

1 **Numerical analysis of the optimum membrane/ionomer water content of**  
2 **PEMFCs: The interaction of Nafion® ionomer content and cathode relative**  
3 **humidity**

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## 30 Abstract

31 A two dimensional, across the channel, isothermal, two-phase flow model for proton exchange membrane  
32 fuel cells (PEMFCs) is developed to investigate the interaction of dry Nafion® ionomer volume fraction ( $L_M^{\text{dry}}$ )  
33 and cathode relative humidity ( $RH_c$ ) in PEMFCs. The agglomerate model is used to describe the catalyst layers  
34 properties, in which the agglomerate is covered by ionomer and liquid water films. The optimum ionomer water  
35 content is suggested by maximising the oxygen diffusion rate through the ionomer film. The effects of  $L_M^{\text{dry}}$  and  
36  $RH_c$  on membrane and ionomer swelling and the cell performance are studied. The predicted current densities at  
37 a fixed cell voltage are analysed by the Kriging surrogate model and used to optimise the  $L_M^{\text{dry}}$  and  $RH_c$  based on  
38 analysing their interaction. The simulation results show that the optimum ionomer water content increases as the  
39 ionomer content increases. At higher current densities, e.g.  $1.0 \text{ A cm}^{-2}$ , the best cell performance is achieved  
40 with  $L_M^{\text{dry}}$  of 10%, corresponding to  $0.3 \text{ mg cm}^{-2}$ , with fully humidified inlet gases. The optimum  $RH_c$  is between  
41 60% to 80% for  $L_M^{\text{dry}}$  of 40%. The modelling results also show that at higher current densities, the optimum  $RH_c$   
42 initially decreases then increases as  $L_M^{\text{dry}}$  increases. The optimum  $RH_c$  decreases from 76% to 73% as  $L_M^{\text{dry}}$   
43 increases from 10% to 30% then it increases up to 85% as  $L_M^{\text{dry}}$  increases to 50%.

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56 **Key words:** proton exchange membrane fuel cell; two-phase flow; membrane and ionomer swelling; ionomer  
57 content; relative humidity; mathematical model

## 58 Nomenclature

|              |   |
|--------------|---|
| $A_s$        | reaction surface area per unit platinum mass, $\text{m}^2 \text{kg}^{-1}$ |
| $a$          | specific area, $\text{m}^{-1}$  |
| $c$          | concentration, $\text{mol m}^{-3}$  |
| $D$          | diffusivity, $\text{m}^2 \text{s}^{-1}$                                   |
| $D_c$        | capillary diffusion coefficient, $\text{m}^2 \text{s}^{-1}$               |
| $D_{ij}$     | Maxwell-Stefan diffusion coefficient matrix, $\text{m}^2 \text{s}^{-1}$   |
| $E$          | effectiveness factor  |
| $E^{cell}$   | cell voltage, V   |
| $EW$         | equivalent weight of membrane, $\text{g mol}^{-1}$                        |
| $F$          | Faraday's constant, $96485 \text{ C mol}^{-1}$                            |
| $f$          | platinum mass ratio to $Pt/C$   |
| $H$          | Henry's constant, $\text{Pa m}^3 \text{mol}^{-1}$                         |
| $i$          | current density, $\text{A m}^{-2}$  |
| $i_0$        | exchange current density, $\text{A m}^{-2}$                               |
| $J(s)$       | Leverett function   |
| $k$          | rate coefficient, $\text{s}^{-1}$   |
| $k_r$        | relative permeability   |
| $k_p$        | hydraulic permeability, $\text{m}^2$                                      |
| $l$          | thickness, m  |
| $L$          | volume fraction   |
| $M_j$        | molecular weight for specie j, $\text{kg mol}^{-1}$                       |
| $M_T$        | Thiele's modulus  |
| $m$          | mass loading, $\text{mg cm}^{-2}$   |
| $N$          | number per volume, $\text{m}^{-3}$  |
| $n$          | number  |
| $p$          | pressure, Pa  |
| $\mathbf{q}$ | unity vector  |
| $\mathbf{R}$ | symmetric correlation matrix  |

|              |   |
|--------------|---|
| $R$          | ideal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ |
| $RH$         | relative humidity   |
| $\mathbf{r}$ | correlation vector  |
| $r$          | radius, m   |
| $S$          | source term   |
| $s$          | liquid water saturation                                       |
| $T$          | temperature, K  |
| $\mathbf{u}$ | velocity vector, $\text{m s}^{-1}$                            |
| $V$          | mole volume, $\text{m}^3$                                     |
| $w$          | mass fraction   |
| $X$          | normalised distance   |
| $\mathbf{x}$ | design matrix of sample                                       |
| $x$          | mole fraction   |
| $Y$          | normalised distance ( $z/(H_{\text{Rib}} + H_{\text{Ch}})$ )  |
| $\%M$        | volume fraction of primary pores occupied by ionomer          |

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60 *Greek*

|               |  |
|---------------|--|
| $\alpha$      | charge transfer coefficient                                |
| $\alpha_w$    | water activity   |
| $\beta$       | known approximation function                               |
| $\lambda$     | water content  |
| $\mu$         | viscosity, Pa s  |
| $\rho$        | density, $\text{kg m}^{-3}$                                |
| $\varepsilon$ | porosity   |
| $\delta$      | thickness of ionomer/liquid water coating, m               |
| $\gamma$      | oxygen diffusion rate through the coating, $\text{s}^{-1}$ |
| $\theta_i$    | unknown correlation parameters                             |
| $\sigma$      | surface tension, $\text{N m}^{-1}$                         |
| $\theta_c$    | contact angle, $^\circ$                                    |

|  |            |  |
|--|------------|--|
|  | $\sigma_s$ | electronic conductivity, S m <sup>-1</sup>         |
|  | $\sigma_M$ | ionic conductivity, S m <sup>-1</sup>              |
|  | $\varphi$  | potential, V                                       |
|  | $\Psi_w$   | association parameter for water (the value is 2.6) |

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62 *Superscripts*

|  |            |             |
|--|------------|-------------|
|  | <i>0</i>   | intrinsic   |
|  | <i>d</i>   | dissolved   |
|  | <i>eff</i> | effective   |
|  | <i>ref</i> | reference   |
|  | <i>eq</i>  | equilibrium |
|  | <i>l</i>   | liquid      |
|  | <i>g</i>   | gas         |

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64 *Subscripts*

|  |             |                           |
|--|-------------|---------------------------|
|  | <i>a</i>    | anode                     |
|  | <i>ads</i>  | adsorption                |
|  | <i>agg</i>  | agglomerate               |
|  | <i>C</i>    | carbon                    |
|  | <i>c</i>    | cathode                   |
|  | <i>CL</i>   | catalyst layer            |
|  | <i>des</i>  | desorption                |
|  | <i>GDL</i>  | gas diffusion layer       |
|  | <i>i</i>    | species i                 |
|  | <i>j</i>    | species j                 |
|  | <i>Kn</i>   | Knudsen diffusion         |
|  | <i>M</i>    | membrane or ionomer in CL |
|  | <i>P</i>    | void space                |
|  | <i>Pt</i>   | platinum                  |
|  | <i>Pt/C</i> | platinum dispersed carbon |

|            |                     |
|------------|---------------------|
| <i>p</i>   | primary pores       |
| <i>r</i>   | relative            |
| <i>S</i>   | GDL penetration     |
| <i>s</i>   | secondary pores     |
| <i>w</i>   | liquid water        |
| <i>sat</i> | saturation          |
| <i>tot</i> | total               |
| <i>vl</i>  | vapour to liquid    |
| <i>vd</i>  | vapour to dissolved |
| <i>dl</i>  | dissolved to liquid |

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# 85 1. Introduction

86 Proton exchange membrane fuel cells (PEMFCs) are promising energy conversion devices for portable and  
87 stationary applications due to their high energy conversion efficiency, power density and environmental  
88 friendliness [1-4]. PEMFCs-batteries and PEMFC-CHP (combined heat and power) systems are emerging  
89 technologies for hybrid automotive and residential applications benefited from their flexibility and scalability  
90 [5-8]. Although significant improvements on PEMFC performance have been achieved over the decades,  
91 sluggish oxygen reduction reaction (ORR) occurred in the cathode catalyst layer (CCL) and inadequate  
92 membrane hydration are hampering to achieve the full potential of PEMFCs [9-13]. Therefore, understanding  
93 electrochemical reactions and associated mass transport in the three dimensional (3D) porous catalyst layers  
94 (CLs) and interaction between membrane/ionomer swelling and cell performance are important, which can be  
95 achieved using ultra-thin layer, pseudo-homogeneous film or spherical-agglomerate models. However, ultra-thin  
96 layer model and pseudo-homogeneous film model cannot resolve the influence of the structural morphology on  
97 the diffusion-reaction processes [14]. On the other hand, spherical-agglomerate model can provide a superior  
98 representation of the porous CL in comparison to ultra-thin layer and pseudo-homogeneous film models [11, 15,  
99 16].

