Supplementary material for: Research of proton exchange membrane fuel cell modeling for the influence of variable-temperature operating conditions on concentration polarization

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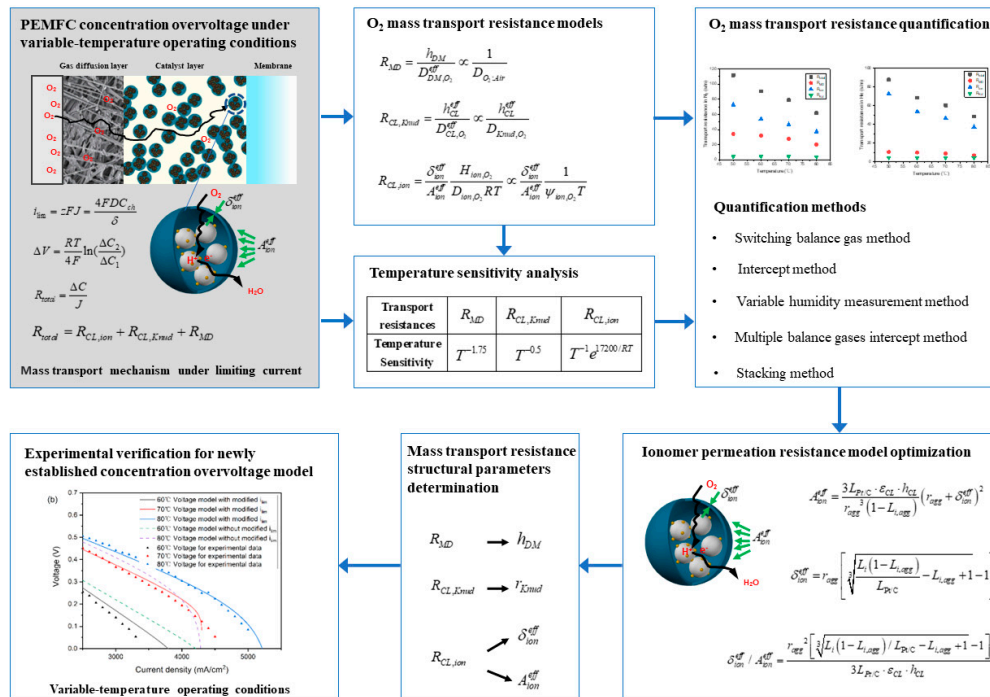
1. Research procedure and methodology

Figure S1. Flowchart of research procedure and methodology

2. Model Description

The Nernst equation is calculated form the difference of Gibbs free energy between reaction products and reactants. When oxygen at the cathode of PEMFC is consumed, which means its partial pressure P_{O_2} decreases, resulting in a concentration gradient of cathode reaction gas. We assume the humidity at cathode is saturated, then the water vapor partial pressure P_{H_2O} remains unchanged. At anode side, the concentration difference caused by reaction of pure hydrogen is much lower than the concentration difference of cathode, therefore the partial pressure of hydrogen P_{H_2} can

be approximately set unchanged. The change of cathode electric potential can be expressed as the correlation function of cathode oxygen partial pressure P_{O_2} variation.

$$\Delta V = \frac{RT}{4F}\ln(P_2) - \frac{RT}{4F}\ln(P_1) = \frac{RT}{4F}\ln(\frac{P_2}{P_1}) \tag{S1}$$

Since the change of oxygen partial pressure is positively correlated with the change of oxygen concentration from the flow channel to the surface of platinum, Equation (S1) can be written.

$$\Delta V = \frac{RT}{4F}\ln(\frac{\Delta C_2}{\Delta C_1}) \tag{S2}$$

ΔC is the oxygen concentration difference between flow channel C_{ch} and the oxygen concentration on platinum surface C_{Pt} of the catalyst. According to Fick's law, the linear diffusion flux equation of cathode oxygen diffusion flux J in the steady-state process is simplified as the change of concentration gradient.

$$J = -D(\frac{\partial C}{\partial x}) = D(\frac{\Delta C}{\delta}) \tag{S3}$$

The cathode current density i can be expressed as oxygen diffusion flux multipling by transport electric charge of ion per mole (equation S4).

$$i = zFJ = \frac{4FD\Delta C}{\delta} \tag{S4}$$

z is oxidant for electron number, for oxygen is 4, F is Faraday constant. When all the oxygen which spreading to the platinum surface of cathode catalyst has been reacted, the cathode catalyst platinum surface oxygen concentration C_{Pt} was equal to zero, the current density of the PEMFC achieved its maximum. At this time ΔC is flow channel oxygen concentration C_{ch}, current density is PEMFC limiting current density $i_{\lim}$.

