mA cm⁻², an altered product composition with ethylene (33% FE) and ethanol (9% FE) along with H₂ (33% FE) is observed. In addition, n-propanol is observed with 7% faradaic efficiency. The results indicate that the composition of the GDE has a severe influence on the electrode performance and setting proper hydrophobicity gradients within the electrode is key toward developing a successful electrochemical CO₂ reduction.

1. Introduction

Increasing anthropogenic carbon dioxide (CO₂) emissions are a major cause of global warming and climate change.[1,2] For this reason, the EU postulates the cross-sectoral reduction of greenhouse gas emissions by 80–95% based on the year 1990 until 2050.[3] In various industries such as steel, cement, aluminum, biogas, waste incineration and paper industry, CO₂ emissions are process-related and thus challenging to avoid. As a consequence, CO₂ capture and utilization (CCU) has become an increasingly attractive research field employing CO₂ as sustainable feedstock for a future production of commodity chemicals and fuels in a closed carbon cycle economy.[4] This allows coupling of the sectors industry, energy, and transport. The collective market size of the potential CCU products is >500 Mt per year, illustrating the potential application of such technologies.[5] Especially power-to-X technologies, involving renewable energy sources are predicted to be a convenient way to convert carbon dioxide into valuables.[6] An additional benefit of these technologies is the storage of electrical energy, which becomes increasingly important when increasing the share of fluctuating renewable energy sources. Power-to-X technologies offer the chance to sustainably produce important substances such as the bulk-chemical ethylene and the fuel substitute ethanol, which are commonly bio- or petroleum-based. However, most power-to-X technologies involving CCU comprise water electrolysis followed by thermally catalyzed CO₂ reduction.[7–9] Especially, synthesis routes based on H₂ and CO₂ toward C₂ alcohols consist of numerous process steps and have comparatively low technical maturity.[10] In contrast, a direct route to commodity chemicals and fuels from CO₂ and water via electrochemical reduction (CO₂R) is desirable and promising to keep investments and operational costs low while potentially increasing the conversion efficiency. Furthermore, CO₂R enables the CO₂ conversion at mild conditions that are typically found in electrolysis cells, avoiding the high temperatures and pressures commonly found in the thermal reduction of CO₂.[11,12]

While this electrochemical process is promising, major hitherto unresolved challenges persist for an industrial CO₂ utilization. Here, especially the poor product formation selectivity,[13–15] the competition with the parasitic hydrogen evolution reaction (HER)[16–18] as well as the low solubility of CO₂ in common electrolytes hampering the CO₂ mass transport have been identified.[19,20] A potential pathway to foster CO₂R, to suppress HER and to simultaneously enable high current densities...
(>200 mA cm$^{-2}$) is the application of gas diffusion electrodes (GDEs) that enable the conversion of gaseous CO$_2$.[21–23] Herein, the preferential CO$_2$ reduction is facilitated in a triple phase boundary between electrolyte, catalyst and gaseous CO$_2$. Likewise, high current densities can be achieved due to ultrathin layers of electrolyte facilitating the mass transport of CO$_2$ to the catalyst surface.[23] The exact working mechanism and with it the prerequisites to assemble functional GDEs are, however, still insufficiently understood and under investigation.[23]

Up to now, most reports on CO$_2$ gas diffusion electrolysis focus on the application of novel catalysts and their design, but not on the investigation of the basic assembly principles of the electrode that defines the catalytic environment and with it the reactivity of a particular catalyst. Along this line, GDEs, selective for CO/H$_2$ syngas mixtures,[24–29] formate$^{[30–32]}$ and C$_2$ products$^{[33–37]}$ were investigated in gas diffusion setups. Especially the formation of C$_2$ products like ethylene, ethanol, and n-propanol using copper-based catalysts are herein of particular interest due to their use as feedstock’s for carbon neutral polymers and fuels.[38–40]

While high selectivities toward, e.g., ethylene at industrially relevant current densities (200 mA cm$^{-2}$) were observed,[45] the electrodes often suffered from gas diffusion layer (GDL) flooding or catalyst abrasion leading to instability after only few hours of electrolysis.[37]

Even though, hitherto only a few strategies were developed to resolve these problems.[42] Notably, the decoupling of the GDL from the current collector component was found to improve the long-term stability due to reduced electrochemical wetting.[46] While this approach affords long-term stable GDE’s and was utilized for various catalytic systems,[42,43] upscaling and the long-term stability due to reduced electrochemical wetting or catalyst abrasion leading to instability after only few hours of electrolysis.[37]

Carbon black-supported Cu catalysts (Cu$_{xx}$) with loadings of 10, 25, and 50 wt% were obtained by a facile two step synthesis involving i) impregnation of the carbon black (CB) with Cu(OAc)$_2$ and ii) subsequent thermal reduction with H$_2$.[52] Powder X-ray diffraction after thermal reduction (Figure S1, Supporting Information) reveals metallic copper (ICDD: 04-0836) as the major Cu species for all catalyst/electrode assemblies. Minor phase impurities of Cu$_2$O (ICDD: 05-0667) and CuO (ICDD: 45-0937), likely due to exposure to air, are present. The crystallite sizes according to Debye-Scherrer are 25 (Cu$_{10}$), 26 (Cu$_{25}$) and 30 nm (Cu$_{50}$). The Cu loadings on CB determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) and thermogravimetric analysis (TGA) were in the anticipated range of 10, 25, or 50 wt%, respectively (Figure S2 and Table S1, Supporting Information). The surface area of the powdered catalysts according to Brunauer, Emmett and Teller (BET) decreases with increasing copper loading from 60 (Cu$_{10}$) to 37 m$^2$ g$^{-1}$ (Cu$_{50}$) (Figure S3 and Table S2, Supporting Information) as copper particles block pores of the carbon black support. Likewise, Hg-intrusion porosimetry shows a peak in pore size at 75 nm, which decreases in intensity with increasing copper loading (Figure S4, Supporting Information).

Subsequently, GDEs were prepared by hot pressing (260 °C, 200 bar) a Cu$_{xx}$/PTFE mixture onto a carbon cloth (CC) with a microporous layer (MPL) serving as a GDL. This process offers a cost-efficient and sustainable alternative to conventional spray-coating techniques. Likewise, it allows for high reproducibility, easy scalability to roll-to-roll manufacturing and no need for additional solvents.

A schematic illustration of the GDEs used within this work is depicted in Figure 1a. In the following, the catalyst layer composition will be referred to as Cu$_{xx}$/PTFE$_yy$ with xx (10–50 wt%) and yy (5–25 wt%) denoting the contribution of the various components in wt%. Unless otherwise stated, we used GDEs with the catalyst layer composition Cu$_{50}$/PTFE$_{15}$.

