Mathematical modelling and operation parameters analysis of proton exchange membrane fuel cell

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Abstract. The fuel cell is a device which can convert chemical energy from fuel into electrical and thermal energy directly. It has advantages like high power density, fast start-up and high conversion efficiency. Its prospects of application in transportation, fixed power supply and standby power generation are great. Fuel cell is a dynamic complex system with multi-phase, multi-scale and multi-physical fields. Based on the working mechanism of fuel cell, this paper establishes a mathematical model to simulate the electrochemical reaction, material and energy transfer process in fuel cell. The parameters such as temperature, pressure, concentration, current and potential, which are difficult to measure, are visualized to deepen the transfer and counter-reaction in fuel cell. In order to provide important scientific basis for the optimal design and system control of the stack, the mechanism should be understood and the optimum reaction conditions should be found.

1. Introduction
When it comes to the worldwide future clean- and renewable-energy, fuel cells are active and inevitable to be talked about due to their important roles in research. The fuel cell is a device which can convert chemical energy from fuel into electrical and thermal energy directly [1-3]. A fuel cell generally consists of three parts, respectively is anode, cathode and electrolyte. Depending on the different electrolyte, the fuel cells technology has 5 main types, including alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), solid oxide fuel cell(SOFC) , and proton exchange membrane fuel cell (PEMFC) [4-5]. Their operating temperatures and the electrolyte types are shown in table 1.

| Fuel Cell type | Operating temperature, °C | Electrolyte type |
|---------------|--------------------------|------------------|
| AFC           | 100                      | Liquid           |
| MCFC          | 500-800                  | Liquid           |
| PAFC          | 60-200                   | Liquid           |
| PEMFC         | 60-100                   | Solid            |
| SOFC          | 1000-1200                | Solid            |

The proton exchange membrane fuel cell(PEMFC) is considered to be the most promising among the diverse fuel cells due to its advantages such as high energy efficiency, noiseless and fast start up and shut down[6].
It is apparently unrealistic to study the mechanism of fuel cells through large-scale series experiments due to the high cost of fuel cells. In fuel cell, the flow, heat transfer, mass transfer and electrochemical processes interact with each other which leads to a multi-phase, multi-scale, multi-physical field dynamic complex system. It is complicated and difficult to directly measure and observe. As a result, a mathematical model is supposed to be established for the electrochemical reaction, material and energy transfer process in fuel cell based on the working mechanism. The simulation visualizes the parameters that are difficult to measure, such as temperature, pressure, concentration, current and potential, deepens the understanding of the transfer and reaction mechanism in fuel cell, searches for the best reaction conditions, and further provides an important scientific basis for the optimal design of the stack and its system control. At present, the research on dynamic characteristics of fuel cell plays an important role in the design, development and practical application of fuel cell, and has developed many branches of disciplines like hydrodynamics, thermodynamics, electrochemistry and computer. Therefore, the research on dynamic characteristics of PEMFC has definite significance in scientific research and engineering application.

Cheddie et al. [7] systematically summarized the work of PEMFC modeling before 2005. The steady-state modeling and simulation of PEMFC stack are summarized as analytical model, semi-empirical model and mechanism model. Promislow et al. [8] elaborated the mathematical problems in the process of PEMFC modeling and the modeling methods of single fuel cell and stack in macro scale. Amphlett et al. [9] earlier proposed a dynamic model of PEMFC, which is a dynamic model of material flow and energy flow inside fuel cell, coupled with a steady-state electrochemical model. The model is mainly used to predict the voltage and temperature output of the stack. Mert et al. [10] analyzed the energy efficiencies and power output of the stack at different operating conditions. They found some positive parameters for the stack output such as stack temperature and operating pressure. At the same time, they also found the negative parameters such as anode and cathode stoichiometry.

This paper uses MATALB/Simulink to establish a mathematical model to simulate the electrochemical reaction, material and energy transfer process in fuel cell. Based on the experimental verification of the correctness of the model, the effects of operating parameters such as temperature and voltage on the output performance of the stack are explored through the model.

2. PEMFC steady state model and simulation

Computer simulations are based on specific assumptions. In order to simplify the working process of fuel cell, the paper makes following assumptions about the working process of fuel cell.

