Research status of thermal management of hydrogen energy proton exchange membrane fuel cell

Jibao Liu\textsuperscript{1a}, Huanyong Cui\textsuperscript{1b}, Lei Gao\textsuperscript{2c}, Jiangtao Wang\textsuperscript{3d}, Meiyan Wang\textsuperscript{2e}, Fajia Li\textsuperscript{1f}

\textsuperscript{1}University of Jinan, Jinan 250022, China;
\textsuperscript{2}Shanghai REFIRE Technology Co., Ltd, Shanghai 200000, China;
\textsuperscript{3}Beijing jingtun Science & Technology Co., Ltd, Beijing 101300, China;
\textsuperscript{a}1934458740@qq.com, \textsuperscript{b}cuihuanyong@163.com, \textsuperscript{c}508712513@qq.com, \textsuperscript{d}3450946913@qq.com, \textsuperscript{e}2159017180@qq.com, \textsuperscript{f}me_lifj@ujn.edu.cn

Abstract—The working principle and advantages of proton exchange membrane fuel cell using renewable energy hydrogen as fuel are introduced, the importance of fuel cell thermal management is emphasized, and the performance influencing factors, heat source and design requirements of proton exchange membrane fuel cell are summarized. According to the current research status of fuel cell related thermal management, the methods of simulation analysis of fuel cell with the help of mathematical model are summarized, and the existing problems and solutions of fuel cell heat dissipation and cold start are summarized.

1. Introduction
Facing the worsening global environmental pollution and energy shortage, new energy and renewable resources have become the focus of the world. In the national strategy of "made in China 2025", China mentioned to vigorously promote the breakthrough development in key fields such as energy saving and new energy vehicles \cite{1}, because the fuel cell reaction process does not involve combustion, breaking the restriction of Carnot cycle, The ideal energy conversion efficiency is more than 80\%, and there is no noise and pollution. It is becoming an ideal way of energy utilization \cite{2}. Among them, proton exchange membrane fuel cell (PEMFC) has the advantages of low operating temperature, no pollution, high specific power and rapid start at room temperature. It has great market potential and broad application prospects in the fields of aerospace power system, motor vehicle power energy conversion, small and medium-sized power generation system and portable mobile power supply \cite{3-6}.

Proton exchange membrane fuel cell belongs to low temperature (60 °C ~ 80 °C) fuel cell. Reasonable temperature conditions during operation have a great impact on the performance of fuel cell. Therefore, it is very necessary to study the heat generation and transfer, temperature field distribution and cooling mode in the fuel cell, including how to discharge the heat generated in the cell to the outside, ensure the uniform temperature distribution in time and space, avoid the occurrence of hot spots, and realize effective heat management.

2. Importance of PEMFC thermal management
PEMFC cell is mainly composed of proton exchange membrane, cathode/anode catalytic layer, cathode/anode gas diffusion layer and cathode/anode collector plate. The flow field is compounded on
the collector plate, and cooling flow channel can also be added. The specific reaction process in the stack is shown in Figure 1 [7] below:

Hydrogen and oxygen are introduced into the anode and cathode respectively, and contact with the catalytic layer and proton exchange membrane through the gas diffusion layer. The following reactions occur under the action of the catalyst:

Anode: \( H_2 \rightarrow 2H^++2e^- \) \hspace{1cm} (1)

Cathode: \( 2H^++1/2O_2+2e^- \rightarrow H_2O \) \hspace{1cm} (2)

Total reaction: \( H_2+1/2O_2 \rightarrow H_2O+\text{thermal energy}+\text{electric energy} \) \hspace{1cm} (3)

Hydrogen protons and electrons generated by oxidation reaction of anode \( H_2 \) reach the cathode through proton exchange membrane and external circuit respectively, and water, thermal energy and electric energy are generated in this process [8-10]. Therefore, effective water heat management is very important to improve the performance of PEMFC.

![Fig. 1 Structure and working principle of PEMFC](image)

Fig. 1 Structure and working principle of PEMFC [7]

The importance of fuel cell thermal management comes from the evaluation of the performance of the fuel cell itself. The regulation and control of heat directly affects the temperature change of the fuel cell itself. To ensure the normal and efficient operation of the fuel cell, its temperature must be kept within the optimal operating temperature range. Therefore, effective and reliable thermal management directly affects the performance of the fuel cell, The importance of fuel cells is self-evident.

