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Transient Gas Distribution in Porous Transport Layers of Polymer Electrolyte Membrane Electrolyzers

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Here, we elucidated the dynamic gas transport behavior in the anode porous transport layer (PTL) of polymer electrolyte membrane (PEM) electrolyzers via in operando synchrotron X-ray imaging. The imaging results showed that the gas saturation in the PTL reached steady state more rapidly with a steep current density ramp-up and a shallow ramp-down (compared to a shallow ramp-up and a steep ramp-down, respectively). Additionally, the gas accumulation was characterized by a faster response time compared to that of the gas removal due to the relatively slow migration of residual gas from the catalyst layer-PTL interface to the flow channels. Furthermore, we investigated the impact of gas response behavior on gas saturation during intermittent electrolyzer operation. Intermittent operation led to an increase in residual gas cacumulation, which negatively impacted the electrolyzer performance. Our results are key for informing design and operating strategies for mitigating such hysteresis effects and improving the performance of PEM electrolyzers when coupled with intermittent renewable energy sources.

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Energy use currently accounts for 75% of the total global carbon dioxide emission in urban cities.¹ Although it is imperative for existing energy infrastructure across the globe to increasingly rely on renewable energy sources, the intermittency of such energy sources hinders their adoption in the power grid.² Electrolysis is an attractive solution to buffer the intermittency of renewable energy technologies and facilitate effective power management, via the electrochemical conversion of excessive power into hydrogen gas.³ In particular, polymer electrolyte membrane (PEM) electrolyzer systems are projected to be the dominant electrolyzer system coupled with renewable energy sources by 2030, due to their relatively low cost and operational flexibility.^{4,5} Currently, several power-tohydrogen pilot plants based on PEM electrolyzers have been installed globally.⁶ However, the overall efficiency of PEM electrolyzers coupled with intermittent renewable energy sources must be improved for the realization of grid-scale power-to-hydrogen plants in future energy infrastructures.

Understanding the effect of intermittent electrolyzer operation on performance is a necessary first step to improve the efficiency of PEM electrolyzers. Several mechanisms leading to material degradation and efficiency losses as well as strategies for improving performance during intermittent operation of PEM electrolyzers have been identified and investigated in previous studies.⁷⁻¹³ The catalyst layer (CL) was significantly degraded when an electrolyzer cell was frequently cycled over the long-term (>1000 hours) between open circuit voltage (OCV) and a high operating current density (i.e. $i = 2 \,\mathrm{A \, cm^{-1}}$ Additionally, the cyclic current operation of the electrolyzer leads to increasing ohmic overpotentials due to the accelerated passivation of the titanium-based porous transport layer (PTL) surface.⁸ Other mechanisms for degradation due to the intermittent operation of the electrolyzer have been suggested, such as delamination at the membrane and catalyst interface¹⁰ and cation contamination of the membrane.⁴ Thanks to these pioneering studies, we now have a fairly good understanding of several degradation and performance loss mechanisms associated with intermittent electrolyzer operation. Despite these extensive efforts to understand the impact of intermittent

electrolyzer operation on the electrochemical performance, the mass transport behavior within the PTL during intermittent operation remains relatively unexplored, even though poor mass transport accounts for up to 25% of electrolyzer performance losses.¹⁴

Significant PEM electrolyzer efficiency losses stem from ineffective mass transport behavior in the anode porous transport layer.¹⁵ Specifically, the undesired accumulation of by-product gas in the anode porous transport layer can significantly obstruct the reactant transport pathways to the reaction sites. However, the twophase flow behavior in the PTL remains poorly understood, owing to the complex two-phase flow dynamics in micro-scale pores where capillary- and viscous-forces govern fluid flow.^{16,17}

An attractive means to understand fluid flow within PTLs is via non-destructive in operando imaging techniques such as neutron and synchrotron X-ray imaging.^{18–26} Key transport phenomena have been identified via in operando imaging, such as insufficient water delivery through the PTL at low water stoichiometry ratios,²³ insensitivity of gas accumulation to flow rate and current density at steady state,²⁴ and increased gas accumulation under the land relative to the channel.²⁵ Although the physical mechanisms of undesired gas accumulation in the anode PTL have been studied extensively, the influence of intermittent electrolyzer operation on the dynamic gas transport behavior in the PTL has yet to be determined.

