Anode partial flooding modelling of proton exchange membrane fuel cells: Model development and validation

Anode partial flooding modelling of Proton Exchange Membrane Fuel Cells: Model development and validation

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Highlights

- A fully coupled 2D, along-the-channel, two-phase flow, non-isothermal, CFD model is developed.
- Temperature rise due to electrochemical reactions, ohmic resistance and water phase-transfer is analysed.
- Mathematical expressions of liquid water saturation against current density at anode and cathode are regressed.
- Relationship between the liquid water saturation at anode and cathode is built.

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Abstract

A two-dimensional along-the-channel computational fluid dynamic (CFD) model, coupled with a two-phase flow model of liquid water and gas transport for a proton exchange membrane (PEM) fuel cell is described. The model considers non-isothermal operation and thus the non-uniform temperature distribution in the cell structure. Water phase-transfer between the vapour, liquid water and dissolved phase is modelled with the combinational transport mechanism through the membrane. Liquid water saturation is simulated inside the electrodes and channels at both the anode and cathode sides. Three types of models are compared for the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) in catalyst layers, including Butler-Volmer (B-V), liquid water saturation corrected B-V and agglomerate mechanisms. Temperature changes in membrane electrode assembly (MEA) and channels due to electrochemical reaction, ohmic resistance and water phase-transfer are analysed as a function of current density. Nonlinear relations of liquid water saturations with respect to current densities at both the anode and cathode are regressed. At low and high current densities, liquid water saturation in the anode linearly increases as a consequence of the linear increase of liquid water saturation in the cathode. In contrast, exponential relation is found to be more accurate at medium current densities.

Key works: PEMFC; liquid water; anode flooding; agglomerate model; non-isothermal; CFD

1. Introduction

Benefiting from high energy efficiency and low emission, proton exchange membrane fuel cells (PEMFCs), play an important role in transiting a carbon intensive economy to sustainable low carbon future [1-4]. In addition, the features of PEMFCs endow a flexibility and scalability for use with batteries and combined heat and power (CHP) system for hybrid automotive and residential use [5-7], as well as energy conversion between winds to electricity [8]. Among the PEMFC family, the medium and low temperature PEMFCs are considered as promising candidates as portable and automotive power sources. However, they can experience certain operating difficulties associated with water transport and flooding during their operation, especially at a high current density [9-11].

Three phases of water co-exist in PEMFCs: as vapor and liquid in porous electrodes and channels, and as a dissolved phase absorbed by membrane and ionomer (membrane and ionomer water uptake). Among three phases, dissolved water can migrate between both electrodes through the membrane under the driving forces of electro-osmotic drag (EOD), back diffusion and hydraulic permeation [12-14]. Liquid water can be generated in terms of water vapor condensation and membrane/ionomer desorption when over-saturated. Simultaneously, liquid water is removed from the MEA (membrane electrode assembly) generally by reactant gases flowing along the channels. If water generation rate is faster than the removal rate, excess water will accumulate in the electrodes and flow channels, leading to a water flooding inside the cell. This flooding can reduce the effective porosity in the porous media and increase the pressure drop along the channel, inhibiting the gas transport to the active sites in catalyst layers (CLs), finally resulting in a decline in the cell performance [15-17]. Water flooding is typically observed at the cathode side due to the fact that water is produced inside the cathode catalyst layers (CCLs) by the oxygen reduction reaction (ORR).

There have been numerous studies of water flooding at the cathode but less consideration of water transport related to the anode. However, hydrogen consumption at the anode could also results in the humidified anode reactant gas becoming supersaturated with water vapor, which can result in transfer to liquid water after condensation. Liquid water movement in hydrophilic and hydrophobic anode gas channel, as well as the effect of hydrogen inlet velocity, operating temperature and channel walls wettability, was numerically studied by Ferreira et al. [18]. Experimental studies have detected liquid water in the anode and that more liquid water was observed at a high anode relative humidity [19, 20]. An in-situ detection scheme of anode flooding, developed by O'Rourke et al. [21], showed that anode flooding could be detected prior to a rapid cell voltage decline, which was considered as an early warning of cathode catalyst damage. As reported by Anderson et al. [22], anode water removal (AWR) could be used as a diagnostic tool to assess cathode water flooding in PEM fuel cells.

Catalyst layers are complex structures and are a difficult to describe and be fully understood in PEMFCs; not only due to their highly compact structure and complex composition but also because of the coupled electrochemical reactions and transport processes occurred. CLs in PEMFCs facilitate electrochemical reactions and produce water at the cathode. To describe the current density produced on each electrode in fuel cell operation, considering the water generated which can partially cover the platinum catalyst surface, (1-s) corrected B-V equation (s is the liquid water saturation, defining as the volume fraction of void space occupied by liquid water) is usually required instead of the traditional B-V equation [23-25]. The electrochemical activity may be further represented using an agglomerate mode, taking into account the increase in ionomer film thickness surrounding the agglomerate due to ionomer swelling. Furthermore, by considering gas transport resistance and the reduction of porosity

due to liquid water occupation, the agglomerate model can also provide a superior representation of the porous CLs in comparison with other models [26, 27].

In fuel cell operation, temperature plays a significant role in achieving a high power performance. A variety of parameters, e.g. electrochemical reaction kinetics, mole fractions in gas mixture, electrolyte conductivity, rate of mass transfer, as well as liquid water saturation, are closely correlated with temperature during fuel cell operation. Within PEMFCs, the temperature distribution across the MEAs and along the flow channels can be either estimated by mathematical modelling technique or detected by experimental measurements [28-31]. Ju et al. [28] developed a three dimensional (3D), single-phase, non-isothermal model through a parametric study for GDL thermal conductivity, gas relative humidity and operating cell voltage. Wang et al. [29] measured the temperature profile within a single PEMFC with the aid of infrared thermal imaging (ITI) and found that the downstream temperature is higher than the upstream, and there was an obvious high temperature section in the outlet of oxygen. Temperature measurement were conducted by Zhang et al. [30] and Lin et al. [31] from which they found a correlation between local temperature rise and local current density, and a temperature rise at backsides of both the anode and cathode flow field plates.

However, up to now, it is still a challenge to fully couple most aspects mentioned above in modelling for a highly accurate evaluation of water flooding in a single PEMFC or stack. In this paper, we fully couple seven sub-models and apply them on a two dimensional (2D), along-the-channel (ATC) geometry for a single PEMFC: (1) agglomerate models for gas transport resistance in CLs, (2) two-phase flow models for liquid water saturation, (3) combinational diffusion models for dissolved water transport through the membrane, (4) non-isothermal models for heat transport in MEA and channels, (5) computational fluid dynamic (CFD) models for gas transport along the channels, (6)

multicomponent diffusion of reactant gases in gas mixture, and (7) ionomer swelling due to non-uniform distribution of water content. The effect of liquid water on the current density are compared based on three mechanisms, including traditional B-V, (1-s) corrected B-V and agglomerate kinetics. Distributions of reactant gas, liquid water and heat within the cell are investigated. The expressions for the relationship between the liquid water saturation on each electrode and current density, as well as the liquid water saturation between anode and cathode, are regressed.

2. Model description

2.1 Assumption

Some additional assumptions were employed in this work in addition to those in the previous papers [35-39]:

1. Steady state, two-phase flow, along the channel model of a PEMFC.
2. Gas flow in the channels is laminar flow and incompressible.
3. Reactant gases enter the gas channels in a direction normal to the channel cross section.
4. Liquid water saturation in channels is continuous.
5. Gas diffusion layers and catalyst layers are isotropic.
6. No liquid water enters the channels at the inlets.
7. Same electrodes and bipolar plates are used in the anode and cathode, respectively.

2.2 Governing equations

The conservation equations of mass, momentum, species, energy and charges are summarized as Eqns. (1) to (4):

$$\nabla \cdot (\rho^g \mathbf{u}^g) = S_m \tag{1}$$

$$\rho^g(\mathbf{u}^g\cdot\nabla\mathbf{u}^g)=\nabla\left[-pI+\mu^g\nabla\mathbf{u}^g+\mu^g(\nabla\mathbf{u}^g)^T-\frac{2}{3}\mu^g(\nabla\cdot\mathbf{u}^g)I\right] \quad (2)$$

$$\rho^g\mathbf{u}^g\cdot\nabla w_i^g-\nabla\cdot[\rho^g\sum_{j=1}^{N}(1-s')D_{ij}(\nabla x_j^g-w_j^g)\frac{\nabla p}{p}+D_i^T\frac{\nabla T}{T}]=M_iS_i^g \quad (3)$$

$$\nabla\cdot[\sum_{i=g,l}(\varepsilon\rho c_p\mathbf{u})_iT]-\nabla\cdot(\sum_{i=g,l,s}k_i\nabla T)=S_T \quad (4)$$

$$\sigma_s^{eff}\nabla\cdot\nabla\varphi_s+\sigma_M^{eff}\nabla\cdot\nabla\varphi_M=0 \quad (5)$$

where ρ (kg m^{-3}) is density, $\mathbf{u}$ (m s^{-1}) is velocity, p (Pa) is pressure, μ (Pa s) is viscosity, M (kg mol^{-1}) is molecular weight, D (m^2 s^{-1}) is diffusion coefficient, D^T (kg m^{-1} s^{-1}) is thermal diffusion coefficient, c_p (J mol^{-1} K^{-1}) is specific heat capacity, k (W m^{-1} K^{-1}) is thermal conductivity, T (K) is temperature, σ (S m^{-1}) is conductivity φ (V) is potential. w is mass fraction, x is mole fraction, ε is volume fraction, s' is corrected liquid water saturation and I is identity matrix. Subscript *i* and *j* represent species *i* and *j* and superscript *g* means gas phase. S is the source term, which is given in detail in Tables 1 to 3. Note that Eq. (1) to Eq. (3) were applied on reactant gas only and the gas velocity in porous electrodes could be related to pressure according to Darcy's law as below:

$$\mathbf{u}^g=-\frac{k_p}{\mu^g}\nabla p \quad (6)$$

where k_p (m^2) is the permeability of the porous media.

For the purpose of describing dissolved and liquid water transport, the following equations were used.

$$\nabla\cdot(n_d\frac{i_M}{F})-\nabla\cdot(D_{w-M}\nabla c_w^d)-\nabla\cdot(\frac{k_{p,M}c_w^d}{\mu_w}\nabla p)=S_w^d \quad (7)$$

$$\nabla\cdot(\rho_w^lD_c\nabla s-\frac{\rho_w^lk_r^l\mu_w^g}{k_r^g\mu_w^l}\mathbf{u}^g)=M_wS_w^l \quad (8)$$

Eq. (7) was developed by applying the diffusive approach to a conservation equation of dissolved water, while Eq. (8) was obtained by applying the volume average approach to the continuity equation

and using Darcy's law for both the liquid and gas phases.

The capillary diffusion coefficient, D_c ($m^2\ s^{-1}$), was calculated using Eq. (9) [32]:

$$D_c = -\frac{k_r^l}{\mu_w^l}\sigma\cos(\theta_c)(\varepsilon k_p)^{1/2}\frac{dJ(s)}{ds} \tag{9}$$

where k_r^l is the relative permeability of liquid phase, μ_w^l (Pa s) is the dynamic viscosity of liquid water, σ ($N\ m^{-1}$) is the surface tension, θ_c (°) is the contact angel, ε is the porosity of the electrode, k_p (m^2) is the permeability of the porous electrode, $J(s)$ is the Leverett function.

The equilibrium membrane/ionomer water content, determined based on water uptake measurement, is given as [33]:

$$\lambda^{eq} = 16.8s + 14.0(1-s) \qquad s > 0 \tag{10}$$

The permeability of gas channels was calculated by Hagen-Poiseuille equation [34].

$$k_{p,ch} = \frac{c_{sf} d_h^2}{32} \tag{11}$$

where c_{sf} is the flow shape factor (1.127 for a square cross-section) and d_h is the hydraulic diameter of a channel, which can be calculated by the relation of the cross-sectional area and wetted perimeter.

The electrochemical reactions inside the catalyst layers according to three different mechanisms, including B-V, (1-s) corrected B-V and agglomerate assumption, can be written as below:

$$i_{BV} = a_{agg}^M i_{0,i}^{ref}\left(\frac{p_i}{c_i^{ref} H_i}\right)^{\gamma}\left[\exp\left(\frac{-\alpha_{Rd,i} F\eta_i}{RT}\right) - \exp\left(\frac{\alpha_{Ox,i} F\eta_i}{RT}\right)\right] \tag{12}$$

$$i_{(1-s)BV} = (1-s)a_{agg}^M i_{0,i}^{ref}\left(\frac{p_i}{c_i^{ref} H_i}\right)^{\gamma}\left[\exp\left(\frac{-\alpha_{Rd,i} F\eta_i}{RT}\right) - \exp\left(\frac{\alpha_{Ox,i} F\eta_i}{RT}\right)\right] \tag{13}$$

$$i_{agg} = nF\left(\frac{p_i}{c_i^{ref} H_i}\right)^{\gamma}\left[\frac{1}{E_{agg} k_{agg}} + \frac{(r_{agg} + \delta_M + \delta_w)}{r_{agg}}\left(\frac{\delta_M}{a_{agg}^M D_{O_2-M}} + \frac{\delta_w}{a_{agg}^w D_{O_2-w}}\right)\right]^{-1} \tag{14}$$

where

$$k_{agg} = \frac{a_{agg}^{M} i_{0,i}^{ref}}{nF}\left[\exp\left(\frac{-\alpha_{Rd,i} F\eta_i}{RT}\right) - \exp\left(\frac{\alpha_{Ox,i} F\eta_i}{RT}\right)\right] \quad (15)$$

The subscript i is for anode and cathode, respectively, and the superscript γ equals to 0.5 for hydrogen oxidation reaction (HOR) in anode and 1.0 for ORR in cathode. The properties of the catalyst layer (porosity, specific area, ionomer and water film thickness), gas transport through the porous electrode (species diffusion in gas mixture and Knudsen diffusion), numerous key parameters and fundamental equations, were listed in Table 4. Details can be found in literature [35-39].

