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# Boosting Membrane Hydration for High Current Densities in Membrane Electrode Assembly CO<sub>2</sub> Electrolysis

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reactant inlet stream. A high current density of 755 mA/cm<sup>2</sup> was reached by humidifying the reactant CO<sub>2</sub> in a MEA electrolyzer cell featuring a CEM. The power density was reduced by up to 30% when the fully humidified reactant  $CO_2$  was introduced while operating at a current density of 575 mA/cm<sup>2</sup>. We reduced the ohmic losses of the electrolyzer by fourfold at 575 mA/cm<sup>2</sup> by fully humidifying the reactant CO<sub>2</sub>. A semiempirical CEM water uptake



model was developed and used to attribute the improved performance to 11% increases in membrane water uptake and ionic conductivity. Our CEM water uptake model showed that the increase in ohmic losses and the limitation of ionic transport were the result of significant dehydration at the central region of the CEM and the anode gas diffusion electrode-CEM interface region, which exhibited a 2.5% drop in water uptake.

**KEYWORDS:** electrocatalytic carbon dioxide reduction, electrolysis, neutron imaging, membrane hydration, membrane electrode assembly

# 1. INTRODUCTION

Global net anthropogenic CO<sub>2</sub> emissions must be reduced by 45% by 2030 in order to prevent more than a 1.5 °C rise in global temperature.<sup>1</sup> The world now faces the challenge of not only needing to mitigate CO<sub>2</sub> emissions but also reducing the current CO<sub>2</sub> concentration levels in the atmosphere. A promising approach to curtailing CO<sub>2</sub> emissions is the electrochemical conversion of CO2 into carbon-neutral fuels powered by renewable energy sources.<sup>2–7</sup>

High current densities (>300 mA/cm<sup>2</sup>) accompanied by low cell voltages (<2 V) to minimize power demands are vital for the successful commercialization of CO2 electrolyzers, as verified by techno-economic models and analyses.<sup>8-11</sup> Current research in the field of CO<sub>2</sub> electrolysis is primarily focused on the development of catalysts to promote selectivity toward the electrochemical CO<sub>2</sub> reduction reactions (eCO<sub>2</sub>RR),<sup>12-14</sup> yet mass transport losses and ohmic losses are key contributors to performance degradation, which have been largely overlooked in the literature.

A variety of CO<sub>2</sub> electrolyzer designs are discussed in the literature, such as the membrane electrode assembly (MEA) design, which features a solid ion conducting polymer electrolyte membrane (PEM) and a cathode and anode gas

diffusion electrode (GDE),<sup>2,15-18</sup> and the three-chamber flow cell design, which includes the addition of an electrolyte buffer layer.<sup>5,13-15,18-20</sup> Among the various designs, the MEA electrolyzer design with an aqueous anode feed is particularly promising due to its high performance, which has been attributed to lower ohmic losses.<sup>21</sup> Introducing an aqueous anode feed allows for the elimination of the electrolyte buffer layer, thereby not only reducing the operating cost by eliminating a cell component but also reducing the distance between the cathode and anode electrode and subsequently reducing ohmic losses.<sup>22</sup> Despite the advantages of the MEA cell configuration, the optimal operating conditions for the CO<sub>2</sub> electrolyzer featuring the MEA design have been largely overlooked. Specifically, the effect of operating conditions on the mass and ionic transport mechanisms needs to be

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investigated to prescribe the optimal operating conditions for the MEA  $CO_2$  electrolyzer performance.

Optimizing operating conditions in electrochemical energy conversion is vital in improving performance and reducing power requirements. The literature has demonstrated that the operating temperature, pressure, and flow rate strongly affect the performance (i.e., cell voltage and product formation) of flow cell  $CO_2$  electrolyzers.<sup>23–25</sup> Reactant humidification has also been shown to significantly impact the performance of other MEA-based electrochemical devices, such as PEM fuel cells.<sup>26-28</sup> For CO<sub>2</sub> electrolyzers, Salvatore et al. reported sharp rises in cell voltage for a flow cell with a bipolar membrane and nonhumidified CO2 supply [relative humidity (RH) of 15%], and they attributed the increase in voltage to membrane dehydration.<sup>29</sup> Liu et al. used a similar approach where they humidified the CO<sub>2</sub> gas stream to maintain the hydration of an anion exchange membrane (AEM).<sup>30</sup> Despite the advancements in AEM-based CO<sub>2</sub> electrolyzers, the cation exchange membrane (CEM) is still the most commonly used PEM for CO<sub>2</sub> electrolyzers.<sup>15,22,31-35</sup> Although important studies have been conducted to examine the humidification effects on product selectivity and cell performances,<sup>29,36</sup> the impact of reactant humidification on ohmic losses and subsequently on ionic transport in CEM-employed MEA CO<sub>2</sub> electrolyzers remains poorly understood.

The ionic conductivity of the sulfonic acid-based CEM is directly proportional to the hydration of the membrane.<sup>26,37</sup> The CEM water uptake,  $\lambda$ , is a measure of the amount of liquid water absorbed by the membrane ionomer per functional group [H<sub>2</sub>O/SO<sub>3</sub><sup>-</sup>] and is used to characterize the hydration state of the CEM. With a dehydrated membrane (low  $\lambda$  value), the ionic transport network within the sulfonic chain narrows and breaks, resulting in elevated ohmic losses and power requirements.<sup>37</sup> Maintaining CEM hydration enhances proton transfer (i.e., reduces ohmic losses), which subsequently improves CO<sub>2</sub> electrolyzer performance. Currently, only indirect methods such as electrochemical impedance spectroscopy (EIS), high frequency resistance (HFR) measurements, and indirect indicators such as membrane swelling behavior have been used to determine the bulk CEM hydration changes.<sup>15,38-40</sup> A direct method is required to quantify liquid water distribution across the membrane to explicate the true hydration changes, to understand the correlation between in operando CEM water uptake and ohmic losses, and to determine the regions of the CEM prone to dehydration in  $CO_2$  electrolyzers.

