Investigation of the transient freeze start behavior of polymer electrolyte fuel cells

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A B S T R A C T

Understanding the water management in polymer electrolyte fuel cells during sub-zero operation is crucial for designing effective freeze start strategies. This study uses sub-second operando X-ray tomographic microscopy to study the effect of warm-up rate and pre-drying on the water dynamics during non-isothermal freeze starts from −30 °C. A faster warm-up rate and cell pre-drying before freezing improved the cell performance during the freeze start. Imaging showed that during the freeze starts no new water clusters were formed in the cathode gas diffusion layer. Temporary catalyst layer detachment from the micro-porous layer was also observed between −20 to 18 °C due to the hygro-mechanical stresses during the sub-zero operation. Isothermal freeze starts were also performed to study the effect of membrane conductivity and local water flux in the catalyst layer during the sub-zero operation. Higher temperatures and lower operating current densities resulted in an increase in the operation time. Imaging results showed water clusters in the cathode gas diffusion layer for the isothermal freeze starts from −15 to 0 °C after 6 C/cm² charge was produced.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are widely regarded as a sustainable and viable alternative to the internal combustion engine for automotive applications due to their high power density and wide range of operating temperatures. In particular for automotive applications, PEFCs are also required to start and operate at sub-zero temperatures [1]. At sub-zero temperatures, water management becomes critical to PEFC operation because the water produced in the cathode catalyst layer (CL) due to the oxygen reduction reaction (ORR) can freeze leading to performance degradation and cell shutdown. Therefore, the rate of cell warm-up during the freeze start is essential to prevent freezing in the cell and provide reliable power output for automotive applications [1,2]. According to the Department of Energy technical targets [3], PEFCs are required to achieve unassisted freeze start from −30 °C and reach 50% rated power in 30 s when starting from −20 °C. Understanding the driving factors for successful PEFC operation at sub-zero conditions is therefore necessary to achieve reliable cell performance during freeze starts.

Water content of the polymer electrolyte membrane (PEM) plays a major role during the freeze start. Low water content in the membrane increases its sorption capacity during the freeze start but could result in high protonic overpotentials. High water content in the membrane could lead to flooding of the catalyst layer and subsequent ice formation and cell shutdown. Cho et al. [4,5] showed that the cell performance degrades at a rate of 2.3% for cells without gas purging to dry excess water prior to cell shutdown and freezing. Several studies [5–8] have therefore, proposed gas purging before cell shutdown at freezing conditions to obtain a successful freeze start and prevent performance degradation. Therefore, efficient water management is crucial for PEFC operation at sub-zero conditions.

Isothermal freeze start experiments [9–13] have widely been used to understand PEFC operation at sub-zero conditions. A general consensus exists among these studies that during the isothermal freeze start the following phases can be identified in the electrochemical performance of the cell: (i) initial decrease in the high frequency resistance (HFR) due to water sorption in the membrane; (ii) a period of constant HFR where the cell power density increases; and (iii) loss of power density due to local ice formation in the membrane electrode assembly (MEA) and loss of active area. For the last stage, the initiation of ice formation in the MEA can be identified by a jump in the HFR [14–16]. For non-isothermal freeze starts, i.e., where the cell temperature is increased from freezing conditions to above 0 °C due to the heat produced by the cell or external heating, an additional phase of power density recovery

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was observed as the cell temperature approached 0 °C [8,17,18]. The power density recovery in this phase was hypothesized to be due to melting of the ice and re-activation of the catalyst layer (CL). Electrochemical measurements during the sub-zero operation of PEFCs provide information about the macro-scale processes in the cell but do not provide information about the localized dynamics in the different layers of the MEA.

Imaging techniques have been used to complement the electrochemical measurements to understand failure mechanisms and MEA degradation. Tabe et al. [10] showed ice formation on the majority of the cathode CL surface for isothermal freeze start at −10 °C while at −20 °C there was very little localized ice formation. Thompson et al. [19,20] performed electron microscopy (SEM) on cathode GDLs post voltage failure during an isothermal freeze start and observed uniform ice formation across the CL cross-section starting from the membrane–CL interface. Kim et al. [21,22] also used SEM to show interfacial delamination at CL-diffusion media (DM) interface due to freeze–thaw cycling. They found that the delamination was limited to the region under the channel and the degree of detachment was dependent upon the DM thickness, DM stiffness, CL cracks and membrane reinforcement. Zhong et al. [23] also showed used 3D X-ray tomography to show crack formation in the membrane and CL delamination at the CL-membrane interface after 20 freeze/thaw cycles. Although post-mortem studies [10,19–23] can provide reasons for cell failure during freeze starts they are not suitable for understanding the transport dynamics during the sub-zero operation.

