

Main factors affecting the lifetime of Proton Exchange Membrane fuel cells in vehicle applications: A review



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HIGHLIGHTS

- Reviewed the PEMFC life degradation during the durability tests and its consequences.
- Reviewed the water management problems: causes, consequence and mitigation methods.
- Reviewed the reactant starvation issues: causes, consequence and mitigation methods.
- Reviewed the effects of the operating parameters on PEMFC dynamic response.
- The conclusion is a guidance for future research of prolong PEM fuel cell life time.

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ABSTRACT

This paper focuses on reviewing the main factors affecting the life time of fuel cells on vehicles. The main difference between fuel cells used in vehicles and fuel cells used as fixed power is the load cycling. Load cycling sometimes leads to water management and gas transport problems, which further leads to degradation of fuel cell performance and attenuation of internal parts. This article is written from the perspective of the fuel cell dynamic cycling as well as its resulting problems of water management and gas starvation, and also analyses the reasons for the degradation of fuel cell life time, and present some mitigation measures during the fuel cell operation.

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1. Introduction

PEM fuel cell system is the main component of a fuel cell vehicle. Compared with other power systems, because of its high power utilization rate and zero emission [1–3], it is considered as one of the most effective power systems for a vehicle [4,5]. To make this technology commercially viable, there are still many challenges. Apart from the high cost of fuel cell systems, high maintenance costs and short lifecycle are the two main issues that need to be addressed [6].

Up to now, while comprehensive studies such as experimental results and reviews have been published in an attempt to

understand the degradation mechanisms of fuel cell components such as electro-catalysts [7–9], membranes [10,11], and bipolar plates [12–14], only a relatively small part of studies aimed at real Proton Exchange Membrane (PEM) fuel cell lifetimes have been conducted, due to the high costs and long testing periods required. To increase sample throughput and reduce the experimental time required, several fuel cell developers and companies, such as Ballard Power Systems, Gore, DuPont, and General Motors, have proposed and implemented different accelerated stress tests (ASTs) to determine the durability and performance of current fuel cell components. Papers published in the last decade on PEM fuel cell degradation and lifetimes are shown in Table 1 [15] and Table 2 [15], which presents work on steady state and accelerated lifetime tests, respectively. Prior to commercializing fuel cell technology, more studies of components and analyses of system failure modes are imperative [15].

Table 1 [15] and Table 2 [15] show that the decay rate of the different evaluation methods; the life of the fuel cell under steady-state operation can be very long, up to 26,300 h; the voltage degradation rate is very large during accelerated durability tests, especially during the cold start-up, the voltage degradation reached 22.5 mV. The life time of PEM fuel cell is a prominent problem in its use, and is also one of the main factors hindering its commercialization. The life time of a fuel cell on a vehicle is about 2500–3000 h [42] much shorter than the life time of a fuel cell operating as a fixed power sources which is over 30 thousand hours [43]. Regarding the application of fuel cells in a vehicle, many factors affect its life time, as fuel cells make use of the air

Table 1
Summary of steady state lifetime tests in the literature [15].

Authors	Test time (h)	Degradation rate	Refs.
Ralph	5000	4 $\mu\text{V h}^{-1}$	[16]
St-Pierre et al.	5000	1 $\mu\text{V h}^{-1}$	[17]
Washington	4700	6 $\mu\text{V h}^{-1}$	[18]
	8000	2.2 $\mu\text{V h}^{-1}$	
Endoh et al.	4000	2 $\mu\text{V h}^{-1}$	[19]
Yamazaki et al.	8000	2–3 $\mu\text{V h}^{-1}$	[20]
St-Pierre and Jia	11,000	2 $\mu\text{V h}^{-1}$	[21]
Fowler et al.	1350	11 $\mu\text{V h}^{-1}$	[22]
Ahn et al.	1800	>4 mV h ⁻¹	[23]
Cheng et al.	4000	3.1 $\mu\text{V h}^{-1}$	[24]
Scholta et al.	2500	20 $\mu\text{V h}^{-1}$	[25]
Cleghorn et al.	26,300	4–6 $\mu\text{V h}^{-1}$	[26]

Table 2
Summary of accelerated durability tests in the literature [15].

Authors	Test time (h)	Degradation rate	Operating conditions	Refs.
Sishtla et al.	5100	6 $\mu\text{V h}^{-1}$	Reformate fuel	[27]
Nakayama	4000	4.3 $\mu\text{V h}^{-1}$	Reformate fuel	[28]
Isono et al.	2000	10 $\mu\text{V h}^{-1}$	Reformate fuel	[29]
Maeda et al.	5000	6 $\mu\text{V h}^{-1}$	Reformate fuel	[30]
Sakamoto et al.		50–90 μV	Per start/stop cycles	[31]
Fowler et al.	600	120 $\mu\text{V h}^{-1}$	Humidity cycles	[32]
Cho et al.		4200 μV	Per thermal cycles	[33]
Knights et al.	13,000	0.5 $\mu\text{V h}^{-1}$	Methane reformate fuel	[34]
			Low humidification	
Oszczipok et al.		22,500 μV	Per cold start-up	[35]
Xie et al.	1916	60 $\mu\text{V h}^{-1}$	Over-saturated humidification	[36]
	1000	54 $\mu\text{V h}^{-1}$		
Yu et al.	2700	21 $\mu\text{V h}^{-1}$	Low humidification	[37]
Endoh et al.	3500	3 $\mu\text{V h}^{-1}$	High temperature, low humidification	[38]
Du et al.	1900	70–800 $\mu\text{V h}^{-1}$	Cold start and hot stop	[39]
Xu et al.	1000	<10 $\mu\text{V h}^{-1}$	High temperature, low humidification	[40]
Owejan et al.		0.212 mV	Per start/stop cycles	[41]

in the outer environment during its operating, hence the impact of environmental pollution factors are a reason for its degradation [44–47]. Fuel cells operating at lower current may cause degradation of the catalyst layer and lead to the reduction of the fuel cells voltage [48,49]. Poor control of the anode and cathode pressure difference, low humidity, high stack temperature, and shortage of reaction gas may lead to gas starvation [50–52]. Successive hydration and dehydration process of the membrane electrode assemble may cause permanent damage to the fuel cells [53]. Effective diagnostic techniques are particularly important to the attenuation and degradation of the fuel cells. Tian et al. [54], through the analysis of experimental data, showed a diagnostic method of practical significance, ensuring that the diagnosis does not open the stack and does not destroy the proper functioning of other single cells.

As to real operation condition in vehicular application, the main character is that fuel cells are always operating at variable load condition [55]. In fuel cells life time evaluation study, load changing, start-stop [56], idling, and high power all have a great impact on fuel cells life time [57,58], while frequent load changing factors in all operating conditions result in performance degradation of the fuel cell with the proportion of 56%, as seen in Fig. 1 [67].

In vehicle applications fuel cells operate under load change conditions. Sudden load changes may result in improper water management and reactant starvation phenomena [59] due to the slow response of the cell to load change, which results in performance loss and short lifetime [60]. As described before the load cycling process has an extreme effect on the fuel cell lifetime, and the issue of load cycling is the issue of fuel gas and vapor ultimately. So far, many researchers conducted research on the load cycling process. Following in this paper summarize their research focus on the problems of water management and dynamic response.

2. Load cycling

2.1. Load cycling aging process

Many scholars studied the dynamic process of the fuel cells degradation in the past. Silva et al. [61] conducted 8 small fuel cells stack load cycling aging test, where they discovered that after 1500 h test the power of the stack have decayed 34%. Since Load cycling has a great impact on the catalyst layer, active area of the catalyst decreased 17.6%. With the carbon corrosion, the thickness of the electrode decreases, and the Teflon ionomer on the catalyst layer also decays severely. Rong [62,63] exploited the rate-dependent isotropic plasticity model, using finite element analysis to

study the microstructure change of the catalyst layer caused by the load cycling process. Simulation indicates that after series of load cycling test, cracker and lamination emerged on the catalyst layer. They pointed out that these phenomena can be used as the basis to judge the fuel cells performance degradation. Jung et al. [64] studied the durability of PEM fuel cells using an accelerated degradation technique. The technique was performed by applying 1.5 V to an MEA with hydrogen and nitrogen feeding to the anode and cathode, respectively, to simulate the high voltage generated during fuel cell shutdown and restart. Bose et al. [65] used a 100 W 10 cells stack conducted load cycling test, and observed irreversible degradation at about 480 h. According to the attenuation, the predicted life of the stack is 1700 h.

In order to simulate the real driving condition of the automotive fuel cells, Liu et al. [66] conducted fuel cells degradation test through load cycling, they found the hydrogen stoichiometric ratio increased due to the pinhole formed in the membrane. On the contrary, the hydrogen permeability keeps constant under steady state. And the fluoride-ion concentration under load cycling is 30 times of under steady state.

