This item was submitted to [Loughborough's Research Repository](#) by the author.
Items in Figshare are protected by copyright, with all rights reserved, unless otherwise indicated.

Two-dimensional simulation of cold start processes for proton exchange membrane fuel cell with different hydrogen flow arrangements

PLEASE CITE THE PUBLISHED VERSION

<https://doi.org/10.1016/j.ijhydene.2020.04.187>

PUBLISHER

Elsevier BV

VERSION

AM (Accepted Manuscript)

PUBLISHER STATEMENT

This paper was accepted for publication in the journal International Journal of Hydrogen Energy and the definitive published version is available at <https://doi.org/10.1016/j.ijhydene.2020.04.187>

LICENCE

CC BY-NC-ND 4.0

REPOSITORY RECORD

Wu, Kangcheng, Xu Xie, Bowen Wang, Zirong Yang, Qing Du, Jin Xuan, Bingfeng Zu, Zhi Liu, and Kui Jiao. 2020. "Two-dimensional Simulation of Cold Start Processes for Proton Exchange Membrane Fuel Cell with Different Hydrogen Flow Arrangements". Loughborough University. <https://hdl.handle.net/2134/12932806.v1>.

Two-dimensional simulation of cold start processes for proton exchange membrane fuel cell with different hydrogen flow arrangements

Kangcheng Wu¹, Xu Xie¹, Bowen Wang¹, Zirong Yang¹, Qing Du¹, Jin Xuan²,
Bingfeng Zu^{3*}, Zhi Liu^{1*}, Kui Jiao^{1*}

¹State Key Laboratory of Engines, Tianjin University, 135 Yaguan Road, Tianjin, 300350, China

²Department of Chemical Engineering, Loughborough University, Loughborough, LE11 3TU,
United Kingdom

³Internal Combustion Engine Research Institute, Tianjin University, 92 Weijin Road, Tianjin,
300072, China

*Corresponding author emails: liuzhi16@tju.edu.cn; kjiao@tju.edu.cn

Abstract

Proton exchange membrane (PEM) fuel cells with an off-gas recirculation anode (ORA) or dead-ended anode (DEA) are widely adopted in engineering. However, those two hydrogen flow arrangements may cause anodic water and nitrogen accumulation in comparison with the flow-through anode (FTA) mode, which causes significant performance degradation. In this paper, a two-dimensional cold-start model is developed with detailed consideration of water phase changes and the nitrogen crossover phenomenon. A simplified electrochemical module is built to calculate the current density distribution in the model. The simulation results are consistent with the experimental data at both subzero temperatures and normal operating temperatures. The effects of hydrogen flow arrangements, flow

24 configurations, and startup strategies are investigated during startup process from
25 subzero to normal operating temperatures. Much less ice is generated in counter-flow
26 cases than in co-flow cases during constant current operation. A relatively lower
27 startup voltage can effectively shorten the cold-start process and enhance the
28 cold-start capacity for the PEM fuel cell. The ORA mode has the best hydrogen flow
29 arrangement due to its general abilities, including higher hydrogen utilization
30 efficiency, higher anodic nitrogen tolerance, better output performance and better
31 startup capability.

32 **Keywords:** PEM fuel cell; Hydrogen flow arrangements; Cold-start process; Start
33 strategies; Flow configurations

34

Nomenclature

a	water activity
A	area (m^2)
ASR	internal resistance of the cell ($\Omega \text{ m}^2$)
c	mole concentration (mol m^{-3})
C_p	specific heat ($\text{J kg}^{-1} \text{ K}^{-1}$)
D	diffusion coefficient ($\text{m}^2 \text{ s}^{-1}$)
EW	equivalent weight of the membrane (kg kmol^{-1})
F	Faraday's constant (C mol^{-1})
h	latent heat (J kg^{-1}); convective heat transfer coefficient ($\text{W m}^{-2} \text{ K}^{-1}$)
I	local current density (A m^{-2})
i	electrochemical reaction rate (A m^{-3})
κ	electrical conductivity (S m^{-1})
K	permeability (m^2)
M	molecular weight (kg mol^{-1})
n	moles of electrons production per mole of

	reactant consumption
n_d	electro-osmotic coefficient
p	pressure (Pa)
p_c	capillary pressure (Pa)
R	ideal gas constant (J K ⁻¹ mol ⁻¹)
s	Saturation
S	source term (mol m ⁻³ s ⁻¹)
ST	stoichiometric ratio
t	time (s)
T	temperature (K)
	voltage (V);
V	volume (m ⁻³)
x, y	coordinate position (m)
<i>Greek symbols</i>	
α	transfer coefficient
δ	thickness (m)
ε	Porosity
η	voltage loss (V)

κ	phase change rate (s^{-1})
θ	contact angle ($^{\circ}$)
λ	water content
μ	dynamic viscosity ($\text{kg m}^{-1} \text{s}^{-1}$)
ρ	density (kg m^{-3})
σ	electrical conductivity (S m^{-1})
ω	volume fraction of ionomer
<i>Superscript and subscripts</i>	
0	standard condition
act	activation loss
ave	Average
c	Cathode
control	control volume
cond	Condensation
eff	Effective
en	Environment
eq	Equilibrium
f	frozen membrane water

fusn	Fusion
g	Gas
H ₂	Hydrogen
H ₂ O	Water
ice	Ice
in	Inlet
lq	super-cooled (liquid) water
nf	nonfrozen membrane water
nernst	Nernst
ohm	Ohmic
out	output; outlet
O ₂	Oxygen
BP	bipolar plate
ref	reference condition
sat	saturation state
vp	water vapor
lq-ice	between liquid water and ice
nf-lq	between nonfrozen membrane water and liquid water

nf-vp	between nonfrozen membrane water and vapor
vp-lq	between vapor and liquid water
vp-ice	between vapor and ice

36 **1. Introduction**

37 Proton exchange membrane (PEM) fuel cell is a potential alternative to the next
38 generation of automobile powertrain due to its high efficiency, high power density,
39 and zero/low emissions [1, 2]. However, the ability of successful and rapid startup
40 from subfreezing temperatures remains great technical obstacles before large-scale
41 commercialization [3, 4]. Therefore, a comprehensive understanding of the startup
42 process from subzero to normal operating temperatures is of vital importance to
43 enhance the performance and durability of the PEM fuel cell [5].

44 To investigate the efforts of operating conditions and design parameters during the
45 cold-start process, many experimental and numerical studies have been conducted.
46 Tajiri et al. [6] compared the effect of the initial temperatures, current density, dry
47 purge and membrane thickness on the cold-start capability by experiments. Jiao et al.
48 [7] investigated the behavior of the cold-start process under different start voltages,
49 initial water contents and initial cell temperatures by simulations. Xie et al. [8]
50 conducted several experiments to investigate the effects of three different
51 ionomer/carbon ratios on the cold-start process and analyzed the consequences with
52 theoretical water transport. Yang et al. [9] studied the influence of various contact
53 angles and porosities of micro-porous layer on the performance of PEM fuel cell
54 during the cold-start process and gave suggestions to the design of the membrane
55 electrode assembly.

