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### A review of automotive proton exchange membrane fuel cell degradation under start-stop operating condition

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#### HIGHLIGHTS

- A comprehensive review of researches on PEMFC degradation in start-stop condition.
- Include degradation mechanism, accelerated lifetime tests and mitigation solutions.
- Further researches should be taken from aspects such as material and strategy.

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#### ABSTRACT

The lifetime of the proton exchange membrane fuel cell (PEMFC) is the main issue restricting its commercialization. During real vehicular applications, the fuel cell engine mainly experiences four dynamic conditions: load changing, start-stop, idling, and high power. Since the start-stop condition has a great impact on the lifetime of fuel cells, it is necessary to fully understand the degradation mechanism of PEMFC under this condition. This paper discusses the background and progresses in related research, analyses the gas distribution process inside the fuel cells during start-stop, and summarises the main mechanism and factors that lead to the degradation. Then, solutions in terms of material improvement and system control are listed. This review can provide a basis for solving the degradation problem in PEMFCs and improving the cell lifetime.

#### 1. Introduction

The proton exchange membrane fuel cell (PEMFC) has a series of advantages such as high efficiency, fast response rate, and zero pollution [1,2]. Thus, it has been applied in new energy vehicles, portable power sources, distributed power plants, etc., with bright future in fields such as transportation, conveyance, and communication [3]. As an automotive power source, PEMFC can start and respond quickly at a relatively low temperature, and it is environmentally friendly and the fuel is also renewable. As a result, PEMFC is considered to be a very promising power source for zero-emission cars [2].

Lifetime is an important parameter to measure the performance of automotive PEMFCs, and currently it is one of the key limiting factors in their commercialisation [4]. As a fixed power supply, PEMFC can reach a lifetime of 30,000 h, while it can only last 2500–3000 h in automotive applications, which is far from the commercial requirement of 5000 h [5–7]. The degradation of fuel cell components is the primary cause of the short service time. The durability of each component is influenced by various factors, including material characteristics and stability,

operating parameters (temperature, humidity, etc.), operating conditions (start-stop, idling, cold start, load changing, etc.), system integration, and contaminants. In order to improve the lifetime of PEMFC, there has been a focus in recent years on studying its degradation mechanism.

The working condition for automotive fuel cell is dynamic during its use. Pei et al. [8] divided the practical operating conditions into four: load changing, start-stop, high power, and idling. As shown in Fig. 1, they found the start-stop condition contributed 33% to the degradation of PEMFC during practical operation. Compared to the idling and high power conditions, start-stop and load changing are more likely to lead to the degradation of key fuel cell materials [9–11]. Yu et al. tested the degradation rate for PEMFC during start-stop cycles, and showed that the start-up and shutdown processes significantly affect the fuel cell lifetime [12]. Therefore, the start-up and shutdown are critical for cell degradation in vehicle applications, and understanding the degradation rates and the mechanisms during start-stop condition should lead to improved automotive fuel cell durability [13,14].

Existing literatures have focused on the theoretical analysis,

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Fig. 1. PEMFC degradation caused by different operating conditions [8].

experimental verification, and mitigation methods and strategies of PEMFC degradation. Reiser et al. [15] first pointed out in 2005 that the reverse current formed during start-up of the stack was the cause of the catalyst corrosion. Zhang et al. reviewed the literatures on the durability of fuel cell catalysts, and pointed out that the corrosion of the carbon catalyst carrier because of fuel starvation and hydrogen-air interface can lead to the loss and degradation of platinum [16]. These researches are significant for the mitigation of PEMFC degradation under frequent start-stop conditions.

In this paper, we review studies on the degradation of fuel cells under start-stop conditions from three perspectives: degradation mechanism, methods and procedures of representative accelerated lifetime tests, and mitigation solutions.

#### 2. Degradation mechanism

The degradation of fuel cell leads to a reduction in the voltage, thus severely reducing its performance. Lin et al. [17] studied the effect of dynamic driving cycle on the performance degradation of PEMFCs. Their accelerated test showed that, with the increase of running time, the open circuit voltage (OCV) of fuel cells decreased gradually and a much more rapid decrease occurred after 280 h of operation (Fig. 2), indicating degradation of the fuel cell lifetime.

