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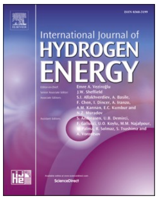

Impact of antifreeze shut-down strategy on performance degradation and freeze start of a proton exchange membrane fuel cell system

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ABSTRACT

Proton exchange membrane fuel cell (PEMFC) systems for heavy-duty applications must operate in cold environments and guarantee durability. This work investigates the influence of methanol solution on performance degradation and freeze-start behavior of a 4 kW PEMFC system. Antifreeze and gas purging shut-down strategies are tested, starting from +3 °C to −20 °C, using 25 and 40 vol % methanol and two stacks with different performance degradation. Results show that methanol has a washing effect on the cells, regenerating performance and leading to negative degradation rates after multiple freeze starts. Moreover, methanol prevents ice formation during subzero storage and ensures reliable freeze starts; the lower the temperature and the higher the methanol concentration, the slower the start-up. Although gas purging yields faster freeze starts, antifreeze start-up time can be optimized, e.g., by oxygen enrichment. This study introduces a novel method to extend PEMFC lifetime while enabling efficient and reliable freeze starts from −40 °C.

1. Introduction

Transportation generates over 15 % of global greenhouse gas emissions (GHG), primarily CO_2 [1]. Proton exchange membrane fuel cell (PEMFC) systems are crucial for decarbonizing this sector due to their zero local emissions, high efficiency, quick refueling, and long driving range. However, challenges remain in standardization, refueling infrastructure, durability, and operation in extreme winter scenarios.

The U.S. Department of Energy (DOE) established targets for FCs in transportation applications, including rapid and efficient freeze starts at −20 °C, unassisted starts at −30 °C, assisted at −40 °C, and a lifetime of 8,000 h [2]. Japan's NEDO set a stricter target: unassisted starts from −40 °C within 30 s [3]. Additionally, Clean Hydrogen JU has set the following FC durability targets for 2030: 30,000 h for heavy-duty vehicles, railway, and aviation, and 80,000 h for maritime applications [4]. Future fuel cell-powered aircraft must meet stricter freeze-thaw durability requirements, as commercial aviation operates in extreme cold environments, experiencing temperatures as low as −40 °C on the ground and down to −56.5 °C at high altitudes (11,000 m) [5]. While fuel cell electric vehicles (FCEVs), namely the Toyota Mirai, Hyundai Nexo, Honda FCV-Clarity, and SAIC Maxus EUNIQ 7, demonstrate start-up capability at −30 °C, the long-term durability of fuel cells under winter conditions remains a critical challenge [6–9].

At subzero temperatures, remaining water in the cells may freeze, expanding its volume by approximately 9 %, which causes mechanical stress [10]. Repeated freeze-and-thaw (F/T) cycles can subsequently lead to damage in the fuel cell components, such as cracks and pinholes in the membrane, delamination at the catalyst layer (CL), and a reduction in the electrochemical active surface area (ECSA) [11–14]. Ice formation blocks reactant flows and decreases the ECSA, resulting in voltage losses and further degradation due to reversal voltage and carbon corrosion [12]. Furthermore, the formed ice can reduce the fuel cell system's freeze-start reliability and efficiency, and even cause failure.

Over the past decade, numerous reviews have addressed the freeze start of PEMFCs, especially for automotive applications. These reviews discuss degradation mechanisms under subzero conditions and mitigation strategies such as gas purging, with more recent works focusing on freeze-start solutions involving thermal management and adaptive control strategies [8,13,15–21]. Additionally, classification of freeze start modes based on the water state enables a targeted optimization for start-up and structural design [22].

Common methods to manage freeze start in automotive PEMFC systems include gas purging to remove residual water at shut-down and rapidly warming the cells above the freezing point during start-up.

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Based on the origin of the heat source, freeze start-ups can be classified into self-starting methods, which rely on heat generated by the cells but may be insufficient in extreme cold environments, and assisted freeze-start methods, which use external power sources (most commonly electric heaters) to raise the temperature. While the latter effectively prevent ice formation, they also reduce the system's overall energy efficiency. To optimize energy consumption and start-up time, particularly at very low temperatures such as −40 °C, hybrid strategies combining both self-starting and assisted methods have been proposed [7,23,24]. In addition, Li et al. enhanced energy efficiency despite using external heating by placing a heating wire (Cr20Ni80) under the cathode ridges [25]. Shi et al. studied the alternating hydrogen pump (AHP) method, which leads to ultra-low degradation [26,27]. Melink et al. presented a novel heating method for freeze-start using a thermochemical metal hybrid, demonstrating its efficiency as it requires no extra energy consumption [28,29].

Solutions to mitigate degradation at subzero temperatures can be classified into three groups: materials and components resistant to freezing, gas purging, and the use of antifreeze during shut-down [8,13,16,18,19]. Non-uniform metal foam flow fields with tailored pore size gradients and microporous layers containing polyphenylene sulfide have both demonstrated improved freeze start performance compared to conventional designs [30,31]. In transportation, PEMFC systems are purged with H2 at the anode and air at the cathode to avoid adding extra components. Optimizing system operating conditions during shut-down can improve the efficiency and reduce the duration of the purge process [32,33]. Additionally, alternative purging methods have been studied to discharge more water, including vacuum-assisted drying, equilibrium, and pressure reduction purging [8,16,17]. However, these approaches have drawbacks: pressure reduction purging slows freeze start-up, equilibrium purging is too time- and energy-consuming, and vacuum drying adds system complexity and may induce mechanical stress [8,17,34–36]. Even with dry gas purging, water redistribution during cool-down occurs due to condensation [17]. To overcome this issue, Ma et al. proposed a delayed secondary purging after membrane equilibrium, and Xu et al. suggested a three-stage closed-loop strategy [37,38]. Both strategies effectively minimized water redistribution during storage, thereby reducing ice formation and facilitating freeze start-up.

Despite these improvements, gas purging cannot completely prevent ice formation during storage, as not all residual water can be effectively removed, especially at −40 °C [39]. Increasing the purge cell temperature raises the saturation vapor pressure, enhancing evaporation and enabling faster water removal [40,41]. However, this can also lead to membrane over-drying or non-uniform drying, resulting in uneven stress that accelerates membrane degradation and compromises freeze-start capability [39,40]. Besides, heating the cells to the effective purge temperature requires higher energy consumption, while lowering the purge temperature avoids drying damage but prolongs shut-down duration. Thus, the dry gas purging method does not meet the stringent requirements of transportation applications for cold-weather PEMFC operation in terms of time, energy, and durability.

An alternative approach involves flooding the cells with an antifreeze solution during shut-down. This method lowers the freezing point, fully preventing ice formation even under extreme winter conditions such as −40 °C, while also reducing shut-down time and parasitic energy consumption [8,11,42–44].

