Effects of Electrode Support Structure on Electrode Microstructure, Transport Properties, and Gas Diffusion within the Gas Diffusion Layer

Nicholas Schwartz,* Jason Harrington, Kirk J. Ziegler, and Philip Cox

ABSTRACT: The effects of gas diffusion layer (GDL) and electrode microstructure, which influence the catalyst layer and catalyst−membrane interface on the performance of a membrane electrode assembly (MEA) for gas-phase electrolysis and the separation of CO\textsubscript{2} were experimentally characterized. Several types of GDL materials, with and without a microporous layer (MPL), were characterized using scanning electron microscopy (SEM) and Brunauer−Emmett−Teller (BET) surface area analysis. The diffusion of reactants through the GDL materials was measured to determine the effects on the microstructure and chemical properties on mass transport. The effects on the GDL structure and chemistry were determined through evaluation of Pt−IrO\textsubscript{2} MEAs with different GDL materials using constant-current measurements. Increasing the thickness of the MPL and hydrophobicity within the GDL assist with retaining water within the membrane and catalyst layers, which results in greater performance at high current densities.

INTRODUCTION

Gas Diffusion Layer (GDL) and Microporous Layer. The permeability of gas through the GDL and membrane has a direct effect on the transport of reactants (e.g., CO\textsubscript{2}, O\textsubscript{2}, and H\textsubscript{2}O) and products through the MEA and thus its performance. GDLs have a dual function in membrane electrode assemblies (MEAs), acting as an electrode support and the material interface between the flow field (structural cell components) and the catalyst layer. GDLs are typically bilayer structures composed of a macroporous carbon fiber layer and a thin microporous dense carbon layer, referred to as the MPL. Mechanical, thermal, and electrical properties are influenced by the carbon fiber layer. The MPL provides a substrate for catalyst deposition and protects the membrane from being damaged or compromised by carbon fibers in the base layer. The mass transport characteristics of the GDL have a significant effect on the overall efficiency and performance of a range of electrochemical systems, including gas-phase electrolysis, fuel cells, and battery air cathodes. Ultimately, the correct choice can affect the size, weight, stability of operation, and thermal management of the system. The GDL influences the mass transport properties of both the reactants and the products to and from the catalyst layer while facilitating the removal of heat and water within the overall cell. Therefore, to maximize the performance of gas-phase electrolysis and CO\textsubscript{2} separation system, we examined the gas permeability of the GDL, gas diffusion electrodes (GDEs), and membrane materials to water and CO\textsubscript{2} to characterize and optimize the intrinsic behavior under the anticipated and realistic operational conditions for the separation of CO\textsubscript{2}. Chemical CO\textsubscript{2} separation from air using MEAs for gas-phase electrolysis and electrochemical pumping could be applied to CO\textsubscript{2} management systems for closed-loop breathing systems such as rebreathers, respiratory protection equipment, spacecraft, and aircraft.

Influence of GDL and Electrode Microstructure on Mass Transport. For humidified and wet gas applications, the humidified gas passes through the GDL via passive diffusion driven by the concentration gradients established by the electrochemical reactions within the cell to the catalyst−membrane interface, where the CO\textsubscript{2} separation reaction occurs. Thus, the gas diffusion and water management properties of the GDL have a significant and critical influence on the overall reaction kinetics by impacting the transport of reactants and products to and from the MEA active sites and

Received: April 29, 2022
Accepted: July 28, 2022
Published: August 16, 2022
thus the reaction environment.\textsuperscript{9,10} The thickness, density, porosity, and tortuosity of the GDL and MPL selected to fabricate and operate the cell can influence the balance of water maintained within the MEA, which impacts the absorption of CO$_2$ at the cathode and the rejection of excess water at the anode. The catalyst layer deposited on the GDL material forms a GDE, which is a microporous matrix of catalyst and ionomer material bound to the MPL surface. The surface structure of the MPL impacts the resulting microstructure of the catalyst layer and electrode and thus the performance and transport properties.\textsuperscript{11–13}