The explanation of fuel cell degradation mechanism and improving their lifetime have become hot research topics. The main reason for performance degradation under start-up and shut-down condition is the formation of the hydrogen-air interface inside the battery. The presence of hydrogen–oxygen interface leads to oxidation reaction in the anode, forming a high potential on the cathode surface and leading to the



Fig. 2. Current voltage-characteristics after different durability test times [17].

oxidation of carbon carrier in the cathode catalyst layer. As a result, Pt particles fall off the catalyst surface, thus decreasing the electrochemically active surface area (ECSA) and performance of the fuel cell. In addition, the uneven distribution of reactive gas can lead to fuel cell degradation.

#### 2.1. Reverse current

Before the start of fuel cell engine, due to the diffusion through the anode exhaust channel and membrane electrode, there will be air in the anode flow field. When activated, hydrogen enters the anode and forms a hydrogen-air interface in the anode flow field. When the fuel cell shuts down, due to the concentration gradient, residual oxygen in the cathode flow field will diffuse through the proton exchange membrane to the anode, forming a hydrogen-air interface with the residual hydrogen there. In addition, when the fuel cell system is shut down, outside air penetrates the fuel cell through the anode channel, also causing the formation of the hydrogen-air interface. The specific processes above are schematically shown in Fig. 3 [12].

United Technologies Corporation (UTC) was the first to propose the presence of hydrogen–oxygen interface in 2000. Reiser et al. [15] proposed in 2005 that the hydrogen-air interface formed inside the fuel cell would cause a high potential in the cathode, which in turn leads to corrosion of the catalyst carbon carrier. This reverse-current decay mechanism has been considered as the basis of PEMFC degradation during start and stop conditions. A one-dimensional steady-state model was proposed [15] to simulate the change of the liquid phase potential along the flow path in the electrolyte when the hydrogen-air interface is generated. A decrease of the liquid-phase potential at the hydrogen-air interface would cause a potential of up to about 1.44 V in the corresponding cathode, as shown in Fig. 4. This high potential would cause corrosion of the carbon carrier in the catalyst layer and performance degradation.

Meyers et al. [18] proposed a more detailed one-dimensional model in 2006 to describe the generation of high cathode potential, as well as further performance degradation due to the uneven gas distribution within the fuel cell. This transient model takes into account the gas transmission along the thickness direction in the membrane electrode, as well as the gas concentration differences along the channel.

Tang et al. [19] pointed out that after the fuel cell shuts down, the residual air and hydrogen would lead to an OCV of about 1.0 V. The presence hydrogen–oxygen interface divides the fuel cell cathode and anode into four regions, as shown in Fig. 5 [10]. Since regions B and C are connected to A through the proton exchange membrane, the potentials in regions A–C are all close to the open circuit voltage (about 1.0 V). Because the cathode potential is 1.0 V higher than the anode, the potential in region D is up to 2.0 V.

Owenjan et al. [20] showed how cathode carbon corrosion develops during start-up/shutdown, and proposed a reverse current model in 2007 to explain the formation of high cathode potential from the aspect of proton and electron movements. As shown in Fig. 6, they argued that the formation of the hydrogen-air interface causes the potential to decrease in the air-covered anode region, the protons move from the cathode to the anode in the opposite direction of the normal movement, forming an air-air cell in the air-filled portion. In order to sustain the oxygen reduction reaction (ORR) at the anode side of the air-air cell, the cathode potential increases until carbon oxidation occurs, supplying protons needed in the anode for ORR.

Yousfi-Steiner et al. [10] proposed that after the hydrogen–oxygen interface is generated, the cell should be regarded as a generator in parallel with an electrolysis cell, rather than two original cells. As shown in Fig. 7, Cell 1 is equal to a generator that has current output, since its cathode and anode are respectively supplied with air and hydrogen. Meanwhile, Cell 2 could be regarded as an electrolysis cell, since both of its electrodes are supplied with air. By calculating the terminal voltage and potential for both devices, it was concluded that a Download English Version:

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