$$i_{\lim} = zFJ = \frac{4FDC_{ch}}{\delta} \tag{S5}$$

In general, the relationship between oxygen concentration at cathode catalyst C_{Pt} and current density of PEMFC i can be obtained by (equation S6).

$$i = zFJ = \frac{4FD(C_{ch} - C_{Pt})}{\delta} \tag{S6}$$

It is assumed that ΔC_1 and ΔC_2 are the concentration differences between limiting current density and general current. The reactant type, reactant concentration, and reactant condition are also to be consider for the model calibration [49]. Then, the analytical formula of PEMFC concentration overvoltage model (equation S7) is obtained by substituting (equation S5), (equation S6) with (equation S2).

$$V_{con} = \frac{RT}{F}\left(\frac{1}{4} + \frac{\Upsilon}{\alpha}\right)\ln(1 - \frac{i}{i_{\lim}})$$
(S7)

The exchange current density analytic equation (equation S8) [43], which is used for the initial value calculation of the exchange current density in order to calibrate the activation overvoltage model.

$$i_0 = i_0^* \ln\left(\frac{P_{O_2}}{P_{O_2}^*}\right)^{\gamma} \exp\left[\frac{-E^{rev}}{RT}\left(1 - \frac{T}{T^*}\right)\right]$$
(S8)

3. Methods for measuring oxygen transport resistance

Table S1- Method for measuring oxygen transport resistances.

Experimental Method	Experimental variable	Theory	Summary
1. Intercept method (Zhaohui Wan) [22].	cathode pressure, cathode oxygen concentration, PEMFC temperature	Using different cathode pressure P_{Ca} condition of $C_{ch}/i_{\lim}$ to calculate R_{total}, ploting R_{total} image in terms of P_{Ca} and get R_{MD}, reverse lengthening image and get intercept of R_{other}, change temperature condition and separate $R_{CL,Knud}$, $R_{CL,ion}$. $R_{other} = R_{CL,Knud} + R_{CL,ion}$	* The method can use a conventional single PEMFC reaction device. * A MEA with a small effective area and a large flow rate of reactive gas are required to reduce the effect of cathode flooding on oxygen transport resistance measurement. * This method requires an adjustable flow mixing device to configure reactive gases with different oxygen concentrations. * This method requires the preparation of an inert balanc gas. * This method needs relatively more experiments.
2. Variable humidity measurement method	cathode pressure, cathode oxygen concentration,	The method to get R_{DM} is same as intercept method. Using the influence of different humidity for $R_{CL,ion}$ to	* The humidity of the cathode has a direct effect on the drying of the proton exchange film (decreased

(Hwanyeong) [4].	cathode humidity	get the separation of $R_{CL,Knud}$ and $R_{CL,ion}$.	conductivity) or the flooding of the cathode gas diffusion layer, catalyst layer, etc. The above interference factors make the method difficult to obtain accurate $R_{CL,ion}$ measurement results. Therefore, this method is rarely used.
3. Switching balance gas method (Nonoyama) [21]	type of cathode balance gases, PEMFC temperature	Using different diffusion coefficient for oxygen in balance gases (N_2、 He) to separate R_{MD}. $$\frac{R_{DM,N_2}}{R_{DM,He}} = \frac{D_{DM,He}^{eff}}{D_{DM,N_2}^{eff}} = \frac{R_{total,N_2} - R_{other}}{R_{total,He} - R_{other}}$$ $$R_{other} = R_{CL,Knud} + R_{CL,ion}$$ Separating $R_{CL,Knud}$, $R_{CL,ion}$ by variable temperature conditions.	* This method requires an adjustable flow mixing device to prepare low concentration reactive gas. * This method requires the preparation of two inert equilibrium gases (e.g. N2, He). * This method needs fewer experiments and it is widely applied.
4. Multiple balance gases intercept method [28].	type of cathode balance gases, PEMFC temperature	Applying the linear relation between reciprocal of total mass transport coefficient k and molecule mass of balance gas, the ionomer phase mass transport coefficient k_e is separated. $$D = \frac{i_l RT\delta}{nFp_{O_2}} = KRT$$ $$\delta = \frac{D}{k_e} = \frac{KRT}{k_e} \quad \frac{1}{k} = \frac{1}{k_g} + \frac{1}{k_e}$$	*In order to improve the test accuracy, it is necessary to prepare a variety of high molecule weight balance gases in advance, which increases the difficulty of the experiment.
5. Stacking method (Baker) [50-52].	cathode pressure, PEMFC temperature, gas diffusion layer of different thickness (carbon paper, microporous layer)	A combination of gas diffusion layers of different thickness is used（carbon paper, microporous layer）to separate R_{MD} from R_{total}.	* This method requires to prepare different thickness of gas diffusion layers (support layer, microporous layer), the preparation is difficult and complicated. * Special gaskets with corresponding thickness to seal the PEMFC for different gas diffusion layers are required. * This method cannot completely separate all three contributions (molecular, Knudsen diffusion, and ionomer permeability) .

