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Supplementary Information

for

Cold Start Mode Classification Based on the Water State for Proton Exchange Membrane Fuel Cells

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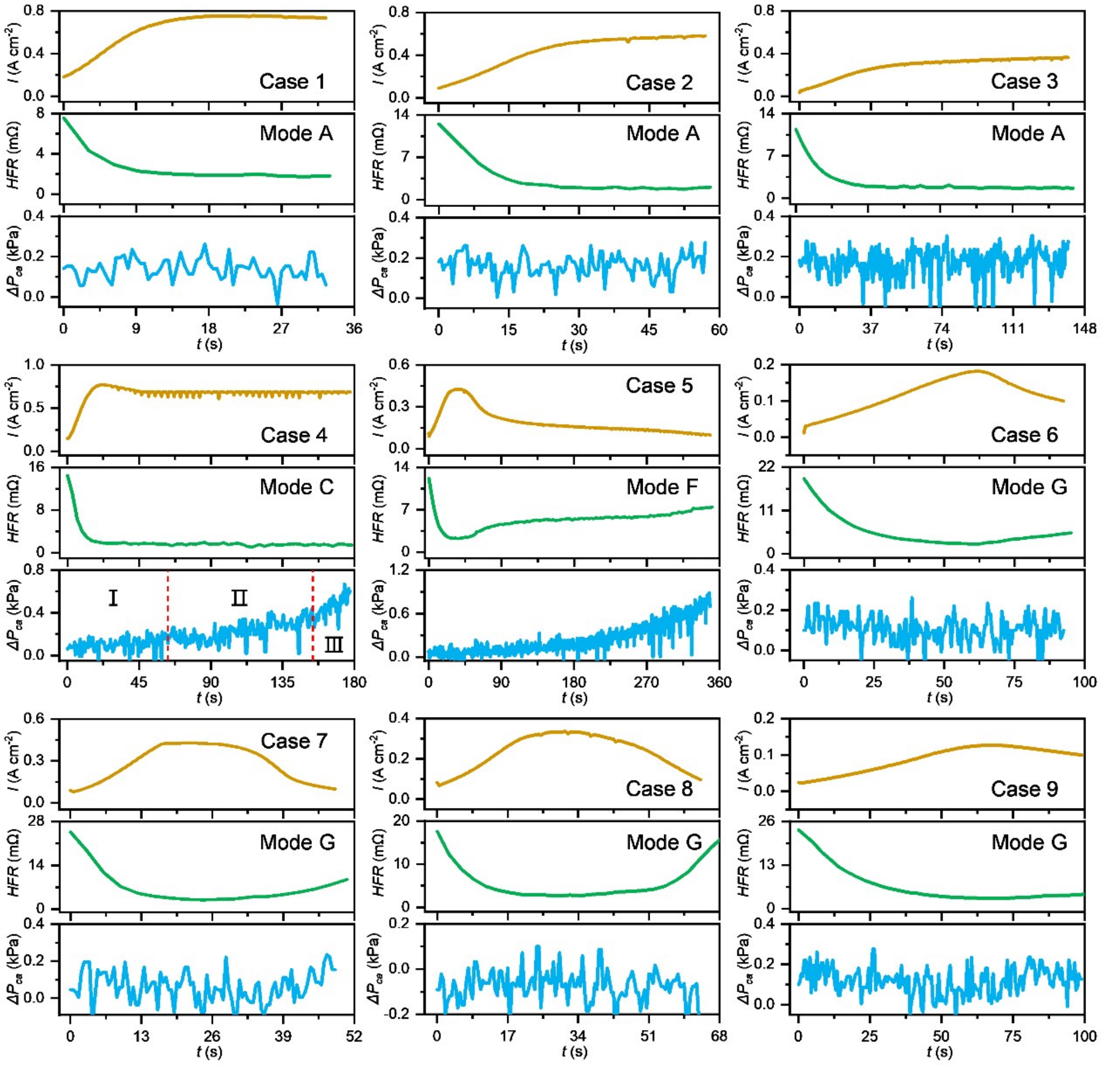

Fig.S1 Parameters of PEM fuel cell cold-start cases in constant voltage mode under different operating conditions

Current density (*I*), high-frequency resistance (*HFR*), type of cold start mode, and cathode pressure drop (*ΔPca*) of Cases 1–9 are shown in Fig.S1. The observable water transport in cases without significant icing mentioned in the subsection *water transport and cathode pressure drop* is annotated in Case 4.

