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Review

A Review on Impact of the Marine Salt Spray Environment on the Performance of Proton Exchange Membrane Fuel Cells

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Abstract: With the escalating global demand for clean energy, the proton exchange membrane fuel cell (PEMFC), as an efficient and environmentally friendly energy conversion device, has emerged as a pivotal component of new power systems, playing a crucial role in achieving global carbon emission reduction targets. At present, the application of PEMFC technology is gradually expanding to the shipping industry and other fields, indicating its potential role in the future transformation of the energy structure. This article focuses on the marine salt spray environment; summarizes the impact of salt ionic contamination on PEMFC performance in recent years; and mainly explores the influence mechanism of the internal components of PEMFC, including the bipolar plate, the gas diffusion layer, catalyst layer, and proton exchange membrane. In addition, this study analyzes and summarizes the polarization curve variations in the marine salt spray environment, as well as the recovery methods after contamination, in order to provide certain references of PEMFC research for marine application.

Keywords: PEMFC; marine salt spray; salt ionic contamination; performance degradation; influence mechanism

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1. Introduction

As an advance electrochemical energy conversion device, PEMFC has exhibited superior performance and significant potentials for a wide range of applications in the energy sector. The working principle and structural schematic of PEMFC are shown in Figure 1. Its working principle is based on the electrochemical reaction of hydrogen and oxygen to generate electrical energy. At the anode, hydrogen is oxidized, and the produced electrons are conducted through the external circuit to the cathode, creating an electric current. Meanwhile, protons pass through the proton exchange membrane to the cathode, where they react with oxygen to produce water [1,2]. The internal structure of PEMFC primarily consists of four components: the bipolar plate, gas diffusion layer, catalyst layer, and proton exchange membrane [3–5]. The schematic diagram of its structure is also shown in Figure 1. The bipolar plate provides gas channels and collects current. The porous structure of the diffusion layer facilitates the transmission and transfer of reaction gases. The catalyst layer primarily consists of Pt/C electrocatalysts, which promote the oxidation of hydrogen and the reduction of oxygen. The proton exchange membrane, typically made of sulfonated perfluorinated sulfonic acid resin, is responsible for conducting protons while isolating gases to prevent direct mixing of hydrogen and oxygen. Due to its advantages such as short start-up time, high energy conversion efficiency, and wide applicability across a broad operating temperature range [6], as well as its “zero emission” feature, which only produces water as a byproduct, PEMFC has attracted widespread attention. Currently, PEMFC has been widely applied in various fields such as new energy vehicles, aerospace vehicles, portable power sources, backup power supplies, and stationary power generation [7,8].

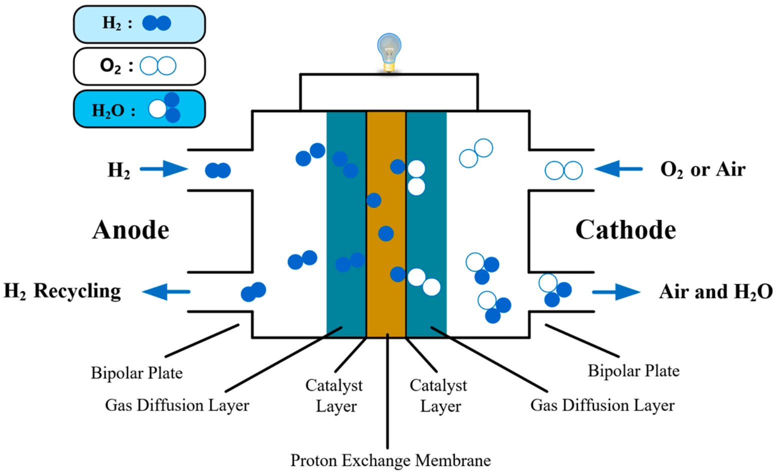

Figure 1. Schematic diagram of the working principle and structure of PEMFC.