2.3 Boundary conditions

At anode inlet (A'-B') and cathode inlet (G-H) as shown in Fig. 1, the temperature, mole fractions of reactant gases in gas mixture, and liquid water saturation are given as below:

$$T = T^{cell},\ x_{w,a}^{0} = \frac{p_{sat} RH_a}{p_a},\quad x_{H_2}^{0} = 1 - x_{H_2O,a,in},\quad s_a = 0 \quad (16)$$

$$T = T^{cell},\ x_{w,c}^{0} = \frac{p_{sat} RH_c}{p_c},\ x_{O_2}^{0} = 0.21(1 - x_{H_2O,c,in}),\ x_{N_2}^{0} = 0.79(1 - x_{H_2O,c,in}),\ s_c = 0 \quad (17)$$

The gas velocities at the inlets of both electrodes are related to their stoichiometry shown as follow:

$$\mathbf{u}_a^{g,0} = \frac{\xi_a RTi^{ref} A_M}{2Fp_a x_{H_2} A_{ch}},\quad \mathbf{u}_c^{g,0} = \frac{\xi_c RTi^{ref} A_M}{4Fp_c x_{O_2} A_{ch}} \quad (18)$$

where i^{ref} is the reference current density (defined as 1.0 A cm^{-2} in this study), ξ_a and ξ_c are the stoichiometry of the anode and cathode, respectively. A_M (m^2) and A_{ch} (m^2) are the effective area of electrode and the cross-sectional area of channel, respectively.

At the inlet and outlet of both the anode and cathode, the pressure was given as a boundary condition.

$$p_a = p_a^0,\quad p_c = p_c^0 \quad (19)$$

The water content on the CL-membrane interfaces of anode (C-C') and cathode (F-F') were defined as Dirichlet boundaries with the values according to the following equations [14, 37-39]:

$$\lambda = 0.043 + 17.81\alpha_w - 39.85\alpha_w^2 + 36.0\alpha_w^3 \quad (20)$$

$$\alpha_w = x_w \frac{p}{p_{sat}} + 2s \quad (21)$$

2.4 Numerical solution

The numerical solution of the fully coupled governing equations was based on the finite element method (FEM). First of all, mesh was developed over the computational domain by dividing it into numerous elements. The distance between each element is known as the step. At each step, the equations accounting for different phenomena were fully coupled and computed with the boundary conditions. Initial value was given to each parameter at the first attempt then followed by an iterative process until the calculation error was smaller than 10^{-5}. Commercial software COMSOL Multiphysics 4.4 was used to implement the fully coupled equations. The key to successfully solving this model is simulating the membrane/ionomer water content, which significantly affects many critical parameters, i.e. ionomer volume fraction, EOD coefficient, ionic conductivity, hydraulic permeability and water diffusivity.

2.5 Mesh independence

Theoretically, the computation error in the solution related to the grid must disappear for an increasingly fine mesh. The effect of mesh on the final simulation results is more significant at high current density due to the increasing impact of mass transport. The current density at a low cell voltage (0.2 V) was therefore taken as the parameter to evaluate nine mesh grids (see Table 5) and determine the influence of the element number on the solution. In this study, the number of elements on various computational domains, including flow channel, GDL, CL and membrane, was investigated with a fixed number of elements (250) along the channel [36]. Three levels of element numbers were studied in each domain, which guaranteed the total number of element increasing at

227 1×10^4 each time. Fig. 2 shows that the current density reaches an asymptotic value while the
228 computation duration increases as the number of elements increases. The current density almost kept
229 as a constant when a finer mesh as Grid 7 was applied. A relative rapidly increase in computational
230 duration was observed from Grid 5 to Grid 7. This indicated that the time consuming step among the
231 computational process was in the catalyst layers, in which numbers of transport and electrochemical
232 processes were involved. In order to reduce the calculation error, finer mesh has to be developed on
233 catalyst layers. Having balancing both the computational accuracy and duration, Grid 6 was selected
234 considering a sufficient reliability to ensure mesh independence with acceptable calculating time.

235 3. Results and discussions

236 3.1 Model validation

237 Fig. 3 shows the comparison of the simulation results with experimental data obtained both
238 in-house and selected from literature [41]. For the in-house case shown in Fig. 3(a), the anode and
239 cathode catalyst layers were made from 20% Pt/C with a Pt loading of 0.1 and 0.4 mg cm^{-2},
240 respectively. 5% Nafion® ionomer solution in de-ionized water was used as binder. The ionomer mass
241 ratios were 20% in the catalyst layers at both the anode and cathode. Nafion® 112 membrane was used
242 as electrolyte sandwiched between anode and cathode. The graphite plates with an active area of 1.0
243 cm × 1.0 cm were grooved with serpentine gas channels with a dimension of 0.1 cm × 0.1 cm. For the
244 case in Fig. 3(b), 40% Pt/C with a platinum loading of 0.4 mg cm^{-2} was used. Serpentine flow field
245 was applied as well with a dimension of the 0.1 cm × 0.1 cm and an active area of 7.2 cm × 7.2 cm.
246 For the formal case, the cell was tested with the cell and gas inlet temperatures at 80 °C under a
247 hydrogen flow rate of 200 sccm at the anode side and an air flow rate of 500 sccm at the cathode side.
248 For the latter case, cell and gas inlet temperatures were 70 °C with the hydrogen flow rate of 1200

sccm and air flow rate of 2200 sccm. Reactant gas pressure and humidity were kept at 1.0 atm and 100% for both cases. The parameters used for model validation and base case in this study are listed in Table 6. The cathode transfer coefficient (α_c) was obtained by fitting the experimental polarisation curves in the kinetics control zone (cell voltage higher than 0.8 V) and the obtained α_c was further verified by the Tafel slope worked out in the model [40]. More details of the membrane electrode assembly (MEA) preparation and cell test can be found elsewhere [37-39, 41].

A good agreement between the simulation results and the experimental data is indicated by Fig. 3 at higher cell voltages, corresponding to lower current densities, due to the slow reaction rate and insignificant mass transport impact. There was a typical drop in cell voltage due to various losses in terms of activation polarization loss, ohmic loss and concentration polarization loss, as the current density increased. A more rapid drop in current density, caused by the increasing mass transport resistance, was observed at high current densities (mass transport control zone), where the departures of simulation results compared with experimental data was clearly observed. The rapid decrease in current density can be explained by the increase in mass transfer losses due to the oxygen diffuses to and then adsorbs on catalyst surface to perform electrochemical reactions, which is determined by both the electrode structure and the reactant provided, e.g. the mole fraction of oxygen against nitrogen and water vapor in air at the cathode side. When the balance between diffusion and consumption rates is achieved, a limit current density is reached. The formation of liquid water inside the electrode void space restricts oxygen diffusion, especially if it is accumulated liquid water near the downstream channel. However, the 2D model in this study failed to fully represent the whole MEA, leading to an under-estimation of the impact of mass transfer losses in the downstream channel. Especially for a large active area in the case of Wang [41], the departure of simulation result and

271 experimental data is more apparent.

272 3.2 Comparison of different mechanisms

273 Three models of describing the effect of liquid water generation were compared, based on the
274 polarization curves, through the reaction mechanism: traditional B-V, (1-s) corrected B-V and
275 agglomerate models. The results are shown in Fig. 4 and the channel lengths are 1 and 10 cm in Fig.
276 4(a) and Fig. 4(b), respectively. The current density predicted using (1-s) corrected B-V model was
277 slightly lower than that by traditional B-V model in the full range of cell voltage. Compared with Fig
278 3, we can see that the agglomerate model is in better agreement with the experimental results, while
279 the (1-s) corrected B-V model still shows limitations in describing the significant mass transport
280 resistance at high current density. This is because the cell performance at high current density is
281 determined by mass transport rather than electrochemical kinetics. Even through the predicted current
282 densities are deduced by considering the partial occupation of platinum active site by liquid water, the
283 (1-s) corrected B-V model fails to take the gas diffusion resistance through the ionomer film into
284 account. More rapid drop in current density was observed at high current densities in Fig. 4(b) in
285 comparison with that in Fig. 4(a), which indicated that the impact of mass transport on cell
286 performance at high current densities was more pronounced for long flow channels than for short
287 channels. This can be explained by the larger fuel concentration gradient and more liquid water
288 accumulation in the downstream channel. It is also clear, due to slow reaction rate and low mass
289 transport impact at low current densities, the results predicted by the agglomerate model were very
290 close to that of B-V model. However, the agglomerate model is capable of capturing the impact of
291 mass transport at high current densities by considering the species transport resistance through the
292 ionomer and liquid water films surrounding agglomerates.

3.3 Distributions of reactant gases

The mole fractions of hydrogen and oxygen within electrode and flow channel at various current densities from 0.2 to 1.4 A cm^{-2} are shown in Fig. 5. It is clear the concentrations of both hydrogen and oxygen decrease along the diffusion direction and the concentration gradient is more apparent at high current densities. Hydrogen consumption near the anode outlet is observed from the distribution of hydrogen mole fraction shown in Fig. 5(a). This can be explained by the electrochemical reaction and the effect of electro-osmotic drag (EOD), especially at high current densities. The increase in current density from 0.6 to 1.0 A cm^{-2} leads to a 69% increase in the rate of hydrogen consumption by HOR and a 63% increase in the water flux under the driving force of EOD. In comparison with hydrogen concentration distribution in flow channel, Fig. 5(b) indicates that, oxygen remains at a very high concentration close to the inlet level in flow channel, in the full range of current densities from 0.2 to 1.4 A cm^{-2}, along the air flow direction. On the contrary, a significant concentration gradient is shown through the diffusion direction as the current density increases, which is in consistence with the previous modelling results of Nguyen et al. [42]. This can be explained by the increase in oxygen consumption due to the accelerated ORR and the presence of large oxygen transport resistance through the electrode. In addition, the more water generated at high current density dilutes the oxygen. The formation of liquid water reduces the porosity of the electrode and increases the thickness of liquid water film surrounding the agglomerate, leading to a further decrease in the oxygen diffusivity through the electrode before it can reach the active sites. However this does not happen at the anode side due to the much easier diffusion of the smaller hydrogen molecular and its relative high mole fraction.

3.4 Distributions of effectiveness factor

315 The effectiveness factors, used to evaluate how effective the catalyst layer is utilized, of the ACL
316 and CCL at various current densities from 0.3 to 1.2 A cm^{-2} are shown in Fig. 6. In Fig. 6(a), X=0 and
317 X=1 represent the interfaces of GDL-CL and CL-membrane of anode, while Y=0 and Y=1 represent
318 the anode inlet and outlet, respectively. In Fig. 6(b), X=0 and X=1 represent the interfaces of
319 membrane-CL and CL-GDL of cathode, while Y=0 and Y=1 represent the cathode outlet and inlet,
320 respectively. The highest effectiveness factors, for both the ACL and CCL, are observed at 0.3 A cm^{-2},
321 which decrease with the increase of the current density to 1.2 A cm^{-2}. The decrease in effectiveness
322 factor can be explained by the increased electrochemical reaction rate as the current density increases.
323 At this stage, the overall reaction rate is mainly determined by the rate of chemical reaction rather
324 than mass transport. As the current density increases, the increase in electrochemical reaction rate
325 leads to a faster consumption of reactant gases relative to the diffusion rate to the active sites. The rate
326 determining process therefore changes from the electrochemical reaction to the reactant gas diffusion.
327 Consequently, along the gas diffusion direction through catalyst layers, the catalyst utilization is
328 higher near the GDL-CL interface (X=0 for anode and X=1 for cathode) than that of the CL-membrane
329 interface (X=1 for anode and X=0 for cathode), which agree with the finding of Sun et al. [26]. It is
330 important to note that the change of the effectiveness factor is not pronounced along the reactant gas
331 flow direction (Y direction). This is because the gases are supplied above stoichiometric requirements.
332 Reactant gases are provided at such rates to guarantee the almost uniform concentrations along the
333 channels. A comparison of Fig. 6(a) and Fig. 6(b) shows a much higher effectiveness factor of ACL
334 than that of CCL, especially at high current densities. The ACL effectiveness factor remains high, ca.
335 80%, for a certain distance along the hydrogen diffusion. On the contrary, due to the large oxygen
336 transport resistance through the cathode, the effectiveness factor of CCL is much lower compared

with that of ACL. The platinum catalyst in the CCL located near the CL-GDL interface cannot be fully utilized, resulting in a waste of expensive catalyst.

3.5 Distributions of current density

Fig. 7 shows the current density distributions within the catalyst layers of anode and cathode at various cell voltages from 0.7 to 0.4 V. The current densities increase in both catalyst layers as the cell voltage decreases. It can be seen that the current densities decrease along the reactant gas diffusion direction at both the anode and cathode, leading to insufficient utilization of the catalyst near the CL-membrane boundary (X=0 for cathode and X=1 for anode). On the contrary, the current densities almost remain constant along the reactant flow direction. It is apparent that the current density distribution in the ACL is more uniform than that in the CCL. In the region near the CL-membrane interface, the anode current density is higher than the cathode current density at a fixed cell voltage. This can be explained by the sluggish ORR in the cathode. Due to the slower ORR in the cathode, the interior of the cathode catalyst layer is not fully utilised, especially at a high current density.