56 To better comprehend the behavior of the PEM fuel cell at subzero temperatures,
57 Morin et al. [10] tested the water management in the PEM fuel cell by small-angle
58 neutron scattering (SANS) and electrochemical impedance spectroscopy (EIS)
59 techniques. The experiments showed that a large current load could lead to
60 dehydration in a thick membrane. Lin et al. [11] used the printed circuit board
61 technology to measure the current density distributions and optimize start strategy for

62 the cold start. Initial voltage load and setup temperature are also investigated in detail
63 [12]. Later, they segmented the PEM fuel cell to study the distribution of internal
64 current density [13] and obtained better understanding of cell behaviors with different
65 flow fields [14]. Jiao et al. [15] launched a 3D model to capture the dynamic features
66 of the cold-start processes in the PEM fuel cell. Then, they investigated the impacts of
67 the initial temperature, load condition and flow arrangement on dynamic
68 performances through in-situ experiments [16]. Gwak et al. [17] performed cold-start
69 simulations for PEM fuel cells from subfreezing to normal operating temperatures and
70 predicted various stages of the processes. They concluded that the co-flow
71 configuration could result in more ice growth and accumulation during subzero
72 temperature operation than the counter-flow case. Zhan et al. [18] tested several
73 reheating methods for a PEM fuel cell stack starting from subfreezing temperatures.
74 The experimental results showed that when the operating temperature exceeded a
75 reference value, e.g., 297 K in this study, the performance of the stack could be
76 improved by humidifying the reactants and circulating the coolant. In those studies,
77 the flow-through anode (FTA) mode is usually adopted due to its operational
78 convenience [19]. However, the FTA mode can suffer from low hydrogen utilization
79 efficiency, which limits the use of this hydrogen supply arrangement in engineering.

80 The dead-ended anode (DEA) mode and off-gas recirculation anode (ORA) mode are
81 widely used in practical applications to enhance the hydrogen utilization efficiency
82 [20]. Compared with the ORA mode, the DEA mode significantly reduces the
83 complexity of hydrogen supply [21]. Many studies have been conducted to investigate
84 the effects of hydrogen supply modes, focusing on the hydrogen efficiency, anodic
85 nitrogen accumulation, and corresponding purge strategies. Chen et al. [21] focused
86 on the optimal purge strategy of the DEA operation and developed a dynamic model
87 to predict the liquid water accumulation in the anode and amount of hydrogen wasted
88 during the purge. The results showed a balance between the maximum
89 thermodynamic efficiency and minimum hydrogen loss during the DEA operation.

90 Yesilyurt et al. [22] presented a dynamic 1D model of the PEM fuel cell in the DEA
91 mode. The computation results showed that the decline of output performance was
92 related to nitrogen crossover and accumulation. Yang et al. [23] built a transient
93 model of the PEM fuel cell with DEA to study the nitrogen crossover and
94 accumulation in varying-load operations. The operating current was considered to
95 affect the nitrogen crossover and purge frequency. The simulation results showed that
96 the model predictions corresponded to the experimental data. Yang et al. [24]
97 examined the current density distributions in the PEM fuel cell in the DEA mode with
98 different boundary conditions. The experimental data indicated that nitrogen first
99 accumulated near the outlet of the anode channel and subsequently diffused to the
100 upstream area, which decreased the local current density at the exit of the anode
101 channel.

102 The PEM fuel cell with ORA has been widely used in vehicles, such as the Toyota
103 Mirai in 2016 and Honda FCX Clarity in 2017 [20]. Bao et al. [25] presented a
104 dynamic 1D model to study the effect of the injection pump on the PEM fuel cell with
105 ORA. The simulation results showed that the 1D fuel cell model had good accuracy
106 and could predict the water flooding in the cathode. Wang et al. [26] simulated the
107 dynamic processes with two different purge strategies in the PEM fuel cell with ORA.
108 He found that a 3% bleed rate was the best choice in consideration of the hydrogen
109 use efficiency and nitrogen accumulation. Ahluwalia and Wang [27] developed a
110 dynamic model to study the nitrogen accumulation during the ORA operation and
111 effects on the performance of the PEM fuel cells with different bleed rates. The
112 investigations indicated that a small bleed rate could make the nitrogen fraction to
113 accumulate over 50% during the operations. Promislow et al. [28] presented an
114 analytical model in the ORA mode to study the best strategy of bleed rate for PEM
115 fuel cells. Wang et al. [29] introduced a quasi-2D dynamic model in the ORA mode
116 and studied the regularities of nitrogen distributions in the anode. The results showed

117 that the PEM fuel cell with ORA performed better in various aspects at normal
118 operating temperatures than those with DEA.

119 However, the studies about the startup processes from subzero to normal temperatures
120 with DEA or ORA are hard to find in the literature. To find the advantages and
121 weaknesses of the three hydrogen flow modes in the start-up processes, numerical or
122 analytical model must be developed to capture the dynamic characteristics in a large
123 range of temperatures. Therefore, we develop a quasi-2D transient multiphase PEM
124 fuel cell model with a simplified electrochemical model in this paper. The differences
125 among the three anode flow arrangements (FTA, DEA, ORA) from subzero to normal
126 operating temperatures are analyzed. The effects of flow configurations (co-flow &
127 counter-flow) and startup strategies (constant current & constant voltage) are also
128 investigated.

129 **2. Mathematical Model**

130 In general, five types of water, including super-cooled water must be considered
131 during startup operation. Hydrogen flow arrangements may affect the water content
132 and local current density distributions. The heat transport can be more complex for
133 subzero environmental temperatures. The gas transport, heat transport and
134 electrochemical reaction must be synthetically considered.

135 **2.1 Model description**

136 Fig. 1 displays a schematic diagram of the quasi-two-dimensional model for the
137 proton exchange membrane (PEM) fuel cell with counter-flow configuration. The
138 entire cell is divided into eleven layers according to structural features, including
139 bioplate (BP), channel (CH), gas diffusion layer (GDL), micro-porous layer (MPL),
140 catalyst layer (CL) and membrane (MEM). Each layer is divided into N segments
141 along the flow direction (Y-axis). The structural parameters and operating conditions
142 are listed in Table 1.

143 In this model, super-cooled water is considered in the water phase change mechanism
 144 during the subzero process [30]. The generated water from electrochemical reactions
 145 is considered to be membrane water and initially absorbed in CCL [4].

146 2.2 Assumptions

147 To simplify the calculation, several assumptions are adopted in the model:

- 148 (1) The flow in channels is laminar due to the low Reynolds number.
- 149 (2) All gas species are treated as ideal gas [5].
- 150 (3) The gas pressure remains constant along the flow direction in the channels
 151 because the pressure drop can be ignored compared to operation atmosphere [29].
- 152 (4) The electric potential is identical all over the surface of the bipolar plate because
 153 of the high electric conductivity of the metal material.
- 154 (5) Considering the real geometry, the diffusion transport along the flow direction
 155 and convection transport in the gas diffusion layer (GDL), micro-porous layer (MPL)
 156 and catalyst layer (CL) can be ignored in comparison with the diffusion and
 157 convection transport in other directions [29].

