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Three-dimensional multi-phase model of PEM fuel cell coupled with improved agglomerate sub-model of catalyst layer

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Abstract

An improved agglomerate sub-model of catalyst layer (CL) involving actual agglomerate size and oxygen local transport characteristics is developed and incorporated into a three-dimensional (3D) multi-phase model of proton exchange membrane (PEM) fuel cell. This makes it capable to consider the effect of Platinum (Pt) loading on oxygen transport and fuel cell performance more accurately. Oxygen local transport resistance near the catalyst surface is divided into three parts caused by liquid water blockage, ionomer coverage and Pt/carbon agglomeration, respectively. The resistances caused by ionomer coverage and Pt/carbon agglomeration are two major sources of oxygen local transport resistance. They have opposite variation trends as Pt loading changes. However, the ionomer resistance increases dramatically when Pt loading is lower than 0.1 mg cm^{-2} because of the much harder transport process through a relatively heavier ionomer coating. The simulation results agree with the experimental data reasonably under different

cathode Pt loadings (from 0.3 to 0.025 mg cm⁻²), for both polarization curves and local transport resistance. In addition, a transport dominance parameter is defined to judge whether the concentration loss predominates the electrochemical reaction. A value greater than 10% can be seen as a symbol of local oxygen starvation. Using this model, fine channel geometry with extremely small channel and rib widths is investigated, and the highest net output power in this study is corresponding to 0.2 and 0.6 mm for channel (rib) width and height.

Keywords

PEM fuel cell; Catalyst layer; Agglomerate model; Pt loading; Oxygen transport; Fine channel geometry

Nomenclature

A	specific surface area (m ⁻¹)
A_{act}	active area (m ²)
a	water activity
a_{ECSA}	electrochemically active surface area (m ² g ⁻¹)
C_i	gas molar concentration (mol m ⁻³)
C_p	specific heat capacity (J mol ⁻¹ K ⁻¹)
D_i	gas diffusivity (m ² s ⁻¹)

E_{rev}	reversible voltage (V)
EW	equivalent weight of ionomer (kg mol^{-1})
F	faraday's constant (C mol^{-1})
H	henry's constant ($\text{Pa m}^3 \text{mol}^{-1}$)
h	latent heat of water (J mol^{-1})
I_{ion}	ionic current density (A m^{-2})
i_0^{ref}	reference exchange current density (A m^{-2})
j	electrochemical reaction rate in current form (A m^{-3})
K	intrinsic permeability (m^2)
k	relative permeability
k^{eff}	effective thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
k_1, k_2	transport resistance coefficient
k_{ele}	collection of electrochemical parameters (A m^{-3})
M	molar mass (kg mol^{-1})
m	specific mass (kg m^{-2})
$\dot{m}$	mass flux ($\text{kg m}^{-2} \text{s}^{-1}$)
N_{O_2}	oxygen molar flux ($\text{mol m}^2 \text{s}^{-1}$)
n	number of catalyst types
n_{agg}	number of Pt/carbon agglomerates per unit volume of catalyst layer (m^{-3})
n_d	electro-osmotic drag coefficient

P	pressure (Pa)
R	transport resistance (s m^{-1})/Universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
RH	relative humidity
r	radius (m)
S	source term ($\text{kg m}^{-3} \text{s}^{-1}$, W m^{-3} ...)
ΔS	entropy change ($\text{J mol}^{-1} \text{K}^{-1}$)
s	liquid water saturation
T	temperature (K)
$\vec{u}$	superficial velocity vector (m s^{-1})
V_{out}	output voltage (V)
x	X direction
Y_i	gas species mass fraction
y	Y direction
z	Z direction

36

37 Greek letters

α	transfer coefficient
γ	phase change rate (s^{-1})
δ	thickness (m)
ε	porosity

$\zeta_{\text{pt/c}}$	platinum weight percentage of Pt/carbon catalyst
$\zeta_{\text{im/c}}$	mass ratio of ionomer to carbon
η	overpotential (V)
θ	correction coefficient
ι	transport dominance
κ_{ele}	electronic conductivity (S m^{-1})
κ_{ion}	ionic conductivity (S m^{-1})
λ	membrane water content
μ	dynamic viscosity ($\text{kg m}^{-1} \text{s}^{-1}$)
ξ	stoichiometric ratio
ρ	density (kg m^{-3})
φ_{ele}	electronic potential (V)
φ_{ion}	ionic potential (V)
χ	mass fraction of different catalyst type
ω	energy parameter (J mol^{-1})

38

39 Subscripts and superscripts

0	standard state
ACL	anode catalyst layer
a	anode

act	active
agg	agglomerate
ave	average
BP	bipolar plate
CL	catalyst layer
CCL	cathode catalyst layer
c	cathode/carbon support
diffu	diffusion
disso	dissolution
ECSA	electrochemically active surface area
eff	effective
ele	electronic
eq	equivalent/equilibrium
GDL	gas diffusion layer
g	gas state/gas mixture
H	Henry's law correction
H ₂ O	water vapor
i	gas species or catalyst type
im	ionomer
im/c	ionomer/carbon

in	inlet
ion	ionic
Kn	Knudsen diffusion
local	local transport
lw	liquid water
l-v	liquid water to water vapor
MEM	membrane
MF	metal foam
MPL	micro-porous layer
m	mass
mw	membrane water
O ₂	Oxygen
out	output
pt	platinum/near platinum surface
p	pore
pt/c	platinum/carbon
pt/im	platinum-ionomer coverage-dependent
pt/o	platinum-oxide coverage-dependent
ref	reference
rev	reversible

sat	saturation
T	temperature
v	water vapor
v-m	water vapor to membrane water
v-l	water vapor to liquid water
*	correction

40

41 **1. Introduction**

42 As one of the most promising energy conversion devices in the future, proton
 43 exchange membrane (PEM) fuel cell has attracted much attention in recent years.
 44 It's adequate for portable, stationary and especially transportation applications due
 45 to little road emissions, low operation temperature and high efficiency [1]. However,
 46 key challenges still obstruct its large-scale commercialization, e.g. the high cost. The
 47 precious metal catalyst — Platinum (Pt) used in catalyst layer (CL) mainly
 48 contributes to the price of membrane electrode assembly (MEA). According to the
 49 2015 review of the U.S. Department of Energy (DOE), the Pt utilization needs to
 50 attain 0.125 g kW^{-1} in order to meet the market demand [2]. Therefore, it is of great
 51 significance to reduce Pt loading appropriately without severely dampening the cell
 52 performance. This requires deep understanding of physicochemical phenomena that
 53 occur in PEM fuel cell catalyst layer.

