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Supporting Information

Coupled carbon corrosion-catalyst layer agglomeration modeling framework for performance degradation of proton exchange membrane fuel cell during startup-shutdown cycles

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Volume fraction of components in the catalyst layer and effective diffusion coefficient of oxygen

In general, the CL is composed of three components: void space, ionomer phase, and solid phase. Obviously, the following equation is given:

$$\varepsilon_{\mathrm{cl}}+L_{\mathrm{i}}+L_{\mathrm{Pt/C}}=1 \tag{S1}$$

in which $L_{\mathrm{Pt/C}}$ is presented as

$$L_{\mathrm{Pt/C}}=\frac{1}{t_{\mathrm{cl}}}\left(\frac{m_{\mathrm{Pt}}}{\rho_{\mathrm{Pt}}}+\frac{m_{\mathrm{C}}}{\rho_{\mathrm{C}}}\right) \tag{S2}$$

L_{i} can be expressed as

$$L_{\mathrm{i}}=\frac{4}{3}\pi\left[r_{\mathrm{agg}}^{3}L_{\mathrm{i,agg}}+\left(\left(r_{\mathrm{agg}}+\delta_{\mathrm{agg}}\right)^{3}-r_{\mathrm{agg}}^{3}\right)\right]\cdot n\Big/V_{\mathrm{tot}} \tag{S3}$$

where n and V_{tot} are defined as the number of agglomerate particles and volume of the whole CL, respectively. n can be written as

$$\begin{aligned} n&=\frac{V_{\mathrm{Pt/C}}}{\left(V_{\mathrm{Pt/C}}\right)_{\mathrm{agg}}} \\ &=\frac{V_{\mathrm{tot}}L_{\mathrm{Pt/C}}}{\frac{4}{3}\pi r_{\mathrm{agg}}^{3}\left(1-L_{\mathrm{i,agg}}\right)} \end{aligned} \tag{S4}$$

where $(V_{\mathrm{Pt/C}})_{\mathrm{agg}}$ and $V_{\mathrm{Pt/C}}$ are the volume of solid phase in a single agglomerate and in the whole CL, respectively. Combining Eqs. S3 and S4, L_{i} can be written as

$$L_{\mathrm{i}}=\frac{L_{\mathrm{Pt/C}}}{r_{\mathrm{agg}}^{3}(1-L_{\mathrm{i,agg}})}\left[r_{\mathrm{agg}}^{3}L_{\mathrm{i,agg}}+\left(\left(r_{\mathrm{agg}}+\delta_{\mathrm{agg}}\right)^{3}-r_{\mathrm{agg}}^{3}\right)\right] \tag{S5}$$

The oxygen reaches the reaction sites through two routes: ionomer phase and void space. Therefore, the effective coefficient of oxygen diffusion can be described using the effective diffusion coefficient of oxygen in ionomer phase and liquid water:[1]

$$D_{\mathrm{O_2}}^{\mathrm{eff}}=\frac{L_{\mathrm{i}}}{L_{\mathrm{i}}+\varepsilon_{\mathrm{cl}}}D_{\mathrm{O_2,i}}^{\mathrm{eff}}+\frac{\varepsilon_{\mathrm{cl}}}{L_{\mathrm{i}}+\varepsilon_{\mathrm{cl}}}D_{\mathrm{O_2,w}}^{\mathrm{eff}} \tag{S6}$$

where $D_{\mathrm{O_2,i}}^{\mathrm{eff}}$ and $D_{\mathrm{O_2,w}}^{\mathrm{eff}}$ are expressed as follows:

$$D_{\mathrm{O_2,i}}^{\mathrm{eff}} = L_{\mathrm{i}}^{1.5} D_{\mathrm{O_2,i}} \qquad \text{[S7]}$$

$$D_{\mathrm{O_2,w}}^{\mathrm{eff}} = \varepsilon_{\mathrm{cl}}^{1.5} D_{\mathrm{O_2,w}} \qquad \text{[S8]}$$

Tables of parameter values used in the model

In the carbon corrosion model, all rate constants are assumed to have an Arrhenius dependence on temperature and can be expressed as

$$k_i = k_i^0 \exp(-E_{\mathrm{a}} / RT) \qquad \text{[S9]}$$

where k_i and k_i^0 ($i = 1, 2, \ldots, 7$) are the rate constant and pre-exponential rate constant of each reaction, respectively. The kinetic parameters used in the carbon corrosion model are given as follows:

Table S1 Kinetic parameters of each reaction in the carbon corrosion model

Parameter	k^0	U	α_{a}	α_{c}	E_{a}
r_1	2.35×10^{-12}	1.00	0.35	N/A	10
r_2	95	0.15	0.65	N/A	110
r_3	2.19×10^{-3}	0.95	0.48	0.65	50
r_4	1.18×10^{-8}	1.09	0.5	N/A	10
r_5	4.22×10^{-14}	1.00	0.5	N/A	10
r_6	2.35×10^{-7}	1.00	0.5	N/A	10
r_7	6.00×10^{-4}	0.57	0.5	0.5	20
Units	$\mathrm{mol\cdot m^{-2}\cdot s^{-1}}$	V	1	1	$\mathrm{kJ\cdot mol^{-1}\cdot K^{-1}}$

The values of more parameters used in the carbon corrosion model and the agglomerate model of CL are given in **Table S2**.

Table S2 Basic parameters used in the modeling framework

Parameters	Symbols	Value/unit	Ref.
Temperature	T	353.15 K	2
Pressure	P	1 atm	2
Mole fraction of oxygen in the cathode side	$\chi_{\mathrm{O_2}}$	0.21	2
Mole fraction of hydrogen in the anode side	$\chi_{\mathrm{H_2}}$	1	2
CL thickness	t_{cl}	10 μm	2
Density of platinum	ρ_{Pt}	21450 $\mathrm{kg \cdot m^{-3}}$	–
Density of carbon	ρ_{C}	1800 $\mathrm{kg \cdot m^{-3}}$	–
Platinum loading	m_{Pt}	0.2 $\mathrm{mg \cdot cm^{-2}}$	2
Carbon loading	m_{C}	0.3 $\mathrm{mg \cdot cm^{-2}}$	2
Cathodic transfer coefficient	α_{c}	1	3
Anodic transfer coefficient	α_{a}	0.5	3
Effective Pt surface ratio	ε_{l}	0.85	–
Electronic conductivity	κ_{s}	72700 $\mathrm{S \cdot m^{-1}}$	3
Ohmic resistance	R_{Ohm}	6.4×10^{-6} $\Omega\cdot\mathrm{m^2}$	4
ECSA of pristine CL	$(\mathrm{ECSA})_0$	59 $\mathrm{m^2 \cdot g^{-1}}$	2
Initial radius of the agglomerate	$r_{0,\mathrm{agg}}$	0.3 μm	Fitted
Initial thickness of ionomer covering film	$\delta_{0,\mathrm{agg}}$	3 nm	Fitted
Initial radius of Pt particles	$r_{0,\mathrm{Pt}}$	2 nm	2
Reference exchange current density	i_0^{ref}	$10^{0.0341T-16.96}$ $\mathrm{mA \cdot cm^{-2}}$	3
Reference oxygen concentration	$C_{\mathrm{O_2}}^{\mathrm{eff}}$	0.8 $\mathrm{mol \cdot m^{-3}}$	–
Henry's constant of oxygen in the ionomer	$H_{\mathrm{O_2,i}}$	0.3125 $\mathrm{atm \cdot m^3 \cdot mol^{-1}}$	3
Henry's constant of oxygen in the water	$H_{\mathrm{O_2,w}}$	1.33exp(-666/T)	3
Pt diffusion coefficient in the ionomer	$D_{\mathrm{Pt,i}}$	1.0×10^{-12} $\mathrm{m^2 \cdot s^{-1}}$	Fitted
Oxygen diffusion coefficient in ionomer	$D_{\mathrm{O_2,i}}$	$1.4276\times10^{-11}\times T-4.2185\times10^{-9}$ $\mathrm{m^2 \cdot s^{-1}}$	3

Surface energy density of Pt	γ	2.37 $J{\cdot}m^{-2}$	5
Molar volume of Pt	Ω	9.27 $m^3{\cdot}mol^{-1}$	6
Ionomer fraction in an agglomerate	$L_{i,agg}$	0.45	–
Partial pressure of water vapors	p_0	47 kPa	–
Concentration of protons	c_+	1 $mol{\cdot}L^{-1}$	–
Frumkin factor	g	3	7
BET surface area	S_{BET}	250 $m^2{\cdot}g^{-1}$	2
Surface concentration of site #	[#]	5.89×10^{-6} $mol{\cdot}m^{-2}$	Fitted
Surface concentration of site *	[*]	1×10^{-4} $mol{\cdot}m^{-2}$	7
Molar mass of water	M_{H_2O}	18 $g{\cdot}mol^{-1}$	–
Molar mass of carbon	M_C	12 $g{\cdot}mol^{-1}$	–
Viscosity of water at 80 °C	μ_{H_2O}	0.3565 mPa·s	–
Molar volume of oxygen	V_{O_2}	25.6 $cm^3{\cdot}mol^{-1}$	–
Association parameter for the water	Ψ	2.26	1