Here, we used in operando synchrotron X-ray imaging to elucidate the transient gas transport behavior in the anode PTL during intermittent electrolyzer operation. Specifically, our results support the advantages of a steep ramp-up and a shallow ramp-down of the operating current density for a faster gas response in the anode PTL (compared to a shallow ramp-up and a steep ramp-down, respectively). Additionally, we observed evidence of residual gas trapping near the CL-PTL interface, leading to a slower gas response behavior during ramp-downs relative to ramp-ups. Finally, the gas accumulation in the anode PTL exhibited hysteresis resulting from the intermittent operation of the electrolyzer based on the power supply of a wind turbine, and this hysteresis negatively affected the performance of the electrolyzer. Our findings revealed the strong dependence of gas response behavior on dynamic operating conditions, and this work informs the design of next generation PEM electrolyzer systems coupled with intermittent renewable energy sources.

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Experimental

In this section, we describe the PEM electrolyzer hardware used for this study and the dynamic operation modes examined to demonstrate the transient behavior of gas accumulation in the anode PTL. Then, we introduce the in operando synchrotron X-ray imaging apparatus and the image processing procedure to quantify the gas content in the anode PTL.

Cell assembly and transient operation modes.—A custom single-cell electrolyzer was specifically designed for X-ray imaging of the membrane-electrode assembly (MEA) in an operating electrolyzer. The active area of the cell was 5 mm long (along the direction traversed by the X-ray beam) and 16 mm wide. We used a commercially available catalyst-coated membrane (CCM) (HYDRion N115, Ion Power) consisting of a Nafion 115 membrane, a cathode platinum catalyst (0.3 mg cm^{-2}) , and an anode iridium catalyst (1.0 mg cm^{-2}). On both sides of the CCM, 0.19 mm-thick commercial carbon papers (TGP-H-060, Toray Industries) were used as anode and cathode PTLs. We used carbon papers instead of conventional titanium-based PTLs to enhance the transparency of the PTL to photons during X-ray imaging. The MEA was compressed between two titanium flow fields with 16 parallel flow channels (0.5 mm wide and 0.5 mm deep) separated by lands (0.5 mm wide). The flow direction of the channel was parallel to the X-ray beam. We controlled the compression of the anode and cathode PTLs via polytetraflouroethylene gaskets (0.15 mm thick).

The transient behavior of gas saturation in the anode PTL was elucidated by operating the custom electrolyzer in two modes of operation: setpoint ramping mode (Fig. 1a) and intermittent-current mode (Fig. 1b). In the setpoint ramping experiment, four ramp slopes (di/dt) were used: $-0.8 \text{ mA cm}^{-2} \text{ s}^{-1}$ (shallow and up), $-1.6 \text{ mA cm}^{-2} \text{ s}^{-1}$ (steep and up), $-0.8 \text{ mA cm}^{-2} \text{ s}^{-1}$ (shallow and down), and $-1.6 \text{ mA cm}^{-2} \text{ s}^{-1}$ (steep and down). For ramp-ups, the current density (i) was increased from 0 to 150 mA cm^{-2} , whereas for ramp-downs, the current density was decreased from 150 to 0 mA/cm². We prescribed these current densities to maintain operating cell potentials (E_{cell}) below 2 V, since the corrosion of carbon-based PTLs becomes significant when $E_{cell} > 2 V.^{26}$ After each ramp, the final current density was held constant until the total duration of operation mode reached 1000 s. In the intermittent-current experiment, a current density profile was extracted from a previously reported power output of a wind turbine (Fig. 1b).²⁷ Specifically, the wind turbine power output was simplified as a series of ramp-ups and rampdowns in current density, where the maximum current density does not exceed 200 mA cm⁻² to avoid corrosion conditions. For a quantitative comparison of the cell performance, we compared the operating cell potential and the gas saturation in the anode PTL at the same current density ($i = 86 \text{ mA cm}^{-2}$) at later points of time. To ensure that the change in the cell potential observed during this experiment is not due to the degradation of the carbon-based PTL, a polarization curve (from 0 mA cm^{-2} to 150 mA cm $^{-2}$ with 15 mA cm $^{-2}$ incremental steps) was obtained before and after the intermittent-current operation experiment. The average deviation between the polarization curves before and after the tests was 5 mV, which was not significant relative to the changes observed during this study.