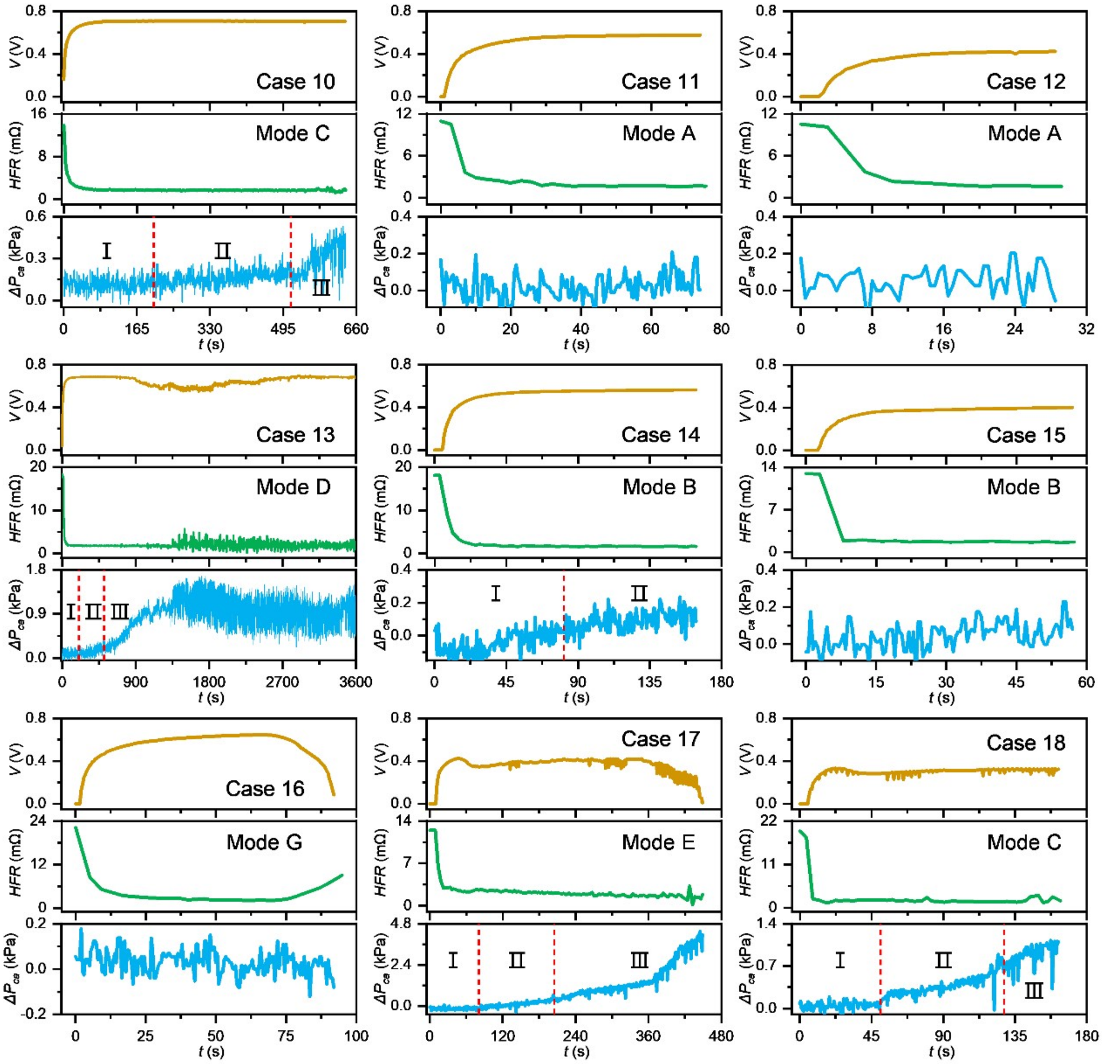

Fig. S2 Parameters of PEM fuel cell cold-start cases in constant current mode under different operating conditions

