



The Conventional Gas Diffusion Electrode May Not Be Resistant to Flooding during CO₂/CO Reduction

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The electrochemical CO_2 or CO reduction to chemicals and fuels using renewable energy is a promising way to reduce anthropogenic carbon emissions. The gas diffusion electrode (GDE) design enables low-carbon manufacturing of target products at a current density (e.g., 500 mA cm⁻²) relevant to industrial requirements. However, the long-term stability of the GDE is restricted by poor water management and flooding, resulting in a significant hydrogen evolution reaction (HER) within almost an hour. The optimization of water management in the GDE demands a thorough understanding of the role of the gas diffusion layer (GDL) and the catalyst layer (CL) distinctively. Herein, the hydrophobicity of the GDL and CL is independently adjusted to investigate their influence on gas transport efficiency and water management. The gas transport efficiency is more enhanced with the increase in hydrophobicity of the GDL than the CL. Direct visualization of water distribution by optical microscope and micro-computed tomography demonstrates that the water flow pattern transfers from the stable displacement to capillary fingering as GDL hydrophobicity increases. Unfortunately, only increasing the hydrophobicity is not sufficient to prevent flooding. A revolutionary change in the design of the GDE structure is essential to maintain the long-term stability of CO₂/CO reduction. © 2022 The Electrochemical Society ("ECS"). Published on behalf of ECS by IOP Publishing Limited. [DOI: 10.1149/1945-7111/ ac9b96]

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The electrochemical reduction of CO₂ into valuable carbon-based chemicals and fuels provides a promising way to mitigate anthropogenic carbon emissions. Among all the CO₂ reduction products, C₂H₄ production on Cu catalyst is recognized as the most desired process due to its relatively larger market volume and decent price.^{1,2} Presently, dimerization of two *CO intermediates or *CO hydrogenation derivatives is widely considered as the rate-determining step for the C₂H₄ production, signifying the importance of *CO coverage, and thereby the CO local concentration.^{3–5} The tandem CO₂ reduction, integrating two consecutive steps of CO₂-to-CO and CO-to-C₂H₄ on two complementary catalysts, can enhance the yield of C₂H₄ by delivering high concentration CO to the Cu surface.^{6,7} Additionally, when tandem CO₂ reduction is implemented in two reactors in series, CO₂ crossover in the AEM-based electrolyzer can be mitigated.^{8,9}

The research on CO_2 reduction transits from H-cell to flow and membrane electrode assembly (MEA) cells by incorporating gas diffusion electrodes (GDEs).^{10,11} A conventional GDE consists of a catalyst layer (CL) which is coated on a hydrophobic gas diffusion layer (GDL) via various means. The reaction is ideally to take place at the triple-phase boundary; however, the triple-phase boundary has a relatively small area in the GDE under the CO_2 reduction conditions.^{12,13} Therefore, the CO_2 reduction mainly happens at the double-phase boundary, where the CO_2 activity, water activity, and ion conductivity are optimal.¹² The double-phase electrochemical CO_2 reduction reaction (CO_2RR) rate is primarily determined by the gas diffusion layer and the gas reactant solubility according to the following equation;

$$j_L = nF\left(\frac{D}{\delta}\right)C_0 \tag{1}$$

coefficient in water $(2.03 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ cm}^2 \text{ s}^{-1} \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ for CO and } 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ cm}^2 \text{ s}^{-1} \text{ cm}^2$ $cm^2 s^{-1}$ for CO₂ at ambient conditions), δ is the diffusion layer in the liquid electrolyte, and C_0 is the bulk concentration of gas reactant. The limiting current density of CO₂RR would reach 3600 mA cm⁻ at a boundary layer of 1 μ m. However, because of one order of magnitude lower solubility of CO (0.99 mM in water at 25 °C) than CO₂ (34 mM) in water, the electrochemical CO reduction reaction (CORR) would only deliver a limiting current density of 77 mA cm⁻² assuming having the same diffusion layer thickness. The CORR demands optimization of water management in the GDE to reduce the CO diffusion layer in the double-phase reaction or increase in the length of the triple-phase boundary to obtain the high current density (>500 mA cm⁻²) relevant to industrial applications.^{1,12} The current GDEs are vulnerable to flooding, imposing huge challenges to the direct CORR and CO2RR that adopts the tandem catalysis strategy involving the CO reduction step.¹