100 During fuel cell operation, ionic conductivity and structure of the membrane and ionomer strongly depend on  
101 their water content and membrane/ionomer swelling. Typically, dry Nafion® membrane/ionomer swells  
102 approximately 20% when fully hydrated by water vapour [17, 18]. Membrane swelling increases the ionic  
103 conductivity and water diffusion coefficient, while ionomer swelling increases the thickness of the ionomer  
104 film surrounding the agglomerate and decreases the void space within the CCL, leading to an increase in species  
105 transport resistance, especially the oxygen diffusion [17]. Depending on the directions of membrane swelling,  
106 two types of membrane deformation can co-exist: the through-plane membrane thickness increase and the in-  
107 plane membrane buckling [19-21]. The through-plane membrane thickness increase is caused by the zero or low  
108 clamping force from gas flow fields to the membrane electrode assembly (MEA) [21]. Due to the fact that the  
109 membrane is constrained between the bipolar plates under a relative high clamping force, membrane swelling  
110 does not occur under the current collector's ribs. However, the membrane thickness increases under the channel  
111 of the gas flow field, which can have a significant impact on the ~~channel-reactant~~ flow in the channel, water-  
112 droplet removal from the gas diffusion layer (GDL) surface, and species transport as the ~~gas-diffusion-layer~~  
113 ~~(GDL)~~ bulges into the channel (see Fig. 3). Moreover, the bulged GDL into the flow channels could lead to a

114 pinhole formation of the membrane under the channel and higher adhesion forces between liquid-water droplet  
115 GDL surfaces [19, 22, 23]. Therefore, water removal would require higher gas flow rate, which would  
116 eventually reduce the cell performance.

117 Water transport through the membrane/ionomer also plays a crucial role in determining the  
118 membrane/ionomer water content [9, 17]. Water transport in fuel cells occurs via three mechanisms: electro-  
119 osmotic drag (EOD), back diffusion and hydraulic permeation. Water exists as three different phases [24, 25]:  
120 dissolved water in the membrane/ionomer (membrane/ionomer absorbed water), water vapour and liquid water  
121 in the porous media. The water phase-transfer occurred in terms of water vapour condensation, liquid water  
122 evaporation, membrane/ionomer water uptake and desorption significantly affect the membrane/ionomer water  
123 content and liquid water saturation [25-28]. Membrane desorption and water vapour condensation are believed  
124 to be the two main sources for liquid water generation in the porous electrode. Therefore, the two-phase flow  
125 between liquid water and reactant gas cannot be neglected. The earliest multi-phase mixture ( $M^2$ ) model for  
126 multi-component transport in capillary porous media was developed by Wang et al. [29], in which the multiple  
127 phases were simplified as constituents of a multi-phase mixture. The  $M^2$  model was combined with the volume  
128 of fluid (VOF) method to describe the liquid water transport in the porous electrode by Wang and his co-  
129 workers [30-32]. Nam and Kaviany [33] studied the water saturation in the porous media and highlighted its  
130 tendency in reducing the effective mass diffusivity. Based on the combined two-phase flow agglomerate model  
131 developed by Lin et al. [34], the liquid water was assumed as a thin film surrounding the agglomerate in the  
132 improved model developed by Shah et al. [17]. Although the membrane swelling, ~~and~~ liquid-water transport,  
133 water-droplet detachment have been investigated by numerous experimental and numerical studies [19-26, 29-  
134 35], very few take the ionomer swelling into consideration.

135 Controlling MEA composition and fuel cell operation conditions can practically improve the cell  
136 performance and durability. Fonseca et al. [36] applied a non-linear control strategy to the PEMFC air supply  
137 subsystem, which is capable of regulating the oxygen stoichiometry and cathode pressure, to prevent side  
138 degradation effects. Bizon [37] maximised the fuel cell net power by optimising the air flow rate based on  
139 extremum seeking (ES) control scheme. Cheng et al. [38] promoted the cell power density using metamodelling  
140 optimal approach in which cell operating temperature, humidification temperatures of anode and cathode,  
141 hydrogen and oxygen stoichiometric flow ratios were studied. The effect of dry ionomer content and relative  
142 humidity ( $RH$ ) of gas inlet on cell performance has been separately studied [27, 39-41]. The combined effects of



143 ionomer content and  $RH$  on cell performance at various current densities are rarely experimentally studied by  
144 Jang et al. [42, 43]. However, their interaction has not been numerically investigated.

145 In this study, a two dimensional, across the channel (ATC), two-phase flow model, based on a spherical-  
146 agglomerate catalyst structure, combined with a comprehensive water phase-transfer and transport mechanism is  
147 developed- with the aim of studying mMembrane and ionomer swelling, liquid water saturation and cell  
148 performance with various dry ionomer content and  $RH_c$ -~~are numerically studied~~. A Kriging surrogate model is  
149 used to optimise the dry ionomer content and  $RH_c$  based on the analysis of their interaction on  
150 membrane/ionomer swelling and cell performance.

## 151 2. Model description

### 152 2.1 Model features and assumptions

153 The model features and main assumptions are listed as follow:

154 (1) *Fuel cell geometry and computational domain.* The 2D representation of the computational domain of a  
155 PEMFC is shown in Fig. 1, which includes five domains, namely anode GDL (domain 1), ACL (domain 2) on  
156 Nafion<sup>®</sup> membrane (domain 3), CCL (domain 4) and cathode GDL (domain 5). The geometric and structural  
157 parameters as well as the material properties of each layer are listed in Table 1.

158 (2) *Reactant transport.* The feed gases at both anode and cathode are treated as ideal gases and are transported  
159 through diffusion in GDL and CL. Assuming the membrane is non-permeable to hydrogen, oxygen and nitrogen.  
160 Only dissolved water and protons for the species transport are accounted through the membrane.

161 (3) *Catalyst layer structure.* The spherical agglomerate model is adopted for the catalyst structure. Assuming  
162 each agglomerate consists of three components: platinum dispersed carbon (Pt/C), ionomer and void space. The  
163 void space within the agglomerate is defined as the *primary pores* and the void space between the agglomerate  
164 is defined as the *secondary pores*. As shown in Fig. 2, the *primary pores* are partially occupied by the ionomer,  
165 whereas the *secondary pores* are partially occupied by the ionomer and liquid water surrounding the  
166 agglomerate.

167 (4) *Liquid water.* Liquid water only exists in the cathode, which is generated by water vapour condensation and  
168 membrane/ionomer desorption. It is assumed that it only exists as the liquid water coating surrounding the  
169 agglomerate. This is because, for the hydrophobic CCL, liquid water is first generated in the *secondary pores*  
170 with the increase in saturation [17, 44].

171 (5) *Dissolved water*. Water absorbed in the membrane/ionomer is in the dissolved phase, which enters the  
172 membrane/ionomer from the vapour phase during water uptake and leaves the membrane in the liquid phase  
173 when the water content reaches complete saturation. The product water in the CCL is generated in the dissolved  
174 phase.

175 (6) *Membrane and ionomer swelling*. As shown in Fig. 3, due to the fact that the catalyst layer is very thin in  
176 comparison to the membrane, it is reasonable to assume that the membrane swelling leads to a half ellipse  
177 through-plane membrane deformation within channel portions at grooved gas flow field while the ionomer  
178 swelling only enlarge the ionomer coating thickness without changing the CCL thickness.