Voltage (*V*), high-frequency resistance (*HFR*), type of cold start mode, and cathode pressure drop (*ΔPca*) of Cases 10–18 are shown in Fig. S2. The observable water transport in cases without significant icing mentioned in the subsection *water transport and cathode pressure drop* is annotated in Cases 10, 13, 14, 17, and 18.

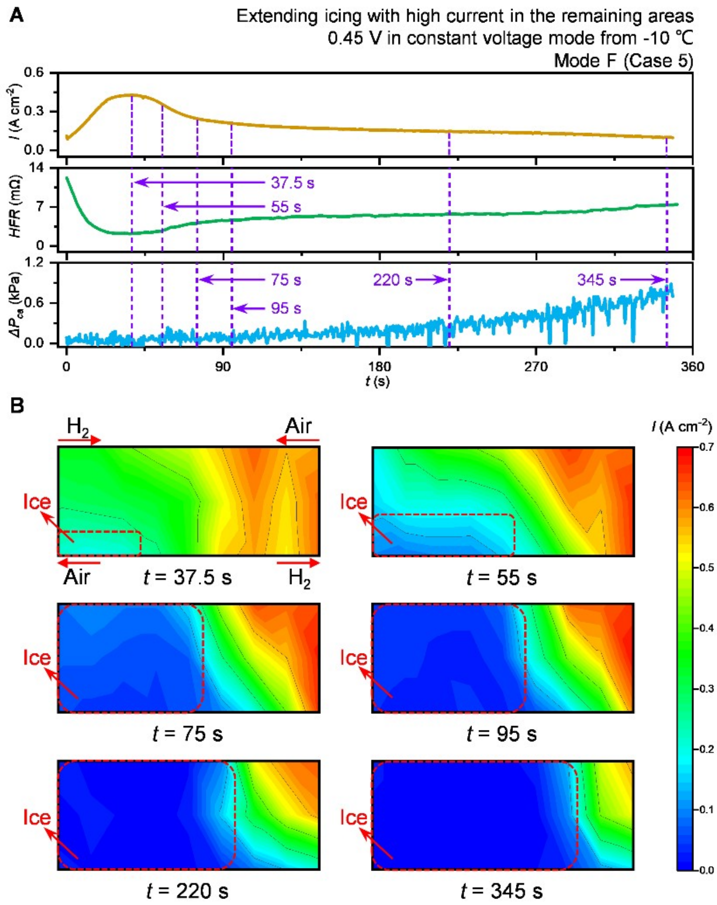

Fig. S3 The failed cold-start process of extending icing with high current in the remaining areas

(A) Current density (*I*), high-frequency resistance (*HFR*), and cathode pressure drop (*ΔPca*) of Case 5, (B) *I* distribution of Case 5.

The cold start process after the output performance of the whole fuel cell peaks is shown in Fig.S3. The local icing in air outlet continues to extend centered on itself while the reaction occurs in the air inlet. At 95 s, the highest current density in the air inlet is 0.69 A cm^{-2}, which is 3.27 times the average current density of the whole fuel cell. Even near the cold start fails, the current density in the air inlet is 0.58 A cm^{-2} when the average current density is 0.10 A cm^{-2}.