54

During the past decades, modeling or simulation has become a powerful tool to investigate the multi-scale transport phenomena and electrochemical reactions inside PEM fuel cell. For catalyst layer, it consists of catalyst (carbon supported Pt), ionomer (Nafion) and void region, which conducts or transfers electron, proton and mass (gas and liquid), respectively. Early CL models like interface model and homogenous model [3, 4] regarded CL as a boundary condition or specified the volume fraction of different phase, which overestimated the fuel cell performance. In fact, the cathode is prone to suffer great concentration loss especially under high current density, due to the slow oxygen transport process. In order to consider the difficulty of oxygen transport and structural details of CL, Ridge et al. [5] firstly introduced the concept of agglomerate into CL modeling. In the agglomerate CL, spherical agglomerates of Pt/carbon clumps coated by ionomer film distributes randomly to form a porous structure. Siegel et al. [6] applied the agglomerate model and predicted the polarization curve with more accuracy. They emphasized the close connection between CL structure and fuel cell performance. Sun et al. [7] developed a two-dimensional agglomerate model and studied the influence of structural parameters. They mentioned that a lower but acceptable Pt loading could be better than higher loading. Actually, lower catalyst loading may provide more void space which is beneficial for gas transport. However, oxygen transport resistance can increase dramatically when Pt loading decreases to a certain level.

Using limiting current measurement, Nissan's research and development center reported higher oxygen transport resistance as Pt loading decreased [8]. The additional resistance was pressure independent and they assumed that it could originate from a thin ionomer film with low permeability. Greszler et al. [9] presented limiting current results of oxygen local transport resistance over a wider range of Pt loadings. The resistance increased greatly when Pt loading was lower than 0.1 mg cm^{-2} because of more oxygen flux through ionomer. And the magnitude was equivalent to the resistance created by 380nm diameter agglomerates with 20nm uniform ionomer coating, assuming bulk diffusion effect only. The geometry size agreed with parameters used in traditional agglomerate models [7, 10]. Nevertheless, it was not supported by microscopic observations, in which the agglomerate diameter mostly ranged from 50nm to 100nm and the ionomer film was just as thin as several nanometers. In other words, traditional agglomerate model did get an advantage on performance predication but still lacked some validity due to the exaggerated geometry size.

Kudo and Suzuki et al. [11, 12] proposed an interfacial resistance and owed its cause to oxygen sorption-desorption through ionomer. After incorporating this dissolution effect into agglomerate model, the geometry dimension of Pt-carbon-ionomer aggregates could fit the scanning electron microscope (SEM) image. They argued that the agglomerate size and ionomer film thickness in previous models could be

just fitting parameters in order to match the experimental data. Hao et al. [13] adopted two interfacial resistances and coupled them with bulk diffusion by assigning two coefficients at gas-ionomer interface and Pt-ionomer interface, respectively. They employed small-size homogeneous-distributed Pt/carbon particles in CL model and gained agreement with the experiments on both polarization curves and transport resistance. Owejan et al.'s [14] experimental work drew a conclusion that the resistance through the ionomer coating was a function of both Pt surface area and Pt particle dispersion. Chen et al. [15] carried out a pore-scale simulation using the lattice Boltzmann method and reconstructed ionomer-coated Pt/carbon particle. The relationship between oxygen local transport resistance and microscopic factors was discussed, including ionomer dissolution and Pt particle dispersion. They concluded that local transport characteristics should be considered when developing agglomerate model. Very recently, Sina et al. [16] conducted a direct measurement of relative gas diffusivity in CL through modified Loschmidt cell method. They also built up an agglomerate-formed CL model by specifying the arrangement of agglomerates which was validated with the measurement data. They emphasized the importance of pore size distribution in catalyst layer and suggested two major ranges. The secondary pores (~200nm in diameter) among agglomerates mainly provides pathways for mass transport, in which bulk diffusion plays a major role. And for primary pores (~20 nm in diameter) inside agglomerates, the Knudsen diffusion becomes dominant and adds difficulty to gas transport. Generally speaking,

the oxygen local transport characteristics may vary remarkably under different Pt loadings, which significantly affects the mass transport property of CL. This Pt loading effect was hardly reflected in traditional agglomerate models because Pt loading only changed the effective reaction area [7, 10]. It's necessary to consider more structural details including Pt loading effect so that the agglomerate model can be more valid and reflect the influence of the CL microstructure more accurately.

Therefore, an improved agglomerate sub-model of CL is firstly developed considering the actual geometry size of agglomerates in this study. At single agglomerate scale, oxygen local transport resistance is clarified with three individual parts caused by liquid water, thin ionomer film and Pt/carbon agglomeration, respectively. The dissolution effect at gas-ionomer interface is coupled with diffusion resistance through the ionomer film. The Pt particle dispersion on carbon support as well as Knudsen diffusion in primary pores is also taken into account. Consequently, the CL model is capable to reflect the influence of Pt loading change more practically. By incorporating the improved agglomerate sub-model into a three-dimensional (3D) multi-phase non-isothermal PEM fuel cell model, it is carefully validated with experimental data under different cathode Pt loadings. To the best of the authors' knowledge, only a few studies have considered detailed local oxygen transport characteristics in CL when using 3D macroscopic PEM fuel cell model. Furthermore, the effects of transport factors and electrochemical factors are

separated through mathematical manipulation, which can derive a transport dominance factor. Using the developed model, some optimized designs of fine channel geometry aiming at reducing concentration loss of PEM fuel cell are studied.

2. Model development

2.1 Agglomerate sub-model of CL

Fig. 1(a) shows the SEM image of CL [16], in which the primary and secondary pores can be clearly seen. And transmission electron microscope (TEM) image of CL sample in Fig. 1(b) gives a deeper view of primary pore and Pt particle dispersion on carbon support. Based on the real CL structure, the schematic of single agglomerate is displayed in Fig. 1(c). The primary pore inside the high-surface-area carbon support is treated as a cylindrical hole for calculation simplicity. In fact, Pt particles are also likely to migrate into primary pores along with agglomeration and coalescence [17], besides depositing onto outer surface of carbon support.