3. Factors affecting PEMFC performance

The performance of PEMFC depends on the influence of various factors on proton exchange membrane. Among the many factors, temperature has the most obvious impact on the performance of PEMFC. Proton exchange membrane has become the key to restrict its temperature characteristics. Temperature can cause the transportation of internal water components, affect the permeability of membrane, the activity of catalyst, the diffusion of gas in the battery, and the occurrence of "water flooding". It can be seen that temperature has a relatively large impact on the performance of PEMFC [11-12].

Mattinoponen et al. [13] studied the influence of PEMFC temperature on current distribution by using a current distribution measurement system, and learned that the main factors affecting its performance will also change with its temperature. Zhang Riqing et al. [14] used the self-made three in one membrane electrode and assembled into a single cell to analyze several factors affecting the performance of the cell, such as Nafion dosage, catalyst dosage, Nafion membrane thickness, anode hydrogen pressure and cathode oxygen pressure. This study provides a reference for the optimal value of each parameter of the single cell. Ma Haipeng et al. [15] used straight single channel to visualize proton exchange membrane single cell, studied the transfer behavior of humidification temperature and gas flow rate on liquid water in cathode channel, and analyzed the phenomenon of "water flooding" with the help of visualization technology.

To judge the performance of PEMFC, the influence of temperature is the top priority. The best temperature can not only ensure the normal operation of its own work, but also maintain the internal
moisture content. The factors affecting the performance of PEMFC are directly or indirectly affected by temperature.

4. PEMFC heat source and heat dissipation mode

For the heat source of PEMFC, irreversible chemical reaction heat and entropy change of electrochemical reaction, Joule heat (heat generation of ohmic polarization), heat brought in by humidified gas, external radiant heat and condensation heat of water vapor generated by reaction. The first two chemical reaction heat and Joule heat are the main heat sources, and other heat is negligible [16].

In the actual working condition of PEMFC, the efficiency of converting internal fuel chemical energy into electrical energy is 40% ~ 60%. Most of the energy in the remaining is still converted into thermal energy, and about 50% of the total capacity will be dissipated through the cooling system [17]. It is necessary to select appropriate heat dissipation methods for PEMFC with different power, mainly as follows:

1) Air cooling: take air as the cooling medium and share it with the reaction air or set a separate channel for transmission to realize heat dissipation. Low convective heat transfer coefficient of air cooling, large heat exchange area required, inconsistent air flow rate and other problems lead to uneven distribution of internal temperature and performance of the battery, which is mostly used in PEMFC power supply equipment with low power (≤ 5kW) [18-19].

2) Liquid cooling: using deionized water or mixed solution of ethylene glycol and water as the cooling medium, relying on the forced convection heat transfer of the coolant and high heat transfer coefficient, the heat dissipation of high-power (> 5kW) PEMFC stack is realized, and the volume of its cooling system is also increased.

The above two cooling methods can be called active cooling or single-phase cooling. They are characterized by using the sensible heat of the cooling medium to take away the waste heat. Usually, a cooling channel is set between the two bipolar plates of the adjacent battery of the stack or a cooling plate with a cooling channel is added to realize forced convective heat transfer.

3) Evaporative cooling: the latent heat of phase change during liquid evaporation is used to take away the heat inside the battery for temperature control. Generally, this method enters the battery from the cathode side together with the coolant and air to participate in the heat absorption and reaction process, which can not only realize the gas humidification but also realize the heat dissipation process, and simplify the complex structure of the system.

4) Heat pipe cooling: with the help of heat pipe (such as copper or aluminum alloy) with good thermal conductivity to maintain uniform temperature on the heat source surface, heat transfer is realized by phase change of its internal working liquid without external equipment power input, and a large amount of heat is transmitted to the outside through its small cross-sectional area [20].

5) Flow boiling cooling: the coolant needs to be set with a separate flow channel and the temperature is constant at the boiling point, changing from liquid to gaseous to realize heat dissipation. Due to the particularity of its cooling mode, deionized water or ethylene glycol aqueous solution cannot be used as the coolant, and the liquid with the characteristics of low boiling point / high latent heat of vaporization and low freezing point shall be selected [21].

The above three types are passive cooling or phase change cooling, which is completed by using the characteristics of absorbing a large amount of heat during phase change. Mramezanizadeh et al. [22] provided a reference matching with PEMFC power for various cooling modes of fuel cells, as shown in Figure 2.
Through the analysis of the heat source and required heat emission of PEMFC, it can be seen that the overall cooling workload is large, and the heat power is basically the same as the power generation power. Therefore, reasonable recycling of PEMFC heat can improve its energy utilization efficiency to a greater extent, significantly reduce the burden of heat dissipation system and effectively ensure the performance of fuel cell. In order to ensure that PEMFC is in heat balance, it is necessary to adapt cooling mode, coolant type, flow and other factors to battery operating conditions.