## 179 **2.2 Numerical methodology**

180 The flowchart of the computation process is shown in Fig.4. The volume fraction of dry ionomer in the CCL  
181 ( $L_M^{\text{dry}}$ ) and cathode relative humidity ( $RH_c$ ) are selected as the independent design variables, 30 sets of samples  
182 with different combination of them are randomly generated using the modified Latin Hypercube Sampling  
183 method [45]. Finite element analysis is performed on the individual samples to simulate their current densities at  
184 a fixed voltage of 0.35 V. Then a Kriging surrogate model [46] of the current density is generated based on the  
185 30 sets of numerical simulation to estimate the other untried combination to avoid large computational burden.  
186 The surrogate model is then employed to investigate the interaction of the two factors and to obtain the optimum  
187 solution of  $L_M^{\text{dry}}$  and  $RH_c$  for the purpose of improving the power output at the given voltage.

## 188 **2.3 Finite element model (Governing equations)**

### 189 **2.3.1 Thicknesses of membrane and ionomer coating in case of swelling**

190 Because the CL is very thin compared with the gas diffusion layer and membrane, the volume increase of CL  
191 therefore can be neglected while the ionomer swelling occurred simultaneously. It is reasonable to assume that  
192 the ionomer swelling only increases the thickness of the ionomer coating surrounding the agglomerate and  
193 decreases the volume fraction of the void space. By further assuming the shape of the swelled membrane is a  
194 half ellipse as shown in Fig. 3, the minor and major radius can be calculated as follow:

$$195 \quad x = \frac{4k_s \lambda l_M (H_{Rib} + H_{Ch})}{\pi H_{Ch}} \quad (1)$$

$$196 \quad y = \frac{H_{Ch}}{2} \quad (2)$$

197 where  $x$  (m) and  $y$  (m) are the minor radius and the major radius, respectively.  $H_{Rib}$  (m) and  $H_{Ch}$  (m) are the  
 198 widths of rib and channel, respectively.  $l_M$  (m) is the membrane thickness. When ionomer swelling, the volume  
 199 fraction of the ionomer in the CCL increases to:

$$200 \quad L_M^{swell} = (1 + k_s \lambda) L_M^{dry} \quad (3)$$

### 201 2.3.2 Catalyst layer property

202 Based on the single-phase and two-phase flow models developed earlier [27, 28, 46], the key parameters used  
 203 for representing the agglomerate structure of the catalyst layer are shown as follow:

$$204 \quad \text{Volume fraction of the platinum dispersed carbon (Pt/C): } L_{Pt/C} = \frac{m_{Pt}}{l_{CL}} \left( \frac{1}{\rho_{Pt}} + \frac{1-f}{f} \frac{1}{\rho_C} \right) \quad (4)$$

$$205 \quad \text{Platinum mass ratio to that of carbon: } f = \frac{m_{Pt}}{m_{Pt} + m_C} \quad (5)$$

$$206 \quad \text{Volume fraction of the solid portion of the GDL penetrating into the CL: } L_S = L_{GDL} (1 - \varepsilon_{GDL}) \quad (6)$$

$$207 \quad \text{Porosity of the CL: } \varepsilon_{CL} = 1 - L_M^{swell} - L_S - L_{Pt/C} \quad (7)$$

$$208 \quad \text{Agglomerate density in the CL: } N_{agg} = \frac{3L_{Pt/C}}{4(1 - \varepsilon_{CL})\pi r_{agg}^3} \quad (8)$$

$$209 \quad \text{Specific areas of the agglomerate without liquid water coating: } a_{agg}^M = \frac{m_{Pt}(1 - \varepsilon_{CL})A_s}{l_{CL}L_{Pt/C}} \quad (9)$$

$$210 \quad \text{Specific area of the agglomerate with liquid water coating: } a_{agg}^w = a_{agg}^M \left( 1 + \frac{\delta_w}{r_{agg}} \right)^2 \quad (10)$$

$$211 \quad \text{Thickness of the ionomer coating: } \delta_M = r_{agg} \left( \sqrt[3]{\frac{(1 - \varepsilon_{CL})(1 - \varepsilon_{CL} - L_S) + L_{Pt/C} \varepsilon_{CL} (1 - \%M)}{L_{Pt/C}}} - 1 \right) \quad (11)$$

$$212 \quad \text{Thickness of the liquid water coating: } \delta_w = \sqrt[3]{(r_{agg} + \delta_M)^3 + \frac{s \varepsilon_{CL} (1 - \varepsilon_{CL}) r_{agg}^3}{L_{Pt/C}}} - (r_{agg} + \delta_M) \quad (12)$$

213 In Eq. (9), the reaction surface area per unit platinum mass is [47]:

$$214 \quad A_s = (227.79 f^3 - 158.57 f^2 - 201.53 f + 159.5) \times 10^3 \quad (13)$$

215 In Eq. (11),  $\%M$  is the volume fraction of the primary pores occupied by the ionomer.

216 Eq. (1) and Eq. (2) are solved on domain 3, the membrane only. Eqns. (3-13) are solved on domains 2 and 4,  
 217 both the anode and cathode CLs.

### 218 2.3.3 Oxygen diffusion and reaction

219 The cathode volumetric current density based on the agglomerate model is [17]

$$220 \quad \nabla i_{c,s} = i_{c,agg} = 4F \frac{p_{O_2}}{H_{O_2}} \left[ \frac{1}{E_{agg} k_{agg}} + \frac{(r_{agg} + \delta)}{\gamma_{agg}} \right]^{-1} \quad (14)$$

221 where  $p_{O_2}$  (Pa) is the partial pressure of oxygen,  $H_{O_2}$  (Pa m<sup>3</sup> mol<sup>-1</sup>) is Henry's constant for dissolved oxygen in  
 222 ionomer/liquid water film,  $k_{agg}$  (s<sup>-1</sup>) is the reaction rate coefficient,  $E_{agg}$  is the effectiveness factor of the  
 223 agglomerate,  $\gamma$  (s<sup>-1</sup>) is the oxygen diffusion rate through the ionomer/liquid water film to the agglomerate  
 224 interface and  $\delta$  (m) is the total thickness of the ionomer and liquid water film.

$$225 \quad \gamma = \frac{\gamma_M \gamma_w}{\gamma_M + \gamma_w}, \quad \gamma_M = \frac{a_{agg}^M D_{O_2-M}}{\delta_M}, \quad \gamma_w = \frac{a_{agg}^w D_{O_2-w}}{\delta_w}, \quad \delta = \delta_M + \delta_w \quad (15)$$

226 The effectiveness factor of the agglomerate is given by

$$227 \quad E_{agg} = \frac{1}{M_{T,agg}} \left[ \frac{1}{\tanh(3M_{T,agg})} - \frac{1}{3M_{T,agg}} \right] \quad (16)$$

228 where  $M_{T,agg}$  is the Thiele's modulus for spherical agglomerate, given as [11, 17]:

$$229 \quad M_{T,agg} = \frac{r_{agg}}{3} \sqrt{\frac{k_{agg}}{D_{O_2,agg}^{eff}}} \quad (17)$$

230 By combining Butler-Volmer (B-V) kinetics with the effectiveness factor of the agglomerate, the reaction rate  
 231 coefficient of the ORR within the agglomerate is represented as:

$$232 \quad k_{agg} = \frac{a_{agg}^M i_{0,c}^{ref}}{4F c_{O_2}^{ref}} \left[ \exp\left(\frac{-\alpha_c F \eta_c}{RT}\right) - \exp\left(\frac{(1-\alpha_c) F \eta_c}{RT}\right) \right] \quad (18)$$

233 Due to the higher diffusivity and permeability of hydrogen into the ionomer and water, the effectiveness factor  
 234 of the hydrogen oxidation reaction (HOR) at anode is set to 1.0. This will simplify the kinetics expression at the  
 235 anode. Thus, the HOR kinetics can be represented by B-V kinetics as [27, 28]:

$$236 \quad \nabla i_{a,s} = i_{a,BV} = a_{agg}^M i_{0,a}^{ref} \left( \frac{p_{H_2}}{c_{H_2}^{ref} H_{H_2}} \right)^{0.5} \left[ \exp\left(\frac{-(1-\alpha_a) F \eta_a}{RT}\right) - \exp\left(\frac{\alpha_a F \eta_a}{RT}\right) \right] \quad (19)$$

237 Because of the weak dependence of the anode charge transfer coefficient ( $\alpha_a$ ), anode reference exchange  
 238 current density ( $i_{0,a}^{ref}$ ) and hydrogen solubility ( $H_{H_2}$ ) on temperature, these parameters are assumed as constant

239 over the operating temperature range. The electrochemical parameters used in this model are listed in Table 2.  
 240 The transport parameters, which are given by the temperature, pressure and/or water content dependent  
 241 expressions, are shown in Table 3.