4. Humidification module and mass flow conversion module

Since this study focuses on cathode oxygen transport resistance of PEMFCs, the cathode/anode inlet air pressure and humidity simulation accuracy are required to be relatively high to simulate real humidification equipment. Therefore, it is necessary to establish a cathode/anode inlet air humidifier module to humidify the reaction gas at a specified flow rate and meet the purpose of cathode/anode inlet air pressure. The humidifier can accurately adjust the inlet pressure of PEMFC cathode/anode by controlling the inlet pressure of humidifier. According to the actual cathode input gas flow, humidity, dry oxygen mole fraction and the setting target of gas output pressure, temperature and humidity of the humidifier, cathode humidifier module can describe detail gas mass flow, pressure, humidity, dry oxygen mole fraction and other parameters at the outlet of the humidifier through the analytical formula of one-dimensional model.

Based on ideal gas state equation, the mass flow rate of cathode gas is.

$$W_{Air} = \frac{dm}{dt} = \frac{M_{Air} \cdot P}{RT} \cdot \frac{dV}{dt} = \frac{P\left(M_{O_2} \cdot x_{O_2} + M_{N_2}\left(1 - x_{O_2}\right)\right)}{RT} \cdot \frac{dV}{dt} \tag{S9}$$

The saturation vapor pressure of the cathode can be calculated by.

$$\log_{10}\left(P_{H_2O}^{sat}\right) = 2.95 \times 10^{-2} \cdot T - 9.19 \times 10^{-5} \cdot T^{-2} + 1.44 \times 10^{-7} \cdot T^{-3} \tag{S10}$$

The specific humidity of cathode can be calculated by.

$$\omega_{ca,atm} = \frac{M_v}{M_{a,ca,in}} \cdot \frac{\phi_{atm} p_{sat}^{atm}}{p_{atm} - \phi_{atm} p_{sat}^{atm}} = \frac{M_v}{M_{a,ca,in}} \cdot \frac{P_{v,ca,in}}{P_{a,ca,in}} \tag{S11}$$

The mass flow rate of dry air at cathode is expressed as.

$$W_{a,ca,in} = \frac{W_{ca,in}}{1 + \omega_{ca,in}} \tag{S12}$$

The modeling principle of anode humidifier module is the same as that of the cathode. There is no need for further elaboration.

Most of the cathode/anode of PEMFC test stand takes the volume flow rate as the unit of inlet gas flow. When estimating the cathode molecule diffusion resistance, it is necessary to convert each inlet gas component (O_2, N_2, $H_2O_{(g)}$) into mass flow rate in advance to facilitate the calculation of actual component content of each gas. Similarly, in the calculation of Nernst reversible voltage, the partial pressure of each gas also needs to be derived from the calculation result of gas mass flow. Therefore, it is necessary to build a mass flow conversion module at the intake port of PEMFC. The crucial physical quantities of the module are calculated as follows.

Oxygen mass fraction

$$y_{O_2} = \frac{M_{O_2} x_{O_2}}{M_{O_2} x_{O_2} + M_{N_2}\left(1 - x_{O_2}\right)} \tag{S13}$$

Nitrogen mass fraction

$$y_{N_2} = 1 - \frac{M_{O_2} x_{O_2}}{M_{O_2} x_{O_2} + M_{N_2}\left(1 - x_{O_2}\right)} \tag{S14}$$

Oxygen mass flow = dry oxygen mass flow * oxygen mass fraction

$$W_{O_2} = \frac{y_{O_2}}{\left(1 + \omega_{ca,atm}\right)} W_{ca,in} \tag{S15}$$

Nitrogen mass flow = dry oxygen mass flow * nitrogen mass fraction

$$W_{N_2} = \frac{y_{N_2}}{\left(1 + \omega_{ca,atm}\right)} W_{ca,in} \tag{S16}$$

Table. S2 operating conditions and parameters of MEA1 [21].