3.6 Distributions of liquid water saturation

The liquid water saturations in both electrodes, including CLs and GDLs, are shown in Fig. 8. The coordinates of X and Y indicate the same geometry as those in Fig. 6. It is clear that the liquid water saturation increases in both electrodes as the current density increases. Also, the liquid water saturation is relatively high near the outlets in both electrodes, indicating more severe water flooding in these areas. This finding is in consistence with the experimental measurement of Iranzo et al. [20]. Comparison of Fig. 8(a) and Fig. 8(b) shows that the gradient of liquid water saturation is greater in cathode electrode than of the anode, especially along the channel direction.

3.7 Distributions of temperature

359 The temperature profiles at various current densities from 0.6 to 1.0 A cm^{-2} are shown in Fig. 9. A
360 non-uniform temperature distribution is clearly indicated. The temperature increases along the air
361 flow and decreases from the cathode to the anode through the membrane with the highest value at the
362 cathode side. The most significant temperature rise, as expected, is observed in the cathode, leading to
363 a ca. 4 °C difference between anode and cathode at 1.0 A cm^{-2}. This temperature increase at the
364 cathode can be explained by both the exothermic ORR and water phase-transfer occurred. The latter
365 comprises ca. 6% of the total heat released at 1.0 A cm^{-2} (Table 7), which is the latent heat associated
366 with water phase change from dissolved water to liquid water during membrane/ionomer desorption.
367 A temperature rise along the cathode flow channel is clearly shown in Fig. 9. This can be explained by
368 the heat released by water phase-transfer as liquid water is pushed downstream to the channel exit by
369 the airflow.

370 As a main heat source, the heat released by ORR comprises more than 90% of the total heat
371 released at 1.0 A cm^{-2}. Similar to the ORR in the cathode, the HOR in the anode occupies more than
372 88% of the total heat change, which therefore can be considered as the main heat source in the anode.
373 Due to the endothermic nature and large contribution of the HOR to the total heat in the anode, the
374 anode is endothermic in full range of current densities. With the increase in current density, the ratio
375 of HOR to the total heat in the anode increases whereas that of ORR to the total heat in the cathode
376 decreases. In the anode, the heat released by ionomer water uptake is the second main heat source,
377 which comprises ca. 10% of the total heat in the anode at 0.2 A cm^{-2}. As the current density increases,
378 there is a decrease in the contribution of the heat released by ionomer water uptake in the anode. This
379 is caused by a relative fast increase in the heat absorption due to the HOR. Although the absolute heat
380 released by ionomer water uptake increases, the ratio decreases from ca. 11% to 3% as the current

density increases from 0.2 to 1.0 A cm^{-2}. Table 7 also shows that the heat contribution of ORR decreases and ionomer desorption increases with the increase in current density in the cathode. This is because more dissolved water is generated at a high current density, which then transfers to liquid water by ionomer desorption after the ionomer is fully saturated.

The detailed temperature profiles at the anode channel-GDL interface are shown in Fig. 10. The temperature increases sharply along the hydrogen flow direction until a maximum temperature is achieved, then slightly decreases near the anode outlet. The maximum temperature is located in the middle of the channel near to the inlet. The temperature rise in the anode is much less than that of the cathode due to the endothermic HOR within the anode catalyst layer (Fig. 9). This increase can be explained by the heat transferred from the cathode and the latent heat released via water phase-transfer. As shown in Table 7, the heat via water phase-transfer approximately comprises 11% of total heat in the anode at 0.2 A cm^{-2}, which decreases to less than 3% as the current density increases to 1.0 A cm^{-2}. Therefore, heat transfer from the cathode is the main heat source contributed to the temperature rise in the anode.

3.8 Comparison of the isothermal and non-isothermal model

Fig. 11 shows the liquid water saturation at the cathode CL-GDL interface at 1.0 A cm^{-2} simulated by both the isothermal and non-isothermal models. The dimensionless coordinate is the same as in Fig. 1. The liquid water saturation increases along the air flowing direction at the cathode GDL-CL interface. By taking the temperature rise into account, the liquid water saturation predicted by the non-isothermal model is slightly smaller than that by the isothermal model, caused by the fast increase in the saturation pressure of water vapour (p_{sat}) with temperature. Specifically, p_{sat} increases from 31.16 to 36.99 kPa as temperature increases from 70 to 74 °C. The increase in the saturation pressure

403 of water vapour, improves the water carrying capacity (WCC) of gas mixture, thus to a certain extent,
404 prohibits the water phase-transfer from vapour to liquid water. Furthermore, the temperature rise is
405 more apparent at a high operating temperature in comparison with a low one [38]. The heat released
406 during fuel cell operation can help mitigate water flooding by improving the WCC of the reactant
407 gases. However, this is at the expense of reducing the effective oxygen concentration of the cathode
408 reactant gas, which may results in a more significant decline in cell performance than that induced by
409 flooding. The mole fraction of oxygen in a fully humidified mixture decreases from 18.24% to 13.34%
410 as temperature increases from 70 to 74 °C, which may lead to oxygen starvation and damage to the
411 cathode. Thus, for a fuel cell operated at a high temperature, the performance may be limited by the
412 excessive moisture in the cathode reactant gas.

413 3.9 Regressed expressions for liquid water saturation

414 Fig. 12 shows the liquid water saturation in both electrodes (including CLs and GDLs) at various
415 current densities. It indicates that the increase of the current density leads to a logarithmic increase in
416 the liquid water saturation, which is greater in the cathode than that in the anode. In addition, the
417 liquid water saturations are slightly larger in CLs than that in GDLs at both electrodes, especially in
418 the cathode due to the water generated via ORR.

419 Mathematical expressions are regressed in terms of logarithmic and exponential equations to fit the
420 average liquid water saturation in both electrodes, as shown in Fig. 13, respectively. Linear
421 logarithmic transform function (Log3P1) and two-phase exponential decay function with time offset
422 (ExpDecay2) were selected as regression functions. The cathode average liquid water saturation (s_c) in
423 Fig. 13(a) could be well fitted by a logarithmic expression (Eq. 22) with a R^2 coefficient of 99.33%.
424 (R^2 is a statistical measure of how close the data to the fitted regression line). However, a large error

of fitting occurs in medium and high current densities when applying the same regression function to the anode average liquid water saturation (s_a). The logarithmic expression (Eq. 23) led to a R^2 coefficient of only 94.26% and a remarkable standard error of parameter c. Thus, the logarithmic expression of s_a - i was considered as an unconfident relationship without enough accuracy. Instead, an exponential expression (Eq. 24), more complex in form in comparison with logarithmic expression, is regressed in Fig. 13(b). It can be seen that the exponential express is more accurate here.

$$s_c = 0.1344 + 0.05912\ln(i + 0.15109) \quad (R^2 > 99.33\%) \tag{22}$$

$$s_a = 0.07405 + 0.01354\ln(i + 3.00567\times10^{-4}) \quad (R^2 > 94.26\%) \tag{23}$$

$$s_a = 0.10232 - 0.06965\exp(-\frac{i + 0.00489}{1.12255}) - 0.0378\exp(-\frac{i + 0.00489}{0.02805}) \quad (R^2 > 99.88) \tag{24}$$

The average liquid water saturations in both electrodes with respect to the current density higher than 0.6 A cm^{-2} are shown in Fig. 14. Log3P1 function, which is used to fit the data plotted, results in accurate expressions (Eq. 25 and Eq. 26) with R^2 greater than 99.9% in both electrodes. This indicates that the changes in the average liquid water saturation in both electrodes follows a logarithmic relationship at current densities higher than 0.6 A cm^{-2}. Comparing Fig. 14 with Fig. 13(b) suggests that, as the current density increases, the increase in the average liquid water saturation in the anode firstly obeys exponential function at low current densities followed by logarithmic function at high current densities. However, it is insufficient to describe the relationship between the anode average liquid water saturation and current density using a logarithmic function in full range of current densities.

$$s_c = 0.11463 + 0.07763\ln(i + 0.40119) \quad (R^2 > 99.99\%) \tag{25}$$

$$s_a = 0.06909 + 0.02897\ln(i + 0.16568) \quad (R^2 > 99.90\%) \tag{26}$$

The relationship between average liquid water saturation in the anode and the cathode is regressed

in Fig. 15. The data plotted can be roughly divided into three segments, corresponding to the liquid water saturation at the low, medium and high levels. In order to guarantee the accuracy, the R^2 coefficient of each regression expression within each segment is controlled greater than 99.9%. The results indicate that at the low and high liquid water saturation, a linear relationship exists between the average liquid water saturations in the anode and the cathode. However, at the medium liquid water saturation, the exponential function is more accurate than the linear relationship. The relation of liquid water saturation at the anode and cathode is similar to the modelling results of Jiang and Wang [43].

As stated by O'Rourke et al. [21], the water flooding in anode could be detected prior to severe damage of cathode catalyst, which could be avoided with the aid of the regressed expressions of the liquid water saturation in the anode and the cathode.

$$s_c = 3.65764 s_a - 1.45542 \times 10^{-4} \quad (R^2 > 99.99\%) \quad \text{low water saturation} \tag{27}$$

$$s_c = \exp(27.0888 s_a^2 + 31.24035 s_a - 4.00174) \quad (R^2 > 99.44\%) \quad \text{medium water saturation} \tag{28}$$

$$s_c = 2.32873 s_a - 0.03044 \quad (R^2 > 99.96\%) \quad \text{high water saturation} \tag{29}$$

4. Conclusion

A two-dimensional, two-phase flow, along-the-channel, non-isothermal, CFD model for a single PEMFC is developed. Water was treated as three different phases: vapour, dissolved and liquid water. The water phase-transfer between each phase, associated with the combinational transport mechanism through the membrane, is numerically studied. Three types of models are compared for hydrogen reduction and oxygen oxidation in catalyst layers, including traditional B-V, (1-s) corrected B-V and agglomerate mechanism. Temperature changes in MEA and channels due to electrochemical reaction, ohmic resistance and water phase change are analysed and the contribution of each heat source is summarised and compared at a variety of current densities. Mathematical expressions for liquid water

saturations against current density at both anode and cathode are regressed and the mathematical relationship between them is developed. Analysis of the simulation results leads to the following insights:

The current density predicted by traditional B-V, (1-s) corrected B-V and agglomerate models are in general agreement with experimental data at low current densities. As the current density increases, by accounting for the extra oxygen diffusion resistance through the ionomer/water film and the loss of catalyst layer porosity due to ionomer swelling, the agglomerate model gives more accurate simulation results in comparison with the others. However, due to significant water flooding in downstream channel, the 2D model developed cannot fit the experimental data very well at high current densities, especially when long flow channels are applied. Due to the more significant transport resistance of oxygen in the cathode than that of hydrogen in the anode, the effectiveness factor of the cathode catalyst layer is much lower than that of the anode catalyst layer.

Water flooding, represented by the liquid water saturation, is prone to occur near the downstream channel of both the anode and cathode. Liquid water saturation is temperature dependent, which requires the non-uniform distribution of temperature predicted by the non-isothermal model. The most significant temperature rise is in the cathode catalyst layer due to the contribution of exothermic ORR, which comprises more than 90% of total heat released. With the increase in the current density, the heat contribution of ORR decreases while ionomer/membrane desorption increases. On the contrary, the endothermic HOR is the main heat source in the anode. At a low current density, the heat released by ionomer/membrane water uptake contributes ca. 10% to the total heat in the anode.

The mathematical expressions for the relationship between the current density and liquid water saturations in both the anode and the cathode are regressed. Nonlinear current density – water

saturation relations are found at both electrodes. It is believed that the liquid water saturation in the cathode presents logarithm relevant to current density. However, the liquid water saturation in the anode increases exponentially as the current density increase. At a high current density greater than 0.6 A cm^{-2}, the liquid water saturations at both electrodes can be described by logarithmic relationship. The relationship between liquid water saturations in the anode and the cathode is also regressed. It is found that at low and high current densities, the relationship can be accurately represented by linear function, but exponential function is believed to be more accurate at medium current densities.