As PEMFC is gradually applied to the field of marine transportation, the environmental difference between the ocean and land presents new challenges for related technological research, especially the salt spray environment in the ocean, which poses higher requirements for the performance and durability of PEMFC. The marine salt spray environment refers to the salt in seawater existing in the form of aerosol particles in the marine atmosphere, mainly due to the disturbance of seawater and complex physical reactions with the air above the sea surface [9]. When these salt aerosol particles enter the PEMFC and dissolve in water, they will exist in the form of ions, which will affect the output performance of PEMFC [10]. The main components in marine salt spray are the same as those in seawater. In addition to O and H elements, the types of elements in seawater can be divided into major, minor, and trace elements according to their contents [11]. Major element refers to those with a content of more than one milligram per kilogram of seawater, accounting for the majority of marine elements, while other minor and trace elements, despite their extremely low content, cannot be ignored [12], as shown in Table 1. Among them, the salt-like substance sodium chloride (NaCl), composed of major elements Na^+ and Cl^-, accounts for the majority of the salt content in seawater, approximately 77.8% [13].

Table 1. Types and classification of elements in marine salt spray environment [14–16].

Categorization	Element Type	Percentage
Major element	Cations: Na^+, Mg^{2+}, Ca^{2+}, K^+, Sr^{2+} Anions: Cl^-, Br^-, $SO_4{}^{2-}$, $HCO_3{}^-$, F^-,	99.9%
Minor and trace elements	Al^{3+}, Cr^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, etc.	0.1%

Air is generally used as the oxidant of fuel cells due to the consideration of economy. When PEMFC is exposed to such an environment, salt ions in the salt spray environment may cause damage to the internal components of PEMFC, thereby affecting the reliability and efficiency of the entire system. Therefore, it is necessary to deeply explore the mechanism of the impact of the marine salt spray environment on the internal components of PEMFC. It is also crucial to analyze the performance variations of PEMFC in this environment and propose corresponding solutions to address the impact of the marine salt spray environment on PEMFC performance.

2. Impact on the Internal Components of PEMFC

The construction of a laboratory simulation environment is particularly important in exploring the performance and durability of PEMFC in the marine salt spray environment. To simulate the actual working conditions of PEMFC in the marine salt spray environment more accurately, many researchers have designed and built specialized salt spray testing platforms. The schematic diagram of the salt spray testing platform is shown in Figure 2. The salt spray testing platform mainly consists of the following modules: gas supply module, humidification module, salt spray module, PEMFC module, and PC control center. The gas supply module is responsible for the supply of hydrogen and air to the fuel cell. The humidification module uses advanced humidification technology to accurately regulate the humidity of the gas, ensuring that the gas reaches the required humidity level. The salt spray module is the core part of the platform, whose main function is to convert salt solution into mist and simulate salt spray conditions in the ocean environment. The design of this module is very important because it directly affects the authenticity of the simulation environment and the accuracy of the experimental results. The salt spray module can uniformly and continuously disperse salt solution into the fuel cell, thereby simulating the impact of the marine salt spray environment on the performance of PEMFC. The PEMFC module and PC control center not only carry out the operation of the fuel cell, but also involve the monitoring and evaluation of PEMFC performance. As the brain of the entire system, the PC control center is responsible for precise control of each module and real-time collection and analysis of data. Through advanced data acquisition systems and control algorithms, the PC control center can ensure the accuracy and repeatability of experiments, providing researchers with detailed experimental data for in-depth analysis of the performance variations of PEMFC in the marine salt spray environment. Therefore, the construction of this salt spray testing platform not only provides a reliable testing method for evaluating the impact of PEMFC in the marine salt spray environment, but also provides valuable data support for research in related fields.

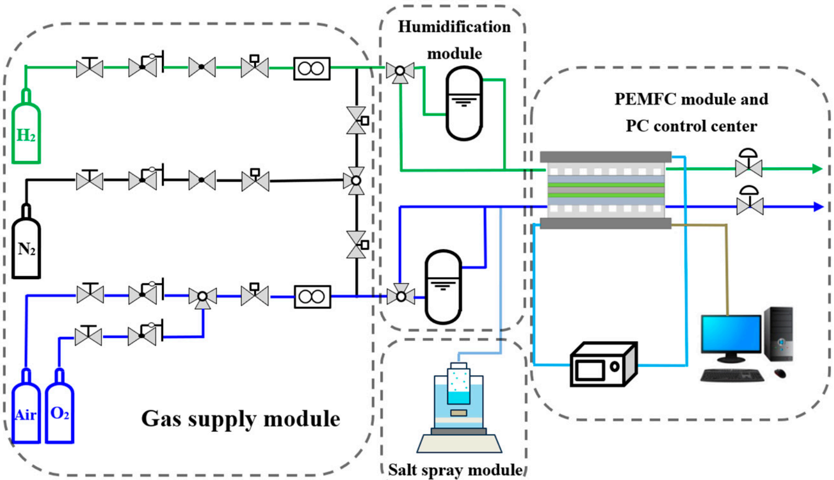

Figure 2. Schematic diagram of PEMFC salt spray test system.