158 2.3 Electrochemical module

159 The output voltage (V_{out} , V) is expressed as follows based on Nernst voltage (V_{nemst} ,
 160 V), the activation overpotential ($\eta_{\text{act,a}}$ and $\eta_{\text{act,c}}$, V), concentration overpotential
 161 ($\eta_{\text{conc,a}}$ and $\eta_{\text{conc,c}}$, V) and ohmic overpotential (η_{ohmic} , V).

$$162 \quad V_{\text{out}} = V_{\text{nernst}} + \eta_{\text{act,a}} + \eta_{\text{act,c}} + \eta_{\text{conc,a}} + \eta_{\text{conc,c}} + \eta_{\text{ohmic}} \quad (1)$$

163 Considering the reactant and product, Nernst voltage is calculated as

$$V_{\text{nernst}} = 1.229 - 0.846 \times 10^{-3} \times (T - 298.0) + \frac{RT}{2F} \ln(p_{\text{H}_2} p_{\text{O}_2}^{0.5}) \quad (2)$$

where p_{H_2} and p_{O_2} (Pa) are the partial pressures for hydrogen and oxygen, respectively.

In this electrochemical module, Tafel equation is applied to calculate the anodic and cathodic activation loss [5]:

$$\eta_{\text{act,a}} = -\frac{RT}{2\alpha_a F} \ln\left(\frac{I / \delta_{\text{CL,a}}}{i_{0,a}}\right) \quad (3)$$

$$\eta_{\text{act,c}} = -\frac{RT}{4\alpha_c F} \ln\left(\frac{I / \delta_{\text{CL,c}}}{i_{0,c}}\right) \quad (4)$$

where α_a and α_c are the transfer coefficients in the anode and cathode in Table 1, respectively; I (A m^{-2}) is the local current density in one segment along the flow direction in the anode channel; $i_{0,a}$ and $i_{0,c}$ (A m^{-3}) are the exchange current densities for the anode and cathode, respectively, and are expressed as

$$i_{0,a} = i_{0,a}^{\text{ref}} (1 - s_{\text{ice}} - s_{\text{liq}}) \left(\frac{c_{\text{H}_2}}{c_{\text{H}_2}^{\text{ref}}} \right)^{0.5} \exp\left(-1400 \left(\frac{1}{T} - \frac{1}{298.15} \right)\right) \quad (5)$$

$$i_{0,c} = i_{0,c}^{\text{ref}} (1 - s_{\text{ice}} - s_{\text{liq}}) \frac{c_{\text{O}_2}}{c_{\text{O}_2}^{\text{ref}}} \exp\left(-7900 \left(\frac{1}{T} - \frac{1}{298.15} \right)\right) \quad (6)$$

where $i_{0,a}^{\text{ref}}$ and $i_{0,c}^{\text{ref}}$ (A m^{-3}) are the reference exchange current densities in the anode and cathode, respectively; s_{ice} and s_{liq} are the ice and liquid water saturation in catalyst layer (CL), respectively.

The anodic concentration loss is usually much smaller than that of the cathode, mainly due to the fast hydrogen oxidation reaction. However, in the DEA or ORA mode,

182 some local positions of the anode catalyst layer may suffer from insufficient hydrogen
 183 as a result of nitrogen and liquid water accumulation, which causes remarkable
 184 concentration loss. Therefore, both anodic and cathodic concentration loss are
 185 considered and calculated as

$$186 \quad \eta_{\text{conc,a}} = \frac{RT}{2\alpha_a F} \ln\left(1 - \frac{I}{I_{\text{D,a}}}\right) \quad (7)$$

$$187 \quad \eta_{\text{conc,c}} = \frac{RT}{4\alpha_c F} \ln\left(1 - \frac{I}{I_{\text{D,c}}}\right) \quad (8)$$

188 In those equations, $I_{\text{D,a}}$ and $I_{\text{D,c}}$ (A m^{-2}) are the limiting current densities and
 189 calculated as [5]

$$190 \quad I_{\text{D,a}} = \frac{2Fc_{\text{H}_2,\text{CH}}}{\frac{\delta_{\text{CL}}/2}{D_{\text{H}_2,\text{CL}}^{\text{eff}}} + \frac{\delta_{\text{MPL}}}{D_{\text{H}_2,\text{MPL}}^{\text{eff}}} + \frac{\delta_{\text{GDL}}}{D_{\text{H}_2,\text{GDL}}^{\text{eff}}}} \quad (9)$$

$$191 \quad I_{\text{D,c}} = \frac{4Fc_{\text{O}_2,\text{CH}}}{\frac{\delta_{\text{CL}}/2}{D_{\text{O}_2,\text{CL}}^{\text{eff}}} + \frac{\delta_{\text{MPL}}}{D_{\text{O}_2,\text{MPL}}^{\text{eff}}} + \frac{\delta_{\text{GDL}}}{D_{\text{O}_2,\text{GDL}}^{\text{eff}}}} \quad (10)$$

192 where $D_{\text{H}_2,\text{CL}}^{\text{eff}}$, $D_{\text{H}_2,\text{MPL}}^{\text{eff}}$, $D_{\text{H}_2,\text{GDL}}^{\text{eff}}$, $D_{\text{O}_2,\text{CL}}^{\text{eff}}$, $D_{\text{O}_2,\text{MPL}}^{\text{eff}}$ and $D_{\text{O}_2,\text{GDL}}^{\text{eff}}$ ($\text{m}^2 \text{s}^{-1}$) are the
 193 diffusivities of reactants in porous layers and are listed in Table 2.

194 The ohmic loss results from the ionic and electronic resistances in the fuel cell
 195 components as follows,

$$196 \quad \eta_{\text{ohmic}} = -\left(\sum ASR\right)I = -\left(\frac{d}{\sigma_{\text{BP}}} + \frac{\delta_{\text{GDL}}}{\sigma_{\text{s,GDL}}^{\text{eff}}} + \frac{\delta_{\text{MPL}}}{\sigma_{\text{s,MPL}}^{\text{eff}}} + \frac{\delta_{\text{CL}}/2}{\sigma_{\text{s,CL}}^{\text{eff}}} + \frac{\delta_{\text{CL}}/2}{\sigma_{\text{m,CL}}^{\text{eff}}} + \frac{\delta_{\text{MEM}}}{\sigma_{\text{MEM}}}\right)I \quad (11)$$

197 The current density distribution can be affected by the local reactant concentrations,
 198 ice volume fraction, liquid water saturation and temperature. Electric boundary

199 conditions are necessary to solve the output voltage and local current densities, and
 200 the electric potentials of all segments in the flow direction are assumed to be identical
 201 [29]. To solve the nonlinear equation system, Newton's method is applied with the
 202 convergence error set as 1×10^{-8} to ensure accuracy.

$$203 \quad \begin{cases} V_{\text{out}} = V_{\text{nernst}}^{(i)} + \eta_{\text{act,a}}^{(i)} + \eta_{\text{act,c}}^{(i)} + \eta_{\text{act,a}}^{(i)} + \eta_{\text{conc,a}}^{(i)} + \eta_{\text{conc,c}}^{(i)} - I^{(i)} ASR^{(i)}, i=1,2,\dots,N \\ \sum_{i=1}^N (I^{(i)} A_{\text{cell}} / N) = I_{\text{ave}} A_{\text{cell}} \end{cases} \quad (12)$$

204 2.4 Conservation Equations

205 The conservation equations of mass, species, nonfrozen membrane water, frozen
 206 membrane water, ice, liquid pressure and energy are solved in the model. In the
 207 calculations, the explicit calculation method is used to enhance calculation efficiency.