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593 # Nomenclature

A_s	reaction surface area per unit platinum mass, $m^2\ kg^{-1}$
a	specific area, m^{-1}
$c_{p,i}$	specific heat capacity of species i, $J\ mol^{-1}\ K^{-1}$
c	concentration, $mol\ m^{-3}$
D	diffusivity, $m^2\ s^{-1}$
D_c	capillary diffusion coefficient, $m^2\ s^{-1}$
D_{ij}	Maxwell-Stefan diffusion coefficient matrix, $m^2\ s^{-1}$
E	effectiveness factor
E^0	open circle potential, V
E_{cell}	cell voltage, V
EW	equivalent weight of Nafion® membrane, $g\ mol^{-1}$
F	Farady's constant, $96485\ C\ mol^{-1}$
f	platinum mass ratio to *Pt/C*
H	Henry's constant, $Pa\ m^3\ mol^{-1}$
i	current density, $A\ m^{-2}$
i_0	exchange current density, $A\ m^{-2}$
J(s)	Leverett function
k	rate coefficient, s^{-1}
k_i	Thermal conductivity of species i, $W\ m^{-1}\ K^{-1}$
k_r	relative permeability
k_p	hydraulic permeability, m^2

l	thickness, m
L	volume fraction
M_j	molecular weight for specie j, kg mol^{-1}
M_T	Thieles's modulus
m	mass loading, mg cm^{-2}
N	number per volume, m^{-3}
n	number
p	pressure, Pa
R	ideal gas constant, 8.314 J mol^{-1} K^{-1}
R_M	membrane resistance, Ω m^{-2}
RH	relative humidity
r	radius, m
S	source term
s	liquid water saturation
T	temperature, K
$\mathbf{u}$	velocity vector, m s^{-1}
V	mole volume, m^3
w	mass fraction
X	normalised distance (x/δ_{CL})
x	mole fraction
Y	normalised distance ($z/(z_{CC}+ z_{Ch})$)
$\%M$	volume fraction of primary pores occupied by ionomer

Greek

α	charge transfer coefficient
α_w	water activity
λ	water content
μ	viscosity, Pa s
ρ	density, kg m^{-3}
ε	porosity
δ	thickness of ionomer/liquid water coating, m
γ	oxygen diffusion rate through the coating, s^{-1}
η	overpotential, V
σ	surface tension, N m^{-1}
θ_c	contact angel, °
σ_s	electronic conductivity, S m^{-1}
σ_M	ionic conductivity, S m^{-1}
φ	potential, V
Ψ_w	association parameter for water (the value is 2.6)

Superscripts

0	intrinsic
d	dissolved
eff	effective
ref	reference

eq	equilibrium
l	liquid
g	gas

597 *Subscripts*

a	anode
ads	adsorption
agg	agglomerate
C	carbon
c	cathode
CL	catalyst layer
des	desorption
GDL	gas diffusion layer
i	species i
j	species j
Kn	Knudsen diffusion
M	Membrane/ionomer
P	void space
Pt	platinum
Pt/C	platinum dispersed carbon
p	primary pores
r	relative
S	GDL penetration

s	secondary pores
T	temperature
w	liquid water
sat	saturation
tot	total
vl	vapour to liquid
vd	vapour to dissolved
dl	dissolved to liquid

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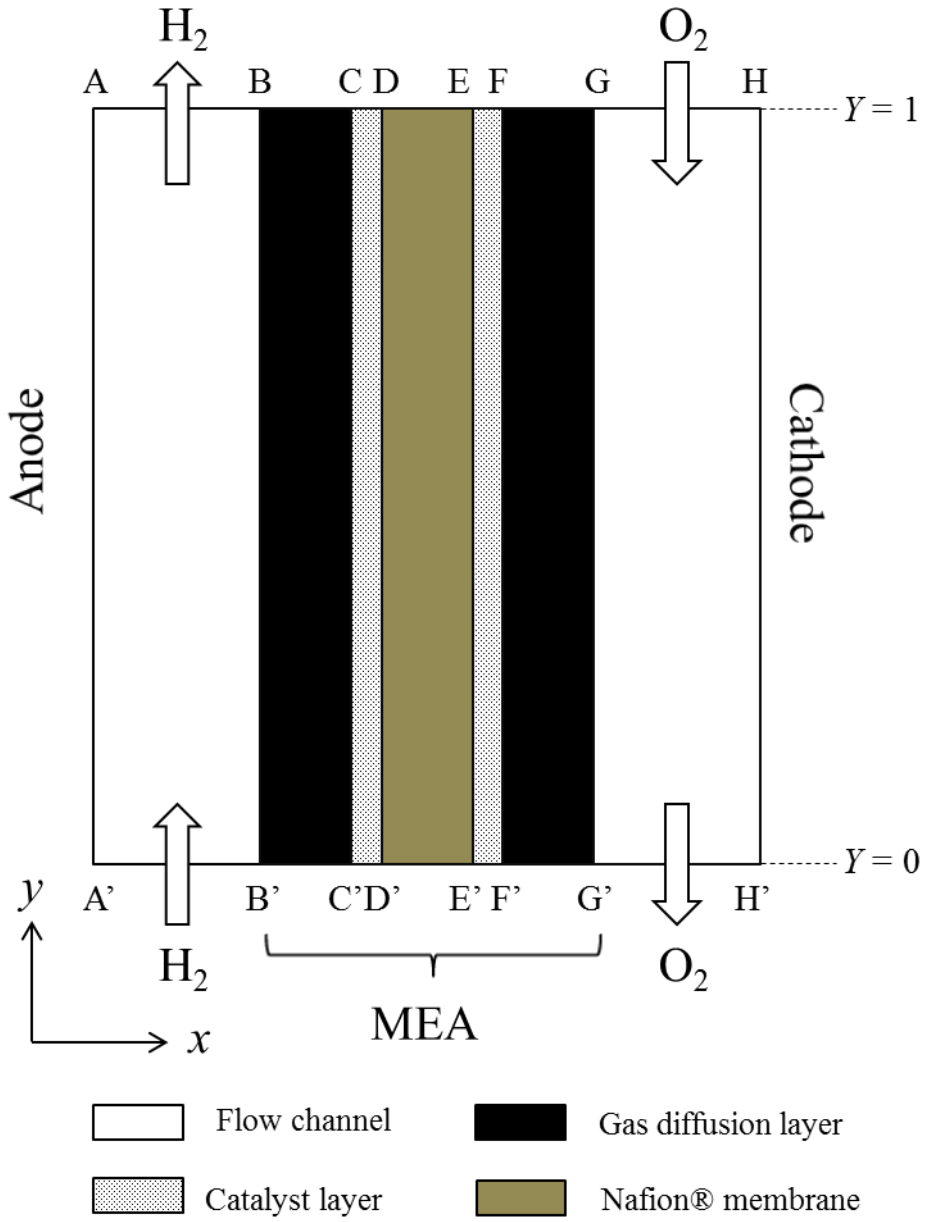


Fig. 1 Schematic of PEMFC unit and modelling domain: A-A' - anode flow channel outer boundary; B-B' - anode flow channel-GDL interface; C-C' - anode GDL-CL interface; D-D' – anode CL-membrane interface; E-E' - cathode CL-membrane interface; F-F' - cathode GDL-CL interface; G-G' – cathode flow channel-GDL interface; H-H' – cathode flow channel outer boundary

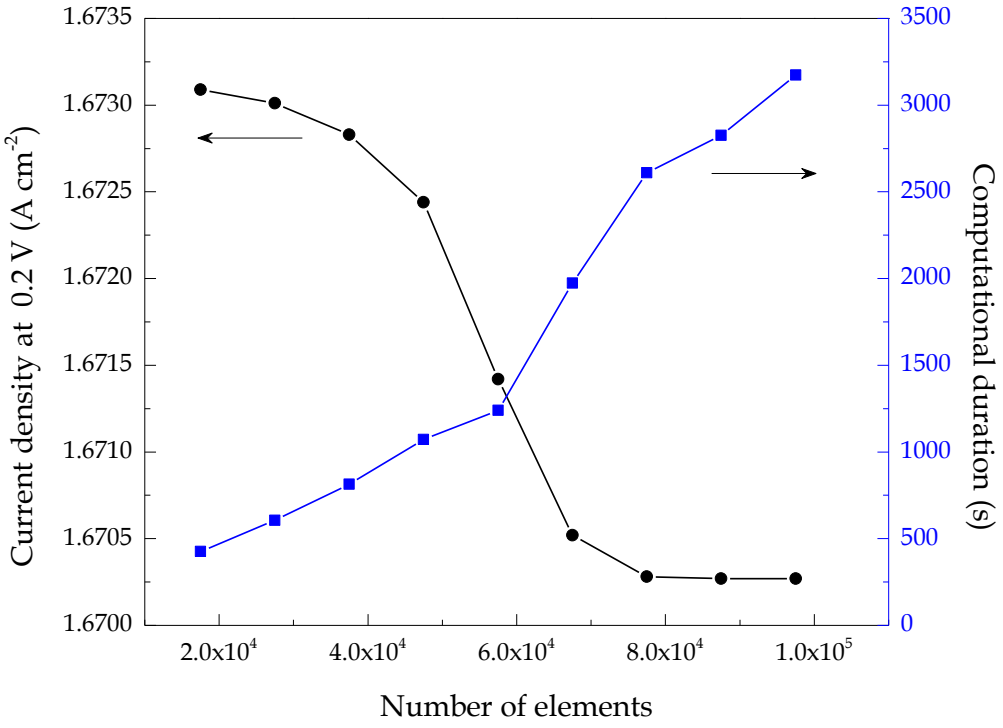
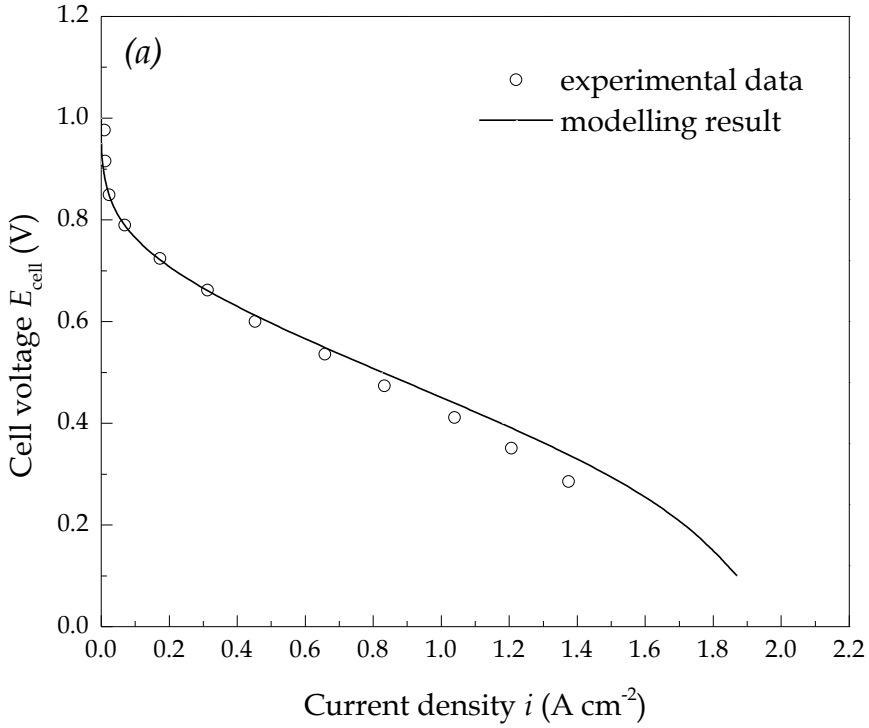


Fig. 2 Effect of mesh characteristics on the current density at 0.2 V



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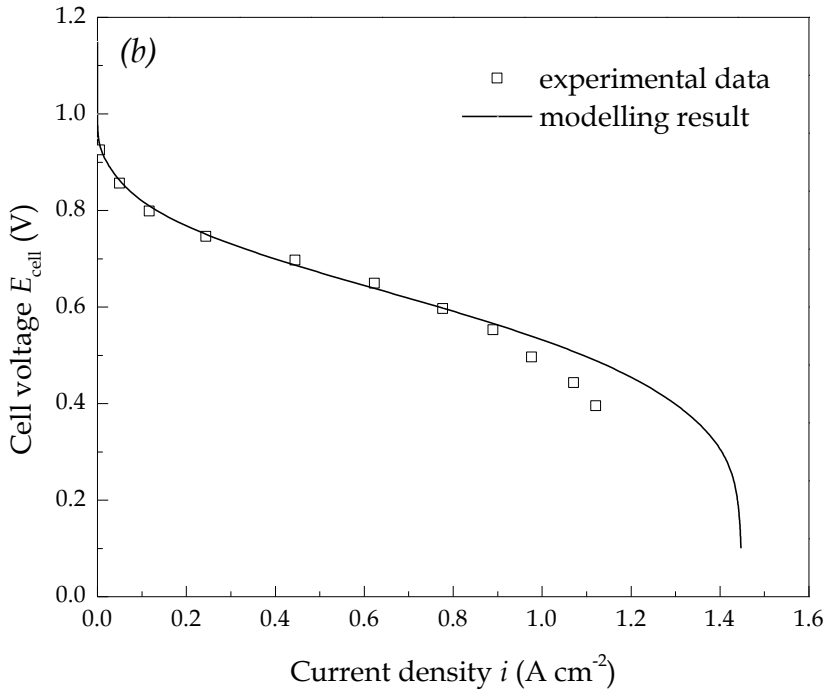

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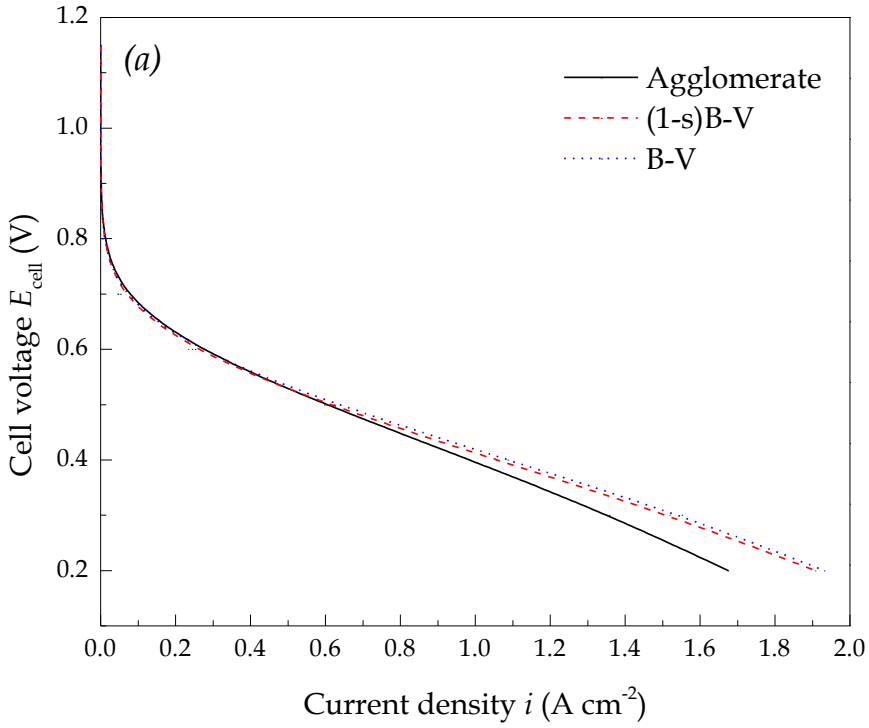
619 Fig.3 Comparison between the modelling results and experimental data for two cases (a) 80 °C, 20% Pt/C, $m_{Pt,a}$ = 0.1 mg
620 cm^{-2}, $m_{Pt,c}$ = 0.4 mg cm^{-2}, effective area: 1.0 cm × 1.0 cm; (b) 70 °C, 40% Pt/C, m_{Pt} = 0.4 mg cm^{-2}, effective area: 7.2 cm ×
621 7.2 cm