Pei et al. [67] studied fuel cells performance degradation under different operating conditions, they distinguished the effect of load changing cycles, start-stop cycles, idling time and high power load four typical driving conditions on PEMFC lifetime. The degradation rate of the fuel cells performance on the simulating driving condition is proved to be a sum of the degradation rates of four typical driving conditions. And they presented a prediction equation for fuel cells lifetime that relates to load changing cycles, start-stop cycles, idling time, high power load conditions, and air pollution factor [67]. Based on the practical data gathered from a fuel cell bus and the test results of a fuel cell stack in laboratory, the calculated lifetime matches the fuel cell bus real working lifetime very well. The study showed that automotive fuel cell lifetime heavily depends on driving cycles. They presented the results of a fuel cell bus trial which run at an average speed of 32 km h⁻¹. After the fuel cell bus ran 35,000 km, in about 1100 h, the cell voltage dropped 10% below the limiting electrical voltage, which caused the fuel cell stack power decrease more rapidly [68].

Fig. 2 [23] shows a fuel cell stack continuous operation 1800 h with hydrogen stoichiometric number was two and oxygen stoichiometric number was four. They observed the uneven cell voltage distribution inside the stack. It operated 300 h under full load and 1500 h under partial load. The continuous operation

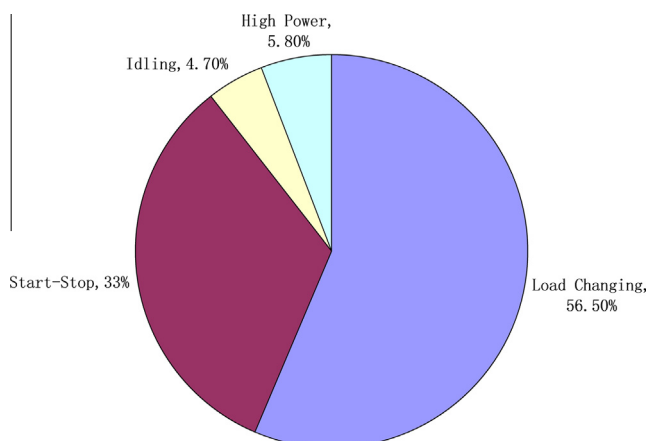


Fig. 1. PEM fuel cell performance degradation rate caused by different operation conditions [67].

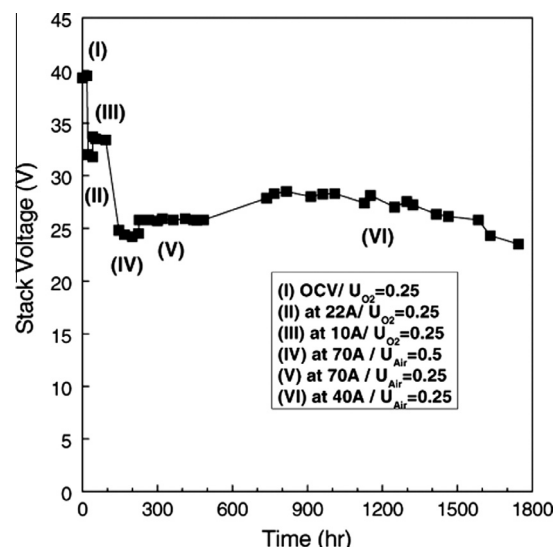


Fig. 2. Performance of a stack during continuous operation [23].

consisted of three periods, the first period from (I) to (III) was a warming-up step, the system operated under partial load. The second period from (IV) to (V) operated under 70 A with full load. At that time, the power of the stack was 1.75 kW. During the third period, the stack operated 12 h under 40 A partial load and the other 12 h under OCV.

As seen in Fig. 2 [23], the stack performance did not decrease during the second period, but slowly dropped during the third period at an average decay rate of 4.37 mV h^{-1} ; then, after continuous operation for 1800 h, the stack showed rapid performance decay. It was postulated that careless operation of the stack might have caused the rapid decay in performance, because the stack was exposed to flooding [69]. Several factors can be at work in stack performance degradation after continuous operation, and these have been investigated with various analytical tools, as will be described in the following sub-sections.

A driving cycle is a specific kind of load changing cycle under simulated vehicle driving conditions. Driving cycles are designed by imitating real vehicle, including start-up, idling, constant load running, variable load acceleration, full power running, and overload running. In order to study the fuel cell performance degradation caused by load cycling, fuel cell load cycling tests were conducted by Pei [67], Lin [69] and Weng [70] et al.

In the test conducted by Pei [68], the load changed from an idling condition to a rated power condition, and the fuel cell performance was measured after every 200 loading cycles. Each day, the researchers used 30 min idling time to warm the fuel cell to above 40°C , then carried out 2000 loading cycles, with a decay rate of 0.000606% per cycle.

Lin et al. [69] studied the dynamic driving cycle effect on performance degradation and micro-structure change of PEM fuel cell. The effective electrode area of the single fuel cell in the test was 50 cm^2 . During the test, the fuel cell was operated at 70°C with ambient back pressure. Anode and cathode sides were 100% humidified at a temperature of 85°C , with a gas utilization of 70% for H_2 and 30% for air. In their experiment, each cycle consisted of six periods (by simulating cold starting, idle running, full power running, continuous loading running and overload running conditions) and lasted for 20 min. The current of overloading was set at 35 A. Driving cycle protocol consisted of continuously running the above cycles. They presented the polarization curves of initial MEA and those measured in time intervals (respectively, after 100, 200, 280 and 370 h running) under driving cycles, as seen in Fig. 3 [69]. With the increase of running time, open circuit voltage of the fuel

cell performance decreased gradually but a much more rapid decrease of voltage was observed after 280 h of operation comparing to the period of 0–280 h. This result shows during a 370 h load cycling operation, and thus the fuel cell severe performance degradation happened after 280 h.

Fig. 4 [69] presented the evolution of voltage versus time under driving cycles, at 0, 200, 500 and 700 mA cm^{-2} current densities respectively. The voltage decreased with time whether under open circuit voltage condition or under higher current density. When the fuel cell operated over 280 h, a much more rapid decrease of voltage was observed comparing to the period of 0–280 h. During 0–280 h operation, the evolution of voltage versus time decreased with a rate of 0.274 mV h^{-1} , while during 280–350 h, a more rapid degradation rate of 2.3 mV h^{-1} was found. The results of Fig. 4 [69] accord with the results of Fig. 3 [69] very well.

2.2. Analysis after operating cycles

After a long period of operating cycles, many micro-scale changes occurred in a fuel cell [71]. Darab [71] observed the catalyst micro-scale structure change using the Electrochemical Impedance Spectroscopy (EIS). Comparing the results before and after load cycling test, they found part of the particle size grew up and agglomerated. The changes of the impedance spectroscopy led to the transform of reaction mechanism. Wu [15] showed the H_2 crossover rate as a function of time, also showed both the Gore reinforced membranes and non-reinforced membranes lifetime during accelerating conditions. Mu et al. [73] showed Pt load changes for an original catalyst-coated membrane (CCM) and a modified CCM under accelerated testing. After 100 h of treatment, the Pt catalyst loss from the modified CCM was radically less than the loss from the original CCM: 0.1 mg cm^{-2} versus 0.32 mg cm^{-2} . They showed fluoride emissions from CCMs in hydrogen peroxide. Both the original and the modified CCM had increasing fluoride emission over time, but the modified CCM emitted more. Fluoride in a fuel cell solution can originate from the degradation of Nafion in the catalyst layers and/or in the Nafion membranes.

After long term load cycling, obvious change occurred in the performance of the fuel cell stack. Pei et al. [72] conducted a 500 h accelerated degradation test on an automotive PEM fuel cell stack with idling cycles, load changing cycles, high power cycles, and start-stop cycles, the stack performance clearly deteriorated. The average cell voltage curve of every cell from 1–14 cells is lower than for cells 15–100. Therefore in the fuel cell stack, performance degradation is more easily occur in the cells in front. They

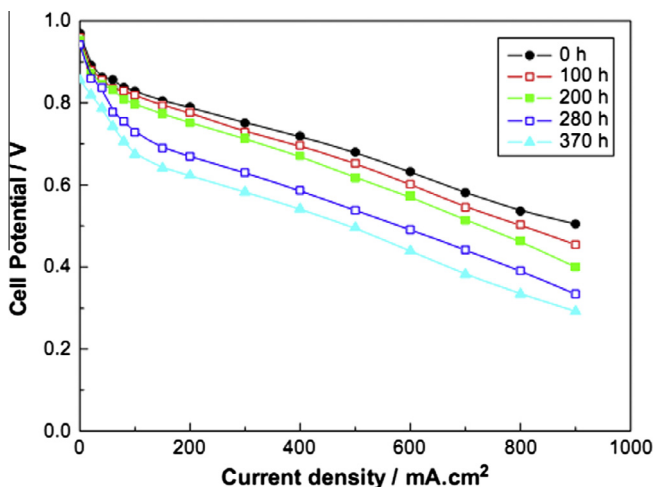


Fig. 3. Current voltage characteristics of an electrode with 50 cm^2 in different durability test time [69].