Cho et al. compared dry gas purging with antifreeze-water solutions (30 % volume of methanol, 30 % ethanol, 35 % ethylene glycol, and 47 % isopropanol) in a single cell subjected to freeze/thaw (F/T) cycles from −10 °C to +80 °C [11]. Among these, the 30 % methanol and 35 % ethylene glycol solutions were selected due to their lower membrane swelling and greater effectiveness in reducing performance degradation rates compared to dry gas purging. Notably, slight performance improvements were observed, with degradation rates of −0.16 % and −0.47 % for methanol and ethylene glycol, respectively. Related studies conducted at the membrane electrode assembly (MEA) level have also demonstrated the beneficial effect of methanol vapor addition to the fuel stream, showing stable operation during F/T cycling and improved durability [45,46]. Similar findings were reported by Knorr et al., who investigated a 40 vol % methanol-water solution in a single cell during F/T cycling from −10 °C to +20 °C and freeze start at −10 °C [43]. They demonstrated that methanol solutions better mitigate performance losses than dry gas purging, reducing degradation rates from 0.25 % per cycle to 0 % at 1.4 A/cm^2. Freeze start capability with antifreeze was tested at −10 °C, but it was limited primarily by the high areal mass density of the 5 × 5 cm^2 cell. In previous work, we conducted a successful freeze start at −10 °C using a 4 kW stack, which has a greater capacity to heat the cells much faster, and a 25 vol % methanol solution [44]. These results indicate that the antifreeze solution effectively prevents degradation during storage and enables successful freeze start-up at the system level. However, previous studies have primarily focused on MEA or single cells, and while promising, the freeze-start performance of PEMFC systems after antifreeze storage requires further investigation to fully understand the freeze-start mechanisms and ensure its reliability. Therefore, a system-level study is essential to validate both the freeze-start capability under varied conditions and the long-term effects of antifreeze before this novel strategy can be implemented in transportation applications.

This experimental work investigates the impact of methanol-based antifreeze solutions on the performance degradation and freeze-start ability of a 4 kW PEMFC system from −20 °C. Parameters examined include stack state of health, methanol volume percentage, and start-up temperature. The results aim to support the development of rapid, energy-efficient start-up and shut-down protocols that enable reliable and quick start-ups from −40 °C, while extending the stack lifetime and thereby meeting the automotive and heavy-duty (HD) requirements for PEMFC systems under extreme winter conditions. This paper is structured as follows: Section 2 describes the setup, test parameters, and procedures. Section 3 presents and discusses results on material compatibility, performance degradation, freeze start, and system integration, limitations and, long-term validation. Finally, Section 4 summarizes the key findings.

2. Methodology

2.1. Test procedures and parameters

To avoid degradation due to freeze storage and enhance the freeze start of PEMFC systems at lower temperatures, two shut-down strategies have been studied: gas purging (the most common method) and an innovative one based on an antifreeze solution.

- **Gas purging.** The gas purging method used in this study begins after stopping the stack operation. It involves blowing dry gases into the anode and cathode volumes to remove the remaining water from the cells, thus reducing the degradation due to freeze storage.
- **Antifreeze solution.** The alternative procedure was conducted when the stack operation was stopped. It consists of flooding the anode and cathode sides with an antifreeze solution before storage at temperatures below 0 °C. This prevents water from freezing and ensures no physical damage because of subzero temperatures.

This study was carried out with two HyPM-HD4 stacks from Hydrogenics. One was in good health, while the other was performance-degraded (12 % of power loss measured at 0.6 V and 15 % at 0.55 V). The parameters and values tested are listed in Table 1.

A methanol–water solution served as the antifreeze, with concentrations of 25 vol % and 40 vol % selected to ensure freezing points below −15 °C and −30 °C, respectively [47]. These temperatures were chosen as representative of freeze starts of PEMFC systems for transportation. −30 °C corresponds to the DOE temperature target for unassisted freeze starts, and no ice formation occurs when unassisted starts

Table 1
Test parameters and values for the stack in a good health state (S1) and the performance-degraded (S2).

Parameter (unit)	Stack (S1)	Stack (S2)
MeOH Volume (%)	0, 25, 40	0, 25
Storage and start-up temperature (°C)	+3, −10, −20	+3, −10
MeOH Removal time (min)	3	6
Cathode oxygen content (%)	21, 35	21

are from −15 °C [2,7,29]. The methanol solution was first tested at +3 °C to study the material compatibility and suitability of this method with the 4-kW PEMFC system, and then at subzero temperatures: −10 °C with the performance-degraded stack and down to −20 °C with the new one. The +3 °C temperature was chosen because previous cell results showed that it prevents methanol from reacting in the catalyst layers while reducing the mechanical stress of the membrane by swelling due to the antifreeze [43]. The start-up procedures were performed once the methanol solution was removed.

Methanol removal times were selected based on a combination of experimental observations, manufacturer guidelines, and findings from previous studies. Visual monitoring during the tests showed that the last methanol droplet exited the stack approximately 2 min after the purge started. To ensure the removal of nearly all methanol and to match the gas purge duration recommended by the stack manufacturer, the duration was extended to 3 min. Additionally, a previous investigation confirmed 3 min as the optimal gas purging time for this stack, as it removes sufficient water at shut-down without over-drying the membrane, thus avoiding a slower freeze start and ice formation [48]. This duration also ensured comparable times between both shut-down strategies. Therefore, the healthy stack (S1) used a 3-min removal protocol. However, for the degraded stack (S2), a longer removal time of 6 min was applied to guarantee thorough elimination of any residual methanol that could further degrade the stack or hinder the freeze start-up.

The test protocol applied in all the experiments is illustrated in Fig. 1. It consists of five major steps: electrochemical characterization, shut-down procedures (gas purging and antifreeze solution), cooling down and storage, start-up, and again, electrochemical characterization. The first electrochemical characterization involves a prior conditioning test at nominal operating conditions, followed by a polarization curve to quantify the irreversible performance degradation of the PEMFC stacks: from 1 A/cm^2 stepwise down to 0.1 A/cm^2 for S1, and likewise from 1.25 A/cm^2 stepwise down to 0.1 A/cm^2 for S2. Then, the stack operation was stopped and the system was cooled down to +40 °C to perform the gas purge procedure suggested by the stack manufacturer (30 nl/min of H_2 at the anode and 400 nl/min of air at the cathode) for 3 min [49]. The system was then further cooled down to +3 °C for the antifreeze experiments, and the stack anode and cathode sides were flooded with the methanol-water solution. The stack temperature was afterwards reduced to the start-up temperature (T_{start}), which, as listed in Table 1, varied from +3 °C to −20 °C, and stored at T_{start} for 1 h when the test temperature was +3 °C, 2 h for −10 °C, and 4 h for −20 °C. Next, the antifreeze solution was removed from the stack by purging it with dry gases (30 nl/min of H_2 at the anode and 400 nl/min of air at the cathode) for different time lengths (3 min for S1 and 6 min for S2). Dry hydrogen and cathode gases (air or 35 % oxygen-enriched) were then supplied, and the open circuit voltage (OCV) was monitored. The freeze start was conducted in potentiostatic mode using the freeze cooling loop to warm the stack faster. For stack S1, a defined voltage control strategy was applied: the system was initially operated at 0.1 V, average cell voltage. Once the current density reached approximately 0.4 A/cm^2, the voltage was increased to 0.2 V to accelerate the heating and power build-up. This current-based triggering ensured a responsive transition point depending on the actual system dynamics, such as temperature and residual methanol concentration. Finally, a polarization curve was performed to measure the reversible performance degradation due to storage with the antifreeze solution and the subsequent start-up at temperatures down to −20 °C.