Water transport mechanism during sub-zero operation of PEFCs can be comparatively different from those at ambient or high temperatures of 50–80 °C [24] (and references within) due to the much lower water carrying capacity of the gas and achievable operating current densities. Several operando imaging studies have therefore, investigated the dynamic transport processes occurring in the PEFC during the freeze start. Santamaria et al. [25] showed ice formation in the cathode flow channels using 3D neutron tomography. The ice content was higher at the cell outlet due to the higher humidity of the gas downstream of the electrochemical reaction. Ishikawa et al. [26,27] used visible and infrared imaging with a transparent cell and showed water accumulation in the GDL was limited to the region under the channel and the degree of detachment was dependent upon the DM thickness, DM stiffness, CL cracks and membrane reinforcement. They also observed ice formation at the CL–GDL interface which was correlated to the performance drop. Neutron imaging has also been used by several studies to investigate the state of water in PEFCs [11–13,15,16]. Mukundan et al. [11] showed that water freezes in the CL close to the membrane and then extends to the GDL. Oberholzer et al. [12] showed the presence of supercooled water in the cell during isothermal freeze starts between −10 and −20 °C and found that lowering the temperature and increasing the current density resulted in lowering of the operational time. Biesdorf et al. [13] used neutron imaging to demonstrate that during isothermal freeze starts water accumulation occurred in the cathode CL and GDL. However, water accumulation in the GDL was limited to the region under the rib. Further, they also showed a dependency of the freezing event and water accumulation on the different GDL coatings and presence/absence of the micro-porous layer (MPL). Stahl et al. [15] showed that freezing of the water produced during sub-zero operation could be limited to a localized area of the cell instead of occurring instantaneously over the entire cell area. Since neutron imaging is limited to a 2D projection of the cell, it is useful for qualitative analysis but cannot provide quantitative measures of local saturation in the 3D geometry. Operando X-ray tomography microscopy (XTM) provides a feasible alternative to analyze spatially resolved water distributions in the GDLs. Mayrhuber et al. [28] used XTM to study the evolution of the water distribution in the GDLs for isothermal freeze starts between −10 to −20 °C. Their results suggest that even at a temperature of −20 °C supercooled water could be observed at high current densities.

Operando imaging studies so far have primarily focused on isothermal freeze starts. Although isothermal freeze starts are ideal for understanding the freezing mechanisms, they do not capture all the transport processes occurring during a non-isothermal freeze start, such as evaporation effects, change in membrane conductivity due to temperature increase and re-activation of the CL due to melting of ice. An understanding of the water dynamics during non-isothermal freeze starts is also necessary to understand the behavior of commercial automotive PEFC stacks [1,2], which have demonstrated successful freeze starts from −30 °C, and further optimize the freeze start strategy.

In this study, sub-second X-ray tomographic microscopy (XTM) is used to study non-isothermal freeze starts in a PEFC. The effect of drying the cell prior to freezing and different warm-up rates from −30 to 0 °C were investigated for the non-isothermal freeze starts. Section 2 describes the details of the experimental setup, freezing setup, X-ray imaging and image processing. Section 3 discusses the electrochemical performance and XTM imaging for the different non-isothermal freeze starts. Isothermal freeze starts were also performed to corroborate the observations from the non-isothermal freeze start experiments.

2. Experimental

2.1. Materials

The PEFC design described by Eller et al. [29] and shown in Fig. 1a was used for the XTM imaging experiments. The flow fields were made of graphic material (BMA5, SGL Technologies) and consisted of two parallel channels which were 0.8 mm wide, 0.3 mm deep and 10 mm long separated by a 0.8 mm wide land region. A commercial catalyst coated membrane (CCM) from W. L. Gore & Associates (Gore® Prime® A510.1/M815.15/C510.4) comprising of a 15 μm thick reinforced Gore-Select membrane® and an anode and cathode Pt loading of 0.1 and 0.4 mg/cm² respectively. The CCM was laser ablated to have an active area of 0.16 cm² (4.5 mm × 3.6 mm). Freudenberg H23C6 GDLs with MPL and hydrophobic treatment (Freudenberg Performance Materials SE & Co. KG) were used for both the anode and cathode. PTFE gaskets having a thickness of 100 μm were used for both the anode and cathode. This resulted in a 20% compression of both the anode and cathode diffusion media (final thickness ca. 200 μm).

2.2. Freezing setup

Fig. 1b shows a schematic of the freezing setup used for the freeze start experiments. The freezing setup previously described by Mayrhuber et al. [28] was modified to cool down the cell to lower temperatures. The cell was cooled using an external dry cold air flow regulated by a mass flow controller. The air was first pre-cooled in the chiller (thermostat) using a stainless steel coil immersed into the coolant in the chiller. The chiller was used to maintain the coolant (30% ethylene glycol solution) at a constant temperature of −10 °C. The pre-cooled air was then fed to the Peltier cooler unit which was made of 12 Peltier elements (CP1 4-71-06L, Laird Technologies, UK), powered using a direct current (DC) power supply (Agilent Technologies, USA). The heat from the Peltier unit was dissipated to the counterflowing coolant.

A 3D printed cooling housing, shown in Fig. 1b, with dimensions 40 × 52 × 105 mm (L × W × H) made of acrylonitrile-butadiene-styrene (ABS) was lowered over the cell in the cell holder. The design of the cooling housing was modified from that used by Mayrhuber et al. [28] to improve heat insulation and prevent snow formation during cooling. The cooling housing also had two rectangular windows with dimensions 8 × 10 mm (W × H) covered with Kapton tape to provide nearly attenuation-free X-ray transmission. The cold air from the Peltier cooler was directed into the housing from the side as shown in the schematic in Fig. 1b. The cell temperature was controlled using the heating pads placed in the flow field and Pt-100 thermocouple placed in the cylindrical holes in the flow field (see Fig. 1a).
Table 1 describes the procedure for the non-isothermal freeze start experiments performed in this study. Before cooling, the cell was operated at a constant current density of 1 A/cm$^2$ for 10 min at 30 °C and 50% RH to achieve steady state hydrated conditions in the MEA. The flow conditions used have a high stoichiometry to suppress gradients along the channel. To study the effect of pre-drying before freezing, two different test conditions were used, i.e., with drying (referred to as dry henceforth) and without drying (referred to as wet henceforth). For the dry freeze start tests, the cell was dried using 50 ml/min of N$_2$ gas at 30 °C and 50% RH for 10 min. This resulted in drying of the GDL and flow fields which was verified using XTM imaging post drying.