We galvanostatically controlled the operating current density and examined the resulting cell potential via a potentiostat (Gamry Reference 3000, Gamry Instruments) to correlate the trends in gas saturation with the cell performance. The liquid water was supplied to both the anode and the cathode at a flow rate of 5 ml min⁻¹ with a peristaltic pump (Masterflex L/S Precision Variable Speed Console Drive, Cole-Parmer). Pulse dampeners were placed downstream of the pump to provide a constant reactant flow rate to the electrolyzer. The electrolyzer cell was operated at room temperature.

In operando synchrotron X-ray imaging and image processing.—We performed in operando synchrotron X-ray imaging to measure the dynamic change in gas content within the anode PTL.



Figure 1. Modes of cell operation performed in this study. (a) Setpoint ramping experiment. The ramp region is highlighted with an orange-shaded background. The ramps were immediately followed by constant current operation. (b) Intermittent-current operation based on a previously reported wind turbine power output (P_{WT}) by Xuan et al.²⁷ A simplified representation of the output power profile involved a series of current ramp-ups and ramp-downs.



Figure 2. In operando imaging experiment setup showing the cathode (C) PTL, CCM, and anode (A) PTL. (a) A schematic of the synchrotron X-ray radiography-based imaging setup. (b) A sample raw image. The flow direction of the channel was parallel to the X-ray beam. The red-dashed box highlights the anode porous transport layer, from which an average bulk gas thickness was determined.

Our custom electrolyzer cell was imaged at the Biomedical Imaging and Therapy Wiggler Insertion Device beamline at the Canadian Light Source Inc. in Saskatoon, Canada.²⁸ Incident X-rays (photon energy level of 30 keV) traversed in the in-plane direction through the MEA, where the in-plane direction refers to the direction shown in Fig. 2a. We used a complementary metal-oxide-semiconductor camera (C11440–22CU, Hamamatsu) to achieve a pixel resolution of 6.5 μ m per pixel and a temporal resolution of 2.5 frames per second. We captured two types of images: a reference image and operational images. Specifically, the reference images were captured in the absence of an applied current, when the PTLs were assumed to be fully saturated with liquid water. Operational images were captured when current was supplied to the electrolyzer.

All images were processed to obtain the average gas thickness in the anode PTL using the following procedure: dark-field correction, beam intensity correction, Beer–Lambert law, and averaging of the pixels that correspond to the anode PTL. First, all images were corrected with dark-field images (images obtained in the absence of the neutron beam) to remove the dark-current noise generated from the electron thermal excitation of the camera.²⁹ After the dark-field correction was applied, the images underwent a beam intensity correction to eliminate the effects of beam intensity decay.³⁰ The readers are directed to Ge et al.³¹ for a thorough description of this correction process.

We applied the Beer–Lambert law to quantify the changes in the water content from the reference state in each pixel (i.e. gas thickness, $t_{gas,pixel}$):

$$t_{gas, pixel} = \frac{1}{\mu} \ln \left(\frac{I_{op}}{I_{ref}} \right)$$
[1]

where μ is the attenuation coefficient of water [3.75 mm^{-1 32}], and I_{op} and I_{ref} are the pixel intensities of operational and reference images, respectively. We used an average of the 10 reference images obtained prior to commencement of each experiment to calculate I_{ref} . Then, the gas saturation at each pixel (S_{pixel}) was determined from the t_{gas,pixel} values as follows:

$$S_{pixel} = \frac{\mathbf{t}_{gas, pixel}}{L_{PTL}\phi}$$
[2]

where L_{PTL} is the length of the PTL in the X-ray beam path [5 mm], and ϕ is the porosity of the PTL [$\phi = 0.62$ after compression]. Two types of saturation values are reported in this work. First, we averaged the gas saturation values within the anode PTL region to obtain average gas saturation (i.e. *S*), and the anode PTL region in the image (indicated as red-dashed box in Fig. 2b) had dimensions of 23 pixels by 2048 pixels (0.15 mm by 13.31 mm). Secondly, the gas saturation values at each pixel in the anode PTL region were averaged in the through-plane direction of the membrane and the flow direction of the channel (*x*-direction in Fig. 2b) to determine the distribution of gas saturation in the through-plane direction (i.e. S_x).