While X-ray imaging has been employed to observe the impact of transient gas behavior on voltage instability, imaging techniques have never been used to quantify liquid water in the membrane of  $CO_2$  electrolyzers.<sup>5</sup> In operando neutron imaging has been shown to be a promising method to directly quantify liquid water distribution across the membrane in electrochemical devices.<sup>41</sup> As neutrons are highly sensitive to hydrogenous molecules, neutron imaging is a promising technique for quantifying liquid water inside a membrane. Hussey et al. measured the in situ water content of a CEM in an operating fuel cell to visualize and understand the hydration changes via neutron imaging.<sup>41</sup>

In this study, we determined the impact of humidifying the  $CO_2$  reactant gas supply on the in operando water uptake and ionic conductivity changes observed in a sulfonated tetra-fluoroethylene-based fluoropolymer CEM (Nafion<sup>*a*</sup>) and the overall power requirements of the MEA  $CO_2$  electrolyzer.

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Furthermore, HFR measurements of the electrolyzer were used to quantify ohmic losses, and high-resolution neutron imaging was used to directly measure the in operando changes of water content across the CEM. We developed a semiempirical water uptake model based on our in operando imaging to determine the impact of reactant humidification on membrane hydration and ionic conductivity. The model was further employed to identify the critical regions of the CEM prone to dehydration during  $CO_2$  electrolyzer operation.

#### 2. EXPERIMENTAL METHODOLOGY

In this section, the fabrication procedure for the GDEs (Section 2.1) and the electrolyzer cell components (Section 2.2) are introduced. The operating conditions of the electrolyzer as well as the procedure for the electrochemical analyses are presented in Section 2.3, followed by a detailed overview of the in operando neutron radiography imaging (Section 2.4). Then, the methods to quantify CEM characteristics such as thickness (Section 2.5) and liquid water content (Section 2.6) are outlined. Finally, a breakdown of the CEM water uptake model is detailed (Section 2.7).

2.1. Gas Diffusion Electrode Fabrication. The GDEs were fabricated in-house by brush-coating a catalyst ink on the surface of the microporous layer (MPL) of a commercially available gas diffusion layer (GDL, Sigracet 29 BC). For this study, carbon-based transport layers were used at the anode rather than conventional titanium porous transport layers. While the titanium transport layers have been optimized for water transport,<sup>38</sup> these layers have potentially damaged the membrane in a compressed cell environment because of their rough surfaces.<sup>42</sup> As we aimed to observe in operando changes in the CEM, we employed a catalyst-coated carbon transport layer to preserve the interfacial CEM structure. To further justify our material choice, transport layers with similar configurations including the MPL and polytetrafluoroethylene (PTFE) coating have been employed in commercial and lab-scale  $CO_2$  electrolyzers.<sup>30,33</sup> The catalyst ink mixture consisted of the catalyst powder, solvents, and ionomer solution. In order to produce gaseous products, silver (Ag) catalyst was used at the cathode to primarily produce CO or H<sub>2</sub> along with the liquid water by-product. The cathode catalyst ink was prepared by dispersing 2.5 g of 80 weight % silver on Vulcan catalyst per milliliter of a solution containing a 1:4 volume ratio of isopropanol to deionized (DI) water. The mixture was sonicated (Q500 Sonica Sonicator) for 2 min prior to adding the D1021 Nafion ionomer dispersion in a 0.3 ionomer-to-carbon mass ratio. The ink solution was then sonicated for 1 h prior to brush-coating the catalyst on the MPL interface of the GDL on a hot plate at 90 °C. After the coating process, the catalyst-coated GDE was dried for 1 h. The anode GDE was prepared using an identical method by dispersing 0.8 g of iridium black catalyst and the ionomer dispersion in a 0.3 ionomer-toiridium mass ratio in the ink solution. The final nominal cathode and anode catalyst loadings were 1.10  $\pm$  0.01 mg/cm<sup>2</sup> and 0.30  $\pm$  $0.02 \text{ mg/cm}^2$ , respectively.

**2.2.** CO<sub>2</sub> Electrolyzer Hardware. The experiments were conducted using an electrolyzer cell customized for neutron imaging. The electrolyzer cell had an active area of 0.80 cm<sup>2</sup> with a traverse length (parallel to the neutron beam) of 5 mm and a width (perpendicular to the neutron beam) of 16 mm. The two flow fields, which also served as the current collectors, were electroplated with gold and titanium for stability against corrosion. Each flow field had 16 channels, which were 0.5 mm wide and 0.5 mm deep, and separated by 0.5 mm wide land regions. The MEA consisted of a Nafion N115 CEM compressed between two GDEs. Both GDEs were compressed by 24% in thickness using 190  $\mu$ m thick PTFE gaskets. An N115 membrane (with a thickness of 127  $\mu$ m) was intentionally selected for its large thickness, which afforded a detailed examination of water content via neutron imaging.

**2.3.** CO<sub>2</sub> Electrolyzer Operating Conditions. The electrolyzer was operated galvanostatically using a potentiostat (Gamry Reference 3000, Gamry Instruments) over a range of current densities



Figure 1. (a) Experimental setup of the  $CO_2$  electrolyzer during neutron visualization. (b) Sample post-image registration radiographic image of the MEA. (c) Corresponding relative intensity profile plotted against the through-plane position of the MEA (x).