**Effects of GDL Microstructure and Poly-(tetrafluoroethylene) (PTFE) Loading on Water Transport.** Hydrophobic properties of the carbon fiber layer and MPL are affected by the macro- and microporous structure, material density, overall porosity, and PTFE content.\textsuperscript{14,15} The balance and management of the water within the membrane and the MEA is dictated by the GDL properties. The capillary pressure–saturation properties within the carbon fiber layer and MPL are affected by the local pore size distribution, carbon structure, and PTFE loading, which influence the hydrodynamic properties in localized regions of the GDL.\textsuperscript{14,15} Small pores in the MPL, in conjunction with the high PTFE loading, limits the liquid water ingress due to the high capillary pressure required to push water into the MPL, which maintains water within the catalyst layer and controls water back diffusion within the MEA. A 5 wt % PTFE loading in the carbon fiber layer is commonly used in commercially available GDL materials as both a binder and to prevent flooding of the material. The MPL used in this study has a 23 wt % PTFE loading, which was determined by Schweiss et al. to have the optimum balance of porosity and hydrophobicity for the carbon fiber paper–carbon MPL layer used in this study.\textsuperscript{7} Adjusting the PTFE content between 5 and 20 wt % on the backing of the MPL\textsuperscript{16} and MPL with different carbon blends has been shown to influence and improve the performance of proton exchange membrane fuel cells depending on the carbon fiber paper–MPL characteristics.\textsuperscript{17–19} The PTFE loading of the MPL and substrate layer, as well as GDL thickness, can be adjusted to optimize cell performance and water management within the GDL.\textsuperscript{20}

## Experimental Methods

Several commercial GDL materials were used to determine how different material properties affect the overall MEA kinetics and behavior for the gas-phase electrolysis and CO$_2$ separation. This study focused on the use of five different GDLs manufactured by Sigracet (10BB, 10BC, 29BC, 34BC, and 39BC), which are used for fuel cells, electrolyzers, and batteries. These GDLs are tailored for high-current density applications with moderate-to-high humidity operation. Analysis of GDL materials through SEM image analysis and gas permeability measurements were made in addition to the manufacturer-reported properties in determining the effect on CO$_2$ separation MEAs.

**Characteristic Physical and Electrochemical Properties.** The GDL materials were cut from a large 41 cm x 45 cm sheet into smaller samples with a cross-sectional area of 54 cm$^2$ (6 cm x 9 cm). Random samples were selected from the cut GDLs for SEM imaging to analyze the macro- and microporous structure and measure the carbon fiber layer, MPL, and overall GDL thickness. Samples of each GDL material were imaged using a SEM (Amray 1845 FE scanning electron microscope). Five measurements of the carbon fiber layer, MPL, and overall thickness were made in five different locations for a total of 25 measurements. An example of an SEM image of a cross-sectioned GDL is shown in Figure 1, where the carbon fiber layer and MPL are identified.

![Figure 1. SEM image of GDL electrode support material with a MPL. The MPL is a dense matrix of PTFE-bound submicron carbon particles, where the carbon fiber layer has aligned isolated fibers.](https://doi.org/10.1021/acsomega.2c02669)

Physical and electrical properties of the GDL materials are listed in Table 1 for the SGL Sigracet 10BB, 10BC, 29BC, 34BC, and 39BC GDL materials.\textsuperscript{21} The 29BC GDL material has been demonstrated as a suitable electrode support material for fuel cells, electrolysis, and gas separation under high-humidity environments.\textsuperscript{12,22,23} SEM images were analyzed to determine the average carbon fiber layer, MPL, and overall thickness with a measure of the thickness layer variability. The manufacturer-specified thicknesses have a reported tolerance range from ±20 to ±30 μm from the average overall GDL thickness,\textsuperscript{21} which is in line with the measurements presented here. The variability in the MPL thickness was greater than the carbon fiber layer based on the measurements. The PTFE content of the MPL for the GDL materials is 23 wt %, with the exception of 10BB, which had 5 wt % PTFE. Deciphering the location of the carbon fiber layer—MPL interface via SEM imaging is the most significant contributor to the MPL thickness variability.\textsuperscript{24}

Given the higher PTFE loading and microporous structure of the MPL, a thicker MPL would be expected to decrease gas permeability and have a more significant effect on the transport properties. High PTFE content results in a more hydrophobic MPL, which helps maintain liquid water within the catalyst layer and membrane. The dense MPL structure leads to a longer, tortuous path length for vapor transport through the GDL, assuming no major voids or channels exist through the structure. The reported gas permeability does not directly correlate with total porosity or MPL thickness. The porosity and permeability values provide a gauge of the carbon layer density and tortuosity of the MPL. Based on a BET analysis, the base PTFE-loaded carbon fiber layer with no MPL, 29-series GDL (Sigracet 29BA), has a surface area of 3.2 m$^2$/g, signifying a large pore size and high porosity layer, whereas the same carbon fiber paper with a MPL was 17.6 m$^2$/g (Sigracet 29BC). This indicates the thin MPL is a dense, small pore size, low porosity layer of high surface area-to-volume ratio carbon particles.