Results and Discussion

In this section, we first describe the transient gas saturation during setpoint ramping operation. Then, we present the evolution in the distribution of gas saturation during setpoint ramping operation. Finally, we detail the transient gas saturation and the resulting performance during intermittent electrolyzer operation.



Figure 3. Evolution of gas saturation in the anode PTL with time. (a, b) Response in the gas saturation during ramp-up ((a) $0.8 \text{ mA cm}^{-2} \text{ s}^{-1}$ and (b) $1.6 \text{ mA cm}^{-2} \text{ s}^{-1}$) followed by constant current operation. (c, d) Response in the gas saturation during ramp-down ((c) $-0.8 \text{ mA cm}^{-2} \text{ s}^{-1}$ and (d) $-1.6 \text{ mA cm}^{-2} \text{ s}^{-1}$) followed by constant open circuit voltage. The ramp regions are highlighted with orange-shaded backgrounds. For all four experiments, the responses of the gas saturation during the ramp exhibited a linear accumulation/removal behavior, and the responses of the gas saturation during constant current operation exhibited logarithmic accumulation/removal behavior.

Transient gas distribution during setpoint ramping operation .- We measured the dynamic evolution of gas saturation in the anode PTL during setpoint ramping operation and observed distinct gas response behaviors (Fig. 3). We observed that the effects of ramp slope on the gas saturations at the end of each ramp (the right edge boundaries of the orange boxes in Fig. 3) were counterintuitive. Specifically, although it is expected that a steeper ramp-up results in a lower volume of gas (since the amount of oxygen produced is proportional to the integral of the current in Fig. 3), a steeper ramp-up led to a 11% higher gas saturation at the end of the ramp (Figs. 3a and 3b). This trend was consistently observed for ramp-downs, where a steeper ramp-down led to a 29% higher gas saturation (Figs. 3c and 3d). These results suggest that the duration of the ramps (regardless of the ramping direction) had a dominating effect on the resulting gas saturation at the end of the ramp, relative to the amount of generated oxygen. A possible explanation is that, considering the ramp-up case, a more gradual increase in the oxygen production rate (i.e. current) suppresses the nucleation of gas pathways within the PTL, whereas a more abrupt increase in the oxygen production rate promotes simultaneous nucleations of gas pathways within the PTL.

We further investigated the gas response behavior by characterizing the gas response time during the setpoint ramping experiments. During the ramp operation, the gas followed a linear accumulation/ removal behavior, whereas during the constant current operation the gas followed a logarithmic accumulation/removal behavior. Hence, for the ramp, we applied a linear fit to the gas response, and used the slope of the linear fit (dS/dt) as a quantitative indicator for the gas response behavior (Fig. 4a). For the constant current, we used a firstorder response function to fit the gas response behavior (Fig. 4b):

$$S = S_i + \Delta S \left(1 - \exp\left(\frac{-t}{\tau}\right) \right)$$
[3]

where S_i is the initial average gas saturation in the anode PTL before the ramp [-], ΔS is the absolute difference between initial average gas saturation and the final average gas saturation in the anode PTL [-], *t* is time [s], and τ is a time constant or the time required for the gas saturation to reach 63% of the final steady-state value [s]. The time constant, τ , was used as a quantitative indicator for the gas response behavior during constant current operation. The *dS/dt* and τ values obtained from the setpoint ramping operation experiments are summarized in Table I.

Gas saturation in the anode porous transport layer reached steady state more rapidly with steep current density ramp-ups and shallow ramp-downs, compared to shallower ramp-ups and steeper ramp-downs, respectively (Table I). During ramp-ups, when *di/dt* increased by a factor of 2 (from 0.8 to $1.6 \text{ mA cm}^{-2} \text{ s}^{-1}$) *dS/dt* increased by a greater factor of 2.4. During ramp-downs, when *di/dt* was increased by a factor of 2 (from $-0.8 \text{ to } -1.6 \text{ mA cm}^{-2} \text{ s}^{-1}$), *dS/dt* increased by only a factor of 1.5. Similar trends were observed during the constant current step after a ramp-down, where a shallower ramp-down resulted in a higher τ (by 24%). These results suggest that a steeper ramp-up and a shallower ramp-down are beneficial for achieving faster gas response behavior in the anode PTL during PEM electrolysis.