208 2.4.1 Mass conservation

209 Gas transport in the channels exists in the form of species diffusion and convection.
 210 To simplify the model, convection is only considered along the flow direction in the
 211 channels, and the convection term is dispersed by the first-order upwind scheme in the
 212 current study [29]. For assumption (3) and the mass conservation equation, the
 213 velocity can be expressed as [29]:

$$214 \quad \frac{\partial}{\partial t} \left(\varepsilon (1 - s_{\text{liq}} - s_{\text{ice}}) \rho_g \right) + \nabla \cdot \left(\rho_g \vec{u}_g \right) = S_m \quad (13)$$

215 where S_m ($\text{mol m}^{-3} \text{s}^{-1}$) is the source term of all gas species in Table 3; ρ_g (kg m^{-3})
 216 is the total gas concentration of segment k in the channel, which can be obtained by
 217 the ideal gas equation [15].

218 2.4.2 Gas species transport

219 The gas species conservation equation can be solved:

$$220 \quad \frac{\partial(\varepsilon(1-s_{\text{liq}}-s_{\text{ice}})\rho_g c_i)}{\partial t} = \frac{\partial^2(\rho_g D_i^{\text{eff}} c_i)}{\partial x^2} + S_i \quad (14)$$

221 where S_i ($\text{mol m}^{-3} \text{s}^{-1}$) is the source term of gas species i in Table 3. Among the
222 porous layers, the convection flux is fixed as zero (mentioned in assumption 5).

223 2.4.3 Membrane water transport

224 In this study, the form of water generated by the electrochemical reaction is assumed
225 to be membrane water, and the conservation equation can be solved:

$$226 \quad \frac{\rho_{\text{MEM}}}{EW} \frac{\partial(\omega \lambda_{\text{nf}})}{\partial t} = \frac{\rho_{\text{MEM}}}{EW} \frac{\partial^2(\omega^{1.5} D_{\text{nf}} \lambda_{\text{nf}})}{\partial x^2} + S_{\text{nmw}} \quad (15)$$

$$227 \quad \frac{\rho_{\text{MEM}}}{EW} \frac{\partial(\omega \lambda_{\text{f}})}{\partial t} = S_{\text{fmw}} \quad (16)$$

228 where S_{nmw} and S_{fmw} ($\text{mol m}^{-3} \text{s}^{-1}$) are the nonfrozen membrane water source
229 term and frozen membrane water source term, respectively, and the detailed phase
230 change functions are presented in Table 3. ρ_{MEM} (kg m^{-3}) is the membrane density
231 and ω_p is the volume fraction of ionomer in the p layer. D_{nf} ($\text{m}^2 \text{s}^{-1}$) is the
232 diffusivity for nonfrozen membrane water and listed in Table 2.

233 2.4.4 Liquid water transport

234 The liquid water saturation conservation equation can be solved:

$$\frac{\partial(\varepsilon \rho_{\text{liq}} s_{\text{liq}})}{\partial t} = \frac{\partial^2 \left(\rho_{\text{liq}} \frac{K_{\text{liq}}}{\mu_{\text{liq}}} p_{\text{liq}} \right)}{\partial x^2} + S_{\text{liq}} \quad (17)$$

where S_{liq} ($\text{mol m}^{-3} \text{ s}^{-1}$) is the liquid water source term in Table 4; K_{liq} ($\text{m}^2 \text{ s}^{-1}$) is the effective liquid permeability. The liquid pressure can be calculated by the relationship of capillary pressure (p_g, P_a) and gas pressure (p_c, P_a) [7] as

$$p_{\text{liq}} = p_g - p_c \quad (18)$$

The correlation equation of capillary pressure can be described by Leverett function [31] and calculated as

$$p_c = \begin{cases} \sigma_{\text{liq}} \cos \theta \left(\frac{\varepsilon}{K_0} \right)^{0.5} \times [1.42 s_{\text{liq}} - 2.12 (s_{\text{liq}})^2 + 1.26 (s_{\text{liq}})^3] & \theta \geq 90^\circ \\ \sigma_{\text{liq}} \cos \theta \left(\frac{\varepsilon}{K_0} \right)^{0.5} \times [1.42 (1 - s_{\text{liq}}) - 2.12 (1 - s_{\text{liq}})^2 + 1.26 (1 - s_{\text{liq}})^3] & \theta < 90^\circ \end{cases} \quad (19)$$

where σ_{liq} (N m^{-1}) is the surface tension coefficient of liquid water; θ ($^\circ$) is the contact angle in Table 1; ε is the porosity; and K_0 (m^2) is the intrinsic permeability.

2.4.5 Ice transport

Freezing point depression [15] is considered in the model defined by the parameters of surface tension of water ($\sigma_{273.15}$, N m^{-1}) at 273.15 K, hydrophobicity (θ , $^\circ$), latent heat of fusion (h_{fusi} , J kg^{-1}) and the pore radius of porous media ($r_{\text{CL,MPL,GDL}}$, m) [31]:

$$T_{\text{FPD}} = \frac{T_N \sigma_{273.15} \cos \theta}{\rho_{\text{ice}} h_{\text{fusi}} r_{\text{CL,MPL,GDL}}} \quad (20)$$

Hence, the actual freezing temperatures in porous media of CL, MPL and GDL can be expressed as:

$$T_{\text{freeze}} = 273.15 - T_{\text{FPD}} \quad (21)$$

The ice saturation conservation equation can be solved:

$$\frac{\partial(\varepsilon s_{\text{ice}} \rho_{\text{ice}})}{\partial t} = S_{\text{ice}} \quad (22)$$

where S_{ice} ($\text{mol m}^{-3} \text{ s}^{-1}$) is the ice source term in Table 4.

2.4.6 Energy conservation

The temperature can be solved by the energy conservation equation:

$$\frac{\partial}{\partial t} ((\rho C_p)^{\text{eff}} T) = \frac{\partial^2 (k_T^{\text{eff}} T)}{\partial x^2} + S_T \quad (23)$$

where S_T (W) is the heat source term in Table 4. k_T^{eff} ($\text{W m}^{-1} \text{ K}^{-1}$) is the effective thermal conductivity. Considering the gas phase and liquid phase, the effective volumetric heat capacity of each layer is defined as [15]:

$$(\rho C_p)^{\text{eff}} = \varepsilon ((s \rho C_p)_{\text{liq}} + (s \rho C_p)_{\text{ice}} + (1 - s_{\text{ice}} - s_{\text{liq}})(\rho C_p)_{\text{g}}) + (1 - \varepsilon - \omega)(\rho C_p)_{\text{s}} + \omega (\rho C_p)_{\text{MEM}} \quad (24)$$

In the model, the BP domain is considered the combination of solid phase (the material of bipolar plate and ice), liquid phase (liquid water) and gas phase (mixed gas including water vapor, hydrogen gas, oxygen gas and nitrogen gas). Therefore, the effective volumetric heat capacity of the BP domain is calculated as [29]:

$$(\rho C_p)_{\text{BP}}^{\text{eff}} = \frac{V_{\text{g}}}{V_{\text{control}}} ((s \rho C_p)_{\text{liq}} + (s \rho C_p)_{\text{ice}} + (1 - s_{\text{ice}} - s_{\text{liq}})(\rho C_p)_{\text{g}}) + \frac{V_{\text{s}}}{V_{\text{control}}} (\rho C_p)_{\text{s}} \quad (25)$$