where j_L is the limiting current density, D is the gas diffusion

The liquid/gas fluid flow scenario in porous structures has been studied for decades. One popular model is an upside-down tree-like liquid water percolation in the porous media.^{15,16} During the reaction, flooding starts from water vapor condensation into micro-droplets oncesaturation is exceeded. These droplets open the channel, converge into micro-flow, and eventually form the main flow driven by capillary action. Conversely, some experimental observations have demonstrated that the primary water transport scenarios are fingering-type and channeling-type flows.^{17–20} Specifically, the water flow will preferentially pass through the spaces with low capillary pressure resistance. Due to the tortuous structure of the GDL, the water percolation diverges, featuring numerous "dead ends" and several main channels breakthrough. Regardless of the debated mechanism, it is generally agreed that the liquid transport in the GDE is driven by capillary action arising from the capillary pressure (P_C) gradient, as shown in Eq. 2.

$$P_C = P_L - P_G = -\frac{2\gamma\cos\theta}{r}$$
[2]

where P_L is the liquid pressure, P_G is the gas pressure, γ is the surface tension, θ is the contact angle, and r is the pore radius. Intuitively assuming cylindrical pores and a well-defined contact angle, as P_C increases, the larger hydrophobic pores are filled first, followed by smaller hydrophobic pores in a hydrophobic GDL.

To improve the hydrophobicity of GDE, a hydrophobic CL is also utilized along with the GDL. The hydrophobic CL is made of fluoropolymers such as polytetrafluoroethylene (PTFE) nanoparticles/dispersion and metal nanoparticle catalysts. A marked improvement in CO₂RR activity and selectivity was observed in the GDE with a hydrophobic CL largely due to the enhanced pore hydrophobicity and gas transport efficiency.¹³ Another type of hydrophobic GDE was fabricated by coating a 20 nm Nafion ionomer layer onto the CL, and the subsequent enhancement in the CO₂RR activity was ascribed to the presence of separate gas and liquid flow channels through the hydrophobic backbone and hydrophilic functional groups, respectively.²¹ Given the hydrophilic nature of metal and metal oxide, flooding in the CL cannot be avoided. Moreover, the hydrophobicity of CL degrades over long-term electrolysis due to the oxidation of carbon substrates and the breakdown of the hydrophobic polymers.^{11,22} Under high current density, the electromigration of electrolytes that contains cations becomes the prevalent cause of flooding in CO₂RR and CORR.²³⁻²⁶ The existing widely used GDE structure is intrinsically incapable of solving these issues.

Herein, a systematic study was performed to investigate the role of GDL in water management and to reveal the water transport mechanism in porous GDE during CO2RR/CORR. To accelerate the assessment of the water management ability of GDL, the CORR was used as a probe reaction instead of the CO₂RR owing to the lower solubility of CO and thus the higher sensitivity of CORR performance to flooding. Note that CORR only represents the scenario of low gas reactant solubility in water and thus sluggish flux to the flooded catalyst surface. In CO₂RR, in addition to flooding, occluding both CL and GDL by (bi)carbonate deposits contributes to performance degradation.²⁷ First, four GDEs with independently adjusted hydrophobicity for CL and GDL were fabricated and tested in the flow cell for CORR to decouple their effect on water management. Then, a CL-free GDE with enhanced GDL hydrophobicity through polydimethylsiloxane (PDMS)-coating was designed to directly observe the time-dependent variation in GDL hydrophobicity as CORR proceeds. In-situ optical microscope and ex situ micro-computed tomography (micro-CT) were employed to qualitatively and quantitively characterize the water distribution in the GDL, respectively. This work suggests that water management in the GDL remains a priority compared with the CL for efficient gas transport. However, both hydrophobic CL and GDL are inadequate to restrain GDE from flooding. Flooding significantly degrades CORR performance within one hour of electrolysis. The water flow pattern in superhydrophobic GDL is consistent with the fingering-type scenario, showing more than 20% pore occupation with water. An effective solution for water management may call for a revolutionary change in the design of GDEs.