242 By taking the Knudsen diffusion into account, the equivalent diffusion coefficient of oxygen in the void space is

$$243 \quad \frac{1}{D_{O_2-P}} = \frac{1}{D_{O_2-g}} + \frac{1}{D_{Kn}} \quad (20)$$

244 According to the assumptions, the secondary pores are partially occupied by the liquid water therefore the  
 245 volume fraction of the void space is reduced. The effective diffusion coefficient of oxygen in the secondary  
 246 pores before reaching the agglomerate is corrected using Bruggeman approximation to account for the presence  
 247 of liquid water as:

$$248 \quad D_{O_2,s}^{eff} = [\varepsilon_s (1 - s_s)]^{1.5} D_{O_2-P} \quad (21)$$

249 where  $s_s$  is the corrected liquid water saturation, defining as the volume fraction of the secondary pores  
 250 occupied by the liquid water, relates to  $s$  via:

$$251 \quad s_s = s \frac{\varepsilon_{CL}}{\varepsilon_s} \quad (22)$$

252  $s$  is the liquid water saturation, defined as the volume fraction of the entire pores occupied by the liquid water.

253 Because no liquid water exists in the primary pores, oxygen diffusion within the agglomerate is calculated by:

$$254 \quad D_{O_2,p}^{eff} = (\varepsilon_{agg,M})^{1.5} D_{O_2-M} + (\varepsilon_{agg,p})^{1.5} D_{O_2-P} \quad (23)$$

255 Eqns. (14-19) are solved on domains 2 and 4, both the anode and cathode CLs. Eqns. (20-23) are solved on  
 256 domains 4 and 5, the cathode GDL and CCL.

### 257 **2.3.4 Two-phase flow model for liquid water transport**

258 By applying the volume average approach to the continuity equation and then utilising Darcy's law for both  
 259 the liquid and gas phases [24-28], the governing equation for the liquid water transport is expressed as:

$$260 \quad \frac{\partial}{\partial t} (\varepsilon \rho_w^l s) + \nabla \cdot (\rho_w^l D_c \nabla s - \frac{\rho_w^l k_r^l \mu_w^g}{k_r^g \mu_w^l} \mathbf{u}^g) = M_w S_w^l \quad (24)$$

261 where  $\varepsilon$  is the porosity of CL or GDL,  $\rho_w^l$  (kg m<sup>-3</sup>) is the liquid water density,  $\mathbf{u}^g$  (m s<sup>-1</sup>) is the velocity vector  
 262 of gas mixture,  $D_c$  (m<sup>2</sup> s<sup>-1</sup>) is defined as the capillary diffusion coefficient,  $M_w$  (kg m<sup>-1</sup>) is the water molecular

263 weight,  $\mu_w^g$  and  $\mu_w^l$  (Pa s) are the dynamic viscosity of liquid water and gas mixture, respectively.  $k_r^g$  and  $k_r^l$   
 264 are the relative permeability of liquid and gas phase, respectively.  
 265 The mole fractions of gas species in the gas mixture can be known using the continuity equation associated with  
 266 Darcy's law and the Maxwell-Stefan equation as follow:

$$267 \quad \nabla \cdot \left( \frac{\rho^g k_p}{\mu^g} \nabla p \right) = -S_m \quad (25)$$

$$268 \quad -\rho^g \mathbf{u}^g \cdot \nabla w_i^g - \nabla \cdot \left[ -\rho^g \sum_{j=1}^N (1-s_j) D_{ij} (\nabla x_j^g - w_j^g) \frac{\nabla p}{p} \right] = -M_i S_i^g \quad (26)$$

269 where  $w_i^g$ ,  $x_j^g$ ,  $M_i$  (kg mol<sup>-1</sup>) are the mass fraction, mole fraction and molecular weight of the species  $i$ ,  
 270 respectively,  $D_{ij}$  (m<sup>2</sup> s<sup>-1</sup>) is the multi-component diffusion coefficient. The source terms,  $S_w^l$ ,  $S_m$  and  $S_i^g$   
 271 (mol m<sup>-3</sup> s<sup>-1</sup>), are given in detail in Table 4 and Table 5.  
 272 Eq. (24) is solved on domains 4 and 5, the cathode GDL and CCL only, while Eqns. (25-26) are solved on all  
 273 domains except domain 3, the membrane.

### 274 2.3.5 Dissolved water transport through the membrane

275 For the dissolved water, by following the traditional diffusive approach, a second order partial differential  
 276 equation (PDE) is developed as follows:

$$277 \quad \frac{\partial}{\partial t} (L_M c_w^d) + \nabla \cdot \left( n_d \frac{i_M}{F} \right) - \nabla \cdot (D_{w-M} \nabla c_w^d) - \nabla \cdot \left( \frac{k_{p,M} c_w^d}{\mu_w} \nabla p \right) = S_w^d \quad (27)$$

278 The term on the left hand side of the equation refers to the water accumulation, water migration by electro-  
 279 osmotic drag (EOD), the back diffusion and the hydraulic permeation, respectively. where  $L_M$  is the volume  
 280 fraction of ionomer ( $L_M=1$  in membrane,  $0 < L_M < 1$  in CL),  $c_w^d$  (mol m<sup>-3</sup>) is the concentration of the dissolved  
 281 water,  $n_d$  is the EOD coefficient,  $D_{w-M}$  (m<sup>2</sup> s) is the diffusion coefficient of water through membrane,  $k_{p,M}$   
 282 (m<sup>2</sup>) is the hydraulic permeability of water in the membrane,  $\mu_w$  (Pa s) is the water viscosity,  $p$  (Pa) is the  
 283 pressure.  $S_w^d$  (mol m<sup>-3</sup> s<sup>-1</sup>) is the source term, which is shown in Table 4 and Table 5.  
 284 Nafion® membrane/ionomer swells when absorbing water until it reaches the saturation level, the concentration  
 285 of dissolved water depends on the water content of the membrane as [17]:

286 
$$c_w^d = \frac{\rho_M}{EW} \frac{\lambda}{1 + k_s \lambda} \quad (28)$$

287 where  $EW$  ( $\text{g mol}^{-1}$ ) is the equivalent weight of membrane,  $\rho_M$  ( $\text{kg m}^{-3}$ ) is the density of dry membrane.

288 The equilibrium water content is determined by empirical correlations which were based on water uptake  
289 measurements [24], given as:

290 
$$\lambda^{eq} = \begin{cases} 0.3 + 6\alpha_w [1 - \tanh(\alpha_w - 0.5)] + 3.9\sqrt{\alpha_w} [1 + \tanh(\frac{\alpha_w - 0.89}{0.23})] & , s \leq 0 \\ 16.8s + 14.0(1 - s) & , s > 0 \end{cases} \quad (29)$$

291 The actual water content is proposed as a function of water activity

292 
$$\lambda = 0.043 + 17.81\alpha_w - 39.85\alpha_w^2 + 36.0\alpha_w^3 \quad \alpha_w \leq 1 \quad (30)$$

293 where  $\alpha_w$  is a function of both water vapour partial pressure and liquid water saturation [26], expressed as:

294 
$$\alpha_w = x_w \frac{P}{P_{sat}} + 2s \quad (31)$$

295 Note that the diffusion coefficient of water through the membrane/ionomer is a function of the  
296 membrane/ionomer temperature and water content via

297 
$$D_{w-M} = \begin{cases} D_{w-M}^0 (2.563 - 0.33\lambda + 2.64 \times 10^{-2} \lambda^2 - 6.71 \times 10^{-4} \lambda^3) & \lambda > 4 \\ D_{w-M}^0 (6.65 - 1.25\lambda) & 3 < \lambda \leq 4 \\ D_{w-M}^0 (2.05D_{w-M}^0 - 3.25) & 2 < \lambda \leq 3 \end{cases} \quad (32)$$