 $(125 \text{ mA/cm}^2 - 755 \text{ mA/cm}^2)$ . In this study, the operating current densities were prescribed to limit the operating cell voltage,  $E_{cell}$ , to 3.6 V to avoid corrosion of GDEs and to achieve economically feasible operating conditions.<sup>8,43</sup> Polarization curves for all electrolyzer operations were obtained during the steady-state operation. Each test consisted of a 10 min purging period (dry gas supply at the cathode, liquid water at the anode, and open-circuit voltage), 5 min of open-circuit voltage operation, and 10 min of constant current operation, followed by galvanostatic EIS tests for each current density step. We observed that 7.5 min was sufficient to achieve steady-state operation, during which the voltage only varied by a maximum of 5%. The electrolyzer voltage reported was calculated by averaging the last 2.5 min of constant current operation at each current density. HFR measurements to quantify ohmic losses during operation were derived from the galvanostatic EIS tests, which were also conducted under steady-state operation across a frequency range of 0.1 Hz to 10 kHz with an amplitude of 10% of the applied current.

The cathode  $CO_2$  gas was supplied at 100 mL/min with varied RH values of 0%, 50%, and 100% via a custom test stand at the Neutron Imaging Facility at the National Institute of Standards and Technology (NIST). A peristaltic pump (Cole-Palmer Masteflex L/S) was used to control the flow of DI water into the anode at 3 mL/min. A pulse dampener was used to alleviate fluctuating pressures from the peristaltic pump. The electrolyzer cell temperature was maintained at 60 °C using a circulating water bath (Fisherbrand Isotemp 4100).

2.4. Neutron Radiographic Imaging. Neutron radiography experiments were performed to visualize in operando changes in the CEM water content at the Beam Tube 2 (BT-2) Neutron Imaging Facility at the NIST Center for Neutron Research (Gaithersburg, MD).<sup>41</sup> A schematic diagram of the electrolyzer and the visualization setup are presented in Figure 1a. The attenuated beam was converted to visible light using a Gd<sub>2</sub>O<sub>2</sub>S:Tb scintillator. The visible light was captured by a scientific complementary metal oxide semiconductor (sCMOS) with a native pixel resolution of 6.5  $\mu$ m and a temporal resolution defined by a frame width of 25 s. An effective pixel pitch of about 15  $\mu$ m was made possible with an 85 mm lens and a PK13 extension tube coupled with the sCMOS camera. The flow channels of the electrolyzer were parallel to the incoming neutron beam, and the captured images were of the attenuated beam passing through the electrolyzer MEA. The captured images displayed a grayscale value for each individual pixel. The grayscale value, a dimensionless count, was proportional to the product of the neutron intensity [1/s] and the integration time [s]. Furthermore, the intensity of the light captured was proportional to the attenuation of the neutron beam through the MEA. As neutrons are highly attenuated by water, the change in intensity between the reference image and each operational image was assumed to be a result of the change in the membrane water content. The reference images for this study were taken during open-circuit

voltage operation, with the fully humidified gas supplied to the cathode and liquid DI water to the anode in order to have a fully hydrated membrane. The operational images were acquired during the 10 min of constant current operation at each current density from  $125 \text{ mA/cm}^2$  to  $575 \text{ mA/cm}^2$ .

All images underwent a three-step correction procedure.<sup>41</sup> First, a median combination of three consecutive raw images was performed to remove gamma spots (noise due to the neutron beam). Specifically, we stored the grayscale value of each pixel from the three consecutive images and formed one frame with the gamma spots eliminated by assigning the respective median grayscale value to each pixel. The next step was removing the hot spots (noise due to electronics) by medianfiltering each frame over a 3 by 3 pixel area. In this step, the grayscale value of each pixel was replaced with the median grayscale value of itself and its adjacent neighboring pixels in the designated area. Finally, an image registration step to correct the images for potential changes in the optical axis (BT-2 beamline-specific beam fluctuations) during imaging was performed. In order to correct the translational movement of the neutron intensity and remove the image artifacts, an image registration step developed by Hussey et al. was used.<sup>44</sup> In this procedure, we utilized the first captured frame to adjust the subsequent images. Upon completing this step, the imaging data were presented with a dimensionless relative intensity value

$$I'(x, y, n) = \frac{I(x, y, n)}{I_o(x, y, n)}$$
(1)

where I' is the relative intensity, I[1/s] is the corrected intensity, and  $I_o$  [1/s] is the corrected intensity of the first frame, all at the x position and y position of frame n. A sample single corrected image of the MEA (post-image registration), highlighting the relative intensity value of each pixel, is presented in Figure 1b, and the corresponding through-plane relative intensity profile of the MEA is shown in Figure 1c.

**2.5. Membrane Thickness.** This section provides the methods of membrane thickness quantification and swelling behavior quantification. The membrane thickness,  $t_m$ , was quantified using the relative intensity profile of the MEA presented in Figure 1c. The rate of change of the relative intensity, M, defined in (1), where x is the through-plane position of the MEA, was used to determine the position of the interface between the GDEs and CEM at the cathode and anode. Specifically, the critical points of M (x-coordinates of the maximum and minimum) were defined as the positions of the interfaces.

$$M = \frac{\mathrm{d}(I')}{\mathrm{d}x} \tag{2}$$

For this study, the membrane thickness was further normalized<sup>45</sup>

$$x_{\rm m}^* = \frac{x_{\rm m}}{t_{\rm m}} \tag{3}$$

where  $x_m^*$  is the normalized membrane through-plane position,  $x_m$  [ $\mu$ m] is the membrane through-plane position, and  $t_m$  [ $\mu$ m] is the membrane thickness. The thickness of the dry membrane ( $\lambda = 0$ ) upon compression of the stack was 123.5  $\mu$ m.<sup>26</sup> The reference image for this study consisted of a fully hydrated membrane ( $\lambda = 22$ )<sup>45</sup> with a thickness of 162.5  $\mu$ m (maximum thickness observed). Membrane swelling reached a maximum difference of 30% between the dry and fully hydrated states, in agreement with other reported values in the literature and thereby justifying the method we implemented to determine membrane thickness.<sup>26,37</sup>