The freezing setup described before was then used to cool down the cell to −30 °C. During the cooling step, gas supply to the cell was stopped. Once the cell temperature reached −30 °C, the freeze start was initiated. During the freeze start, dry gases were supplied to the cell without humidification. Two different warm-up strategies, namely rapid and slow, were investigated in this study. For the rapid warm-up, the cell temperature was increased from −30 to 0 °C in 30 s and the cell voltage was ramped down to 0.1 V in 15 s and then kept constant. For the slow warm-up, the cell temperature was increased from −30 to 0 °C in 60 s and the cell voltage was ramped down to 0.2 V in 15 s and then kept constant. Above 0 °C, the cell was operated at a constant current density of 0.25 A/cm$^2$ for both the warm-up strategies. For the experiments in this study with the imaging cell, the cell warm-up was done using external heating from the heating pads because the active area of the cell (0.16 cm$^2$) was much smaller than the cross-sectional area of the GDL and membrane (see Fig. 1a) and hence insufficient to provide the necessary heat for the thermal mass of the cell. The non-isothermal freeze starts in this work correspond to unassisted freeze starts in the real world. The heating rate and electrochemical operating conditions chosen in this work were such that they represent an unassisted freeze start for a commercial automotive fuel cell stack [1,2]. During the freeze starts, the 1 kHz high frequency resistance of the cell was monitored using a Tsuruga E3566 AC milliohm meter.

In addition to the non-isothermal freeze starts, isothermal freeze starts were also performed at several sub-zero temperatures. For all isothermal freeze starts, the cells were dried prior to cooling and the same procedure described in Table 1 was used. Once the desired temperature was achieved the cells were operated at a constant current density of 0.3 A/cm$^2$ (for imaging tests) until cell shutdown while maintaining the cell temperature constant using external cooling.

2.3. Freeze start protocols

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2.4. XTM imaging

Operando XTM imaging was performed at the TOMCAT (X02DA) beamline at the Swiss Light Source (SLS) [30]. A polychromatic beam obtained using a 2.9 T superbend magnet and 400 mA ring current and filtered by 1 mm Si and 20 mm pyrolytic graphite was used [30, 31]. The tomographic scans were acquired using the TOMCAT in-house developed GigaFRoST camera system [32] (which combines the pco.Dimax imaging chip with a continuous ~8 GB/s data readout system) coupled with a 4x macroscope (Optique Peter) [33] and a 150 μm thick LuAG:Ce scintillator. At the 4x magnification used for
imaging, a voxel edge length of 2.75 μm was achieved. Operando XTM scans were obtained with an exposure time of 0.6 ms and frame time of 0.83 ms. A total of 301 projections were obtained resulting in a scan time of 0.25 s. The field of view for the XTM scans was 2016 × 2016 pixels (5.54 × 5.54 mm). 3D reconstructions were obtained from the projections using the Paganin approach [34]. At the end of the experiments, a high quality dry reference scan was taken with 2001 projections and same exposure and frame time as the operando scans.

For the operando imaging experiments, the cell was mounted vertically in the cell holder on the rotation stage with the heating pads at the bottom and the cooling housing was lowered around the cell. In-beam (cell centered at the window in the cooling housing) and out-of-beam positions were adjusted prior to imaging. During the non-isothermal freeze starts, 10 scans were performed at equal intervals (3 s for rapid and 6 s for slow) during cell warm-up from −30 to 0 °C and 20 scans were performed at 6 s interval during cell warm-up from 0 s to 30 °C. For the isothermal freeze starts, scans were performed at intervals of 10 s until cell shutdown.

2.5. Image processing

3D reconstructions of the XTM scans were first cropped to the region of interest (ROI) in the through-plane (TP) direction, which in this case was the cathode GDL and channel. The ROI also included the cathode MPL even though it was not used in the segmentation. The cropped 3D domains were registered to the reference low quality (LQ) dry scan (same number of projections as operando scans, i.e., 301) using SimpleElastix [35]. It was found that using the LQ dry scan instead of the scan with more projections (HQ dry scan) resulted in a better registration of the domains and reduction in the noise when obtaining difference images for water segmentation. The HQ dry scan was then subtracted from the registered operando scans to obtain the difference image containing only the water clusters. To threshold the water clusters from the difference images, a three step segmentation was used. For the first step, a lenient global threshold value was chosen which captured all the liquid clusters in the difference images but also a lot of noise. In the second step, the difference images were de-noised using a 3D median filter with radius of 3 voxels followed by a 3D anisotropic diffusion (AD) filter with 3 iterations. A strict global threshold was then applied on the de-noised images to obtain water clusters but ensuring that no noise was captured. In the final step, the connected liquid clusters from the lenient segmentation which had a corresponding cluster (smaller) in the strict segmentation were identified and used as the segmented water distribution.

To segment the GDL fibrous structure, the high quality (HQ) dry scan ROI was first aligned to the LQ dry scan so that it could be merged with the segmented water distributions post solid phase segmentation. The HQ dry scan images were then de-noised using a 3D anisotropic diffusion filter with 3 iterations followed by contrast enhancement using a Gaussian filter with σ of 1. The de-noised images were segmented using a global threshold value to obtain the GDL fiber structure. In the current study, no distinction was made between the GDL fibers and binder material. The GDL solid structure was then merged with the segmented water distributions to obtain the saturation profiles.