Figure 1. a) Schematic illustration of a GDE used in this work. The electrodes consist of i) an optional ionomer coating, ii) a PTFE bound catalyst layer, iii) a microporous layer, and iv) a GDL. b) Cross-sectional SEM micrograph of a representative Cu$_{50}$/PTFE$_{15}$ GDE. The scale bar is 250 μm.
As highlighted in the cross-sectional scanning electron microscopy (SEM) images of the GDEs (Figure 1b), the electrodes consist of interwoven, a rather thick catalytic layer and GDL. The typical catalyst layer thickness ranges from 320 to 415 μm depending on the exact composition (Figures S3–S7 and Table S3, Supporting Information). The variation in thickness mainly stems from varying compressibility of different catalyst layer compositions. While our hot-pressing method yields an unusually thick catalyst layer, we believe that this is advantageous for subsequent manipulations of the catalyst layer hydrophilicity by adjusting its composition. This opens the possibility for implanting hydrophilicity gradients in the catalyst layer which is favorable as a high performance GDE should provide high surface wettability with the electrolyte but also exhibit bulk hydrophobicity to limit flooding of the catalyst layer.

### 2.2. Electrochemical Testing

For the electrochemical evaluation of the gas diffusion electrodes, we constructed an electrochemical cell (Figure S8, Supporting Information) ensuring a controlled CO\(_2\) flow and pressure. Ideally, GDEs are operated in a bypass mode meaning that neither CO\(_2\) nor product gases cross the catalytic layer and reach the electrolyte. In this setup, solely liquid products will diffuse into the electrolyte. The exhaust gas stream was directly connected to the injection port of a GC instrument, where its composition was periodically monitored. We defined standard operating conditions (SOC) at an electrolysis potential of \(-1.4\) V versus reversible hydrogen electrode (RHE) (iR corrected), a CO\(_2\) flow of 5 mL min\(^{-1}\) and a CO\(_2\) pressure of 100 mbar in 0.5 M KHCO\(_3\) (the electrolyte pressure on the electrode is ≤5 mbar resulting from the hydrostatic pressure of max. 5 cm electrolyte column). At SOC, Cu\(_{50}/\)PTFE\(_{15}\) gas diffusion electrodes operate at a current density of 32 mA cm\(^{-2}\) after 2 h electrolysis (Figure S9, Supporting Information), with the main products being H\(_2\) (46%), CO (6%), and formate (20%) (Table S4, Supporting Information). Furthermore, traces of ethylene (0.3%), ethanol (0.2%), and n-propanol (0.2%) were detected and will not further be discussed within this work unless significant quantities (>1% faradaic efficiency) are observed for the described experiments. The total FE after electrolysis at SOC using Cu\(_{50}/\)PTFE\(_{15}\) GDEs is, however, insufficient at 73%. The significant losses in FE can be assigned to insufficient separation of gaseous and liquid phase by the GDE resulting in gas breakthrough and thus loss of gaseous products. The liquid products should however be unaffected by this effect. Thus, as long as gas breakthrough is occurring, the main indicator for the CO\(_2\)R performance should be liquid products, as the composition of the broken-through gas is not identified. Noteworthy, the gas breakthrough occurred despite prior cathodic polarization to ensure proper wetting of the GDE. The reproducibility of these experiments was confirmed by repeating the experiments at SOC a total of six times with electrodes cut from multiple electrode sheets and prepared with different catalyst batches (Note S1, Supporting Information). The relative errors from these experiments can be extrapolated to the parameter and compositions variation presented herein, as this represents the error with respect to the electrolysis setup.

Furthermore, we explored the electrolysis parameters differential pressure at the electrode (positive CO\(_2\) pressure differential) from 25 to 150 mbar, the CO\(_2\) gas flow from 2.5 to 20 mL min\(^{-1}\), and the electrolysis potential starting from SOC (Note S2, Figures S10–S12, and Table S5, Supporting Information). Here, the Cu\(_{50}/\)PTFE\(_{15}\) gas diffusion electrodes showed a stable operation at pressures <150 mbar and mass transport limitation at flow rates <5 mL min\(^{-1}\). Higher flow rates lead to significant dilution of the product gases, which is undesirable for potential industrial scale applications. However, increasing the electrolysis potential from \(-1.4\) to \(-1.8\) V versus RHE results in gas breakthrough caused by an increased production of gaseous products (due to a higher current density of 55 mA cm\(^{-2}\) compared to 32 mA cm\(^{-2}\) at SOC) ultimately leading to decreased faradaic efficiencies on the gas side of the electrode. Thus, operation of Cu\(_{50}/\)PTFE\(_{15}\) electrodes at higher electrolysis potentials/current densities is not favorable and further improvement of the catalyst layer with respect to its hydrophobicity and porosity is needed to enable high performance CO\(_2\)R at high current densities with proper separation of the gas stream from the liquid electrolyte.

### 2.3. PTFE Content

We anticipated that the observed behavior with gas breakthrough is indicative for a shift of the catalytic region (three phase boundary) closer to the electrolyte and thus a nonoptimal electrode composition with unfavorable electrode porosity and wettabillity. This low surface wettabillity is supported by the water contact angle of 152° ± 7° for Cu\(_{50}/\)PTFE\(_{15}\) GDEs (Table 1; Table S6, Supporting Information). The shift of the catalytic region is strongly dependent on the surface wettabillity, as the depth of electrolyte penetration into the catalyst layer decreases with increasing contact angle according to the Washburn equation.[53] It is noteworthy that the electrolysis conditions might lead to electrocapillary forces, which can reduce the actual contact angle under electric bias.[34] The electroless contact angle, however, still gives insight into the general wetting behavior of the catalyst layers. Likewise, the porosity was analyzed by means of N\(_2\) adsorption experiments (Figure S13, Supporting Information) and suggests a macroporous structure with little micro- or mesoporous contributions and a BET surface area (with respect to the complete electrode composite consisting of CL and GDL) of the Cu\(_{50}/\)PTFE\(_{15}\) GDEs of 20 m\(^2\) g\(^{-1}\) (compared to 37 m\(^2\) g\(^{-1}\) for the powdered, as synthesized Cu\(_{50}\) catalyst and 13 m\(^2\) g\(^{-1}\) for a bare gas diffusion layer). To receive further information on the pore sizes and their distribution, Hg-intrusion porosimetry was performed (Figure S14, Supporting Information). For Cu\(_{50}/\)PTFE\(_{15}\) GDEs, a broad range of pores between 75 and 100 000 nm is observed which account for 65% of the total pore volume of the electrode. This range represents the carbon cloth fabric of the GDL which shows a similar pore size distribution with a high percentile contribution of this range to the cumulative pore volume. A broad maximum in this range is observed between 4000 and 100 000 nm. Pores between 4 and 75 nm contribute 35% to the total pore volume of the Cu\(_{50}/\)PTFE\(_{15}\) GDE.
Here, a peak in relative pore sizes is observed at 50 nm, which is shifted toward smaller pores as compared to the pure Cu50 catalyst (75 nm) as the electrode is pressed at high pressures during fabrication. This peak can be assigned to the catalyst layer.

