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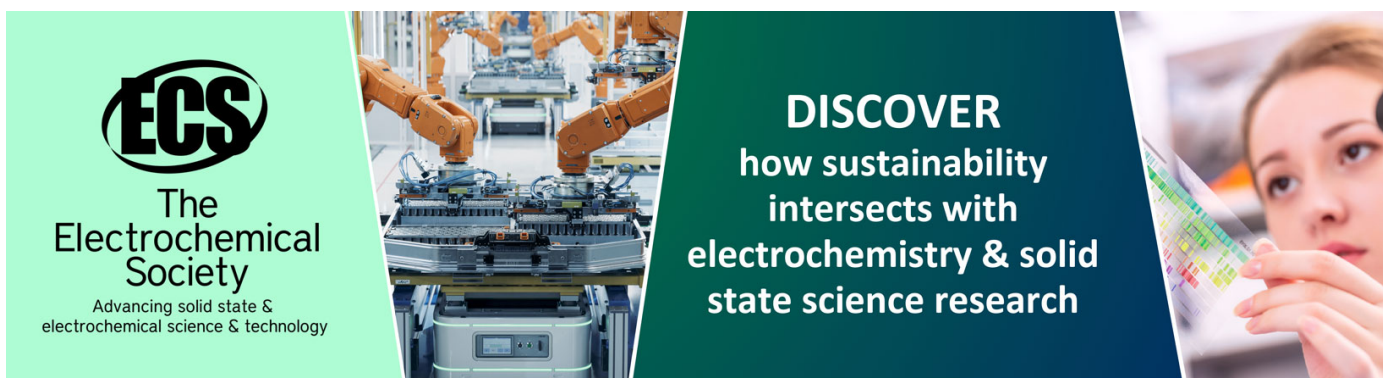
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To cite this article: Ke Xu *et al* 2020 *IOP Conf. Ser.: Earth Environ. Sci.* **558** 052041

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The review of the degradation mechanism of the catalyst layer of membrane electrode assembly in the proton exchange membrane fuel cell

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Abstract. With the rapid depletion of fossil reserves, unstable prices of fossil commodities and the negative effect of fossil fuel on the environment, the demand for clean energy power generation increases. Proton exchange membrane (PEM) fuel cells are a prominent technology for power generation in a variety of applications such as fuel cell vehicles, portable power supplies, stationary power stations and submarines. With their high power density, low emission, low operating temperature, high efficiency, noiseless operation and simplicity of design and operation, PEM fuel cells have a number of attractive advantages over traditional power sources. In this paper, the degradation mechanism of the catalyst layer of the membrane electrode assembly and the core component of the proton exchange membrane fuel cell are summarized. Besides, the degradation mechanism of the Pt-based catalyst, carbon support and Nafion ionomer are obtained. Considering the agglomeration and growth of Pt catalyst, Pt loss and migration, active site pollution and other micro processes, the degradation of catalyst is analyzed in depth. Furthermore, the carbon corrosion process is studied under the normal operation, fuel starvation of the anode and partial hydrogen coverage of the anode processes. In addition, the chemical degradation of Nafion ionomer and the effect of the length of the side chain to the electrode structure are discussed. Eventually, the improved strategies for the failure of the catalyst layer of the membrane electrode assembly are proposed, in the hope to provide useful guidance for the development of long-life proton exchange membrane fuel cells in commercialization.

Keywords: Proton Exchange Membrane Fuel Cell; Membrane Electrode Assembly; Catalyst Layer; Degradation Mechanism; Mitigation Strategy.

1. Introduction

With the increase of environmental pollution and fossil energy consumption, the demand for clean energy had risen. Proton exchange membrane fuel cell (PEMFC) owns the advantages of clean, quiet,