As seen in Fig. 1 (c), the oxygen local transport resistance in this agglomerate sub-model is divided into three parts:

1. The resistance caused by liquid water in secondary pores (R_{lw} , s m⁻¹), which can be expressed by Fick's diffusion:

$$R_{lw} = \frac{\delta_{lw}^{eq}}{D_{O_2, lw}} \quad (1)$$

where δ_{lw}^{eq} (m) is the equivalent water film thickness and $D_{O_2, lw}$ ($m^2 s^{-1}$) the oxygen diffusivity in water. Actually, liquid water only occupies part of void space and can be removed by capillary effect, which means that a continuous water film on ionomer surface may not exist, therefore, the equivalent film thickness is assumed:

$$\delta_{lw}^{eq} = \frac{s \varepsilon_{CL}}{A_{im}} \quad (2)$$

where s , ε_{CL} and A_{im} (m^{-1}) are the liquid water saturation, porosity of CL and specific surface area of ionomer film, respectively.

2. The resistance caused by thin ionomer film (R_{im} , $s m^{-1}$), which consists of dissolution part and diffusion part:

$$R_{im} = R_{im, disso} + R_{im, diffu} \quad (3)$$

$$R_{im, diffu} = \frac{\delta_{im}}{D_{O_2, im}} \quad (4)$$

where δ_{im} (m) is the thickness of thin ionomer film and $D_{O_2, im}$ ($m^2 s^{-1}$) the oxygen diffusivity in ionomer. The dissolution resistance is usually coupled with the diffusion resistance through a coefficient. In Hao et al.'s [13] work, the specific surface area ratio of ionomer to Pt (A_{im} / A_{pt}) was adopted to modify the diffusion in ionomer film. It can be applied to relate these two resistances so that the dissolution effect is considered:

$$R_{im, disso} = k_1 \frac{A_{im}}{A_{pt}} R_{im, diffu} \quad (5)$$

178 where k_1 is set as a undetermined coefficient.

179 3. The resistance caused by Pt/carbon agglomeration (R_{pt} , s m⁻¹). In primary pores,
180 transport resistance could be a complicated mixing hindrance. Besides liquid water
181 and ionomer, the Knudsen diffusion should be considered as earlier mentioned:

$$182 \quad R_{pt} = \frac{\delta_{pt}^{eq}}{D_{O_2,pt}^{eq}} \quad (6)$$

$$183 \quad \frac{1}{D_{O_2,pt}^{eq}} = \frac{1}{D_{O_2,im}} + \frac{1}{D_{O_2,lw}} + \frac{1}{D_{O_2,Kn}} \quad (7)$$

$$184 \quad D_{O_2,Kn} = \frac{8r_p}{3} \sqrt{\frac{RT}{2\pi M}} \quad (8)$$

185 where $D_{O_2,pt}^{eq}$ (m² s⁻¹) is the equivalent oxygen diffusion coefficient in primary pores,
186 $D_{O_2,Kn}$ (m² s⁻¹) the Knudsen diffusion coefficient, R (J mol⁻¹ K⁻¹) the universal gas
187 constant, T (K) the local temperature and M (kg mol⁻¹) the molecular weight of
188 oxygen. And the equivalent diffusion length (δ_{pt}^{eq} , m) is simply assumed to be half of
189 carbon support radius (r_c , m). The pore radius (r_p , m) is calculated based on the
190 assumption that all the pores are placed together with the cylindrical shape:

$$191 \quad r_p = \sqrt{\frac{4\varepsilon_c}{3}} r_c \quad (9)$$

192 where ε_c is the porosity of carbon support. It should be noted that this resistance is
193 only valid for Pt particles that fall into primary pores so that a correction is
194 necessary:

$$195 \quad R_{pt}^* = k_2 R_{pt} \quad (10)$$

196 where k_2 is correction coefficient which should be associated with the Pt loading,

or more exactly, with the Pt weight percentage of Pt/carbon catalyst (Pt/C percentage). As mentioned before, the Pt particle dispersion is also a significant factor affecting oxygen transport and consumption. Pt particles are prone to get concentrated at high Pt/C percentage [14] and the deposition into primary pores may increase. On the contrary, Pt particles are more dispersed at low Pt/C percentage. Herein, the correction coefficient is assumed to equal an average Pt/C percentage, which has the same value as actual Pt/C percentage when only one kind of Pt/carbon catalyst is used.

$$k_2 = \zeta_{pt/c}^{ave} = \frac{\sum_{i=1}^n \zeta_{pt/c,i} \chi_i}{\sum_{j=1}^n \zeta_{pt/c,j} \chi_j} \quad (11)$$

where $\zeta_{pt/c,i}$, χ_i and n are the Pt/C percentage, mass fraction of different catalyst type and the number of types, respectively.

In total, the total oxygen local transport resistance (R_{local} , s m⁻¹) from secondary pores to Pt surface is:

$$R_{local} = R_{lw} + R_{im} + R_{pt}^* = R_{lw} + \left(k_1 \frac{A_{im}}{A_{pt}} + 1 \right) R_{im,diffu} + k_2 R_{pt} \quad (12)$$

Overall, oxygen local transport resistance in Eq. (12) can be seen as a function of Pt surface area and Pt particle dispersion just as Owejan concluded [14]. In addition, Henry's law is used to describe the concentration drop at gas-ionomer interface:

$$C_{O_2}^H = \frac{C_{O_2}^g RT}{H_{O_2}} \quad (13)$$

where $C_{O_2}^H$ (mol m⁻³) represents the oxygen concentration at the gas-ionomer interface and H_{O_2} (Pa m³ mol⁻¹) is the Henry's constant of oxygen in ionomer. Then the oxygen flux (N_{O_2} , mol m⁻² s⁻¹) can be obtained:

$$N_{O_2} = \frac{C_{O_2}^H - C_{O_2}^{pt}}{R_{local}} \quad (14)$$

The oxygen that arrives at Pt surface (effective) is assumed to be consumed by electrochemical reaction immediately:

$$N_{O_2} A_{im} = \frac{j_c}{4F} \quad (15)$$

where j_c (A m⁻³) is the reaction rate and F (C mol⁻¹) the Faraday constant. Number of agglomerates per unit volume of CL can be calculated using the compositional and structural parameters:

$$n_{agg} = \frac{m_{pt}}{\delta_{CL}} \left[\frac{1}{\rho_{pt}} + \left(\frac{1}{\zeta_{pt/c}} - 1 \right) \frac{1}{\rho_c} \right] \frac{3}{4\pi r_c^3} \quad (16)$$

where m_{pt} (mg cm⁻²) is the Pt loading, δ_{CL} (m) the CL thickness and ρ_{pt}, ρ_c (kg m⁻³) the density of platinum and carbon, respectively. And the ionomer film thickness is calculated using the mass ratio of ionomer to carbon (I/C ratio):

$$\delta_{im} = \frac{\zeta_{im/c} m_{pt}}{\rho_{im} \delta_{CL} n_{agg} 4\pi r_c^2} \left(\frac{1}{\zeta_{pt/c}} - 1 \right) \quad (17)$$

where $\zeta_{im/c}$ is the I/C ratio and ρ_{im} (kg m⁻³) the dry ionomer density. Moreover, the specific surface area of ionomer and Pt can be obtained by:

$$A_{\text{im}} = 4\pi (r_c + \delta_{\text{im}})^2 n_{\text{agg}} \quad (18)$$

$$A_{\text{pt}} = \frac{m_{\text{pt}} a_{\text{ECSA}}}{\delta_{\text{CL}}} \quad (19)$$

where a_{ECSA} ($\text{m}^2 \text{g}^{-1}$) is the electrochemically active surface area (ECSA).

In addition, the volume fractions of three phase in CL are given as below:

Solid phase (carbon and Pt):

$$\varepsilon_{\text{pt/c}} = \frac{m_{\text{pt}}}{\delta_{\text{CL}}} \left[\frac{1}{\rho_{\text{pt}}} + \left(\frac{1}{\zeta_{\text{pt/c}}} - 1 \right) \frac{1}{\rho_c} \right] \quad (20)$$

Electrolyte phase (ionomer or Nafion):

$$\varepsilon_{\text{im}} = \frac{\zeta_{\text{im/c}} m_{\text{pt}}}{\delta_{\text{CL}} \rho_{\text{im}}} \left(\frac{1}{\zeta_{\text{pt/c}}} - 1 \right) \left(1 + \frac{M_{\text{lw}} \rho_{\text{im}}}{\rho_{\text{lw}} EW} \lambda \right) \quad (21)$$

Pore phase (porosity):

$$\varepsilon_{\text{CL}} = 1 - \varepsilon_{\text{pt/c}} - \varepsilon_{\text{im}} \quad (22)$$

where M_{lw} (kg mol^{-1}) and ρ_{lw} (kg m^{-3}) are the molecular weight and density of liquid water, EW (kg mol^{-1}) the equivalent weight of ionomer and λ the membrane water content.

2.2 Three-dimensional multi-phase model

The agglomerate sub-model developed in this study is incorporated into a 3D multi-phase non-isothermal model. The conservation equations involved in this model are summarized as below:

252 Mass:
$$\frac{\partial}{\partial t}(\varepsilon(1-s)\rho_g) + \nabla \cdot (\rho_g \vec{u}_g) = S_m \quad (23)$$

253 Momentum:

254
$$\begin{aligned} & \frac{\partial}{\partial t} \left(\frac{\rho_g \vec{u}_g}{\varepsilon(1-s)} \right) + \nabla \cdot \left(\frac{\rho_g \vec{u}_g \vec{u}_g}{\varepsilon^2(1-s)^2} \right) = -\nabla P_g + \\ & \mu_g \nabla \cdot \left(\nabla \left(\frac{\vec{u}_g}{\varepsilon(1-s)} \right) + \nabla \left(\frac{\vec{u}_g^\top}{\varepsilon(1-s)} \right) \right) - \frac{2}{3} \mu_g \nabla \cdot \left(\nabla \left(\frac{\vec{u}_g}{\varepsilon(1-s)} \right) \right) + S_u \end{aligned} \quad (24)$$

255 Species:
$$\frac{\partial}{\partial t}(\varepsilon(1-s)\rho_g Y_i) + \nabla \cdot (\rho_g \vec{u}_g Y_i) = \nabla \cdot (\rho_g D_i^{\text{eff}} \nabla Y_i) + S_i \quad (25)$$

256 Energy:

257
$$\begin{aligned} & \frac{\partial}{\partial t} \left(\varepsilon s \rho_{l,w} C_{p,l,w} T_l + \varepsilon(1-s) \rho_g C_{p,g} T_g \right) + \nabla \cdot (\varepsilon s \rho_{l,w} \vec{u}_{l,w} T_l + \varepsilon(1-s) \rho_g \vec{u}_g T_g) \\ & = \nabla \cdot (k^{\text{eff}} \nabla T) + S_T \end{aligned} \quad (26)$$

258 where ρ_g (kg mol⁻¹), $\vec{u}_g$, $\vec{u}_{l,w}$ (m s⁻¹), P_g (Pa), μ_g (kg m⁻¹ s⁻¹), ε , s , Y_i , D_i^{eff} (m² s⁻¹), $C_{p,g}$,

259 $C_{p,l,w}$ (J mol⁻¹ K⁻¹), T (K) and k^{eff} (W m⁻¹ K⁻¹) are the gas mixture density,

260 superficial velocity vector, pressure and dynamic viscosity of gas mixture, porosity

261 (“1” for channel), liquid water saturation, mass fraction and effective diffusion

262 coefficient of species “i” (i represents hydrogen, oxygen or water vapor), specific

263 heat capacity, temperature and effective thermal conductivity, respectively.