Hence, we altered the wettability and gas porosity of the catalytic layer by addition of various PTFE amounts to counter this effect. In total, PTFE contents from 5 to 25 wt% with respect to the carbon black content in the catalyst layer were applied. With increasing PTFE content, the BET surface area slightly decreased from 23 m² g⁻¹ (Cu50/PTFE05) to 20 m² g⁻¹ (Cu50/PTFE25) reducing the porosity of the catalyst layer by blocking pores with additional PTFE fibers (Table 1; Figure S15 in the Supporting Information). The pore size distribution remains mostly unchanged with a slight shift of the peak pore size from 50 nm (Cu50/PTFE05 and Cu50/PTFE10) to 60 nm (Cu50/PTFE15) and Cu50/PTFE25) with decreasing PTFE content (Figure 2a; Figure S16, Supporting Information). While at 5 wt% PTFE, a water contact angle of 131° ± 8° was obtained showing improved surface wettability compared to Cu50/PTFE15 electrodes, it did not notably change upon application of a PTFE content of 10 wt% (147° ± 8°) (Table 1; Table S6, Supporting Information). As the surface contact angle is influenced by the surface hydrophilicity and roughness, a direct correlation between the contact angle and bulk hydrophilicity of the electrodes is not applicable.⁹ Thus, we performed H₂O vapor physisorption analysis of GDEs with varying PTFE contents. Here, the H₂O sorption isotherms normalized to the specific BET surface area are presented as a metric for the hydrophilicity of the sample (Figure 2b). Notably, the H₂O sorption and thus the hydrophilicity decreases with increasing PTFE content in the catalyst layer. While at lower partial pressures (p/p₀ ≤ 0.2) this effect is not as pronounced, the H₂O uptake in the range from 0.2 < p/p₀ < 0.8 clearly shows the above-mentioned trend. It is noteworthy that at p/p₀ ≥ 0.8 the H₂O uptake shows a significant increase as result of H₂O condensation due to capillary effects impeding conclusions in this range (compare to Figure S15 in the Supporting Information). Thus, we will only discuss the H₂O physisorption in the range 0 < p/p₀ < 0.8. The electrocatalytic performance is altered significantly with the different PTFE contents (Figure 2c). Here, we observed a drop in current density from 34 mA cm⁻² (Cu50/PTFE05) to 29 mA cm⁻² (Cu50/PTFE25) at −1.4 V versus RHE in 0.5 M H₂CO₃ with increasing PTFE content (Figure S17, Supporting Information), as the electrical conductivity (Table 1) and double layer capacitance, representing the electrochemical surface areas (ECSA), of the electrodes decrease accordingly (Figure S18, Supporting Information). At the same time, the total CO₂R faradaic efficiency increases from 15% (Cu50/PTFE05) to 26% (Cu50/PTFE15) and then levels off at PTFE contents over 15 wt%. At the same time, the faradaic efficiency toward H₂ evolution herein is nearly unaffected (44–48%) from the PTFE content. Summarizing these dependencies, PTFE contents higher than 15 wt% reduce the overall electrode performance due to increased electrical resistivity of the electrode (Table 1). Furthermore, significant crack formation is observed in SEM micrographs after 2 h electrosynthesis using Cu50/PTFE05 and Cu50/PTFE15 electrodes, supporting mechanical instability of the electrodes (Figure S19, Supporting Information). All electrodes showed agglomeration of copper particles after electrosynthesis to some extent. Likewise, PTFE contents below 10 wt% cause mechanical instability of the catalyst layer during electrosynthesis and lead to faster breakthrough of gas through the GDE eventually resulting in a loss of total faradaic efficiency. Higher PTFE contents (≥15 wt%) in the catalyst layer lead to decreased wetting of the catalyst layer thus enhancing CO₂ mass transport in the porous matrix facilitating higher CO₂R rates. Therefore, we identified a PTFE content of 15 wt% as optimal for the further experiments.

Table 1. Experimentally determined copper loadings, contact angles, BET surface areas, and water sorption of the utilized GDEs with catalyst layers composed of varying PTFE contents and copper catalysts loadings as well as additives.

| Code                | Cu (wt%) | PTFE (wt%) | Additive/ ionomer⁹ | Cu [mg cm⁻²] | Spec. resistivity [mΩ cm⁻²] | ΘH₂O [°] | BET [m² g⁻¹] | H₂O sorption [cm³ m⁻²] |
|---------------------|----------|------------|--------------------|-------------|--------------------------|---------|-------------|---------------------|
| Cu50/PTFE05         | 50       | 5          | –                  | 14.9        | 152                      | 131 ± 8 | 23          | 0.070               |
| Cu50/PTFE10         | 50       | 10         | –                  | 11.1        | 115                      | 147 ± 8 | 22          | 0.050               |
| Cu50/PTFE15         | 50       | 15         | –                  | 12.4        | 117                      | 152 ± 7 | 19          | 0.047               |
| Cu50/PTFE25         | 50       | 25         | –                  | 15.3        | 160                      | 147 ± 4 | 20          | 0.036               |
| Cu50/PTFE10/AC      | 10       | 15         | –                  | 1.7         | 113                      | 145 ± 6 | 27          | 0.039               |
| Cu50/PTFE15/Nafion  | 25       | 15         | –                  | 5.1         | 121                      | 139 ± 6 | 26          | 0.043               |
| Cu50/PTFE15/CNT     | 50       | 15         | –                  | 12.4        | 117                      | 152 ± 7 | 20          | 0.047               |
| Cu50/PTFE15/FAA3    | 50       | 15         | FAA-3-film         |             | 12.4                      | 74 ± 4 | 30          | 0.110               |
| Cu50/PTFE15/Sust.   | 50       | 15         | Sust. XA-9         | 12.4        | 157                      | 56 ± 6  | 36          | 0.067               |