2.2. Setup

The setup used in this experimental investigation was developed at the German Aerospace Center (DLR) to operate at subzero temperatures. The setup consists of a PEMFC liquid-cooled stack (Hydrogenics HyPM-HD4) with a rated power of 4 kW, 40 cells, an ECSA of 200 cm^2 per cell, and graphite bipolar plates. This setup has been used in previous investigations for freeze starts of the PEMFC system down to −30 °C using the gas purging shut-down strategy and is described in detail in Ref. [7].

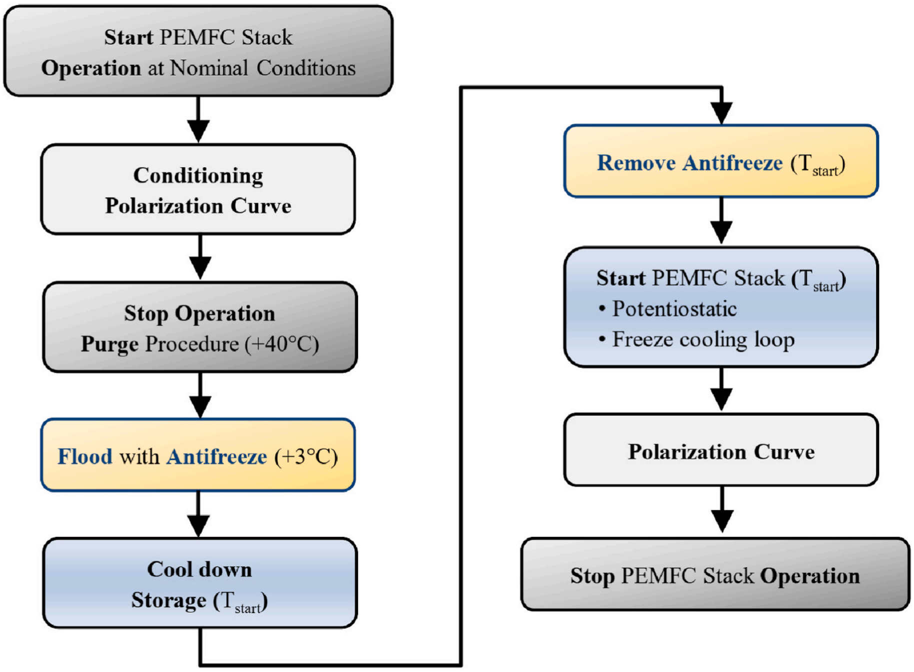

Fig. 1. - Test protocol.

To investigate the antifreeze approach, an antifreeze module (described in Ref. [44]) was added to the test bench and is presented in Fig. 2. The antifreeze module enables flooding the anode and cathode volumes with the methanol-water solution, flushing it with deionized (DI) water if required, and later removing the methanol-water solution. The stack is flooded with antifreeze by pumping the methanol-water solution from the anode and cathode methanol (MeOH) tanks while the hydrogen and cathode gas supply is closed. In reverse, the antifreeze removal process is performed by purging hydrogen at the anode and air at the cathode, while the supply from the (MeOH and DI-H_2O) tanks is closed. The hydrogen purge valve remains open in both processes. During the emptying process, the methanol-water solution was recollected into the methanol tanks.

3. Results and discussion

3.1. Material compatibility and performance degradation

Previous studies have demonstrated the antifreeze compatibility with the PEMFC materials. First, a single cell was tested with a 40 vol % methanol-water solution for 112 h, and then the 4 kW system used in this study was tested with a 25 vol % methanol-water solution for 1 h. After removing the antifreeze, both setups could start at temperatures above 0 °C without inducing performance losses [43,44].

In this work, to quantify the impact of the antifreeze solution on PEMFC performance degradation, j-V characteristics were measured at +60 °C. Fig. 3 compares the polarization curves of both stacks (S1 in a good health state and S2, which had degraded performance before this investigation) before filling them with a methanol-water solution (25 % volume of methanol) versus those obtained after storing them with the antifreeze at +3 °C for 1 h, removing it for 2 min, and then starting at +3 °C. Fig. 3 demonstrates that using the methanol-water solution does not cause performance losses in either stack. On the contrary, the cell potentials increased, especially for the performance-degraded one (S2) at current densities roughly above 0.6 A/cm^2. Namely, the average cell voltage of S2 increased by 8 % at 1.25 A/cm^2. This performance improvement aligns with previous studies [43,44].

When using the antifreeze solution, the observed performance enhancement may result from its washing effect, which removes contaminants from the cells. Various degrading substances, such as airborne pollutants, Pt oxides, and CO, can accumulate in both the catalyst and the gas diffusion layers. Pt oxidation deactivates the catalyst surface by forming inactive PtOx species that hinder the oxygen reduction reaction (ORR), thereby lowering current generation. Likewise, CO adsorption poisons the catalyst by occupying active Pt sites, blocking hydrogen and oxygen reactants from reaching those sites, and hence reducing electrochemical performance. Consequently, the presence of these contaminants leads to performance losses [12,50]. In contrast, the methanol-water solution helps remove these contaminants through redox reactions and the scavenging effect of the liquid solution, which is subsequently purged from the cells with dry gas. Methanol reduces PtOx to metallic Pt and facilitates CO removal by generating reactive intermediates during its oxidation [51]. Therefore, methanol not only physically cleans the cells but also chemically restores the catalyst surface, partially recovering catalytic activity. As a result, some performance degradation is reversed, enhancing the long-term durability of the fuel cell.

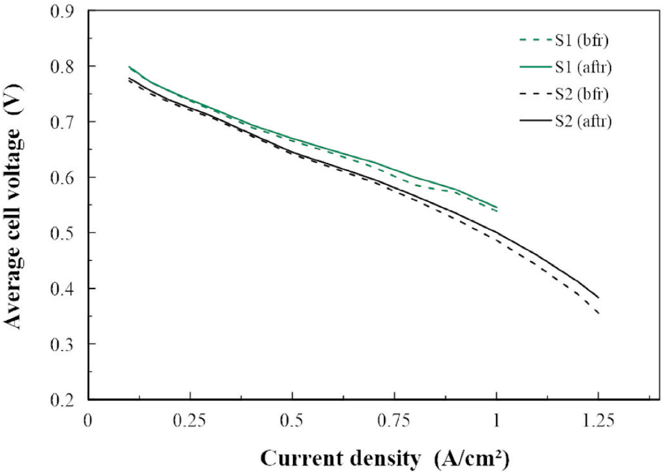

Fig. 3. - Average cell voltage as a function of current density before (bfr) and after (aftr) filling the cells with antifreeze (25 vol % methanol) for both stacks: stack S1 (in green) and stack S2 (in black).