298 
$$D_{w-M}^0 = 1.0 \times 10^{-10} \exp[2416(1/303 - 1/T)] \quad (33)$$

299 Eqns. (27-33) are solved on domains 2, 3 and 4, both the anode and cathode CLs and the membrane.

### 300 2.3.6 Charge transport

301 In CLs of anode and cathode, conservation of the charge balance leads to the following equation as:

302 
$$\nabla i_s + \nabla i_M = 0 \quad (34)$$

303 According to Ohm's law, the governing equations for the electronic and ionic charge transport are

304 
$$i_s = -\sigma_s^{eff} \nabla \phi_s, \quad i_M = -\sigma_M^{eff} \nabla \phi_M \quad (35)$$

305 where  $\phi_s$  and  $\phi_M$  (V) are the potential of solid phase and electrolyte phase, respectively.  $\sigma_s^{eff}$  and  $\sigma_M^{eff}$  ( $\text{S m}^{-1}$ )  
306 are the effective electronic and ionic conductivity of the catalyst layer, respectively. The effective electronic  
307 conductivity is estimated using a Bruggeman correction as it provides a good approximation for effective

308 electronic conductivity [48], whereas the effective ionic conductivity estimated using the equation developed by  
 309 Kamarajugadda et al. [49] as:

$$310 \quad \sigma_s^{eff} = (L_{Pt/C})^{1.5} \sigma_s \quad (36)$$

$$311 \quad \sigma_M^{eff} = (1 - \varepsilon_{CL}) \left[ 1 + \frac{(\varepsilon_{agg,M} - 1)}{(1 + \delta_M / r_{agg} + a_0)^3} \right] \sigma_M \quad (37)$$

312 The intrinsic membrane/ionomer electronic and ionic conductivities are given in Table 1 and Table 3. Eqns. (34-  
 313 37) are solved on all domains.

## 314 2.4 Kriging surrogate model

315 In simulation-based design optimisation, an objective function usually requires a large number of simulations,  
 316 which might be too computationally expensive to achieve even with a high-performance computer. In this work,  
 317 a surrogate model known as Kriging based on deterministic simulation is used to replace the realistic unknown  
 318 model to investigate and optimise the initial ionomer content and relative humidity for a practical PEMFC. In  
 319 general, the Kriging model combines a global model plus a localised departure, and can be formulated as:

$$320 \quad f(\mathbf{x}) = \beta + z(\mathbf{x}) \quad (38)$$

321 where  $f(\mathbf{x})$  is the unknown function of interest,  $\beta$  denotes a known approximation function (usually  
 322 polynomial), and  $z(\mathbf{x})$  stands for a stochastic component in terms of zero mean and variance  $s^2$  with the  
 323 Gaussian distribution. Let  $\hat{f}(\mathbf{x})$  be an approximation function to the true function  $f(\mathbf{x})$ . By minimising the  
 324 mean squared error between  $f(\mathbf{x})$  and  $\hat{f}(\mathbf{x})$ ,  $\hat{f}(\mathbf{x})$  can be calculated as:

$$325 \quad \hat{f}(\mathbf{x}) = \hat{\beta} + \mathbf{r}^T(\mathbf{x}) \mathbf{R}^{-1} (\mathbf{f} - \hat{\beta} \mathbf{q}) \quad (39)$$

326 where  $\mathbf{R}^{-1}$  is the inverse of correlation matrix  $\mathbf{R}$ ,  $\mathbf{r}$  is the correlation vector,  $\mathbf{f}$  is the observed data at  $n_s$   
 327 sample points, and  $\mathbf{q}$  is the unity vector with  $n_s$  components,  $\hat{\beta}$  is the vector of estimated regression  
 328 parameters.

$$329 \quad \hat{\beta} = (\mathbf{q}^T \mathbf{R}^{-1} \mathbf{q})^{-1} \mathbf{q} \mathbf{R}^{-1} \mathbf{f} \quad (40)$$

330 And the random variables are correlated to each other using the basis function of

$$331 \quad R(\mathbf{x}^j, \mathbf{x}^k) = \exp \left( - \sum_{i=1}^m \theta_i |x_i^j - x_i^k|^2 \right), \quad (j = 1, \dots, n_s, k = 1, \dots, n_s) \quad (41)$$

332 The Kriging surrogate model was shown in detail elsewhere [47].



## 333 2.5 Boundary conditions

334 The back pressures at the inlet of anode (A'-A'') and cathode (F'-F'') are defined as  $p_a$  (Pa) and  $p_c$  (Pa),  
335 respectively. The water content on the CL-membrane interfaces of anode (C-C') and cathode (D-D') are defined  
336 as the Dirichlet boundaries with their values given by Eq. (30). The liquid water saturation at the inlet of cathode  
337 (F'-F'') is also defined as the Dirichlet boundary with the value of zero. The mole fraction of the species at the  
338 inlets of anode (A'-A'') and cathode (F'-F'') are calculated by the following equations:

$$339 \quad x_{H_2O,a,in} = \frac{p_{sat}RH_a}{p_a}, \quad x_{H_2,a,in} = 1 - x_{H_2O,a,in} \quad (42)$$

$$340 \quad x_{H_2O,c,in} = \frac{p_{sat}RH_c}{p_c}, \quad x_{O_2,c,in} = 0.21(1 - x_{H_2O,c,in}), \quad x_{N_2,c,in} = 0.79(1 - x_{H_2O,c,in}) \quad (43)$$

## 341 2.6 Numerical solution

342 The commercial software COMSOL Multiphysics 4.3a is used to implement the fully coupled equations in  
343 which Eqns. (26), (34) and (35) are pre-defined whereas the other equations are added as individual equations.  
344 The key to successfully solve this model is the membrane/ionomer water content due to the strong effect on the  
345 critical parameters, i.e. ionomer volume fraction, EOD coefficient, ionic conductivity, hydraulic permeability  
346 and water diffusivity. The numerical solution of all equations is based on the finite element method (FEM). The  
347 computational geometry consists of 8040 elements, the distance between each element is known as the step. At  
348 each step, the used equations accounting for the different phenomena are fully coupled.

## 349 3. Result and discussion

### 350 3.1 Model validation

351 The simulation results obtained by both the single-phase and two-phase flow models are validated by the  
352 experimental data as shown in Fig. 5. In the single-phase flow model, all species are assumed to be existed in  
353 gaseous phase, which leads to an invalidation of Eq. (24). In the two-phase flow model, the liquid water  
354 formation and transport are considered. The models are validated at two operating temperatures, 60 and 80 °C.  
355 For the MEA, the anode is made from 20% Pt/C (VulcanXC-72) with platinum loading of 0.1 mg cm<sup>-2</sup> and the  
356 cathode is made from 50% Pt/C (VulcanXC-72) with platinum loading of 0.4 mg cm<sup>-2</sup>, respectively. The  
357 ionomer mass ratios are 20% in the catalyst layers of both the anode and cathode. The Nafion® 112 membrane is  
358 sandwiched between the cathode and the anode. The cell body is made of stainless steel with the active areas of

359 the electrodes of  $1.0 \text{ cm} \times 1.0 \text{ cm}$ . The cell is thermostatically controlled by cartridge heaters. Pure hydrogen  
360 and air are supplied as the reactants which are humidified by passing through an external humidifier. The  
361 operating conditions are fuel cell and gas inlet temperatures of 60 and 80 °C, gas pressure of 1.0 atm, anode and  
362 cathode gas humidity of 100%, hydrogen stoichiometry of 1.2 and air stoichiometry of 2.0 corresponding to a  
363 reference current density of  $1.0 \text{ A cm}^{-2}$ . The MEA preparation and fuel cell test are shown in detail in reference  
364 [27, 28]. The parameters used for model validation and base case condition are listed in Table 6. Note that the  
365 cathode transfer coefficient ( $\alpha_c$ ) for model validation is obtained by fitting the experimental polarisation curve  
366 in the kinetic control zone (cell voltage higher than 0.8 V) [27]. It is apparent from Fig. 5 that, due to the weak  
367 mass transport impact at higher cell voltages (i.e. lower current densities), both models give very close  
368 simulation results in agreement with the experimental data. With increasing current density there is the typical  
369 decrease in cell voltage. At higher current densities there is a rapid fall in cell voltage caused by mass transport  
370 restrictions. By accounting for the mass transport resistance of oxygen diffusing through the liquid water coating  
371 and considering the reduction in void space resulting from liquid water occupation (flooding), the two-phase  
372 flow model gives reasonable predictions of the polarisation curves. The potential profiles of the solid and  
373 electrolyte phases at the current density of  $1.0 \text{ A cm}^{-2}$  are shown in Fig. 6. The  $x$  coordinate is the thickness of  
374 the CCL and the  $y$  coordinate is the total width of the rib and channel of the current collector.  $x = 0$  indicates the  
375 CCL-membrane interface while  $x = 15 \text{ }\mu\text{m}$  indicates the CCL-GDL interface.  $y = 0$  and  $y = 1250 \text{ }\mu\text{m}$  indicate  
376 the bottom boundary of the channel and upper boundary of the rib, respectively. Fig. 6 shows that the maximum  
377 differences of the solid phase potential and electrolyte potential are  $4.2 \times 10^{-3}$  and  $7.1 \times 10^{-2}$  V, respectively. Along  
378 the  $x$  direction, the potential gradients of solid and electrolyte phases across each agglomerate are  $2.8 \times 10^{-4}$  and  
379  $4.73 \times 10^{-3}$  V, which are  $3.36 \times 10^{-6}$  and  $5.68 \times 10^{-5}$  V along the  $y$  direction, respectively. As a result, the constant  
380 potential profiles across the agglomerate through the entire CL are reasonable.