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high-efficiency and pollution-free, which is applied in various scenarios, such as fuel cell vehicles, energy storage power stations, stationary combined heat and power supply, backup power, offshore power generation [1-3]. According to the plan proposed by the Department of Energy of United States, the lifetime for fuel cell vehicles is at least 5000 h, above 20000 h for fuel cell buses and 40000 h for stationary applications [4]. The currently commercialized product, Toyota Mirai vehicle which is equipped with the proton exchange membrane fuel cell technology, can operate at minus 30°C and reach the maximum output power up to 114 kw. Panasonic's combined heat and power product, Ene-farm has produced 700 W of proton exchange membrane fuel cell home-used energy storage products, which can provide users with combined heat and power services, with the operating lifetime up to 40000 h. Therefore, the preparation of long-life proton exchange membrane fuel cells with high durability is an essential step of the development in the field of fuel cell technology. Membrane electrode assembly (MEA), the core component of PEMFC, is the position where hydrogen and oxygen react. The decay degree of MEA largely affects the durability of fuel cell, which is determinant to the life of fuel cell. Therefore, the development of high durability and long-life membrane electrode is of great significance to promote the commercial application of proton exchange membrane fuel cell. As the reaction position of the membrane electrode assembly, the catalytic layer plays an important role in improving the performance and durability of the electrode. Currently, most research for the catalyst layer of membrane electrode assembly used in PEMFC focuses on the design for improving battery performance, such as highly active catalyst design, high performance membrane composition and structural design. However, we lack the durability study of PEMFC, especially the study for the degradation mechanism of the catalyst layer of membrane electrode assembly in PEMFC. This paper summarized the degradation mechanism of Pt-based catalyst, carbon corrosion and Nafion ionomer attenuation in the catalytic layer of the membrane electrode assembly in PEMFC. Besides, several mitigation strategies have been proposed to guide the design for the catalyst layer with high durability in PEMFC, which can facilitate its commercial application.

2. The principle and structure of membrane electrode assembly in proton exchange membrane fuel cell

A proton exchange membrane fuel cell is an electrochemical device that converts fuel chemical energy into electrical energy. It consists of a membrane electrode assembly, a flow field plate, an end plate and seals. As the core component of proton exchange membrane fuel cell, membrane electrode assembly is composed of catalytic layer, proton exchange membrane and gas diffusion layer. The catalytic layer is generally composed of Pt-based catalyst, carbon support and Nafion ionomer. The proton exchange membrane generally adopts perfluorosulfonic acid membrane. Currently, it mainly comes from Nafion series membrane produced by DuPont, Gore series membrane developed by Gore, Aquivion membrane produced by 3M. The gas diffusion layer is generally composed of a microporous layer and a gas diffusion base layer which is made by carbon paper or carbon cloth. Hydrogen and oxygen through the gas passage flow field plate reach the anode and cathode of the fuel cell, respectively. Then cross through the gas diffusion layer of the anode and cathode, and arrive at the catalyst layer. Under the action of the anode catalyst, hydrogen dissociates into hydrated protons and electrons. The hydrated protons are transferred to the cathode side through the sulfonic acid group of the proton exchange membrane, and the electrons are transferred to the cathode through the external circuit. The oxygen molecules on the cathode side are combined with the hydrated protons and electrons to generate water molecules. During the electrochemical reaction, in addition to generating electrical energy, it also releases thermal energy. The theoretical thermodynamic efficiency of proton exchange membrane fuel cell up to 83%, the actual efficiency of the stack is 50%-60%, much higher than that of the heat engine of 20%-40%.

3. Catalytic layer degradation mechanism

The degradation of the catalytic layer mainly includes the degradation of the Pt -based catalyst, the catalyst support and the Nafion ionomer. Their degradation results in the reduction of the electrochemically active area, and the performance for fuel cell is further reduced.

3.1. *Platinum-based catalyst degradation mechanism*

The degradation mechanism of Pt-based catalyst mainly includes: (1) Pt particle agglomeration and growth, (2) Pt loss and migration, (3) contamination of active sites caused by impurities [5]. These reduce the active area of the catalyst or increase the contact resistance with the catalyst support, so that the activity of the catalytic layer is significantly attenuated during long-term operation.

The agglomeration and growth of Pt particles is the most important mechanism of catalyst degradation in PEMFC. It is generally believed that Pt nanoparticles tend to agglomerate into large particles due to their high surface energy relative to large particles, leading to the reduction in active area [6]. Ferreira et al. analyzed the degradation performance of the membrane electrode assembly in PEMFC after 2000 h operation under open circuit conditions, found that Pt particles were dissolved in the Nafion ionomer phase and then deposited on the surface of large particles, resulting in larger Pt particle size. This process is called “Ostwald ripening” [7]. Padgett found that Ostwald ripening is the degradation mechanism that causes Pt nanoparticles to turn into coarse particles. The lower the porosity of the carbon support, the catalyst particles are more prone to go through severe coarsening phenomenon. Therefore, the author uses porous carbon with higher porosity as a carrier to reduce agglomeration, and proposes a strategy for the mitigation of Pt-based catalyst decay [8].