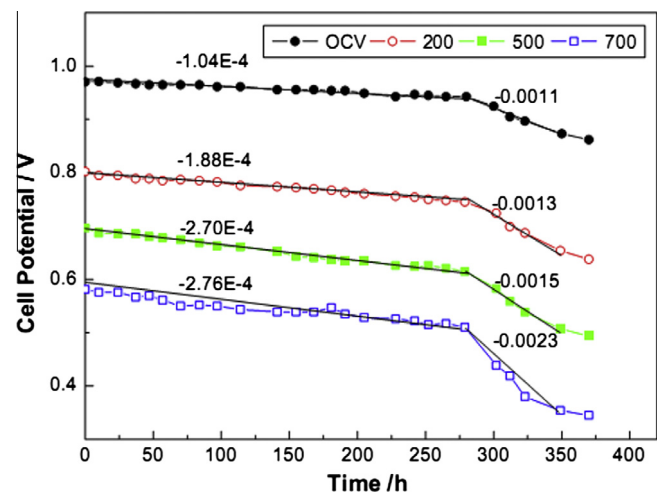


Fig. 4. Evolution of voltage versus time under driving cycles [69].

compared the polarization curve of different small cells within primary cells. The small cells taken from the air-outlet parts of primary cells display the worst performance overall and have the lowest open circuit potentials. Their polarization curves drop rapidly in the ohmic potential loss region, and their maximum current density is less than 300 mA cm^{-2} . The small cells taken from the hydrogen-outlet parts of primary cells also perform poorly, sometimes even worse than the air-outlet parts. The small cells taken from the air-inlet, middle parts display average performance, while the small cells taken from the hydrogen-inlet parts have the best performance, which performs even better than a new cell, with an open circuit potential of more than 0.85 V. The polarization curves of the hydrogen-inlet cells drop gently in the ohmic potential loss region. Their maximum current density is the highest, which is more than 1000 mA cm^{-2} . They also showed the electrochemically active surface area coefficients of the different parts in every cell. The coefficients of the hydrogen-inlet parts are the largest, indicating that the catalysts in these areas are the most active after a long working time.

3. Water management

Water management, ensuring the normal operation of the PEM fuel cells, also is a key issue of PEM fuel cells performance improvement and life extension [74]. Recent studies showed that water management is of vital importance to ensure stable operation, high efficiency and to maintain the power density of PEM fuel cells in the long run [75–77].

Yan et al. [78] described seven modes of water transmission in the PEM. They are production of water from cathode reaction, removal with air, back diffusion, humidification of the air supply, humidification of the hydrogen supply, and removal by circulating hydrogen. As seen in Fig. 5 [79]. In the seven modes, the gas–liquid two-phase flow increased the difficulty of water management. The core issue is keeping the balance of the water inside, which maintains sufficient water of the membrane and improves the proton conduction rate, whilst avoiding of flooding and membrane dehydration.

Water management, which significantly affects catalyst and membrane degradation, is of vital importance for a PEMFC's lifetime. Poor water management causes dehydration and flooding.

Dehydration is an important issue. Dehydration causes mechanical stress in the membrane that leads to failures (tearing and cracking), and accelerates the chemical degradation of PEM fuel cells [19]. RH cycling (rather than steady-state operation) further accelerates membrane degradation. Severe dehydration will cause

irreversible membrane degradation (delamination, pinholes) within about 100 s [75]. Thomas [80] analyzed the membrane dehydration by nonlinear frequency response. He found that the proton conductivity on the catalyst layer side decreased, which lead to the decrease of the catalyst active area and the increase of the charge transfer resistance. Panha [81] studied the fuel cells performance degradation by the reactant humidity cycling tests. Their studies mainly focused on the membrane degradation caused by acceleration degradation tests.

Flooding is another common issue in PEMFC operation. As reactant gas humidity increases, Platinum dissolution–precipitation and carbon support corrosion accelerate. Too much water can block the flow channels and pores of the GDL and lead instantly to reactant starvation, which can induce catalyst support degradation.

In the load changing process, it is important to know how the automotive fuel cell humidity with a large area behaves in various parts of the flow field. Weng et al. [70] using a segmented fuel cell to study the effect of inhomogeneous humidification on the local aging of the MEAs. The active area of the MEA was divided into eight segments along the flow channels. The effects of the local humidification of the MEA were measured by high-frequency resistance (HFR). The HFR was higher in segment 1 due to drying out of the membrane, which occurred because less water was present to humidify it. When the gas shifted downstream, the amount of water increased, the membrane was humidified, and the HFR decreased. They also observed that when the loading changed from a large to a small current, the HFR was lower due to the low temperature of the membrane, and the water content was sufficient in segments 1–4. The HFR value was found to increase with increasing temperature. In segments 5–8 the HFR was steady because there was sufficient water from upstream to humidify the membrane. The HFR increased in segments 1–7 when the loading was changed from a large current to a small one, because the membrane was still at a higher temperature and water production decreased, so the membrane's water content dropped. When the gas shifted downstream it took up more water, which humidified the membrane. This phenomenon caused the HFR to overshoot then ease up in the last segments. There was also flooding in segment 8 because the water produced in prior segments passed to segment 8 when the system shifted from a large to a small load, causing the HFR to undershoot due to that flooding. When the flooding was removed, the HFR stabilized [70]. An aging experiment under current cycling conditions comprised 450 cycles in total, taking about 150 h. Polarization test and linear sweep voltammetry (LSV) were conducted every 50 cycles. In the segment 1 near gas inlet the cell performance degradation very fast, because of low relative humidity, is easier to dry during loading. The segment 8 near the outlet decays slower, because it is during good humidification [70].

3.1. Low Relative Humidity (RH)

3.1.1. Impact on fuel cell performance

During the PEM fuel cells operation, hydrogen ions (protons) form from the anode catalyst layer across the membrane to the cathode. Protons in the membrane transfer in the form of hydrated protons. The more protons transferring through the membrane, the more water moves from the anode to the cathode. Water content in the membrane largely determines the electrical conductivity and the efficiency of the fuel cell power generation. With water infiltration and reaction, water decreases on the anode side and increases on the cathode side leads to membrane dehydration at the anode side. Because of the water vapor concentration difference, the water molecules also transfer to the anode due to back diffusion.

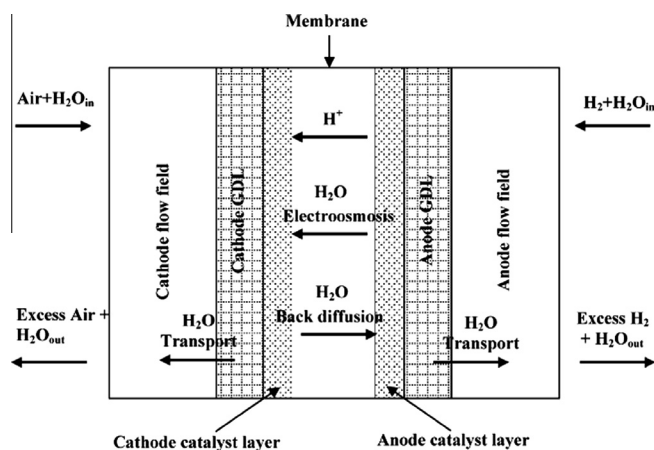


Fig. 5. Schematic picture of water movement inside a PEM fuel cell [79].

When the water content in the membrane is moderate, the best fuel cell conductivity can be achieved. The ohmic resistance is then relatively small and the power efficiency is maximized. Less water in the membrane leads to membrane dehydration which disadvantages proton transfer, greatly reducing its conductivity. This increases ohmic resistance and decreases power generation efficiency. In order to maintain the membrane sufficiently hydration, methods need to be found to add water vapor on the anode side, which results from water loss caused by the electric osmotic drag. The anode hydrogen must be well humidified. If air, instead of pure oxygen is used at the cathode, the oxygen concentration at the cathode will be much less. To obtain a higher oxygen concentration it is generally required to increase the air flow rate, and then more water is carried away by air flow at the cathode side of the membrane. Therefore, the cathode air must also be humidified.

In the case of membrane electrode dehydration, membrane electrical conductivity decreases and ohmic resistance increases. The internal fuel cell voltage loss will thus be even more serious, leading to the fuel cell polarization curve decrease with the drop in RH. Fig. 6 [75] and Fig. 7 [82] are fuel cell polarization and resistance curves for different RHs.

As can be seen from Fig. 7 [82], when the relative humidity is about 75–100%, the ohmic loss is the minimal. When the relative humidity is too low, reducing the membrane's ability to carry protons, the membrane resistance increases. When the relative humidity is too high, supersaturated vapor will form liquid water, which blocks the flow channels, leading to the increase of electrode resistance.

Low RH also makes thermal management of the fuel cell difficult. As the membrane resistance increases, the output voltage drops. To achieve the same power, the output current must increase. Thus, the fuel cell temperature rises, further decreasing the RH and making the membrane more hydrophobic. The result is the continuous deterioration in fuel cell performance.