**Measure Gas Permeability of GDL and Electrodes.** GDL gas permeability measurements were made by controlling the volume flux of air through a 20 cm$^2$ sample area (3.8 cm x 5.3 cm) of GDL and gas diffusion-based electrodes. The experimental apparatus and method for measuring the permeability are shown in Figure 2. Based on Darcy’s law,
Table 1. Properties of GDL Materials\textsuperscript{7,21}

| parameter                          | 10BB  | 10BC  | 29BC  | 34BC  | 39BC  |
|------------------------------------|-------|-------|-------|-------|-------|
| basic weight\textsuperscript{a} (g/m\textsuperscript{2}) | 125   | 135   | 90    | 140   | 105   |
| porosity\textsuperscript{a} (%)   | 84    | 82    | 40    | 83    | 50    |
| permeability\textsuperscript{a} $\times 10^{-12}$ (m\textsuperscript{2}) | 0.76  | 0.37  | 0.16  | 0.07  | 0.27  |
| through plane resistance\textsuperscript{a} (mΩ-cm\textsuperscript{2}) | <15   | <16   | <12   | <15   | <12   |
| reported GDL thickness\textsuperscript{a} (μm) | 420   | 420   | 235   | 315   | 325   |
| overall thickness (μm)             | 395 ± 17 | 371 ± 19 | 234 ± 16 | 297 ± 16 | 328 ± 21 |
| carbon fiber thickness (μm)        | 298 ± 34 | 229 ± 54 | 154 ± 19 | 192 ± 40 | 216 ± 50 |
| MPL thickness (μm)                 | 93 ± 34  | 134 ± 44 | 80 ± 19  | 104 ± 36 | 110 ± 45 |

\textsuperscript{a}Manufacturer-reported values.

the volume flux—pressure drop relationship would result in a linear relationship directly proportional to the permeability.\textsuperscript{15,26} Gas flow was regulated using a mass flow controller (Alicat MC-500SCCM), which was passed through a membrane-based humidifier prior to entering the temperature-controlled flow chamber to produce a saturated air stream.

The flow chamber maintained a uniform, laminar gas flow at the set-point temperature through the GDL material. Gas flow ranged from 0 to 10.0 cm\textsuperscript{3}/cm\textsuperscript{2}-min for the GDL with the lowest permeability and up to 0–145.0 cm\textsuperscript{3}/cm\textsuperscript{2}-min for the highest permeability GDL. Two high-resolution pressure transducers (Dwyer 605-0 and 605-3 Magnehelic Indicating Transmitter) were used to measure the pressure drop across the GDL with ±2% of full scale for ranges of 0–1.245 mbar (0–0.5 in H\textsubscript{2}O) and 0–7.472 mbar (0–3.0 in H\textsubscript{2}O), respectively. The gas passed through the GDL into a covered exhaust port that ensured the gas flow was undisturbed and protected from changes in the temperature or interference from the flow of ambient air.

Pt black (Alfa Aesar, 12755) cathodes and IrO\textsubscript{2} black (Alfa Aesar, 43396) anodes were prepared by spray-casting a catalyst–ionomer (Fuma-Tech, FAA-3) dispersion with a 75:25 ratio (by mass) onto a 6 cm × 9 cm sheet of SGL 29BC, controlling the catalyst loading by the amount of dispersion deposited onto the GDL. Electrodes were dried at 50 °C for 12 h, and the final catalyst loading was determined by measuring the amount of catalyst and ionomer deposited on the GDL (calculated by the difference in mass with the initial GDL sheet). The permeability of anode and cathode electrodes with loadings ranging from 0.4 to 2.7 mg catalyst/cm\textsuperscript{2} were measured to determine how the catalyst layer affects the gas permeability. For each electrode sample, the flow rate was varied (volume flux) to ensure a large pressure drop across the range of the transducer was measured. Measurements were repeated five times with the same electrode sample. The lowest loading of 0.4 mg IrO\textsubscript{2}/cm\textsuperscript{2} was evaluated with a gas flow rate from 0 to 40.0 cm\textsuperscript{3}/cm\textsuperscript{2}-min, whereas the highest loading 2.7 mg IrO\textsubscript{2}/cm\textsuperscript{2} ranged from 0 to 3.9 cm\textsuperscript{3}/cm\textsuperscript{2}-min.