1) The model is a one-dimensional lumped parameter model.
2) The distribution of humidity and temperature inside the fuel cell is uniform.
3) Reaction gases are ideal gases, which obey the law of ideal gases.
4) There is no difference between each single fuel cell, and multiple single fuel cells are connected in series to form a stack.
5) The temperatures of fuel cell stack is constant.

![Figure 1. The fuel cell equivalent circuit.](image)
Due to the existence of irreversible loss in fuel cell (as shown in Figure 1), the actual cell electromotive force is smaller than the theoretical electromotive force. The irreversible loss of fuel cell is generally referred to as polarization overpotential or overvoltage. There are three main reasons for the generation of overvoltage: 1) activation overvoltage; 2) ohmic overvoltage; 3) concentration overvoltage[11].

According to the empirical formula of output characteristics of proton exchange membrane fuel cell (PEMFC) established by J. C. Amphlett [9], the output voltage of PEMFC single cell is below:

$$V_{cell} = E_{Nernst} - V_{act} - V_{ohm} - V_{con}$$

(1)

where $E_{Nernst}$ is thermodynamic potential, $V$; $V_{act}$ is activation overvoltage, $V$; $V_{ohm}$ is ohmic overvoltage, $V$; $V_{con}$ is concentration overvoltage, $V$.

Proton exchange membrane fuel cells are all used in the form of a stack. For a stack of cells connected in series, the voltage is:

$$V_{stack} = NV_{cell}$$

(2)

where N is the number of PEMFC single cell.

The thermodynamic electromotive force ($E_{Nernst}$) of a fuel cell refers to the open circuit voltage when the fuel cell is operated under no load conditions. In the model, it can be derived from the Nernst equation[12]:

$$E_{Nernst} = \frac{\Delta G}{2F} + \frac{\Delta S}{2F}(T - T_{ref}) + RT\left[\ln(P_{H2}) + \frac{1}{2}\ln(P_{O2})\right]$$

(3)

where $\Delta G$ is Gibbs free energy J/mol; $F$ is the faraday constant, C/mol; $\Delta S$ is the entropy change, J/mol; $P_{H2}$ is partial pressure of hydrogen at the anode, atm; $P_{O2}$ is partial pressure of oxygen at the cathode, atm; $T$ is working temperature, K; $T_{ref}$ is reference temperature, K; $R$ is the ideal gas constant, J/mol·K. The thermodynamics data are shown in table 2.

### Table 2. The thermodynamics data[12].

| Parameter | $\Delta H$/kJ·mol$^{-1}$ | $\Delta G$/kJ·mol$^{-1}$ | $\Delta S$/J·mol$^{-1}$ |
|-----------|--------------------------|--------------------------|--------------------------|
| H$_2$(g)  | 0                        | 0                        | 130.59                   |
| O$_2$(g)  | 0                        | 0                        | 205.03                   |
| H$_2$O(l) | -285.84                  | -237.19                  | 69.94                    |

Bring the parameters in the table into the equation to get the empirical equation of thermodynamic electromotive force:

$$E_{Nernst} = 1.229 - 8.5\times10^{-4}(T - 298.15) + 4.308\times10^{-5}T\left[\ln(P_{H2}) + 1/2\ln(P_{O2})\right]$$

(4)

The activation overvoltage ($V_{act}$) of the fuel cell is caused by the activation polarization of the fuel cell, which is used to activate the electrochemical reaction. The voltage drop at this stage is mainly affected by the adsorption and desorption dynamics of the catalyst. The activation overvoltage can be expressed as follows[5]:

$$V_{act} = \varepsilon_1 + \varepsilon_2 T + \varepsilon_3 T \ln\left(C_{H2}\right) + \varepsilon_4 T \ln I$$

(5)