3.1.2. The effects of different anode and cathode gas humidity

3.1.2.1. The role of air-side humidity and low RH effects. A moist membrane has higher electrical conductivity and better fuel cell performance. When RH is constant in the anode inlet, water diffusion from the cathode to the anode increases the membrane's water content. But under working conditions with a high current density, the amount of water carrying protons will be greater than the water diffusing from cathode to anode. Therefore, if the cathode has low humidity, the fuel cell performance improves when the anode RH is increased. When the anode humidity increases,

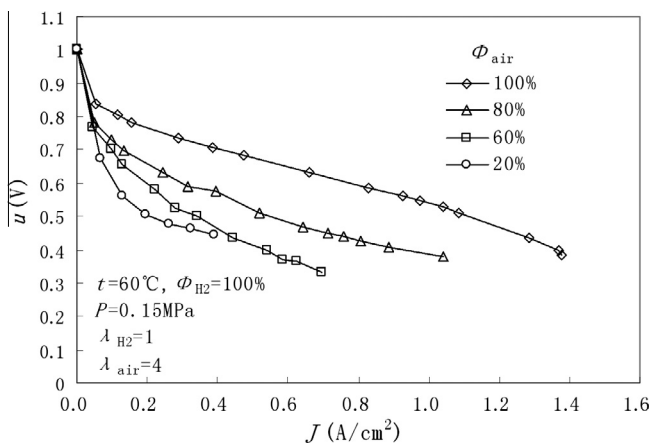


Fig. 6. PEM fuel cell polarization curves under different RH [75].

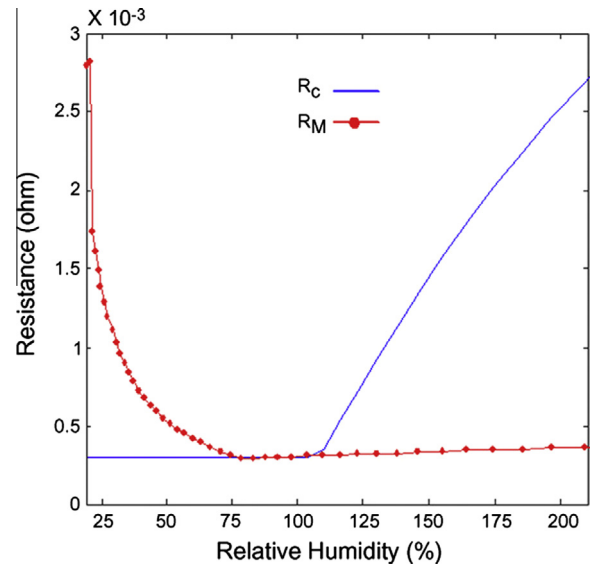


Fig. 7. Effect of RH on fuel cell internal resistances (R_c = electrode resistance, R_m = membrane resistance) [82].

this humidification can to some extent compensate for the loss of membrane water content. High RH at the cathode causes a decline in the partial pressure of oxygen in the air, and even a flooding phenomenon, which results in decreased fuel cell performance [78].

On the other hand, since the fuel cell's electrochemical reaction produces water, the RH is generally too high for oxygen export. The membrane moisture content will not be uniform when the cathode RH is low. This results in lower RH in the gas intake area and higher RH in the gas export area, thus making the current density uneven [82].

3.1.2.2. The role of hydrogen-side humidity and low RH effects. Similarly, if the anode RH is very low, e.g. 10%, membrane performance increases with anode humidification. If the cathode RH is high, the membrane can be humidified through water back diffusion from cathode to anode when the hydrogen humidification is low. On the other hand, if the hydrogen humidity increases, the hydrogen partial pressure drops, and under this situation the hydrogen humidity has little effect on cell performance.

In general, to improve fuel cell performance, keeping the cathode humidity at 100% while reducing anode humidity is more effective than keeping anode humidity at 100% while reducing cathode humidity. This is mainly because maintaining 100% RH at the cathode side can basically ensure the membrane humidification. Particularly with a low operating voltage, the cathode produces large amounts of liquid water, and water from the back diffusion wetting membrane at the anode side. At this point water flooding becomes the key issue. Reducing the anode humidity can direct more water to the anode by back diffusion, which alleviates water flooding at the cathode and reduces mass transfer loss, thereby increasing fuel cell performance [78].

3.2. Flooding

If the PEM membrane water content is too high, liquid water will form saturated water vapor. Diffused liquid water will then dilute the concentration of the reactive gas and block the cathode gas diffusion layer channel, reducing the speed of the oxygen transport and the efficiency of fuel cell power generation. Then the flooding occurs. Flooding immediately increases the mass transport losses, which means the transport rate of the reactants is significantly

reduced. Water blocks the GDL pores, preventing the reactants from reaching the catalysts and thus leading to gas starvation and an immediate drop in cell potential. As seen in Fig. 8 [83], cathode flooding has a negative effect on the fuel cell performance. Under high current density (over 0.55 A cm^{-2}), the cathode oxygen partial pressure drop caused severe cells voltage drop. They also indicated that cathode pressure drop from 1.5 kPa to 3 kPa, voltage decreased from 0.9 V to one third of the initial (cells operation temperature, 51°C ; hydrogen flow rate, equivalent to 2.0 A cm^{-2} , air flow rate, equivalent to 2.8 A cm^{-2} , atmospheric pressure; hydrogen temperature, 50°C ; air temperature, 27°C) [83].

Flooding also has a negative effect on PEMFC durability. Too much water accelerates the corrosion of the electrodes, the catalyst layers, the gas diffusion media, and the membrane [84]. Corrosion in turn increases ohmic losses. Dissolved catalyst particles and impurities can also be transported into the membrane, replacing H^+ ions and reducing the proton conductivity over time, eventually leading to cell failure [85]. It takes much longer to accumulate water at the anode [86], but the accumulated water in the anode side can also cause fuel starvation with subsequent carbon corrosion in the catalyst layer, which has very serious consequence. Maintaining appropriate water content is one of the most effective ways to improve fuel cell power generation efficiency and the service life.

In the past few years, the importance of water management in relation to the proper functioning of fuel cells has motivated much research on liquid water transport and effects on cell performance and durability [87]. Many scholars use different equipment for liquid water visualization inside the fuel cells [88–96]. Feindel [88], Feindel [89] applied magnetic resonance imaging technology, Park [90], Zhang [91], Ludlow [92] applied neutron imaging technology, Jin [93], Chan [94] used electron microscopy imaging technology, Tobias [95], Deevanhxay [96] used the X-ray radiography. Many researchers conducted experiments on the water transports inside the fuel cells [97,98]; others modeled on the water transport inside the fuel cells [99–103]; whilst others studied the flooding diagnostic methods [98,104–106] and the dehydration diagnostic methods [107]. Also there are many researchers who focused on the reviewing research of water transport, water management and flooding caused performance degradation and life attenuation problems [74,79,101,107,108].

3.3. Solution of water management problem

Since water management significantly affects the lifetime of the PEMFC, efficient management strategies are needed.

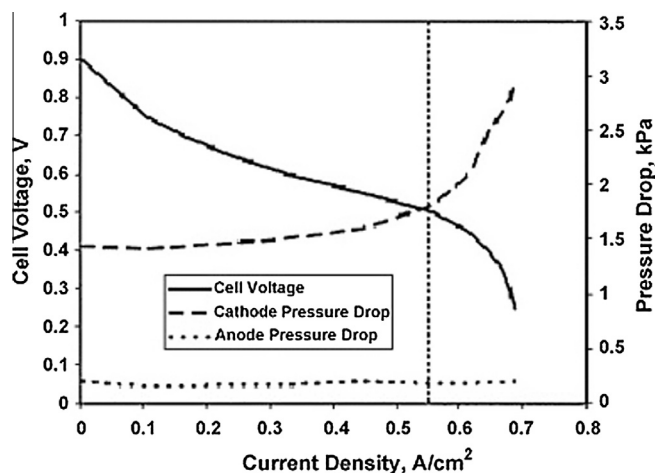


Fig. 8. Cell voltage and pressure drop change with current density [83].

It has been proven that membrane resistance is higher when dehydration occurs. To diagnose membrane dehydration, membrane resistance measurement is used to indicate the levels of dehydration. Three resistance measurement methods present a good compromise between simplicity, invasiveness, and reliability [107]: current interrupt (CI), AC resistance (ACR) and high-frequency resistance (HFR). All are based on the cell's response to certain situations. The easiest way to diagnose flooding is to monitor the pressure drop. Before beginning the diagnosis, the normal pressure drop curve should be tested for comparison, which is the baseline for the diagnosis. If the pressure drop is seriously larger than normal, flooding is supposed to have occurred.

Many scholars have proposed a lot of water management measures, which try to lower the influence of poor water management on fuel cell life. During these measures to reduce the pressure, temperature gradient and counter flows design are relatively easy to implement.

3.3.1. Proper reactant humidity

In general, reactant gas is humidified before entering the fuel cell. However, some scholars proposed that the reactant gas does not need to be humidified before entering the fuel cells [109]. In this case, operating parameters (e.g. gas flow rate, active area, current density and temperature) have to match properly, so that the generated water is able to humidify the membrane effectively. Such an operating mode is called 'self-humidify mode' [110]. Wang et al. [111] designed a gas distribution media, which was coated with a silica particle/poly composite. The gas distribution media has a superhydrophobic surface, which is to the advantage of water management and shows low resistance to gas transport. Performance testing indicates that the PEM fuel cell equipped with this kind of GDMs offers the best performance, compared with the PEM fuel cell with raw GDM (untreated with surface coating) and conventional GDM.