Effects of GDL and MPL on the Electrode Structure and Pt–IrO\textsubscript{2} MEA Performance. Pt and IrO\textsubscript{2} electrodes were made using the previously developed catalyst inks to screen-print each ink onto 216 cm\textsuperscript{2} of the SGL Sigracet 10BB, 10BC, 29BC, 34BC, and 39BC GDL materials.\textsuperscript{29} Electrodes were dried to remove organic solvents from the catalyst ink before undergoing an ion exchange treatment by soaking in 1 M NaOH solution for 2 h to exchange the as-received bromide (Br\textsuperscript{−}) ion in the ionomer (Fuma-Tech, FAA-3) with hydroxide ions (OH\textsuperscript{−}). Next, the electrodes were rinsed to remove any excess hydroxide or contaminants and dried. Pt and IrO\textsubscript{2} electrodes were cut into 54 cm × 9 cm sheet of SGL Sigracet 10BB, 10BC, 29BC, 34BC, and 39BC GDL materials. Then, a 29BC-based Pt cathode served as the control electrode to evaluate 10BB, 10BC, 29BC, 34BC, and 39BC GDL-based electrodes. Impedance measurements between 0.1 Hz and 10 kHz and linear sweep measurements at 5 mV/s from −0.3 to −2.2 V with air at 2.1 cm\textsuperscript{3}/cm\textsuperscript{2}-min.
Humidified to 100% RH at 25 °C were made after the MEA was assembled and the cell was hydrated with 2.1 cm$^3$/cm$^2$·min of air for 30 min. These initial baseline impedance measurements ensured the MEA was properly assembled and the electrochemical characteristics (high-frequency resistance) were comparable prior to performing additional electrochemical tests. Constant-current measurements were carried out with applied current densities between 2 and 10 mA/cm$^2$ for 1.1 cm$^3$/cm$^2$·min, 4 and 20 mA/cm$^2$ for 2.1 cm$^3$/cm$^2$·min, and 4 and 36 mA/cm$^2$ for 4.2 cm$^3$/cm$^2$·min of the 5% CO$_2$ humidified gas mixture applied to the cathode and no airflow on the anode side of the cell. The effluent CO$_2$ concentration leaving the cathode side of the flow cell was measured with a CO$_2$ sensor (Amphenol SGX Sensortech IR11GM_1) and LabVIEW-programmed control and data acquisition system over time to determine the steady-state concentration for 10 min at each applied current density.

### RESULTS AND DISCUSSION

**Gas Permeability through GDL Materials.** The gas permeability was calculated from the measured pressure differential across the GDL over the change in volume flux for each GDL material, where the slope is proportional to the gas permeability and GDL thickness. A high-value slope indicates a low gas permeability—higher resistance of gas flow through the GDL, whereas a low slope is observed for GDL materials with higher gas permeability. The 10BB GDL had the highest gas permeability at 1.0 × 10$^{-12}$ m$^2$, where the manufacturer-reported value was 0.76 × 10$^{-12}$ m$^2$. Low gas permeability was measured with the 34BC GDL with 0.03 × 10$^{-12}$ m$^2$ (manufacturer-reported value of 0.07 × 10$^{-12}$ m$^2$). The intermediate gas permeability was measured with the 10BC, 29BC, and 39BC. The gas permeability was 0.34, 0.13, and 0.16 × 10$^{-12}$ m$^2$ for 10BC, 29BC, and 39BC, respectively (Figure 3).

Based on these results, the gas permeability is influenced by the microstructure, density, and thickness of the MPL and GDL porosity. The measured gas permeability for the GDLs agrees with the manufacturer-reported values; however, there is no discernible individual direct relationship between MPL thickness, porosity, and overall thickness. These measurements provide a qualitative measurement of the structure of the GDL and MPL because the magnitude of the gas permeability is influenced by the combined effects of microstructure, material density, and tortuosity of the MPL. The mass transfer of reactants and products from the electrode layer is directly affected by the gas permeability of the GDL. Low-gas permeability GDL materials decrease the overall mass transfer and could limit the rate of diffusion of reactants to the electrode; however, these materials could maintain liquid water within the electrode layer and membrane, helping to maintain the membrane’s water content and conductivity. In comparison, high-gas permeability GDL materials allow reactants and products to move more easily from the electrode layer with less mass transport limitations.

The temperature and humidity were varied using the base (standard) 29BC GDL material to determine how these variables influence gas permeability. For the use of CO$_2$ separation from closed-breathing loops, the temperature would be between 35 and 40 °C with 100% relative humidity. Measured gas permeability for the 29BC GDL at 25 °C with 0 and 100% humidity, as well as at higher temperatures, is listed in Table 2.

The effects of temperature and humidity appear to be negligible in the range evaluated; however, the gas permeability would most likely be affected if the gas stream became condensing and the GDL material became saturated with water (flooded). Within an MEA, the GDL can be exposed to excess water, which could lead to capillary condensation within the microporous structure of the MPL. This flooding of the GDL...
would be observed by a drastic increase in pressure drop across the GDL, effectively restricting the gas flow.

