The influence of operating parameters on the performance of PEMWE electrolytic cell

Dugang Kang [1, 2, *], Lin Ma [1, 2, a], Yanyun Huang [1, 2, b], Yongjun Qiu[1, 2, c], Ligui Kang [1, 2, d], Song Huang [1, 2, e]

[1] Chongqing Special Equipment Inspection and Research Institute, Chongqing 401121, China

[2] Key Laboratory of Electromechanical Equipment Security in Western Complex Environment for State Market Regulation, Chongqing 401121, China

* Corresponding Author Email: kangdugang@cqtj.org, [a]malin@cqtj.org, [b]huangyanyun@cqtj.org, [c]qiuyongjun@cqtj.org, [d]kangligui@cqtj.org, [e]huangsong@cqtj.org

Abstract. Proton exchange membrane (PEM) is considered the most promising green hydrogen production technology in the future. The proton exchange membrane electrolysis cell (PEMEC) involves a complex process of multiple physical fields, including charge transfer, gas transfer, and heat transfer, during operation. Increasing the inlet water flow rate within a certain range is beneficial for increasing the output performance of the electrolysis cell and can also reduce the average temperature of the proton exchange membrane. But when the inlet flow rate increases to a certain amount, it has no effect. As the electrolysis voltage increases, the electrochemical performance of the electrolysis cell also increases, and the temperature of the proton exchange membrane and the current density of the catalytic layer also increase with the increase of voltage.

Keywords: PEMWE, Electrolytic cell performance, Voltage step, Water flow rate, Electrolytic voltage.

1. Introduction

Hydrogen fuel can burn under different conditions, providing a large amount of thermal energy, thereby reducing the total emissions of greenhouse gases and air pollutants. At present, three types of electrolysis cells using different types of electrolytes have been developed [1]. The water electrolysis hydrogen production process mainly includes alkaline electrolysis water hydrogen production process (AEC) and proton exchange membrane electrolysis water hydrogen production process (PEMWE) and high solid oxide electrolyte hydrogen production process (SOEC). Compared with existing AEC technologies, PEMWE hydrogen production has a higher current density (>1 A/cm2), overall efficiency (70%~90%), and produces a higher volume fraction of hydrogen (>99.99%), which can be directly used in hydrogen fuel cells [2].

PEM electrolysis cell is an electrochemical energy converter that uses electro oxidation of water to form oxygen and protons on the anode side (as shown in Figure 1). After oxygen is formed, it detaches from the device, and protons pass through proton exchange membranes, while electrons circulate through external circuits. On the cathode side, electrons reduce protons to produce hydrogen gas [3].

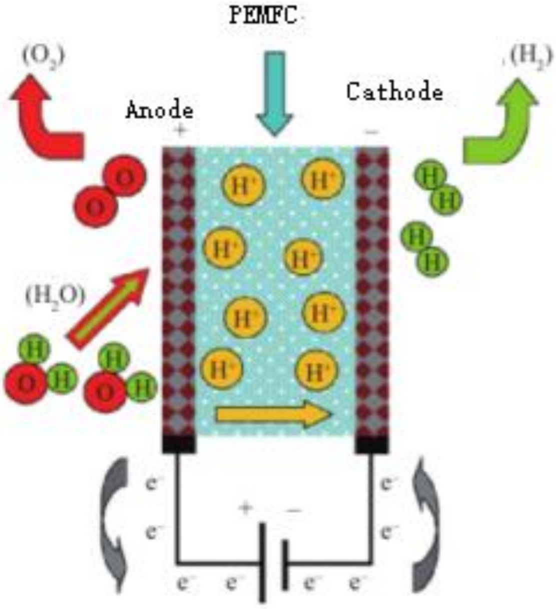


Figure 1. Working principle of proton exchange membrane electrolysis cell

Nie et al. modeled a gas-liquid two-phase flow field plate confined to the anode side of PEMWE [4]. They used numerical three-dimensional dynamic simulation to examine the different components of PEMWE, and paid more attention to the flow patterns inside the electrolytic cell. They used FLUENT to simulate the generation rate and distribution of hydrogen/oxygen in the flow field and found the pressure and velocity distribution [5].