Experimental

Fabrication of conventional gas diffusion electrodes.—The Cu catalyst ink was prepared by dispersing 16 mg of Cu nanoparticles (25 nm, MilliporeSigma) in 16 ml isopropanol solvent, followed by ultrasonication for 15 min Then, $x \ \mu l$ 6.0 wt% PTFE suspension, which was prepared by diluting 60.0 wt% PTFE suspension (Fuel Cell Store) with water, was added to the catalyst ink, where x is 100, 200, and 300 μ l corresponding to 33.3 wt%, 66.7 wt%, and 100.0 wt % of PTFE with reference to the Cu. The catalyst ink was further ultrasonicated for another 15 min Afterward, the catalyst ink was sprayed onto a $4.0 \times 4.0 \text{ cm}^2$ GDL (SGL Sigracet 39BB and Toray 090). The GDL was weighed before and after spraying catalyst to quantify and control the loading of CL. The Cu loading for these electrodes is around 0.35 mg cm⁻². The fabricated GDEs are denoted

as SGL-Cu-PTFE-33, SGL-Cu-PTFE-66, SGL-Cu-PTFE-100, and Toray-Cu-PTFE-66.

Fabrication of the PDMS-coated CL-free gas diffusion electrodes.—100 ml of 5.0 mM CuCl₂ (MilliporeSigma) was prepared as the electrodeposition electrolyte. The solvent for the electrolyte was prepared by mixing 50 ml deionized water and 50 ml isopropanol. The electrodeposition was conducted by a potentiostatic/galvanostatic station (Solartron EnergyLab XM), during which a total current of 2.0 mA was applied for 1000 s to grow Cu onto a $4.0 \times 6.0 \text{ cm}^2$ GDL (Sigracet 39BB). The prepared GDE is named GDL/Cu. A PDMS (Polymer Source Inc.) solution was prepared by dissolving a certain amount of PDMS into 100.0 μ l isopropanol to control the PDMS loading varying from 0 to 20.0 wt% in reference to the weight of GDL/Cu. The 100.0 μ l of PDMS solution was drop cast onto the GDL/Cu. After annealing in a tube furnace under Ar flow at 200 °C for 10 h, the derived GDE is named GDL/Cu/PDMS-*x*, where *x* refers to the PDMS content.

Electrochemical CO reduction test.—The activity of all the aforementioned GDEs was tested in a customized flow cell comprising the GDE cathode, Sustainion anion exchange membrane, and Ni foam anode. Both anolyte and catholyte were 1.0 M KOH streams supplied at a flow rate of 0.5 ml min^{-1} by a peristaltic pump (Harvard Apparatus P70–7000). The dry CO feedstock was supplied to the flow cell at 100.0 sccm regulated by a mass flow controller (Alicat Scientific MC-100SCCM-D). The cell voltage was controlled by a potentiostatic/galvanostatic station. At the same time, the cathode potential was monitored, in reference to a saturated calomel electrode (SCE) by the multi-channel function of the Solartron EnergyLab XM. The gas composition in the outlet stream was analyzed by on-line gas chromatography (GC, Agilent 7890B), while the liquid products were identified and quantified by ¹H nuclear magnetic resonance spectroscopy (Bruker AV400).