3. Results and discussion

3.1. Non-isothermal freeze starts

Non-isothermal freeze start experiments with operando XTM imaging were carried out to understand the water dynamics in the PEFC during the sub-zero operation. As described in Section 2.3, four different types of non-isothermal freeze starts, namely, rapid-dry, rapid-wet, slow-dry and slow-wet, were analyzed. These labels indicate the warm-up time from −30 to 0 °C (30 s for rapid and 60 s for slow) and if the cell was pre-dried before freezing (dry) or not (wet).

Figs. 1c and 1d show the electrochemical performance for the rapid-dry and rapid-wet freeze starts respectively and Fig. 1e shows the corresponding temperature ramp during the rapid freeze start. At sub-zero conditions, the cell was operated in a potentiostatic mode and the corresponding behavior of the current density and HFR resembles the typical behavior observed during a non-isothermal freeze start [8]. From Figs. 1c and 1d, it can be observed that lowering the cell voltage resulted in an increase in the current density to a maximum and a reduction of the HFR during the first 10 s of operation. The reduction in HFR is due to water sorption into the membrane resulting in an improvement in the membrane conductivity. Water in the membrane can exist in two states, namely non-frozen, which does not freeze even at −120 °C, and frozen bound, which can freeze below −20 °C [36,37]. Huo et al. [38] proposed that once the membrane and ionomer are saturated, water desorption occurs from the ionomer in vapor and liquid form in the CL pores leading to subsequent ice formation. Ice formation and propagation would result in a decrease in the current density which can be observed in Figs. 1c and 1d after 10 s. Additionally, a jump in the HFR is observed at 10 s which has been attributed to the onset of ice formation in the CL by previous studies [14–16]. Ice formation after 10 s of operation would be similar to the results of Huo et al. [38] who observed ice formation initiation after 9 s when starting from −20 °C.

Cryo-SEM imaging of CL by Li et al. [39] showed that the ice formation in the CL was close to the CL–MPL interface when operating at −25 °C and constant voltage (similar to the sub-zero operating conditions in this study). Tabe et al. [10] also showed that at −20 °C the ice formation on the CL surface was localized to a small region. Based on these studies, it can be hypothesized that the ice formation in the CL was localized and likely closer to the CL–MPL interface. Low protonic conductivity at sub-zero temperatures [40] likely results in a shift of the ORR to the CL-membrane interface. As a result, the region near the CL-membrane interface would be warmer which suppresses ice formation close to the membrane [41]. The produced water migrates from the warmer CL-membrane interface to the colder CL–MPL interface where it eventually freezes [39]. Ice formation in the CL, inferred from the jump in the HFR [14–16], likely results in a blockage of the gas pathways and a decrease in the cell performance as shown in Figs. 1c and 1d. To further understand the effect of temperature on ionic conductivity and water transport, isothermal freeze start experiments were performed which are discussed in the next section.

As the cell temperature was increased above −6 °C (r = 25 s in Figs. 1c and 1d), the current density was found to increase likely due to melting of the ice in the CL and improvement of the ionic conductivity. This phase of power recovery was also observed by other studies [8,17] for non-isothermal freeze starts. Similar electrochemical behavior was also observed for the slow-dry and slow-wet freeze starts (see Fig. S1 in Supplementary Information) with the power recovery phase delayed to nearly 44 s due to the slower warm-up rate. Although only one non-isothermal freeze start of each type was performed for the operando imaging, the electrochemical behavior during the freeze start was found to be reproducible for multiple cells (see Fig. S2 in Supplementary Information).

Comparison of Figs. 1c and 1d also shows the difference between the electrochemical behavior of the rapid freeze start with and without pre-drying. The performance during the rapid-wet freeze start is significantly worse than the rapid-dry freeze start. The height of the initial current density peak is nearly 5 times smaller for the rapid-wet freeze start due to the lower water uptake capacity of the membrane and CL. Table 2 shows the total charge produced during sub-zero operation and the voltage at 0 °C for the different non-isothermal freeze starts. The freeze starts with pre-drying show higher performance and much higher cell voltage at 0 °C than the ones without pre-drying. Additionally, for the wet freeze starts (both rapid-wet and slow-wet), the cell performance recovery phase is significantly delayed to higher temperatures compared to the pre-dried freeze starts. Further, for the
Table 2
Comparison of electrochemical performance for the non-isothermal freeze starts.

| Type       | Charge produced in the first 30 s [C/cm²] | Charge produced until 0 °C [C/cm²] | Voltage at 0 °C [V] |
|------------|-----------------------------------------|-----------------------------------|---------------------|
| rapid-dry  | 5.95                                    | 5.95                              | 0.455               |
| rapid-wet  | 1.75                                    | 1.75                              | 0.039               |
| slow-dry   | 3.45                                    | 11.61                             | 0.372               |
| slow-wet   | 0.23                                    | 2.27                              | 0.094               |

Fig. 2. Through-plane (TP) XTM slices for the rapid-wet freeze start at different temperatures. Water clusters in the GDL are indicated with blue color. The red circles show CL detachment at the CL–MPL interface which was observed between temperatures of −20 to 18 °C at multiple locations in the cell. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Operando XTM imaging was used to gain further insights into the water transport processes during the PEFC freeze starts. For the freeze starts with pre-drying (rapid-dry and slow-dry), no water clusters were observed in the cathode GDL during operation (XTM slices for rapid-dry and slow-dry freeze start at different temperatures are shown in Figs. S3 and S4 in Supplementary Information). Fig. 2 shows the XTM slices for rapid-wet freeze start at different temperatures with the water slow-wet freeze start (shown in Fig. S1 in Supplementary Information) the voltage at the end of the freeze start (at 30 °C) was nearly 180 mV lower than for the slow-dry case.