In order to conduct in-depth research on the influence of various parameters on multiphase flow transport, it is necessary to conduct parameter visualization research at the microscopic scale. Due to the opaque nature of electrolytic cells, there have been limitations in the visualization research of neutron radiography and synchronous radiography operations so far. Establishing mathematical models for porous diffusion layers and conducting numerical simulations has become an effective way to reveal the coupling mechanism of flow transfer and energy mass conversion within the diffusion layer [6]. The internal material transfer of proton exchange membrane electrolysis cell mainly includes the transfer of water inside the electrolysis cell, as well as the cross transfer of various internal gases. From this, single-phase models and gas-liquid two-phase models can be established, but there is relatively little research in this area [7].

2. Model description

This article is based on COMSOL software to establish three-dimensional, single-phase, non-isothermal, steady-state/transient models. By changing the operating parameters (inlet flow rate, voltage), the polarization curve, hydrogen mass fraction distribution, PEM temperature distribution, and catalytic layer current density distribution were studied to explore their impact on the performance of the electrolytic cell.

2.1. Grid partitioning

The grid division of the proton exchange membrane single channel electrolysis cell model is shown in Figure 2. The grid type is a regular hexahedron grid, which is used for model calculation. Compared with other forms of grids, it has advantages such as faster calculation speed, easier convergence, and more convenient calculation of the number of grid nodes. Due to the fact that the catalytic layer is the main site of chemical reactions, with significant physical and chemical changes, it is necessary to mesh the membrane electrode area to determine the high convergence of simulation calculations and more accurately describe the transfer phenomenon inside the electrolytic cell.

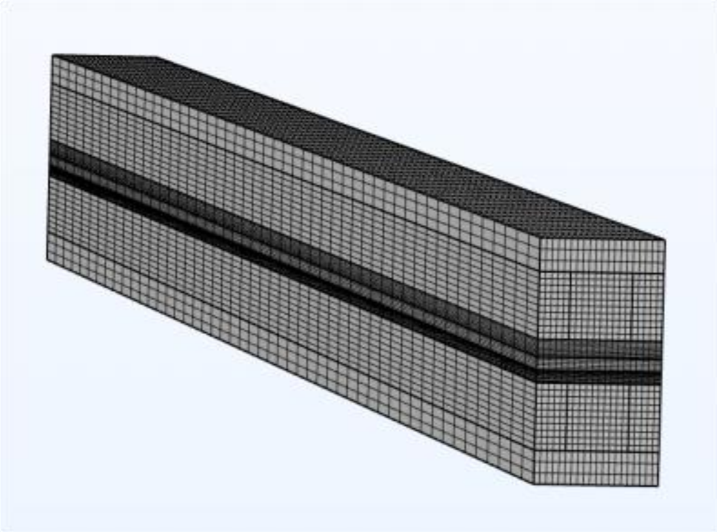


Figure 2. Grid division of single channel electrolytic cell

2.2. Model validation

When using COMSOL simulation, the size of the grid division will to some extent affect the accuracy of the final simulation results. If the number of grids is too small, it can also cause significant deviation in the simulation results; A large number of grids will increase the computational workload of the simulation, and sometimes it can also cause calculation errors or non-convergence of results. Therefore, choosing an appropriate number of grids can not only improve the accuracy of simulation calculations but also reduce the computational workload.

As shown in Figure 3, the model selected a total of six sets of unit numbers, including 15000, 23000, 34000, 39600, 52000, and 65000. From the figure, it can be seen that when the number of grids is less than 34000, the number of grids increases and the current density rapidly decreases, indicating a strong correlation between the two. However, when the number of grids increases by a certain amount, such as when the number of grids in this model increases to 65000, there is not much change in the result of further increasing the number of grids. On the contrary, it will also increase the computational cost of simulation. Therefore, selecting 65000 grids is the most appropriate choice for the model in this article.