264

265 In channel, the liquid water is assumed to be in mist state [18] and thus the liquid

266 water saturation conservation equation [19] is solved, in which liquid water velocity

267 ($\vec{u}_{l,w}$) equals to gas velocity ($\vec{u}_g$):

268
$$\frac{\partial}{\partial t}(\rho_{l,w} \varepsilon s) + \nabla \cdot (\rho_{l,w} \vec{u}_{l,w} s) = S_{l,w} \quad (27)$$

269 And liquid pressure conservation equation is solved in the porous electrodes in order

270 to consider the liquid water saturation jump at the interfaces:

$$271 \quad \frac{\partial}{\partial t}(\rho_{\text{lw}} \varepsilon s) = \nabla \cdot \left(\rho_{\text{lw}} \frac{K k_{\text{lw}}}{\mu_{\text{lw}}} \nabla P_{\text{lw}} \right) + S_{\text{lw}} \quad (28)$$

272 where K (m^2) and k_{lw} are the intrinsic permeability of porous media and relative
 273 permeability of liquid water. Then the liquid water saturation can be obtained
 274 through the Leverett-J function [20].

275

276 Other conservation equations concerning the electrochemical reaction are:

$$277 \quad \text{Membrane water: } \frac{\rho_{\text{m}}}{E W} \frac{\partial}{\partial t} (\varepsilon_{\text{m}} \lambda) + \nabla \cdot \left(\frac{n_d}{F} I_{\text{ion}} \right) = \frac{\rho_{\text{m}}}{E W} \nabla \cdot (D^{\text{eff}}_{\text{m}} \nabla \lambda) + S \quad (29)$$

$$278 \quad \text{Electronic potential: } 0 = \nabla \cdot (\kappa_{\text{ele}}^{\text{eff}} \nabla \varphi_{\text{ele}}) + S_{\text{ele}} \quad (30)$$

$$279 \quad \text{Ionic potential: } 0 = \nabla \cdot (\kappa_{\text{ion}}^{\text{eff}} \nabla \varphi_{\text{ion}}) + S_{\text{ion}} \quad (31)$$

280 where n_d , I_{ion} (A m^{-2}), $D_{\text{mw}}^{\text{eff}}$ ($\text{m}^2 \text{ s}^{-1}$), $\kappa_{\text{ele}}^{\text{eff}}$ and $\kappa_{\text{ion}}^{\text{eff}}$ (S m^{-1}) represent the
 281 electro-osmotic drag (EOD) coefficient, the ionic current density, the effective
 282 diffusion coefficient of membrane water, the effective electron and ion conductivity,
 283 respectively. The source terms in electronic and ionic potential conservation
 284 equations are calculated through the Butler-Volmer equations (B-V equations):

$$285 \quad j_{\text{a}} = i_{0,\text{a}}^{\text{ref}} A_{\text{pt}} \theta_{\text{T,a}} \left(\frac{C_{\text{H}_2}}{C_{\text{H}_2}^{\text{ref}}} \right)^{0.5} \left(\exp \left(\frac{2F\alpha_{\text{a}}}{RT} \eta_{\text{a}} \right) - \exp \left(-\frac{2F\alpha_{\text{c}}}{RT} \eta_{\text{a}} \right) \right) \quad (32)$$

$$286 \quad j_{\text{c}} = i_{0,\text{c}}^{\text{ref}} A_{\text{pt}} \theta_{\text{T,c}} \left(\frac{C_{\text{O}_2}^{\text{pt}}}{C_{\text{O}_2}^{\text{ref}}} \right) \left(\exp \left(-\frac{4F\alpha_{\text{c}}}{RT} \eta_{\text{c}} \right) - \exp \left(\frac{4F\alpha_{\text{a}}}{RT} \eta_{\text{c}} \right) \right) \quad (33)$$

$$287 \quad \theta_{\text{T,a}} = \exp \left(\frac{-1400(353.15 - T)}{353.15T} \right), \quad \theta_{\text{T,c}} = \exp \left(\frac{-7900(353.15 - T)}{353.15T} \right) \quad (34)$$

288 where i_0^{ref} (A m^{-2}), θ_{T} , $C_{\text{H}_2}^{\text{ref}}$, $C_{\text{O}_2}^{\text{ref}}$ (mol m^{-3}), α and η (V) are the reference exchange
 289 current density, the temperature correction coefficient, the reference molar
 290 concentration of hydrogen and oxygen, the transfer coefficient and the overpotential,
 291 respectively. According to Subramanian et al.'s work [21], excess oxygen around Pt
 292 surface may have negative effect on electrochemical reaction under very low current
 293 density. The Pt-oxide coverage-dependent correction coefficient fitted by Hao et al.
 294 [13] is introduced to revise the cathode B-V equation. In addition, excess ionomer
 295 coverage is also harmful to the catalyst activity. So another Pt-ionomer
 296 coverage-dependent correction coefficient is fitted in this study based on
 297 experimental data [14].

$$298 \quad j_c = i_{0,c}^{\text{ref}} A_{\text{pt}} \theta_{\text{T,c}} \theta_{\text{pt/im}} (1 - \theta_{\text{pt/o}}) \left(\frac{C_{\text{O}_2}^{\text{pt}}}{C_{\text{O}_2}^{\text{ref}}} \right) \left(\exp \left(-\frac{4F\alpha_c}{RT} \eta_c - \frac{\omega \theta_{\text{pt/o}}}{RT} \right) - \exp \left(\frac{4F\alpha_a}{RT} \eta_c \right) \right) \quad (35)$$

$$299 \quad \theta_{\text{pt/o}} = \frac{1}{1 + e^{22.4(0.818 - E)}}, \quad \theta_{\text{pt/im}} = 1 - \exp \left[-30.6 \left(\frac{\zeta_{\text{pt/c}}}{\zeta_{\text{im/c}} (1 - \zeta_{\text{pt/c}})} \right)^{2.6} \right] \quad (36)$$