Decreasing the warm-up rate results in a lower performance in the first 30 s but nearly doubles the total charge produced until 0 °C. For the slow warm-up freeze starts, the higher charge produced until 0 °C was due to the longer sub-zero operation time and hence the average current density did not differ significantly between the rapid and slow warm-ups. The performance recovery phase for both the rapid and slow warm-up with pre-drying was found to start around −6 °C. The cell voltage at 0 °C was nearly 80 mV higher for the rapid-dry freeze start compared to the slow-dry freeze start thereby, demonstrating the advantage of a faster warm-up time for the cell performance. The cell voltage at 0 °C varied less than 85 mV with the warm-up rate but more significantly (nearly 300–400 mV) with the pre-drying.
clustering highlighted in blue color. For the freeze starts without pre-drying, ice was observed in the cathode GDL (rapid-wet shown in Fig. 2 and slow-wet shown in Fig. S5 in Supplementary Information) at sub-zero temperatures due to water accumulation from the pre-operation phase. XTM imaging does not directly provide sufficient information to differentiate between the liquid and ice form for the water clusters. It is assumed here that the water clusters in the GDL at −30 °C are in ice form and eventually thaw as the temperature increases. However, even for these cases no new water/ice clusters and no growth of the existing water/ice clusters was observed in the cathode GDL during the operation. Further, the size of the water clusters was found to decrease as the cell temperature increased above 0 °C due to evaporation, as can be seen qualitatively from Figs. 2d and 2e.

Fig. 3a shows the overall saturation in the cathode GDL for the freeze starts without pre-drying at different cell temperatures. There was a difference of 4% between the rapid-wet and slow-wet initial saturation at −30 °C. This was due to a difference in the water accumulation during the pre-operation phase. Although the pre-operation phase for both freeze starts was the same, i.e., constant current density operation at 1 A/cm² for 5 min at 30 °C and 50% RH on both anode and cathode as described in Table 1, there was some variability observed in the GDL saturation. For both cases, the saturation remained constant at sub-zero temperatures and decreased almost linearly with temperatures above 0 °C due to evaporation. The rate of evaporation, which is proportional to the slope of overall saturation, was different for the two cases due to a difference in the initial saturation. However, the final saturation value for both cases was relatively similar with a difference of 1.3%.

Figs. 3b and 3c show the in-plane and through-plane saturation profiles for the rapid-wet freeze start. The in-plane saturation profiles shown in Figs. 3b were obtained by averaging the saturation in the GDL over each 2D through-plane slice parallel to the gas channels for every temperature. Similarly, the through-plane saturation profiles in Fig. 3c were obtained by averaging the GDL saturation over each 2D through-plane slice parallel to the gas channels for the rapid-wet freeze start at different temperatures. The water accumulation from the pre-operation phase was limited to the region under the rib as shown in Fig. 3b and Fig. 4. There was negligible change in the water distribution and saturation profiles up to 0 °C beyond which the saturation profiles decreased uniformly due to evaporation.

The through-plane saturation profiles shown in Fig. 3c show two peaks at 40 μm and 125 μm from the MPL interface. During the pre-operation phase, water transport in the GDL was governed by capillary transport and water accumulation was limited to under the rib region (as shown by the saturation profiles at −30 °C in Fig. 3b, which are assumed to have remained unchanged during the freezing step). This resulted in a local peak in the GDL saturation close to the GDL–rib interface (at 125 μm from the MPL interface) because the water network cannot continue to grow in the through-plane direction. This can also be seen in the through-plane projected water volumes in Fig. 4. The saturation peak at 40 μm from the MPL interface is a consequence of the blocked capillary fingering at the GDL–rib interface, which results in lateral growth of the water network within the GDL during the pre-operation phase. During the non-isothermal freeze start, the through-plane saturation profiles also decreased uniformly when the temperature was increased above 0 °C. Although not shown here similar behavior was also observed for the cathode GDL saturation for the slow-wet freeze start. The results of XTM imaging indicate that during the non-isothermal freeze starts, irrespective of pre-drying, no additional water/ice formation was observed in the GDL. Thus, the water produced during these freeze starts likely exists in the CL or MPL and freezes in these layers or leaves the cell in vapor form.