**2.6. Membrane Liquid Water Content.** This section details the use of the neutron radiography images in order to calculate the liquid water content of the membrane. The change in liquid water content was quantified by calculating the reduction in liquid water volume in the CEM between the reference image (fully hydrated) and each operating image, as follows

$$V_{w,m}(x_m^*, n) = \alpha \cdot l_y \cdot P \cdot t_{w,avg}(x_m^*, n)$$
(4)

where  $V_{w,m}$  [mm<sup>3</sup>] is the volumetric change in liquid water in the CEM at the  $x_m^*$  position in image frame *n*,  $l_y$  [mm] is the thickness of the membrane perpendicular to the neutron beam in the *y* direction, *P* [mm] is the pixel resolution, and  $t_{w,avg}$  [mm] is the average water thickness change of the membrane at the  $x_m^*$  position in image frame *n*. Because of the normalization of the membrane thickness (direction *x* in Figure 1b), a linear interpolation for the relative intensity values was performed in order to quantify the true volumetric liquid water change,  $V_{w,m}$ . Because of the membrane swelling and shrinkage during operation, a correction factor for the pixel size was required to calculate the true change in water volume. The correction factor,  $\alpha$ , as seen in (3), is defined as

$$\alpha = \frac{t_{\rm m}}{t_{\rm m,ref}} \tag{5}$$

where  $t_m [\mu m]$  is the measured membrane thickness, and  $t_{m,ref} [\mu m]$  is the measured thickness of a fully hydrated membrane from the reference image. The water thickness change,  $t_w$ , was calculated from the neutron images using the relation defined by the Beer–Lambert law<sup>41</sup>

$$t_{\rm w}(x_{\rm m}^{*}, y, n) = -\sqrt{-\frac{\ln\left(\frac{I_{\rm op}(x_{\rm m}^{*}, y, n)}{I_{\rm ref}(x_{\rm m}^{*}, y, n)}\right)}{\beta_{\rm w}} + \left(\frac{\Sigma_{\rm w}}{2\beta_{\rm w}}\right)^{2}} - \frac{\Sigma_{\rm w}}{2\beta_{\rm w}}}{2\beta_{\rm w}}$$
(6)

where  $I_{op}$  [1/s] and  $I_{ref}$  [1/s] are the measured pixel intensities in the corrected operational and reference images, respectively, at  $x_m^*$  position and y position in image frame n, and  $\Sigma_w$  [0.38483 mm<sup>-1</sup>] and  $\beta_w$  [-0.00947 mm<sup>-2</sup>] are the fixed parameters of the NIST neutron beam. Hussey et al. measured the changes in neutron absorbance with a range of water thickness values and used a nonlinear least-square fit to obtain accurate water thickness measured at BT-2. The two parameters,  $\Sigma_w$  and  $\beta_{w}$ , were the fitted values that gave the most accurate water thickness values when the water thickness through the beam was <5 mm. In order to calculate the average water thickness change,  $t_{w,avg}$ , from (3), the water thickness change,  $t_{w,w}$  was averaged in the y direction as follows

$$t_{\rm w,avg}(x_{\rm m}^*, n) = \frac{1}{N_y} \sum_{i=0}^{N_y} t_{\rm w}(x_{\rm m}^*, y_i, n)$$
<sup>(7)</sup>

where  $N_y$  is the number of pixels in the *y* direction. For this study, as a fully hydrated membrane was used as a reference, the results showed water thickness changes below zero ( $t_w < 0$ ). This negative value was attributed to the loss of liquid water content in the CEM compared to the reference state.

For each current density step, the final six images (spanning 2.5 min) were averaged to obtain imaging results during steady-state

operation and to minimize noise. A sample processed image of the change in liquid water volume of a CEM is presented in Figure 2a,

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**Figure 2.** Liquid water volume change  $(V_{w,m})$  across the CEM is quantified using (3) to (6). (a) Sample processed image highlighting the volumetric liquid change in the CEM. (b) Corresponding  $V_{w,m}$  profile across the normalized through-plane position  $(x_m^*)$  of the CEM.

and the corresponding through-plane profile of the change in liquid water volume of the CEM is shown in Figure 2b. The cathode GDE and anode GDE were on the left and right sides, respectively, of the membrane, as indicated in Figure 2b. The through-plane water profile of the membrane is presented as a function of the normalized membrane thickness,  $x_{m}^*$ , as defined in (2).

**2.7. Membrane Water Uptake Model.** We presented a onedimensional semiempirical isothermal model to highlight the water uptake and ionic conductivity of the CEM during  $CO_2$  electrolysis operation. This model elucidated the impact of reactant humidification for MEA  $CO_2$  electrolyzers by revealing the changes in membrane hydration and ionic transport. Furthermore, the model was used to identify the critical regions of the CEM prone to dehydration during operation. This model was developed using the following inputs:

- Change in membrane liquid water content (via neutron imaging), V<sub>w,m</sub> [mm<sup>3</sup>]
- 2. Membrane thickness (via neutron imaging),  $t_{\rm m}$  [ $\mu$ m]
- 3. Operating electrolyzer temperature, T[°C]
- 4. Water uptake of fully hydrated membrane (reference image),  $\lambda$  [H<sub>2</sub>O/SO<sub>3</sub><sup>-</sup>]

The model was developed to predict the following characteristics of the CEM:

- 1. Membrane liquid water saturation, S [%]
- 2. Membrane water uptake profile,  $\lambda [H_2O/SO_3^-]$
- 3. Bulk membrane ionic conductivity,  $\sigma_m$  [S/m]

The following assumptions and boundary conditions were used to develop the model:

- 1. Fully hydrated membrane thickness was 162.5 µm with a water uptake value of 22 across the membrane.
- 2. The pore volume of a fully hydrated membrane was equivalent to the total water volume of the membrane.
- 3. During membrane swelling, the solid membrane material,  $V_{\rm s,m'}$  did not change.
- 4. Membrane swelling behavior was anisotropic and solely occurred in the through-plane position of the CEM. This change was quantified by measuring the membrane thickness.