2.1. Impact on the Bipolar Plate

The bipolar plate assembly primarily serves to support electrode materials, collect and conduct electrons, and facilitate water and thermal managements within the PEMFC [17,18]. Common bipolar plates include the graphite bipolar plate, composite bipolar plate, and metal bipolar plate. The choice of material for these bipolar plates has a decisive impact on the stability and conductivity of fuel cells [19]. Current research focuses on the corrosion phenomena of the PEMFC bipolar plate caused by Cl^- and F^- anions in the marine salt spray environment. Lædre et al. [20] conducted constant potential and dynamic potential tests on the AISI 316L stainless steel bipolar plate in acidic solutions to investigate the corrosion effect of chloride concentration on the stainless steel bipolar plate. It was found that when the Cl^- concentration in the solution was 10 ppm, the contaminated bipolar plate remained almost unchanged without significant corrosion. However, when the Cl^- concentration reached 100 ppm, significant pitting corrosion occurred on the bipolar plate under high Cl^- content conditions. Scanning electron microscope (SEM) images of the fresh and the contaminated bipolar plate with 100 ppm Cl^- are shown in Figure 3.

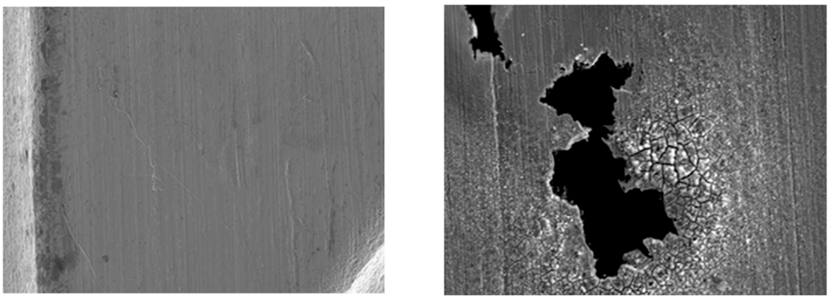

Figure 3. SEM images of the original state (**left**) and pitting corrosion on the surface after 100 ppm Cl^- contamination (**right**) of AISI 316L bipolar plate [20].

Yang et al. [21] analyzed the corrosion behavior of PEMFC with SS316L as the bipolar plate under different F^- concentrations by means of electrochemical technology and SEM. It was found that the corrosion resistance of SS316L is decreased with the increase in F^- concentration in the solution. Pitting corrosion occurred under all set operating conditions, and the higher the F^- concentration, the more severe the pitting corrosion. At the same time, the author analyzed the surface roughness of the bipolar plate in the following research [22]; put forward the empirical corrosion model of the exponential decay of the corrosion current of the bipolar plate with the polarization time [23]; and also found that, in most cases, the local corrosion of the bipolar plate is more serious at the cathode side of the PEMFC [24]. Xuan et al. [25] also systematically studied the corrosion performance of the bipolar plate in the cathode environment of F^- simulated PEMFC in 0–200 ppm HF with different concentrations. In addition, the author conducted surface analysis, the water contact angle (WCA) test, and interface contact resistance (ICR) measurement. The results also showed that the higher the F^- concentration, the more obvious the corrosion effect on the bipolar plate. They also found that the passive film could not be formed spontaneously in PEMFC solution with an F^- concentration higher than 20 ppm. However, different from the findings of Yang et al. [21], it was found that the increase in F^- concentration would not cause pitting corrosion of SS304 but would reduce the oxidation degree and roughness of its surface. As shown in Figure 4, the scratches caused by sandpaper polishing are still visible, and only a few tiny corrosion products can be observed nearby at high magnification.

Therefore, the potential hazards represented by Cl^- and F^- in the salt spray environment, especially the corrosion phenomenon, must be fully considered for the bipolar plate. Existing studies have shown higher concentrations of Cl^- and F^- ions have a more pronounced effect on the corrosion of bipolar plate. Therefore, it is necessary to develop coating technology or other surface modification methods suitable for stainless steel materials for the low-cost, high-performance PEMFC stainless steel bipolar plate.