### 381 **3.2. Effect of membrane and ionomer swelling**

382 Fig. 7 shows the effect of membrane and ionomer swelling on the cell performance. The polarisation curves  
383 are obtained in four conditions: considering membrane swelling only, considering ionomer swelling only,  
384 considering both and neglecting both. At lower current densities, the four polarisation curves almost overlap  
385 each other due to the weak mass transport influence. The predicted current densities are almost identical to each  
386 condition, because both the effects of Nafion® membrane swelling and ionomer swelling can be neglected. As  
387 the current densities increase, the current densities predicted by the model neglecting the membrane and

388 ionomer swelling are greater than that considering the membrane and ionomer swelling. At higher current  
389 densities, by ignoring the membrane and ionomer swellings, the two-phase flow model overestimates the current  
390 densities at higher current densities, where mass transport impact is significant. The relatively higher predicted  
391 current densities can be explained by three reasons: firstly, the unchanged porosity of the cathode catalyst layer  
392 when the ionomer swelling is not considered; secondly, the thicknesses of the ionomer coatings surrounding the  
393 agglomerate are constants without considering the ionomer swelling, finally, the constant reactant gas transport  
394 resistance when the MEA bulge is not included. In base case condition, the original catalyst layer porosity and  
395 ionomer coating thickness are 30.5% and 133.2 nm, respectively. The porosity decreases to 23.6% and the  
396 ionomer coating thickness increases to 168.5 nm at 1.0 A cm<sup>-2</sup> when the ionomer swelling is taken into account.  
397 It is also clear in Fig. 7 that the polarisation curve obtained by considering the membrane swelling only is very  
398 close to that considering the ionomer swelling only. This indicates that the effects of ionomer swelling and  
399 membrane swelling are of equal importance.

### 400 3.3 Optimal ionomer water content

401 According to the agglomerate assumption of the catalyst layer, oxygen need to diffuse through the ionomer  
402 and liquid water coatings before reaching the platinum particle surface (see Fig. 2). Due to the fact that, above  
403 70 °C, the diffusion coefficient of oxygen through the liquid water is more than ten times bigger than that  
404 through the ionomer [50], the ionomer coating therefore has more significant impact on oxygen transport. In the  
405 absence of a liquid water coating, the oxygen diffusion flux can be described by the dimensionless Fick's law  
406 [51] shown as follow:

$$407 \quad \vec{N}_{O_2-M} = -\nu c_{O_2}^0 \nabla C_{O_2} \quad (44)$$

408 where  $c_{O_2}^0$  (mol m<sup>-3</sup>) is the oxygen concentration at the outer boundary of the ionomer coating,  $C_{O_2}$  is the  
409 dimensionless oxygen concentration, the parameter  $\nu$ , is the quotient of oxygen diffusion coefficient and the  
410 ionomer film thickness, which represents to the oxygen diffusion rate through the ionomer film.

$$411 \quad \nu = \frac{D_{O_2-M}}{\delta_M} \text{ (m s}^{-1}\text{)} \quad (45)$$

412 The boundary condition for Eq. (44) is:

$$413 \quad \begin{cases} X = 0, & C_{O_2} = 1 \\ X = 1, & \nabla C_{O_2} = 0 \end{cases} \quad (46)$$

414 As increase in ionomer water content results in increases in both the oxygen diffusion coefficient and ionomer  
415 film thickness, and hence optimal ionomer water content theoretically exists, with a maximum value of parameter  
416  $\nu$ .

417 The effect of ionomer water content on parameter  $\nu$  with different volume fractions of dry ionomer is shown  
418 in Fig. 8. The platinum loading, platinum mass ratio and catalyst layer thickness are fixed at  $0.4 \text{ mg cm}^{-2}$ , 40%,  
419 and  $15 \text{ }\mu\text{m}$ , respectively. The results in Fig. 8 show that the optimal water content is higher as the dry ionomer  
420 volume fraction increases. This can be explained by the ionomer coating thicknesses at different dry ionomer  
421 volume fractions. Specifically, the ionomer coating is thicker when a larger dry ionomer volume fraction is  
422 adopted. The increase in thickness of the thicker ionomer film is smaller than that of the thinner film. For  
423 example, the dry ionomer films are  $7.96 \times 10^{-8} \text{ m}$  and  $1.33 \times 10^{-7} \text{ m}$  for the dry ionomer volume fraction of 30%  
424 and 40%, respectively. At the ionomer water content of 14, the ionomer film thicknesses increase by 118.8%  
425 and 70.4%, respectively. However, the increase in oxygen diffusivity is a constant. As a result of the increase in  
426 water content, the increase in parameter  $\nu$  with higher ionomer content is more significant than that of a lower  
427 ionomer content.

### 428 **3.4 Orthogonal test**

429 An orthogonal test on the cell performance is carried out. Four parameters, including platinum loading,  
430 platinum mass ratio, dry ionomer volume fraction and catalyst layer thickness, with three levels are investigated  
431 by nice tests. The orthogonal design and test results are shown in Table 7 and Table 8, respectively.

432 In Table 8, the agglomerate specific area, ionomer coating thickness, porosity of the secondary pores, proton  
433 conductivity, parameter  $\nu$ , and the predicted current densities and liquid water coating thicknesses at different  
434 cell voltages are investigated. It is clear that the highest current densities at the cell voltages of 0.9, 0.5 and 0.3  
435 V are observed in case 7, case 4 and case 4, respectively. The proton conductivity and the specific area of case 7  
436 are the largest and second biggest among the nice cases, which indicate that the oxygen reduction kinetics and  
437 the proton conductivity are the two most important factors determining the cell performance at high cell  
438 voltages. The highest current densities at the cell voltage of 0.5 and 0.3 V are observed in case 4, although no  
439 studied parameters are extreme values. The predicted current densities in Case 8 are also very high at 0.5 and  
440 0.3 V, which are quite close to the current densities obtained from case 4. All parameters in case 8, except the  
441 specific area, are more optimal compared to that in case 4. This indicates that the oxygen reduction kinetics is  
442 also very important at low cell voltages. Similarly, all parameters in case 9, except the porosity, are more  
443 optimal than that in case 4. However, the predicted current densities are much lower, especially at lower cell

444 voltages. This indicates the importance of the porosity. Therefore, the gas transport is another factor determining  
445 the cell performance at low cell voltages. In intermediate cell voltages, cell performance is under a mixed  
446 control where the impacts of proton conductivity, kinetics and gas transport are of equal importance.