The saturation of liquid water in the membrane was calculated by measuring the water thickness across the CEM from the neutron images. The water saturation across the normalized through-plane

position of the CEM was determined as the percentage of liquid water occupying the pore volume of the membrane as follows  $^{46}$ 

$$S(x_{\rm m}^*, n) = \left[1 + \frac{t_{\rm w,avg}(x_{\rm m}^*, n)}{l_z \cdot \varepsilon_{\rm m}}\right] \times 100\%$$
(8)

where S [%] is the liquid water saturation across the normalized through-plane position of the membrane at the  $x_m^*$  position in image frame n,  $l_z$  [mm] is the distance traversed (parallel) to the neutron beam, and  $\varepsilon_m$  is the local porosity of the membrane.

There is currently an absence of literature concerning the relationship between membrane pore volume and membrane thickness. Weber and Newman reported a maximum water volume percent of 43% in a fully hydrated membrane ( $\lambda = 22$ ) and further assumed that value to be the maximum pore volume of the membrane.47 For our model, we assumed that the fully hydrated membrane porosity was 43%. As there was significant membrane swelling up to 30% observed via the neutron radiography images for this study, the local porosity of the membrane was assumed to change linearly with the membrane thickness change. We assumed that the dimensions of the CEM (parallel  $(l_z)$  and perpendicular  $(l_y)$  to the beam) were fixed; therefore, membrane swelling was assumed to be constrained to the through-plane direction of the CEM. This assumption was made as the membrane was supported by gasketcompressed GDEs on both sides of the CEM active area that suppressed any potential inhomogeneous swelling in the membrane.<sup>41</sup> The CEM was composed of a solid membrane polymer material and a void pore space, and we assumed that when the membrane swelled, changes to the overall volume were attributed to the growth of membrane pore volumes. It was assumed that the volume of the solid polymer membrane remained constant, and we therefore determined membrane porosity as a function of the membrane thickness as follows

$$\varepsilon_{\rm m} = \frac{V_{\rm p,m}}{V_{\rm m}} = \frac{V_{\rm m} - V_{\rm s,m}}{V_{\rm m}} = 1 - \frac{V_{\rm s,m}}{V_{\rm m}} = 1 - \frac{V_{\rm s,m}}{l_y \cdot l_z \cdot t_{\rm m}}$$
(9)

where  $\varepsilon_{\rm m}$  is the membrane porosity,  $V_{\rm m}$  [mm<sup>3</sup>] is the total membrane volume,  $V_{\rm p,m}$  [mm<sup>3</sup>] is the membrane pore volume, and  $V_{\rm s,m}$  [mm<sup>3</sup>] is the fixed solid membrane polymer volume in the active area of our electrolyzer. The solid membrane polymer volume,  $V_{\rm s,m}$ , was determined by assuming a porosity of 43.0%<sup>47</sup> of our reference CEM, which was a fully hydrated membrane with a thickness of 162.5  $\mu$ m. Table 1 outlines the measured and reported membrane thickness

 Table 1. Measured and Reported Membrane Thickness and

 Membrane Porosity Values at Various Membrane

 Conditions and Cathode Inlet RH Conditions<sup>a</sup>

membrane condition	inlet cathode (RH) [%]	membrane thickness $(t_{\rm m}) \; [\mu { m m}]$	membrane porosity ( $\varepsilon_{\rm m}$ )		
dry membrane		123.5 <sup>26</sup>	0.250		
	0	130	0.288		
	50	136.5	0.321		
	100	143	0.352		
full hydration		162.5	0.430 <sup>47</sup>		
<sup>a</sup> The membrane thickness and peresity values were used as inputs for					

"The membrane thickness and porosity values were used as inputs for the membrane water uptake model presented in Section 2.7.

(1) and membrane porosity (8) values at various membrane conditions (dry and fully hydrated) and cathode inlet RH conditions (0%, 50%, and 100%), which were used as inputs to the membrane water uptake model.

As liquid water was supplied as a reactant at the anode and produced as a by-product of the eCO<sub>2</sub>RR at the cathode, the presence of this liquid water necessitated a water uptake value in the membrane greater than or equal to 14 (as  $\lambda < 14$  is for vapor).<sup>48</sup> Furthermore, the water uptake was less than or equal to 22 (completely hydrated

membrane).<sup>45</sup> The through-plane water uptake in the membrane was defined as  $^{49}$ 

$$\lambda(x_{\rm m}^*, n) = 14 + 8 \cdot S(x_{\rm m}^*, n) \qquad \text{for } 0 < S(x_{\rm m}^*, n) < 1 \qquad (10)$$

where  $\lambda [H_2O/SO_3^-]$  is the water uptake value, and *S* is the measured liquid water saturation at position  $x_m^*$  in image frame *n*. The bulk saturation,  $S_{\text{bulk}}$  and bulk water uptake,  $\lambda_{\text{bulk}}$  of the CEM were quantified by averaging the saturation and water uptake values across the CEM through-plane position, respectively. To further relate the modeled water uptake profile to the performance of the CO<sub>2</sub> electrolyzer and the membrane behavior, Springer et al. defined the ionic conductivity of the Nafion membrane as a function of the bulk membrane water uptake<sup>48</sup>

$$\sigma_{\rm m} = (0.5139\lambda_{\rm bulk} - 0.326) \cdot \exp\left[1268\left(\frac{1}{303} - \frac{1}{T+273}\right)\right]$$
(11)

where  $\sigma_m$  [S/m] is the ionic conductivity of the membrane and T [°C] is the operating electrolyzer temperature. The electrochemical performance, specifically the HFR measurements, was attributed to the membrane ionic conductivity during the electrolyzer operation. Collectively, this semiempirical model [(7) to (10)] was employed to determine the effects of reactant humidification and operating current density on CEM hydration, ionic transport limitations, and, subsequently, overall power requirements for MEA CO<sub>2</sub> electrolyzers.