CL detachment was observed during the non-isothermal freeze starts between the cathode CL and MPL as shown by the red circles in Fig. 2 (and Figs. S3, S4 and S5 in Supplementary Information). The detachment was observed at several locations in the cell under the channel region. The CL detachment occurred at the same locations for all the non-isothermal freeze starts between temperatures of 20 to 18 °C. Fig. 5 (top) shows a cropped section highlighting the through-plane and in-plane cross-sections at the detached location at different temperatures for the slow-dry freeze start. The CL detachment from the MPL was likely due to the hygro-mechanical and thermo-mechanical stresses on the CCM. During the non-isothermal freeze start, the HFR reduces from 0.3 to nearly 0.1 Ω cm² as the temperature increases from −30 to −20 °C indicating hydration of the membrane which could induce mechanical stress on the CCM. The HFR remains nearly constant between 0.06 and 0.07 Ω cm² between temperatures of −20 to 18 °C. Increase in temperature above 18 °C resulted in an increase in the HFR (value of 0.1 Ω cm² at 24 °C) indicative of membrane drying. Drying of the membrane resulted in alleviation of the stress on the CCM consequently, resulting in the flattening of the CL–MPL interface and disappearance of the CL detachment. Similar CL detachment restricted to under the channel region was also observed by Kim et al. [21,22] for
their thermal cycling experiments. However, unlike the observations of Kim et al. [21,22] the CL detachment from the MPL surface in our freeze starts was temporary and only observed between the –20 to 18 °C. Above 18 °C, there was no detachment at the CL–MPL interface due to flattening out of the CCM (as can be seen in Fig. 2e). Since, Kim et al. [21,22] used a wider temperature range (–40 to 70 °C) and higher number of cycles (30) than in this study, it is expected that the hygro and thermal stresses on the CCM resulted in a permanent detachment of the CL from the diffusion media compared to the temporary temperature dependent detachment observed for the shorter cycles in this study.

Fig. 5 (top) also highlights the appearance and disappearance of water clusters in the gap formed at the CL–MPL interface due to the CL detachment. Water clusters were observed in these gaps at several locations for all non-isothermal freeze starts. The water volume in the gaps was visibly larger after the cell temperature increased above 0 °C. An increase in temperature would result in a shift of the ORR from the CL-membrane interface at near the MPL interface with an increase in cell temperature. This could be due to a shift in the ORR from the CL-membrane interface at –30 °C towards the CL–MPL interface at 0 °C and above due to an increase in the protonic conductivity of the membrane [40].

3.2. Isothermal freeze starts

It was deduced from the non-isothermal freeze start behavior that the performance drop after cell startup was due to localized ice formation in the CL. It was hypothesized that the low protonic conductivity of the membrane at –30 °C resulted in a shift of the ORR towards the CL-membrane interface and only a localized region of the CL was active. This could have resulted in local ice formation in the CL close to the colder CL–MPL interface [39,41]. Consequently, isothermal freeze starts were performed at different temperatures and current densities in order to probe the effect of membrane conductivity and local water flux in the CL.

The steps for the isothermal freeze starts were similar to those described in Table 1, i.e., pre-operation, drying and cooling. For the freeze start, the cells were operated at a constant current density of 0.3 A/cm² (unless mentioned otherwise) until cell shutdown. Fig. 6 shows the total charge produced until cell shutdown for the isothermal freeze starts at different temperatures and current densities. A drop in the current density to less than 10% of the set value was used as the criterion for cell shutdown. The total charge was computed by integrating the current density until the criterion was met. Since the cell was operated in a galvanostatic mode, the total charge produced was proportional to the operation time.

Fig. 6a shows the variation of the total charge produced for isothermal freeze starts at different temperatures at a constant current density of 0.3 A/cm². An increase in temperature results in a nearly exponential increase in the total charge produced with no performance failure observed for the isothermal freeze start at 0 °C and –10 °C (repeat). For 0 °C, it can be expected that the CL was at a temperature above 0 °C due to the heat produced from the ORR. The value shown in Fig. 6a
in the operating temperature and consequently, an increase in the membrane conductivity resulted in proton transport deeper into the CL and “activation” of a larger fraction of the CL. Since the current density was the same irrespective of operating temperature, this resulted in a decrease in the local water flux in the CL. Further, an increase in temperature also reduces the probability of the freezing event due to an increase in the activation barrier for phase change [43]. The combined effect of improved protonic conductivity, lower local water flux and delayed freezing event resulted in an increase in the total charge produced from 1.74 to 102.2 C/cm$^2$ for isothermal freeze starts from −30 to −5 °C.

To probe the local water flux in the CL, isothermal freeze starts were performed at −24 °C with different operating current densities. Fig. 6b shows the total charge produced during the isothermal freeze starts at −24 °C for different current densities. A decrease in the operating current density resulted in an increase in the operation time and total charge produced. These results support the hypothesis that a decrease in the local water flux in the CL can help to delay ice formation in the CL and improve cell operation. The variation of the isothermal freeze start operation time with current density agrees well with the results reported by Thompson et al. [19] and Oberholzer et al. [12] who also observed an improvement in the operation time with a decrease in the current density. These results were however contrary to the observations of Mayrhuber et al. [28] who noted that higher current densities facilitated supercooled water transport to the GDL and hence increased operation time. The difference between the observations of this study and that of Mayrhuber et al. [28] could be attributed to the effect of the MPL used in this study. Since MPLs have a low thermal conductivity, they reduce the heat transported from the cathode CL to the GDL thereby, increasing the temperature in the CL. It is likely that for the studies of Mayrhuber et al. [28] at low current densities, the heat produced in the CL was not sufficient to increase the temperature and hence, resulted in earlier ice formation and performance failure.

XTM operando imaging was also performed for the isothermal freeze starts on Cell 1 to understand the water transport dynamics. XTM imaging scans were performed every 10 s during the isothermal freeze starts. Water clusters were observed in the reconstructed GDL domains for all isothermal freeze starts after 20 s of operation. XTM imaging is unable to provide direct information about the phase of the water clusters (liquid or ice). The advantage of operando imaging of the isothermal freeze starts every 10 s until performance failure is that the transient evolution and growth of the water clusters can be observed. Image analysis showed that the water cluster growth in the GDL was similar to the capillary transport observed for liquid water at elevated temperatures, concluding that the water is in the supercooled liquid form for the isothermal freeze starts at sub-zero temperatures. Several studies in literature [12,13,26–28] have also demonstrated that supercooled water can exist in the GDL and channels during isothermal freeze starts up to −20 °C. Mayrhuber et al. [28] also performed operando XTM imaging and observed similar capillary transport network of supercooled water. They proposed that the established supercooled water networks improved the freeze start performance as they delayed ice formation in the CL. Based on these studies and the XTM imaging results, it can be assumed that the water observed in the GDL during the isothermal freeze starts at sub-zero temperatures is initially in a supercooled liquid form and eventually freezes before cell shutdown.