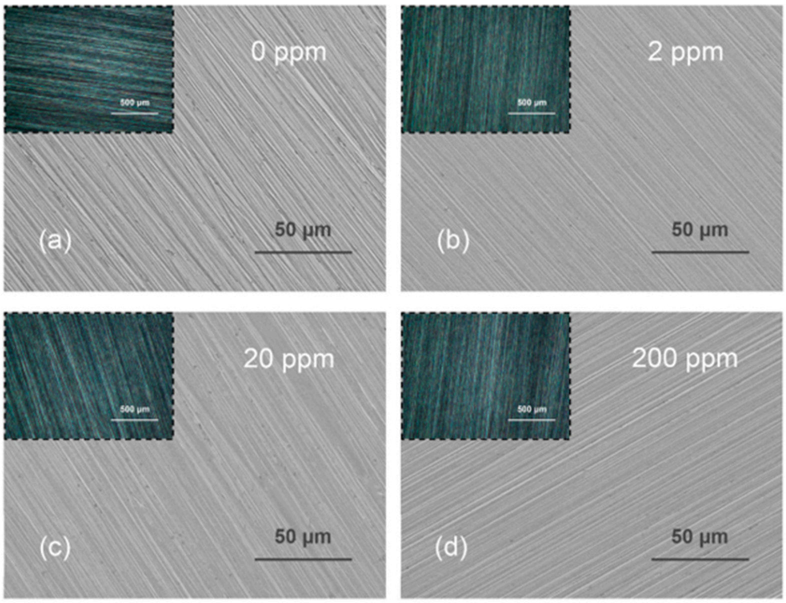

Figure 4. SEM surface topography of SS304 bipolar plate in solutions of different F^- concentrations accompanied by air bubbling: (**a**) 0 ppm; (**b**) 2 ppm; (**c**) 20 ppm; (**d**) 200 ppm [25].

2.2. Impact on the Gas Diffusion Layer

The gas diffusion layer is usually composed of carbon paper or carbon cloth. The high density of fibers makes it have a unique pore structure. It is crucial for mass transfer and water management. [26,27]. Polytetrafluoroethylene (PTFE), as the most common coating material, greatly improves the hydrophobicity of the gas diffusion layer, reduces the water adsorption on its surface, and improves the gas diffusion efficiency. At the same time, it maintains a certain hydrophilicity to ensure the proper transmission of water to ensure the performance of PEMFC [28,29]. However, when salt ions in the marine salt spray environment enter the gas diffusion layer, they mostly affect the hydrophobicity of the gas diffusion layer in the form of a white deposit.

Uemura et al. [30] introduced 1 µm sea salt aerosol into the cathode of the fuel cell and found white NaCl particles in the gas diffusion layer. These NaCl particles not only adhered to the gas diffusion layer, but also invaded the area near the catalyst layer. Nakajima et al. [31] conducted an accelerated degradation test by directly injecting NaCl solution into the cathode. After injection for 5 h, they found that the mass transfer resistance of PEMFC increased by about 2.5 times, which was speculated to be due to the decrease in hydrophobicity of the gas diffusion layer. In addition, Yan et al. [32] introduced NaCl salt spray into the running PEMFC and also observed that white precipitation adhered to the carbon fiber in the gas diffusion layer. Wen et al. [33,34] not only found that NaCl particles are evenly distributed on the carbon fibers in the gas diffusion layer, but also showed that NaCl exists in the form of crystal, and the crystal presents a regular cubic structure. The authors also found that in the environment of a specific NaCl concentration, the crystal distribution become closer and closer with the increasing time. Under a certain test time, the number of crystals was also significantly different under different NaCl concentrations. The higher the concentration was, the more the number of crystals. Uddin et al. [35] introduced a solution containing Ca^{2+} into the cathode channel of the PEMFC. Salt deposits could be seen inside the gas diffusion layer, as shown in Figure 5. It was found that salt deposition was the main reason for the decline and fluctuation of the cell voltage, which led to the loss of mass transfer.