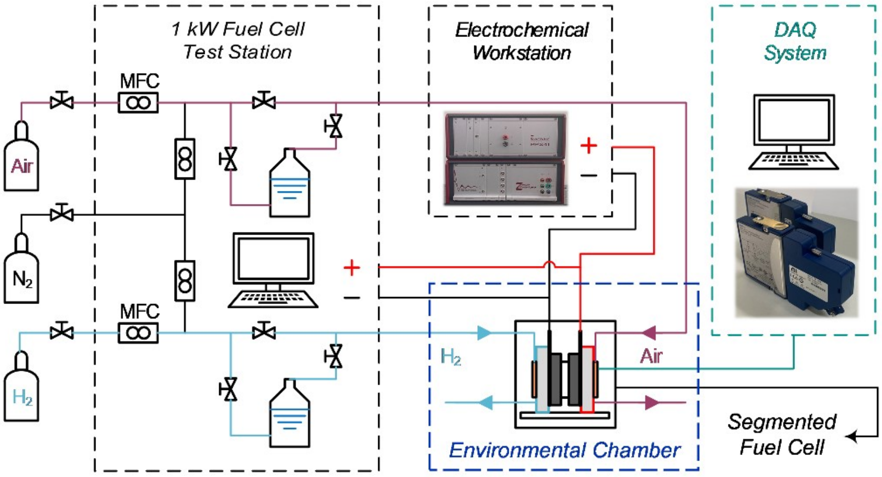

Fig. S4 Schematic diagram of the PEM fuel cell cold-start experimental system

The experimental system to measure the parameters for PEM fuel cells during the cold start processes primarily consists of four main components: a 1 kW fuel cell test station (that can control the gas flow and supply the electrical load), an electrochemical workstation (that can be used to measure HFR and other electrochemical diagnostics), an environmental chamber (that can provide a stable environmental temperature ranging from -50 °C to 200 °C), and a DAQ system (that can acquire voltage and temperature signals at a frequency of 10 Hz). The segmented fuel cell is used as a test object in this study, and the purity of gases is 99.999%.