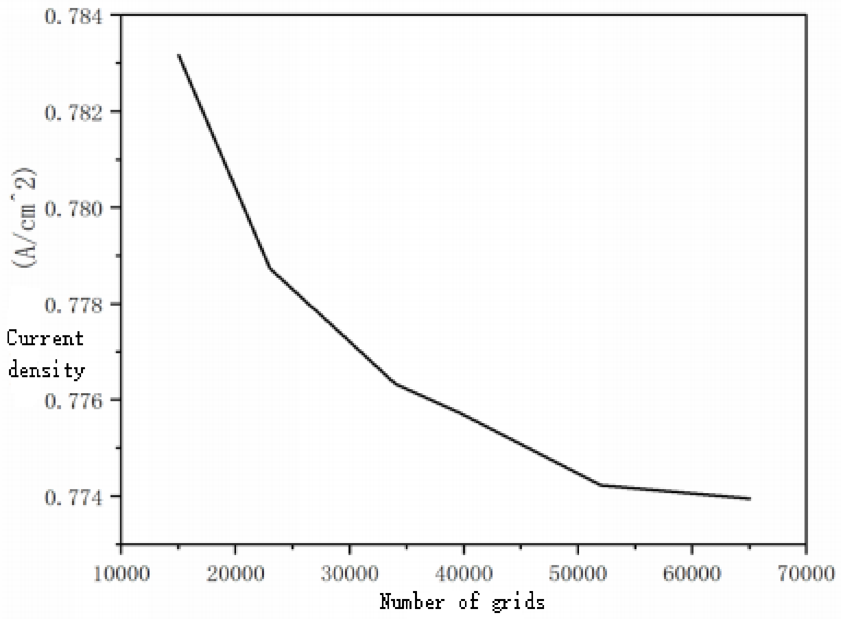


Figure 3. Grid independence verification

3. The effect of inlet flow rate on the output performance of PEMWE

Water plays an important role in the electrolytic cell, as both a reactant participating in chemical reactions and a substance exchanging heat with the cell, while also carrying the generated gas away from the cell. Therefore, this section will study and analyze the impact of water inlet flow rate on the performance of the electrolytic cell.

3.1. Electrolytic cell output performance

Based on the inlet flow rate of 0.5m/s (flow rate of 3ml/min), the polarization curves of the electrolytic cell under different inlet flow rates are shown in Figure 4. It can be seen that the output performance at an inlet flow rate of 1.25m/s is much higher than that at an inlet flow rate of 0.125m/s. This is because the increase in inlet flow rate can accelerate the removal of gas in the channel, indirectly strengthening the gas discharge from the diffusion layer and catalytic layer. The polarization curve at an inlet flow rate of 1.25m/s is basically consistent with that at an inlet flow rate of 0.5m/s, and the temperature distribution of the proton exchange membrane between the two is also similar. It can be seen that the polarization curve of the proton exchange membrane electrolysis cell and the PEM temperature distribution map can mutually confirm and jointly characterize the output performance of the proton exchange membrane electrolysis cell.