Physical characterization of gas diffusion electrodes.-The front surface (CL side facing the electrolyte), the back surface (GDL side facing the flow channel), and the cross-sectional area of the GDEs were imaged by scanning electron microscopy (SEM, FEI SCIOS DualBeam). The SEM samples for the cross-sectional area imaging were prepared by breaking the electrodes in the liquid N_2 . The GDL pore size distribution was characterized by the Langmuir adsorption/desorption isotherm.²⁸ The in situ optical images were taken by optical microscope (Keyence VIIX-2000E). A customized open-head cell comprising cathode GDE (1.0 cm² active area), Ni foam anode, and 1.0 M KOH electrolyte was manufactured for the in situ imaging. The volume of the electrolyte compartment is 1.0 ml. During the in situ imaging, a constant current density of 100 mA cm^{-2} was applied to the cell controlled by a power supply (BK Precision XLN3640-GL). Optical photos were taken every 10 min The ex situ micro-CT was conducted using Siemens Inveon PET/SPECT/CT. The Fourier-transform infrared spectroscopy (FTIR) spectra for all samples were performed on the Nicolet 6700 FTIR Spectrophotometer.

Results and Discussion

Identification of the origin of sluggish CO transport.—To diagnose the influence of CL and GDL hydrophobicity on the CO transport distinctively, four GDEs were fabricated by varying the hydrophobicity in CL and GDL independently. The first three types of GDEs were prepared based on the same GDL (SGL Sigracet 39BB) containing 5 wt% PTFE, while the CL had different PTFE contents of 33.3 wt%, 66.7 wt%, and 100.0 wt%, denoted as SGL-Cu-PTFE-33, SGL-Cu-PTFE-66, and SGL-Cu-PTFE-100, respectively. Note that CORR was selected as the probe reaction to evaluate gas transport efficiency because CORR is more sensitive to flooding than CO_2RR due to the lower solubility of CO in water (0.99 mM at 20 °C) than CO_2 . When a fresh SGL-Cu-PTFE-33 GDE

was used for 10 min testing for each applied potential, the SGL-Cu-PTFE-33 exhibited remarkable CO reduction performance. Specifically, the fresh SGL-Cu-PTFE-33 delivered close to unity C_{2+} Faradaic efficiency (FE) and a partial current density of C_{2+} (j_{C2+}) of 600 mA cm⁻² at -0.60 V vs RHE (Figs. 1a and 1b). The FE of C₂₊ declined to 75%, while j_{C2+} further increased to 1100 mA cm⁻² at -0.84 V vs RHE. This short-term performance rivals most of the peer-reported performances.¹⁰ However, during the long-term CORR at a constant total current density (j_{total}) , e.g., $400\,\text{mA}\,\text{cm}^{-2},$ the FE of C_{2+} degraded from 80% to 16% within 90 min, accompanied by a cathodic shift of potential from -0.60 to -0.85 V vs RHE (Figs. 1c and 1d). As expected, the FE of H₂ rapidly increased from 10% at 10 min to 60% at 90 min After disassembling the electrolyzer, a significant amount of water was observed in the flow channel. The water comes from the catholyte penetration into the GDE, indicating severe GDE flooding. We hypothesized that CORR performance declines due to sluggish CO transport in the flooded GDE. The increased cathodic shift of potential is due to the mass transport overpotential seen in flooded systems.29

To mitigate flooding in the CL, we sought to prepare GDEs with a higher PTFE content in the CL, which increases the CL hydrophobicity. As the PTFE content increased, the FE of C_{2+} after 90-min. electrolysis rose from 16% on the SGL-Cu-PTFE-33 to 24% on the SGL-Cu-PTFE-66 and then further to 32% on the SGL-Cu-PTFE-100 (Fig. S1). The spent SGL-Cu-PTFE-66 maintained a water contact angle of 125°, suggesting that the CL preserved considerable hydrophobicity after 90-min. CORR (Fig. S2). The CL thickness increased from 1 μ m for the SGL-Cu to 2 μ m for the SGL-Cu-PTFE-100 (Fig. S3). The increased CL thickness extended the gas diffusion distance, which is supposed to reduce the gas transport efficiency. However, the CORR performance still increased with the increase of PTFE content, further demonstrating the significance of the CL hydrophobicity in gas transport. Nevertheless, increasing the hydrophobicity in CL alone is insufficient to manage the water for efficient CORR. The GDL comprising 300 μ m carbon fiber paper and a 60 μ m microporous layer (MPL) as a water barrier also plays a vital role in water management (Fig. S3). Improving water management in GDL may be more effective in maintaining CO flux to the catalyst surface. Therefore, a more hydrophobic GDL (Toray-090) with a higher PTFE content (30 wt%) was used to prepare the fourth GDE (denoted as Toray-Cu-PTFE-66). The stability of CORR performance was relatively improved for Toray-Cu-PTFE-66, as revealed by the relatively constant FE of C₂₊ in the first 60 min However, the FE of C₂₊ still gradually declined to 57% at 90 min (Fig. S4). Compared with the CL, an increase in hydrophobicity of the GDL exhibits a more pronounced improvement in durability.