Pt loss and migration is another degradation mechanism for Pt-based catalyst. Ferreira and More et al. observed Pt enrichment between the cathode and membrane interface [9]. Guilminot et al. found Pt enrichment at the interface between anode and membrane [10]. Sabawa et al. observed Pt enrichment in the membrane during the freeze-thaw cycle experiment [11]. This phenomenon is mainly due to the influence of many factors on the migration and redistribution of Pt, including potential, operating time, potential cycle times, battery operating conditions, membrane permeability and other component conditions. Brian et al. used a 3D analysis method to study the Pt degradation on different carbon supports. The electron tomography results show that the agglomeration of Pt nanoparticles mainly occur at the edge of the aggregated graphitized carbon particles, resulting in poor Pt dispersion in the accelerated degradation test [12].

Contamination of active sites caused by impurities is also an important mechanism affecting the degradation of Pt-based catalysts. Generally speaking, according to different sources of pollution, impurity pollution can be divided into two categories: one being the gas pollution derived from the reaction gas and air, such as CH₄, CO, CO₂, H₂S, NH₃, NO, NO₂, SO₂, SO₃ and O₃ [13]. And another type including the system derived from the contaminants, such as metal ions from the system component and silicon (such as a pair of metal plates, films, sealing gasket) [14]. Considering the effective time, the poisoning dose and the reversibility of the poisoning effect, different pollutants exhibit different poisoning effects on the Pt catalyst. The most common contaminants are CO, which are typically the byproduct from the reforming of natural gas. A small amount of CO in the fuel cell inlet gas is preferentially adsorbed on Pt catalytically active sites, blocking the passage of H₂ contact sites and reducing catalyst activity. Even trace CO impurities derived from the reaction gas can cause fuel cell performance degradation due to anode kinetic loss, especially during long-term operation [15]. Hassan et al. obtained the PtW/C catalyst exhibit better performance than that of the Pt/C catalyst. This is because the doping of tungsten adjusts the electronic structure of Pt and reduces its CO adsorption performance [16]. Bilondi et al. studied the effect of CO pollution on the hydrogen side of PEM fuel cells by simulation and experiment, when 53 ppm CO was applied at 0.6 V, the current density decreased from 2 A·cm⁻² to 0.2 A·cm⁻². When pure hydrogen was added for 60 min, most of the properties were recovered [17]. Sulfur-containing substances such as H₂S and SO₂ can cause irreversible decay of the catalyst and reduce battery performance. Mohtadi et al. adopt cyclic voltammetry to detect two kinds of sulfur-containing substances on the Pt surface at the cathode side exposed to SO₂ or H₂S atmosphere, which are strong adsorption and weak adsorption on the Pt surface, respectively [18]. Prithi et al. studied the recovery of battery performance after SO₂ poisoning and found that the adsorption of sulfur on platinum led to the decrease in catalyst utilization. Recovery experiments show that sulfur is irreversibly adsorbed on the catalyst surface in the low current density region, and SO₂ will rapidly hydrolyze to

form sulfuric acid at higher current density in the presence of water, resulting in partial performance recovery [19].

3.2. Carbon Corrosion Mechanism

Nano Pt particles are usually distributed on carbon to obtain maximum utilization and reduce costs. However, under the conditions of high temperature, high water content and high potential, carbon carrier is easy to degrade, which is generally known as carbon oxidation or carbon corrosion. Carbon corrosion is an important degradation mechanism, which can damage the performance of PEMFC by destroying the connectivity of catalyst, destroying the pore structure of electrode, losing hydrophobicity and increasing the particle size of catalyst. Generally speaking, carbon corrosion mainly occurs under three conditions: normal operation potential, insufficient hydrogen supply to anode and partial hydrogen coverage of anode.

Carbon corrosion occurs as a chemical or electrochemical process under normal operating potential. Furthermore, carbon oxidation takes place in two ways: one is the formation of oxygen-containing groups on the surface due to incomplete oxidation, and the other is complete oxidation to produce CO_2 . The potential has a great influence on carbon corrosion. Kangasniemi et al. observed obvious oxidation of carbon surface under the experimental conditions of potential higher than 0.5 V at 65 °C and 1.0 V at room temperature [20]. Merzdorf et al. studied the mechanism of carbon corrosion by on-line analysis of cathode outlet gas composition by using non dispersive infrared technology. The results show that carbon corrosion is the main cause of fuel cell performance degradation, and the carbon carrier corrosion phenomenon is obvious between 1 and 1.5 V [21]. In addition, carbon is easily oxidized at a low potential in the presence of Pt [22].