⁹ The Cu loading in wt% is referred to the copper loading in the catalyst; ⁰ The loading of the additive was 10 wt% with respect to the total mass of the catalyst layer; ¹ Through-plane resistivity under a compression load of 0.2 MPa; ² The error was estimated from twelve independent drops on the electrode surface (Table S5, Supporting Information); ³ BET surface area normalized H₂O physisorption in cm³ m⁻² at p/p₀ = 0.5. Higher H₂O adsorption refers to higher hydrophilicity; ⁴ The ionomer coating is an electrical insulator.
2.4. Copper Loading

Additionally, the Cu-loading in the catalyst layer was varied in the range of 1.9–14.8 mg cm$^{-2}$ referred as Cu$_{10}$/PTFE$_{15}$ and Cu$_{50}$/PTFE$_{15}$, respectively. While the BET surface was unchanged in Cu$_{25}$/PTFE$_{15}$ (26 m$^2$ g$^{-1}$) and Cu$_{10}$/PTFE$_{15}$ (27 m$^2$ g$^{-1}$), at a higher Cu-mass loading of 50 wt% the surface area notably decreases to 20 m$^2$ g$^{-1}$ (Cu$_{50}$/PTFE$_{15}$) (Figure S20, Supporting Information). On the contrary, the pore size distribution from Hg-intrusion porosimetry appears, opposed to the bare catalysts, similar for Cu$_{xx}$/PTFE$_{yy}$ electrodes (Figure 2d; Figure S21, Supporting Information). Thus, the pore size distribution is rather controlled by the fabrication method of the electrode rather than the catalysts properties. The surface wettability increased marginally with lower Cu-mass loadings, as the contact angle decreases to 139° ± 6° (Cu$_{25}$/PTFE$_{15}$) or 145° ± 6° (Cu$_{10}$/PTFE$_{15}$), respectively (Table 1; Table S6, Supporting Information). Contrary, the surface area normalized H$_2$O sorption decreases slightly with lower Cu-mass loading (Figure 2e) from 0.047 cm$^3$ m$^{-2}$ (Cu$_{50}$/PTFE$_{15}$) to 0.043 cm$^3$ m$^{-2}$ (Cu$_{50}$/PTFE$_{15}$) and 0.039 cm$^3$ m$^{-2}$ (Cu$_{10}$/PTFE$_{15}$) at p/p$_0$ = 0.5. This behavior clearly reveals a discrepancy between surface wettability and bulk hydrophilicity caused by surface roughness. With respect to electrode performance, the Cu-loading does not significantly influence the current densities (Figure S22, Supporting Information), double layer-capacitance (Figure S23, Supporting Information), the product composition (Figure 2f), as well as electrode morphology after electrolysis (Figure S24, Supporting Information). We therefore hypothesize that a considerable portion of pore volume of the carbon black support is blocked with copper particles at elevated mass loadings. The observation shows that the catalyst accessibility in GDEs can antagonize the effect of a higher catalyst surface.

2.5. Catalyst Layer Hydrophobicity

While we could improve the CO$_2$R performance of the GDEs by tailoring the PTFE content, a large portion of the faradaic efficiency is lost by gas evolution on the electrolyte site. We anticipated that the wettability and porosity of the catalyst layer is not sufficiently tuned to achieve an optimal performance. Thus, we prepared Cu$_{50}$/PTFE$_{15}$ GDEs with supplementary 10 wt% activated charcoal (AC) as hydrophilic additive as well as multiwalled carbon nanotubes (CNTs) as porosity modulator with respect to the catalyst layer mass.

Introducing these additives to the GDE catalyst layer the BET surface area is perceptibly increased from 20 m$^2$ g$^{-1}$ (Cu$_{50}$/PTFE$_{15}$) to 29 m$^2$ g$^{-1}$ (Cu$_{50}$/PTFE$_{15}$/CNT) or 45 m$^2$ g$^{-1}$ (Cu$_{50}$/PTFE$_{15}$/AC) by the addition of the extra carbon matrix and can be correlated to the enhanced surface area of the utilized additives (Table S7, Supporting Information). Furthermore, the N$_2$ sorption isotherms showed that the addition of AC as well as multiwalled carbon nanotubes (CNTs) as porosity modulator with respect to the catalyst layer mass.

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more pronounced for Cu50/PTFE15/AC electrodes. On the contrary, the pore size distribution in the meso- to macro porous range from Hg-intrusion porosimetry does not show significant changes upon modification with AC or CNT additives (Figure 3a; Figure S27, Supporting Information). In contrast to additive-free electrodes, the surface wettability increased significantly for AC (72° ± 9°) and did not significantly alter for CNT (144° ± 9°) modified electrodes (Table 1). A similar trend is observed in the relative H2O sorption. Introduction of CNT only slightly increased the H2O uptake to 0.056 cm3 m−2 at p/p0 = 0.5 (Figure 3b). Contrary, the Cu50/PTFE15/AC electrode shows perceptibly higher H2O uptake at 0.21 cm3 m−2 implying higher bulk hydrophilicity. This can be attributed to the high ash content and thus high availability of hydrophilic sites in the material (Table S6, Supporting Information).

Notably, electrochemical performance tests at SOC showed that the decreased hydrophobicity improved the total faradaic efficiencies at comparable current densities of ≈35 mA cm−2 (Figure S28, Supporting Information), with unaltered H2:CO ratios (Figure 3c). The Cu50/PTFE15/AC GDEs exhibit quantitative conversion of electrons in H2 evolution as well as CO2R products. A significantly smaller FE (34%) was observed for Cu50/PTFE15/CNT GDEs. We assume that this behavior reflects the suppressed gas cross-over to the electrolyte site and is in accordance with our visual experimental observations. Moreover, we observed a slightly improved faradaic efficiency toward formate (23% for Cu50/PTFE15/AC compared to 20% for Cu50/PTFE15) using AC electrodes while the ratio of the H2 and CO did not change. Upon CNT-modification, solely formate is observed with a total CO2R faradaic efficiency of (6%). We assume that this improvement for Cu50/PTFE15/AC electrodes is due to enhanced wettability of the catalyst layer by the hydrophilic nature of the AC additive. Concurrently, the porosity still enables transport of gaseous reactants and products to the GDL. Upon CNT-modification, severe crack formation during electrolysis coupled with the retaining low surface wettability as observed for Cu50/PTFE15 electrodes enables undesirable flow-through operation of the electrode, reducing the overall performance (Figure S29, Supporting Information). Our experiments thus show that the optimization of catalyst layer hydrophobicity allows an liquid–gas product separation but does not significantly alter the overall reactivity of the gas diffusion electrode.