We further investigated the gas response behavior by comparing the dS/dt values between ramp-ups and ramp-downs and observed that the time response for gas accumulation was faster than the time

 Table I. Summary of the resulting fitting parameters for the rampconstant current experiments.

$di/dt \ [\text{mA cm}^{-2} \ \text{s}^{-1}]$	$dS/dt \ [\mathrm{cm \ s}^{-1}]$	τ [s]
0.8	1.03×10^{-4}	204.9
1.6	2.45×10^{-4}	197.5
-0.8	-7.00×10^{-5}	277.8
-1.6	-1.03×10^{-4}	343.4



Figure 4. Fitting results for the ramp operation and constant current operation. (a) Linear fit during the ramp operation at $di/dt = 0.8 \text{ mA cm}^{-2} \text{ s}^{-1}$. (b) Logarithmic fit during the constant current operation at $di/dt = 0.8 \text{ mA cm}^{-2} \text{ s}^{-1}$. The resulting fitting parameters are summarized in Table I.

response for gas removal (Table I). Specifically, during the steeper ramps, dS/dt for ramp-up was 47% larger than dS/dt for ramp-down. During the shallower ramps, dS/dt for ramp-up was 138% larger than dS/dt for ramp-down. This trend in slower gas response for ramp-downs was also evident from the gas evolution curves (Fig. 3), where during the ramp-up the gas saturation reached a plateau within 1000 s (Figs. 3a and 3b), whereas during the ramp-down the gas saturation did not plateau within 1000 s (Figs. 3c and 3d). We attribute the slower gas response behavior during gas removal to the relatively slow migration of residual gas from the anode porous transport layer to the flow channels. A previous work reported the



Figure 5. Evolution of gas distribution from the CL-PTL interface (x = 0.00 mm) to the PTL-FF interface (x = 0.15 mm). (a)–(b) Response in gas saturation during ramp-up (a) and ramp-down (b), with red-background markers indicating the time at which the distribution in gas saturation was quantified. (c)–(d) Change in the distribution of gas saturation with respect to time during ramp-up (c) and ramp-down (d). We observed that gas preferentially accumulated near the CL-PTL interface, which resulted in residual gas largely present also near the CL-PTL interface.

presence of residual gas in the PTL subsequent to the physical displacement of the gas phase by the liquid water phase.²² According to a classical study on enhanced gas recovery from natural reservoirs via liquid water flooding, residual gas exits the system via diffusion, which is much slower than via physical displacement by liquid water.³³ We propose that the removal mechanism in the PTL is similar, evidenced by the slower rate of gas removal from the PTL relative to the rate of gas accumulation in the PTL.

Distribution of gas saturation during setpoint ramping operation.-We further investigated the accumulation of residual gas in the PTL by examining the through-plane gas distribution during the setpoint ramping experiment (Fig. 5). The through-plane gas distributions were compared at five points of time; pre-ramp ($t_a =$ 50 s), post-ramp ($t_b = 144$ s), 5 min ($t_c = 350$ s), 10 min ($t_d = 650$ s), and 15 min ($t_e = 950$ s) from t_a (Figs. 5a and 5b). When current was applied and gas was initially generated, the gas preferentially accumulated at $x = 13 \mu m$, which corresponds to the average pore size (i.e. $\sim 18 \,\mu m^{34}$) of the PTL used in this work. Previous works $^{35-37}$ have reported that the CL inherently intrudes into the PTL during cell assembly, resulting in a heterogeneous CL-PTL interface. The presence of preferential gas accumulation at 13 μ m from the theoretical location of the CL-PTL interface (determined based on the PTFE gasket thickness used) indicates that the majority of the contact points between the CL and PTL resided near the x =13 μ m plane (this region was herein referred to as "near the CL-PTL interface"). We assumed that preferential gas accumulation near the CL-PTL interface negatively affected the performance via the hindrance of liquid water transport to the reaction sites. Gas also accumulated near the flow field and PTL interface, but the quantity was negligible relative to the gas near the CL-PTL interface.