Gas Permeability through Electrodes. Several anode and cathode electrodes with varying catalyst loading were prepared to measure the gas permeability through electrodes. Although they can also have a possible effect on the gas permeability for this study, the catalyst particle size and ionomer level were fixed at 75:25 black catalyst to FAA-3 ionomer (deposited by screen printing), which was found to be the optimal formulation in a previous study of the MEA fabrication parameters. Within an MEA, gaseous reactants and products must diffuse from the flow channels, where it is convectively well mixed in the cell through the GDL to the catalyst layer deposited on the MPL of the GDL. Gas permeability measurements at 25 °C with 100% relative humidity with catalyst loading varying from 0.4 up to 2.7 mg/cm² are shown in Figure 4.

As the catalyst loading increased, the gas permeability decreased for the anode and cathode. Higher catalyst loadings lead to a thicker layer with more of the catalyst–ionomer matrix composed of 75:25 ratio of catalyst/ionomer deposited on the electrode surface. Both the catalyst and ionomer added more material onto the microporous structure of the MPL, restricting gas flow through the material.

Figure 4. Measured gas permeability for Pt cathode and IrO₂ anode with different catalyst loadings on the baseline 29BC GDL material. Increasing the catalyst loading resulted in more catalyst–ionomer matrix (25 wt % ionomer) deposited on the MPL, which increased the resistance to flow.

Figure 5. Effluent CO₂ concentration versus current density for MEAs with varying GDL materials with the standard anode and cathode. Measured effluent CO₂ concentration varying the current density between 4 and 20 mA/cm² of the electrode active area at 4 mA/cm² intervals with 2.1 cm³/min feed of 5% CO₂ gas mixture. (A) Different Pt cathodes were tested against a standard IrO₂ anode with the 29BC GDL (electrode support material) to quantify the effects of each GDL on MEA performance. Most GDLs, with the exception of the 10BB, had little effect on the overall performance compared to the baseline 29BC-based electrodes. (B) Different IrO₂ anodes evaluated against a standard 29BC-based cathode showing the 10BC, 34BC, and 39BC GDL showed an improvement in the MEA performance over the full range of current densities.

Gas Permeability through Electrodes. Several anode and cathode electrodes with varying catalyst loading were prepared to measure the gas permeability through electrodes. Although they can also have a possible effect on the gas permeability for this study, the catalyst particle size and ionomer level were fixed at 75:25 black catalyst to FAA-3 ionomer (deposited by screen printing), which was found to be the optimal formulation in a previous study of the MEA fabrication parameters. Within an MEA, gaseous reactants and products must diffuse from the flow channels, where it is convectively well mixed in the cell through the GDL to the catalyst layer deposited on the MPL of the GDL. Gas permeability measurements at 25 °C with 100% relative humidity with catalyst loading varying from 0.4 up to 2.7 mg/cm² are shown in Figure 4.

As the catalyst loading increased, the gas permeability decreased for the anode and cathode. Higher catalyst loadings lead to a thicker layer with more of the catalyst–ionomer matrix composed of 75:25 ratio of catalyst/ionomer deposited on the electrode surface. Both the catalyst and ionomer added more material onto the microporous structure of the MPL, restricting gas flow through the material.

As the GDLs assist with distributing reactants and products around the catalyst layer, the GDLs provide a catalyst layer support and influence water management within the MEA. Increasing catalyst loading could increase MEA performance by providing a more active catalyst area; however, too high loading can lead to mass transfer limitations observed by the decrease in gas permeability. Additionally, higher catalyst loading leads to a thicker catalyst layer, which increases the path length for ions formed in the reaction, ultimately slowing ion transport through the MEA.

MEA Kinetics within the Pt–IrO₂ MEA. To determine the effects of the GDL on MEA performance and separation kinetics, several MEAs were evaluated through a series of tests with the standard 29BC-based anode and cathode. This allowed for the anode and cathode performance to be decoupled and evaluated independently. IrO₂ anodes and Pt cathodes with the SGL Sigracet 10BB, 10BC, 29BC, 34BC, and 39BC GDL material were prepared and assembled with a SGL
29BC-based standard electrode (anode or cathode). Figure 5A shows the measured effluent concentration from a cell feed with a 5% CO₂ gas mixture at 2.1 cm³/cm²·min of the electrode active area at 100% RH at 25 °C while varying the current density between 4 and 20 mA/cm² at 4 mA/cm²·min intervals for Pt cathodes in an MEA with the standard SGL 29BC-based IrO₂ anode. Experiments were repeated for different IrO₂ anodes in an MEA with the standard 29BC-based cathode (Figure 5B). Steady-state, constant-current measurements quantify the rate of CO₂ separation and the overall MEA performance of the cell.