PEMFC operating conditions	Value
cathode pressure	150kPa
cathode flow	650cm^3 /min
oxygen concentration	1%
Cathode stoichiometric	8
balance gases concentration	N$_2$ 99%，He 99%
cathode humidity	90%
PEMFC temperature	50°C 60°C 70°C 80°C
MEA parameters	Value
proton exchange membrane type	NRE211 25.4μm
Pt loading	0.2mg/cm^2
carbon paper thickness	200μm
microporous layer thickness	70μm
effective area of PEMFC	1cm^2
I/C ratio	0.8

Table. S3 operating conditions and parameters of MEA2 [22].

PEMFC operating conditions	Value
cathode pressure	150, 200, 250, 300kPa
cathode flow	4000cm^3/min
oxygen concentration	0.5%, 1%, 1.5%, 2%
Cathode stoichiometric	>14
cathode humidity	70%

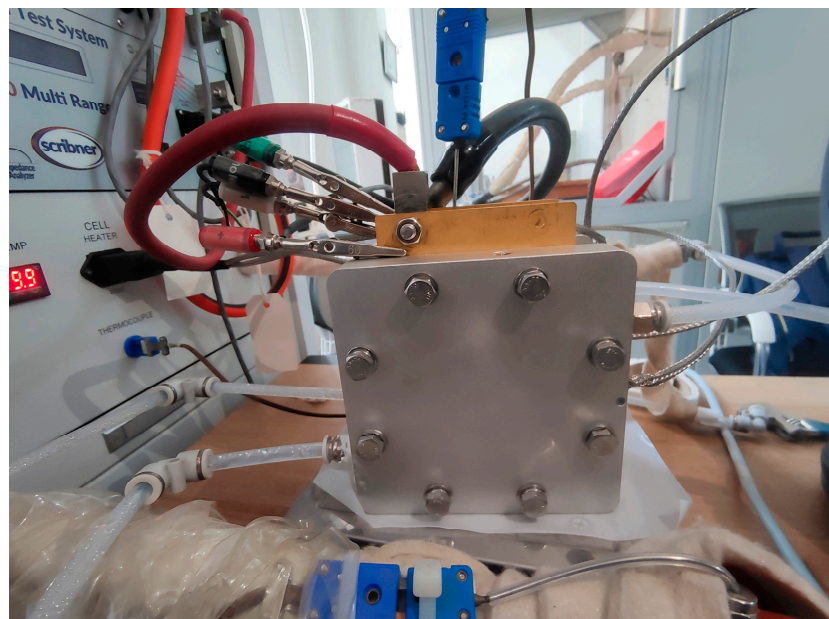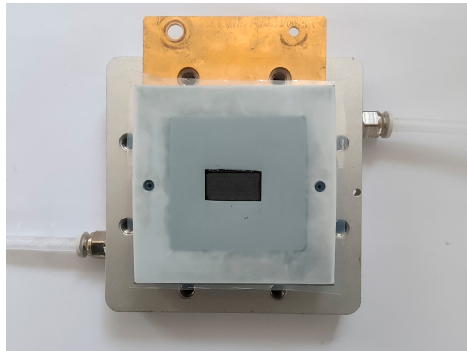| PEMFC temperature	40℃ 50℃ 60℃ 70℃
MEA parameters	**Value**
proton exchange membrane model	EW870 15μm
Pt loading	0.4mg/cm^2
thickness of gas diffusion layer	250μm
effective area of PEMFC	2 cm^2
I/C ratio	0.8

5. Fuel cell test bench

Figure S2. 2cm^2 single fuel cell.

6. Structural parameters of MEA model

Table. S4 structural parameters of MEA1.

MEA1 catalyst	Value
h_{DM} , thickness of gas diffusion layer m	0.000110
r_{Knud} , catalyst pore radius m	0.00000015
h_{CL} ,effective thickness of catalyst layer m	0.0000069

r_{agg}, effects of agglomerate radius m	0.000000099
ε_{CL}, pore volume fraction of catalyst layer	0.537
$L_{i,agg}$, volume fraction of ionomer in agglomerates	0.4

Table. S5 structural parameters of MEA2.