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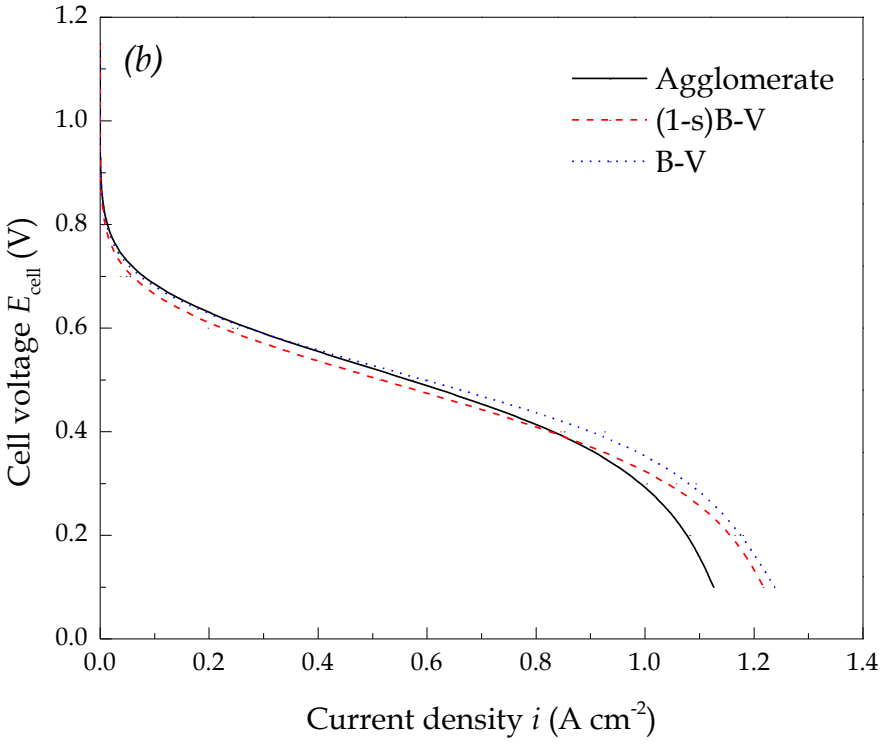

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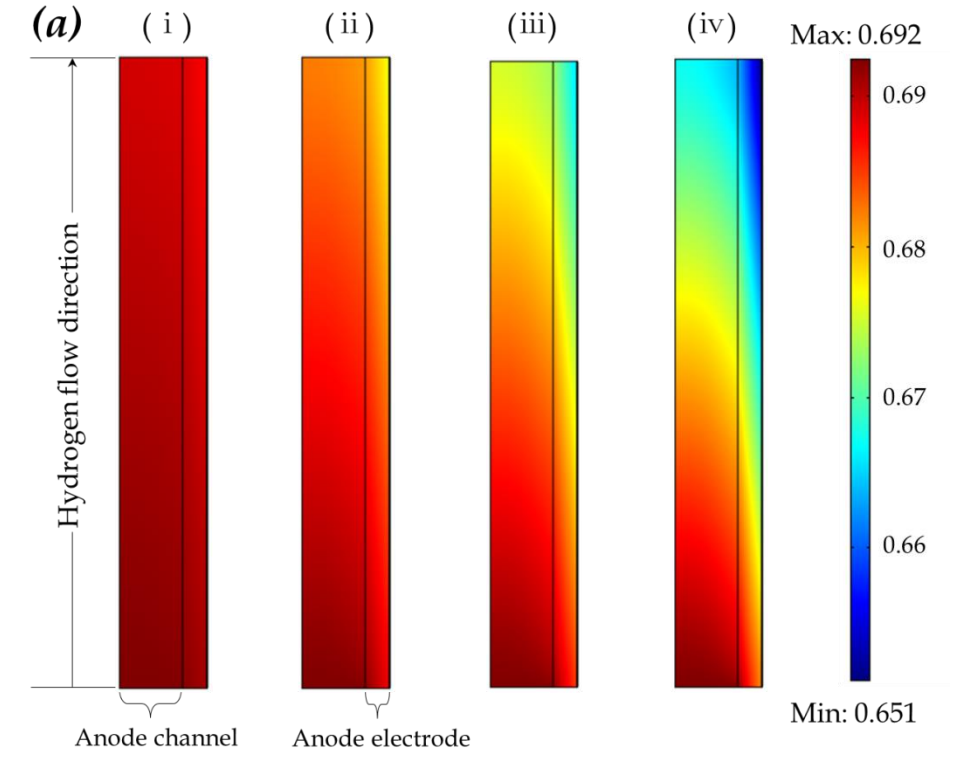
624 Fig.4 Comparison of three mechanisms for (a) a short 1 cm channel and (b) a long 10 cm channel



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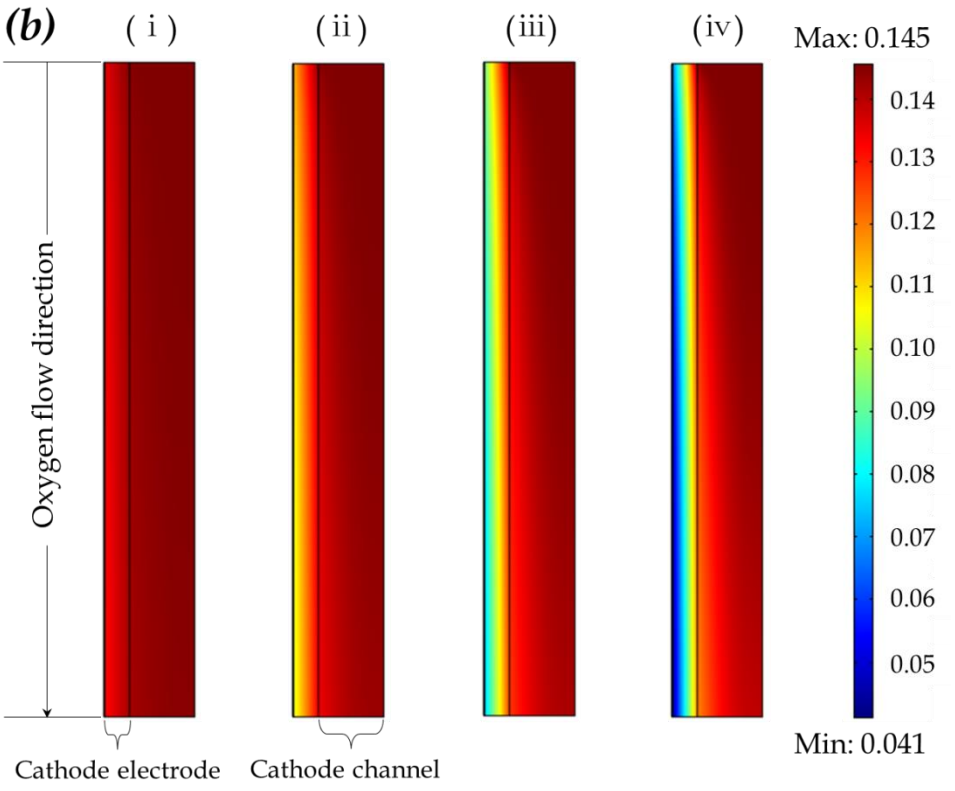

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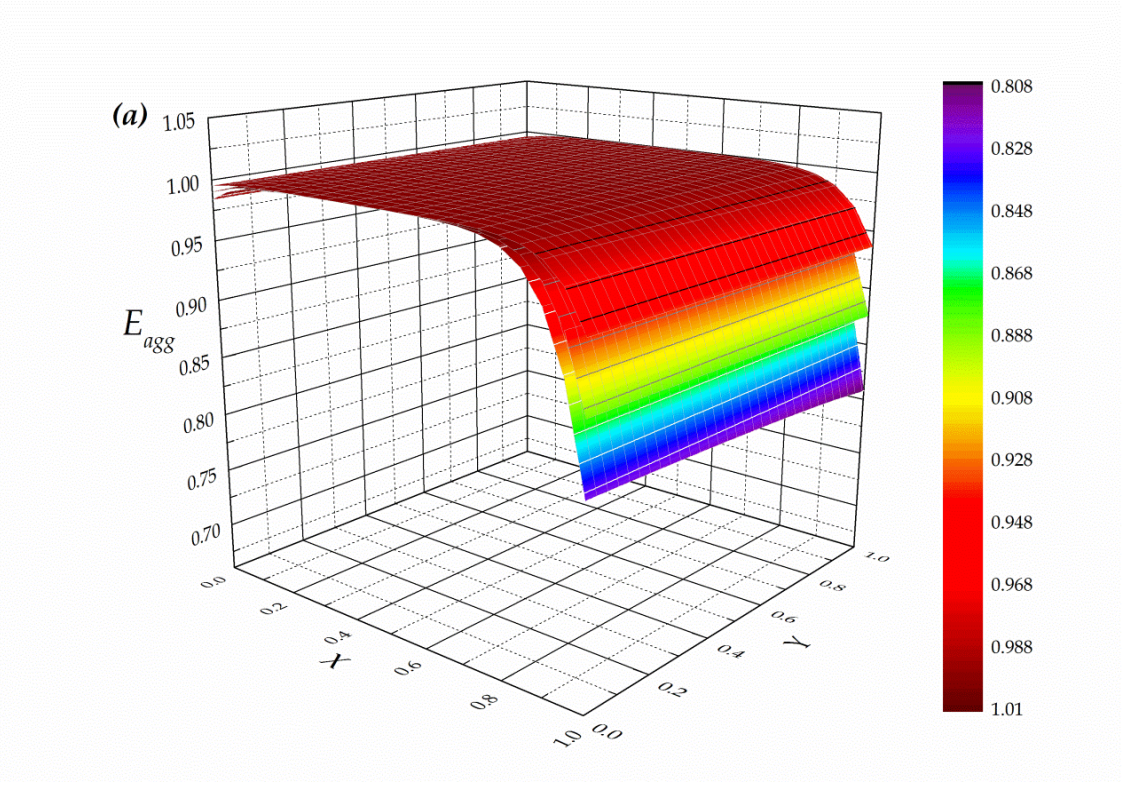
628 Fig.5 Distribution of mole fractions of (a) hydrogen and (b) oxygen at various current densities at (i) 0.2, (ii) 0.6, (iii) 1.0

629 and (iv) 1.4 A cm^{-2}



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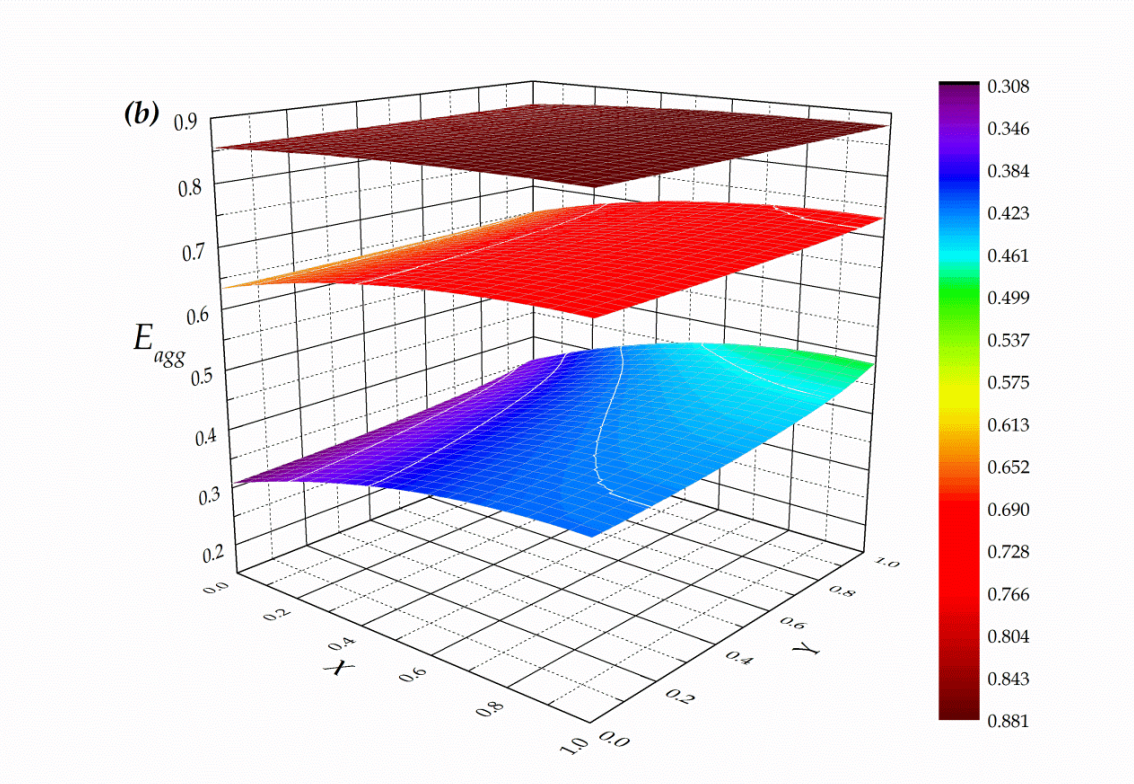