### 2.6. Electrode Coating and Surface pH

Notably, the simple decrease of catalyst layer hydrophobicity with a hydrophilic additive improved the overall electrode performance and separation of gaseous and liquid products by wetting the catalyst layer and thus creating a barrier for gas evolution on the electrolyte site. However, the CO2R selectivity was still unsatisfying. Thus, we further optimized the catalyst layer with respect to the local pH, as it has been shown to be crucial for efficient CO2R.[56,57] Furthermore, ionomer modifications have been shown to enhance the combined hydrophobic and hydrophilic properties necessary for efficient CO2R.[58,59] A straightforward method to enable such a local pH change,
while providing high surface wettability, is by modifying the catalyst layer with an additional ionomic coating. Ultimately, a hydrophilicity gradient is implemented by adding a hydrophilic ionomer coating to the bulk hydrophobic catalyst layer.

Thus, we subsequently coated Cu50/PTFE15 GDEs with either Nafion D-521 (Nafion), FAA-3 or Sustainix AX-9 (Sust.) ionomers with a loading of 3 mg cm⁻² generating either a highly acidic (Nafion) or an alkaline environment (Sust. and FAA-3) on the catalyst layer. The thickness of the ionomer coating is in the range between 6 and 7 µm (Figure S30, Supporting Information). Noteworthy, the BET surface area increases upon modification of the Cu50/PTFE15 with ionomer coatings. While for Nafion (37 m² g⁻¹) and Sust. (36 m² g⁻¹) modification the BET surface area is nearly doubled, for a FAA-3 coating (30 m² g⁻¹) an increase by 50% is observed as compared to pristine Cu50/PTFE15 electrodes (20 m² g⁻¹) (Table 1; Figure S31, Supporting Information). This can be explained by increasing porosity of the ionomer film upon drying in vacuum as seen in SEM images (Figure S32, Supporting Information). Hg-intrusions porosimetry reveals changes in the pore size distribution in the micrometer range (1000–100 000 nm) as well as sub-100 nm range (Figure 3d; Figure S33, Supporting Information). In the former case, an increased contribution of the micrometer pores is observed for Nafion and Sust.-modified electrodes, which is likely due to cracks in the ionomer coating. In the sub-100 nm range, the pore size peak at 50 nm shifts to 60 nm for alkaline (FAA-3 and Sust.) and to 75 nm for acidic (Nafion) coatings. The very low contact angles of 92° ± 9° (Cu50/PTFE15/Nafion), 74° ± 4° (Cu50/PTFE15/FAA3) and 56° ± 6° (Cu50/PTFE15/Sust.) indicate high surface wettability of the ionomer coated electrodes (Table 1; Table S6, Supporting Information). Along this line, the H₂O uptake at p/p₀ = 0.5 increases in comparison to pristine Cu50/PTFE15 electrodes. While acidic modification with Nafion drastically increases the H₂O uptake (Figure 3e) to 0.371 cm³ m⁻², upon alkaline modification the increased H₂O uptake is less pronounced for Cu50/PTFE15/FAA3 (0.110 cm³ m⁻²) and Cu50/PTFE15/Sust. (0.067 cm³ m⁻²). Worth mentioning is, however, that the contact angle and H₂O physisorption results show a contrasting trend. This again shows the huge discrepancy between surface wettability via contact angle measurements and bulk hydrophilicity analysis of the electrode as described above.

Again, electrochemical testing was performed under the above described SOC and the product compositions was analyzed after 2 h electrolysis. The CO₂R performance is clearly influenced by the electrode coating and with it, the local pH within the GDE, as was recently shown by in situ infrared spectroscopy on polycrystalline Cu electrode surfaces.[56] The current density is mostly independent of the nature of the ionomer coating (Figure S34, Supporting Information). On the contrary, the double layer significantly decreases upon ionomer coating (Figure S35, Supporting Information) as the penetration of the electrolyte into the pore system is blocked by the ionomer film. While the acidic surface modification (Cu50/PTFE15/Nafion) leads to slightly increased total CO₂R efficiency (31%) compared to pristine electrodes with formate and CO faradaic efficiencies of 22% and 12%, respectively (Figure 3f), H₂ remained the main product (FE 59%). Similarly, modification of the Cu50/PTFE15 electrodes was conducted with the FAA-3 ionomer typically being a constituent of anion exchange membranes. The electrochemical performance of the obtained electrodes, however, was very similar to that of Cu50/PTFE15/Nafion and H₂ (70%), formate (15%), and CO (9%) were observed. Nevertheless, compared to Nafion-coated catalyst layers, the C₂+ products ethylene (2.8%), ethanol (1.1%), and n-propanol (1.1%) were likewise detected suggesting that an alkaline environment in the FAA-3-modified catalyst layer seems to impair CO₂R selectivity but improves C–C coupling efficiency. Therefore, we applied the Sust. ionomer that was previously shown to provide high conductivity at lowest area specific resistance.[60] Upon modification of the catalyst layer surface with Sust. ionomer, the electrochemical CO₂R performance is significantly improved. Notably, H₂ evolution could be massively suppressed to 28% faradaic efficiency along with a major increase of the main CO₂R products formate and CO. These CO₂R products were generated with a faradaic efficiency of 37% and 27%, respectively. Likewise, formation of the C₃+, products ethylene (1.7%), ethanol (3.2%), and n-propanol (2.0%) was observed as minor by-products. The fact that the FAA-3 or Sust. ionomer coated Cu50/PTFE15 electrodes reveal C₂+ products while the uncoated electrodes did not, suggests that the selectivity is significantly influenced by the alkalinity in the catalyst layer as was recently suggested by Smith and coworkers.[24]

2.7. Toward Industrially Relevant Conditions

We have shown that especially the wetting characteristics of the catalyst layer and the chemical nature of the ionomer play crucial roles in tailoring the CO₂R performance of GDEs. While we improved the selectivity for CO₂R to an overall faradaic yield of 71% by coating of the catalyst layer with Sust. ionomer layer, the performance with respect to current densities and overpotentials, reaching 30 mA cm⁻² at −1.4 V versus RHE is insufficient for any industrial application.[61] We first changed the electrolyte from 0.5 m KHCO₃ (35 mS cm⁻¹) to 1 m KOH, which exhibits significantly higher conductivity (201 mS cm⁻¹).[62–64] In line with this change, the overpotential at a current density of 30 mA cm⁻² is tremendously reduced from −1.43 V in 0.5 m KHCO₃ to −0.69 V versus RHE in 1 m KOH (Figure 4a). Electrolysis experiments at the same current densities revealed comparable faradaic efficiencies for H₂ (31%) and CO (26%) for 1 m KOH as compared to the experiments in KHCO₃. Notably, KOH facilitates the formation of the C₂+ products ethylene (4.4%), ethanol (7.7%), and n-propanol (3.1%) at the cost of lowered formate FE (27%) (compare Cu50/PTFE15/Sust. in Table S8 and 25 mA cm⁻² in Table S9, respectively, in the Supporting Information). We attribute this phenomenon to the high concentration of hydroxide ions, which was shown to facilitate C–C coupling in CO₂R with same Cu-based GDEs.[17,57,65] Under such high pH conditions, the CO hydrogenation on Cu catalysts is predicted to be kinetically hindered paving the way for C–C coupling to occur.[19,66]