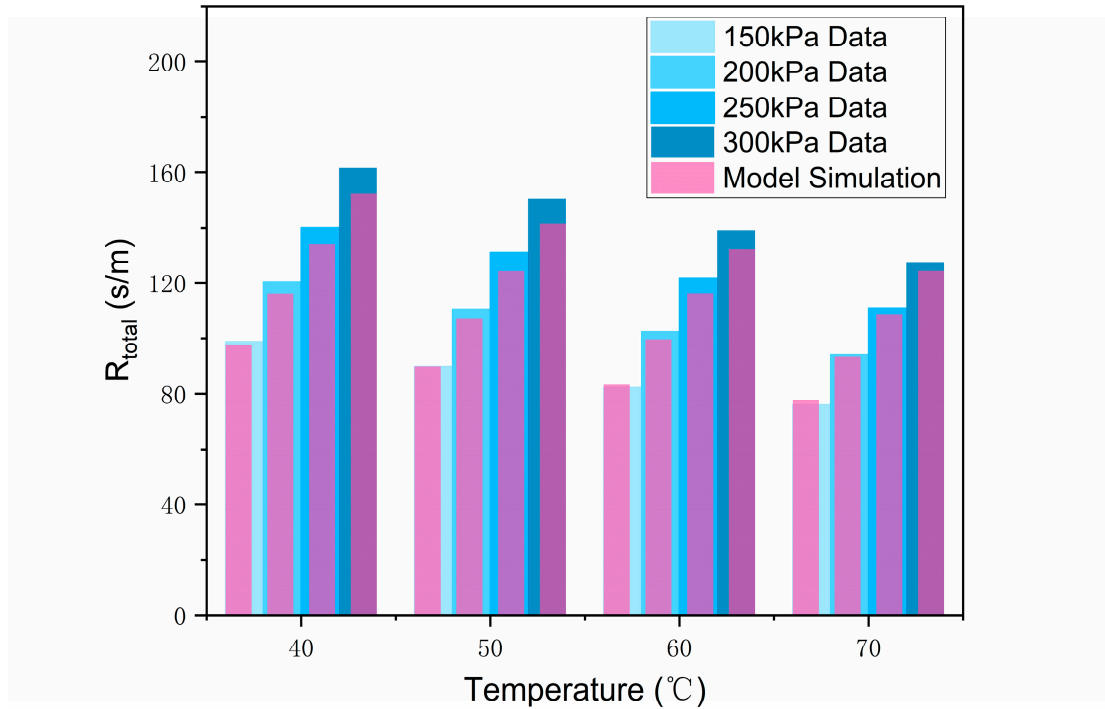| MEA1 catalyst	Value
h_{DM}, thickness of gas diffusion layer m	0.000250
r_{Knud}, catalyst pore radius m	0.0000005
h_{CL}, effective thickness of catalyst layer m	0.000071
r_{agg}, effects of agglomerate radius m	0.000000050
ε_{CL}, pore volume fraction of catalyst layer	0.537
$L_{i,agg}$, volume fraction of ionomer in agglomerates	0.4

7. Oxygen transport resistances simulation

Figure S3. Oxygen transport resistances simulation result compared with experiment data.