As demonstrated in Fig. 3, the antifreeze washing effect particularly

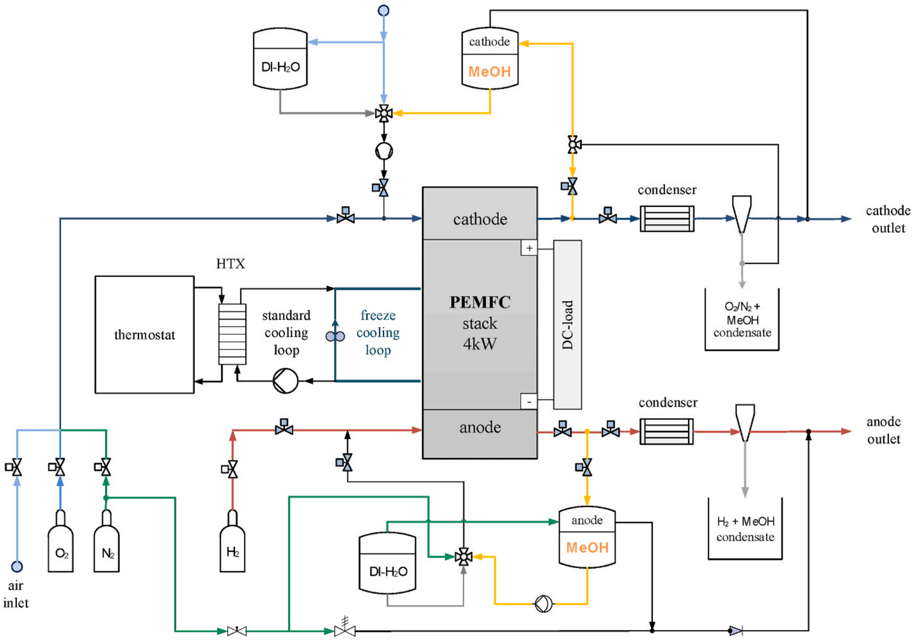

Fig. 2. - Schematic diagram of the 4-kW PEMFC system with the antifreeze module.

applies to performance-degraded fuel cells whose losses are associated with contaminant degradation mechanisms, like stack S2 in this investigation. Accordingly, using an antifreeze solution is recommended as a regeneration process for fuel cells, especially for automotive and HD applications. This process also has the advantage that the stacks can be restored onboard while parked without disassembling them from the system, thus reducing maintenance time and costs. In aviation, a ground trolley could even manage the regeneration process (including methanol filling and removal), hence avoiding any added weight to the aircraft fuel cell systems.

The results of the performance degradation due to freeze start using the methanol storage solution are presented in Fig. 4. This degradation was calculated by comparing the current density at an average cell voltage of 0.6 V before the first freeze start (0) (i.e., after the start-up at +3 °C) and after repeating several freeze starts for both stacks, at temperatures down to −20 °C for S1 and −10 °C for S2. To ensure that the solution's freezing point remained below the freeze start-up temperature, both stacks were soaked in a 25 vol % methanol-water solution for the start-ups at −10 °C and a 40 vol % solution for the start-ups at −20 °C performed with S1. For both stacks, the current density evolution after multiple freeze starts followed a similar trend: an initial performance improvement, followed by a decline back to baseline levels, and then stable operation. The improvement lasted longer for the stack in a better health state, despite starting at lower temperatures ($T \geq -20$ °C). The average performance degradation rate was −0.97 % for 16 freeze starts at $T \geq -20$ °C with S1, and −1.31 % for 10 freeze starts at $T = -10$ °C with S2. This aligns with Cho and Knorr's results, who, after several thermal cycles down to −10 °C using a methanol solution, observed a performance improvement at 0.6 V and fully mitigated the performance losses at current densities up to 1.4 A/cm^2, respectively [11,43].

As shown in Fig. 4, the methanol solution eliminates performance degradation due to freezing conditions. This is because the antifreeze prevented ice formation during storage. Methanol solutions can ensure that no water freezes in the cells at extremely low temperatures, such as −30 °C using a 40 vol % methanol-water solution and at −40 °C with a 50 vol %, respectively [47]. Ice formation during storage can cause various physical damages to the cells, constrain the transport of reactants, and reduce the ECSA, thereby hindering the freeze start. This may lead to carbon corrosion, local fuel starvation, and cell voltage losses, resulting in degradation and, consequently, a reduction in fuel cell lifetime [11,38]. However, the absence of performance degradation when using the antifreeze strategy ensures that the PEMFC system's efficiency and long-term durability increase. By fully eliminating ice formation during storage, the antifreeze solution also assists in lowering the freeze start-up temperature of the system, below which the stack cannot start without auxiliary heat input. This occurs because the catalyst layer pores are initially free, allowing more water to freeze there before they become blocked with ice, which would lead to a failed freeze start.

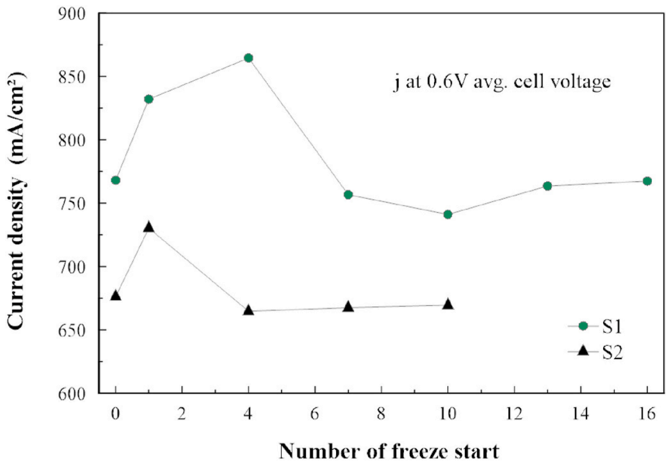

Fig. 4. - Influence of freeze starts on current density at 0.6 V average cell voltage before (0) and at +60 °C stack temperature after some freeze starts: at $T \geq -20$ °C for S1 and at $T = -10$ °C for S2.

In addition to preventing ice formation and recovering performance losses, the potential risks associated with the long-term use of methanol in PEMFC systems must be considered. Residual methanol may lead to CO formation, reducing catalytic activity, while repeated exposure to the antifreeze solution over multiple F/T cycles may alter the gas diffusion layer (GDL) hydrophobicity or induce swelling of the membrane and MEA, which can cause flooding and reduce fuel cell efficiency [12,50,52,53]. Furthermore, methanol concentrations up to 200 ppm in hydrogen result in reversible performance loss, although the recovery time increases drastically with higher methanol concentrations [54]. Despite these concerns, no degradation was observed after 16 freeze starts, demonstrating strong short- and medium-term reliability. To address these potential drawbacks, CO-tolerant catalysts are recommended, along with stable materials for GDL and microporous layer (MPL) to maintain effective water management [51,53]. It should also be noted that methanol-based antifreeze solutions cause slightly more membrane swelling than pure water but less than other alcohol-based refrigerants, and it can be further mitigated by employing reinforced membranes and controlling humidity to prevent overhydration and dimensional stress [11,55,56]. Residual methanol can be minimized through proper purging, start-up, and shut-down protocols. Additionally, optimized cooling system design, humidity control, and operating parameters help reduce the effects of any remaining methanol while preserving overall system integrity. With these considerations, the significant benefits of the antifreeze solution in regenerating stack performance and preventing freeze-related damage strongly support its application in PEMFC systems for transportation.