# 3. RESULTS AND DISCUSSION

This section highlights the improved electrochemical performance of the MEA  $CO_2$  electrolyzer, which resulted from humidifying the  $CO_2$  reactant supply (Section 3.1). We correlated the performance improvement with the volumetric change in liquid water content and water uptake of the CEM (Section 3.2). Finally, the effect of increasing current density on the liquid water content and water uptake profile across the CEM is presented in detail (Section 3.3).

3.1. Effect of Increasing RH on CO<sub>2</sub> Electrolyzer Electrochemical Performance. The effect of reactant humidity on the electrolyzer voltage over a range of current densities  $(125 \text{ mA/cm}^2 - 755 \text{ mA/cm}^2)$  is presented in Figure 3. For current densities up to  $575 \text{ mA/cm}^2$ , the electrolyzer operated with three levels of inlet humidification (0%, 50%, and 100%); however, the cell voltage exceeded the limiting voltage of 3.6 V for current densities above 575 mA/cm<sup>2</sup> when 0% RH was supplied to the reactant. With 50% and 100% RH, current densities of 665 mA/cm<sup>2</sup> and 755 mA/cm<sup>2</sup> were achieved, respectively. Increasing reactant humidification resulted in not only higher current density operation but also lower power requirements (indicated by the lower cell voltage). Specifically, the required power density decreased by 30% (from 1.88 W/cm<sup>2</sup> to 1.32 W/cm<sup>2</sup>) when increasing the RH from 0% to 100% at a current density of 575 mA/cm<sup>2</sup>. This decrease in power density is particularly attractive for the widespread dissemination of CO<sub>2</sub> electrolyzer technologies.

We further characterized the electrochemical performance of the electrolyzer, specifically the ohmic losses in this case, to examine the benefits of humidifying the  $CO_2$  reactants by examining the HFR (Figure 4). The HFR values were consistently lower for the humidified reactant. We demonstrated a striking fourfold decrease in ohmic losses during the electrolyzer operation at a current density of 575 mA/cm<sup>2</sup> by fully humidifying the reactant  $CO_2$ .

**3.2. Effect of Increasing RH on the Change of Liquid Water Content in the CEM.** We quantified the change in the CEM liquid water content and further modeled the water



**Figure 3.** Polarization curves of the electrolyzer operation at humidification levels of 0% (dry gas), 50%, and 100% of  $CO_2$  gas supply at the cathode inlet. The uncertainty bars show the deviation in voltage measurements for four sets of repeated experiments. For each operating current density, a lower electrolyzer potential was measured with the increasing relative humidification of  $CO_2$ . Higher current density operation (755 mA/cm<sup>2</sup>) was attained at higher levels of humidification (100% RH).



Figure 4. HFR measurements as a function of  $CO_2$  gas inlet RH at operating current densities. The uncertainty bars show the deviation in voltage measurements for four sets of repeated experiments. For each operating current density, a lower HFR measurement was attained with increasing RH, suggesting reduced ohmic losses and improved ionic transport across the CEM.

uptake profile across the membrane as a function of RH to explain the influence of the reactant RH and changes in HFR. We expected enhanced membrane hydration with increasing reactant humidification level because of the significant reduction in ohmic losses that was observed (Figure 4). The liquid water content across the normalized through-plane position of the CEM as a function of the reactant humidification level at 575 mA/cm<sup>2</sup> is presented in Figure 5a. As we increased the RH, the liquid water content was higher in all regions of the CEM. Overall, the liquid water volume of the CEM increased by 60% (from 176 mm<sup>3</sup> to 281 mm<sup>3</sup>) when the supply was changed from dry (0% RH) to fully humidified (100% RH). We further correlated this change



**Figure 5.** (a) Relative change in water volume across the CEM at 575 mA/cm<sup>2</sup> as a function of  $CO_2$  gas inlet RH and (b) corresponding water uptake profile determined via the model. With increasing RH, a higher water content across the CEM is observed. With dry gas supply, significant water loss and membrane dehydration is observed, whereas with high humidification levels, there is an increase in the CEM water uptake.

in liquid water content in the membrane to the water saturation. Our imaging results showed that the fraction of pore space filled with liquid water increased from 54% to 80% with full humidification of the reactant while operating at 575 mA/cm<sup>2</sup>. Table 2 outlines the bulk water saturation values at

Table 2. Model Outputs of the Bulk Water Saturation, Bulk Water Uptake, and Ionic Conductivity of the CEM at Low  $(215 \text{ mA/cm}^2)$  and High  $(575 \text{ mA/cm}^2)$  Operating Current Densities with Changing Inlet RH

current density ( <i>i</i> ) [mA/cm <sup>2</sup> ]	cathode RH [%]	bulk water saturation (S <sub>bulk</sub> ) [%]	bulk water uptake ( $\lambda_{\text{bulk}}$ ) [H <sub>2</sub> O/SO <sub>3</sub> <sup>-</sup> ]	ionic conductivity $(\sigma_{\rm m}) [{ m S/m}]$
215	0	67.27	19.38	78.07
	50	71.88	19.75	79.61
	100	87.17	20.77	83.86
575	0	53.78	18.30	73.57
	50	69.62	19.57	78.86
	100	80.27	20.30	81.90

different RH inlets for low (215 mA/cm<sup>2</sup>) and high (575 mA/cm<sup>2</sup>) current densities. Consistent trends of water volume in the CEM as a function of RH were observed for lower operating current densities (<575 mA/cm<sup>2</sup>), highlighting the dominating effect of reactant humidification on the liquid water content in the CEM. The additional liquid water in the CEM with a higher reactant RH resulted in an increase of hydrated sulfonic acid group clusters in the membrane. This change in the membrane structure provided more pathways and channels for facilitating enhanced proton transfer. Therefore, the increase in CEM hydration reduced the power requirements for protonic transfer in the membrane, subsequently reducing ohmic losses.