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633 Fig.6 Effectiveness factor of (a) anode CL and (b) cathode CL at various current densities (from up down: 0.3, 0.7 and 1.2 A
634 cm^{-2})

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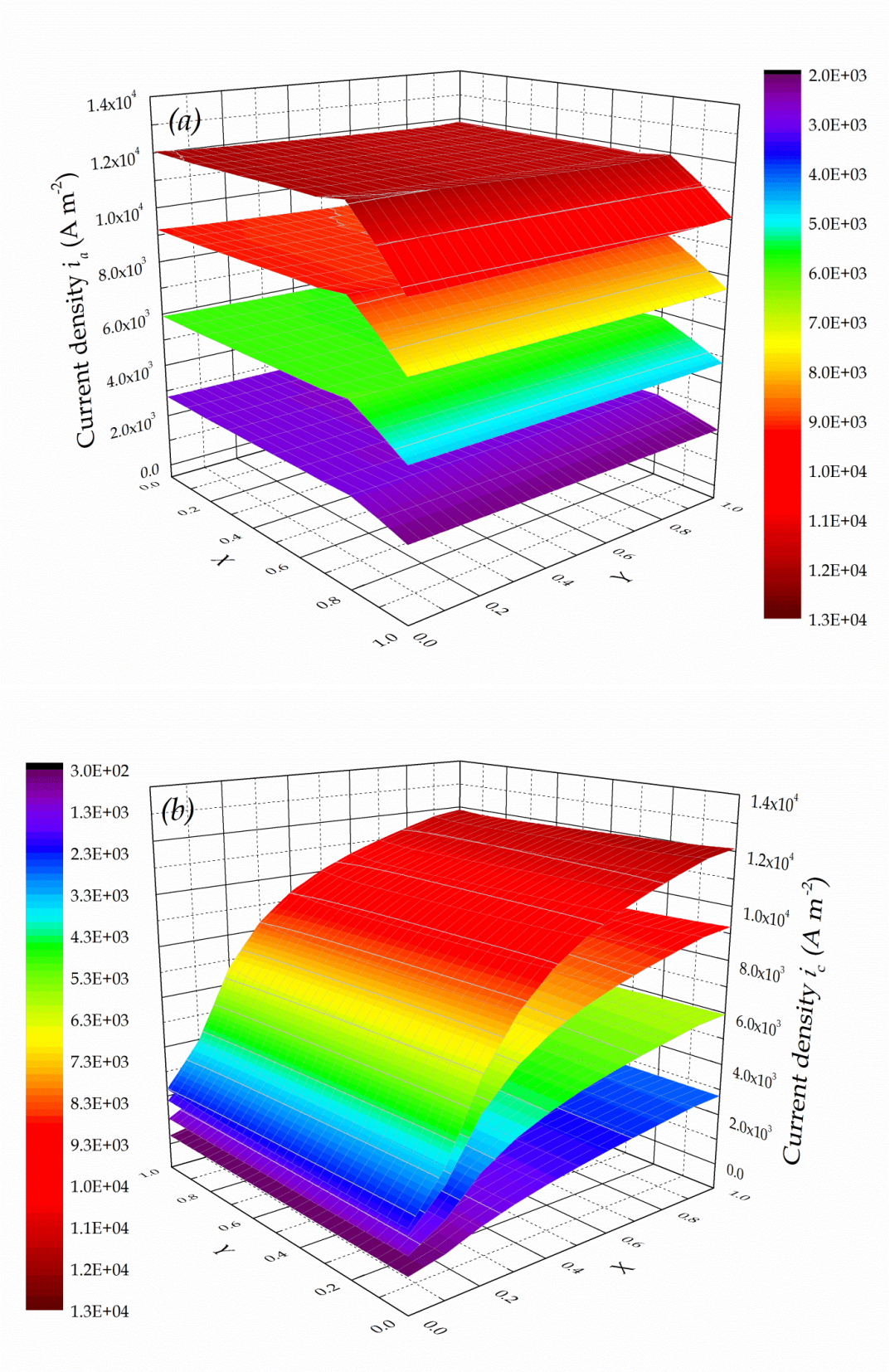

Fig. 7 Current density distribution within (a) the anode CL and (b) the cathode CL (from top down 0.7, 0.6, 0.5 and 0.4 V)

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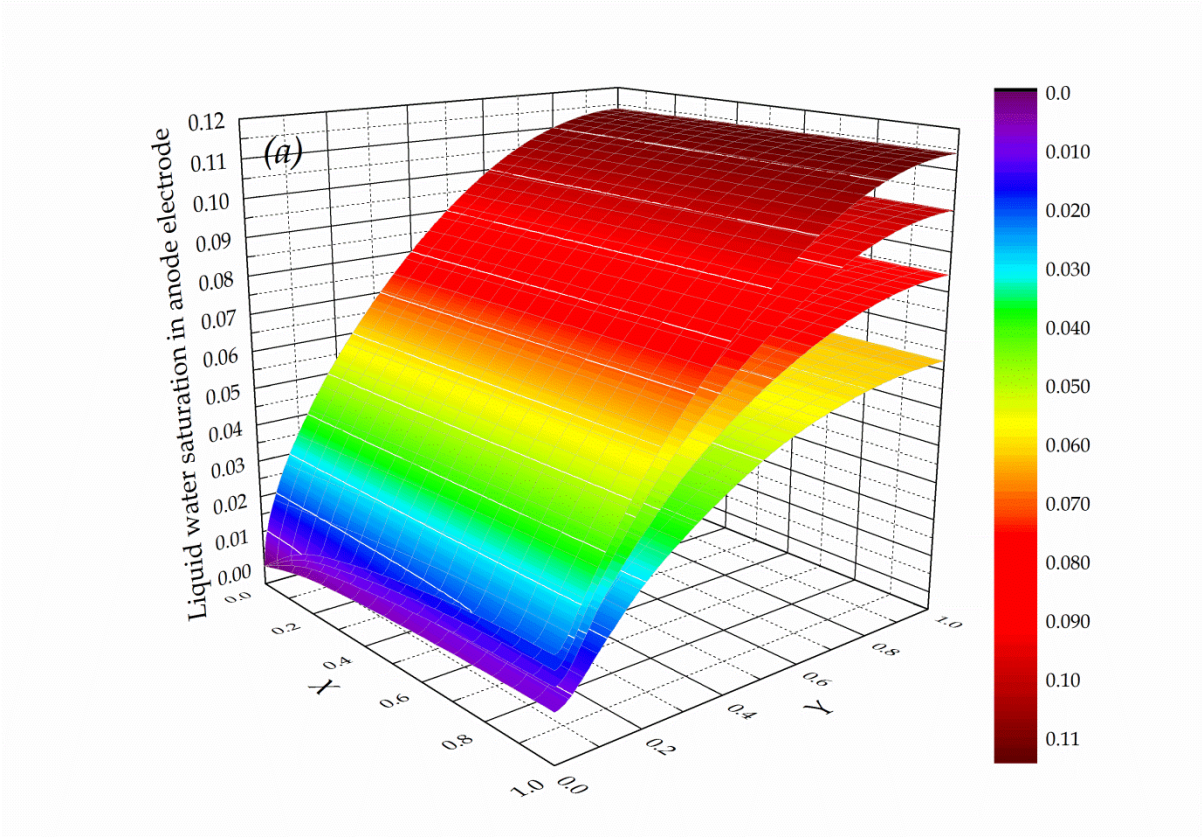

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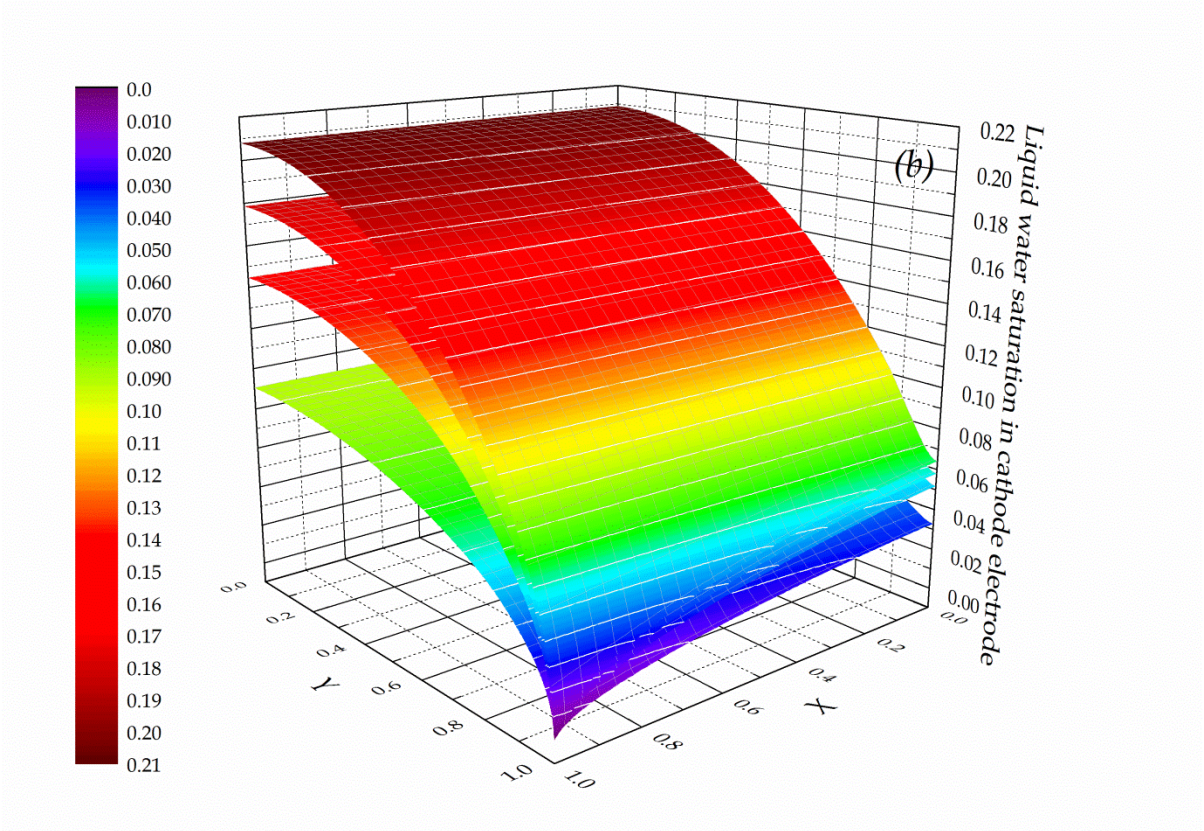
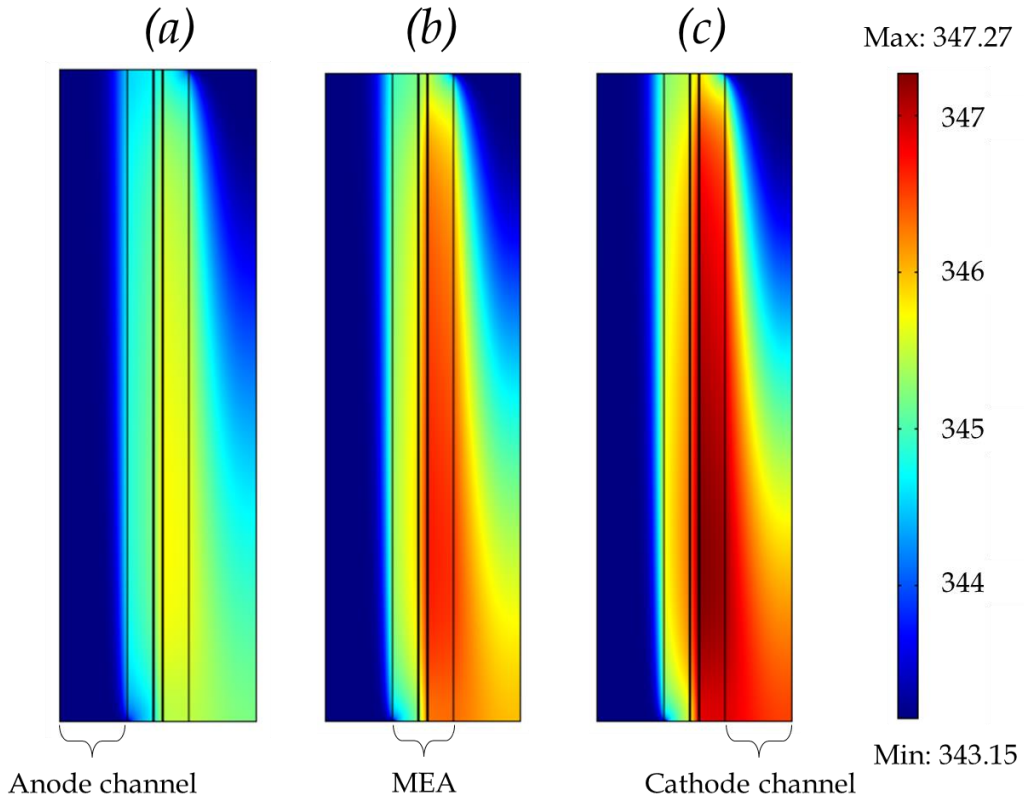