The Pt cathode is less affected by the selection of GDL materials, where most GDLs had similar performance, with the exception of the 10BB GDL. Because the SGL 10BB GDL has a significantly higher gas permeability, higher performance was expected due to higher gas diffusion of reactants to the electrode to increase the reaction rate. This could be attributed to water loss in the catalyst layer, which could slow the absorption and reaction step. Low PTFE content would lead to lower membrane water content and lower conductivity as water diffuses out of the GDL. Based on results for the IrO₂ anodes against the standard 29BC-based Pt cathode, faster kinetics were observed with the SGL 10BC, 34BC, and 39BC GDLs. As products (rejected CO₂ and liquid water) are generated at the anode, diffusion and mass transfer away from the catalyst layer are required for faster kinetics. The SGL 10BC, 34BC, and 39BC GDLs all have thicker MPL layers and might keep more water and moisture within the membrane and the catalyst layer in the MEA. This can lead to flooding of the layer and potentially restrict the release of CO₂ due to flooding of the GDL structure. Retaining more water with the thicker MPL increases the concentration at the cathode, which drives the forward reaction and higher absorption rates of CO₂. For both the Pt and IrO₂ electrodes, the SGL 39BC GDL had the highest measured MEA performance.

Pt and IrO₂ electrodes with the 29BC and 39BC GDLs were used to determine the performance of the MEA with different GDL materials (Figure 6).

The baseline 29BC-based Pt cathode and 29BC-based IrO₂ anode were assembled into the standard MEA (29BC−29BC), and the effluent concentration was measured over a range of current densities at flow rates of 1.1, 2.1, and 4.2 cm³/cm²·min of the 5% CO₂ gas mixture with 100% RH at 25 °C (red curve in Figure 6). Electrodes with the 39BC GDL were assembled into an MEA (39BC−39BC), which was evaluated under the same conditions (gray curve in Figure 6).

The lowest flow rate conditions saw no discernible difference in MEA performance over the range in current density. For the moderate and high flow rates, the 39BC−39BC MEA appeared to have higher performance compared to the 29BC−29BC MEA at higher current densities—above 16 mA/cm² for the flow of 2.1 cm³/cm²·min of the electrode active area and greater than 20 mA/cm² for 4.2 cm³/cm²·min of electrode active area gas mixture humidified to 100% RH at 25 °C. Under these flow conditions and at lower current densities below 16 mA/cm² (kinetically controlled regime), the 29BC−29BC MEA had slightly higher performance, which was attributed to lower ohmic resistances. Based on the moderate and high flow rate conditions, the MEA transitioned from a kinetically controlled regime to a mass transport controlled regime. At higher current densities, the CO₂ and H₂O reactants became mass transport limited because the diffusion of CO₂ to the catalyst layer limited the reaction rate while the H₂O was being pulled across the membrane. The difference in the 29BC−29BC and 39BC−39BC MEA at the higher current densities revealed the 39BC GDL kept more water in the membrane and near the cathode catalyst layer. Improved water management and retention in the membrane and electrodes enhanced the reaction kinetics at higher current densities, as water is driven across the MEA through the electrochemical reaction and electroosmotic drag. Back diffusion of water due to the high concentration at the anode and holdup by the anode MPL replenishes the water in the membrane and the cathode catalyst layer. The 39BC had a higher gas permeability and thicker MPL compared to the 29BC GDL material. At 2.1 cm³/cm²·min of electrode active area and 20 mA/cm², the effluent concentration was 0.24% CO₂ and 0.07% CO₂ for the
29BC- and 39BC-based MEA, respectively. Under high flow conditions of 4.2 cm³/min, the concentrations were 0.76% CO₂ for the 29BC-based MEA and 0.45% CO₂ for the 39BC-based MEA.