The accumulation of gas near the CL-PTL interface exhibited steady state behavior five minutes after the ramp (i.e. t_c) (Fig. 5c). In contrast to the ramp-up case, the gas saturation near the CL-PTL interface did not recover to the original gas saturation $S_x = 0$, despite a 15 min-flush after the ramp-down (i.e. t_e) (Fig. 5d). We attributed this relatively slower removal rate of residual gas to the relatively long diffusion pathways from the gas to the flow channels. As previously stated, we expect the residual gas to exit the system via diffusion, which is a relatively slower process than the physical displacement by liquid water. The diffusion rate of the gaseous species is dependent on the species concentration and the length of the diffusion pathway from the location of the considered species to the exit according to Fick's law of diffusion where the oxygen exits at the flow channel in this experiment. Since the residual gas preferentially accumulated near the CL-PTL interface (which was located further from the flow channels relative to the bulk of the PTL), a relatively lower diffusion rate of the gaseous species near the CL-PTL interface was assumed compare to the diffusion rate of the gaseous species within the bulk of the PTL. Thus, we demonstrate that the gas removal rate was relatively slower than gas accumulation, not only due to the generally slow diffusion process (relative to the physical displacement by liquid water) but also due to the longer diffusion pathway of residual gas from the CL-PTL interface to the flow channels.

Transient gas saturation during intermittent-current operation.—Our results thus far demonstrate that the gas response rate is strongly dependent on the slope (i.e. shallow and steep) and direction (i.e. up and down) of the ramp. We exploited these observations to understand how the identified trends in gas response rate influence the accumulative gas volume in the PTL during



Figure 6. Hysteresis in gas saturation and overpotential during intermittentcurrent operation. (a) The resulting gas saturation in the anode PTL of the electrolyzer. (b) The resulting electrochemical performance of the electrolyzer. The circular markers indicate points of identical current density (i =86 mA cm⁻²) during the experiment ($t_1 =$ 76.8 s, $t_2 =$ 216.8 s, $t_3 =$ 502.0 s). We observed a gradual increase in gas saturation and cell potential over time, despite identical current density operation.

intermittent electrolyzer operation, and the subsequent effects of the accumulative gas volume on the electrochemical performance.

Intermittent electrolyzer operation led to an increase in residual gas accumulation, resulting in a negative effect on the electrolyzer performance (Fig. 6). The gas saturation in the PTL exhibited hysteresis, whereby the gas volume at identical operating current densities was higher relative to an earlier point in time (Fig. 6a). We compared the gas saturation at three points in time ($t_1 = 76.8$ s, $t_2 =$ 216.8 s, $t_3 = 502.0$ s) at which the operating current density was 86 mA cm^{-2} . Strikingly, the gas saturation in the anode PTL increased gradually between these three points, despite operating at the same current density. We observed a 19% increase in gas saturation between t_1 and t_3 (from 0.087 to 0.103). According to Faraday's law, the rate of gas introduced from the reaction sites to the PTL is directly proportional to the operating current density. We attributed the observed hysteresis in anode PTL gas volume to the slower rate of gas removal relative to the rate of gas accumulation in the PTL. Gas hysteresis effects were consistently observed in a repeated trial of the intermittent operating current experiment. The insufficient removal of residual gas during the ramp-downs during the intermittent operation of the electrolyzer led to an overall increase in the residual gas saturation in the PTL.

The hysteresis effect of gas saturation in the PTL was accompanied by a gradual increase in the cell overpotential (Fig. 6b). We compared t_1 and t_3 , and observed a 6% increase in the cell overpotential (from 0.51 V to 0.55 V). We further confirmed that



Figure 7. Analysis of performance hysteresis during intermittent-current operation. (a) Three operating regions discussed in (b): t_1 , t_2 , and t_3 are points of identical current density introduced in Fig. 6, and $t_{1'} = 61.0$ s, $t_{2'} = 198.2$ s, and $t_{3'} = 467.4$ s are points in time when local current density maxima were reached prior to t_1 , t_2 , and t_3 , respectively. (b) Hysteresis in cell performance throughout operation. The cell performance gradually increased over time regardless of the local current density maxima (i.e. $t_{1'}$, $t_{2'}$, and $t_{3'}$), thereby illustrating hysteresis effects.