5. Design requirements and modeling and Simulation of thermal management

(1) Ensure the overall temperature change. Perfluorosulfonic acid membrane is widely used in PEMFC. If the battery temperature is too low, it will aggravate the phenomenon of electrode internal polarization and reduce the output voltage, resulting in the deterioration of battery performance; If the temperature is too high, it will lead to dehydration, shrinkage and even rupture of the proton exchange membrane, which will seriously cause the water loss of the proton exchange membrane and accelerate the attenuation of the proton exchange membrane and catalyst.

(2) Keep component temperature balanced. The temperature uniformity of each internal part is conducive to the evaporation, condensation and distribution of water, so as to avoid dehydration and final rupture on one side of the proton exchange membrane and water flooding on the other side.

(3) Control the overall temperature bearing limit. Most components of PEMFC system have temperature tolerance limits, so it is necessary to ensure that the whole stack operates within its temperature tolerance. If the local temperature distribution of the stack is uneven and higher than 100 °C, micropores will appear in the proton exchange membrane, and hydrogen will penetrate into the air system, causing serious safety accidents [23].

At present, the research on the models to describe the output performance of fuel cells according to the changes of internal parameters and external characterization at home and abroad is complex. There are three common types: mechanism model, empirical model and equivalent circuit model [24]. The mechanism model is based on a reasonable assumption, and the influence of internal temperature, material distribution and other parameters on the battery output characteristics is analyzed by using the electrochemical reaction law. The establishment of simultaneous equations increases its complexity and accuracy. The empirical model does not need to analyze the internal reaction parameters of fuel cell, and summarizes the output characteristic law through its external characterization and big data statistical analysis. The external reference value is mainly obtained from the volt ampere characteristic curve. The model is easy to understand, but it also lacks the investigation of the internal reaction parameters of the battery. The equivalent circuit model is to construct an equivalent circuit through circuit elements to simulate the internal polarization characteristics of fuel cells and express the output characteristics of the system.
The importance of fuel cell thermal management is clarified in the previous article, so it is necessary to optimize the design. Through the constraints of design requirements and the analysis of modeling and Simulation of thermal management, the thermal management problem of PEMFC is improved by combining theory with practice, so that the whole design process is more perfect, which not only ensures the performance of fuel cell, but also shortens the design and research and development cycle, It reduces the consumption of research and development funds.

6. PEMFC cold start at low temperature
Low temperature cold start of PEMFC refers to the process of successful start-up and operation to normal working temperature (about 60 ℃ ~ 80 ℃) at ambient temperature below 0 ℃. In the below zero environment, the reaction product water of fuel cell will freeze due to low temperature, resulting in the decline of fuel cell performance and failure to start. Whether it is used as a portable mobile power supply or as a power supply equipment for new energy vehicles, PEMFC will inevitably encounter starting and operation in a low temperature environment below 0 ℃. In this environment, the following problems mainly occur:

(1) The water generated by the reaction at the cathode catalytic layer will freeze, hinder or stop the reaction of the reaction gas, and the electrode active material is completely covered;
(2) The humidification of the reaction gas and the freezing of the water directly cause that the reaction gas cannot enter the reaction area through the flow channel;
(3) The densities of water and ice at 0 ℃ are 0.9998g/cm³ and 0.9168g/cm³ respectively. When water freezes, it will produce 9% volume expansion. If unreasonable repeated freezing/melting cycles are carried out inside the stack, it will cause the decline of internal single cell performance, and even lead to the decline of stack performance and irreversible damage such as physical deformation or breakdown of component structure [25].

At present, researchers have taken some measures to solve the cold start problem of fuel cell in low temperature environment:

(1) Safe shutdown: the residual water in the reactor is treated in advance by purging before and after shutdown to ensure that there is no freezing problem during startup. Tajirie et al. [26] used humidified gas to purge the internal gas of the stack for a long time in order to ensure that the membrane is not excessively dry. The experimental effect is good but time-consuming. Secondly, by using antifreeze materials or structures inside the stack, the internal damage caused by freezing can be reduced, resulting in performance degradation. Ko et al. [27] [28] proposed to alleviate the problem of internal expansion damage by adding a bifunctional microporous layer between the gas diffusion layer and the catalyst coating membrane, and verified that this method can guarantee the performance of the battery.