Although the gas purging strategy can mitigate degradation caused by freeze storage, it can not guarantee its complete elimination, particularly in extremely low-freezing environments, or at least not without consuming a significant amount of parasitic energy and time during shut-down. Moreover, the dry gas purging strategy can lead to membrane degradation due to over- and/or non-uniform drying [12]. In contrast, the antifreeze solution is an efficient and damage-free strategy that can entirely remove fuel cell degradation due to freeze storage, as shown by these results. Therefore, we advocate the antifreeze solution for shut-downs in automotive and HD applications (aviation, maritime, and on-/off-*road* transport), as this approach meets the stringent sector targets in terms of shut-down efficiency, costs, and stack durability, even under extreme winter conditions down to −40 °C.

3.2. *Freeze start*

3.2.1. *Start-up performance*

To investigate the freeze-start ability of the PEMFC system after flooding the stack with a methanol solution, both storage strategies studied (gas purging and antifreeze solution) have been tested under different start-up operating parameters at subzero temperatures with the two stacks mentioned above: one in a good health state (S1) and the other performance-degraded (S2). This work defines freeze start as the time required for the stack to reach 50 % of its rated power.

Fig. 5 compares the freeze starts of stack S1 at −10 °C after filling it with a 25 % volume of methanol solution and two different cathode gases during the start-up (air and 35 % oxygen-enriched) with a freeze start using the gas purging strategy. Likewise, Fig. 6(a) contrasts the freeze starts of stack S2 at −10 °C and 25 % volume of methanol solution with two freeze starts using the gas purging solution and different voltage strategies. The stack-rated power percentage and the evolution of the coolant outlet temperature are illustrated in Fig. 5(a) for stack S1 and in Fig. 6(a) for stack S2, respectively. The voltage strategies applied

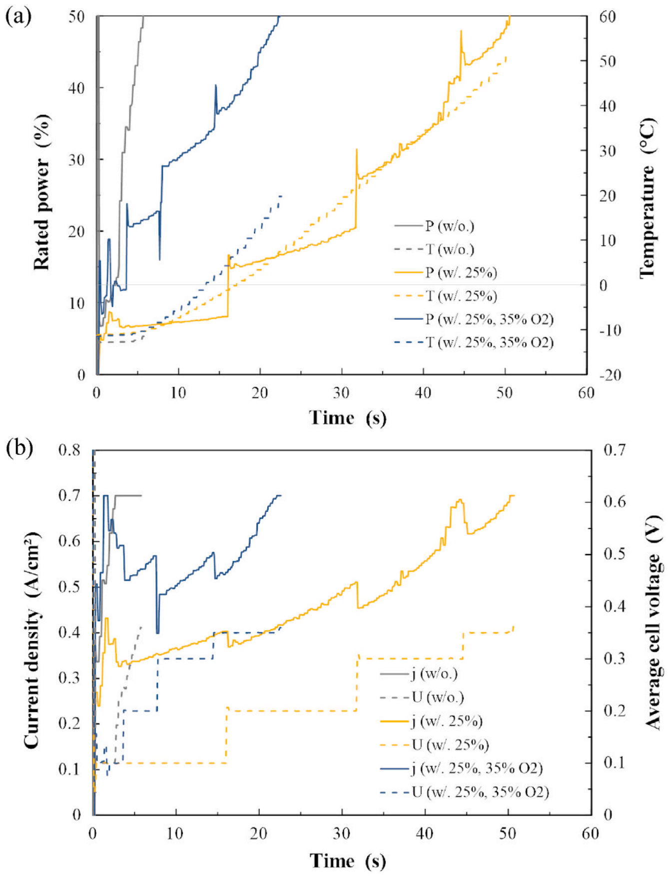

Fig. 5. - Freeze start experiments at −10 °C of stack S1 without the methanol solution (w/o.) and with 25 % of methanol: air (w/. 25 %) and oxygen-enriched (w/. 25 %, 35 % O_2): (a) stack-rated power and coolant outlet temperature, and (b) current density and average cell voltage as a function of time.

as a function of current density are depicted in Fig. 5(b) for stack S1 and Fig. 6(b) for stack S2.

As illustrated in Figs. 5 and 6, both stacks demonstrated reliable and relatively fast start-up at −10 °C after being flooded with the methanol solution during freeze storage. In both cases, current density and power generation continuously increased for each voltage step. Since the water and heat production are proportional to the current, this increase indicates that no significant ice formation occurred during either freeze start-up procedures. This aligns with previous investigations, which found that unassisted and safe starts without water freezing can be achieved at temperatures from about −15 °C, thereby avoiding degradation due to ice formation [7,29].

The experimental results of this investigation have shown that a safe and relatively quick start-up of a PEMFC system from subzero temperatures after being stored with a methanol solution is possible, even for a performance-degraded stack. Two reasons explain why the previous investigation from Knorr et al. in a single cell conversely showed poor freeze-start ability after using the antifreeze [43]. The first and most influential reason is that a 5 × 5 cm^2 single cell has an extremely low capacity to heat the thermal mass of the setup compared to a 4-kW PEMFC stack [44]. This suggests that quicker freeze starts can be achieved using the antifreeze solution by reducing the setup's thermal mass to be heated or increasing the heat power generation, for instance, by using stacks made of stainless steel bipolar plates or higher power stacks used for HD applications (typically ranging from around 100 kW to the MW-range) [57,58]. The second reason is that the cell voltage was set to 0.6 V, which does not favor waste heat production to warm the stack more quickly. The lower the start-up voltage, the faster and more robust the freeze start [57].

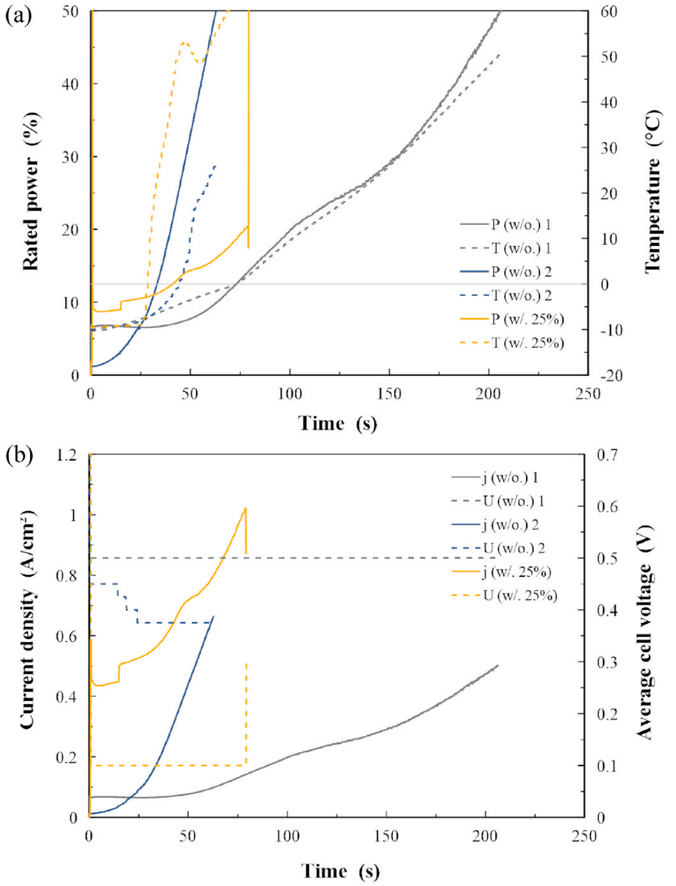

Fig. 6. - Freeze start experiments at −10 °C of the stack S2 with a 25 % volume methanol solution (w/. 25 %) and without methanol for two different voltage strategies (w/o. 1 and w/o. 2): (a) stack-rated power and coolant outlet temperature, and (b) current density and average cell voltage as a function of time.