the performance hysteresis observed in Fig. 6b occurred gradually over time and was relatively insensitive to the local maximum current densities prior to ramping down to t_1 , t_2 , and t_3 (Fig. 7). Specifically, we examined the polarization behavior at each local maximum current density prior to t_1 , t_2 , and t_3 (Fig. 7a), and we observed that the gradual increase in cell potential from t_1 to t_3 was insensitive to the operating current densities at $t_{1'}$, $t_{2'}$, and $t_{3'}$, respectively (Fig. 7b). If the proceeding current density dominated this increase in potential, the slope of the potential drop in Fig. 7b would be a function of the local current density maxima. However, we observed that the slopes of the potential drops were similar, further confirming the presence of hysteresis effects. At low operating current densities (i.e. $i = 86 \text{ mA cm}^{-2}$), the kinetic overpotential dominated the cell overpotential,¹⁴ implying that the kinetic overpotential increased between t_1 and t_3 . The increased kinetic overpotential was attributed to the physical shielding of reaction sites by the accumulated residual gas, consequently leading to reduced electrochemical surface areas. The increase in overpotential was consistently greater than 5% from six repeated electrochemical tests. The hypothesized decrease in electrochemical surface area was confirmed by observing a preferential accumulation of residual gas near the CL-PTL interface (Fig. 5). Under low constant current operation, the cell overpotential is known to stabilize rapidly (<10 s) since the reaction sites are fully saturated with liquid water.

It is important to note that the anode PTL used in this study was a carbon fiber-based PTL rather than a conventional titanium-based PTL. The carbon-based PTL used in this study exhibited a bulk porosity that is comparable to conventional titanium PTLs (63%) but

was less hydrophilic than titanium PTLs ($80^{\circ 38}$ compared to $50^{\circ 39}$). A less hydrophilic PTL may have promoted gas accumulation in the PTL, potentially leading to more residual gas than what would be expected in a conventional PTL. However, the wettability of the untreated carbon-based PTL was still hydrophilic ($\theta < 90^{\circ}$), therefore the gas accumulation hysteresis is expected to be highly relevant in a conventional PTL.

Here, we demonstrated for the first time the existence of gas accumulation hysteresis, which persisted up to 500 s during intermittent operation due to the insufficient rate of residual gas removal from the PTL. Although we demonstrated this hysteresis effect on a relatively small-scale electrolyzer (designed with an active area of 5 mm by 16 mm for sufficient X-ray transmission), the hysteresis effect is also expected to be strongly relevant in large-scale electrolyzers, which typically operate over a wider range of current densities (up to 3 A cm^{-2} ⁴). Specifically, factors such as larger active areas accompanied by more heterogeneous liquid water distributions and ramp-downs from high current density operation are both expected to lead to higher volumes of residual gas and subsequently more severe gas accumulation hysteresis. Furthermore, these results present potential opportunities for designing strategies to mitigate such hysteresis effects for improved dynamic operation.

Conclusions

In this study, we investigated the dynamic gas response behavior in the anode PTL under intermittent electrolyzer operation via in operando synchrotron X-ray imaging. Intermittent operation of PEM electrolyzers is highly relevant for PEM electrolyzer systems coupled with intermittent renewable energy sources (such as wind and solar), but the majority of previous works on intermittent electrolyzer operation have been focused on material degradation; the dynamic mass transport behavior remains relatively unexplored.

We conducted two in operando imaging experiments. In the first experiment, the electrolyzer underwent a setpoint ramping operation to identify the dependence of the gas response rate on the ramp slope and direction. The current was ramped from OCV to an operating current setpoint (or from a setpoint current and then back down to OCV), immediately followed by a period of constant current (or OCV). We observed that a steep ramp-up and a shallow ramp-down led to a more rapid (and more favorable) gas response. Furthermore, we observed evidence of residual gas near the CL-PTL interface during gas removal, which led to a slower time response during ramp-downs relative to ramp-ups. In our second experiment, we determined the impact of intermittent operation on the gas response in the electrolyzer. To the best of the authors' knowledge, we are the first to identify hysteresis effects in the PEM electrolyzer PTL as a result of intermittent operation, whereby the accumulative gas volume increased over time, despite the identical operating current densities. Specifically, we observed up to a 19% increase in gas volume at two points in time, even though the operating current densities ($i = 86 \text{ mA cm}^{-2}$) were identical. This increase in gas volume was attributed to the residual gas accumulation during operation, evidenced by our results from the first experiment. The gas accumulation led to a 6% increase in cell overpotential, which was attributed to a reduction in the electrochemical surface area. Our results can be used to inform design strategies for mitigating such hysteresis effects and improve the performance of PEM electrolyzers coupled with intermittent renewable energy sources.

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