(2) Rapid cold start: the external heating device is installed to realize rapid temperature rise start, but it will increase the overall volume, cost and energy consumption of the battery. The internal heating method is not the same. Toyota Mirai uses short circuit or near short circuit to realize short-time heating and cold start, but the risk coefficient of short-circuit behavior is high. Some researchers also control the supply of reactants during the working process of the stack to cause the occurrence of internal electrode overpotential to realize the heating of internal resistance, or reduce the pressing force of the stack and increase the internal resistance to realize the heating [29].

The problem of fuel cell cold start cannot be avoided. Therefore, researchers have adopted different strategies to achieve the normal working state of fuel cell and ensure the overall safety and reliability. Obviously, the solutions to this cold start problem need to be realized in two aspects: safe shutdown and rapid cold start, This problem will also continue to be studied as a hot spot and technical difficulty.

7. Conclusion
Based on the results and discussions presented above, the conclusions are obtained as below:

(1) Thermal management is of far-reaching significance to the performance of proton exchange membrane fuel cells. It is the analysis and heat treatment of the fuel cell heat source, which directly
affects the overall temperature of the fuel cell. At the same time, the temperature has an impact on the internal water distribution and water content of the fuel cell. Therefore, water management and thermal management are closely related and coupled. Effective hydrothermal management ensures the stability and safety of fuel cell performance.

(2) Working temperature is one of the most important control parameters of fuel cell. From the internal water dispersion, membrane permeability, catalyst activity, gas diffusion, “water flooding” and other phenomena to the performance of fuel cell performance, it shows the importance of working temperature. At the same time, it is also the focus and difficulty of cell stack heat dissipation and cold start research.

(3) There are many sources of heat in fuel cells, among which the main heat sources are chemical reaction heat and Joule heat. In the research process, the heat brought by other heat sources accounts for too little and can be ignored.

(4) For PEMFC, the heat dissipation treatment method will be selected according to the power required for the application of fuel cell. Among them, the heat dissipation method of phase change material has obvious advantages and has become a research hotspot.

(5) With the help of mathematical modeling, select an appropriate modeling method to simulate and analyze the actual working conditions of fuel cell, significantly shorten the design optimization and operation test cycle of fuel cell, and reduce the investment of test funds in the process of research and development.

The hydrothermal management of PEMFC has always been a research direction of continuous innovation and optimization, but the investment in its research and development process has also increased. By constantly imposing design requirements on research and development products, with the help of mathematical model simulation analysis and theoretical guidance, it has obviously promoted the progress of this research and development direction.

Acknowledgments
This work was financially supported by the National Key R&D Program of China (2019YFB1504605).

References
[1] http://www.gov.cn/zhengce/zhengceku/2015-05/19/content_9784.htm
[2] Wang Ju, Zhu Xinyi. Overview of demonstration and application of fuel cell vehicles at home and abroad [J]. Solar energy, 2017 (8): 31-34.
[3] Huang Zhuo, Tu hailing, Zhang Ji qiang, et al. Research development and application of proton exchange membrane fuel cells [M]. Beijing: Metallurgical Industry Press, 2000:5-29.
[4] Yi Baolian. Fuel cells – Principle technology and application [M] Beijing: Chemical Industry Press, 2003.
[5] Ren Xueyou. Research progress of proton exchange membrane fuel cells [J]. China Engineering Science, 2005. 7 (01): 86-94.
[6] Fu Tiantian. Overview of the development of hydrogen fuel cells for electric vehicles [J]. Power supply technology, 2017,41 (4): 651-653.
[7] Wang Jihua, Ju Yusheng, Yi zhenggen, et al. Overview of fuel cell technology development and application status (I) [J]. Modern vehicle power, 2018 (5): 7-11.
[8] Appleby A J, Foukes F R. Fuel cell handbook[M]. New York:Van Reinhold, 1989.
[9] Yi Baolian. Principle, technical status and Prospect of fuel cell [J]. Battery industry, 2003,8 (1): 16-22.
[10] Hu Qingsong. Research progress of hydrogen fuel cell [J]. Automotive practical technology, 2017 (21): 114 - 116.
[11] OWEJAN J P, OWEJAN J E, GU W B, et al. Water transport mechanisms in PEMFC gas diffusion layers [J]. J. Electrochem.Soc,2010,157(10):1 456-1 464.
[12] Wang Xu, Zhang Rui, Wang xumin. Overview of research on performance thermal management of proton exchange membrane fuel cells [J]. Special purpose vehicles, 2020 (09): 76-80.
[13] Matti Noponen, Tuomas Mennola, Mikko Mikkola, et al. Measurement of current distribution in a free-breathing PEMFC [J]. J Power Sources, 2002, 106(1).