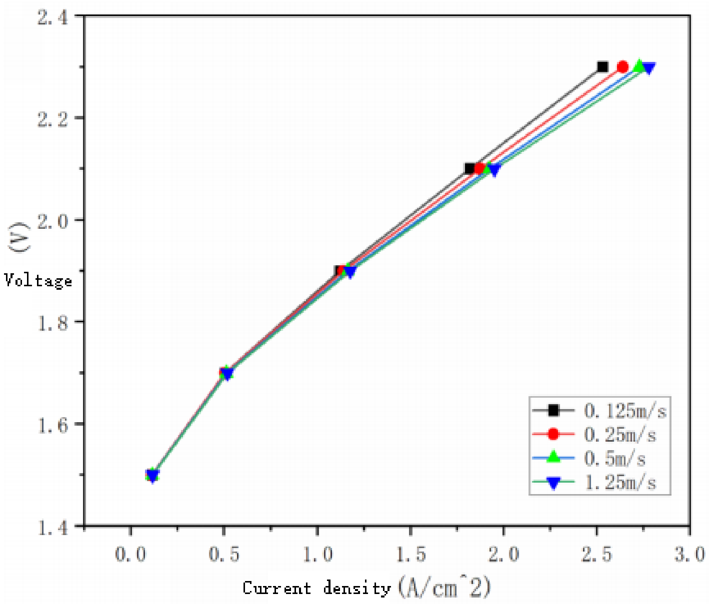


Figure 4. Polarity curves under different inlet flow velocities

3.2. Membrane temperature distribution

According to the Arrhenius equation, the higher the temperature, the faster the chemical reaction rate. Therefore, the working temperature of the electrolytic cell has a significant impact on its performance. Within the specified working temperature range, higher temperature electrolytic cells have better characteristics. However, if the specified working temperature range is too high, it may cause the evaporation rate of water during the reaction with the membrane electrode to be too fast, resulting in "membrane drying" phenomenon, leading to an increase in internal resistance and a decrease in output characteristics of the PEM electrolytic cell. So, the temperature distribution of PEM can indirectly reflect the quality of its output characteristics. Figure 5 shows the temperature distribution of proton exchange membranes under different inlet flow rates. It can be seen that as the inlet flow rate increases, the temperature of the proton exchange membrane also decreases. As shown by the polarization curve in Figure 15, as the flow rate increases, the output performance of the electrolytic cell improves and the heat generated is relatively more. However, an increase in flow rate also enhances the heat dissipation of the electrolytic cell. So, under the dual effect of both, the temperature of the proton exchange membrane decreases with the increase of flow rate.