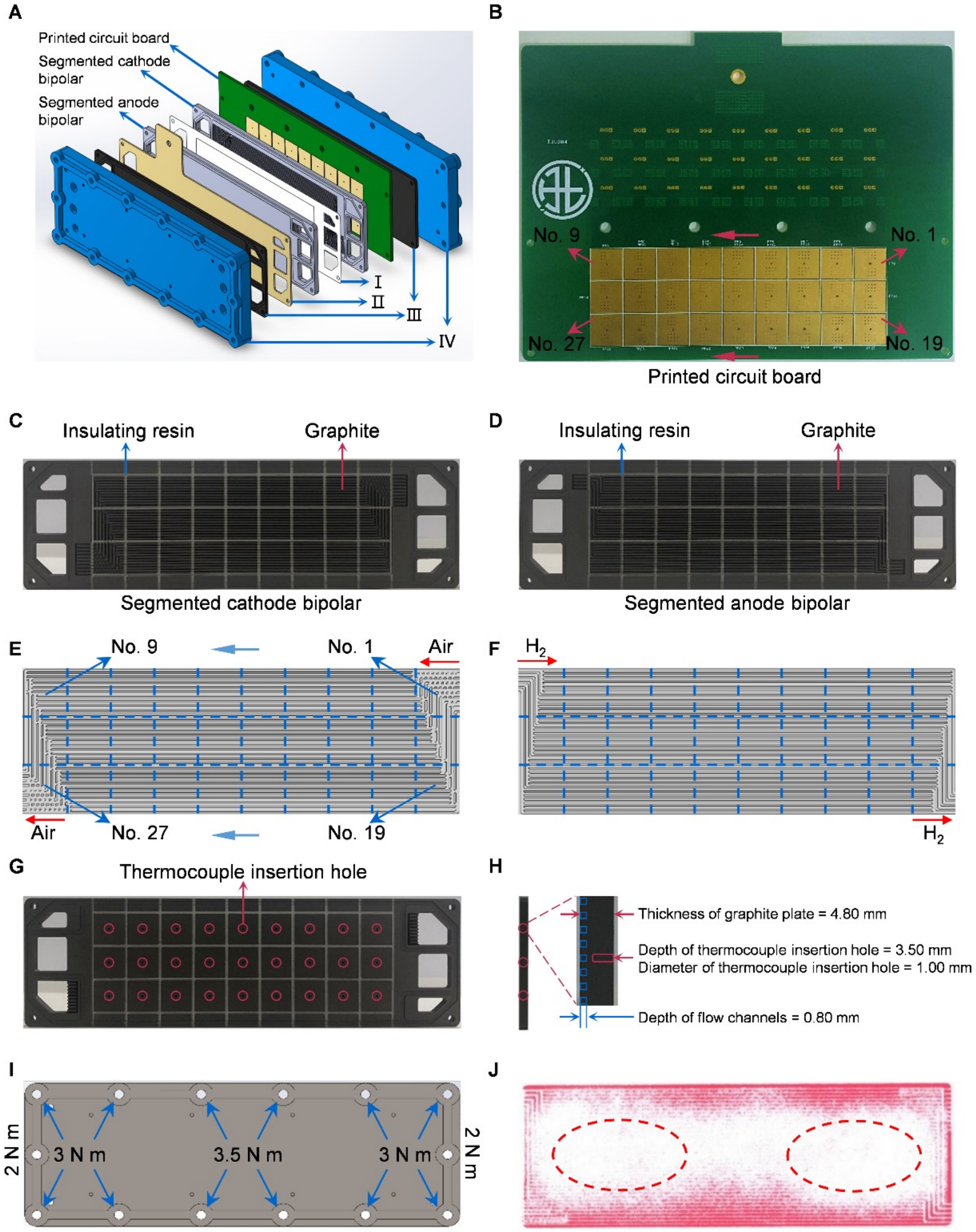

Fig. S5 Schematic diagram of segmented fuel cell design

(A) Assembly drawing of the segmented fuel cell. The printed circuit board (PCB) is used instead of the cathode current collector in the traditional fuel cells. Graphite is used for both the cathode and anode bipolar plate bodied to ensure the validity of in-situ measurement results. I is the membrane electrode assembly, II is the anode current collector, III are the insulating plates, and IV are the end plates.

(B) The side of PCB attached to the cathode bipolar plate (horizontally mirrored figure). The gold-plated copper blocks that collect the current are named No. 1 to No. 9 from right to left and No. 1 to No. 19 from top to bottom.

(C–D) Segmented bipolars of cathode (horizontally mirrored figure) and anode. The activation area in the graphite bipolar plates is segmented by the insulating resin (transparent areas marked by blue arrow) into 27 equal areas.

(E–F) Flow fields of cathode (horizontally mirrored figure) and anode. The segmented cathode bipolar plate is named in the same rule as PCB.

(G–H) Front and side views of the back of the cathode bipolar plate. The red circles in the back are the insertion holes for thermocouples with a depth of 3.50 mm and a diameter of 1.00 mm. The thickness of the whole cathode bipolar plate is 4.80 mm, and the depth of the flow channels which are marked by blue lines is 0.80 mm.

(I) Torque values applied on the bolts. (J) Contact pressure detected by the pressure-sensitive films. The torque applied to the different bolts to clamp the PEM fuel cell is shown in Fig. S5I, such that the pressure distribution inside the fuel cell is formed as shown in Fig. S5J. The pressure in the red circles areas of Fig. S5J is lower than the others, i.e., other areas of the fuel cell structures are in closer contact. Therefore, more heat loss in the areas between the two red circles occurs due to the closer contact during the PEM fuel cell cold start processes.