Carbon corrosion is prone to occur when the anode hydrogen supply is insufficient (fuel starvation) [23]. By using transmission electron microscopy, element distribution and electrochemical methods, Taniguchi et al. analyzed the attenuation of cathode catalyst caused by insufficient hydrogen gas supply at anode. It was found that the active area of electrocatalyst was obviously lost due to the corrosion of carbon support, and the active area began to decay after 1s of battery reverse polarity [24].

Partial hydrogen coverage of the anode caused carbon corrosion. Raiser et al. used a simplified mathematical method to simulate carbon corrosion, and summarized the conditions under which oxygen flows from the cathode side through the membrane to the anode and causes reverse current, thereby causing permanent damage to the PEMFC cathode [25]. Meyers and Darling established a model of the reverse current mechanism, explaining that carbon corrosion caused by local fuel shortages can be mitigated by fine system control and design [26]. At the same time, Fuller and Gray established a partial hydrogen coverage model for the anode side, and found that the higher the potential, the worse the conductivity of ionomer. Besides, the stronger the permeability of oxygen through the membrane, the easier carbon corrosion occurred [27].

3.3. Nafion Ionomer Degradation Mechanism

Nafion ionomer is an important part of the catalytic layer. It plays a role of conducting protons and ensuring water transfer in the catalytic layer, the structure of the Nafion ionomer can be seen in FIGURE.1(a). Nafion ionomer is mainly composed of poly perfluorosulfonic acid resin (PFSA) molecules, the distribution and content of which in the catalytic layer directly affect the ion/electron transfer in the catalytic layer [28]. Its attenuation and dissolution directly lead to the ion/electron conductivity and mass transfer ability of the membrane electrode assembly decrease. The branched chain length of the ionomer affects the performance and lifetime of PEMFC. Ozden et al. found that compared with the long branched chain ionomer, the surface microstructure damage of the electrode surface composed of short branched ionomer after 60 cycles of freeze-thaw cycle is less, which improves the performance and durability of PEMFC. The decay process first occurs by ionomer swelling and pore expansion, then the separation of large catalytic layer sheet and microporous layer occurs, and finally develops into the form of high surface corrosion. As shown in FIGURE.1(b, c), the delamination of

catalytic layer and microporous layer after attenuation and the electrode difference caused by the two ionomers can be clearly observed [29].

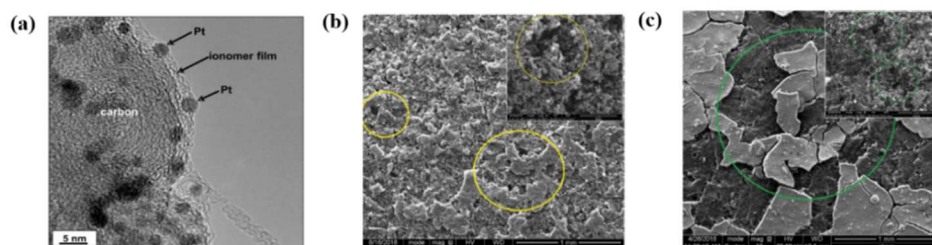


Figure 1. The structure of ionomer and the morphology of the degraded electrode with different ionomers: (a) TEM image of the microstructure of the Pt/ionomer/carbon three-phase interface (b) Surface morphology of the electrode made of short-side-chain ionomer at 60 cycles (c) Surface morphology of the electrode made of long-side-chain ionomer at 60 cycles

Hydrogen peroxide, hydroxyl radicals or other pollutants generated in the fuel cell reaction all damage the ionomer structure of the catalytic layer by attacking PFSA. Both Nafion ionomer and proton exchange membrane are composed of PFSA molecules, and the degradation mechanism is also very similar, but there are also differences, mainly reflected in the following two aspects. On the one hand, the Nafion ionomer in the catalytic layer is located at the active site of the reaction. Since many free radicals may be removed by the Pt catalyst, the decay of the Nafion ionomer is slower than in the membrane [30]. On the other hand, the Nafion ionomer in the catalytic layer is exposed to more water (from the product and inlet water) and intermediates during operation. In general, compared with Pt catalyst and carbon support, Nafion ionomer network in the catalytic layer is difficult to distinguish by the traditional morphology characterization method, so it is difficult to judge the decay process by the morphology change. However, many research groups have made important progress in the study of Nafion ionomer decay in the catalytic layer. Balogun et al. analyzed the degradation of short-chain branched Aquivion and long-chain branched Nafion ionomers are also composed of PFSA molecules by using EIS technology, and found that the membrane electrode composed of short-chain branched Aquivion ionomers was made of Nafion ionomers. The ohmic resistance of the membrane electrode is 46.6% lower, the output power density is 23.3% higher, and the impedance results show that the short branched chain has less degradation than the long branched ionomer [31].