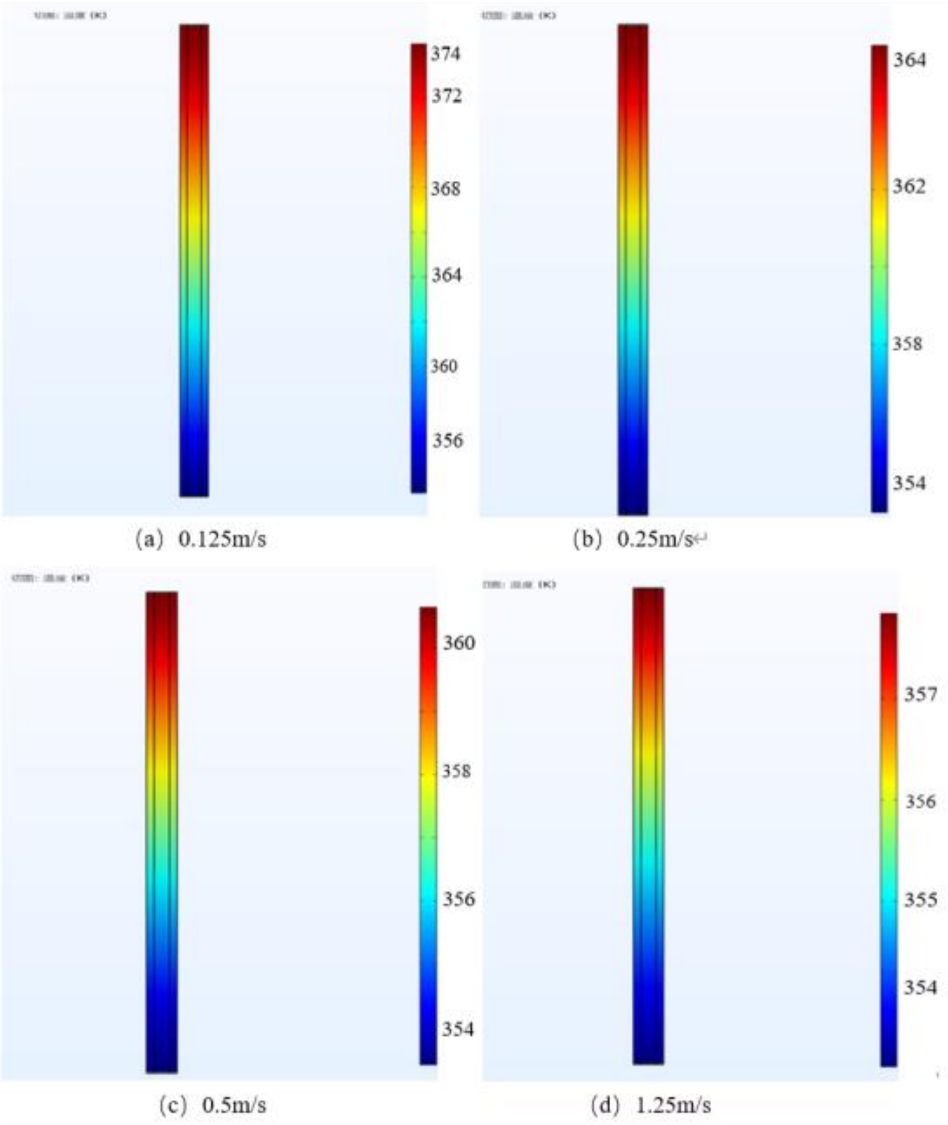


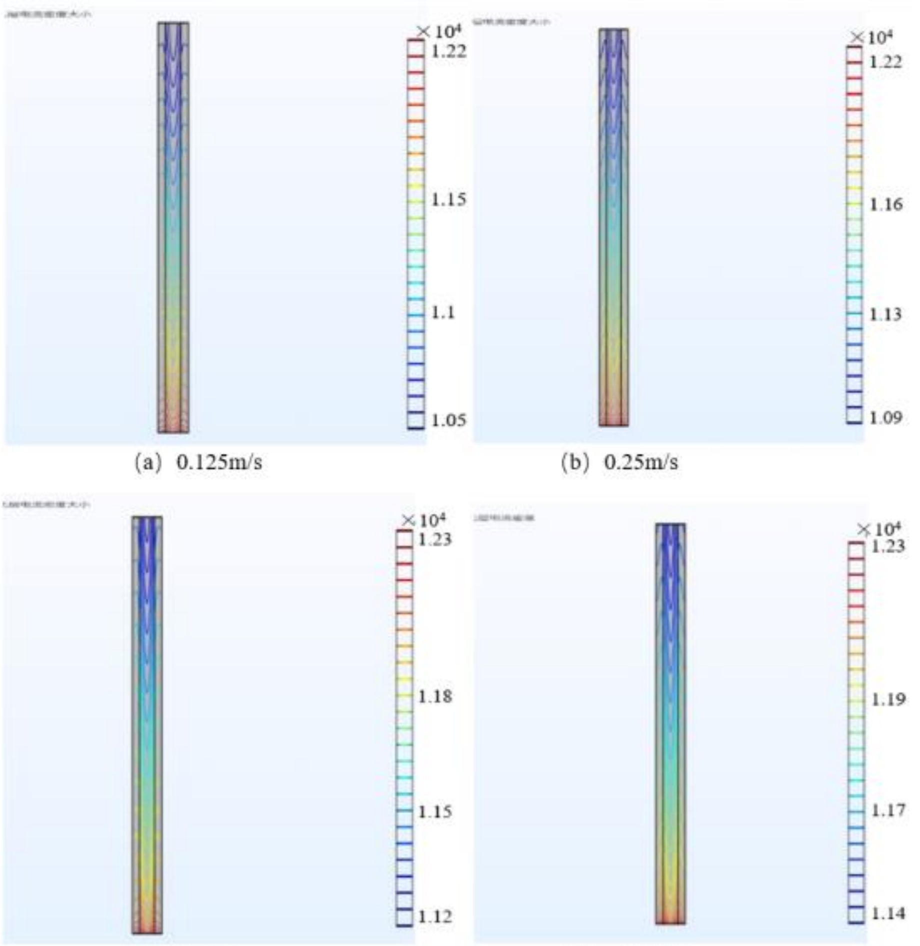
Figure 5. Temperature distribution of proton exchange membrane under different inlet flow rates

Table 1. Proton exchange membrane temperature under different inlet flow rates

current velocity (m/s)	0.125	0.25	0.5	1.25
Maximum (K)	374	364	360	357
Average (K)	365.5	360.2	357.32	355.84
Minimum (K)	356	354	354	354

3.3. Distribution of current density in catalytic layer

As the import flow rate continues to increase, the average current density of the catalytic layer also increases. When the inlet flow rate increases to a certain amount, the current density basically does not increase with the increase of water supply flow rate. Figure 6 shows the current density distribution of the catalytic layer under different inlet flow rates. The current density distribution with an inlet flow rate of 1.25m/s is basically consistent with the inlet flow rate of 0.5m/s, which precisely illustrates this point. It can also be inferred from Figure 4 that the polarization curves of the two have a high degree of overlap, which can be confirmed.