Furthermore, since current densities of 30 mA cm⁻² are far away from any industrial application scenario, we subsequently performed galvanostatic electrolysis experiments with the Sust.-modified Cu GDEs in 1 m KOH with current densities
of 25, 50, 100, 200, 300, and 400 mA cm$^{-2}$ Non-iR-corrected potentials (the distance between working and reference electrode is $\approx 25$ mm) required to reach these current densities after 2 h electrolysis are $-0.72$, $-0.89$, $-1.41$, $-1.85$, $-2.49$, and $-2.92$ V versus RHE, respectively (Figure 4b) Depending on the applied current density, a shift in the applied potential is observed. For current densities $\leq 200$ mA cm$^{-2}$, a more negative potential indicates decreased conductivity of the electrolyte, which can be assigned to changes of the electrolyte pH by carbonate buffering via dissolution of CO$_{2}$ in the electrolyte (Table S8, Supporting Information). This carbonate formation leads to a higher resistivity of the electrolyte due to lowered ionic strength. On the contrary, the positive shift for current densities $\geq 300$ mA cm$^{-2}$ may indicate flooded operation of the electrode under high current densities.[67]

In fact, the selectivity for H$_{2}$, C$_{1}$, and C$_{2}$+ products is largely influenced by the current density (Figure 4c). Besides the main products (H$_{2}$, CO, ethylene, ethanol and n-propanol), traces of ethane are detected with faradaic efficiencies <0.3% (Table S9, Supporting Information). While an increase from 25 to 50 mA cm$^{-2}$ slightly reduced the C$_{2}$+ faradaic efficiency at the expense of higher H$_{2}$ evolution, a further increase in current density to 100 mA cm$^{-2}$ leads to an increase in C$_{2}$+ faradaic efficiency of 19% with an ethylene yield of 12%. Equally, the faradaic efficiency of C$_{1}$ products decreases continuously from 53% (25 mA cm$^{-2}$) to 48% (100 mA cm$^{-2}$). At a current density of 200 mA cm$^{-2}$, the suppression of C$_{1}$ product formation is significantly more noticeable, resulting in C$_{1}$ faradaic efficiency of solely 27% as well as faradaic efficiencies of 33% for H$_{2}$ and 47% for C$_{2}$+ products. This sudden change in C$_{2}$+ selectivity implies a changed reaction mechanism and can be explained by an increase in local pH due to high proton consumption at high current densities together with the phenomenon's described above.[65,68,69] The composition of the product gas stream is 37.0 vol% H$_{2}$, 10.8 vol% CO, and 6.2 vol% ethylene along with traces of ethane (250 ppm) as well as CO$_{2}$ (Table S10, Supporting Information). However, further increasing the current density to 300 and 400 mA cm$^{-2}$, the total detected faradaic efficiency decreased significantly to 67% at 400 mA cm$^{-2}$. During these experiments, we observed perceptible gas evolution on the electrolyte site suggesting limited transport of gaseous products to the gas side. We assume this effect is due to rapid electrowetting of the catalyst layer at such high current densities, thus blocking the gas transport. Furthermore, carbonate formation resulting in blocked pores and thus hindered CO$_{2}$ mass transport can facilitate increasing H$_{2}$ evolution.[70] Along this line, we observed a significantly increased H$_{2}$ evolution with faradaic efficiencies of 53 (300 mA cm$^{-2}$) and 51% (400 mA cm$^{-2}$). The faradaic efficiency for carbonaceous products decreased to a total of 30% and 16% at 300 and 400 mA cm$^{-2}$, respectively. This observation likewise confirms the CO$_{2}$ mass transport limitation by increased electrowetting and increasing carbonate formation at higher current densities. In fact, we further observed a decreased efficiency toward
CO₂ reduction products after 2 h electrolysis in comparison to 1 h electrolysis at 300 and 400 mA cm⁻², supporting the high degree of electrowetting (Table S9, Supporting Information).

To further evaluate the influence of the applied current density on the product distribution, we depict the partial current densities as a function of the measured voltage (Figure 4d–f). While the H₂ partial current density steadily increases with higher measured voltages, the C₁ and C₂⁺ reach maximum partial current densities at a voltage of −1.85 V versus RHE (200 mA cm⁻²) with 55 and 94 mA cm⁻², respectively. According to a Bezier interpolation of the data, the C₂⁺ partial current density becomes higher at voltages more negative than −1.6 V versus RHE. At even higher voltages, the partial current densities for the CO₂ reduction products ceases, indicating before-mentioned mass transport limitations due to electrowetting and pore blocking by carbonate formation. Subsequently, HER becomes the favored process.

So far, we showed that the ionomer coating of the catalyst layer with Sustanion providing a promising performance toward C₂⁺ products at elevated current densities. However, optimization with respect to the flooding of the electrode is still needed. Thus, we opted to tune the ionomer coating thickness by adjusting the loading in the range from 1.5 to 9.0 mg cm⁻² (Figure 5a,b; Table S11, Supporting Information). At lower loadings (<3 mg cm⁻²), the ionomer coating thickness only slightly increases from 1.8 to 6.8 µm, indicating intrusion of the ionomer into the pores. Contrary, at higher loadings ≥3 mg cm⁻², the thickness increases linearly with a slope of 9.4 µm mg⁻¹ cm⁻² up to 65 µm at a loading of 9 mg cm⁻², suggesting growth of a membrane film on the catalyst layer. The H₂O-physisorption and thus hydrophilicity of the electrodes increase accordingly with higher ionomer coatings (Figure S36, Supporting Information). In fact, the coating thickness has a drastic influence on the performance of the GDE at a current density of 200 mA cm⁻² in 1 m KOH (Figure 5c–f). The electrolysis potential range between −1.8 and −2.0 V versus RHE and does not show any notable trend with respect to the ionomer film thickness (Figure S37, Supporting Information). Without any ionomer coating the total faradaic efficiency suffers from significant gas breakthrough (see Video S1 in the Supporting Information) reaching only 24% proving unsuitability of non-coated Cu₅₀/PTFE₁₅ electrodes at high current density operation. Accordingly, the faradaic efficiencies for CO₂R products is low at 3.1% with contributions from CO (1.8%), formate (0.7%), and ethylene (0.5%). Furthermore, ethanol (<0.1%) and n-propanol (0.1%) were detected in traces. Thus, the partial current densities for CO₂R products are negligible. Consequently, a comparatively (with respect to the overall detected products) high H₂ faradaic efficiency (21%) is detected. While the low overall faradaic efficiency for gaseous products can be attributed to the