300 where ω (J mol^{-1}) is the energy parameter, E (V) the cathode potential vs.
 301 Reversible Hydrogen Electrode (RHE), $\theta_{\text{pt/o}}$ the Pt-oxide coverage-dependent
 302 correction coefficient and $\theta_{\text{pt/im}}$ the Pt-ionomer coverage-dependent correction
 303 coefficient. Combine Eq. (12), (13), (14), (15) and (35) together and oxygen local
 304 transport resistance can be taken into account:

$$305 \quad \frac{j_c}{4FA_{\text{im}}} = \frac{RTC_{\text{O}_2}^g / H_{\text{O}_2}}{\frac{4FA_{\text{im}} C_{\text{O}_2}^{\text{ref}}}{k_{\text{ele}}} + R_{\text{lw}} + \left(k_1 \frac{A_{\text{im}}}{A_{\text{pt}}} + 1 \right) R_{\text{im,diffu}} + k_2 R_{\text{pt}}} \quad (37)$$

$$k_{\text{ele}} = i_{0,\text{c}}^{\text{ref}} A_{\text{pt}} \theta_{\text{T,c}} \theta_{\text{pt/im}} (1 - \theta_{\text{pt/o}}) \left(\exp\left(-\frac{4F\alpha_{\text{c}}}{RT} \eta_{\text{c}} - \frac{\omega \theta_{\text{pt/o}}}{RT}\right) - \exp\left(\frac{4F\alpha_{\text{a}}}{RT} \eta_{\text{c}}\right) \right) \quad (38)$$

where the first term in the denominator of right side in Eq. (37) can be regarded as another resistance term—electrochemical resistance (R_{ele} , s m^{-1}):

$$R_{\text{ele}} = \frac{4FA_{\text{im}} C_{\text{O}_2}^{\text{ref}}}{k_{\text{ele}}} \quad (39)$$

It should be noted that the relative magnitudes of the electrochemical resistance (R_{ele}) against the local transport resistance (R_{local}) indicates the control of electrochemical factors or transport factors on the cathode CL reaction. With respect to the anode side, B-V equation is corrected only by Henry's law at gas-ionomer interface due to the good permeability of hydrogen and inapparent concentration loss compared with the cathode side.

$$j_{\text{a}} = i_{0,\text{a}}^{\text{ref}} A_{\text{pt}} \theta_{\text{T,a}} \left(\frac{RTC_{\text{H}_2}^{\text{g}}}{H_{\text{H}_2} C_{\text{H}_2}^{\text{ref}}} \right)^{0.5} \left(\exp\left(\frac{2F\alpha_{\text{a}}}{RT} \eta_{\text{a}}\right) - \exp\left(-\frac{2F\alpha_{\text{c}}}{RT} \eta_{\text{a}}\right) \right) \quad (40)$$

where H_{H_2} ($\text{Pa m}^3 \text{ mol}^{-1}$) is the Henry's constant of hydrogen in ionomer.

The mass flow rate and constant pressure are specified at inlet and outlet boundaries, respectively:

$$\dot{m}_{\text{a}} = \frac{j_{\text{a}} \xi_{\text{a}} A_{\text{act}}^{\text{a}} \rho_{\text{g}}^{\text{a}}}{2FC_{\text{H}_2}}, \quad C_{\text{H}_2} = \frac{P_{\text{g,out}}^{\text{a}} + \Delta P_{\text{g}}^{\text{a}} - RH_{\text{a}} P_{\text{sat}}}{RT} \quad (41)$$

$$\dot{m}_{\text{c}} = \frac{j_{\text{c}} \xi_{\text{c}} A_{\text{act}}^{\text{c}} \rho_{\text{g}}^{\text{c}}}{4FC_{\text{O}_2}}, \quad C_{\text{O}_2} = \frac{0.21(P_{\text{g,out}}^{\text{c}} + \Delta P_{\text{g}}^{\text{c}} - RH_{\text{c}} P_{\text{sat}})}{RT} \quad (42)$$

where ξ , A_{act} (m^2), RH and P_{sat} (Pa) are stoichiometric ratio, active area, relative

humidity and water saturation pressure, respectively. And boundary conditions (B.C.s) of electronic potential are defined with the total overpotential to anode side and zero potential to cathode side:

$$\varphi_{\text{ele}}^{\text{a}} = E_{\text{rev}} - V_{\text{out}} , \varphi_{\text{ele}}^{\text{c}} = 0 \quad (43)$$

where E_{rev} (V) is the reversible thermodynamic voltage and V_{out} (V) the output voltage. Additionally, constant surface temperature is specified to all the surrounding walls. Physical and transport parameters are listed in Table 1 and more detailed information can be found in Ref. [22]. And Table 2 gives the source terms of the above conservation equations.

3. Results and discussion

A typical single channel computational domain including bipolar plates (BPs), flow channels (CHs), gas diffusion layers (GDLs), micro-porous layer (MPLs), CLs and proton exchange membrane (PEM) is shown in Fig. 2. This study is conducted with the help of the commercial computational fluid dynamics (CFD) software FLUENT, and the user-defined function (UDF) is used. Grid independence is tested by comparing the calculated current density at the same output voltage using different mesh density. The results are shown in Table 3 and mesh 4 is adopted in this study.

3.1 Model validation

For the 3D multi-phase model of PEM fuel cell, the polarization curve and ohmic

loss have been validated in previous work [23]. In this study, the simulated polarization curves are further compared with experimental data under different cathode Pt loadings without carbon dilution (from 0.3 to 0.025 mg cm⁻²). Fig. 3 shows the comparison and the consistency is acceptable. The maximum current density deviation doesn't exceed 0.1A cm⁻² and the corresponding maximum validation error (%) is smaller than 15% for single data point. In addition, Fig. 4 compares simulated polarization curves using different CL models under 0.2 mg cm⁻² cathode Pt loading. Obviously, homogeneous model overestimate cell performance markedly. With the solution methods of Sun et al. [7], traditional large-size agglomerate model (agglomerate diameter 380nm, ionomer film thickness 20nm) gains similar results with improved small-size agglomerate model developed by this study (agglomerate diameter 50nm, ionomer film thickness 8nm). This also supports the conclusion of Greszler et al. [9] and proves the validity of current model. Moreover, Fig. 5 gives the results of oxygen local transport resistance and similar preceding work in the open literature is also exhibited [24, 25]. R_{local} by this study falls into the range of existing studies and matches the data of Owejan et al. [14] reasonably. In this validation, the undetermined parameter (k_1) in Eq. (5) is assigned as 0.15. Design and model parameters of validation cases are listed in Table 4 and the 5 different CL formulations can be found in Table 5.