**Fig. 6c** shows the overall saturation evolution with operation time for isothermal freeze starts at 0, −10 and −15 °C. For the isothermal freeze starts, an increase in operation time with operating temperature resulted in an accumulation of water in the cathode CL and channel. Until 20 s of operation, negligible saturation was observed in the cathode GDL. Based on this result, imaging was not performed for freeze starts at −20 °C and lower because the total charge produced for those freeze starts was not sufficient for water transport to the GDL. This could also explain the absence of new water clusters in the

![Graph](image-url)
GDL during the non-isothermal freeze starts because the total charge produced up to 0 °C (Table 2) was less than 6 C/cm² for most freeze starts except the slow-dry freeze start. As shown in Fig. 5 (top), for the slow-dry freeze start water clusters were observed in the gaps formed at the CL-MPL interface due to CL detachment and hence, the water might have accumulated in the MPL or transported as vapor. For the freeze starts at −15, −10 and 0 °C, the saturation as a function of operation time is identical until the cell shutdown due to ice formation in the CL. As discussed before, one of the isothermal freeze starts for −10 °C failed earlier likely due to early ice formation in the CL.

Figs. 7a and 7b show the in-plane and through-plane saturation profiles for the isothermal freeze start at −15 °C respectively. An increase in operation time leads to an increase in water accumulation in the GDL which is confined to under the rib regions and close to MPL-GDL interface. Figs. 7c and 7d show the in-plane and through-plane saturation profiles for the isothermal freeze start at 0 °C respectively. For the 0 °C isothermal freeze start, initially the water was confined under the rib region but after 200 s some water accumulation was observed under the channel with the saturation value under the rib increasing to nearly 0.45. In the through-plane direction, water accumulation started at the MPL-GDL interface and increased in the GDL during operation. After 200 s, a saturation peak was observed to be developing close to the rib-GDL interface which increased significantly to nearly double the saturation at the MPL-GDL interface at 600 s of operation.

To visualize the spatial distribution of water in the cathode GDL and channels, in-plane and through-plane projected water volume fraction contour plots are shown in Fig. 8 for the isothermal freeze starts at −15 and 0 °C at different operation times. Fig. 8 shows that the water accumulation in the GDL was limited to under the rib region for the isothermal freeze starts at 0 and −15 °C. Similar water distributions were also observed for the isothermal freeze start at −10 °C. For the −15 °C isothermal freeze start, water droplets were observed in both channels after 30 s which were connected to the liquid network in the GDL. As shown in Fig. 8 for the −15 °C isothermal freeze start, at 50 s there was an increase in the size of the water droplets in the channels as well as a growth of the water network in the GDL both in the in-plane and through-plane directions. For the 0 °C isothermal freeze start, the water distribution in the GDL at 50 s is similar to that observed for the −15 °C freeze start at 50 s. Although not shown here, for all the isothermal freeze starts, the water distribution in the GDL at the same operation time was nearly identical. For the 0 °C isothermal freeze start, the longer operation times resulted in much higher water accumulation under the rib region both in the in-plane and through-plane region. The growth of liquid droplets in the channels was due to the low flowrate of 50 Nml/min (channel gas velocity of 1.73 m/s) used in this study. At 600 s, there was significant water accumulation in the channels with the right channel nearly fully flooded and as a result, water clusters can be observed in the GDL under both the channels.

The water distribution in the GDL for the isothermal experiments shows that water networks were established from the CL to the GDL after 20 s of operation. At −15 °C, cell failure occurred even though the overall saturation in the GDL was less than 2% whereas at 0 °C no cell shutdown was observed with a saturation in the GDL of more than 16% and one of the cathode gas channels fully flooded. The similar water distributions observed for the 0, −10 and −15 °C freeze starts at same operation times could be due to: (a) presence of MPL which regulated the capillary transport from the CL to the GDL and/or (b) similar ORR distribution in the CL. For the latter to be true, the membrane conductivity should not limit the ORR distribution. While the protonic conductivity of the membrane can vary by nearly an order of magnitude between −30 and −15 °C [40] and hence result in a difference in the ORR distribution in the CL, the absolute value of the membrane conductivity at −15 and 0 °C is much higher. Since the operating current density is relatively small (0.3 A/cm²), the protonic conductivity at −15 °C and above might be sufficient to activate nearly the entire CL and result in a similar ORR distribution. In this case, the total operation time for the freeze starts is only governed by the
probability of freezing in the CL which increases with a decrease in temperature. In the absence of an MPL, water distributions in the GDL might give a direct indication about the underlying ORR distribution.