270 2.5 Nitrogen transport

271 The nitrogen transport across the membrane is decided by the nitrogen pressure
 272 difference between anodic and cathodic catalyst layers and membrane hydration. The
 273 nitrogen crossover flux is calculated as [28]:

$$274 \quad J_{N_2, cro} = K_{N_2} \frac{p_{N_2, c} - p_{N_2, a}}{\delta_m} \quad (26)$$

275 where $p_{N_2, a}$ and $p_{N_2, c}$ (Pa) are the partial pressures on the two sides of the
 276 membrane. K_{N_2} (mol m⁻¹ s⁻¹ Pa⁻¹) is the nitrogen permeability of Nafion and is
 277 expressed as [29]:

$$278 \quad K_{N_2} = (0.0295 + 1.21f_v - 1.93f_v^2) \times 10^{-14} \times \exp \left[\frac{E_{N_2}}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right] \quad (27)$$

279 where, E_{N_2} is the nitrogen activation energy (24000 J mol⁻¹); T_{ref} is the reference
 280 temperature (303 K) [27]; V_w (m³ mol⁻¹) and V_m (m³ mol⁻¹) are the molar volumes
 281 of liquid water and dry membrane, respectively; and f_v (-) is the volume fraction of
 282 water content and is calculated as

$$283 \quad f_v = \frac{\lambda_m V_w}{V_m + \lambda_m V_w} \quad (28)$$

284 2.6 Boundary conditions

285 In the model, the method of heat transfer between the bipolar plate surface and the
 286 environment is heat convection. Thus, the heat transfer can be expressed as [15]:

$$287 \quad Q = h(T_{en} - T_{BP}) A_{BP} \quad (29)$$

288 where Q (J s^{-1}) denotes the heat transfer rate between the bipolar plate surface and
 289 environment; h ($\text{W m}^{-2} \text{K}^{-1}$) is the heat transfer coefficient in Table 1; A_{BP} (m^2) is
 290 the surface area of the bipolar plate; and T_{en} and T_{BP} (K) are the temperatures of the
 291 environment and bipolar plate surface, respectively.

292 For the flow configurations, co-flow and counter-flow are used in the model. For the
 293 co-flow configuration, the inlets of the anode and cathode are on the same side of the
 294 channels; for the counter-flow configuration, it is the reverse.

295 Hydrogen flow arrangements can be divided into three modes as FTA, DEA, and
 296 ORA. For each mode, the boundary conditions for the anode channels are different.
 297 For the FTA mode, the flow velocities and concentrations at the inlets of flow
 298 channels are calculated as

$$299 \quad u_{\text{a,in}} = \frac{ST_{\text{a}} I_{\text{ave}} A_{\text{cell}}}{2F c_{\text{H}_2,\text{in}} A_{\text{ACH}}}, \quad u_{\text{c,in}} = \frac{ST_{\text{c}} I_{\text{ave}} A_{\text{cell}}}{4F c_{\text{O}_2} A_{\text{CCH}}} \quad (30)$$

$$300 \quad c_{\text{H}_2,\text{in}} = \frac{p_{\text{g}}^{\text{a}} - RH_{\text{a}} p_{\text{sat}}}{RT_{\text{in}}^{\text{a}}}, \quad c_{\text{O}_2,\text{in}} = \frac{0.21(p_{\text{g}}^{\text{c}} - RH_{\text{c}} p_{\text{sat}})}{RT_{\text{in}}^{\text{c}}} \quad (31)$$

301 Here, ST_{a} and ST_{c} are the stoichiometry ratios for the anode and cathode. I_{ave}
 302 (A m^{-2}) is the average current density for the cell. A_{ACH} and A_{CCH} (m^2) are the gas
 303 flow flux areas at the anode and cathode, respectively. A_{cell} (m^2) is the total active
 304 surface area. The inlet gas is assumed to be fully preheated, and the inlet gas
 305 temperatures are equal to the local cell temperature.

306 For the DEA mode, the flow velocities at the outlet of anode channel and the inlet of
 307 the cathode channel are calculated as

$$u_{a,in} = 0, \quad u_{c,in} = \frac{ST_c I_{ave} A_{cell}}{4Fc_{O_2} A_{CCH}} \quad (32)$$

$$c_{H_2,out} = c_{H_2,ACH}^{t-\Delta t}, \quad c_{O_2,in} = \frac{0.21(p_g^c - RH_c p_{sat})}{RT_{in}^c} \quad (33)$$

where $c_{H_2,ACH}^{t-\Delta t}$ (mol m⁻³) is the hydrogen concentration at the outlet of the anode channel in the previous time step.

For the ORA mode, the flow from the outlet is assumed as being reserved and recirculated at the new time step [29]. The inlet flow velocities (m s⁻¹) are calculated as

$$u_{a,in} = \frac{ST_a \frac{I_{ave}}{2F} A_{cell} + \phi_{N_2,out}^{t-\Delta t} + \phi_{vp,out}^{t-\Delta t}}{c_{total} A_{ACH}}, \quad u_{c,in} = \frac{ST_c I_{ave} A_{cell}}{4Fc_{O_2} A_{CCH}} \quad (34)$$

$$c_{H_2,in} = c_{total} - \frac{\phi_{N_2,out}^{t-\Delta t} + \phi_{vp,out}^{t-\Delta t}}{A_{ACH} \cdot u_a}, \quad c_{O_2,in} = \frac{0.21(p_g^c - RH_c p_{sat})}{RT_{in}^c} \quad (35)$$

where $\phi_{N_2,out}^{t-\Delta t}$ and $\phi_{vp,out}^{t-\Delta t}$ (mol s⁻¹) are the nitrogen flux and vapor flux, respectively, at the outlet of the anode channel (ACH) at $t-\Delta t$; $c_{N_2,out}^{t-\Delta t}$ and $c_{vp,out}^{t-\Delta t}$ (mol m⁻³) are the nitrogen and vapor concentrations, respectively, at the outlet of ACH at $t-\Delta t$ and c_{total} (mol m⁻³) is the sum of all gas component concentrations at the ACH inlet based on the ideal gas equation.

$$\phi_{N_2,out}^{t-\Delta t} = c_{N_2,out}^{t-\Delta t} A_{ACH} u_{a,out}^{t-\Delta t} \quad (36)$$

$$\phi_{vp,out}^{t-\Delta t} = c_{vp,out}^{t-\Delta t} A_{ACH} u_{a,out}^{t-\Delta t} \quad (37)$$

324 2.7 Solution procedures

325 The numerical model is solved by a self-written program and run by MATLAB. In
326 this model, the size of a single time step is fixed as 1×10^{-6} s to avoid divergence and
327 guarantee calculation accuracy due to the explicit scheme applied to disperse control
328 equations. The grid-independency has been tested, and the difference in cell voltage
329 between 5 segments and 10 segments is less than 1 %. Considering the computational
330 efficiency, 5 segments is suitable for calculation [29]. To comprehend how the
331 mathematical model works, Fig. 2 shows the flow chart of the calculation process. In
332 Fig. 2, the physical variables include the velocity, gas species, membrane water,
333 liquid water, ice and temperature.

334 3. Results and discussion

335 In the paper, the features of three hydrogen flow arrangements, flow-through anode
336 (FTA), dead-ended anode (DEA) and off-gas recirculation anode (ORA), are analyzed
337 in detail to investigate their effects on startup processes from subzero to normal
338 operating temperatures. The comparisons between two flow configurations (co-flow
339 or counter-flow) and two start-up strategies (high start voltage or low start voltage)
340 are also analyzed in detail.