Hydrophobicity of the PDMS-coated CL-free GDE.-To directly observe the hydrophobicity of GDL before and after CORR, we designed the CL-free GDE (denoted as GDL/Cu), which was prepared by electrodepositing Cu cubic particles into GDL. The dispersed Cu cubic particles with uniform 250 nm size are spaced at a distance of 500 nm. The dispersed Cu cubic particles serve as catalysts instead of the conventional CL. The GDL is still exposed after electrodepositing the Cu catalysts (Figs. 2a and 2b, Figs. S5 and S6). The water contact angle before and after electrodepositing Cu remained 145°, further confirming the significant exposure of the GDL (Figs. 2c and 2d). The hydrophobicity of the front surface (MPL side) of the GDL/Cu electrode was further enhanced by PDMS coating, as indicated by the higher average water contact angle of 147.3° for the GDL/Cu/PDMS-20 electrode. Note that the apparent contact angle is only an indicator of the electrode surface hydrophobicity. The hydrophobicity of micropores primarily governs water management. Figure 2f shows the FTIR spectra of GDL, GDL/Cu, and GDL/Cu/PDMS-20. The strong peaks at 1146 and



Figure 1. (a) The Faradaic efficiency of all CO reduction products and (b) the total current density vs the potential for SGL-Cu-PTFE-33 when a fresh GDE is operated for a short period of 10 min at each applied potential. The test was conducted in a flow cell with 1 M KOH as a catholyte. (c) The Faradaic efficiency of all CO reduction products and (d) the corresponding cathode potential as a function of operation time on the SGL-Cu-PTFE-33. The test was conducted in a flow cell with 1 M KOH catholyte at a constant total current density of 400 mA cm⁻².



Figure 2. (a), (b) SEM images of the front GDL surface of the GDL/Cu/PDMS-20 electrode. The MPL is directly exposed, and the bright square particles in Fig. b are the Cu nanocubes. (c)–(e) the apparent water contact angle on the front surface of bare GDL (c), GDL/Cu (d), and GDL/Cu/PDMS-20 (e). (f) The FT-IR spectra of bare GDL, GDL/Cu, and GDL/Cu/PDMS-20.

 1202 cm^{-1} appear on all three electrodes corresponding to the vibration of C-O and C-F bonds, respectively. The strong absorption at 609 cm⁻¹ on GDL/Cu and GDL/Cu/PDMS reveals the existence of the Cu-O bond, indicating the formation of copper oxide species. The success of PDMS coating is proved by the absorption peaks at 795, 1010, 1255, and 2942 cm⁻¹ ascribing to Si–CH₃, Si–O–Si, Si–CH₃, and –CH₃, respectively. Meanwhile, the absorption peak at 1080 cm⁻¹, attributed to Si–O–C, suggests that the PDMS chemically bonds to the carbon substrate. This chemical bond is expected to preserve PDMS over a long-period CORR or CO₂RR.