Where: $I$ is the load current of the fuel cell (A); $\varepsilon_1$, $\varepsilon_2$, $\varepsilon_3$, $\varepsilon_4$ is the empirical parameter, the data in the universally applicable steady-state electrochemical model adopted in this paper are below:

$$\varepsilon_1 = -0.9514$$

$$\varepsilon_2 = 0.00286 + 0.0002ln(A) + 4.3\times10^{-5}ln\left(C_{H2}\right)$$

$$\varepsilon_3 = 7.4\times10^{-5}$$

$$\varepsilon_4 = -1.87\times10^{-4}$$
CO₂ is the oxygen concentration (mol/cm³) at the cathode gas-liquid interface, and C₇H₆ is the hydrogen concentration (mol/cm³) at the anode gas-liquid interface. It can be expressed by Henry's law as:

\[
C_{O_2} = \frac{P_{O_2}}{5.08 \times 10^6 \exp(-498/T)}
\]

\[
C_{H_2} = \frac{P_{H_2}}{9.174 \times 10^6 \exp(-77/T)}
\]

Ohmic overvoltage of fuel cells refers to the voltage drop caused by ohmic impedance when ions migrate in electrolytes and electrons move in electrodes. In fuel cell, the impedance of electrolyte and electrode obeys Ohm's law in general, so ohmic overvoltage can be expressed as:

\[
V_{ohm} = IR_{ohm} = I(R_m + R_c)
\]

Where \( R_{ohm} \) is equivalent ohmic resistance, \( \Omega \); \( R_m \) is resistance to proton transfer through the membrane, \( \Omega \); \( R_c \) is contact resistance to electron flow, \( \Omega \).

Because ion charge transfer is more difficult than electron charge transfer, which plays a major role in ohmic resistance, the impedance effect of electrons passing through the membrane can be neglected.

\[
R_w = \frac{r_m L}{A}
\]

where \( L \) is membrane thickness, cm; \( A \) is membrane active area, cm²; \( r_m \) is the membrane specific resistivity, \( \Omega \cdot \) cm, and \( r_m \) can be expressed as[12] :

\[
r_m = 181.6 \times \left[ 1 + 0.03 \left( \frac{I}{A} \right) + 0.062 \left( \frac{T}{303} \right)^2 \left( \frac{I}{A} \right)^{2.5} \right]
\]

\[
\lambda - 0.634 - 3 \left( \frac{I}{A} \right) \exp \left( 4.18 \left( \frac{T-303}{T} \right) \right)
\]

where \( \lambda \) is a specific coefficient for every type of membrane:

\[
\lambda = \begin{cases} 
0.043 + 1.781a - 3.985a^2 + 3.6a^3, & a < 1 \\
1 + 1.4(a - 1), & 1 \leq a \leq 3 \\
1.68, & a > 3 
\end{cases}
\]

Fuel cell concentration overvoltage(\( V_{con} \)) is a voltage drop caused by the inadequate supply of hydrogen and oxygen, which prevents the reactant from maintaining an appropriate concentration on the surface of the electrode. Concentration overvoltage mainly occurs at the condition of high current density. At this time, the reason why concentration overvoltage occurs is that fuel gas and oxidant not supplying the required gas concentration on the electrode surface in time. Concentration overvoltage of fuel cells can be expressed as:

\[
V_{con} = w \exp(ni)
\]

where \( i \) is current density, A/cm²; \( n \) is product growth rate of electrochemical reaction in catalytic layer; \( w \) is coefficient of mass transfer.

\[
w = \begin{cases} 
1.1 \times 10^{-1} - 1.2 \times 10^{-6}(T - 273.15), & T \geq 312.15K \\
3.3 \times 10^{-1} - 8.2 \times 10^{-5}(T - 273.15), & T < 312.15K 
\end{cases}
\]

The efficiency of the stack is:

\[
\eta = u_f \frac{V_{cell}}{E_{Nernst}}
\]

Where \( u_f \) is fuel availability, evaluated as 0.95.
3. Experiment
In order to verify the accuracy of the mathematical model, the relevant verification experiment was conducted. The experimental equipment is shown in figure 2.