341 3.1 Model validation

342 To verify the model accuracy, simulation results are compared with data from
343 self-designed experiments. Fig. 3 shows that the model has been validated against
344 experimental data for cold-start processes and cell polarization curves. In Fig. 3 (a),
345 the simulation and results reasonably match with the experimental evolutions of cell
346 voltage and ohmic loss voltage in the failed and successful cold-start processes from
347 -6 °C and -9 °C; the initial membrane water content was $\lambda = 3.24, 4.59, 2.33$. The
348 operating current density was constant at 1000 A m^{-2} . The FTA mode and

counter-flow configuration are applied in experiments by default. In Fig. 3 (a), the most error rate of cell voltage between simulation and experiment is approximately 4%. This error rate is within the allowed range. In Fig. 3 (b), the simulation results are consistent with the experimental data with different inlet relative humidities. The relative modeling parameters (Table 1) such as geometric parameters and electrochemical parameters are kept constant in those operations. The predictions of the model are consistent with the experimental data, and the reasonable modeling accuracy is acquired at different operating temperatures. The validations of the DEA and ORA modes have been done in the previous work [29, 34]. Fig. 3 (c) shows the comparison of dynamic performances of the PEM fuel cells with DEA between model prediction and experiment [32]. The boundary conditions of the model are the same as those in the experiments [32]. Fig. 3 (d) shows the comparison of the dynamic performances of the PEM fuel cells with the ORA between the experiment [33] and model prediction. The grid-independency has also been tested in the dynamic process in Fig. 3 (d). There is no big influence for the dynamic performance when the grid number is growing from 5 to 10.

3.2 Effects of the flow configurations on the hydrogen flow arrangements

In this section, three successful startup processes from subzero temperature of the PEM fuel cell with different hydrogen flow arrangements are discussed in detail. To investigate the effects of different flow configurations on the cold-start capacity, galvanostatic operation (1000 A m^{-2}) is adopted to guarantee the same generating rate of water in the cells.

Figure 4 displays the evolutions of the output voltage with three hydrogen flow arrangements starting from 267.15 K with constant-current operation at 1000 A m^{-2} and no humidity at the inlets. During the entire processes, the output voltages change in a wide range due to the membrane hydration and ice accumulation [5]. In Figs. 4 (a) and 4 (b), the hydrogen flow arrangements have very small effects on the

performances in the first 200 s. From 200 s to 900 s, the output voltages generally decrease, and in DEA mode, the largest voltage drop appears with both flow configurations. At 900 s, cell voltages in the DEA mode and FTA mode can differ by 40 mV at most. Simultaneously, the cell voltages are approximately 15 mV higher in co-flow case than in counter-flow cases. Among the three hydrogen flow arrangements, the output performance is always the best in the FTA mode and the worst in the DEA mode.

Figure 5 presents the evolutions of ice saturation in the cathode catalyst layer (CCL) in the first 150 s. The hydrogen flow arrangements slightly affect the ice saturation distributions in the first 150 s, especially in the counter-flow modes. Most ice saturation during the cold-start process in the co-flow modes is over 0.50 but less than 0.25 in the counter-flow modes. Combined with Fig. 4, the difference in ice formation accumulation in two flow configurations can be explained by the ability of self-humidification ability. Stronger self-humidification can promote a better cell performance at temperatures above freezing and lead to more ice formation and accumulation in CCL at subzero temperatures [17]. Affected by current density distributions, more water is generated close to the upstream cathode channel in the co-flow mode than in the counter-flow mode. More water in the co-flow mode can be absorbed in the downstream membrane in the form of vapor.

Figure 6 displays the evolutions of the current density distribution (Fig. 6 (a)), temperature distribution (Fig. 6 (b)) and nitrogen concentration distribution (Fig. 6 (c)) with three hydrogen flow arrangements in the counter-flow mode. The current density distributions in the FTA and ORA modes are similar but differ from that in the DEA mode, especially after 300 s (Fig. 6 (a)). At 900 s, the local current density near the anode exit in the DEA mode is the minimum and lower than 150 A m^{-2} , but in the FTA mode and ORA mode, it is the maximum along the channel. The variation tendency of the temperature distribution is similar to that of the current density

distribution (Fig. 6 (b)); since the local current density can directly affect the ohmic heat power and other heat sources. The current density in the DEA mode decreases below 450 A m^{-2} near the exit of the anode channel at 750 s, and the heating power cannot satisfy the heat loss from the cell into the cold environment. Later temperature near the inlet of cathode is approximately the freezing point in the DEA mode at 900 s in Fig. 6(b), which may lead a failing startup process. The nitrogen distributions are quite different in three cases due to hydrogen flow arrangements (Fig. 6 (c)). The nitrogen concentration relatively uniformly distributes in the ORA mode, but most of the nitrogen concentrates in the downstream area of anode catalyst layer in the DEA mode. Comparing with the results in Fig. 6 (a) and (c), the local current density decreases when the nitrogen concentration increases from 0 to 43.0 mol m^{-3} in the DEA mode. Although the problems of nitrogen crossover and gathering also exist in the ORA mode, the anode recirculation loops can force nitrogen convection and the maximum of nitrogen concentration in the anode catalyst layer is approximately 27 mol m^{-3} at 900 s while hydrogen remains relatively adequate for electrochemical reaction. More nitrogen concentration and more nonuniform nitrogen distribution are the main reasons [22, 23, 32] that cause the worst performance to the DEA mode as shown in Fig. 4.

Figure 7 shows the evolutions of hydrogen use efficiencies of PEM fuel cells with three hydrogen flow arrangements during the startup processes. The hydrogen use efficiency (η) is calculated as [29]:

$$\eta = \frac{\sum (I_{\text{ave}} V_{\text{out}}) A_{\text{cell}}}{\sum (u_{\text{a,in}} c_{\text{H}_2, \text{in}}) M_{\text{H}_2} LHV_{\text{H}_2} A_{\text{ACH}}} \quad (38)$$

here LHV_{H_2} (J kg^{-1}) is the lower heating value of hydrogen, and M_{H_2} (kg mol^{-1}) is the molar mass of hydrogen gas. The efficiencies in the DEA and ORA modes are often nearly identical and much larger than that in the FTA mode. However, after 500

s, a clear decline in efficiency appears in the DEA mode, which implies that the nitrogen crossover causes a larger activation loss in ACL than in ORA mode [26, 29].

3.3 Effects of the startup voltages on the hydrogen flow arrangements

Generally, 0.65 V is considered as a common operating voltage when the fuel cell works at a state of high output power and high hydrogen use efficiency in normal temperature operation [35, 36]. Therefore, a successful cold start with constant-voltage operation at 0.65 V from subzero to normal operating temperatures has strong practical significance for automobile applications. However, under the requirement of rapid start from subzero temperature, startup with a low voltage operation is considered an effective method for a rapid cold start [15]. In this section, the effects of startup voltages on PEM fuel cells with three hydrogen flow arrangements are analyzed in detail and relative conditions are listed in Table 1. In the following content, all cases with the counter-flow configuration are arranged as default. The flow rates of gases are calculated by the output current at the last time step and stoichiometric ratio.