Under the 'self-humidify mode', the dry gas flows in and contacts with the diffusion layer, and thus a portion of water carried by the diffusion layer would be dried away for humidifying gases. In order to maintain the inner balance of the self-humidifying mode, the reaction gas humidification water must be less than the oxidation–reduction generated water. As long as there is liquid water inside the fuel cell, it will be involved in the dry gas humidification. In the self-humidify mode, we have to lower the operation temperature of the fuel cell to prevent the generated water from being removed by the waste gas. Actually, under the self-humidify mode, the fuel cell operation temperature must be below 60°C to avoid membrane dehydration [112]. Buechi [109] observed that the fuel cells performance under no humidification is reduced by 40% compared with the well humidification cells. The authors explained this phenomenon as being as a result of too low water content of the membrane, which leads to the moisture gradient.

Evaporates in the cathode gas flow channel and transfers through the membrane from the cathode to the anode are the two cathode water transfer processes. Usually, water removes from anode to cathode through membrane is called the electronic osmosis process. Water removes from cathode to anode through the membrane is called the reverse osmosis process. Reverse osmosis is affected by many factors, such as the anode flow rate. Natarajan et al. [113] studied fuel cells with chunking electrode operated under constant pressure. They found that increasing the anode humidity would decrease the reverse osmosis process, which lead to uneven current density distribution and more chunking electrode exposure to flooding.

Drying one or both reactant gases is another restoration measure during flooding, which promotes the evaporation of the liquid water [17].

3.3.2. Proper reactant temperature

A suitable cell temperature that maintains sufficient membrane hydration is suggested for cell operating temperature [114]. Improving the fuel cell reaction temperature will increase the saturation pressure. At the same time, the surface tension and the viscosity of the liquid water will decrease, thus increasing the evaporation rate [83]. The liquid water inside the fuel cell evaporates, hence the threat of flooding removed. He et al. [83] observed a fuel cell exposed to flooding. They fixed the other operation parameters, and flooding was removed after a 40–50 °C temperature rise. Hosseinzadeh et al. [115] pointed out that higher the operating temperature, higher the mass flow is needed for humidification and water production cannot meet this requirement. This effect can be partly improved by reducing the temperature gradient when the operating temperature increases.

As shown from the gas temperature and relative humidity curves in Fig. 9 [82], the gas RH range is not large. When membrane dehydration occurs, reducing the fuel cell temperature or gas excessive coefficient will increase the gas RH.

If membrane dehydration occurs, raising the humidification temperature will help to bring more water into the flow field, and lowering the operation temperature prevents too much water from flowing away. Another method is increasing the current density to generate more water to humidify the membrane. The extra power that results from increasing the current density can be stored in batteries [75].

3.3.3. Proper anode and cathode pressure

Under normal working conditions, pressure in both sides of the membrane is constant. The electric-osmosis is much greater than the reverse osmosis [107]. Voss et al. [116] designed a fuel cell whose cathode pressure is greater than the anode pressure, thus eliminating the above phenomenon. Then they observed improvements of the performance. Most cathodes generated water osmoses to the anode side eliminating the flooding effectively. This particular design is suitable for fuel cells with large area flow field, since the manufacturing cost and difficulty will decrease with the increase of the fuel cell area. Because a large pressure difference between the anode and the cathode may cause mechanical damage of the membrane, the pressure difference should not exceed 500 mbar [107].

Rodatz et al. [117] used the pressure pulse method to remove water droplets. The pressure waves generated by pumping pushed the gas into the fuel cells instantaneously. The pumping pressure is

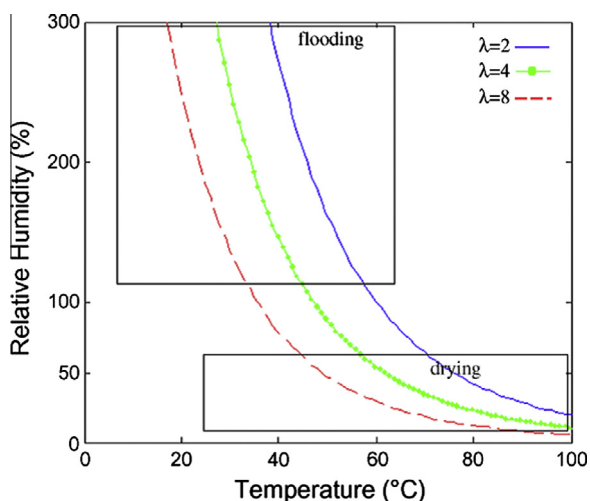


Fig. 9. Temperature and RH curve under different stoichiometry ratios [82].

higher than the normal operating pressure. Another method is to put the outlet into a pressure vessel to increase the inlet and outlet pressure gradient. Then the internal flow rate increased, thus purging the droplets inside the fuel cells.

Tang et al. [118] reported a Vacuum-assisted drying method which increased the water evaporation and diffusion rate by mean of reducing the boiling point of water. This method is applied to a single PEM fuel cell and compared with the method of purging water using dry N₂. Electrochemical impedance spectroscopy (EIS) was used to monitor the drying process. Experimental results showed the vacuum-assisted drying method provides a higher water removal rate than the dry N₂ purging method.

3.3.4. Control reactant gas flow rate

Too low a flow rate into the fuel cells is to the disadvantage of removing liquid water, even further leading to gas starvation. In practice, the reactant gas flow into the fuel cells is more than the quantity required for reaction, as the air stoichiometry generally is greater than two [112].

Natarajan et al. [113] studied the chunking fuel cells operating at constant voltage mode, and pointed out that the flow of liquid water is a strong function of air velocity. Reducing the inlet flow rate of the cathode led to the liquid water being evaporated and purged by the flow gas decrease. Under this condition, the inlet gas is easier to saturate and the flooding area shifts near to the gas inlet. Generally, lower reactant gas flow rate leads to the current density being unevenly distributed. They also found that there was a serious current decrease on some electrode blocks. On the contrary, increasing the gas flow rate postponed the current decrease, but lead to flooding and current decrease near the outlet. They explained it as due to the membrane near the outlet drying by the air, and then the internal resistance increase. Hakenjos et al. [119] found increasing the reactant gas flow rate would increase the fuel cell performance, as the excess reactant coefficients increase, the purge effect is strengthened. They also detected the temperature is higher where liquid water exists, caused mainly by the condensate formation enthalpy [119]. Moreno et al. [120] showed anode purging is required to avoid flooding. A cathodic fan is conducted to forced air convection to improve water transport, further helping the water management.

Obviously, the influence of gas flow rate on the fuel cells life time needs to be of deep concern. Wahdame et al. [121] studied the importance of gas flow rate management. They pointed out that the fuel cells durability is closely related to the gas flow rate. For example, decreasing the pressure inside the fuel cells may cause an increase in the internal mechanical stress, uneven flow rate and uneven water distribution, leading to hot spots inside.

3.3.5. Proper fuel cell stack design

Fuel cells design, especially the flow field design, is the key to water management. One of the flooding Mitigation methods of the conventional parallel flow field is to increase flow rate or temperature, to accelerate evaporation [113]. Nguyen [122] and Wood [123] conducted an experiment comparing the interdigitate flow field and parallel flow field, and found the inter digitate flow field better for higher current density; the performance was 50–100% higher. Inter digitate flow fields are more resistant to flooding and provide a more uniform reactant gas supply.

Liu et al. [124] compared 3 kinds of flow field design (inter digitate, series and parallel flow field). During operation, inter digitate and series flow field flooding occurred later and the flooding area was smaller. Jiao et al. [125] investigated the characteristics of liquid water removal form GDL experimentally. Visualization of liquid water transport has been conducted by using transparent flow channel, and liquid water removal from GDL under the land was observed for all the tested inlet air flow rates. The conclusions

of their study confirmed that cross flow is practically effective to remove the liquid water accumulate in GDL under the land area.

Proper fuel cell components design accelerates the evacuation of the liquid water [107]. The gas diffusion layer of the fuel cells contains a tetrafluoroethylene for its high hydrophobicity [126]. Performance loss caused by accumulation of liquid water could be reduced by adding hydrophobic particles into the gas diffusion layer, or by increasing the porosity of electrode at the cathode outlet where the liquid water accumulated. Some of the methods involve putting some carbon clothes inside the carbon fiber paper, on which some holes and slots are made to facilitate the accumulation of water [34]. Lin et al. [127] found that coated aluminum bipolar plates demonstrate the hydrophobic property than the raw material.

Qin et al. [128] applied a novel PEM fuel cell flow channel consists of a hydrophilic plate in the flow channel, and analyzed water removal and transport in the flow channel numerically. They carried out a parametric study to determine the optimal values for the surface contact angle, the length and height of the plate. The results showed that the liquid water droplet on the membrane-electrode assembly (MEA) surface can be removed effectively using the novel flow channel [128].