[14] Zhang Riqing, He Yan, Zhou Zhentao. Research on the electrical performance of proton exchange membrane fuel cells [A]. Ministry of science and technology of the people's Republic of China, China Association for science and technology, hydrogen energy professional committee of China solar energy society International Hydrogen Energy Association. Proceedings of the second international hydrogen energy forum youth hydrogen energy forum [C]. China solar energy society, 2003:5.

[15] Ma Haipeng, Zhang Huamin, Hu Jun, et al. Effects of humidification temperature and gas flow rate on liquid water distribution and drainage in PEMFC cathode channel [J]. Journal of chemical industry, 2007(09): 2357-2362.

[16] Kandlikar S G, Lu Z J. Thermal management issues in a PEMFC stack-A brief review of current status [J]. Applied Thermal Engineering, 2009, 29(7): 1 276-1280.

[17] Li Zhonghua, Du Chuanjin, Hou Xianjun. Research on thermal management of proton exchange membrane fuel cells [J]. East China power, 2007(02): 19-22.

[18] Meter Q, Ronaszegi K, Robinson J B, et al. Combined current and temperature mapping in an air-cooled, open cathode polymer electrolyte fuel cell under steady-state and dynamic conditions[J]. J Power Sources, 2015, 297(31): 315-322.

[19] Bu Qingyuan, Li Qi, Chen Weirong, et al. Experiment and Simulation of cathode fan system of air-cooled PEMFC reactor [J]. Journal of chemical engineering, 2015, 66(10): 211-217. Power sources, 2006156 (1): 114-118.

[20] Lei Dongqiang, Wang Xiuchun, Zhu Weili, et al. Research on the application of heat pipe technology in transformers [J]. Transformers, 2007(04): 37-40.

[21] Hou Jian, Yang Zheng, He Ting, et al. Research progress on thermal management of proton exchange membrane fuel cells [J]. J Central South University (Natural Science Edition), 2021, 52(01): 19-30.

[22] Ramezanizadeh M, Nazari M A, Ahmadi M H, et al. A review on the approaches applied for cooling fuel cells[J]. International Journal of Heat and Mass Transfer, 2019, 139(AUG.): 517-525.

[23] Puji, Qin Xiaojin, Lu Yan, et al. Design and research of fuel cell thermal management system [J]. Automotive abstracts, 2019 (04): 24-27.

[24] Yang Duo, Pan Rui, Wang Yujie, et al. Dynamic modeling and simulation of proton exchange membrane fuel cell [A]. Professional Committee of system simulation of Chinese society of automation, professional committee of simulation technology application of Chinese society of system simulation. Proceedings of the 18th Annual Academic Conference of China system simulation technology and its application 18th CCSSTA 2017 [C]. Professional Committee of system simulation of Chinese society of automation, 2017.5:

[25] Ma Jianxin, Gao Xin, Zhang Cunman, et al. Cold starting Mechanism and Cold Starting Strategy of proton exchange membrane fuel cell [J]. Power technology, 2009, 33(07): 533-540.

[26] Kazuya Tajiri, Yuichiro Tabuchi, Fumio Kagami, et al. Effects of operating and design parameters on PEFC cold start[J]. J Power Sources, DOI: 10.1016/j.jpowsour.2006.12.017.

[27] Johan Ko, Whan-Gi Kim, Young-Don Lim, et al. Improving the cold-start capability of polymer electrolyte fuel cells (PEFCs) by using a dual-function micro-porous layer (MPL): Numerical simulations[J]. Int J Hydrogen Energy, DOI: 10.1016/j.ijhydene.2012.06.026.

[28] Ko, Johan, Ju, Hyunchul. Numerical evaluation of a dual-function micro-porous layer under subzero and normal operating temperatures for use in automotive fuel cells[J]. Int J Hydrogen Energy, DOI: 10.1016/j.ijhydene.2013.07.060. membrane fuel cell [J]. Battery, 2018, 48(03): 202-205.

[29] Li Jie, Sun Tiesheng, Zhang Guangmeng, et al. Research progress on thermal management and cold start of PEMFC engine [J]. Battery, 2020, 50(04): 383-387.