Figure 8 shows the evolutions of the average output current density with three hydrogen flow arrangements with different voltage operations at 0.65 V and 0.3 V. The average output current densities of three hydrogen flow arrangements in the 0.65-V cases are from 650-1050 A m⁻². At 0.3 V, they are 4000-12000 A m⁻². In comparison with the processes at two operation voltages, the average output current densities of three modes obviously vary at 0.65 V, especially at 250 s, with similar trends to the other low-current operations in Fig. 4 (b). However, at 0.3 V, the cell performance of the DEA mode starts to decrease when the performances of the other modes continuously increase at 75 s, which is caused by the nitrogen crossover and accumulation in the anode [33, 34].

453 Figure 9 displays the evolutions of the ice accumulation distributions in CCL with
454 constant-voltage operations at 0.65 V and 0.3 V. Obviously, during the startup
455 processes, the ice saturation can be over 0.25 in the 0.65-V cases but less than 0.1 in
456 the 0.3-V cases. In 0.3-V cases, there is ice for fewer than 10 s due to the large
457 voltage loss and heat source. Although the larger current in the 0.3-V cases can result
458 in a faster rate of water formation, starting at 0.3 V is better in terms of cold-start
459 capacity.

460 Figure 10 presents the evolutions of the current density distributions (Fig. 10 (a)),
461 temperature distributions (Fig. 10 (b)) and nitrogen concentration distributions (Fig.
462 10 (c)) with a constant-voltage operation at 0.65 V. The FTA and ORA modes have
463 similar trends of current density distribution in the entire processes. At the same place
464 of the channel, the local current density in the FTA mode is a little higher than that in
465 the ORA mode, which corresponds to the curves of FTA and ORA modes in Fig. 8 (a).
466 In the DEA mode, the local current density at the fifth segment decreases over time
467 due to the nitrogen concentration accumulation. The effect of nitrogen accumulation
468 on the ORA mode is not as obvious as that in the DEA mode. Compared with the
469 FTA mode, the nitrogen crossover and gathering slightly affect the output
470 performance in the ORA mode. The same reason is presented in section 4.2. In Fig.
471 10 (c), the highest temperatures are approximately 280 K in the processes and locate
472 near the inlet of the cathode channel in the FTA and ORA modes. In the DEA mode,
473 the highest temperature is at the middle of CCL due to the distribution of local current
474 density.

475 Figure 11 displays the evolutions of the current density distribution (Fig. 11 (a)),
476 temperature (Fig. 11 (b)) and nitrogen concentration distribution (Fig. 11 (c)) with a
477 constant-voltage operation at 0.3 V. The local current densities in the 0.3-V cases
478 exceed 10000 A m^{-2} at 80 s. In the DEA mode, the local current density near the exit
479 of the anode gradually decreases after 60 s because the nitrogen concentration

480 increases to a high level in Fig. 11 (a). According to the experimental results [37], a
481 larger operating current can accelerate the rate of nitrogen crossover and
482 accumulation in the anode, which can be verified in the 0.3-V cases. As we expected,
483 the startup with a low voltage operation can accelerate the process of heating the cell
484 and lead to a rapidly successful cold start. At 80 s, the highest temperatures can
485 exceed 340 K in three modes. For three hydrogen flow arrangements, the differences
486 among temperature distributions can be ignored in a short start time.

487 Generally, the 0.3-V cases have an advantage over the 0.65-V cases with the shorter
488 heating-up time and better uniformity. In the simulation results, the startup with 0.3-V
489 operation can motivate a huge current density and shorten the cold-start process, and
490 the effort of nitrogen crossover can be safely ignored in the DEA and ORA cases
491 compared with the FTA cases due to the startup of 80 s.

492 **4. Conclusion**

493 In the study, the dynamic characteristics in the start-up process with different
494 hydrogen flow arrangements are systematically analyzed for the PEM fuel cell. Based
495 on the numerical investigations, the major conclusions are as follows:

- 496 1. During startup processes, co-flow cases can cause much more ice formation
497 accumulation in CCL than the counter-flow cases. The hydrogen flow
498 arrangements can hardly affect the ice formation distributions.
- 499 2. Starting at a low operating voltage can remarkably shorten the start time and
500 effectively avoid the hydrogen starvation in PEM fuel cells with a dead-ended
501 anode or an off-gas recirculation anode during the startup processes.
- 502 3. The PEM fuel cell with an off-gas recirculation anode or a flow-through anode
503 has similar dynamic characters in startup processes in terms of ice formation, local
504 current density and temperature distributions.

505 4. A PEM fuel cell with a low voltage operation, an off-gas recirculation anode and a
506 counter-flow configuration is the ideal combination during the cold-start process
507 in the items of the best hydrogen utilization efficiency, good anodic nitrogen
508 tolerance, high output performance and good cold-start capacity.

509 In general, the development of the quasi-2D cold-start model and the relative work
510 presented in the study are expected to assist the selections of hydrogen supply
511 arrangements and startup strategies for the cold-start process of the PEM fuel cell. In
512 the future, the more complicated strategy should be considered in the cold-start
513 process including a variable load and heating the coolant. The cold-start model can
514 also be combined with AI technology so that the faster prediction and optimization
515 can be achieved in a few seconds [38, 39]. More practical applications such as online
516 control for PEM fuel cell can be based on the model [39].

517

518 **Acknowledgements**

519 This research is supported by the National Key Research and Development Program
520 of China (Grant No. 2018YFB0105505), National Natural Science Foundation of
521 China for Excellent Young Scholars (Grant No. 51622606), Natural Science
522 Foundation for Outstanding Young Scholars of Tianjin (Grant No. 18JCQJC46700)
523 and China-UK International Cooperation and Exchange Project (Newton Advanced
524 Fellowship) , which is jointly supported by the National Natural Science Foundation
525 of China (Grant No. 51861130359) and the UK Royal Society (Grant No.
526 NAF\R1\180146).

527 **References**

- 528 [1] Jiao K, Ni M. Challenges and opportunities in modelling of proton exchange
529 membrane fuel cells (PEMFC)[J]. International Journal of Energy Research, 2017,
530 41(13).
- 531 [2] Liu F, Zhao F, Liu Z, et al. The impact of fuel cell vehicle deployment on road
532 transport greenhouse gas emissions: The China case[J]. International Journal of
533 Hydrogen Energy, 2018, 43(50): 22604-22621.
- 534 [3] Amamou A , Kandidayeni M , Boulon L, et al. Real time adaptive efficient cold
535 start strategy for proton exchange membrane fuel cells[J]. Applied Energy, 2018,
536 216:21-30.
- 537 [4] Chen H, Song Z , Zhao X , et al. A review of durability test protocols of the
538 proton exchange membrane fuel cells for vehicle[J]. Applied Energy, 2018,
539 224:289-299.
- 540 [5] Luo Y, Jiao K. Cold start of proton exchange membrane fuel cell[J]. Progress in
541 Energy and Combustion Science, 2017, 64: 29-61.
- 542 [6] Tajiri K, Tabuchi Y, Kagami F, et al. Effects of operating and design parameters
543 on PEFC cold start[J]. Journal of Power Sources, 2007, 165(1):279-286.
- 544 [7] Jiao K, Li X. Effects of various operating and initial conditions on cold start
545 performance of polymer electrolyte membrane fuel cells[J]. International Journal
546 of Hydrogen Energy, 2009, 34(19):8171-8184.
- 547 [8] Xie X, Zhang G, Zhou J, et al. Experimental and theoretical analysis of
548 ionomer/carbon ratio effect on PEM fuel cell cold start operation[J]. International
549 Journal of Hydrogen Energy, 2017, 42(17): 12521-12530.
- 550 [9] Yang Z, Du Q, Huo S, et al. Effect of membrane electrode assembly design on
551 the cold start process of proton exchange membrane fuel cells[J]. International
552 Journal of Hydrogen Energy, 2017,42(40):25372-25387.
- 553 [10] Morin A, Peng Z, Jestin J, et al. Water management in proton exchange
554 membrane fuel cell at sub-zero temperatures: An in operando SANS-EIS coupled
555 study[J]. Solid State Ionics, 2013, 252:56-61.