(a) 0.125m/s (b) 0.25m/s

(c) 0.5m/s (d) 1.25m/s

Figure 6. Distribution of catalytic layer current density under different inlet flow rates

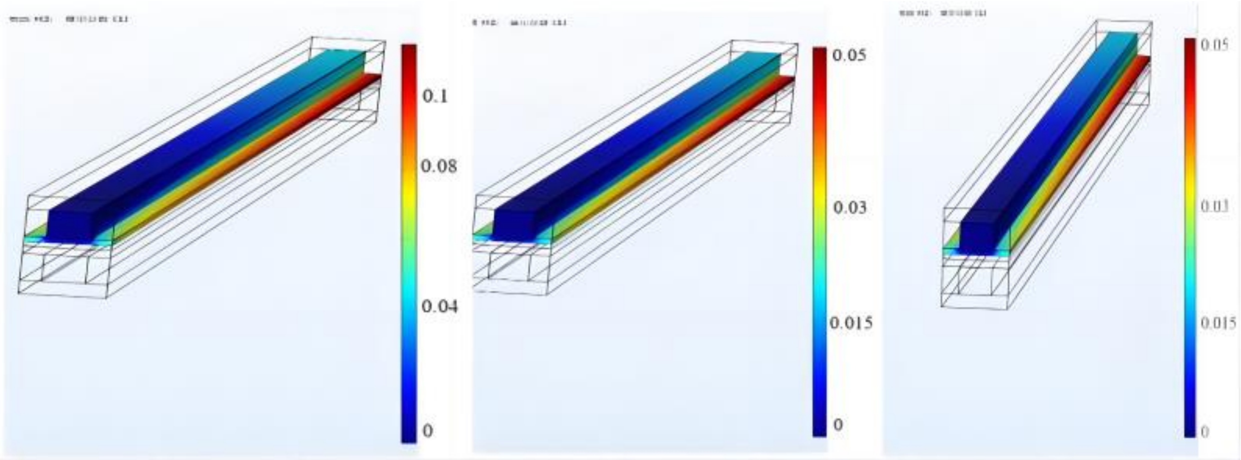
4. The influence of electrolytic cell voltage on the output performance of PEMWE

For a given electrolysis cell, according to Ohm's law, the current increases with the increase of voltage, and the reaction rate also increases accordingly. Therefore, the voltage of the electrolysis cell plays a crucial role in the output performance of the proton exchange membrane electrolysis cell. The national standard stipulates that the boundary voltage of the electrolytic cell is 1.9V, which is the rated voltage. Therefore, in this section, a model with a porosity of 0.8 for the anode and cathode diffusion layer and an inlet flow rate of 0.5m/s was established with a low load of 1.4V and an overload of 2.3V. The hydrogen mass fraction distribution, PEM membrane temperature distribution, and catalytic layer current density of the electrolytic cell were analyzed under different operating conditions, in order to better understand the impact of electrolytic cell voltage on the output performance of PEMEC.

4.1. Distribution of hydrogen mass fraction

As shown in Figure 7, as the voltage of the electrolytic cell increases, the reaction efficiency increases, so the generated hydrogen and oxygen also increase continuously with the voltage of the electrolytic cell. It can be seen from the cloud map that when overloaded, the mass distribution of hydrogen gas at the cathode diffusion layer and cathode flow channel is much larger than when overloaded. On the contrary, compared to the rated voltage, the hydrogen mass fraction at low load is not much lower, which is consistent with the results reflected in the polarization curve. At 1.4V to

1.9V, there is not much difference in current density, but there is a significant change in current density between 1.9V and 2.4V.