8. Concentration overvoltage model validation at 250 kPa cathode pressure
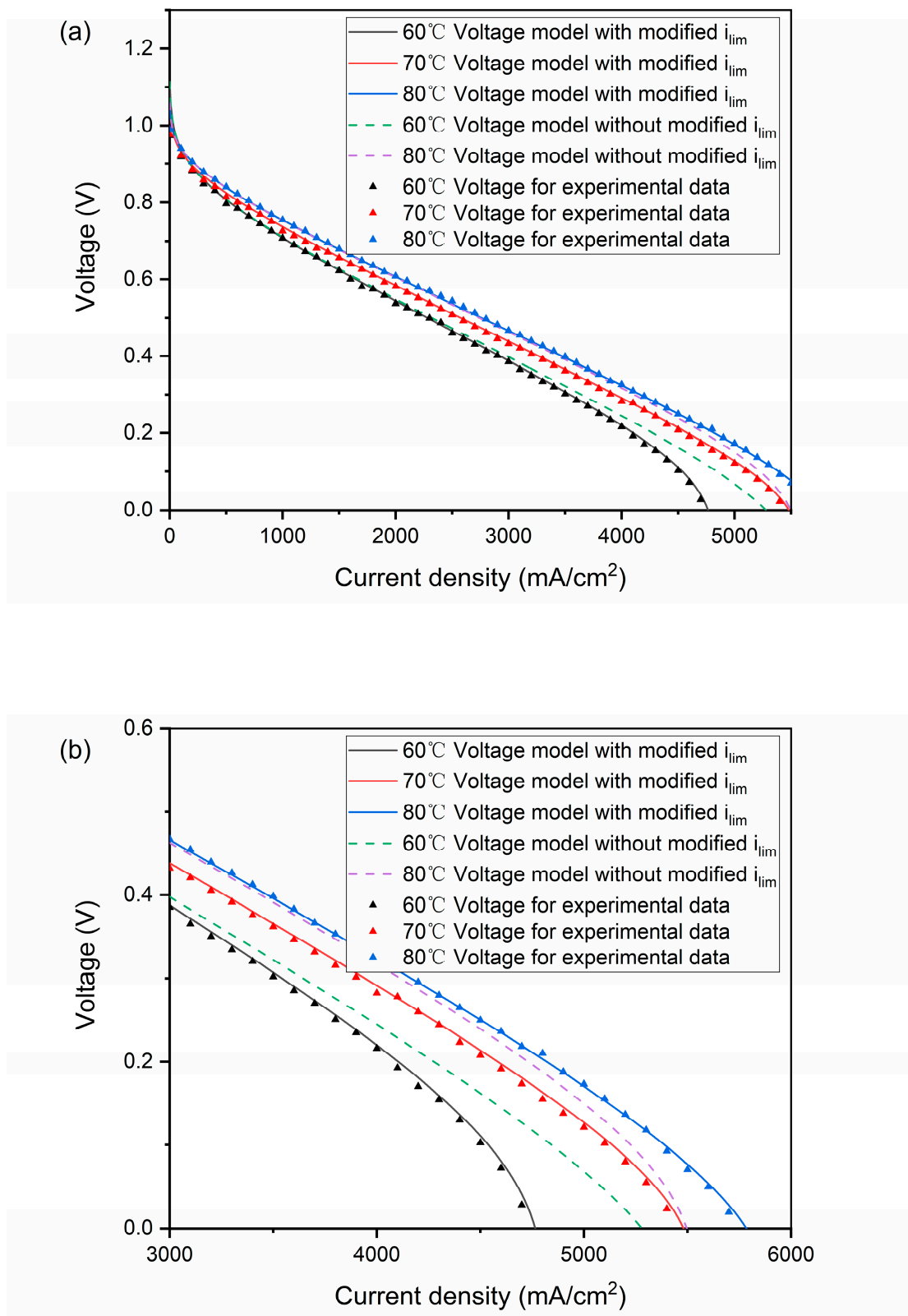
Figure S4. Concentration overvoltage model validation with polarization curve at 250

kPa cathode pressure for MEA2. (a) General diagram of polarization curve. (b) Partial enlargement of polarization curve.

9. Methods for measuring oxygen transport resistance in detail

The total oxygen transport resistance is composed of three mass transport subresistances, namely the ionomer/water membrane permeation resistance, the Knudsen diffusion resistance and the molecular diffusion resistance, i.e. $R_{total} = R_{CL,ion} + R_{CL,Knud} + R_{MD}$ .Based on Faraday's law

$$R_{total} = \frac{\Delta C}{J} = \frac{4F}{i} \Delta C = \frac{4F}{i_{\lim}} \frac{P - P_w}{RT} x^{inlet}_{O_2},$$ ΔC is the difference in oxygen concentration between the flow channel and the catalyst at the platinum surface, in the situation of limiting current, ΔC is the oxygen concentration in flow channel. Therefore, R_{total} can be obtained simply by measuring the limiting current density $i_{\lim}$.

For $R_{CL,ion}$, $R_{CL,Knud}$ and R_{MD} detailed quantification, the "switching balance gas" method can be applied indirectly to obtain them. The core idea of the quantification method is to separate $R_{CL,ion}$, $R_{CL,Knud}$, and R_{MD} one by one by taking advantage of the different sensitivity of each oxygen transport subresistance by temperature and balance gas type. The switching balance gas method uses oxygen transport subresistance for pressure sensitivity to divide R_{total} into R_{MD} and R_{other} , where

$$R_{other} = R_{CL,ion} + R_{CL,Knud} \quad (S17).$$

Then the total oxygen transport resistance in nitrogen and helium can be expressed as

$$R_{total(N_2)} = R_{MD(N_2)} + R_{other} \text{ (S18) and } R_{total(He)} = R_{MD(He)} + R_{other} \text{ (S19)}.$$