3.2 Local transport characteristics

In Fig. 6, the total local transport resistance (R_{local}) and two partial resistances (R_{im} , R_{pt}^*) under different Pt loadings are shown. The transport resistance caused by liquid water (R_{lw}) is neglected because of its much smaller value (two orders of magnitude smaller than the others). Opposite variation trends of the ionomer coverage resistance and the Pt/carbon agglomeration resistance can be clearly seen as Pt loading (Pt/C percentage) changes. For all the 5 CL formulations, I/C ratio (0.95) is constant but Pt/C percentage is different so that the different Pt loading represents different Pt/C percentage, i.e. different Pt particle density on carbon support. Higher Pt loading results in inevitable deposition of Pt particles and the correction coefficient (k_2) gains a larger value. Contrarily, oxygen may go through a longer and rougher “road” in ionomer film under lower Pt/C percentage (R_{im} rises). When Pt loading is lower than 0.1 mg cm^{-2} , the total local transport resistance sharply goes up due to the much larger value of the specific area ratio ($A_{\text{im}} / A_{\text{pt}}$). Although the agglomeration effect decreases as less Pt particles deposit into primary pores, it cannot offset the growth of the ionomer resistance. In other words, a relatively heavier ionomer coating causes severe oxygen transport loss under extreme low Pt loadings.

Instead, a slight increase of the total resistance is observed when Pt loading changes from 0.2 to 0.3 mg cm^{-2} . The negative effect of agglomeration and deposition is more obvious because the ionomer resistance changes indistinctively. The finding

seems to be only supported by Owejan et al.'s [14] experimental data, not by others (e.g. Sakai et al. [24]). But it should be noted that, during Owejan et al.'s experiments, the CL thickness were kept unchanged within the capability of coating method, which is different from other studies. The calculated CL porosities almost hold a constant (~ 0.5) because the carbon and ionomer loadings basically maintain the same. In this case, excess Pt loading may also be detrimental to oxygen transport due to higher Pt particle density. Generally speaking, the compositional parameters used to prepare the catalyst layer ink influence the structural topology of CL (e.g. Pt particle density) and hence affect the oxygen local transport characteristics. Based on the above analysis, a possible way to mitigate the negative effect on oxygen transport can be concluded. Through the optimization of coating method and electrode design, it's promising to avoid the catalyst being completely or heavily covered by ionomer and disperse the Pt particles more evenly on carbon support.

3.3 Transport dominance parameter

The electrochemical resistance (R_{ele}) expressed by Eq. (39) is a collection of electrochemical parameters related to oxygen reduction reaction (ORR). It has the same unit with transport resistance (s m^{-1}) and represents the last step before oxygen is consumed. By comparing the local transport resistance with the electrochemical resistance, a transport dominance parameter (ι) can be derived:

$$\iota = \frac{R_{\text{local}}}{R_{\text{ele}} + R_{\text{local}}} \times 100\% \quad (44)$$

Fig. 7 shows the polarization curves and the corresponding transport dominance curves with more complete data under three cathode Pt loadings (0.2, 0.1, 0.05 mg cm⁻²). The concentration loss region is highlighted. As seen from Fig. 7, the electrochemical factors dominate the cathode ORR under low and middle current densities as the value of transport dominance is fairly small. However, a turning appears as current density continues to increase indicating the transport factors begin to play a major role. After the turning, the transport dominance increases dramatically near the limiting current density (3A cm⁻²) which means the electrochemical reaction is suffering severe concentration loss. Therefore, the transport dominance parameter can be used to judge whether the oxygen starvation shows up under a certain output condition. According to the turning range in Fig. 7, a value greater than 10% can represent a symbol of obvious concentration loss.

3.4 Fine channel geometry design

In view of the hard transport process of oxygen as explained above, besides the optimization of CL preparation, the cathode flow field design is also of great significance in providing sufficient oxygen supply. The common flow fields usually consist of channel and rib. Limited by the machining precision, the wide rib (mostly 0.5-0.8 mm) can affect the fuel cell performance due to the non-uniform distribution

of reactant gas. So far, some novel flow fields have developed 3D structure based on the rib/channel design such as air-guide plate and converging/diverging channel [26, 27]. Others jumped out of the “channel and rib” pattern such as 3D fine mesh flow field and metal foam flow field [28, 29]. These novel structures successfully avoid the bad effect of rib and greatly increase fuel cell performance.

In fact, with the fast development of manufacturing technology, we can imagine that the widths of channel and rib may be reduced to extremely small (about 0.1 mm). Then the effects of rib are likely to be negligible. As a consequence, using the model developed in this study, 8 cases are set up regarding PEM fuel cell with fine flow channel and rib, which are shown in Table 6. Case 1-6 give different groups of fine channel widths and channel heights considering the 0.1-0.2 mm width range. The metal foam channel (without real structure) is considered in case 7 and case 8 uses traditional channel width as comparison. For these 8 cases, some operation conditions are reset to better agree with technology actuality of the state of the art fuel cell vehicles, including relative humidity (anode 0.2 & cathode 0.3) and stoichiometry ratio (anode 1.2 & cathode 2.0). In addition, cathode Pt loading uses the 0.2 mg cm^{-2} formulation in Table 5 and the anode reference exchange current density is adjusted within reasonable range.

As shown in Fig. 8, the narrower the channel cross section area is, the higher the

limiting current density. As for the metal foam channel (case 7), it also performs well under high current density. However, the pumping loss needs to be considered due to the narrow inlet area, which is calculated by:

$$W_{\text{pump}} = \Delta P \bar{u}_{\text{in}} A_{\text{in}} / A_{\text{act}} / \eta \quad (45)$$

where ΔP (Pa), $\bar{u}_{\text{in}}$ (m s⁻¹), A_{in} (m²), A_{act} (m²), η are pressure drop, average inlet velocity, inlet area, active area and air compressor efficiency (70% is used [23]). As

a result, case 3, 5 gives the best net power density at intermediate output voltage. In addition, the pumping loss and transport dominance at 0.3V output voltage are displayed of the 8 cases in Fig. 9. The extreme narrow width (0.1mm) causes high pumping loss owing to the intake resistance. Case 6 and 8 both have a relatively large value of transport dominance (about 12%), indicating that concentration loss is obvious, which can also be seen in Fig. 8. It's worth noting that case 7 has nearly the same pumping loss as case 5 but much lower transport dominance possibly because of the homogeneous porous media hypothesis. Considering better aspect ratio of channel cross section, 0.2-width/0.6-height channel geometry (case 5) stands out as the best among the fine channel geometry designs. And the transport dominance at 0.3V is still lower than 10%.