## CONCLUSIONS

The effects of the GDL microstructure (thickness, carbon fiber layer, MPL) and chemistry (PTFE loading) influence the mass transport of reactants to and product from the catalyst layer and, ultimately, the electrode behavior. Thickness of the carbon fiber and MPL increased the mass transport resistance (lower permeability), where the microporous layer affected the kinetics at the electrode–membrane interface. Gas permeability for electrodes decreased with increasing catalyst loading. Catalyst and ionomer loadings increase the total active catalyst area and conductive ionomer but increase the mass transport influenced by catalyst loading, GDL properties, and electrodes layer. The overall MEA performance and kinetics were with different electrode support materials. Based on the (lower permeability), where the microporous layer affected the membrane interface. Gas permeability for electrodes decreased with increasing catalyst loading. Catalyst and ionomer loadings increase the total active catalyst area and conductive ionomer but increase the mass transport resistance of reactants and products into and out of the catalyst layer. The overall MEA performance and kinetics were influenced by catalyst loading, GDL properties, and electrodes with different electrode support materials. Based on the relationship between the measured effluent CO₂ concentration and current density, the cathode is less impacted by the GDL in comparison to the anode. The electrodes with the low-PTFE-loaded GDL had a lower performance for the anode and cathode, which was attributed to poor water retention in the membrane and the catalyst layer. The highest MEA performance was measured with SGL 10BC, 34BC, and 39BC GDLs for both the Pt and IrO₂ electrodes. Evaluation of a 29BC–29BC (baseline) and 39BC–39BC MEA revealed the kinetics and rate of CO₂ removal can be improved with different GDLs. Both 29BC- and 39BC-based MEAs transitioned from the kinetic controlled to mass transport controlled regime at higher current densities, above 16 mA/cm² at 2.1 cm³/min of the electrode active area and 22 mA/cm² at 4.2 cm³/min of electrode active area. The 39BC-based MEA had greater performance, which was attributed to more water in the membrane and catalyst layer at the cathode, as the 39BC GDL has a thicker MPL and lower gas permeability. Changes in the electrode supporting GDL materials to increase the thickness of the MPL and PTFE content to retain more water within the membrane and catalyst layers lead to higher performance at high current densities.

## ACKNOWLEDGMENTS

The authors would like to thank the program sponsors and the support of those at the U.S. Army Combat Capabilities Development Command Chemical Biological Center.

## REFERENCES

1. Jayakumar, A.; Sethu, S. P.; Ramos, M.; Robertson, J.; Al-Jumaily, A. A technical review on gas diffusion, mechanism and medium of PEM fuel cell. *Ionics* 2015, 21, 1–18.
2. Morgan, J. M.; Datta, R. Understanding the gas diffusion layer in proton exchange membrane fuel cells. I. How its structural characteristics affect diffusion and performance. *J. Power Sources* 2014, 251, 269–278.
3. Ismail, M. S.; Ingham, D. B.; Hughes, K. J.; Ma, L.; Pourkashanian, M. Effective diffusivity of polymer electrolyte fuel cell gas diffusion layers: An overview and numerical study. *Int. J. Hydrogen Energy* 2015, 40, 10994–11010.
4. Endrődi, B.; Bencsik, G.; Darvas, F.; Jones, R.; Rajeshwar, K.; Jankó, C. Continuous-flow electroreduction of carbon dioxide. *Prog. Energy Combust. Sci.* 2017, 62, 133–154.
5. Manzi-Orezzoli, V.; Siegwart, M.; Scheuble, D.; Chen, Y.-C.; Schmidt, T. J.; Boillat, P. Impact of the Microporous Layer on Gas Diffusion Layers with Patterned Wettability I: Material Design and Characterization. *J. Electrochem. Soc.* 2020, 167, No. 064516.
6. Chen, Y.; Jiang, C.; Cho, C. Characterization of effective in-plane electrical resistivity of a gas diffusion layer in polymer electrolyte membrane fuel cells through freezethaw thermal cycles. *Energies* 2020, 13, 145.
7. Schweiss, R.; Meiser, C.; Damjanovic, T.; Galbati, I.; Haak, N. SíGRACET Gas Diffusion Layers for PEM Fuel Cells, Electrolyzers and Batteries. In *SíGRACET Gas Diffusion Layer, GDL Group, 2016.*
8. Phillips, R. K.; Fries, B. R.; Hicks, A. D.; Bellervois, J.; Hoofar, M. Ex-situ Measurement of Properties of Gas Diffusion Layers of PEM Fuel Cells. *Energy Procedia* 2012, 29, 486–495.
9. Sinha, P. K.; Mukherjee, P. P.; Wang, C.-Y. Impact of GDL structure and wettability on water management in polymer electrolyte fuel cells. *J. Mater. Chem.* 2007, 17, 3089–3103.
10. Zenyuk, I. V.; Lamibrac, A.; Eller, J.; Parkinson, D. Y.; Marone, F.; Büchi, F. N.; Weber, A. Z. Investigating Evaporation in Gas Diffusion Layers for Fuel Cells with X-ray Computed Tomography. *J. Phys. Chem.* 2016, 120, 28701–28711.
11. Nakano, R.; Iguro, T.; Kim, B.; Fushinobu, K. In Investigation of Transport-Reaction Phenomena in Multi-Layered PEFC Cathode Catalyst Layer, ASME 2017 International Mechanical Engineering Congress and Exposition, IMECE 2017; American Society of Mechanical Engineers (ASME): Tampa, FL, United States, November 3–9, 2017.
12. Lin, G.; Nguyen, T. V. Effect of Thickness and Hydrophobic Polymer Content of the Gas Diffusion Layer on ElectrodeFlooding Level in a PEMFC. *J. Electrochem. Soc.* 2005, 152, A1942.
13. El-kharouf, A.; Mason, T. J.; Brett, D. J. L.; Pollet, B. G. Ex-situ characterisation of gas diffusion layers for proton exchange membrane fuel cells. *J. Power Sources* 2012, 218, 393–404.
14. Yoneda, M.; Takimoto, M.; Koshizuka, S. Effects of Microstructure of Gas Diffusion Layer on Two-Phase Flow Transport Properties. *ECS Trans.* 2007, 11, 629–635.
15. Lin, G.; Liu, S.; Qi, G.; Song, Y.; Li, T.; Liu, F.; Hu, Y. Effect of pore size distribution in the gas diffusion layer adjusted by composite carbon black on fuel cell performance. *Int. J. Energy Res.* 2020, 45, 7689–7702.
16. Ismail, M. S.; Damjanovic, T.; Ingham, D. B.; Ma, L.; Pourkashanian, M. Effect of polytetrafluoroethylene-treatment and microporous layer-coating on the in-plane permeability of gas diffusion layers used in proton exchange membrane fuel cells. *J. Power Sources* 2010, 195, 6619–6628.
17. Schweiss, R.; Ottinger, O. The importance of carbon materials in micro-porous layer in gas diffusion layers for proton exchange membrane fuel cells. *Carbon* 2015, 93, 1079.
(18) Mukundan, R.; Davey, J.; Rau, K.; Langlois, D.; Spernjak, D.; Fairweather, J.; Artjushkova, K.; Schweiss, R.; Borup, R. Degradation of Gas Diffusion Layers in PEM Fuel Cells during Drive Cycle Operation. *ECS Meet. Abstr. 2013*, 58, 1425.