The diffusion coefficient of oxygen in a multicomponent gas (nitrogen/water, vapor or helium/water, vapor) can be expressed as

$$D_{O_2:N_2} = \left(\sum_{\substack{j=1 \\ j \neq A}}^{Nc} \frac{x_j}{D_{A:j}} \right)^{-1} = \left(\frac{W_{N_2} \cdot M_{Ca,in}}{W_{Ca,in} \cdot M_{N_2} \cdot D_{O_2:N_2}} + \frac{W_{Va} \cdot M_{Ca,in}}{W_{Ca,in} \cdot M_{Va} \cdot D_{O_2:Va}} \right)^{-1} \text{ (S20)}.$$

$$D_{O_2:He} = \left(\sum_{\substack{j=1 \\ j \neq A}}^{Nc} \frac{x_j}{D_{A:j}} \right)^{-1} = \left(\frac{W_{He} \cdot M_{Ca,in}}{W_{Ca,in} \cdot M_{He} \cdot D_{O_2:N_2}} + \frac{W_{Va} \cdot M_{Ca,in}}{W_{Ca,in} \cdot M_{Va} \cdot D_{O_2:Va}} \right)^{-1} \text{ (S21).}$$

x_j can be expressed as the molar fraction of helium, nitrogen, and water vapor.

We associate equation (S19) with (S18).

$$\begin{cases} R_{MD(N_2)} = R_{total(N_2)} - R_{other} & \text{（S18）} \\ \\ R_{MD(He)} = R_{total(He)} - R_{other} & \text{（S19）} \end{cases}$$

When switching reaction balance gas (%1 oxygen/%99 nitrogen switching to %1 oxygen/%99 helium), $R_{CL,ion}$, $R_{CL,Knud}$ are not affected by the switching of balance gas, i.e. R_{other} has zero sensitivity for switching balance gas. According to equations (S20) and (S21), R_{MD} is highly sensitive to the reaction balance gas. Placing zero sensitivity variables (0 sensitivity to reaction balance gas) on one side of the equation, equation (S22) can be obtained by equation (S18) and (S19).

$$\frac{R_{MD(N_2)}}{R_{MD(He)}} = \frac{D_{O_2:He}}{D_{O_2:N_2}} = \frac{R_{total(N_2)} - R_{other}}{R_{total(He)} - R_{other}} \text{ (S22)}。$$

By calculating R_{total} and $\dfrac{D_{O_2:He}}{D_{O_2:N_2}}$, then R_{other} can be obtained. Nonoyama set 4 PEMFC temperature measurement points (50°C, 60°C, 70°C, 80°C) for oxygen transport resistance measurement, then 4 R_{other} values and 4 R_{MD} values can be obtained with the same procedure above.

$$R_{CL,Knud} = \frac{2}{3r_{Knud}} \left(\frac{8RT}{\pi M_A} \right)^{-0.5} \text{ (S23) and } R_{CL,ion} = \frac{\delta_{ion}^{eff}}{A_{ion}^{eff}} \frac{H_{ion,O_2}}{D_{ion,O_2} RT} \text{ (S24),}$$

In Equation (8), the ratio of diffusion coefficient D_{ion,O_2} to Henry's constant H_{ion,O_2} is

$$\frac{D_{ion,O_2}}{H_{ion,O_2}} = 3.27 \times 10^{-15} \exp[1.28(RH)] \times \exp[\frac{17200}{R} (\frac{1}{323.15} - \frac{1}{T})] \text{ (S25).}$$

From this we conclude that the temperature sensitivity of $R_{CL,Knud}$ and $R_{CL,ion}$ is

$T^{-0.5}$ and $T^{-1}e^{17200/RT}$, respectively.

Therefore, $R_{CL,Knud} \propto T^{-0.5}$, $R_{CL,ion} \propto T^{-1}e^{17200/RT}$.

Since r_{Knud}, δ_{ion}^{eff}, and A_{ion}^{eff} are the hard-to-measure structural parameters of $R_{CL,Knud}$ and $R_{CL,ion}$, respectively. We consider r_{Knud}, δ_{ion}^{eff}, and A_{ion}^{eff} as unknown quantities. We make

$$R_{CL,Knud} = AT^{-0.5} \text{ (S26)}, \quad R_{CL,ion} = BT^{-1}e^{17200/RT} \text{ (S27)}.$$

A and B are the coefficients of $R_{CL,Knud}$ and $R_{CL,ion}$, respectively, then

$$R_{other} = AT^{-0.5} + BT^{-1}e^{17200/RT} \text{ (S28)}.$$

The R_{other} values for four PEMFC temperature measurement points (50°C, 60°C, 70°C, 80°C) have been quantified. Then the coefficients A and B can be considered as solutions of the quadratic equation of equation (S28). The solutions A and B of equation (S28) are brought into equations (S26) and (S27), then $R_{CL,Knud}$ and $R_{CL,ion}$ at different temperature conditions are obtained.