To understand the roles of PTFE and PDMS on the hydrophobicity of GDL/Cu/PDMS-20 electrode, EDX elemental mapping was applied to investigate their distribution on the front surface (MPL side), the back surface (carbon fiber layer side), and the crosssectional area of the GDL/Cu/PDMS-20 electrode. The distribution of PTFE and PDMS is reflected by the characteristic X-ray emission from the K shell of F and Si elements, respectively. The GDL and GDL/Cu possess uniform PTFE distribution on the front surface of the electrode, which gives them decent hydrophobicity, as indicated by the large water contact angle (Figs. 3a-3d and Fig. S7). Moreover, the uniform PTFE distribution also leads to an increase in the breakthrough pressure. It is the minimum capillary pressure that the reservoir pressure must overcome to flow into the pores of a porous structure. Unfortunately, the PTFE distribution over the back surface and along the thickness direction is uneven. The carbon fiber layer at the back surface comprises interwoven carbon fibers of approximately 15 μ m in diameter, forming tortuous pores with a diameter over 100 μ m (Figs. S8 and S9). These fibers are mostly covered with PTFE coating. However, these pores accommodate a significant amount of micro carbon platelets, which are almost PTFE-free (Figs. 3e-3h and Figs. S8 and S9). The elemental mapping along the thickness direction discloses that the PTFE stays concentrated at the top surface of the MPL, but it remains very diluted inside the MPL (Figs. 3i-31). The PTFE distribution over the bare GDL and the GDL/Cu is similar to the GDL/Cu/PDMS-20 (Figs. S10 and S11). Therefore, although the front and the back surfaces of bare GDL and GDL/Cu remain hydrophobic (Fig. S7), there is a significant possibility for the inside of the bare GDL and GDL/Cu to be hydrophilic. The PDMS modification complements the PTFE coating. The PDMS not just uniformly coats the front surface of the MPL, but also penetrates the whole MPL with 50 μ m

thickness, which significantly increases the breakthrough pressure (Figs. 3d and 3l). In the carbon fiber layer, the carbon platelets inside the pores are also covered by PDMS and become hydrophobic (Fig. 3h and Fig. S10).

Linkage between the microstructure of PDMS-coated CL-free GDE and CORR performance.—A combination of ex situ SEM imaging and flow cell analysis can systematically probe the impact of PDMS content on the electrochemical performance of the electrode. The electrochemical performance of GDE depends on its ability to deliver CO to the catalyst surface and to drag away excess water. Six CL-free GDEs with a PDMS content varying from 0 to 20% were assembled into the flow cell and tested independently at a current density of 100 mA cm⁻². The outlet gas stream composition and cathode potential were monitored periodically.

Figure 4 shows that the FEs of C_2H_4 and overall C_{2+} products degrade over time. The GDL/Cu without PDMS degrades at the fastest rate. The FEs of C₂H₄ and C₂₊ were initially 31% and 86%, respectively, and decreased by 74% and 62% in one hour. In comparison, H_2 FE surged from an initial value of 19% to 64% in one hour (Figs. S12 and S13). The spent GDL/Cu was characterized by SEM and goniometer immediately after CORR to observe the surface morphology and the water contact angle. As shown in Fig. S14, the water contact angle of the GDL/Cu decreased from 145° to around 68°. Together with the direct observation of the electrolyte in the gas flow channel, we conclude that the GDL/Cu was flooded. However, after rinsing the spent GDL/Cu with deionized water and blow-drving, the electrode turns back to be hydrophobic (Fig. S14). Therefore, the small water contact angle on the spent GDL/Cu before rinsing does not necessarily represent the change of surface properties but may be due to a large amount of water residing in the GDL and the resultant increase in the water adhesion force. The water dragged by electro-osmosis probably invades the GDL due to the electro-wetting effect, which is inevitable for the conventional GDL regardless of its hydrophobicity.^{11,23} Increasing the PDMS content enhances the stability of CO reduction gradually (Fig. 4). The FEs of C₂H₄ and C₂₊ for GDL/Cu/PDMS-15 declined by only 27% and 34%, respectively, after one-hour CORR. Further increasing the PDMS content only improves stability slightly. The spent GDL/Cu/PDMS-20 still maintained hydrophobicity, as indicated by the large water contact angle of 143° (Fig. S15). It should



Figure 3. (a) SEM image and (b)–(d) EDX elemental (C, F, and Si) mapping for the front surface (MPL side) of the GDL/Cu/PDMS-20 electrode. (e)–(l) Analogous data for the back surface (carbon fiber layer side) (e)–(h) and the cross-sectional area (i)–(l) of the GDL/Cu/PDMS-20 electrode.