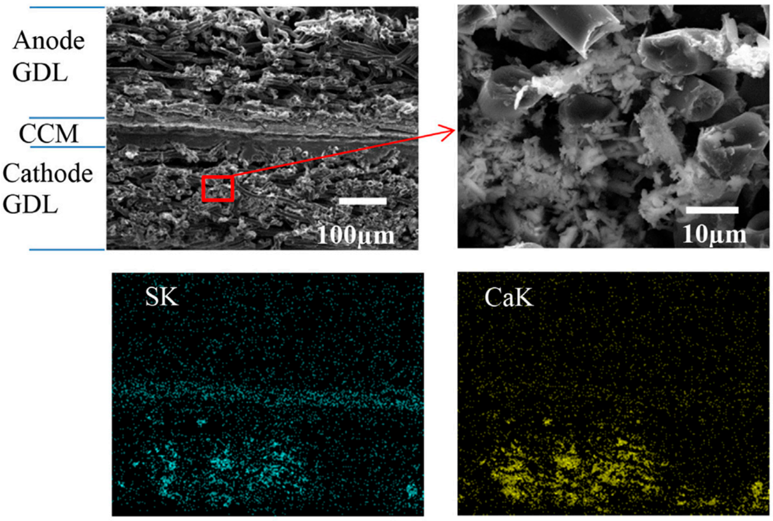

Figure 5. SEM images of MEA cross-section after the galvanostatic test with an enlarged view of cathode gas diffusion layer [35].

As an important component of PEMFC, the gas diffusion layer is closely related to the transport of reactants and liquid water inside PEMFC. Salt ions in the marine salt spray environment enter the interior of PEMFC, and the formation of white deposits of NaCl or other salts can be observed on the carbon fibers in the gas diffusion layer, usually in the form of crystals. These white deposits can reduce the hydrophobicity of the gas diffusion layer, affecting the distribution and transport of substances, and thus affecting the efficiency of PEMFC. To address this phenomenon, more targeted coating techniques and surface modifications can be used on the gas diffusion layer, or a gradient design can be employed structurally to mitigate the hydrophobic effects caused by marine salt spray environments.

2.3. Impact on the Catalyst Layer

The catalyst layer provides a place for the electrochemical reaction of PEMFC. It is generally a random porous structure with a thickness of about 10 µm, and is composed of platinum (Pt) nanoparticles, carbon carrier particles, ionomers, and pores [36]. The catalyst layer is crucial to the efficiency and performance of the PEMFC, which not only promotes the oxygen reduction reaction (ORR), but also ensures the effective conduction of protons and electrons [37].

For the cations in the marine salt spray environment, it was found that cations could affect the ORR occurring on the catalyst layer. Qi et al. [38] investigated the electrocatalytic activity of Pt/C catalysts in the presence of Ca^{2+} on ORR. It was found that Ca^{2+} cation contamination could be absorbed by perfluorinated ionomers, and Ca^{2+} would reduce the availability of Pt active sites at high concentrations. Excessive Ca^{2+} would disrupt the charge distribution near the Pt surface and limit the adsorption of O_2 molecules on Pt particles.

Researchers also investigate anion contaminations in the catalytic layer. For the anion contaminations in the marine salt spray environment, represented by Cl^-, Cl^- has strong adsorption capacity and is easily adsorbed on the surface of the Pt catalyst. This adsorption will occupy the active sites of the Pt catalyst, thereby reducing the number of active sites available for catalytic reactions. In addition, the presence of Cl^- can affect the surface electrochemical environment of Pt catalysts. The surface sites of Pt catalysts usually carry positive charges, and Cl^- is a strongly electronegative ion. When it adsorbs on the surface of Pt catalysts, some of the positive charges will be neutralized. This is due to the complexation reaction between the two, forming a chloride complex composed of Pt-Cl bonds (see Formulas (1) and (2)), which promotes the dissolution of the Pt catalyst. These reasons directly lead to the decrease in electrochemical surface area (ECSA).