644 Fig.8 Liquid water saturation in CLs and GDLs of (a) anode and (b) cathode at various current densities (i = 0.2, 0.6, 1.0 and

645 1.4 A cm^{-2} from down up)



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647 Fig.9 Temperature profiles at various current densities at (a) 0.6, (b) 0.8 and (c) 1.0 A cm^{-2}

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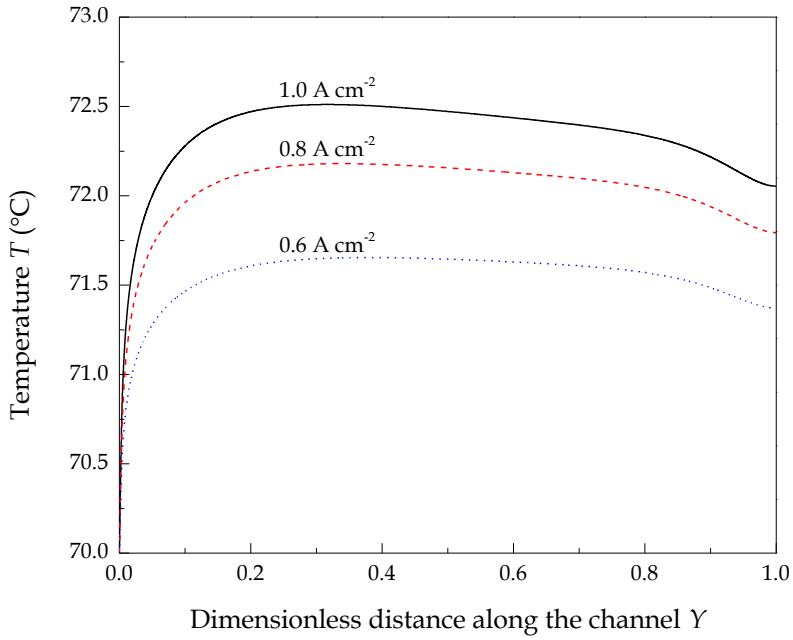
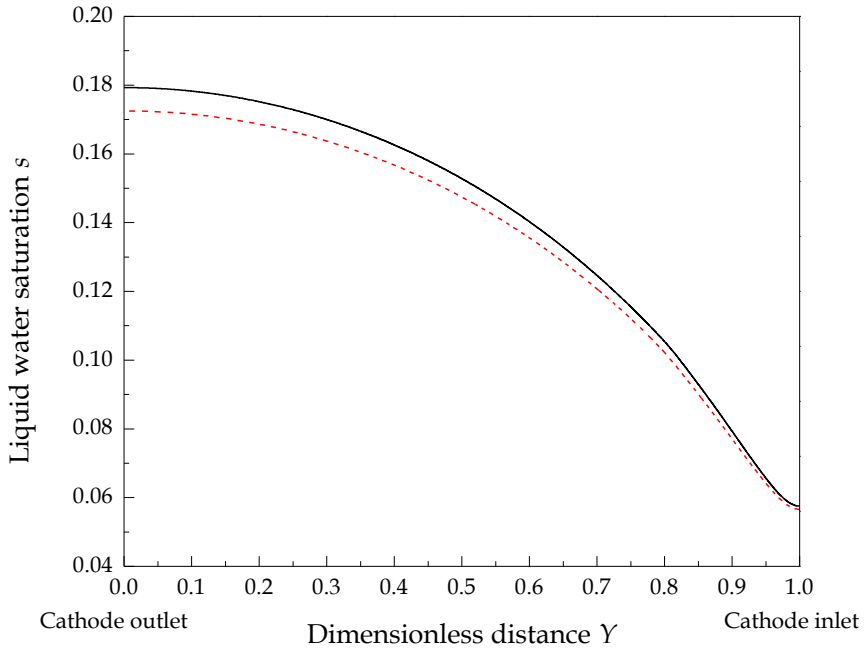


649

650 Fig.10 Detailed temperature profiles at anode channel-GDL interface at various current densities at (a) 0.6, (b) 0.8 and (c)

651 1.0 A cm^{-2}

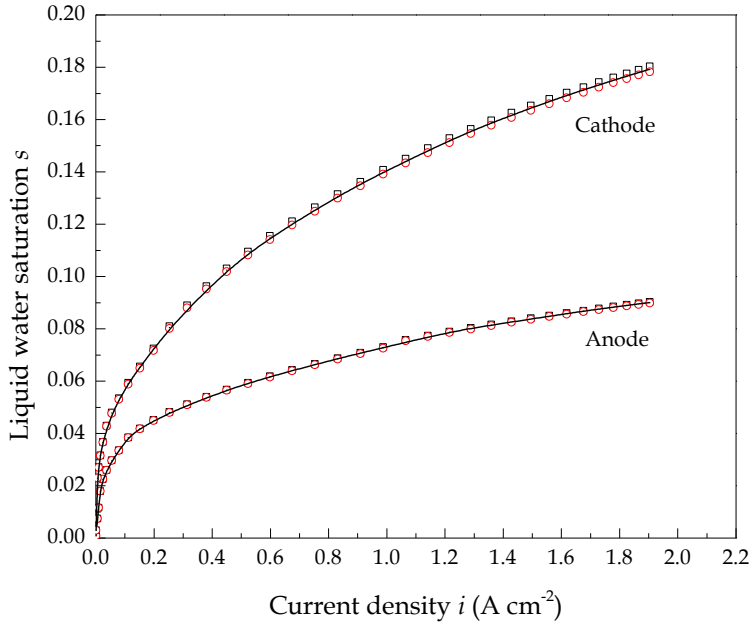


652

653 Fig. 11 Comparison of liquid water saturation at the cathode CL-GDL interface at 1.0 A cm^{-2}, predicted by isothermal and

654 non-isothermal models; Solid line - isothermal model prediction, Dash line - non-isothermal model prediction.

655

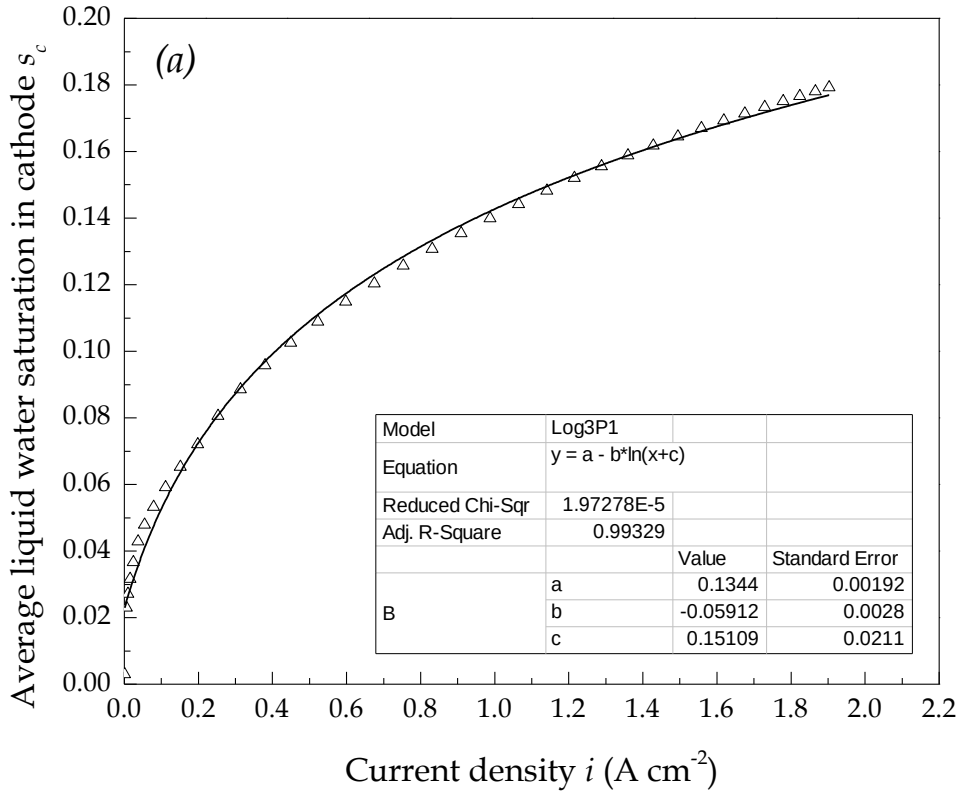


656

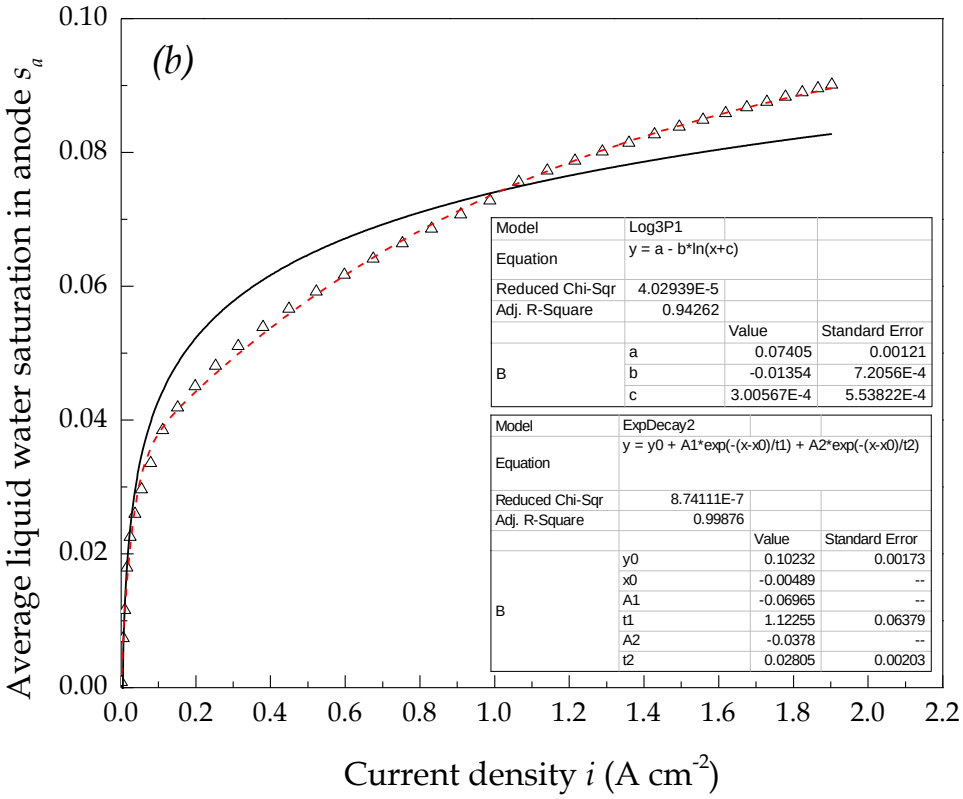
657

658 Fig. 12 Average liquid water saturation in both electrodes at various current densities: □- in catalyst layer, ○- in gas diffusion

659 layer, solid line – average value of CLs and GDLs



660

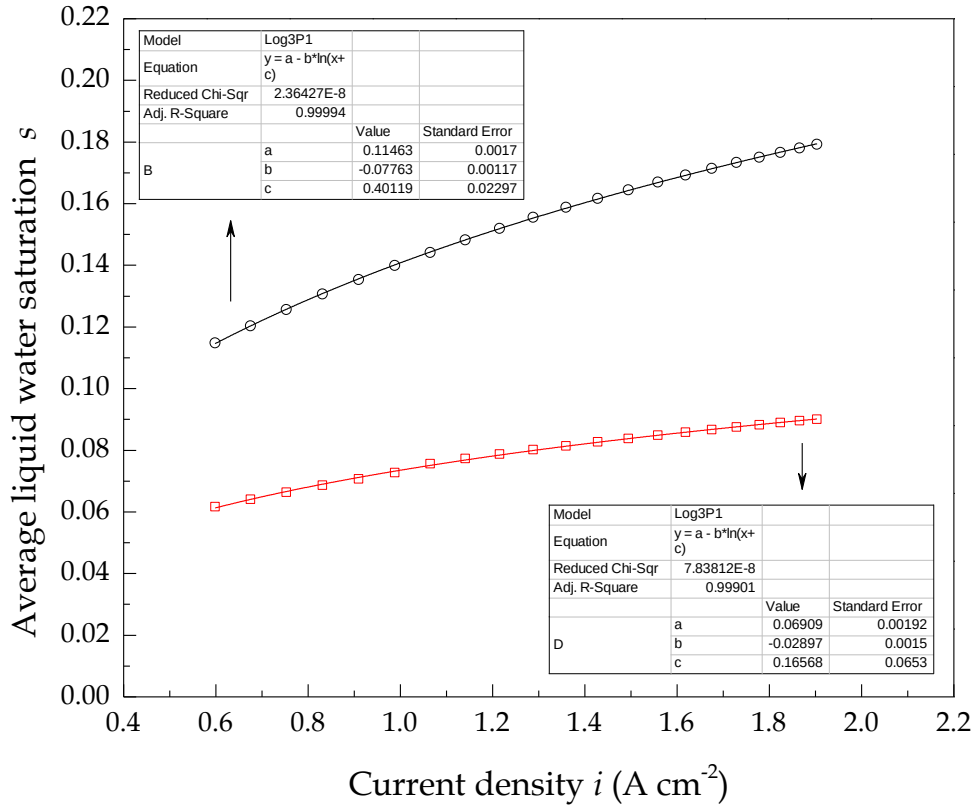


661

662 Fig. 13 Regression expressions of the liquid water saturation versus current density in (a) cathode (b) anode; ∆-average

663 liquid water saturation, solid line - Log3P1 function fitted, dash line: ExpDecay2 function fitted.