4. Membrane electrode catalytic layer attenuation mitigation strategy

(1) Pt catalyst alloyed or modified by other metals

In order to improve durability of the catalysts of PEMFC in long-term operation, many studies have been done by trying to avoid serious loss of activity caused by Pt migration and growth by alloying Pt based catalysts or modifying them with other metals. This method can reduce Pt loading and fuel cell cost. The most common alloying elements with Pt are transition metal elements, including Co, Ni, Cu and Pd. The improved durability of PtCo catalysts is due to their special structure and improved surface electronic properties, which can provide more active sites for the reaction. Chong et al synthesized the PtCo alloy catalyst by pyrolysis of imidazolium ester framework containing cobalt and zinc as precursor. The catalyst was used in PEMFC with ultra-low Pt loading of $0.035 \text{ mg} \cdot \text{cm}^{-2}$, and its mass activity was $1.77 \text{ A} \cdot \text{mg}^{-1}_{\text{Pt}}$ at 0.9 V, which exceeded DOE objectives of $0.44 \text{ A} \cdot \text{mg}^{-1}_{\text{Pt}}$ [32]. Li et al. synthesized PtNi/C oxygen reduction catalyst. The results showed that the mass activity of PtNi/C was 19 times higher than that of Pt/C at RDE scale, and the power generation performance and durability of PtNi/C catalyst at MEA scale were better than those of commercial Pt/C catalyst. The performance of single cell assembled with PtNi/C catalyst was 0.712 V and $881.6 \text{ mW} \cdot \text{cm}^{-2}$ at the current density of $1 \text{ A} \cdot \text{cm}^{-2}$ [33].

(2) Optimized design of catalytic layer structure to improve battery performance

Optimizing the structure of the catalytic layer is also beneficial to improve the durability of the membrane electrode. Zheng et al. designed a gradient cathode catalyst layer for proton exchange membrane fuel cells. Through numerical simulation, it was found that the multilayer structure design alleviates the Pt loss at the interface between the catalyst layer and the membrane, which is conducive to improve the durability of the fuel cell [34].

(3) Development of highly graphitized carbon supports or strengthening the interaction between catalysts and supports

One mitigation strategy is to reduce the negative impact of carbon oxidation on fuel cell performance by using more stable materials as catalyst supports. Yu et al. proved that the catalyst supported on the carbon carrier with higher graphitization degree showed higher carbon corrosion resistance [35]. Forouzandeh et al. treated the carbon support by using a pentafluorophenyl surface functionalization method, and the resulting new catalyst support has a corrosion resistance that is 50-80% higher than that of a commercial carbon black support. It is believed that this is related to the decrease of surface active sites and the increase of surface hydrophobicity [36]. Although the highly graphitized carbon has high carbon corrosion resistance, its surface area is low. At the same time, particles have a surface graphitized carbon inherently hydrophobic, unable to promote Pt dispersion effectively, which results in a lower utilization of platinum, thus hindering their widespread use [37]. And even if highly graphitized materials are used, the carbon decay will not be mitigated under severe conditions. This is because a high degree of graphitization can only slow down the kinetic process of carbon oxidation reaction, but it will not change the mechanism of oxidation reaction.

5. Conclusion

The degradation of the catalytic layer of the membrane electrode in PEMFC occurs in every component, including catalyst, carbon support and ionomer. The changes of active components and microstructure in the catalytic layer affect the performance and durability of fuel cells. In this paper, we hope to design a low-cost, high-performance and long-life proton exchange membrane fuel cell through the analysis and research on the degradation mechanism of the catalytic layer of the membrane electrode, so as to promote its commercial application in the field of clean energy power generation.

Acknowledgments

This work was financially supported by State Grid Corporation Technology Support Project: Research on Key Technology of Membrane Electrode of Proton Exchange Membrane Fuel Cell Suitable for Variable Load (Contract No. 2018-2020-SGGR0000DLJS1800814).

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