The thinner the fuel cell membrane the better its mechanical durability is, but its ohmic resistance is also higher. Especially in large current density, the movement of water is mainly caused by electronic drag phenomenon, which leads to massive water transfer to cathode side with flooding forming, and humidity in the membrane and anode side is lower. Local membrane dehydration increases the ohmic loss. Flooding increases the concentration loss. Dehydration decreases active area of the anode catalyst, thus increasing the activation loss [129].

3.3.6. Proper current density

The water generated is proportional to the current density. When flooding decreases the current density, the water generated is reduced. With the decreasing current density, the reactant gas decreases, thus leaving more gas in flow channels to purge the liquid water, which contributes to the recovery of flooding.

3.3.7. Clean reaction gas

Chen et al. [130] applied non-steady state model which took into account the effect of the impurities on the membrane, to study the conduction properties of water in the membrane, as well as the influencing factors of its characteristic time to reach steady-state. The results showed that higher initial current density, larger water flux from anode to cathode, lower operation current density and lower impurities content on the membrane are accelerating the water dynamic response.

4. Dynamic response

Dynamic behavior is a key property in vehicular application of PEM fuel cells [131]. Understanding the dynamic behavior of the PEM fuel cell is essential to achieve longer fuel cell lifetime and better performance [60]. Dynamic response of the PEM fuel cell is a very complex process; affected by its structure, operational modes and many other factors [132]. With different parameters, the dynamic response of a fuel cell varies widely. When the external load changes, the fuel cell goes through a transient fluctuation process, which in turn affects parameters such as the gas excessive coefficient, the temperature, the pressure, and the humidity. The parameters' fluctuation also leads to fuel cell degradation.

The studies concerning the test of fuel cell dynamic response was very limited, mainly recorded experiment data of different working conditions, without in-depth study on the relevant

mechanism. This is mainly because with the new test methods available today, it is difficult to observe the physical changes inside. Hamelin et al. [133] were the first to conduct the research on dynamic response of PEM fuel cells. They applied the Ballard MK5-E to observe voltage undershoot, voltage overshoot, and current reverse. The response time of the system was 0.15 s, which is much shorter than those reported in new research. Their study gave no explanation of the short response time. Kim et al. [134,135] carried out a series of tests on the influences of the gas and fuel stoichiometric ratio, the flow field design and the step voltage on the fuel cells dynamic performance. Their work focused on the process of load changing from normal to gas starvation, which represented the limits of working conditions. Tang et al. [136] conducted experiments using the fuel cell with Nexa module to study the factors which affect the dynamic response. They conducted five tests, including start, stop, step loading, regular loading, and irregular loading. The fuel cell performance recovering was found during the purge process under specific loads. The overshoot and undershoot phenomenon were observed during the test, but the charge capacitance effect was not observed during the current overshoot. The change of the voltage peaks follows the changes of the current. The operating temperature changes rapidly in responses to the changes in loads, which was very smoothly with no obvious overshoot and undershoot. The gas flow rate directly follows the load changing, but not proportionally, it also depended on the reaction inside and the water condition. Their experiment results are a good model validation of the fuel cell and a reference of control and management.

Many researchers studied on modeling the PEM fuel cells dynamic response. Fonseca et al. [137] built a PEM fuel cells dynamic model. A nonlinear differential flatness control was applied on the PEM fuel cells air supply system. The control parameters were cathode pressure and oxygen stoichiometric ratio. The control system was validated by the dynamic model. Meidanshahi [138] built a one-dimensional dynamic model to study the dynamic response of the PEM fuel cells. The steady state operation parameters were optimized using a DE algorithm. They compared the result of the fuzzy control algorithm with the result of a traditional PI algorithm, and indicated that the average power density of the fuzzy control algorithm responses faster. Yerramalla [139] and Pathapati [140] built a dynamic response model, which modeled fuel and gas time domain variation in the flow channels to study the voltage overshoot and undershoot phenomenon. Loo et al. [132] built a one-dimensional two phase PEM fuel cells dynamic model to study the fuel cells dynamic response, by which they predicted the fuel cells transient response, activation and ohmic over potential, water saturation, and water content of the membrane. With the current density increasing, the fuel cells voltage dropped, response time of the membrane humidity was 50 s. About 150–200 s after the voltage drop came the flooding. They found a certain fuel cell, with the design parameters fixed, the dynamic response was affected by many operating parameters.

4.1. Dynamic response characteristics and influencing factors

The dynamic response of the PEM fuel cells was influenced by many parameters, mainly the structural and operational parameters. The structural parameters include gas diffusion layer [141], channel size [142] etc. Cho et al. [141] studied the influence of the membrane water balance on the transient response of the PEM fuel cells. They found the gas diffusion layer with a larger cellular structure has a better dynamic response character, because the large cellular structure could balance the pressure gradient along the direction of the gas diffusion layer. Kim et al. [142] analyzed the dynamic response of an air-blowing PEM fuel cell affected by the channel size and operation parameters. The water

management parameters including operating temperature, fuel voltage, and anode humidity are calculated through impedance analysis applying EIS tests.

Many factors affect the dynamic response of fuel cells, which including the loading speed, loading rate, stoichiometric ratio, temperature, humidity and pressure. The following will introduce them in detail.

4.1.1. Loading range

Fig. 10 [143] shows a single fuel cell dynamic response curve of voltage under different loadings, with the anode and the cathode stoichiometric ratios both are 3. This is a typical dynamic response curve that cannot meet the load requirements due to restricted air flow [143]. The negative voltage pulse process can be observed from the group loading curves. The larger the load, the more negative the voltage pulse amplitude, and more time is required to reach a new steady-state value.

4.1.2. Loading speed

Fig. 11 [144] presents a change in voltage for a group of dynamic response curves of a single fuel cell stack with different loading times and average voltage [144]. The shorter the time is and the faster the voltage load, the greater is the magnitude of the voltage negative pulse. When loads, the electrode potential and overall fuel cell voltage drop, sometimes even leading to a negative voltage because the cathode lacks oxygen. Therefore, to improve the fuel cell stack's stability and longevity, we should try to reduce the loading speed and extend the loading time.

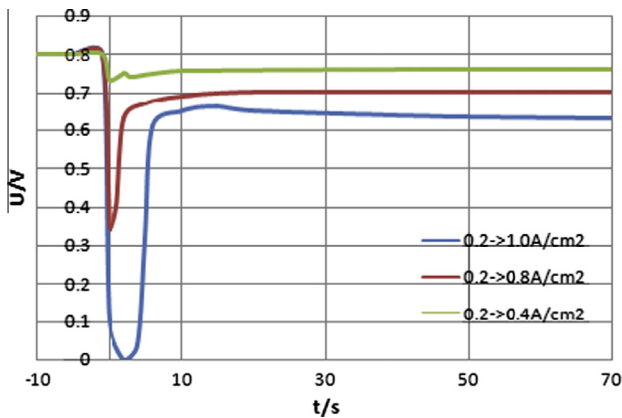


Fig. 10. Dynamic response curves under different loading range [143].

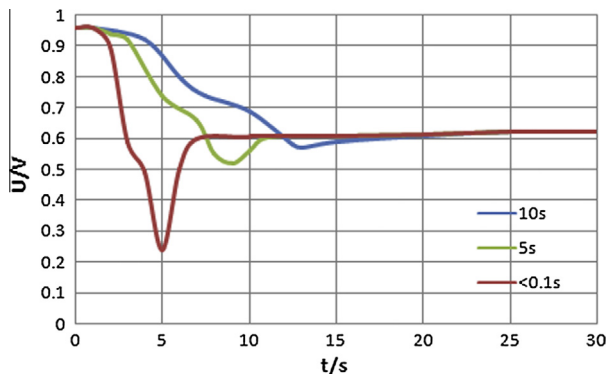


Fig. 11. Dynamic response curves under different loading speed [144].

4.1.3. Stoichiometric ratio

Cho et al. [145] did an experiment analyzing the effects of the stoichiometric ratio on dynamic response. Fig. 12 [145] shows when the stoichiometric ratio of H_2 and air change, the fuel cell voltage undergoes basically the same process of change, also as the gas stoichiometric ratio increases, the dynamic response and voltage change accelerate.

4.1.4. Humidity

Humidity is another important factor affecting the dynamic response of a fuel cell. Fig. 13 [145] is a 100–200 A dynamic voltage response curve with different gas humidity. At 100% humidity, the dynamic response is optimal. If the loading process is changed and there is insufficient water supply, result in membrane dehydration and decreasing of the membrane ionic conductivity, with a corresponding increase in voltage drop. In Fig. 13 [145] it is evident that the cathode gas humidity has a slightly larger impact on the fuel cell dynamic response than the anode gas humidity [145].