Figure 4. The change of Faradaic efficiency of (a) C_2H_4 and (b) C_{2+} products and (c) the cathode potential vs time on the GDL/Cu and GDL/Cu/PDMS with the PDMS content varying from 3% to 20% for CO reduction. The CO reduction was conducted in a flow cell using a 1 M KOH electrolyte at 100 mA cm⁻² total current density.

be noted that the pore size of the GDL approximately ranges from 5 to 20 nm (Fig. S16). Coating the PDMS slightly narrows the pores, as illustrated by the decrease in mean pore size from 10.54 to 8.90 nm. Given the slight change in the mean pore size and the significant overlap of pore size distribution, the effect of pore size change on gas transport after PDMS coating is supposed to be negligible. It is noteworthy that the Cu particles are cracked to various degrees after the one-hour electrochemical reaction (Fig. S17). The morphology change of Cu particles does not necessarily cause a decrease in catalytic performance because some of the introduced defects are more active for CO reduction.

In-situ and ex situ characterization of water transport in GDL.—To understand the water flow scenario in the GDL, in situ characterization was conducted to monitor the water percolation in GDL during CORR. As shown in Fig. 5a and Fig. S18a, we designed a particular electrolyzer with an open-top so that the cross-sectional

area of GDE is exposed. CO gas stream was fed to the electrolyzer to create a comparable environment to the flow cell. An optical microscope with $500 \times$ magnification was placed right above the cathode electrode during electrolysis. For the GDL/Cu/PDMS-20, the GDL maintained an almost dry condition with sparse droplets scattered on the cross-sectional area during the first 30 min (Figs. 5c -5e), agreeing with the relatively constant CO reduction activity within the first 30 min After that, the number of droplets increased, accompanied by the appearance of some large droplets (Figs. 5f-5h). The droplet size was proportional to the quantity of the water flow in the GDL. Note that the water contact angle on the cross-sectional area was visually large (Fig. S18), illustrating a good hydrophobicity of the MPL. Referring to the existing mechanism of liquid transport through the GDL, the randomly scattered droplets across the crosssectional area support the fingering-type flow, which spreads across the network (Fig. 5b).¹⁸ In contrast, according to Fig. S19, the water flooding in GDL/Cu resembles stable displacement, where liquid



Figure 5. (a) Schematic of in situ optical microscope characterization of the GDE. (b) Schematic of the predicted fingering-type water flow pattern in the GDL. (c)–(h) The optical microscope images of droplets distribution along the thickness direction of the GDL/Cu/PDMS-20 electrode at different reaction periods.



Figure 6. (a)–(o) Micro-CT images of the GDL/Cu/PDMS-20 taken layer by layer down the thickness (vertical) direction in 17 μ m interval. The area marked by cyan color corresponds to the Hounsfield unit value ranging from -50 to 50, representing water distribution. 0 μ m represents the front surface (MPL) facing the electrolyte side, while 238 μ m is the back surface (carbon fiber layer) facing the flow channel. (p) The water fraction over each different slice across the thickness of GDL/Cu (grey) and GDL/Cu/PDMS-20 (cyan).

flow occupies most of the pores and displaces the gas.¹⁹ The difference in liquid transport mechanisms inside the pores arises from different inner hydrophobicity.