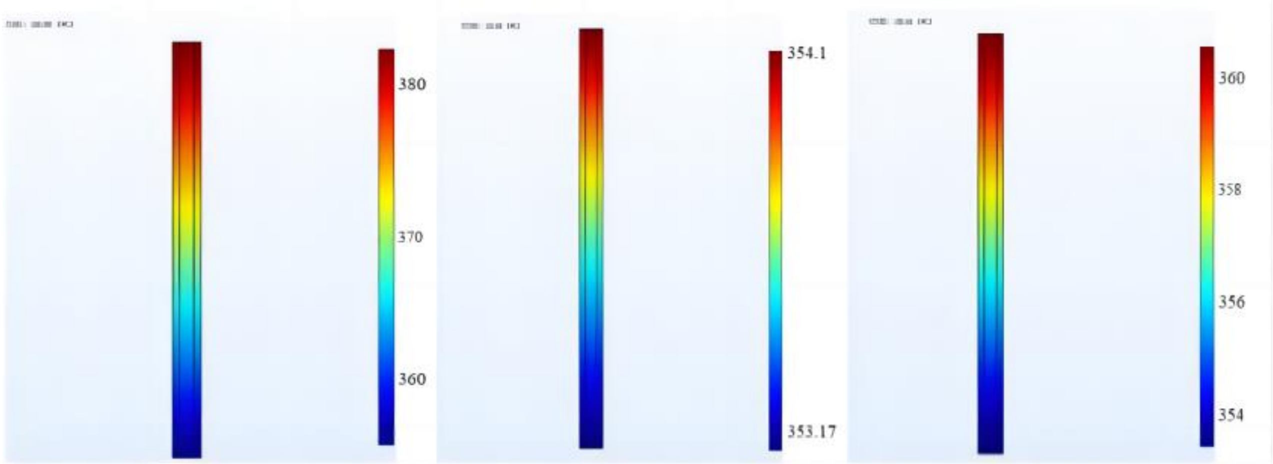


(a) 1.4V (low load) (b) 1.9V (rated) (c) 2.3V (overload)

Figure 7. Distribution of hydrogen mass fraction under different operating conditions

4.2. Membrane temperature distribution

The two most important parts that affect the temperature of the electrolytic cell are the proton exchange membrane and the catalytic layer. The proton exchange membrane serves as the channel for proton transport, while the catalytic layer is the main site for chemical reactions. Next, the temperature distribution of the proton exchange membrane under different voltage conditions will be analyzed. Figure 8 shows the temperature distribution of the proton exchange membrane at an inlet temperature of 80℃, while Table 7 shows its maximum, average, and minimum values. From the graph, it can be seen that the temperature of the proton exchange membrane remains almost unchanged when the voltage is between 1.4V and 1.9V. Subsequently, as the voltage increased from 1.9V to 2.3V, the temperature of the proton exchange membrane increased exponentially. For a given electrolysis cell, according to Ohm's law, the current increases with the increase of voltage, resulting in more Ohmic heat, especially for the proton exchange membrane with the highest Ohmic impedance. The heat is sequentially transferred to the anode catalytic layer, diffusion layer, anode bipolar plate, and water in the anode flow channel. Due to the continuous flow of water into and out of the electrolytic cell, which carries away heat, the temperature of the liquid in the flow channel is the lowest.



(a) 1.4V (low load) (b) 1.9V (rated) (c) 2.3V (overload)

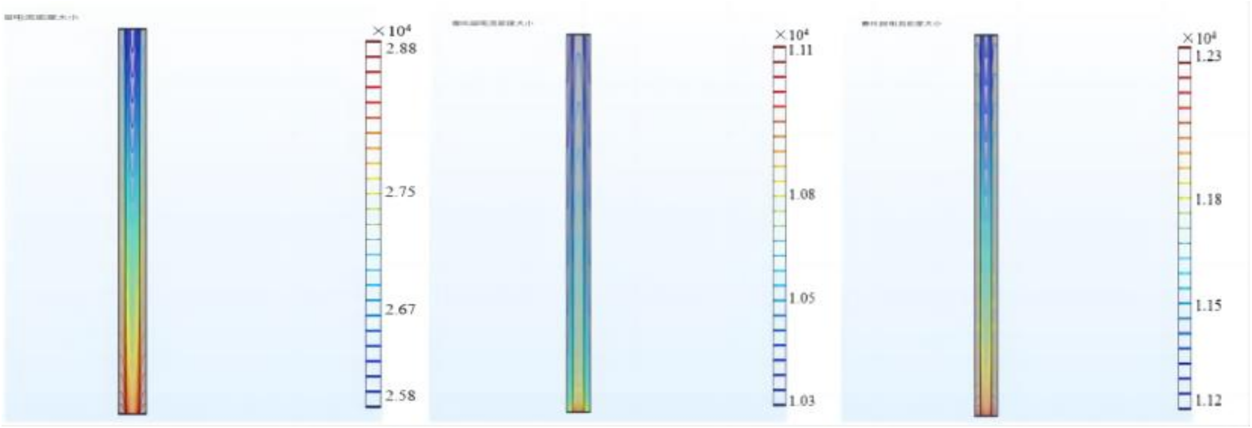
Figure 8. Temperature distribution of PEM under different working conditions