4.2. Gas starvation is the key factor affecting the fuel cell dynamic performance

The above analysis indicates that the loading speed, loading range, stoichiometric ratio, and the humidity affect the dynamic

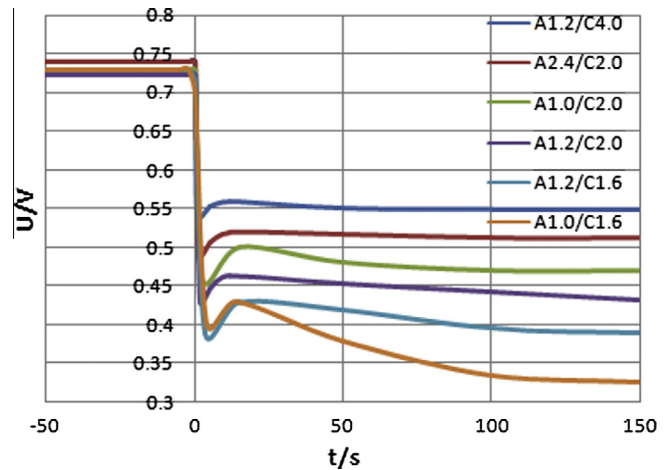


Fig. 12. Dynamic voltage response curves under different reactant stoichiometry ratio [145].

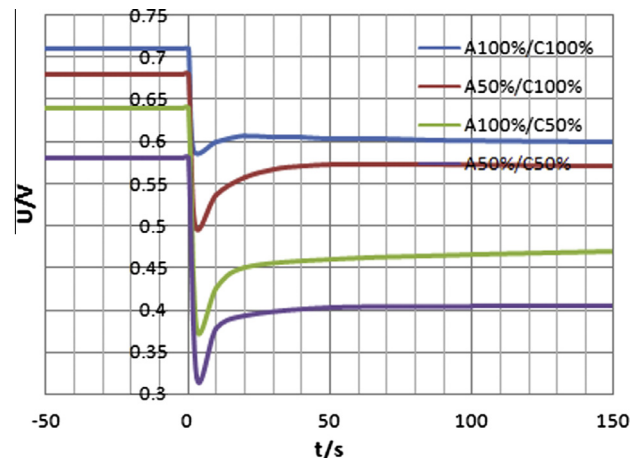


Fig. 13. Dynamic voltage response curves under different humidity [145].

response of vehicle used fuel cells. Fig. 13 [145] shows that the fuel cells obtain a good dynamic performance in the case of the cathode and anode when both are 100% humidified.

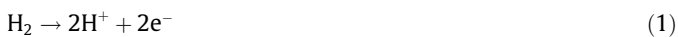
During the loading process the fuel cells require more reaction gas, but the gas flow rate in the channels is far less than the speed of current change. Thus the gas starvation caused by the large loading speed, large loading range and small excess coefficient, is the key factor affecting the fuel cell dynamic response.

In the load changing process, it is important to know how the automotive fuel cell gas supply with a large area behaves in various parts of the flow field. Weng et al. [70] studied the voltage fluctuation in a segmented fuel cell with current cycling between 700 and 70 mA cm⁻². They found in segments 5–8 in the downstream of the fuel cell, the gas in the electrode could not be supplied quickly enough when the load suddenly increases from 70 mA cm⁻² to 700 mA cm⁻² [70].

Starvation, which describes the operating conditions of fuel cells in sub-stoichiometric fuel or oxidant feeding, is a potential cause of fuel cell failure. Reactant starvation can be divided into local starvation and overall starvation. Local starvation is insufficient reactant gas supply in partial area of the catalyst layer. The performance deterioration of external current and voltage is not very obviously. Overall starvation is insufficient reactant gas supply in cell level or stack level, the performance deterioration of external current and voltage is obviously.

The local starvation of the PEM fuel cell leads to the carbon corrosion of the MEA, which further causes catalyst loss and performance degradation [146].

In normal conditions, the hydrogen at the anode is oxidized according to:



At the cathode, oxygen is reduced according to:



The global reaction is therefore:



Besides water, it also releases electricity and heat.

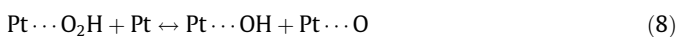
Reactions (1) and (2) actually occur in several successive steps. Adsorption of H atoms, according to [147,148]:



Hydrogen discharge step, according to [147,148]:



Damjanovic et al. [149] and Sepa et al. [150] explained O₂ reduction reaction mechanism, which was summarized by Xu et al. [151]:



When local starvation, carbon corrosion occurs [148]:



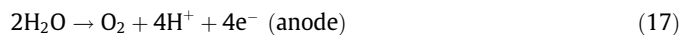
Ball et al. [152] showed that carbon corrosion occurs in three successive steps [148]:



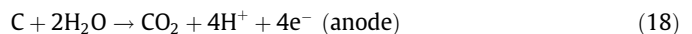
Local starvation further leads to catalyst dissolution and reprecipitation. The Pt particles have been proved to dissolve into Pt²⁺, according to the following mechanism [148,153,154]:



Cathode or anode overall starvation may causes hydrogen generation at the anode and oxygen generation at the cathode. Under anode starvation, current density reduction leads to a high anode potential [52]. In this case, water electrolysis at the anode side generates hydrogen or oxygen. The reaction of generates oxygen at the anode:



When lack of hydrogen, the carbon corrosion at the anode side occurs:



Similarly, under cathode starvation, the reaction of the cathode generates hydrogen. The normal reaction at the cathode side (Eq. (2)) changes to [52]:



The fuel cell voltage reverse occurs due to the existence of oxygen at the anode side and hydrogen at the cathode side.

Many factors will lead to local starvation in a fuel cell: poor cell design or machining, leading to uneven mass distribution in the flow fields; poor stack design or assembly, causing uneven flux distribution between cells; poor water management, resulting in channel blockage by flooding; poor heat management during cold start-up, causing ice blockage; membrane electrode assembly degradation caused the increase of hydrogen permeability, the hydrogen through membrane before reacts to form proton; existence of contaminant gas decreases the partial pressure of reactant gas; contaminant blocks the gas diffusion layer, prevents the reactant gas form contacting the catalyst layer. Overall starvation mainly caused by control module failure and incorrect operation, inducing sub-stoichiometric gas feeding [52].

Load cycling is one of the main reasons causing the gas starvation of fuel cells in vehicular application [155]. Many scholars have studied the fuel cells starvation. Ohs et al. [156] built a two-dimensional steady model to study the fuel cells gas starvation during transient load changing. They diluted the reactant gas by nitrogen to create a gas starvation condition, and then observed carbon corrosion and water electrolysis at the cathode. The model also included the factors of hydrogen permeation and local condensate water. The results indicated that the fuel cell's voltage dropped rapidly where the gas starvation occurred. Serious carbon corrosion and water electrolysis happened at the cathode when the voltage gradient of the electrode and the membrane was greater than 1.2 V. Li et al. [157] simulated the fuel cell gas starvation during dynamic loading. They presented a diagnosing method for fuel cell gas starvation, which compared voltage response time constant and pressure response time constant. The method was validated by experiment. A two-dimensional numerical single cell model was built by Yang et al. [158], which was applied to simulate the voltage reverse phenomenon of the fuel cell. They observed the water electrolysis phenomenon at the catalyst layer near the cathode inlet. Hu et al. [159] built a two-dimensional prediction model along the flow channel, and predicted the carbon corrosion of the cathode catalyst layer. Simulation results indicated higher operating

voltage, lower proton conduction rate, and higher oxygen penetration rate would accelerate the carbon corrosion.

4.2.1. Feed starvation at the anode side

It is possible for one or more MEAs in a stack, or even a complete stack in a multi-stack system, to show a reverse in polarity during fuel cell operation. Various circumstances can result in a fuel cell being driven into voltage reversal by the other cells in the series stack, and severe damage to the MEAs may result. The most likely reason for cell reversal is reactant starvation of the MEA at the anode, due to inadequate fuel supply. Fuel and oxidant starvation can occur during a sudden change in reactant demand, such as start-up and load change. Taniguchi et al. [50] analyzed electro-catalyst degradation during fuel starvation and found anode ruthenium dissolution and cathode platinum sintering. Sanyo Electronics reported a fuel cell performance degradation caused by reactant starvation in a national R&D project on PEMFCs [160]. Kim et al. [134] reported a vacuum effect during anode starvation, which causes the anode gas to be drawn from the stack manifold and ambient air to be inhaled into the fuel cell. By cyclic voltammetry (CV) measurements, Kang et al. [161] also detected cell reversal when the fuel supply was inadequate.

Cell reversal occurs when the fuel cell stack is loaded and not enough fuel is supplied to the anode. Drawing excessive current from any single cell—i.e., more than its fuel delivery can produce—can lead to cell reversal. Taniguchi et al. carried out an experiment using a single cell that imitates cell reversal in a stack. After cell reversal degradation under conditions of 100% fuel utilization, using external direct-current power sources, various characterizations were carried out. The potential change in the cell terminal voltage and individual electrodes during the cell reversal experiment was measured using a cell connected to a reference electrode by an electrolyte junction [50].