### 447 **3.5 Membrane/ionomer water content**

448 The profiles of membrane/ionomer water content at the cell voltage of 0.3 V with different  $RH_c$  are shown in  
449 Fig. 9. It is clear that the effect of relative humidity on the membrane/ionomer water content is apparent. As  
450 shown in conditions of (a) to (c), due to the effect of electro-osmotic drag (EOD), the membrane/ionomer water  
451 content is non-uniform since the anode dehydrates and the cathode is prone to be water saturated with higher  
452 relative humidity, especially on the region under the land. The lowest water contents, with values around 3.5 for  
453 various relative humidity from 40 to 80%, are observed at the anode CL-GDL interfaces. The situation is  
454 different when the relative humidity is lower than 30% shown in condition (d). The cathode ionomer water  
455 content is lower than that of the anode. With this low relative humidity, the ionomer in the CCL is hard to be  
456 saturated by the water migrated from the anode. In other words, the ionomer water absorption (water uptake) is  
457 more significant in determining the ionomer water content in comparison to the EOD. It is also apparent that, at  
458 lower relative humidity, e.g. lower than 60%, the ionomer in the CCL cannot be fully saturated. The water  
459 migrated from the anode under EOD effect is insufficient. With the increase in  $RH_c$  from 30% to 80%, anode  
460 dehydration is more severe. This is because that higher relative humidity increases the current density, which  
461 leads to more water migration through the membrane from the anode to the cathode and results in more severe  
462 dehydration on the anode side. As shown in Fig. 8 and Fig. 9, the optimal water content for the cathode side is  
463 approximate 13. The relative humidity between 60% and 80% is believed to satisfy this requirement. Moreover,  
464 the cathode ionomer water content is higher under the land than under the channel. This is explained by the  
465 higher water migration flux driven by the force of EOD under the land. In addition, lower relative humidity  
466 decreases the membrane swelling. The minor radii of the swollen membrane are 10.3  $\mu\text{m}$  and 7.3  $\mu\text{m}$  with  $RH_c$   
467 of 60% and 30%, respectively.

### 468 **3.6 Effect of relative humidity on ionomer swelling**

469 The effect of  $RH_c$  on the ionomer volume fraction within the CCL is shown in Fig. 10. Two levels of  $RH_c$  of  
470 60% and 80% are compared. The boundaries of  $X=0$  and  $X=1$  refer to the interfaces of CL-membrane (D-D')  
471 and CL-GDL (E-E'). The boundaries of  $Y=0$  and  $Y=1$  refer to the lower boundary of the flow channel (D'-E')  
472 and the upper boundary of the current collector (D-E) as shown in Fig. 1, respectively. At a cell voltage of 0.3 V,

473 the corresponding current density is 0.92 and 0.96 A cm<sup>-2</sup> for  $RH_c$  of 60% and 80%, respectively. When the  
474 relative humidity is lower than 60%, the ionomer volume fraction is greater near the cathode CL-membrane  
475 interface than that near the GDL-CL interface as shown in Fig. 10 (a). In this situation, the lower relative  
476 humidity reduces the ionomer water absorption due to the lower mole fraction of water vapour, leading to  
477 unsaturated ionomer. Due to the effect of EOD, the dissolved water, which migrates through the membrane from  
478 anode to cathode, is firstly absorbed by the ionomer near the cathode CL-membrane interface. This will lead to a  
479 greater ionomer swelling on this region. However, when  $RH_c$  is higher than 80%, the ionomer in the CCL is  
480 sufficiently saturated with water vapour and, as shown in Fig. 10 (b), similar to the distribution of the ionomer  
481 water content, the highest ionomer volume fraction (swelling) is observed at the cathode CL-GDL interface  
482 under the land. The observed higher ionomer volume fraction near the cathode CL-GDL interface in comparison  
483 to that of the CL-membrane interface indicates that ionomer water absorption (water uptake) is the main process  
484 determining the ionomer water content rather than EOD when  $RH_c$  is higher than 80%. The EOD effects are  
485 more pronounced closer to the membrane with  $RH_c$  lower than 60%.

### 486 **3.7 Effect of relative humidity on cell performance**

487 The predicted polarisation curves for different operating  $RH_c$  are shown in Fig. 11. The polarisation curves can  
488 be roughly divided into three segments. As the relative humidity increases, the cell performance initially  
489 decreases at lower current densities then increases at medium current densities and finally decreases again at  
490 higher current densities. At lower current densities, the lower  $RH_c$  is of benefit to the cell performance because a  
491 lower  $RH_c$  increases the oxygen fraction of the cathode gas inlet and increases the catalyst layer porosity by  
492 reducing the ionomer swelling. Even though the oxygen diffusion coefficient through the ionomer is reduced by  
493 the lower relative humidity, the negative effect is not significant due to the slight impact of mass transport at  
494 lower current densities. At medium current densities, the electrode is under mixed kinetics and mass transport  
495 control. In this condition, the increase in cathode relative humidity increases the oxygen diffusion rate through  
496 the ionomer coating and results in an increase in ORR rate until liquid water is generated at higher current  
497 densities. However, the thickness of the ionomer coating increases more significantly at higher  $RH_c$ . As shown  
498 in Table 9, the ionomer film thickness increases approximately 26% with  $RH_c$  of 80% at the current density of  
499 1.0 A cm<sup>-2</sup>, but only increases 8% with  $RH_c$  of 40%.

### 500 **3.8 Effect of dry ionomer content on cell performance**

501 The predicted polarisation curves and the agglomerate effectiveness factors for cells with various dry ionomer  
502 loadings are shown in the Fig. 12 and Fig. 13. The platinum loading, platinum mass fraction, and catalyst layer

503 thickness are set to constants of  $0.4 \text{ mg cm}^{-2}$ ,  $0.4$  and  $15 \mu\text{m}$ , respectively. The ionomer volume fraction can be  
504 transformed to its mass loading according to  $m_M^{dry} = \rho_M l_{CL} L_M^{dry}$ . As shown in Fig. 12, the increase in dry  
505 ionomer loading increases the current densities at higher cell voltages whereas decreases the current densities at  
506 lower cell voltages. The improvement in the cell performance at higher cell voltages is because a higher  
507 ionomer loading increases the proton conductivity by reinforcing the contact between agglomerates with thicker  
508 ionomer coating [27].

509 Due to the fact that the electrochemical reaction rate is relative slow at higher cell voltages, the overall rate is  
510 therefore mainly control by the proton transport rate [46]. As a result, the increase in ionomer loading is of  
511 benefit to the cell performance. However, at media and low cell voltages, the impact of mass transport becomes  
512 significant. The increase in ionmomer loading decreases the porosity and increases the mass transport resistance.  
513 It is clear that the current densities at medium and low cell voltages drop rapidly as the ionomer loading  
514 increases to  $1.65 \text{ mg cm}^{-2}$ . The obtained optimal dry ionomer loading is between  $0.2$  to  $0.30 \text{ mg cm}^{-2}$ , which  
515 agrees well with the experimental results of Passalacqua et.al [39] and Kim et.al [52].

516 Fig. 13 shows that the effectiveness factor decreases as the ionomer loading increases. The effectiveness  
517 decreases along two directions: from GDL-CL interface to CL-membrane interface and from the region under  
518 the channel to that under the land, which leads to insufficient utilisation of the platinum catalyst near the  
519 membrane and under the land. The highest effectiveness factors are observed at the GDL-CL interface under the  
520 channel due to the relative high oxygen concentration on this region.

### 521 **3.9 Liquid water saturation and membrane swelling**

522 Since the membrane and ionomer swellings strongly depend on their water content, it is plausible to operate  
523 the cell under less wet conditions. However, this is at the expense of proton conductivity which may cause a  
524 greater decline in fuel cell performance than what swelling initiates. Controlling the access of external water to  
525 the cell through relative humidity can minimise the effect of swelling. Fig. 14 shows the profiles of the liquid  
526 water saturation within the cathode porous electrode with two levels of  $RH_c$ , 80% and 100%. It is apparent that  
527 liquid water mainly generates and accumulates within the CCL and GDL under the land and lower relative  
528 humidity decreases the liquid water saturation at high current densities. The liquid water saturation is  
529 proportional to the cathode relative humidity. It can be seen that flooding is less severe and the two-phase flow  
530 region is reduced as the relative humidity decreases. Specifically, the decrease in  $RH_c$  from 100% to 80%  
531 reduces the average liquid water saturation from 7.3% to 6.2%, until no liquid water flooding ( $s = 0$ ) when  $RH_c$   
532 decreases to lower than 40%. The decrease in relative humidity also reduces the membrane swelling. For

533 example, the minor radius of the swollen membrane ellipse decreases from 10.9 to 7.3  $\mu\text{m}$  as  $RH_c$  decreases  
534 from 60% to 30%. Also, as indicated in Table 9, the thickness of the ionomer coating increases as the relative  
535 humidity and current density increase. The increase in  $RH_c$  from 40% to 60% leads to an increase in ionomer  
536 coating thickness from 143.9 to 157.8 nm at 1.0 A  $\text{cm}^{-2}$ . When the ionomer is completely saturated, the ionomer  
537 coating thickness keeps as a constant value of 168.2 nm. It can be concluded that applying lower cathode  
538 relative humidity reduces both the membrane and ionomer swelling.