For a given initial start-up temperature, the freeze start duration and performance depend on the stack's health and the storage and operating parameters strategies applied, as shown in Figs. 5 and 6. By comparing both figures, the influence of the stacks' health is evident. All the freeze starts of stack S1 were faster than those of the performance-degraded stack S2, regardless of the shut-down procedure (gas purging or antifreeze solution) and the applied start-up operating parameters. Although using an antifreeze solution instead of gas purging seems to lead to slower freeze starts, this slowdown can be minimized or even overcome by applying improved operating parameters strategies during the freeze start. By way of example, Fig. 5 shows that after using the antifreeze solution at shut-down, feeding the cathode with oxygen enrichment (35 % of volume) instead of air, shortened the freeze start by half, hence considerably reducing the start-up time difference between using gas purging and the antifreeze solution. The improved freeze-start with the antifreeze solution achieved 50 % of the rated power in less than 25 s, meeting the DOE technical targets for fuel cell systems and stacks for transportation applications [2]. This is because operating during the start-up with a higher oxygen concentration in the cathode increases the oxygen partial pressure, which reduces activation and mass transport losses while improving the overall efficiency, and consequently, higher current densities can be achieved quickly, allowing faster cell warming [59].

The freeze-start performance with antifreeze can also be enhanced using optimized voltage strategies. As shown in Fig. 6, the start-up with the methanol solution (operated at a variable voltage strategy with $U_{start} = 0.1$ V) was similar to the one with gas purging (depicted in blue and at a variable voltage lower than 0.5 V). The antifreeze start-up was even much faster than the one using gas purging (in gray, constant voltage with $U_{start} = 0.5$ V), as operating at a lower voltage resulted in higher current and heat generation, which warmed the cells more quickly. Although the antifreeze led to a reliable freeze-start performance (no relevant current drop occurred), the rated power rose considerably once the voltage was increased when reaching high current density ($j > 1$ A/cm^2). Therefore, increasing the voltage with the current and starting with a very low voltage ($U_{start} = 0.1$ V) is considered a more suitable voltage start-up strategy to enhance the freeze-start performance, and it was applied to all tests with stack S1.

3.2.2. Influence of methanol percentage and start-up temperature

Using a methanol-water solution during freeze storage avoids ice formation in the cells at much lower temperatures since the antifreeze alters the freezing point. The temperature at which the solution begins to freeze can be lowered by increasing the methanol percentage. Namely, 25 % of methanol volume in water avoids freezing at temperatures down to −15 °C (temperature threshold found for unassisted starts without water ice formation during the start-up with the same kind of stack used in this investigation), 40 % at −30 °C (Toyota, Hyundai, Honda and SAIC FCEVs proven freeze start-up temperature), and 50 % at −40 °C (DOE temperature target for an assisted start-up and NEDO's for a start-up without external heat sources) [2,3,7,8,47]. This study investigates the influence of the methanol percentage in the methanol-water solution and the start-up temperature on the PEMFC system freeze performance with stack S1. The methanol volume percentage range studied varied from 0 % to 40 %, and the temperature from +3 °C to −20 °C. The time to remove the methanol solution before the start-up was set to 3 min, and the start-up voltage strategy (increasing with the current) performed is shown in the following figures (Figs. 7 and 8), which summarize the results of the methanol percentage influence and the start-up temperature, respectively.

Fig. 7 depicts the influence of the methanol solution volume percentage on the freeze performance. It compares the start-up of stack S1 at −10 °C after filling it with a 25 % volume of methanol solution, a 40 % volume, and without using the methanol solution during freeze storage. Likewise, Fig. 8 illustrates the influence of the start-up temperature by comparing the starting performance of stack S1 after storing it with a 40 % volume of methanol solution at different start-up temperatures: +3 °C, −10 °C, and −20 °C. The freeze start test at −20 °C with a 40 % volume of methanol solution was conducted four times, and the results are presented in Fig. 9.

Fig. 7 shows that the freeze start without methanol reaches 50 % of its rated power in less than 5 s at a temperature below 0 °C. In contrast, the start-up tests with methanol-water solutions (25 % and 40 %) take longer, achieving 50 % power at temperatures above approximately +50 °C. Both freeze tests with methanol exhibit similar performance (continuous current increasing for each voltage step), and a higher percentage of methanol corresponds to a slower freeze start. These results indicate that although the 3-min removal time allows the PEMFC system to start reliably at −10 °C, it seems insufficient to entirely eliminate the methanol from the anode and cathode sides, which may partially impede the electrodes' gas flows and the electrochemical reaction. As a result, less current is generated, and consequently, cells are warmed more slowly. This phenomenon is intensified at higher methanol percentages, since a greater amount of methanol remains in the

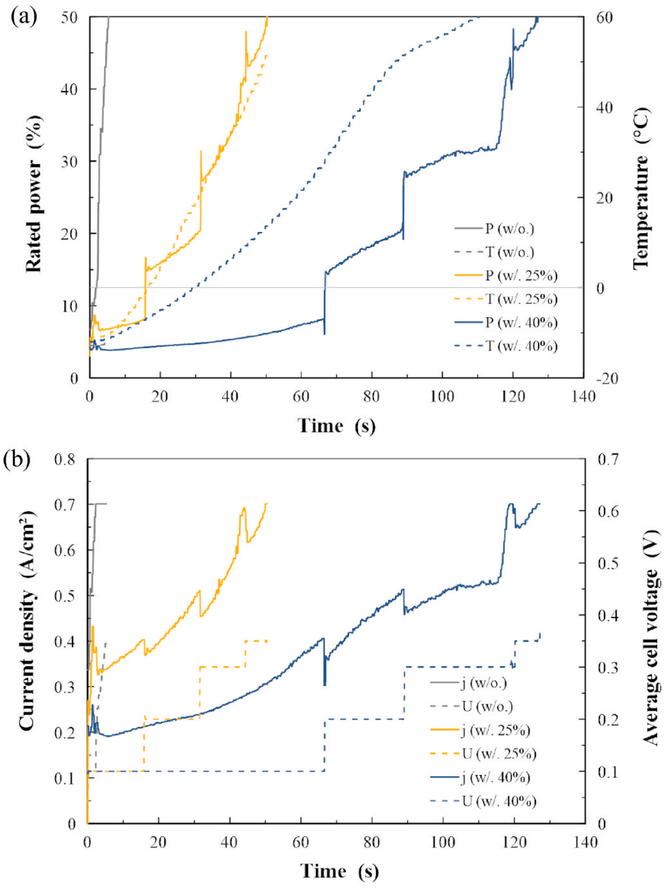

Fig. 7. - Freeze start experiments at −10 °C of the stack S1 without the methanol solution (w/o.), with 25 % volume of methanol solution (w/. 25 %) and with 40 % (w/. 40 %): (a) stack-rated power and coolant outlet temperature, and (b) current density and average cell voltage as a function of time.