Additionally, the oxygen molar concentration distribution in the middle plane of cathode CL and current density distribution in the middle plane of membrane (case 5, 7 and 8, 2.0 A cm⁻²) are shown in Fig. 10, respectively. The metal foam channel

(case 7) gives the most uniform oxygen distribution at in-plane direction and fine channel geometry case (case 5) also performs better than traditional channel geometry case (case 8). As for current density distribution, both case 5 and 7 are much more uniform than case 8. It should be noted that the output voltage of case 5 (0.6V) is a little higher than that of case 7 (0.58V). This agrees with the conclusion of Kumar et al. [30] that the rib-channel structure can perform better than the metal foam under the same permeability. Using the Hagen–Poiseuille equation [31], the equivalent permeability of normal flow channel can be obtained through the hydraulic diameter. The permeability of the fine channel geometry (case 5) is calculated to be $3.2 \times 10^{-9} \text{ m}^2$ which is close to the metal foam permeability adopted in this study ($1.0 \times 10^{-9} \text{ m}^2$). Hence, fine channel geometry has the competence to further improve the PEM fuel cell performance.

4. Conclusion

In this study, an improved agglomerate sub-model of catalyst layer (CL) in proton exchange membrane (PEM) fuel cell is developed with the consideration of reasonable agglomerate size and Pt loading effect on oxygen transport. The oxygen local transport characteristics before arriving at the catalyst surface is clarified with detail by analyzing the composition of transport resistance at single agglomerate scale. The local transport resistance is separated into three individual resistance terms, namely the liquid water resistance, ionomer coverage resistance and

Pt/carbon agglomeration resistance. The Pt particle dispersion, the dissolution effect at gas-ionomer interface and Knudsen diffusion in primary pores are taken into account. The final expression of local transport resistance (Eq. (12)) is related to catalyst layer formulation parameters, including Pt loading, Pt weight percentage of Pt/carbon catalyst (Pt/C percentage) and mass ratio of ionomer to carbon (I/C ratio), which agrees with conclusions of former studies. In addition, by separating the electrochemical part and transport part in cathode B-V equation, a transport dominance parameter is derived. It can be used to evaluate the control of transport factors on reaction rate compared with the influence of electrochemical factors. According to the turning range, a value larger than 10% can be seen as a sign of local oxygen starvation. The sub-model is further coupled into a three-dimensional multi-phase PEM fuel cell model. An optimization research of fine channel geometry with extremely small channel (rib) width is conducted. Main conclusions are summarized as below:

- The local transport resistance mainly comes from the ionomer coverage and Pt/carbon agglomeration and they manifest opposite variation trends. Under extreme low Pt loading ($< 0.1 \text{ mg cm}^{-2}$), the ionomer resistance increases dramatically and becomes dominant possibly due to the relatively heavier ionomer coating. The transport pathway of oxygen flux should be much more complicated in this case.

- On the other hand, the agglomeration resistance is more evidently and causes a

slight increase of local transport resistance when Pt loading increases to 0.3 mg cm⁻². The reason is that Pt particles get more concentrated so that a larger proportion of them is likely to deposit into primary pores. Consequently, excess Pt loading may also be harmful to oxygen transport because of the high Pt particle density, even though the porosity of CL keeps unchanged.

– In general, from the perspective of oxygen local transport, it's highly recommended to optimize the structural topology of CL by improving the coating method, e.g. avoiding heavy ionomer coverage and dispersing the Pt particles more evenly on carbon support.

– With the expectation of manufacturing technology, fine channel geometry is found to greatly improve the uniformity of gas distribution and increase fuel cell performance effectively. The optimized channel width and height are 0.2 and 0.6 mm, respectively, which gives the highest net power density. And the transport dominance at 0.3V output voltage is still acceptable (< 10%). As a result, the fine channel and rib can serve as another competitive choice to improve the oxygen distribution and sufficiency regarding the flow field design of PEM fuel cell.

The large-scale commercialization of PEM fuel cell is urgently needed as a more clean and efficient energy conversion device. The analysis of the Pt loading effect on oxygen transport can help understand the underlying transport phenomena inside PEM fuel cell and fine channel geometry design may provide a potential idea to the

R&D. Also, the current model still fails to reflect the real microscopic transport mechanism in ionomer due to lack of knowledge. There exists fitting empirical coefficients in this study, which may be short of universality. And the Pt loading effect on the coupled electrochemical kinetics and transport phenomena needs further investigation, which also remains a future task in follow-up studies.

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637

638 **Figure and table captions**

639 Fig. 1. (a) SEM image of CL showing the secondary and primary pores [16]; (b)
640 TEM image of CL sample; (c) Schematic of single agglomerate and the three parts
641 of oxygen local transport resistance.

642 Fig. 2 Computational domain and mesh.

643 Fig. 3. Comparison of polarization curves between simulation results of this study
644 and experimental data under different cathode Pt loadings [14].

645 Fig. 4. Comparison of simulated polarization curves using homogeneous model,
646 traditional large-size agglomerate model (agglomerate diameter 380nm, ionomer
647 film thickness 20nm) and improved small-size agglomerate model (agglomerate
648 diameter 50nm, ionomer film thickness 8nm) under 0.2 mg cm⁻² cathode Pt loading.

649 Fig. 5. Comparison of local transport resistance between simulation results of this
650 study and other similar experimental results from the literature under different
651 cathode Pt loadings [14, 24, 25].

652 Fig. 6. The simulated total local transport resistance and two partial resistances
653 under different cathode Pt loadings.

654 Fig. 7. Polarization curves and corresponding transport dominance curves under 0.2,
655 0.1, 0.05 mg cm⁻² cathode Pt loadings.

656 Fig. 8. Polarization curves and net power density of the 8 cases.

657 Fig. 9. Pumping loss and transport dominance of the 8 cases at 0.3V output voltage.

658 Fig. 10. Comparisons of (a) oxygen molar concentration distribution in the middle
659 plane of cathode CL; (b) current density distribution in the middle plane of
660 membrane among case 5, 7 and 8. (“MF” stands for metal foam)

661

662 Table 1. Physical and transport parameters.

663 Table 2. Source terms.

664 Table 3. Grid independence test results.

665 Table 4. Design and model parameters of the validation cases.

666 Table 5. Catalyst layer formulations of the 5 cathode Pt loadings [14].

667 Table 6. Design parameters of the 8 different channel geometry cases.