The values of $R_{CL,ion}$ $R_{CL,Knud}$ and R_{MD} can be obtained by indirect measurements of using switching reaction balance gases method. Due to the complexity and irregularity of the structure of gas diffusion layer, microporous layer and catalyst layer, the hard-to-measure structural parameters h_{DM}, r_{Knud}, δ_{ion}^{eff} and A_{ion}^{eff} are the numerical values we need to fit within a reasonable range after determining the oxygen transport subresistances.

Similar to the method of "switching balance gas", the "intercept method" can be used to separate each value of $R_{CL,ion}$, $R_{CL,Knud}$ and R_{MD}.

Firstly, equation $R_{total} = \dfrac{\Delta C}{J} = \dfrac{4F}{i}\Delta C = \dfrac{4F}{i_{\lim}}\dfrac{P - P_w}{RT}x_{O_2}^{inlet}$ is used to obtain R_{total} at different inlet pressures under limiting current condition. The image of the function is plotted with horizontal coordinate P and vertical coordinate R_{total}. Since for R_{total}, R_{MD}

is positively correlated with P, while $R_{CL,ion}$ and $R_{CL,Knud}$ are not affected by P, therefore R_{total} is linearly correlated with P. When $P=0$, it is considered that $R_{MD}=0$. When the R_{total}-P linear image is extended in the reverse direction, the image is at the intersection point of the vertical axis R_{total}, that means when $P=0$, $R_{total}=R_{other}$. At this time, R_{other1} is separated at the temperature T_1. Subsequently, R_{total} measurement experiments are carried out at different temperature conditions. Then, at different temperature conditions, R_{other} can be quantitatively obtained. The quantification $R_{CL,ion}$ and $R_{CL,Knud}$ methods are the same as the switching reaction balance gas method, which is not repeated here. Similarly, the mass transport structural parameters h_{DM}, r_{Knud}, δ_{ion}^{eff}, and A_{ion}^{eff} are also the numerical values that need to be fitted in our manuscript.

Reference
[4] Oh H, Lee YI, Lee G, Min K, Yi JS. Experimental dissection of oxygen transport resistance in the components of a polymer electrolyte membrane fuel cell. J POWER SOURCES. 2017; 345:67-77.
[21] Nonoyama N, Okazaki S, Weber AZ, Ikogi Y, Yoshida T. Analysis of Oxygen-Transport Diffusion Resistance in Proton-Exchange-Membrane Fuel Cells. J ELECTROCHEM SOC. 2011; 158:B416.
[22] Wan, Z.; Liu, S.; Zhong, Q.; Jin, A.; Pan, M. Mechanism of improving oxygen transport resistance of polytetrafluoroethylene in catalyst layer for polymer electrolyte fuel cells. Int. J. Hydrogen Energy 2018, 43, 7456–7464.
[28] Correa JM, Farret FA, Popov VA, Simoes MG. Sensitivity Analysis of the Modeling Parameters Used in Simulation of Proton Exchange Membrane Fuel Cells. IEEE T ENERGY CONVER. 2005; 20:211-8.
[48] Striednig M, Cochet M, Boillat P, Schmidt TJ, Büchi FN. A model based investigation of evaporative cooling for polymer electrolyte fuel cells – Stack level analysis. J POWER SOURCES. 2022; 517:230706.
[49] Zihrul P, Hartung I, Kirsch S, Huebner G, Hasché F, Gasteiger HA. Voltage Cycling Induced Losses in Electrochemically Active Surface Area and in H2/Air-Performance of PEM Fuel Cells. J ELECTROCHEM SOC. 2016; 163:F492-8.

[50]Baker DR, Caulk DA, Neyerlin KC, Murphy MW. Measurement of Oxygen Transport Resistance in PEM Fuel Cells by Limiting Current Methods. J ELECTROCHEM SOC. 2009; 156:B991.

[51]Schuler T, Chowdhury A, Freiberg AT, Sneed B, Spingler FB, Tucker MC, et al. Fuel-Cell Catalyst-Layer Resistance via Hydrogen Limiting-Current Measurements. J ELECTROCHEM SOC. 2019; 166:F3020-31.

[52]Beuscher U. Experimental Method to Determine the Mass Transport Resistance of a Polymer Electrolyte Fuel Cell. J ELECTROCHEM SOC. 2006; 153:A1788.