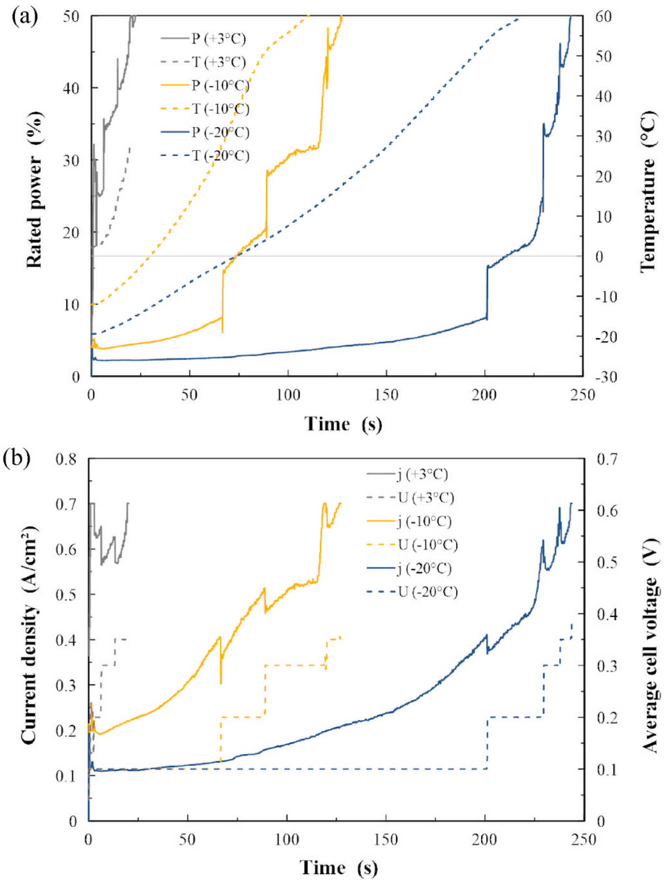

Fig. 8. - Start-up experiments of the stack S1 after storage with a 40 % volume methanol solution at +3 °C, −10 °C, and −20 °C: (a) stack-rated power and coolant outlet temperature, and (b) current density and average cell voltage as a function of time.

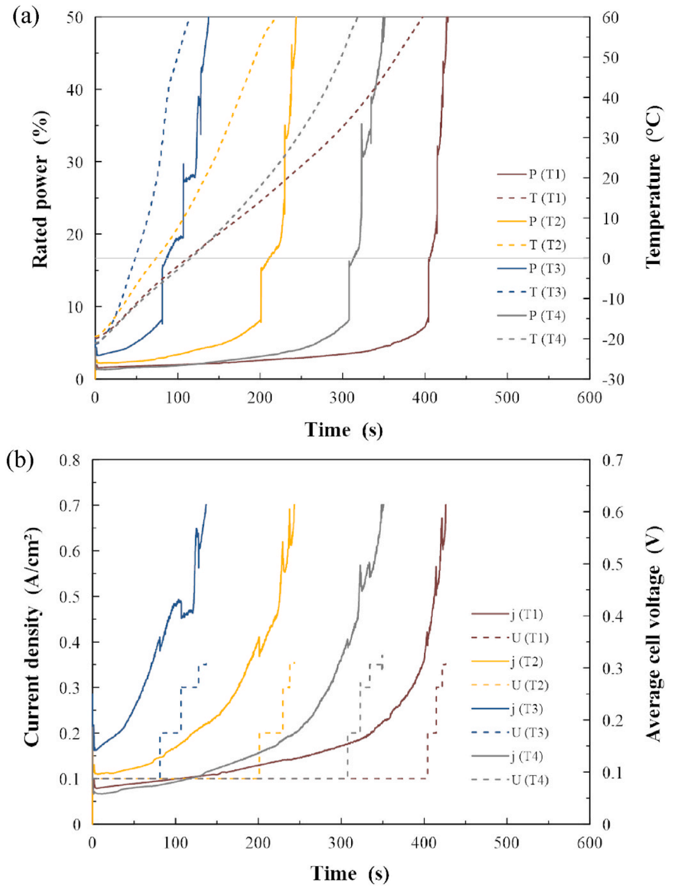

Fig. 9. - Tests repetitions (T1–T4) of the stack S1 after storage with a 40 % volume methanol solution and start-up at −20 °C: (a) stack-rated power and coolant outlet temperature, and (b) current density and average cell voltage as a function of time.

cells before start-up, as shown in Fig. 7 by the prolonged freeze start-up duration of the 40 % test. The difference in start-up duration between the 25 % and 40 % methanol tests also reflects the impact of the current-based voltage control strategy. In both cases, the system started at 0.1 V, and the voltage was increased to 0.2 V only once a current density of ~0.4 A/cm^2 was reached. Since higher methanol concentrations slow down the initial current build-up, this trigger point was delayed in the 40 % case, resulting in a longer 0.1 V phase. Once the system reached 0.2 V, the power trajectories became more comparable, indicating a convergence in system dynamics after overcoming initial methanol-related limitations.

All freeze-start experiments conducted after storing the stack with a 40 % methanol-water solution were successful and exhibited similar performance: the start-up was slower with the start-up temperature decrease, as illustrated in Fig. 8. This result was expected since the start-up temperature strongly affects the freeze-start. Indeed, there is a critical temperature below which an unassisted freeze-start is unsuccessful because all pores are plugged with ice before reaching the melting point [7,57].

All start-ups shown in Fig. 8 used the same voltage control strategy, with the voltage increase from 0.1 V to 0.2 V triggered at 0,4 A/cm^2. The time required to reach this trigger point increased with decreasing temperature, as colder conditions further suppress reaction kinetics and methanol related inhibition. However, after storing the stack with 40 % methanol, it was always possible to start the PEMFC system at −20 °C without significant ice formation during the start-up, as indicated by the continuous current generation in Fig. 9. Although the freeze-start performance is similar in all tests, the start-up duration varies from 2 min to 7 min, as illustrated in Fig. 9. The variation in start-up time is influenced by the current-controlled voltage strategy applied during all freeze-start experiments. The system remained at 0.1 V until a current density of ~0.4 A/cm^2 was reached. Due to differing levels of residual methanol and resulting inhibition, this threshold was reached at varying times, causing the observed spread in start-up duration (2–7 min). However, once the switch to 0.2 V occurred, the performance evolution quickly converged, indicating consistent system behavior beyond the inhibition phase. In contrast, freeze starts down to −30 °C from a previous study performed with the same setup and using the gas purging shut-down strategy, showed highly reproducible start-up times [7]. Likewise, the tests carried out with the 25 % volume of methanol solution at −10 °C also exhibited minimal variation in the start-up time duration. These results suggest that it is not the antifreeze solution strategy itself that causes start-up variability, but rather the presence of residual methanol at −20 °C, highlighting the importance of effective removal protocols under very low temperature conditions. The standard 3-min removal protocol appears to be insufficient to fully eliminate high methanol concentrations such as 40 %, which is associated with additional issues when starting at very low temperatures.