### 539 **3.10 The interaction of dry ionomer content and relative humidity**

540 The current density plot of the surrogate model at the cell voltage of 0.35 V is given in Fig. 15. It is used to  
541 show the interaction of dry ionomer volume fraction ( $L_M^{\text{dry}}$ ) and cathode relative humidity ( $RH_c$ ) and their effect  
542 on the cell performance. It can be observed that the predicted current density is lower with  $RH_c$  smaller than 60%  
543 and there is an abrupt rise in current density around the relative humidity of 60%. With a further increase in  $RH_c$ ,  
544 e.g. from 60% to 90%, current density decreases from the peak. The reason for this tendency is that the initial  
545 increase in relative humidity increases the ionomer water content within the CCL, which increases the oxygen  
546 diffusion rate and proton conductivity to a maximum threshold. The further increase in relative humidity results  
547 in liquid water generation without improving the mass transport rate after the optimum relative humidity is  
548 achieved. For example, for a MEA in a base case condition, with  $RH_c$  of 40% at the cell voltage of 0.3 V, the  
549 parameter  $\nu$  and proton conductivity of the CCL are  $5.8 \times 10^{-3} \text{ m s}^{-1}$  and  $1.59 \text{ S m}^{-1}$ , respectively, which increase  
550 to  $7.2 \times 10^{-3} \text{ m s}^{-1}$  and  $6.02 \text{ S m}^{-1}$ , respectively, when  $RH_c$  increases to 80%. As a consequence, an optimum  $RH_c$   
551 exists and it increases as  $L_M^{\text{dry}}$  increases at the first glance. The optimum  $RH_c$  with various  $L_M^{\text{dry}}$  is shown in Fig.  
552 16. In consistence with the experimental measurement [42, 43], the optimum  $RH_c$  initially decreases from 76%  
553 to 73% as  $L_M^{\text{dry}}$  increases from 10% to 30%. This is because, when the ionomer content is low, the proton  
554 conductivity plays a more important role in determining the cell performance rather than the oxygen transport  
555 resistance. With the further increase in  $L_M^{\text{dry}}$  from 30% to 50%, the optimum  $RH_c$  increases to 85%. In this  
556 condition, the oxygen diffusion rate through the ionomer coating replaces the proton conductivity to control the  
557 cell performance. Thus, higher ionomer water content is required of improving the oxygen transport coefficient,  
558 resulting in more ionomer water uptake as the ionomer content increases. It is also indicated in Fig. 8 that a  
559 higher ionomer water content benefits the oxygen diffusion rate with a higher ionomer content compared to a  
560 lower ionomer content. In short, the modelling results indicate that the optimum cathode relative humidity  
561 initially decreases then increases as the dry ionomer volume fraction increases from 10% to 50%. Note that the



562 variation behaviour changes according to the MEA fabrication method and probably the preparation conditions.  
563 Therefore, more studies are needed for model validation due to limited available experimental data so far. On  
564 the other hand, the predicted current density decreases slowly as  $L_M^{\text{dry}}$  increases from 10% to 50% while  $RH_c$  is  
565 fixed at higher than 60%. By comparing the increment of the current density along both the  $x$  and  $y$  axis, it  
566 shows that the effect of relative humidity is more significant than that of dry ionomer content. It can be  
567 concluded that the oxygen diffusion rate and proton conductivity of the CCL is more sensitive to relative  
568 humidity in comparison to ionomer content.

569 Applying the optimum cathode relative humidity ( $RH_c = 75\%$ ) and ionomer content ( $L_M^{\text{dry}} = 10\%$ ) without  
570 changing other parameters in the base case condition, the improved polarisation curve and power density are  
571 shown in Fig. 17. It is clear that the optimum  $RH_c$  and  $L_M^{\text{dry}}$  improve the cell performance at the cell voltages  
572 smaller than 0.35 V. The grey area is the increment of cell output. At higher cell voltages, corresponding to  
573 lower current densities, there is very little change in the predicted polarisation curves. Looking back to Fig. 11  
574 and Fig. 12, the decrease in  $RH_c$  increases the cell performance at higher cell voltages, on the contrary, the  
575 decrease in  $L_M^{\text{dry}}$  decreases the cell performance. Simultaneous decreases in  $RH_c$  and  $L_M^{\text{dry}}$  offset their individual  
576 effect on the cell performance, leading to an almost unchanged polarisation curve at higher cell voltages.

## 577 4. Conclusions

578 An across the channel, two dimensional, isothermal, steady state, two-phase flow model for a PEMFC is  
579 developed by fully coupling several electrochemical and transport processes occurring simultaneously, namely  
580 (1) oxygen diffusion-reaction process from the outer boundary of the ionomer and liquid water coating to the  
581 platinum surface inside the agglomerates; (2) membrane and ionomer swelling associated to their water content;  
582 (3) non-uniform membrane/ionomer water content determined by the combinational water transport mechanism;  
583 (4) combinational water transport mechanisms through the membrane under the forces of electro-osmotic drag  
584 (EOD), back diffusion and hydraulic permeation; (5) water phase-transfer between water vapour, dissolved  
585 water and liquid water; (6) two-phase flow process between liquid water and reactant gases.

586 An optimum ionomer water content is proposed by maximising the oxygen diffusion rate through the ionomer  
587 film surrounding the agglomerate, which is dependent on the ionomer content. Specifically, it becomes higher as  
588 the ionomer content increases. The initial dry ionomer content in the CCL and the relative humidity of the  
589 cathode gas inlet are investigated in terms of their effects on the membrane/ionomer water content and swelling,  
590 liquid water saturation, and fuel cell performance. The simulation results show that, at lower current densities,

591 higher ionomer content and lower relative humidity are of benefit to the cell performance. However, lower  
 592 ionomer content and higher relative humidity improve the cell performance at higher current densities. Ionomer  
 593 water absorption (water uptake) is the main mechanism in determining the ionomer water content instead of  
 594 EOD when the relative humidity is higher than 80%.

595 A Kriging surrogate model is used for the dry ionomer volume fraction and cathode relative humidity based  
 596 on analysing their interaction on membrane/ionomer swelling and cell performance. The modelling results show  
 597 that the effect of relative humidity is more significant in comparison to the ionomer content. At higher current  
 598 densities, the optimum relative humidity increases as the ionomer content increases. The optimum cathode  
 599 relative humidity initially decreases from 76% to 73% as the dry ionomer volume fraction increases from 10%  
 600 to 30%, and then it increases up to 85% as the dry ionomer volume fraction increases to 50%. The dry ionomer  
 601 volume fraction of 10%, corresponding to 0.3 mg cm<sup>-2</sup>, and cathode relative humidity of 75% yield the best cell  
 602 performance, which improves the cell power density by 14.5% at 0.35 V.

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## 606 Appendix

607 By assuming the shape of the swollen membrane is a half ellipse as shown in Fig. 3, the increased area of the  
 608 swollen membrane ( $A_M^{swell}$ ) can be expressed as the product of PI, the minor radius ( $x$ ) and major radius ( $y$ ) as  
 609 follow:

$$610 \quad \frac{\pi xy}{2} = A_M^{swell} \quad (A.1)$$

611 The membrane swells in contact with water leading to an increase in the volume, as shown in Fig. 3, the  
 612 increased membrane area ( $A_M^{swell}$ ) can be also related to the membrane thickness ( $l_M$ ), membrane width  
 613 ( $H_{Rib} + H_{Ch}$ ), membrane water content ( $\lambda$ ) and swelling coefficient ( $k_s$ ) as follow:

$$614 \quad A_M^{swell} = (H_{Rib} + H_{Ch}) \cdot l_M \cdot k_s \cdot \lambda \quad (A.2)$$

615 It is clear that the major radius of the ellipse equals to the half width of the flow channels, gives

$$616 \quad y = \frac{H_{Ch}}{2} \quad (A.3)$$

617 Combing Eq. (A.1) to (A.3), the minor radius of the ellipse is obtained as:

$$x = \frac{4(H_{Rib} + H_{Ch}) \cdot l_M \cdot k_s \cdot \lambda}{\pi d_{Ch}} \quad (\text{A.4})$$

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