The modeled water uptake profile across the CEM is presented in Figure 5b. With an increasing inlet RH, the water uptake profile across the CEM exhibited higher  $\lambda$  values. Specifically, at 575 mA/cm<sup>2</sup>, the water uptake increased by 11% (from 18.3 to 20.3) when a fully humidified reactant was introduced. However, it was critical to note that the center of the membrane experienced the most significant dehydration during operation. While supplying the dry reactant and operating at 575  $mA/cm^2$ , the lowest water uptake value was 16.70 at the center of the CEM-the area most prone to membrane dehydration. On the other hand, the two membrane interface regions in contact with the cathode and anode GDEs experienced a significantly less dehydration. This phenomenon was due to the constant supply of liquid water at the anode and water accumulation at the cathode as a result of water transport and water generation from the eCO<sub>2</sub>RR. Furthermore, Ge et al. showed a significant temperature increase (up to 10 °C) in the CEM at high current density operations (>100 mA/cm<sup>2</sup>) during the operation of similar MEA design PEM fuel cells, which further explicated the membrane dehydration observed here.49 Similar trends were seen for the 0% and 50% RH cases, as listed in Table 2. HFR measurements illustrated that lower ohmic losses were associated with higher RH, which was a result of higher CEM hydration and ionic conductivity, as shown in Figure 5b. Specifically, from 0% to a 100% RH gas supply, at 575 mA/ cm<sup>2</sup>, the ionic conductivity of the membrane increased by approximately 11.3% (73.57 S/m to 81.90 S/m). Table 2 outlines the bulk water uptake and ionic conductivity of the CEM for a range of reactant RH conditions for low (215 mA/  $\rm cm^2)$  and high (575 mA/cm^2) current densities. The consistent trend of observing higher CEM water uptake and ionic conductivity with increasing RH indicates the significant impact of reactant humidification on reducing ohmic losses and subsequently improving electrolyzer performance.

**3.3. Effect of Increasing Current Density on the Change of Liquid Water Content in the CEM.** In this section, we examine the impact of reactant humidification on electrolyzer performance as a function of the operating current density. Understanding how cell performance changes with current density is particularly important for minimizing the power requirements of  $CO_2$  electrolyzer operation.

As highlighted by the HFR measurements, ohmic losses increased with increasing current density for all the three RH conditions, which we attributed to membrane dehydration. In order to quantify the dehydration, the change in the liquid water content of the membrane was used to model the water uptake profile across the CEM. Figure 6 shows the calculated water uptake profile across the CEM as a function of the operating current density, with 100% RH obtained from the model presented in Section 2.7.

A net decrease in bulk membrane water uptake with increasing current density was observed by quantifying the membrane water content. The CEM experienced a reduction in water uptake when the current density increased from 215 mA/cm<sup>2</sup> to 575 mA/cm<sup>2</sup>. During this operating current density range, the ionic conductivity decreased (83.86 S/m to 81.90 S/m) and the HFR increased (0.35  $\Omega$  to 0.53  $\Omega$  cm<sup>2</sup>). Furthermore, as shown in Figure 4, HFR drastically increased at operating current densities above 575 mA/cm<sup>2</sup>. Understanding the membrane hydration behavior in response to increasing density is critical to explicate these changes in HFR and CEM ionic conductivity.

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**Figure 6.** Water uptake across the CEM as a function of operating current densities, with  $CO_2$  gas supplied at 100% RH. A net decrease in the overall membrane water content is observed with increasing current density. Furthermore, an induced water gradient across the CEM is formed with a higher water uptake at the cathode GDE–CEM interface and a lower water uptake at the anode GDE–CEM interface.

We observed distinct behaviors in the CEM water content depending on the region of the membrane, and ultimately we detected a water gradient across the membrane. As shown in Figure 6, the normalized through-plane position of the membrane was divided into three significant regions:

- (i) cathode GDE-CEM interface region
- (ii) central CEM region
- (iii) anode GDE-CEM interface region

At each region of the CEM, the water uptake behaved differently in response to increasing the current density. In region (i), the water uptake in the membrane increased, whereas in regions (ii) and (iii), the membrane experienced dehydration, causing a drop in the water uptake with the increasing current density. However, it is important to note that operating at higher current densities led to little or no membrane dehydration in region (iii). This further showed that at higher current density operation, the central region of the membrane is susceptible to the greatest amount of water loss. For instance, we observed a 3.0% decrease in the CEM water uptake in the central region of the membrane when increasing the current density from 575 mA/cm<sup>2</sup> to 575 mA/cm<sup>2</sup> with 100% RH supply.

The induced water gradient across the CEM was attributed to liquid water transport across the CEM and by-product generation at the cathode and anode catalyst GDEs, both phenomena which were significantly impacted by the operating current density.

The water transport phenomena impacting the induced water gradient across the CEM were defined as the rate of liquid water crossover from the anode to the cathode because of the following two water transport mechanisms: (1) electroosmotic drag (EOD) and (2) water diffusion. As EOD was directly proportional to the operating current density and CEM water uptake,<sup>50</sup> with increasing current density, a higher flux of liquid water is transported through the CEM. The dehydration observed in region (ii) and region (iii) of the CEM was a result of water molecules transferring to the

cathode side via protonic transfer, and, as a result, region (i) experienced a higher water uptake, as seen in Figure 6. This transport phenomenon has been recognized in other electro-chemical devices, such as fuel cells<sup>49,51</sup> and water electrolyzers,<sup>52</sup> and is expected to play a critical role in understanding ohmic losses and CEM hydration in MEA CO<sub>2</sub> electrolyzers. The second transport phenomenon, water diffusion, occurred as a result of a water concentration gradient between the anode and cathode. With increasing current density, the water uptake at the liquid-saturated anode side (region (iii)) decreased and the water uptake at the vapor-saturated cathode side (region (i)) increased, as shown in Figure 6. As the water concentration difference between the anode and cathode decreased with increasing current density, the contribution of water diffusion to the overall flux of water transport decreased. Therefore, as the operating current density increased, EOD was the more dominant mode of water transport across the CEM.