![Figure 2. The layout of experimental equipment.](image)

3.1. Experimental steps
(1) Clean the circuit at least twice with deionized water so that the conductivity of cooling water in the pipeline can be reduced to less than 10μs/cm.
(2) Open the valve of hydrogen cylinder and oxygen cylinder, check the pressure of the pressure relief valve at the outlet of the cylinder, and ensure that the outlet pressure is normal.
(3) Check the position of single voltage interface carefully and open the patrol instrument after checking it correctly.
(4) Start the PLC, open the STEP7 and WINCC interface, and check the pressure sensor and temperature sensor to ensure that the sensor is normal. Then start the load box.
(5) Click on the boot button on the WINCC interface. After opening the throttle valves of the hydrogen side and the oxygen side exhaust air conditioning for 20 seconds, the system will be closed completely and the system will enter the closed cycle state.
(6) Check whether the single voltage values are within the normal range in the single voltage inspection interface to ensure that no single fuel cell voltage is too low.
(7) When the temperature of the stack reaches 353K, the load current is adjusted to 20A, and the load current is adjusted every 3-5 minutes, the adjustment range is 20A. Record relevant data which are shown in table 3.

3.2. Experimental results

| current/A | 0  | 20 | 40 | 60 | 80 | 100 | 120 | 140 | 160 | 180 | 200 | 220 | 240 |
|-----------|----|----|----|----|----|-----|-----|-----|-----|-----|-----|-----|-----|
| voltage/V | 102.9 | 90.6 | 88.3 | 86.7 | 84.5 | 83.1 | 80.6 | 78.8 | 76.6 | 74.3 | 72.1 | 69.3 | 66.6 |

4. Analysis of steady-state model
Based on the MATLAB/Simulink software and the above empirical formula, the steady state model of the stack is established. The input of the model includes the working temperature of the fuel cell, the operating pressure of hydrogen and oxygen, the load current of the stack, the output of the model...
includes the voltage of the stack, the power of the stack and the efficiency of the fuel cell. The specific simulation diagram is shown in Figure 3.

Figure 3. The steady-state characteristic simulation diagram.

Figure 4 shows a comparison between the simulation and experimental values of the steady-state model of the stack. In order to eliminate the influence of the size of the fuel cell membrane area on the experimental results, the current value is converted to the current value of the unit area for comparison. After the operation of the fuel cell system, the simulation value is in good agreement with the experimental value, and the maximum error is not more than 7% and the experimental value is higher than the simulation value. There are two main reasons for this phenomenon: (1) When the stack is in normal operation, the ohmic overvoltage plays a major role, so the output voltage is close to a linear relationship with the current. From equations (8)-(11), it can be seen that the magnitude of ohmic overvoltage is closely related to the humidity of hydrogen and oxygen. In this experiment, a humidifier is used to humidify the gas. The mass flow of hydrogen and oxygen goes up with the increase of current density. Therefore, in the actual experiment, hydrogen and oxygen are under
The humidified state, so the ohmic overvoltage in the actual experiment is less than the simulation value. (2) The internal electrochemical reaction of fuel cell is exothermic reaction. The stack temperature measured in the experiment and the working temperature set in the simulation model is the external temperature of the stack. Because of the influence of thermal resistance, convective heat transfer and heat dissipation, the external temperature of the stack is lower than that of the single cell. The catalyst activity rises with increasing temperature, so the simulation value is smaller.

Figure 5. The performance curve under different temperature conditions.

Figure 6. The performance curve under different pressure conditions.

Figure 5 shows the simulation curve of the fuel cell performance of the stack working at different temperatures. With the temperature rising from 313K to 353K, the output performance of the fuel cell is obviously improved. The reason is that the catalytic layer of fuel cell materials contains catalysts, and the activity of catalysts goes up with the increase of temperature. At the same time, the increase of temperature also helps the water diffusion coefficient and gas diffusion coefficient in the membrane to rise, which increases the mass transfer in the membrane and decreases the resistance of the membrane, so the output performance of the stack is improved.

Figure 6 shows the fuel cell performance curve of the stack under different pressure conditions. As we can see from the figure, the output performance of the stack is also improving as the operating pressure of the stack gas rises from 1 bar to 3 bar. Because the thermodynamic electromotive force of the stack goes up with the increase of operating pressure, the output performance of the stack is improved when the overvoltage is constant.
Figure 7. The performance curve under different membrane thickness conditions.