![Figure 5](https://example.com/figure5.png)

**Figure 5.** a) Cross-sectional micrograph of a Cu₅₀/PTFE₁₅ electrode coated with 10 wt% Sustainion XA-9 at 1000× magnification (scale bar: 25 µm). The catalyst layer and ionomer coating are highlighted in cyan and green. b) Dependency of the coating thickness on the mass loading of Sustainion XA-9 on the catalyst layer. At loadings <3.0 mg cm⁻², the increase in thickness is reduced compared to ≥3.0 mg cm⁻² as the porous catalyst layer is mostly soaked with the ionomer solution during the first cycle. The dashed line represents a linear fit for loadings ≥3.0 mg cm⁻². c) Faradaic efficiencies after 2 h galvanostatic electrolysis using Cu₅₀/PTFE₁₅/Sust. Electrodes with a Sustainion XA-9 loading of 0.0, 1.5, 3.0, 4.5, 6.0, and 9.0 mg cm⁻². The H₂ (orange), CO (blue), formate (light blue), ethylene (dark green), ethanol (green), and n-propanol (light green) faradaic efficiencies are shown. The columns are grouped in H₂ (orange), C₁ (blue), and C₂⁺ products (green) for visualization of the C₂⁺ selectivity. (d)–(f) show the partial current densities as a function of the measured potential using the same color code as previously described for faradaic efficiencies.
gas breakthrough, the low amounts of liquid products (formate, ethanol, and n-propanol) suggest inefficient operation of the gas diffusion electrode likely in a flooded state. At a low coating thickness (1.8 µm), the performance suffers as H2 evolution dominates with a faradaic efficiency of 52%. C1 and C2 products form in equal quantity at 19% faradaic efficiency, whereas formate (12%) and ethylene (12%) are the main CO2R products. Increasing the ionomer loading to 3 mg cm⁻², the performance drastically improves to before mentioned performance for Cu50/PTFE15/Sust. Electrodes at 200 mA cm⁻² show high faradaic efficiencies for C2 (47%) and ethylene (33%). The decreased performance at 1.5 mg cm⁻² is likely caused by increased electrowetting of the electrode, as the ionomer film acts as a barrier for the aqueous electrolyte to the electrode. Further increasing the ionomer loading to 4.5 mg cm⁻² slightly reduces the efficiency toward C2 and C2, products with 23% and 40% at the cost of increased H2 evolution (42%). At loadings >4.5 mg cm⁻² Sust., the H2 evolution becomes more pronounced with 53% (6 mg cm⁻²) and 50% (9 mg cm⁻²). The C1 product faradaic efficiency stays within the margin of errors (Table S11, Supporting Information) between 16% and 20% for 6 and 9 mg cm⁻², respectively. On the contrary, the C2, efficiency first decreases to 19% for 6 mg cm⁻² loading followed by an increase to 29% for 9 mg cm⁻². The sudden increase in performance at very high Sust. loadings and thus thick coating appears surprising, the performance with thicker coatings is worse compared to the optimal coating thickness between 6 and 25 µm. We assume that the mass transport of hydroxide ions from the catalyst is hampered with thick ionomer coatings, increasing the likelihood of carbonation in the catalyst layer, thus decreasing the local pH toward more neutral conditions. Furthermore, the decreased presence of liquid water in the catalyst layer resulting from a thick ionomer barrier might enhance this phenomenon as formed carbonate cannot dissolve into the electrolyte, blocking the pores and thus pathways for CO2 diffusion. This results in less efficient CO2 reduction, increasing H2 evolution.⁶⁷,⁷²

3. Conclusion

In summary, we prepared a series of Cu-GDEs with PTFE bound catalyst layers using a facile dry-pressing method and could allocate the influence of the composition on the performance of these GDEs. We show that the composition severely affects the overall performance of the electrodes. Although good performances of a GDE for CO2R is often accompanied with high hydrophobicity, we could show that this is only the case for the GDL. By using GDEs with a thick, PTFE-bound catalyst layer, we could show that high hydrophobicity of this layer reduces the overall performance with respect to product separation, as gaseous products break through at the electrolyte site due to bad wettability of the catalyst layer. We likewise were able to improve the product separation by improving the wettability of the catalyst layer using hydrophilic activated charcoal or ionomers additive in/on the catalyst layer. However, the desired selectivity for C2 products was solely achieved by coating the catalyst layer with the anionic ionomers FAA-3 and Sust. This way, we provide high bulk hydrophobicity, while improving the surface wettability. Especially the latter ionomer did not only improve the product separation and C2, product outcome, but also significantly boosted the CO2R selectivity with formate and CO as main products in 37% and 27% FE, respectively.

In order to test the electrodes toward industrially more relevant conditions, we investigated the Sust.-modified electrodes in 1 m KOH electrolyte, yielding reduced overpotentials and slightly favorable product distributions, namely, C2, products are favored. By increasing the current density from 25 to 200 mA cm⁻² we could further improve the C2 selectivity, reaching C2, faradaic efficiencies of up to 47% at 200 mA cm⁻². Furthermore, we observed high CO (10.8 vol%) and ethylene (6.2 vol%) concentrations in the output gas stream, which might be further increased by altering the CO2 gas feed flow. However, at higher current densities, the flooding of the GDE via electrowetting disabled stable electrolysis. This observation, however, shows that the current density plays a pivotal role in the performance of these copper GDEs. Moreover, we could show that the selectivity of the electrode could be modified just by electrode design, which further increases the flexibility as well as product diversity and paves another route for optimization of the copper-based CO2 electrolysis compared to other strategies such as catalyst optimization via particle size, morphology, or surface chemistry.⁷³,⁷⁴ We further optimized the Sust. coating of the GDE with respect to the coating thickness. The ideal coating thickness is in the range between 6 and 25 µm. While thinner films accelerated electrowetting induced flooding of the catalyst layer, thicker films limit the hydroxide transport from the catalyst layer yielding increased carbonate formation which blocks CO2 diffusion pathways and ultimately disfavors CO2R.