(19) Schweiss, R.; Steeb, M.; Wilde, P.; Schubert, T. Enhancement of proton exchange membrane fuel cell performance by doping microporous layers of gas diffusion layers with multiwall carbon nanotubes. *J. Power Sources* 2012, 220, 79–83.

(20) Zhao, C.; Xing, S.; Liu, W.; Chen, M.; Wang, H. Performance improvement for air-cooled open-cathode proton exchange membrane fuel cell with different design parameters of the gas diffusion layer. *Prog. Nat. Sci.: Mater. Int. 2020*, 30, 825–831.

(21) SIGRACET GDL Gas Diffusion Layer 2D Non-Woven Fabric. TDS TLRS.033.01; SGL CARBON GmbH, 2015.

(22) Schwartz, N.; Diez, D.; Cox, P.; Hill, J. In *Efficient Carbon Dioxide Separation Using Membrane Electrode Assemblies with High Selectivity*, AIChE Annual Meeting; San Francisco, 2016.

(23) Schwartz, N.; Cox, P.; Harrington, J.; Hill, J. *Synergistic and Smart Micro-Controls for Enhanced SCBA Equipment*; Department of Defense, 2017.

(24) Simon, C.; Hasché, F.; Gasteiger, H. A. Influence of the Gas Diffusion Layer Compression on the Oxygen Transport in PEM Fuel Cells at High Water Saturation Levels. *J. Electrochem. Soc. 2017*, 164, F591–F599.

(25) Ismail, M. S.; Borman, D.; Damjanovic, T.; Ingham, D. B.; Pourkashanian, M. On the through-plane permeability of microporous layer-coated gas diffusion layers used in proton exchange membrane fuel cells. *Int. J. Hydrogen Energy 2011*, 36, 10392–10402.

(26) Orogbemi, O. M.; Ingham, D. B.; Ismail, M. S.; Hughes, K. J.; Ma, L.; Pourkashanian, M. On the gas permeability of the microporous layer used in polymer electrolyte fuel cells. *J. Energy Inst. 2018*, 91, 894–901.

(27) Schwartz, N.; Harrington, J.; Ziegler, K.; Cox, P. Improving Catalytic Activity in the Electrochemical Separation of CO₂ Using Membrane Electrode Assemblies. *J. Electrochem. Soc. 2022*, 169, No. 014510.