List of Symbols

a_{eff}	Effective catalyst surface area per unit volume, m^{-1}
a_{agg}	Effective agglomerate surface area per unit volume, m^{-1}
c_+	Concentration of protons, $mol{\cdot}L^{-1}$
C_{O_2}	Oxygen concentration, $mol{\cdot}m^{-3}$
C_{Pt}	Equilibrium concentration of solute Pt^{2+}, $mol{\cdot}m^{-3}$
D_{O_2}	Oxygen diffusion coefficient, $m^2{\cdot}s^{-1}$
E_a	Activation energy, $J{\cdot}mol^{-1}$
E_r	Agglomerate effectiveness factor
E_{rev}	Reversible potential of the reaction of hydrogen and oxygen, V
F	Faraday’s constant, 96485 $C{\cdot}mol^{-1}$

$H_{O_2,\mathrm{i}}$	Henry's constant of oxygen in ionomer, atm·m^3·mol^{-1}
$H_{O_2,\mathrm{w}}$	Henry's constant of oxygen in water, atm·m^3·mol^{-1}
i	Current density, mA·cm^{-2}
i_0^{ref}	Reference exchange current density, mA·cm^{-2}
I_{tot}	Total current density, mA·cm^{-2}
k_{c}	Electrochemical reaction rate constant
L_{i}	Volume fraction of ionomer phase in CL
$L_{\mathrm{i,agg}}$	Volume fraction of ionomer phase in the agglomerate
$L_{\mathrm{Pt/C}}$	Volume fraction of solid phase in CL
m	Mass loading per unit cross-sectional area, kg·m^{-2}
M	Molar mass, kg·mol^{-1}
n	Total number of agglomerates
N_{C}	Number of moles of carbon per unit cross-sectional area, mol·m^{-2}
N_{O_2}	Oxygen mole flux, mol·m^{-2}·s^{-1}
N'_{O_2}	Oxygen mole flux in ionomer film, mol·m^{-2}·s^{-1}
p_0	Partial pressure of water vapors, atm
P	Gas pressure, atm
r_{agg}	Radius of an agglomerate, m
$r_{0,\mathrm{Pt}}$	Initial radius of Pt particles, m
$r_{t,\mathrm{Pt}}$	Radius of degraded Pt particles, m
R	Universal gas constant, 8.314 J·mol^{-1}·K^{-1}
R_{agg}	Oxygen consumption rate based on agglomerate volume, mol·m^{-3}·s^{-1}
R_{O_2}	Oxygen consumption rate based on catalyst volume, mol·m^{-3}·s^{-1}
R_{Ohm}	Ohmic resistance, Ω·m^2
S_{ac}	Actual platinum surface area per mass, m^2·kg^{-1}
t_{cl}	Thickness of catalyst layer, m
V_{ave}	Average value of cyclic voltage, V
V_{O_2}	Molar volume of oxygen, m^3·mol^{-1}

Greek

α_a	Anodic transfer coefficient
α_c	Cathodic transfer coefficient
δ_agg	Thickness of ionomer covering film, m
η_local	Local overpotential within the CL, V
ε_1	Effective Pt surface ratio
ε_cl	Catalyst layer porosity
λ	Local water content of the ionomer phase
θ	Fraction of coverage
κ_l	Bulk protonic conductivity, $\mathrm{S \cdot m^{-1}}$
κ_s	Bulk electronic conductivity, $\mathrm{S \cdot m^{-1}}$
γ	Interfacial energy surface density, $\mathrm{J \cdot m^{-2}}$
Ω	Molar volume of Pt, $\mathrm{m^3 \cdot mol^{-1}}$
ρ	Density, $\mathrm{kg \cdot m^{-3}}$
μ	Viscosity, m·Pa·s
χ	Mole fraction
ϕ_L	Thiele modulus

Subscripts and superscripts

agg	Agglomerate
ave	Average
C	Carbon
cl	Catalyst layer
eff	Effective
g	Gas
i	Ionomer
max	Maximum
min	Minimum
Pt	Platinum

ref	Reference
rev	Reversible
s	Solid
w	Water

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