Overall, we present a scalable and reproducible method for the preparation of stable GDEs for the highly flexible electrochemical CO2 reduction using a dry-pressing process. We likewise highlight the tunability of the hydrophobicity and porosity via this dry-pressing pathway. Furthermore, we decoupled the wettability of the electrodes surface from the bulk hydrophobicity by applying a coating ionomeric film onto the electrode surface. Especially a high bulk hydrophobicity coupled with a good surface wettability in Cu50/PTFE15/Sust. electrodes offers a good performance with high product selectivity for CO2R at industrially relevant current densities. This emphasizes the importance of the electrode design for high performance CO2R.

4. Experimental Section

General: Copper(II) acetate hydrate (98%, Alfa Aesar), ENSACO 250 G carbon black (Imerys Graphite & Carbon), DyneonTM PTFE Powder TF 1750 (3M), multwallaided CNTs (United Nanotech), Dopetac Sulfo 100 activated charcoal (AdFiS GmbH), KHCO3 (Merck), and KOH (Carl Roth) were used as received without further purification. Carbon cloth GDLs with 10% microporous coating were purchased from Quinter (CeTech W1S1009 with 10% MPL and PTFE). Ionomers were either purchased as 5 wt% solution (Nafion D-521, Alfa Aesar and Sustainion XA-9, dioxide materials) or as a shredded film (FAA-3-film, furnatech BWT GmbH), which was then dissolved in n-propanol to form a 5 wt% solution. Unless otherwise stated, MilliQ quality water (≥18.2 MΩ cm) was used for all experiments. All potentials in this manuscript are referred to the RHE.

Catalyst Synthesis: The Cuxx catalysts with Cu-loadings of 10, 25, or 50 wt% were synthesized according to an adopted literature procedure.⁸² Briefly, in a 1000 mL round bottom flask, copper(II)acetate (3.14 g for Cu50, 9.42 g for Cu25, or 28.26 g for Cu50) was dissolved in
deionized water (500 mL). Subsequently, carbon black (9.0 g) was added and the mixture was sonicated for 3 h. Then, the water was removed using a rotary evaporator (60 °C bath temperature, 60 mbar) yielding a black powder, which was dried overnight at 105 °C and then ground to a fine powder. Finally, the copper(II) acetate was thermally reduced in a tubular furnace under H2 atmosphere at 240 °C for 6 h.

Electrode Preparation: The catalyst layers were made of a powder mixture, the copper catalyst immobilized on carbon black (Cu90, Cu85, or Cu70) and PTFE as a binder. The catalyst loadings as well as PTFE contents are always related to the mass of carbon black in the catalyst layer. For presentation of the catalyst layer composition, the abbreviation CuX/PTFE/Y (Add.) was used, where X describes the copper mass fraction with respect to carbon black (xCu), Y as the mass fraction of PTFE in % by weight (xPTFE), and Add. as the type of additive used for this electrode.

For electrode fabrication, the respective CuX, catalyst, PTFE amount, and optionally additive (Dopetac Sulfo 100, AC or MWCNT, CNT) were mixed in an IKA M-20 universal blade mill for 1 min. Electrodes were hot-pressed using a Polystat 300 S laboratory scale press. Here, 2.0 ± 0.2 g of the catalyst/PTFE mixture was manually doctor bladed in a mask (90 × 70 × 3 mm). The mixture was hot-pressed on a GDL with the MPL facing the catalyst/PTFE mixture at 260 °C and 3.6 kN cm⁻² for 10 min. This pressing step resulted in a 95 ± 7.5 µm catalyst layer (as the pressing step was performed without any frame) on the carbon cloth substrate. For electrochemical characterization, circular electrodes with a diameter of 22 mm were cut from the large sheet using a punch. For ionomer modification of the catalyst layer, a thin film of the respective ionomer was deposited via drop-casting with 5 wt% solutions of either Nafion 115 or Cu50/PTFE15 gas diffusion electrodes consisted of 92 wt% Cu90 catalyst (thus 46 wt% Cu and CB, respectively) and 8 wt% PTFE with respect to the total catalyst layer mass.

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were calculated according to Equation (3), where $z$ is the number of electrons for the respective product, $F$ is the Faraday constant, $i$ is the current, and $x_{\text{prod}}$ is the mole fraction of the product in the gas stream ($x_{\text{gas}}$) corrected by the CO$_2$ loss within the system. Herein and due to its inertness, N$_2$ was used as an internal standard and the ratio of input N$_2$ ($x_{\text{N2,input}}$) versus output N$_2$ mole fractions ($x_{\text{N2,output}}$) served as correction factor that was determined by GC analysis. Furthermore, $F$ represents the CO$_2$ pressure (absolute), $F_i$ the initial CO$_2$ volume flow of, $R$ the gas constant and $T$ the temperature.

$$FE = \frac{zF}{i} x_{\text{prod}} \frac{p_{F_i}}{RT}, \text{with} x_{\text{prod}} = x_{\text{gas}} \frac{x_{\text{N2,input}}}{x_{\text{N2,output}}} \tag{3}$$

Electrolyte samples were analyzed with respect to their formate, acetate, methanol, ethanol, and n-propanol concentrations by subjecting them to GC-MS as well as HPLC analysis. For alcohol analysis, a Shimadzu GCMS-QP2020 system equipped with a HS-20 trap sampling system and a SH-Rtx-200MS column (0.25 mm ID, 30 m) was used. Organic acids were quantified on a HPLC 1200 with a BinPump1200, an Autosampler ALS1200, and a DAD detector at 210 nm. As column, a Phenomenex Rezex ROA-organics 300×8 mm, 8% was used. The samples were diluted 1:5 in 5 m H$_2$SO$_4$ before analysis. The pH of the electrolyte was analyzed before and after electrolysis using a pH Schott TA20plus autotitrator in pH measuring mode.

Polarization curves were recorded in galvanostatic mode. Each current density step was held for 2 min to reach steady state conditions. The double layer capacitance representing the ECSA was determined by cycling the electrode in the range from 0.1 V < $E_{\text{cell}}$ < 0.2 V for 10 cycles at scan rates of 10, 20, 30, 40, 50, and 60 mV s$^{-1}$. From these measurements, the 10th cycle was taken for evaluation of the electrochemical surface area by a method described elsewhere.[77] The measured potential during ECSA measurements was corrected by the internal resistance, which was determined prior the cyclic voltammetric scans using the GetRU function.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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### Conflict of Interest

The authors declare no conflict of interest.

### Author Contributions

K.J.P., D.S., and U.-P.A. planned and performed all materials preparation and electrochemical experiments, and analyzed the data. J.T. and R.M. performed and analyzed the H$_2$O physisorption data. F.M. and S.S. provided context for the industrial relevance of this work. All authors prepared the manuscript. U.-P.A. was responsible for supervision.

### Keywords

carbon dioxide, copper, electrocatalysis, ethylene, gas diffusion electrodes

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