Table S1. Cases roughly classified based on water states

	No significant icing	Significant icing
No water transport into flow channels	Case 1 Successful/32.5 s/20.69 C cm^{-2}	Case 6 Failed/92.5 s/10.89 C cm^{-2}
	Case 2 Successful/56.8 s/24.93 C cm^{-2}	Case 7 Failed/48.5 s/13.67 C cm^{-2}
	Case 3 Successful/139.6 s/39.38 C cm^{-2}	Case 8 Failed/63.5 s/14.67 C cm^{-2}
	Case 11 Successful/73.9 s/36.95 C cm^{-2}	Case 9 Failed/99 s/8.80 C cm^{-2}
	Case 12 Successful/28.5 s/22.80 C cm^{-2}	Case 16 Failed/92.0 s/18.40 C cm^{-2}
	Case 14 Successful/163.9 s/81.95 C cm^{-2}	
	Case 15 Successful/56.8 s/45.44 C cm^{-2}	
Water transport into flow channels	Case 4 Successful/177.3 s/118.80 C cm^{-2}	Case 5 Failed/348.5 s/66.11 C cm^{-2}
	Case 10 Successful/636.3 s/127.26 C cm^{-2}	Case 17 Failed/444.0 s/222.00 C cm^{-2}
	Case 13 Thermal equilibrium/3600.0 s/ 720.00 C cm^{-2}	
	Case 18 Successful/162.3 s/129.84 C cm^{-2}	

The cold start cases are classified roughly based on the water state and the start-up result, duration and the average accumulated charge of each case are listed in the table.

Table S2. The operating condition parameters

Parameter		Value
Conditioning	Temperature of supplied gases	70 ℃
	Relative humidity of supplied gases	100%
	Absolute pressure at outlets	1 atm
	Temperature of the PEM fuel cell	70 ℃
	Voltage	0.4 V
	Duration	0.5 h
Purging	Completion condition: HFR	11 mΩ
	Relative humidity of nitrogen	0
	Absolute pressure at outlets	1 atm
	Temperature of nitrogen	25 ℃
Cooling down	Duration	6 h
	Environmental temperature	-5, -10, and -15 ℃
Starting up	Start-up voltage in CV mode	0.3, 0.45, and 0.6 V
	Start-up current density in CC mode	0.2, 0.5, and 0.8 A cm^{-2}
	Mass flow rate of gases	0.56 slpm (anode) and 2.27 slpm (cathode) for CV mode/stoichiometry ratios of 1.5 (anode) and 2.5 (cathode) for CC mode
	Relative humidity of gases	0
	Absolute pressure at outlets	1 atm

The test procedure of PEM fuel cell cold start consists of four major steps: conditioning, purging, cooling down, and starting up.

Segmented fuel cell design

The SFC design is shown in Fig. S5A PCB is used instead of the cathode current collector in traditional fuel cells, as shown in Fig. S5A. The PEM fuel cell has a counter-flow arrangement with an activation area of 108 cm^2. A dot-parallel flow field (Fig. S5E) for the cathode and a parallel flow field (Fig. S5F) for the anode is used in the cold start experiments. The end plates of the PEM fuel cell are clamped by bolts with (1) different torques around the activation area to ensure tightness and (2) lower contact resistance to obtain excellent electrical performance. Fig. S5I shows the torque values applied on the 14 bolts clamping the fuel cell; the contact pressure between the bipolar plate and gas diffusion layer detected by pressure-sensitive films (200 μm, Fuji LLW) is shown in Fig. S5J. A multilayer PCB with an integrated sampling resistor is used to replace the cathode current collector plate, instead of graphite plates, to ensure the in-situ measurement results. The fuel cell is divided into nine equal parts along the long side and three equal parts along the short side to form 27 segments. Further, the segments in the cathode inlet and outlet areas are marked as No. 1 and No. 27, respectively, as shown in Fig. S5E. The cathode graphite bipolar plate is divided into 27 segments by epoxy resin material with excellent electrical insulation for collecting current through the PCB board. The preparation process of segmented graphite bipolar plates follows the similar approaches reported by Strickland et al.[1] Simultaneously, a hole with a diameter of 1 mm is set in the middle of every graphite bipolar plate segmented for inserting a K-type thermocouple to measure the temperature distribution, as shown in Fig. S5G and S5H. The rationality of the entire PEMFC has been verified through numerical investigations, and the reliability of the SFC has been verified through experiments.[2,3]