Table 2. Values of proton exchange membrane temperature under different voltages

Voltage (V)	1.4	1.6	1.9	2.3
Maximum (K)	354	361	360	380
Average (K)	353.73	354.59	357.28	369.33
Minimum (K)	353	353	354	360

4.3. Distribution of current density in catalytic layer

The current density of the catalytic layer is closely related to its temperature. Generally speaking, the higher the temperature, the higher the density of the catalytic layer. Figure 9 shows that the average current density of the catalytic layer increases with the increase of voltage. When the voltage is between 1.4V and 1.9V, there is almost no significant change in the current density of the catalytic layer. Subsequently, as the voltage increased from 1.9V to 2.3V, the current density of the catalytic layer increased exponentially. It can be seen that this trend of change is basically consistent with the temperature change trend of the proton exchange membrane in Figure 8.



1.4V (low load) (b) 1.9V (rated) (c) 2.3V (overload)

Figure 9. Current density distribution of catalytic layer under different operating conditions

5. Conclusion

Increasing the inlet water flow rate can promote the discharge of gas from the flow channel, indirectly strengthening the gas discharge from the diffusion layer and catalytic layer, which is conducive to increasing the output performance of the electrolytic cell. At the same time, increasing the flow rate is conducive to carrying heat out of the electrolytic cell, and the average temperature of the proton exchange membrane also decreases. However, when the inlet flow rate increases to a certain amount, increasing the flow rate again has little effect on the output performance of the electrolytic cell.

As the electrolysis voltage increases, the electrochemical performance of the electrolysis cell also increases, and the temperature of the proton exchange membrane and the current density of the catalytic layer also increase with the increase of voltage. When the voltage is between 1.4V and 1.9V, the temperature of the proton exchange membrane and the current density of the catalytic layer remain almost unchanged. Subsequently, as the voltage increased from 1.9V to 2.3V, the temperature of the proton exchange membrane and the current density of the catalytic layer increased exponentially.

Acknowledgments

This work was financially supported the Special Project for Performance Incentive and Guidance of Research Institutions in Chongqing (No. CSTC2022JXJL70006) and the scientific research planning project of Chongqing Municipal administration for Market supervision Bureau (No.: CQSJKJ2020014).

References

[1] Kang Z, Mo J, Yang G, Li Y, Talley DA, Retterer ST, et al. thin film surface modifications of thin/tunable liquid/gas diffusion layers for high-efficiency proton exchange membrane electrolyzer cells. Applied Energy. 2017, 206: 983 - 90.

[2] Kang Z, Mo J, Yang G, Retterer ST, Cullen DA, Toops TJ, et al. Investigation of thin/well tunable liquid/gas diffusion layers exhibiting superior multifunctional performance in low temperature electrolytic water splitting. Energy & Environmental ence. 2016, 10: 166 - 75.

[3] Maier M, Dodwell J, Ziesche R, Tan C, Heenan T, Majasan J, et al. Mass transport in polymer electrolyte membrane water electrolyser liquid-gas diffusion layers: a combined neutron imaging and X-ray computed tomography study. Journal of Power Sources. 2020, 455: 227968.

[4] Zinser A, Papakonstantinou G, Sundmacher K. Analysis of mass transport processes in the anodic porous transport layer in PEM water electrolysers. International Journal of Hydrogen Energy. 2019, 44: 28077 - 87.

[5] Haverkort J W. A theoretical analysis of the optimal electrode thickness and porosity. Electrochemical Acta. 2019, 295: 846 - 60.

[6] Zhang Z Q, Xing X H, Simulation and experiment of heat and mass transfer in a proton exchange membrane electrolysis cell. International Journal of Hydrogen Energy. 2020, 45: 20184 - 20193.

[7] Jude O, Majasan, Jason I.S, et al. Two-phase flow behaviour and performance of polymer. electrolyte membrane electrolysers: Electrochemical and optical characterization. International Journal of Hydrogen Energy. 2018, 43: 15659 - 15672.