The second critical mechanism for the induced water gradient was the product formation at the cathode and anode GDEs. For this CEM-based MEA CO<sub>2</sub> electrolyzer, the oxygen evolution reaction (OER) occurred at the anode, whereas for the cathode, the eCO<sub>2</sub>RR (faradaic efficiency of 4.3%), which resulted in  $\mathrm{CO}_{(g)}$  and  $\mathrm{H}_2\mathrm{O}_{(l)}\text{,}$  as well as the hydrogen evolution reaction (HER). The measured faradaic efficiency was below that of the state-of-the-art CO<sub>2</sub> electrolyzers, and this is largely due to the custom cell design, which was intentionally optimized for the in operando neutron imaging experiments, the study of gas product formation, and the employment of a thicker CEM. However, elucidating the drastic changes in membrane hydration was critical for reducing ohmic losses and achieving commercial-scale operation of this unique MEA CO<sub>2</sub> electrolyzer with a humidified reactant feed and simultaneous gas and liquid product generation. According to Faraday's law of electrolysis, the amount of product from the cathodic and anodic reactions was directly proportional to the operating current density. At the anode, the rate of O2 production increased with current density according to Faraday's law. With a higher  $O_{2(g)}$  production, more liquid water was displaced from the microporous anode GDE as the oxygen gas bubbles occupied the pore space. This led to a formation of a gas barrier at the anode porous transport layer. While supplying at 100% RH, the 2.3% decrease in water uptake in region (iii), with increasing current density from 215 mA/cm<sup>2</sup> to 575 mA/ cm<sup>2</sup>, was indicative of the formation of a gas barrier layer near the anode GDE-CEM interface. This accumulation of gas near the GDE-CEM interface contributed to the dehydration of the membrane, which manifested as a higher HFR, as shown in Figure 4. Although we acknowledge that PTFE-coated carbon transport layers (i.e., SGL 29BC) would further limit reactant water transport in the anode because of its hydrophobic surface, this oxygen gas barrier has also been seen in porous structures optimized for water transport, such as titanium porous transport layers, starting at 100 mA/ cm<sup>2,53,54</sup> Furthermore, our previous studies showed that the gas saturation at the anode PTL does not change noticeably until the critical current density range is reached  $(i > 7000 \text{ mA/cm}^2)$ , and these conditions were not achieved in this study.<sup>55</sup> At the cathode, gas generation was assumed to be the dominant by-product, but liquid water was also generated as a result of the eCO<sub>2</sub>RR, thereby adding to the water flux at the cathode. The water flux at the cathode, in turn, hydrated the membrane in region (i), the cathode GDE-

CEM interface, with increasing current density, as demonstrated in Figure 6. Although this MEA CO<sub>2</sub> electrolyzer exhibited low CO faradaic efficiency, understanding the worstcase scenario conditions where the cell experiences severe membrane dryout was critical for informing the design and operation for reduced power requirements. When CO<sub>2</sub> electrolyzers are commercialized, operating conditions are expected to vary widely, especially when coupled with renewable intermittent power sources, such as wind or solar. The unexpected changes in operation potentially increase ohmic losses, substantially reducing the performance. The results of this study showcased the impact of humidification of the inlet stream and its importance in maintaining membrane hydration to maintain low ohmic losses. Additionally, with revisions to the cell design to inhibit the HER, further improvement in membrane hydration can be achieved via a higher faradaic efficiency of CO and a subsequent increase in H<sub>2</sub>O formation at the cathode. In a future study, we will incorporate a cell configuration that closely replicates that of a commercial device to better inform state-of-the-art CO<sub>2</sub> electrolysis technology development.

# 4. CONCLUSIONS

In this work, we demonstrated a high current density operation (up to 755 mA/cm<sup>2</sup>) of a CEM-based MEA  $CO_2$  electrolyzer by increasing the humidification of the reactant  $CO_2$  supply at the cathode. With the humidified supply, the 11% increase in CEM water uptake reduced the ohmic losses by fourfold, enhancing the ionic transport and CEM ionic conductivity. With the higher membrane water uptake, there was a reduced power demand for CO<sub>2</sub> electrolysis (up to 30% reduction). Upon achieving higher current density operations, we observed an increase in Ohmic losses due to membrane dehydration, once again highlighting the importance of humidifying the reactant supply. Our semiempirical water uptake model showed that the central CEM region and the anode GDE-CEM interface region were most prone to dehydration with increasing current density. The CEM experienced up to 3% loss in water uptake in this region, causing a spike in electrolyzer power requirements. Based on the results observed from this study, we recommend that humidified CO<sub>2</sub> supply is a prerequisite for higher current density and lower power density operations of CEM-based MEA CO2 electrolyzers. Our results demonstrate the benefits of humidifying the reactant CO<sub>2</sub> supply to the cathode for improved membrane hydration and the subsequent reduction in power density for the MEA CO<sub>2</sub> electrolyzer. Furthermore, we highlight that the critical membrane regions (central CEM and anode GDE-CEM interface regions) experienced dehydration when operating at commercial-scale current densities. These findings are critical for determining the optimal operating conditions and advancements in CEM structures for CO<sub>2</sub> electrolyzers.

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# Notes

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# ADDITIONAL NOTE

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