Experimental system

The experimental system to measure the parameters (such as current density and temperature distributions) of PEM fuel cells during the cold start processes primarily consists of four main components--a 1 kW fuel cell test station, an electrochemical workstation, an environmental chamber, and a DAQ system (Fig.S4). The 1 kW fuel cell test station (NBT-1000W, NBT) can measure the current and voltage of the whole cell through the load station. It can control and record the parameters of the gases (air, hydrogen, and nitrogen) entering the cell, including the mass flow rate, temperature, relative humidity (RH), and pressure. The electrochemical workstation (Zennium

Pro., Zahner) can measure HFR and other electrochemical diagnostics. The environmental chamber (H/GDW-50L, HuSheng Test Instrument) can provide a stable environmental temperature ranging from -50 °C to 200 °C with an error of less than 0.5 °C, as the start-up temperature of the cell. The DAQ system comprises multi-channel voltage acquisition cards (NI-9205, National Instruments) and temperature acquisition cards (NI-9214, National Instruments). Labview is employed to control the DAQ program and record the distribution data at a frequency of 10 Hz.

Test procedures

The test procedures for the cold start testing consist of four major steps: conditioning, purging, cooling down, and starting up. The parameters of operating conditions are listed in Table S2. The conditioning step includes operating the PEM fuel cell at 70 °C, 0.4 V, and 1 atm for 30 min. Hydrogen and air are supplied to the anode and cathode with 100% RH at 70 °C with stoichiometry ratios of 1.5 and 2.5 corresponding to the current density, respectively. After the conditioning step, the PEM fuel cell is cooled down to 25 °C. Dry nitrogen at 25 °C with a mass flow rate of 2 slpm is supplied to both the anode and cathode simultaneously for the purging step while detecting HFR at 1000 Hz frequency. When the cell is purged to a fixed HFR value, the anode/cathode nitrogen mass flow is adjusted to 1 slpm. Similarly, the mass flow is adjusted from 1 slpm to 0.5 slpm and further from 0.5 slpm to zero. After these operations, the cell's HFR value will stabilize around the value instead of dropping again, indicating that most of the residual water in the cell is purged away to form a relatively dry cell environment.[4] In this study, this fixed value is set as 11 mΩ, which is far from the HFR value (approximately 2 mΩ) during the normal operation of the PEM fuel cell.

After completing the purge step, the temperature in the environmental chamber is set as the desired start-up temperature (including -5, -10, and -15 °C in this study), and the fuel cell will be frozen for 6 h when the inside temperature stabilizes. Finally, two cold start strategies are used to test the cold start-up capability, namely CC mode and CV mode. During the cold start processes in CC mode, dry hydrogen and air are supplied to the anode and cathode, and the stoichiometry ratios are 1.5 and 2.5 corresponding to the current density. The cold start-up is considered to be failed when the cell voltage is lower than 0.1 V. During the cold start processes in CV mode, dry hydrogen at a mass flow of 0.56 slpm and dry air at a mass flow of 2.27 slpm (equivalent to stoichiometry ratios of 1.5 and 2.5 at 0.5 A cm^{-2}) are supplied to the anode and cathode, respectively. The start-up fails when the current density is lower than 0.1 A cm^{-2}. Regardless of CC or CV mode, when the temperatures of all temperature acquisition points in the SFC are higher than 0 °C (the freezing point of water), the cold start-up is considered to be successful. In this study, the cold start processes of every operating condition are repeated three times.

References

1 D. G. Strickland, S. Litster and J. G. Santiago, *J. Power Sources*, 2007, **174**, 272-281.
2 T. Miao, C. Tongsh, J. Wang, P. Cheng, J. Liang, Z. Wang, W. Chen, C. Zhang, F. Xi, Q. Du, B. Wang, F. Bai and K. Jiao, *Energy*, 2022, **239**, 121922.
3 G. Zhang, X. Xie, B. Xie, Q. Du and K. Jiao, *Int. J. Heat Mass Transf.* 2019, **130**, 555-563.
4 K. Tajiri, C. Wang and Y. Tabuchi, *Electrochim. Acta*, 2008, **53**, 6337-6343.