664



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667 Fig. 14 Regression expressions of the average liquid water saturation in both electrodes versus current density at the current

668 density > 0.6 A cm^{-2}, □- in anode electrode,○- in cathode electrode, solid lines - Log3P1 function fitted

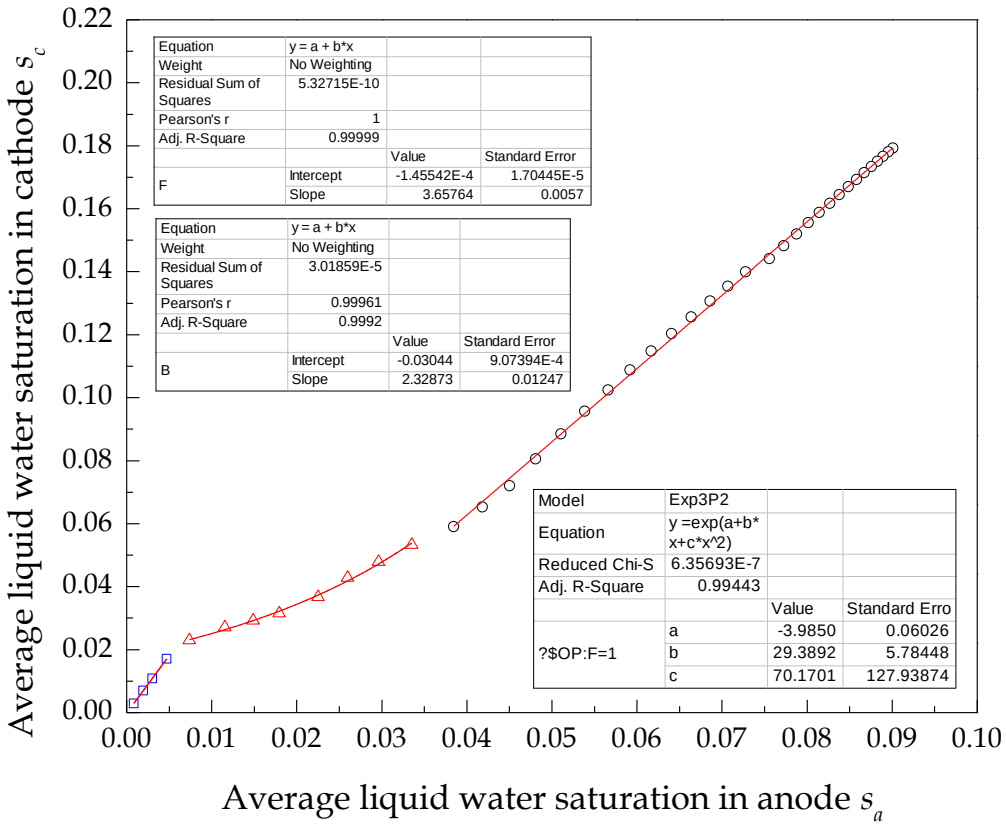

Fig. 15 Relationship between the average liquid water saturation in the anode and the cathode

Table 1 Conservation of water in different phases

	Channels	GDLs	CLs
Water vapour S_w^v	$-S_w^{vl}$	$-S_w^{vl}$	$-S_w^{vd}-S_w^{vl}$
Liquid water S_w^l	S_w^{vl}	S_w^{vl}	$S_w^{dl}+S_w^{vl}$
Dissolved water	0	0	$S_w^{r,i}+S_w^{vd}-S_w^{dl}$

Note: superscript i represents the anode or cathode, the unit for each source term is (mol m^{-3} s^{-1}).

Table 2 Conservation of heat

Membr	CLs	GDLs	Channels
S_T^M	$S_T^{dl} + S_T^{vl} + S_T^{vd} + S_T^{r,i} + S_T^{s,i} + S_T^M$	$S_T^{vl} + S_T^{s,i}$	S_T^{vl}

Note: superscript *i* represents the anode or cathode, the unit for each source term is (W m^{-3}).

687 Table 3 Source terms

Source terms	Unit	Domain
$S_m = M_{H_2} S_{H_2}^g + M_{O_2} S_{O_2}^g + M_w S_w^v$	kg m^{-3} s^{-1}	GDLs, CLs and channels
$S_{H_2}^g = \frac{i_a}{2F}$	mol m^{-3} s^{-1}	ACL
$S_{O_2}^g = \frac{i_c}{4F}$	mol m^{-3} s^{-1}	CCL
$S_w^{rc} = \frac{i_c}{2F}$	mol m^{-3} s^{-1}	CCL
$S_w^{vd} = k_{ads}(c_w^{eq} - c_w^d) \quad c_w^d < c_w^{eq}$	mol m^{-3} s^{-1}	ACL and CCL
$S_w^{dl} = k_{des}(c_w^d - c_w^{eq}) \quad c_w^d \geq c_w^{eq}$	mol m^{-3} s^{-1}	ACL and CCL
$S_T^{sa} = \frac{i_a^2}{\sigma_{GDL,a}^{eff}}$	W m^{-3}	Anode GDL
$S_T^{sc} = \frac{i_c^2}{\sigma_{GDL,c}^{eff}}$	W m^{-3}	Cathode GDL
$S_T^M = \frac{i_M^2}{\sigma_M^{eff}}$	W m^{-3}	Membrane, ACL and CCL
$S_T^{ra} = -\lvert i_a \rvert [\frac{T \nabla S_a}{2F}]$	W m^{-3}	ACL
$S_T^{rc} = \lvert i_c \rvert [\lvert \eta_c \rvert - \frac{T \nabla S_c}{4F}]$	W m^{-3}	CCL
$S_T^{vd} = M_w S_w^{vd} \nabla h_w^{vd}$	W m^{-3}	ACL and CCL
$S_T^{dl} = M_w S_w^{dl} \nabla h_w^{dl}$	W m^{-3}	ACL and CCL
$S_T^{vl} = M_w S_w^{vl} \nabla h_w^{vl}$	W m^{-3}	CLs, GDLs and channels
$S_w^{vl} = \begin{cases} k_{con} \frac{\varepsilon(1-s) x_w^g}{RT} (x_w^g p^g - p_{sat}) & x_w^g p^g \geq p_{sat} \\ k_{eva} \frac{\varepsilon s \rho_w^l}{M_w} (p_{sat} - x_w^g p^g) & x_w^g p^g < p_{sat} \end{cases}$	mol m^{-3} s^{-1}	CLs, GDLs and channels

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692 Table 4 Expressions of key parameters

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Description	Expression	Reference
Volume fraction of Pt/C	$L_{Pt/C}=\frac{m_{Pt}}{l_{CL}}(\frac{1}{\rho_{Pt}}+\frac{1-f}{f}\frac{1}{\rho_C})$	[36]
Porosity of catalyst layer	$\varepsilon_{CL}=1-L_M-L_{GDL}(1-\varepsilon_{GDL})-L_{Pt/C}$	[36]
Agglomerate density of catalyst layer	$N_{agg}=\frac{3L_{Pt/C}}{4(1-\varepsilon_{CL})\pi r_{agg}^{3}}$	[36]
Specific area of agglomerate	$a_{agg}=\frac{m_{Pt}A_s}{l_{CL}}\frac{(1-\varepsilon_{CL})}{L_{Pt/C}}$	[36]
Reaction surface area per unit platinum mass	$A_s=(227.79f^3-158.57f^2-201.53f+159.5)\times10^3$	[38]
Dry ionomer film thickness surrounding the agglomerate	$\delta_M=r_{agg}(\sqrt[3]{\frac{(1-\varepsilon_{CL})(1-\varepsilon_{CL}-L_S)+L_{Pt/C}\varepsilon_{CL}(1-\%M)}{L_{Pt/C}}}-1)$	[38]
Liquid water film thickness surrounding the agglomerate	$\delta_w=\sqrt[3]{(r_{agg}+\delta_M)^3+\frac{s\varepsilon_{CL}(1-\varepsilon_{CL})r_{agg}^3}{L_{Pt/C}}}-(r_{agg}+\delta_M)$	[38]
Concentration of dissolved water	$c_w^d=\rho_M\lambda/EW(1+k_s\lambda)$	[27]
Water content	$\lambda=0.043+17.81\alpha_w-39.85\alpha_w^2+36.0\alpha_w^3$	[35]
Water activity	$\alpha_w=x_wp/p_{sat}+2s$	[14]
Vapor saturation pressure	$p_{sat}=9.531\times10^{-4}(T-237)^4-3.123\times10^{-2}(T-237)^3+3.451(T-237)^2+20.96(T-237)+611.0$	[35-39]
Effective electronic conductivity of catalyst layer	$\sigma_s^{eff}=(L_{Pt/C})^{1.5}\sigma_s$	[37-39]
Effective ionic conductivity of catalyst layer	$\sigma_M^{eff}=(1-\varepsilon_{CL})\left[1+\frac{(\%M\varepsilon_{CL}-1)}{(1+\delta/r_{agg}+a_0)^3}\right]\sigma_M$	[37-39]
Knudsen diffusivity of species i	$D_{Kn}=\frac{d_{avg}}{3}\sqrt{\frac{8R_gT}{\pi M_i}}$	[36]

Intrinsic diffusivity of species i	$D_{i-g}^{0}=\dfrac{1-x_i}{\sum_{j\neq i}^{n} x_j / D_{i-j}^{0}}$	[36]
Equivalent diffusivity of species i	$D_{i-P}^{0}=\dfrac{D_{i-g}^{0} D_{Kn}}{D_{i-g}^{0}+D_{Kn}}$	[36]
Diffusivity of oxygen through ionomer film	$D_{O_2-M}=1.3926\times10^{-10}\lambda^{0.708}\exp(\dfrac{T-273}{106.65})$ $-1.6461\times10^{-10}\lambda^{0.708}+5.2\times10^{-10}$	[38]

Table 5 Mesh characters

	Channe	GDLs	CLs	Membr	Total elements
Grid 1	10	10	10	10	17500
Grid 2	30	10	10	10	27500
Grid 3	50	10	10	10	37500
Grid 4	50	30	10	10	47500
Grid 5	50	50	10	10	57500
Grid 6	50	50	30	10	67500
Grid 7	50	50	50	10	77500
Grid 8	50	50	50	50	87500
Grid 9	50	50	50	90	97500

701 Table 6 Parameters used for model validation and base case condition in the study

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Symbol	Description (unit)	In house	Wang [41]	Base case
δ_{GDL}	GDL thickness (m)	3.0×10^{-4}	3.0×10^{-4}	3.8×10^{-4}
δ_{CL}	CL thickness (m)	1.5×10^{-5}	1.29×10^{-5}	1.5×10^{-5}
δ_{M}	Membrane thickness (m)	5.5×10^{-5}	1.08×10^{-4}	1.2×10^{-4}
ε_{GDL}	GDL porosity	0.40	0.40	0.40
m_{Pt}	Platinum loading (mg cm^{-2})	0.10 (anode) 0.40	0.40	0.40
f	Platinum mass ratio	20%	40%	40%
L_{M}	Volume fraction of ionomer	13.3%	32.5%	40%
T	Operating temperature (°C)	80.0	70.0	70.0
p	Operating pressure (atm)	1.0	1.0	1.0
α_{c}	Cathode transfer coefficient	0.6	2.0	0.7
r_{agg}	Agglomerate radius (m)	1.0×10^{-6}	1.0×10^{-6}	1.0×10^{-6}

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Table 7 Terms of thermal sources at various current densities with a single PEMFC

Thermal source (W m^{-3})	0.2 A cm^{-2}		0.6 A cm^{-2}		1.0 A cm^{-2}	
	Anode	Cathode	Anode	Cathode	Anode	Cathode
S_{vd}^{T}	4.88×10^{6} (11.36%)	2.04×10^{6} (1.04%)	5.46×10^{6} (4.56%)	3.23×10^{5} (0.053%	5.54×10^{6} (2.84%)	7.93×10^{3} (0.00078
S_{dl}^{T}	2.09×10^{3} (0.0049%)	1.80×10^{6} (0.92%)	4.55×10^{3} (0.0038	2.78×10^{7} (4.58%)	1.38×10^{3} (0.00071	6.23×10^{7} (6.11%)
S_{vl}^{T}	6.85×10^{4} (0.16%)	9.89×10^{4} (0.051%	2.08×10^{5} (0.17%)	3.03×10^{5} (0.050%	3.49×10^{5} (0.18%)	5.15×10^{5} (0.051%
S_{HOR}^{T}	-3.80×10^{7}	----	-1.14×10^{8}	---	-1.89×10^{8}	---
S_{ORR}^{T}	---	1.91×10^{8} (97.82%	---	5.76×10^{8} (94.88%	---	9.50×10^{8} (93.15%
S_{s}^{T}	3.33×10^{3} (0.0078	3.16×10^{3} (0.0016	3.02×10^{4} (0.025%	2.86×10^{4} (0.0047	8.23×10^{4} (0.042%	7.81×10^{4} (0.0077
$S_{M,i}^{T}$	9.65×10^{3} (0.023%	3.15×10^{5} (0.16%)	8.66×10^{4} (0.072%	2.65×10^{6} (0.44%)	2.34×10^{5} (0.12%)	6.91×10^{6} (0.68%)
Total	4.30×10^{7}	1.95×10^{8}	1.20×10^{8}	6.07×10^{8}	1.95×10^{8}	1.02×10^{9}

Note: total means the sum of the absolute value of each item; the values in brackets are the percentage of each item corresponded to the total heat of the anode and cathode, respectively.