Figure 7 shows the simulation curve of the fuel cell performance of the stack working at different membrane thickness. The simulation parameters are setting as constant values, and the stack temperature, operating pressure, current density respectively sets as 353K, 1.5atm, and 0.4A/cm². The simulation curve shows that, with the membrane thickness rising from 0.005 to 0.015cm, the output voltage decreases continuously. The phenomenon is caused by an increase in ohmic overvoltage. There are two main reasons cause the ohmic overvoltage, the one is the electrical resistance, and the other is the resistance to the flow of ions in the membrane. The flowing resistance of ions goes up with the membrane thickness, so the ohmic overvoltage goes up with the increase of membrane thickness. Therefore, the membrane thickness should be as thin as possible in the practical application.

5. PEMFC dynamic model and simulation

In fuel cells, electrons and hydrogen ions are concentrated on the surface of electrodes and electrolytes due to the action of electrostatic field. A voltage will be generated between them. Charge and energy will be stored on or near the surface of electrodes/electrolytes, which is similar to an equivalent capacitance. Therefore, when the load current suddenly changes, the activation overvoltage and concentration overvoltage need a certain transition time instead of changing as immediately as ohmic overvoltage.

As shown in Figure 8, the effect of the double charge layer can be represented by adding an equivalent capacitance to the circuit. R_{ohm} represents ohmic overvoltage and R_{a} represents equivalent resistance. The dynamic characteristics of single cell are mainly reflected in the dynamic voltage changes on capacitor C and its parallel equivalent polarization resistance. If the total polarization overvoltage is equal, the dynamic characteristics of single cell can be described by differential equation as follows:

$$\frac{d\nu}{dt} = \frac{I}{C} - \frac{\nu}{R_{a} C}$$

(15)

Where C is the charge capacitance of double electrode layer, evaluated as 0.016F/cm².

Figure 8. The equivalent circuit diagram.
6. Analysis of dynamic model

Based on the above steady-state model, a dynamic model is established. The specific simulation diagram is shown in Figure 9.

Figure 10 shows the curve of current density with time. In the simulation, the loading of load current completely imitates the loading mode of load current during the operation of the experiment. The load is adjusted every 5-10 minutes in the experiment. In order to shorten the simulation time, the load adjustment time is set to 10s in the model. Between 0-130s, the magnitude of each 10s adjustment is +20A. Between 130-250s, the adjustment range is -20A every 10 seconds. From the simulation curve, it can be seen that when the load current changes step by step, the output voltage is gently transited to a certain value due to the role of the charge layer capacitance, and then stabilizes at that value. By comparing the simulation curve with the experimental data curve, it can be found that the coincidence between the experimental data and the simulation data goes up with the increase of current density (as shown in Figure 11). Therefore, the simulation process of the dynamic model is close to the actual working process of the stack, which has a certain guiding significance for predicting the output performance of the stack.

![Figure 9. The dynamic characteristic simulation diagram.](image)

![Figure 10. The curve of current density with time.](image)
Figure 11. The comparison between the simulation and experimental values.

Figure 12. The curve of power with time.

Figure 12 shows the power curve of the stack with time. It can be seen from the diagram that the output power of the stack grows with the increase of the load current. In the partial amplification diagram, when the load current suddenly changes, the output power will overshoot. It is because when the load current suddenly changes, the output voltage does not change immediately. Instead, there is a transition time, which can lead to overshoots.

Figure 13. The curve of efficiency with time.

Figure 13 shows the curve of fuel cell efficiency with time, which is very similar to the output voltage curve. Formula (2-14) shows that the fuel cell efficiency is proportional to the output voltage. The efficiency decreases with the increase of load current. When the load current is 100 mA/cm², the efficiency can reach 65%, and when the load current is 1300 mA/cm², the efficiency can be reduced to
48%. It also draws the same conclusion that the output power and efficiency cannot be obtained at the same time when the stack is running as the steady-state model, and the relationship between the output power and efficiency of the fuel cell should be considered comprehensively.

7. Conclusions
Based on the MATLAB/Simulink software, the steady-state model and dynamic model of proton exchange membrane fuel cell are established respectively. The experiment value is basically consistent with the simulation value, and the maximum error is less than 7%. The simulation model can be pretty realistic and objective stack operation. On the basis of steady state model and dynamic model, the influence of operation parameters such as stack temperature and operating pressure on the output performance of fuel cell is analyzed, which provides a practical simulation platform for the study of fuel cell performance and has a certain guiding significance for predicting the output performance of fuel cell under different operating conditions.

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