- 556 [11]Lin R, Weng Y, Lin X, et al. Rapid cold start of proton exchange membrane fuel
557 cells by the printed circuit board technology[J]. International Journal of Hydrogen
558 Energy, 2014, 39(32): 18369-18378.
- 559 [12]Lin R, Lin X, Weng Y, et al. Evolution of thermal drifting during and after cold
560 start of proton exchange membrane fuel cell by segmented cell technology[J].
561 International Journal of Hydrogen Energy, 2015, 40(23): 7370-7381.
- 562 [13]Lin R, Ren Y S, Lin X W, et al. Investigation of the internal behavior in
563 segmented PEMFCs of different flow fields during cold start process[J]. Energy,
564 2017, 123: 367-377.
- 565 [14]Zhu Y, Lin R, Jiang Z, et al. Investigation on cold start of polymer electrolyte
566 membrane fuel cells with different cathode serpentine flow fields[J]. International
567 Journal of Hydrogen Energy, 2019, 44(14): 7505-7517.
- 568 [15]Jiao K, Li X. Three-dimensional multiphase modeling of cold start processes in
569 polymer electrolyte membrane fuel cells[J]. Electrochimica Acta, 2009, 54(27):
570 6876-6891.
- 571 [16]Jiao K, Alaefour I E, Karimi G, et al. Cold start characteristics of proton
572 exchange membrane fuel cells[J]. international journal of hydrogen energy, 2011,
573 36(18): 11832-11845.
- 574 [17]Gwak G, Ko J, Ju H. Numerical investigation of cold-start behavior of
575 polymer-electrolyte fuel-cells from subzero to normal operating
576 temperatures—effects of cell boundary and operating conditions[J]. International
577 Journal of Hydrogen Energy, 2014, 39(36): 21927-21937.
- 578 [18]Zhigang Z, Chong Y, Zhangrong H, et al. Experimental study on different
579 preheating methods for the cold-start of PEMFC stacks[J]. Energy, 2018,
580 162:1029-1040.
- 581 [19]Liu Y, Lehnert W, Jan En H , et al. A review of high-temperature polymer
582 electrolyte membrane fuel-cell (HT-PEMFC)-based auxiliary power units for
583 diesel-powered road vehicles[J]. Journal of Power Sources, 2016, 311:91-102.

- 584 [20]Guangjin W, Yi Y, Hai L, et al. Progress on design and development of polymer
585 electrolyte membrane fuel cell systems for vehicle applications: A review[J]. Fuel
586 Processing Technology, 2018, 179:203-228.
- 587 [21]Chen J, Siegel J B, Stefanopoulou A G, et al. Optimization of purge cycle for
588 dead-ended anode fuel cell operation[J]. International Journal of Hydrogen
589 Energy, 2013, 38(12):5092-5105.
- 590 [22]Yesilyurt S, Siegel J B, Stefanopoulou A G. Modeling and experiments of voltage
591 transients of polymer electrolyte membrane fuel cells with the dead-ended
592 anode[J]. Journal of Fuel Cell Science and Technology, 2012, 9(2): 021012.
- 593 [23]Yang C W, Chen Y S. A mathematical model to study the performance of a
594 proton exchange membrane fuel cell in a dead-ended anode mode[J]. Applied
595 Energy, 2014, 130: 113-121.
- 596 [24]Yang Y, Zhang X, Guo L, et al. Overall and local effects of operating conditions
597 in PEM fuel cells with dead-ended anode[J]. International Journal of Hydrogen
598 Energy, 2017, 42(7): 4690-4698.
- 599 [25]Bao C, Ouyang M, Yi B. Modeling and control of air stream and hydrogen flow
600 with recirculation in a PEM fuel cell system—I. Control-oriented modeling[J].
601 International journal of hydrogen energy, 2006, 31(13): 1879-1896.
- 602 [26]Wang B, Deng H, Jiao K. Purge strategy optimization of proton exchange
603 membrane fuel cell with anode recirculation[J]. Applied Energy, 2018, 225: 1-13.
- 604 [27]Ahluwalia R K, Wang X. Buildup of nitrogen in direct hydrogen
605 polymer-electrolyte fuel cell stacks[J]. Journal of Power Sources, 2007, 171(1):
606 63-71.
- 607 [28]Promislow K, St-Pierre J, Wetton B. A simple, analytic model of polymer
608 electrolyte membrane fuel cell anode recirculation at operating power including
609 nitrogen crossover[J]. Journal of Power Sources, 2011, 196(23): 10050-10056.

610 [29]Wang B, Wu K, Yang Z, et al. A quasi-2D transient model of proton exchange
 611 membrane fuel cell with anode recirculation[J]. Energy conversion and
 612 management, 2018, 171: 1463-1475.

613 [30]Huo S, Jiao K, Park J W. On the water transport behavior and phase transition
 614 mechanisms in cold start operation of PEM fuel cell[J]. Applied Energy, 2019,
 615 233: 776-788.

616 [31]Jiao K, Li X. Water transport in polymer electrolyte membrane fuel cells[J].
 617 Progress in Energy & Combustion Science, 2011, 37(3):221-291.

618 [32]Chen Y S, Yang C W, Lee J Y. Implementation and evaluation for anode purging
 619 of a fuel cell based on nitrogen concentration[J]. Applied Energy, 2014,
 620 113(1):1519-1524.

621 [33]Lee, Heng-Yi, Su, et al. A gas management strategy for anode recirculation in a
 622 proton exchange membrane fuel cell[J]. International Journal of Hydrogen
 623 Energy, 2018, 43(7):3803-3808.

624 [34]Wang B, Wu K, Xi F, et al. Numerical analysis of operating conditions effects on
 625 PEMFC with anode recirculation[J]. Energy, 2019, 173(4):844-856.

626 [35]Livshits V, Ulus A, Peled E. High-power H₂/Br₂ fuel cell[J]. Electrochemistry
 627 communications, 2006, 8(8): 1358-1362.

628 [36]Mathias M F, Makharia R, Gasteiger H A, et al. Two fuel cell cars in every
 629 garage[J]. Electrochem. Soc. Interface, 2005, 14(3): 24-35.

630 [37]Rabbani R A , Rokni M . Effect of nitrogen crossover on purging strategy in PEM
 631 fuel cell systems[J]. Applied Energy, 2013, 111(11):1061-1070.

632 [38]A. Bejan. AI and freedom for evolution in energy science[J]. Energy and AI,
 633 accepted.

634 [39]Wang B, Zhang G, Wang H, et al. Multi-Physics-Resolved Digital Twin of
 635 Proton Exchange Membrane Fuel Cells with A Data-Driven Surrogate Model[J].
 636 Energy and AI, accepted.