Taniguchi [50] showed the change in cell terminal voltage with time, as well as time-dependent changes in the anode and cathode potentials. According to their results, as soon as the experiment started, the cell terminal voltage rapidly dropped and became negative, and the MEA changed polarity due to cell reversal. After this initial rapid drop, the cell terminal voltage showed a steady decrease with time. Cell voltage reversal occurs when the anode potential increases. When the anode potential rapidly increased to nearly 1.5 V, it became more positive than the cathode potential. This result indicated that the anode potential increased as soon as the experiment had started, until water electrolysis occurred because the anode was starved of fuel.

Taniguchi [50] also found that ruthenium dissolution from individual catalyst particles occurred in the anode catalyst layer, with the most severe degradation occurring in the anode plane and the area close to the outlet region.

Patterson et al. [162] studied the catalyst layer corrosion which was caused by local anode gas starvation. They placed a barrier inside the anode flow channel. After 100 h operation, severe corrosion appeared on the catalyst layer near the border of the barrier; however no corrosion was observed on the catalyst layer elsewhere. Fuel starvation causes severe and permanent damage to the PEMFC electro-catalysts, and even momentary starvation must be absolutely avoided.

4.2.2. Feed starvation at the cathode side

Oxidant (air) starvation can also occur during operation. Since water is produced at the PEMFC cathode via three processes—transport by humidified reactants, water generation from the cathode reaction, and transport via electro-osmotic drag associated with proton transport across the PEM—condensed liquid water present within the cathode tends to block oxygen from accessing the electro-catalyst. A sudden change in oxygen demand, such as

at start-up and load change, and water accumulation during long-term operation can cause air starvation.

Rao et al. [163] reported air starvation through numerical simulation, and found that it is not enough to control a lumped oxygen excess ratio (OER) parameter to avoid oxygen starvation. The variation in the process gain suggests that a nonlinear control approach is most likely needed to solve the problem of oxygen starvation.

Taniguchi et al. [51] found degradation caused by air starvation to be much smaller than under anode starvation because of the large difference in anode degradation. However, long-term operation (for a few tens of minutes) under the air-starved condition led to accelerated degradation in the electrode and in PEMFC performance. Therefore, air starvation also has to be avoided to prevent a dramatic decrease in fuel cells performance.

Shen et al. [164] found that with increased current density and decreased air stoichiometry, the voltage difference between the inlet and outlet increased. When loaded dynamically in load following mode, the fuel cell would suffer a temporary voltage fluctuation due to air starvation because the air response rate lagged behind the loading rate. They suggested that if the pre-supplied air stoichiometry was 1.5, the fuel cell would not suffer from any air starvation at the loading transient.

Liu et al. [52] measured the current distribution during the cathode starvation. They observed severe local current drop at the oxidant starvation affected area, and indicated the oxidant is unevenly distributed on the catalyst layer. However, unaffected area is insensitive to the oxidant starvation.

Natarajan et al. [165] studied the local current density distribution for 4 h through various oxidant flow rate and temperature. The main consequence they observed of oxidant starvation was the decrease of reaction flow rate and current density in segment downstream.

4.3. Measures to improve the dynamic response

When fuel cell load changes rapidly from low to high, gas starvation easily occurs. On account of the irreversible consequence of the gas starvation, effective diagnoses method is important. As said before, under fuel starvation, the fuel cell voltage will decrease sharply or even to negative in a fuel cell stack. In this case, the gas starvation is easy to detect by monitoring voltages of individual cells or groups of cells [166]. Others gas starvation diagnosis methods reported in the literature are based on current distribution monitoring inside individual cells. This method needs preliminary electrode segmentation [52,113,167]. Due to its complexity, it is not practical to diagnose gas starvation during the fuel cell stack operating. Others detected the fuel cell starvation by combining various parameters, including polarization curve study (for the individual cell or all the cells) [52], temperature distribution analysis, CO₂ detection near the cathode outlet (to detect the carbon corrosion), and gas flow direction test of the fuel cell outlet [168]. The last method is predicated on the observation that no starvation could occur as long as the exhaust gas flow out the stack assembly towards ambient and was patented by Reiser [168]. The fuel cell load was disconnected in the case of inward flow direction at the gas outlet. However, this method cannot detect a fuel starvation caused by cathode gas permeation into the anode [148].

During operation the usual approach to mitigate this is to provide enough air before the loads, but the drawback is that this increases fuel cell parasitic power and decreases the system overall efficiency. There have been many studies of the problems related to fuel cells starvation. The majority focused on gas starvation prevention than to the mitigation of its effects. The best mitigation method was careful cell-stack design and control method to ensure uniform fuel distribution [148].

Halalay et al. [146] studied using hydrogen storage material in the anode, which was applied to supply hydrogen proton during gas starvation caused by transient loading or local flooding. They tested three kinds of electrode materials containing TiO_2 , WSi_2 and WO_3 , and the results indicated that the electrode containing WO_3 was the best choice.

He et al. [169] and Ahn et al. [170] presented an air supply system using a static feed forward control and a static feedback control, together with the integrator to ensure that the oxygen stoichiometric ratio was adapted to any load condition. A variable voltage controlled air blower, the voltage of which was changed following the load, thus prevented the cathode side gas starvation. A two-phase flow model was built to verify the feasibility of the system.

Kim et al. [131] firstly built a steady state thermal isolation model to analyze the mass transport and the water transport inside the membrane. A timing control was applied to optimize the oxygen stoichiometry, to avoid the gas starvation. The fuel cell stack and a battery were connected by a bi-directional DC/DC convertor, in order to realize an even power distribution. A dynamic evolution control (DEC) offered sufficient pulse-width modulation (PWM) to ensure fast response of the DC/DC convertor.

Pathapati et al. [140] conducted research on the measures to improve the fuel cell dynamic response. He tested the fuel cell voltage changed with the current density from 50 mA cm^{-2} to 500 mA cm^{-2} , with the air stoichiometric number of 1.1, 1.3, and 1.5 respectively. With the growth of pre-supply air stoichiometric number, the performance of the dynamic response of the fuel cell raised, becoming more stable and faster. When the air stoichiometric number reached 1.5, starvation did not occur.

5. Conclusion

This paper reviews the main factors that affect PEM fuel cells in vehicular application, and summarizes some mitigation measures.

Load cycling is the main character of fuel cells in vehicular application, and is also the main cause of fuel cells life degradation. Load cycling leads to water management and dynamic response two main problems.

During load changing process, the current density of the fuel cell changes frequently. In large current density, the reaction inside generates a lot of liquid water, while a sudden load reduction, the flow rate of the gas within the flow channel is reduced, and then the water content of the gas reduces resulting in a large number of liquid water condense; similarly, during a sudden load increase, the flow rate of the gas within the flow channel is increased, the water content of the gas increases resulting in a large number of reaction formation water driven away and then leads to membrane dehydration.

Flooding and dehydration both have great impact on the fuel cell life time. If too much water vapor, liquid water will be formed in the pores of porous media of PEM fuel cell electrode, which prevents the reaction gas pass to the catalyst layer of the channel, and intensifies the concentration polarization. The reaction gas is diluted by the water vapor, thus the concentration of the gas in the electrochemical reaction interface reduces, and the reaction rate reduces. The active sites on the catalyst layer were flooded by the liquid water. Membrane dehydration increases the proton transmission resistance, intensifies the ohmic polarization, accelerates the membrane degradation, causes the carbon atom on the carrier be oxidized to carbon dioxide, and reduces the activity of catalyst interface.

Fuel cells' flooding is usually diagnosed by observing the voltage, which appeared to be a marked fall. Two main methods to solve the flooding problem are: (i) opening the pulse valve allows

the hydrogen gas to purge the liquid water out of flow channels; (ii) raising the operating temperature to decrease the relative humidity of the reactant gas; (iii) optimizing the fuel cell operation parameters and structure parameters. Membrane dehydration can be mitigated by reducing fuel cells reaction temperature or lower air stoichiometric number.

Reactant gas flow rate is far less than the current change rate, thus the fuel cell dynamic response is the key. Poor dynamic response more easily leads to anode or cathode gas starvation during load cycling. Gas starvation is one of the most critical faulty conditions of the fuel cell during operation, the prevention of which requires appropriate reactant gas supply and distribution. Uneven current density distribution leads to the fuel cell local starvation, and then increases the fuel cell local potential, further promotes the carbon corrosion and the loss of platinum catalyst layer. One of the methods mitigates the gas starvation is using hydrogen storage material in the anode, which supplies hydrogen proton during gas starvation caused by transient loading or locally flooding. Another is applying the advanced gas supply system to realize the reactant gas supply meets the fuel cells load change.

There are challenges in the research of water management and gas starvation problems. Reliable detection methods and feasible mitigation methods are the key to solve the problems. Future approaches should focus on the following aspects: (i) a greater understanding of the fundamental processes of the water transport and the reactant gas dynamic response, which provides theory basis to measures of the water management and the improvement of dynamic response; (ii) advanced material development, such as thin but strong proton exchange membrane that facilitates easy water removal through the membrane and improves the reliability of the thin membrane, a gas diffusion layer with both higher hydrophilic and higher gas permeability; (iii) appropriate structural design, especially the flow field design, improves the water removal and the dynamic response; (iv) advanced control techniques, ensure the fuel cell operates appropriately and avoids of the critical and faulty operation.

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