Similar to the non-isothermal freeze starts CL detachment at the CL–MPL interface was also observed for the isothermal freeze starts. The locations of the CL detachment were identical to those observed during the non-isothermal freeze starts. Fig. 5 (bottom) shows the gap formed at the CL–MPL interface due to CL detachment for the −15 °C isothermal freeze start at different operation times at the same location as shown earlier for the slow-dry freeze start in Fig. 5 (top). Detachment at the CL–MPL interface can be observed after 10 s of operation and was found to have water droplets after 20 s of operation as shown in Fig. 5 (bottom). However, after 30 s of operation, no water clusters were observed in the gap. A similar behavior was also observed for the 0 °C isothermal freeze start. Unlike the non-isothermal freeze starts where the CCM returned to a non bent state with increase in temperature, the CL detachment was observed during the entire operation for the isothermal freeze starts. Since, the operating temperature was constant and CL detachment was observed after 10 s of operation during which the HFR reduced to nearly 0.1 Ω cm² (same as for the non-isothermal freeze starts), it can be deduced that the CL detachment at the CL–MPL interface was mainly due to the hygro-mechanical stress on the CCM at sub-zero operating temperatures. Although not observed in this study, these stresses could result in permanent CL detachment from the MPL surface as observed by Kim et al. [21,22]. As a result, water could accumulate in these gaps resulting in significant mass transport losses even at high temperature operation. Further, CL detachment from the MPL could also reduce the structural integrity of the MEA making it more susceptible to physical degradation.

4. Conclusions

Non-isothermal freeze starts were performed to study the PEFC behavior at sub-zero operating conditions. The effect of pre-drying the cell prior to freezing and warm-up rate from −30 to 0 °C were investigated. It was found that pre-drying the cell resulted in a better performance during sub-zero operation due to a higher water uptake capacity of the membrane and CL. Based on the electrochemical performance of the cell during the non-isothermal freeze starts, it was hypothesized that the low protonic conductivity of the membrane resulted in a shift of the ORR to the CL-membrane interface and local freezing of this region resulted in performance degradation. A performance recovery phase beginning at a cell temperature of −6 °C for the pre-dried freeze starts was also observed which was attributed to the melting of ice in the CL. The warm-up rate was found to influence the start of the performance recovery phase with the rapid warm-ups resulting in an earlier increase in cell temperature and consequently, electrochemical performance. For the freeze starts without pre-drying, the performance recovery phase was delayed to higher temperatures of 6–10 °C likely due to more ice accumulation in the CL.

Sub-second operando XTM imaging was performed to visualize the water transport in the cell during the freeze starts. Imaging results showed that no new (or growth of existing) water clusters were observed in the cathode GDL during any of the non-isothermal freeze starts indicating that water accumulation and freezing was limited to the CL and/or MPL. No new water clusters were observed in the cathode GDL even at temperatures above 0 °C indicating vapor dominated water transport in the MEA. For the freeze starts without pre-drying, water clusters present from the pre-operation stage were found to evaporate as the cell temperature was increased above 0 °C.

Isothermal freeze starts were also performed at different temperatures and current densities to understand the effect of membrane conductivity during the freeze starts. An increase in the isothermal freeze start temperature resulted in an increase in operation time and total charge produced prior to cell failure. The increase in operation time with an increase in temperature could be due to an increase in membrane conductivity leading to activation of a larger fraction of the CL and reduced probability of freezing. Operation time and total charge produced prior to cell failure decreased with an increase in current density likely due to an increase in the local water flux in the CL leading to water accumulation and ice formation. XTM imaging of isothermal freeze starts with temperatures of −15, −10 and 0 °C showed that water clusters appeared in the GDL after 20 s of operation. The water distribution in the GDL was similar for all the isothermal freeze starts at the same operation times which was likely due to the MPL regulating the capillary water transport from the CL to the GDL and/or similar ORR distributions in the CL for the freeze starts with temperatures −15 °C and above due to much higher membrane conductivities at these temperatures.

XTM imaging also showed temporary CL detachment under the channel for both the non-isothermal and isothermal freeze starts due to the thermal stress on the CCM. For the non-isothermal freeze starts, the CL detachment at the CL–MPL interface was observed between temperatures of −20 to 18 °C with the CCM returning to its original
position at higher temperatures. Water droplets were also observed in the gaps formed at the CL–MPL interface due to the CL detachment during the non-isothermal freeze start. For the isothermal freeze starts, the gaps formed due to CL detachment were present throughout the operation and water clusters were observed therein. Although the CL detachment from the MPL surface observed in this study was temporary, a permanent deformation of the CCM might occur if the operating temperature range is higher and after a large number of thermal cycles. This could lead to water accumulation at the CL–MPL interface and also make the MEA more prone to physical degradation.

The results of the current study indicate water transport in the GDL during non-isothermal freeze starts was predominantly in the vapor phase. This could be due to the heat-pipe effect introduced by the MPL and/or the use of dry (∼0% RH) gases during the freeze starts. To understand the role of the MPL during non-isothermal freeze starts, GDL materials with and without MPLs could be used. Although dry gases were used in the current study, it must be noted that ambient air used for automotive applications and recirculating hydrogen can have a finite humidity. Therefore, future studies should also investigate the effect of gas humidity during sub-zero PEFC operation.

CRediT authorship contribution statement

Mayank Sabharwal: Conceptualization, Methodology, Software, Formal analysis, Data curation, Investigation, Writing - original draft, Writing - review & editing, Visualization. Felix N. Büchi: Conceptualization, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition. Shinya Nagashima: Project administration, Conceptualization, Writing - review & editing. Frederica Marone: Investigation, Writing - review & editing, Resources. Jens Eller: Conceptualization, Supervision, Project administration, Methodology, Data curation, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.jpowsour.2020.229447.

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