To capture the water distribution inside the GDL pores, micro-CT was performed as a non-destructive, ex situ characterization tool. The spent GDL/Cu and GDL/Cu/PDMS-20 were sealed immediately after the one-hour CORR to prevent water evaporation. A fresh GDL was also characterized as the benchmark. The micro-CT imaged the electrode in the thickness direction slice by slice with 17 μ m resolution. The area with Hounsfield unit value ranging from -50 to 50 was identified as water. The visualization of water distribution in each slice of the GDL/Cu/PDMS-20 electrode is displayed in Figs. 6a–6o. Water is scattered randomly, resembling the fingering flow revealed by in situ optical microscope characterization. The

water fraction in each slice was calculated by counting the pixel of the water area over the entire imaging area. Note that each pixel point in the images represents the average value in a cubic volume of $17 \times 17 \times 17 \ \mu m^3$. For the spent GDL/Cu/PDMS-20, water mainly stays in the MPL within the top 68 μ m thickness, while the rest of the GDL remains unwetted (Fig. 6p). The slice of 34 μ m contains 7.5% water out of the image area, corresponding to 24% of the pores occupied by water when taking the MPL porosity into consideration (Fig. S20). However, the dry pore cannot guarantee efficient gas transport because some gas may be trapped by the looping water flow pathway. Therefore, the actual volume blocked by water should be more than 24%. The spent GDL/Cu exhibits a much higher water fraction (10% to 20% per image area) for each slice than GDL/Cu/ PDMS-20 except for the last two slices adjacent to the gas flow channel. Moreover, the maximum occupation of the pores by water reaches 40% (Figs. S20 and 21). The higher water fraction translates to more sluggish CO transport, which is detrimental to the activity toward CORR.

According to the experimental observations, increasing the GDL and CL hydrophobicity can alter the water flow pattern inside the GDE, but it cannot prevent the GDE from flooding. The conventional GDE structure has shown excellent stability in other reactions like water electrolysis and fuel cell.^{30,31} However, the electrochemical CO₂ or CO reduction possesses more sophisticated reaction scenarios. First, the electrochemical CO₂ or CO reduction involves reactants in both gas and liquid phases, rather than the simple liquid phase reactant in water electrolysis. Thus, the GDE must compromise the activity of gas and liquid phase reactants in the CL to ensure sufficient reaction kinetics. Second, the electrochemical CO or CO₂ reduction involves electrolytes in various concentrations rather than pure water in the fuel cell.³² Hence, electro-osmosis will speed up the flooding and thereby restrict gas availability. The conventional GDE structure is intrinsically prone to flooding, resulting in poor stability of CORR and CO₂RR. Future research on solving flooding should focus on changing the reaction conditions to neutral electrolytes like pure water or transforming the structure of GDE.

Conclusions

In this work, we have investigated the role of GDL in water management during electrochemical CORR. The influence of GDL and CL on flooding is differentiated by independently modifying their hydrophobicity. A more pronounced improvement in gas transport was observed with increased hydrophobicity of the GDL than the CL. It is also hereby established that flooding happens regardless of whether the GDL maintains hydrophobicity during the CO reduction test or not. Increasing the GDL hydrophobicity by adding PDMS alters the water flooding pattern. On the CL-free GDL/Cu electrode without PDMS, flooding exhibits stable displacement, which significantly occupies the pores in GDL. In contrast, flooding exhibits a fingering-type flow pattern after the PDMS modification, showing much less pore occupation. The different flooding patterns translate into distinct gas transport efficiency. However, even though the PDMS-coated GDL/Cu exhibits a significantly lower water fraction than GDL/Cu, the space wetted by water is still thick enough to cause sluggish CO transport, resulting in rapid degradation of CORR performance. Taken together, modifying the hydrophobicity of both CL and GDL only influences the water flow pattern but cannot restrain the CL flooding. The flooding may mainly come from the electroosmotic flow driven

by the applied potential. The GDE that combats the flooding issue must have significant regions maintaining sustainable hydrophobicity even during electrolysis operation. A revolutionary change in the structure of GDE should be considered for the long-term stable operation of CORR and CO_2RR .

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