During start-up, residual methanol can temporarily block catalyst sites and hinder water and gas transport, further reducing current generation and prolonging the freeze start-up duration [43]. As shown in Fig. 9, the different initial current densities at 0.1 V demonstrate how residual methanol impacts catalyst activity, leading to variations in the start-up duration. Indeed, once the voltage increases to 0.2 V, the time differences decrease, indicating that the system overcomes the initial inhibitory effects of residual methanol. Therefore, further investigation of the methanol removal time as a function of the methanol percentage and the start-up temperature is necessary, especially for methanol percentages above 25 % and temperatures at or below −20 °C. This will allow the development of optimized methanol removal protocols that shorten the freeze-start duration while ensuring its reproducibility, even from extremely low temperatures.

In conclusion, filling the stack with a 40 % methanol solution guarantees no damage from icing during freeze storage while allowing reliable unassisted freeze starts without degradation, as demonstrated by the freeze experiments at −20 °C. These findings suggest that repeatedly starting at very low temperatures (at least −30 °C) without degradation is feasible when the stack is stored with 40 % methanol. However, at very low temperatures such as −30 °C, using the antifreeze solution combined with optimized removal protocol and start-up operating parameters may not be sufficient to achieve rapid start-ups. Integrating these strategies with hybrid heating methods presents significant potential to shorten the freeze start-up duration while enhancing system efficiency under harsh cold conditions, especially down to −40 °C. This integration could expand the reliable operational range of PEMFC systems, enabling their deployment in severe winter climates while meeting the stringent performance and durability requirements for automotive and heavy-duty applications.

Therefore, the antifreeze solution and removal protocol should next be investigated for freeze start at lower temperatures, down to −40 °C, followed by studies combining this approach with optimized operating and thermal start-up strategies.

3.3. *System integration, limitations, and long-term validation*

While the experimental results demonstrate the feasibility of the antifreeze solution for freeze-start operations, potential system-level limitations related to scalability and safety must also be addressed. The methanol concentrations used in this study, 25 % and 40 % by volume, are within the flammable range. For example, the flash point of the 40 % mixture is approximately +32 °C [60]. Although such temperatures may occasionally occur during summer conditions, freeze-start operations would not be required in those scenarios, and the system would remain inactive. In the current concept, the injection and removal of the antifreeze solution are limited to ambient temperatures below +3 °C, reducing the risk of vapor formation and ignition. However, methanol volume scales with the internal gas volume of the anode and cathode sides, which could become a critical factor when applying the concept to larger stacks. For transport applications, one possible solution could involve isolating methanol storage and handling within a dedicated freeze-storage module. This unit would be used to fill the stack with antifreeze after shut-down and drain it again before start-up, ensuring safe storage at subzero temperatures without ice formation. In this way, the freeze-storage module adds value by preserving stack integrity during frozen standby periods, while maintaining the core system architecture unchanged.

Although the methanol-based antifreeze protocol has proven effective in preventing ice formation and even in recovering PEMFC stack performance after multiple F/T cycles, further studies involving more than 1,000 consecutive freeze cycles are necessary to fully validate its long-term reliability and durability under realistic operating conditions. While current short-term experiments yield promising outcomes, it is essential to verify performance consistency and the absence of cumulative degradation over a large number of storage and start-up events. These extended tests should encompass a wide range of operating conditions, fuel cell stack aging states, and methanol concentrations to reflect realistic long-term scenarios. Insights from such investigations will be critical to establishing the method's suitability for commercial applications requiring high-frequency start-stop operations and compliance with stringent durability standards.

4. Conclusions

This investigation proposes an antifreeze-based storage strategy for PEMFC systems, where cells are flooded with a methanol-water solution to prevent ice formation and eliminate degradation due to subzero storage. Experimental tests conducted at temperatures ranging from +3 °C down to −20 °C with two stacks – one healthy and one performance-degraded – demonstrate the effectiveness of this novel method compared to conventional dry gas purging.

Findings indicate that the antifreeze strategy not only avoids performance losses but can even enhance stack performance. After storing the degraded stack in a 25 vol % solution and starting at +3 °C, it exhibited an 8 % increase in average cell voltage at 1.25 A/cm^2. Additionally, negative degradation rates were observed over repeated freeze starts: −0.97 % after 16 start-ups down to −20 °C for the healthy stack, and −1.31 % after 10 start-ups at −10 °C for the degraded one. These results suggest that the methanol solution reverses degradation linked to contaminant accumulation, highlighting its potential as a regeneration method.

All freeze starts following antifreeze storage have demonstrated consistent reliability. Although freeze starts were slower when using antifreeze, the start-up duration was influenced more by the stack condition and the start-up operating strategy rather than the storage method itself. Improving start-up operating parameters also enabled rapid start-ups with antifreeze. For example, applying oxygen enrichment (35 %) at the cathode halved the time required for the healthy stack to reach 50 % of its rated power at −10 °C, reducing it from 50 s to 22 s.

The freeze start duration increased as temperature decreased and methanol concentration increased: at −10 °C, it took 50 s with 25 vol % and 127 s with 40 vol %. However, the 3-min removal protocol appears to be insufficient for the 40 vol % concentration, as the start-up duration at −20 °C varied widely between 2 min and 7 min. Despite these variations, start-up performance remained consistent across tests. These results suggest that unassisted starts from −30 °C or even −40 °C are feasible with the antifreeze strategy, as it effectively prevents ice-induced pore blockages during storage.

Further research should focus on developing optimized methanol removal and start-up protocols to enable efficient, fast, and robust start-ups from −40 °C, while ensuring reproducibility of start-up times. Additionally, long-term validation is necessary to confirm durability and commercial viability.

In conclusion, the antifreeze strategy prevents complete freeze-related degradation, enables efficient shut-down procedures, and ensures reliable freeze starts, making it a promising approach for applications demanding high durability and efficiency, including HD industries (aviation, maritime, and on/off-road). Particularly in applications where ultra-rapid start-up is less critical, such as aerospace, the antifreeze strategy's superior ability to extend stack lifetime makes it a valuable option for ensuring long-term reliability.

This paper recommends the antifreeze strategy as a key enabler for enhancing the durability and freeze-start capability of PEMFC systems operating under extreme environmental conditions, with temperatures as low as −40 °C.

CRediT authorship contribution statement

G. Montaner Ríos: Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization, Writing – review & editing. **F. Becker:** Writing – review & editing, Methodology. **J. Schirmer:** Supervision, Funding acquisition. **C. Gentner:** Writing – review & editing, Funding acquisition. Technical implementation. **A. Ansar:** Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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