$$\mathrm{Pt} + 4Cl^{-} \rightarrow PtCl_4^{2-} + 2e^{-} \tag{1}$$

$$\mathrm{Pt} + 6Cl^{-} \rightarrow PtCl_6^{2-} + 4e^{-} \tag{2}$$

Matsouka et al. [39] investigated the performance of single fuel cells contaminated with four anions: Cl^-, F^-, $NO_3{}^-$, and $SO_4{}^{2-}$. They found that the ECSA of the catalyst layer in a single cell contaminated with Cl^- decreased by about 25%. Li et al. [40] conducted a contamination test by injecting ppm level HCl pollutant into PEMFC. The results showed that no matter whether the PEMFC was introduced from the anode or cathode, the characteristics of the cell voltage during chloride contamination were first sudden drop and then reached a stable state. The main reason for the decline of PEMFC performance was that the charge transfer resistance increased due to the active site of the Cl^- blocking catalyst, and the formation of chloride complex enhanced the dissolution of Pt, resulting in the decrease in ECSA. The authors also found that when Cl^- was introduced into the anode side, the ECSA of the cathode and anode decreased by 28% and 15% respectively. When Cl^- was introduced into the cathode side, the ECSA of the cathode and anode were reduced by 25% and 14%, respectively. It was speculated that when Cl^- is injected into the anode side, it could migrate from the anode to the cathode side, resulting in a greater reduction in cathode ECSA than anode ECSA.

Yadav et al. [41] studied the effect of Cl^- on the dissolution of electrochemically deposited Pt and found that platinum chloride complexes were formed, and the presence of only 10 ppm Cl^- led to Pt dissolution. Pavlišič et al. [42] summarized three reasons for the corrosion phenomenon of PEMFC catalysts: Firstly, it reduced the Pt dissolution potential. Secondly, it increased the total amount of dissolved Pt. At the same time, the presence of chloride would enhance the anodic dissolution of Pt. And it was found that even a very small amount of 10^{-6} mol/L chloride can lead to a 21% increase in platinum dissolution. Li et al. [43] found that chloride contamination mainly led to an increase in the charge transfer resistance and mass transfer resistance, and the impact of charge transfer resistance is the greatest. They also found that the current density, relative humidity, and temperature also seriously affect the degree of chloride concentration on PEMFC. Uddin et al. [44] found that Cl^- acted as a site blocker, leading to a decrease in the peak values of hydrogen adsorption and desorption in cells. The conclusion was also drawn that Cl^- occupied Pt active sites and forms chlorides to accelerate Pt dissolution, thereby reducing the electrochemical active area of the catalyst layer.

Park et al. [45] found that the particle size of the Pt catalyst before NaCl contamination was approximately 5 nm or smaller but increased to 10 nm after contamination at 0.9 V. The presence of NaCl contaminants caused some dissolved Pt ions to redeposit, resulting in an increase in particle size, as shown in Figure 6. The author concluded that the decrease in ECSA and the decline in PEMFC performance were mainly due to the loss of Pt catalyst rather than the adsorption of Cl^- ions. Baturina et al. [46] studied the performance degradation of PEMFC exposed to 4 ppm HCl in air under different voltage conditions. The growth of Pt nanoparticles on the cathode was analyzed by HR-TEM images of catalyst samples scraped off from CCM, maintained at voltages of 0.4 and 0.6 V. The results showed that as the voltage increased, the Cl^- coverage of Pt nanoparticle electrocatalysts increased. In addition, compared to maintaining the voltage of the PEMFC at 0.4 V, it was easier to observe Pt aggregation when the battery was kept at 0.6 V. They analyzed that under 0.6 V conditions, it was easier to promote the dissolution of Pt catalyst, and the formed chloroplatinate ions would promote the growth and aggregation of Pt nano ions, which would further reduce the active surface area of the catalyst. Schmidt et al. [47] found that the effect of Cl^- adsorption on Pt resulting in ORR activity depends largely on the crystal structure of Pt.

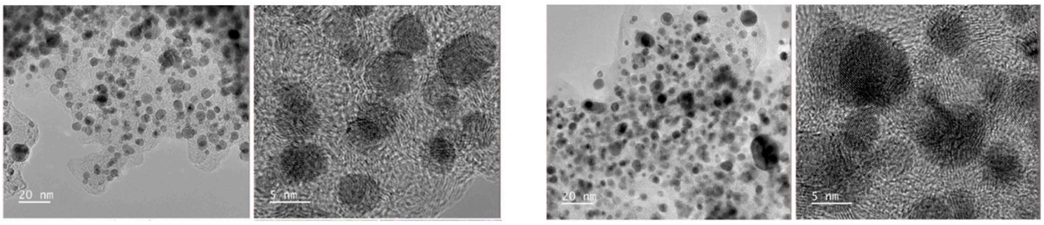

Figure 6. HR-TEM images before (**left**) and after (**right**) NaCl contamination at 0.9 V [45].

The above studies indicate that the impact of the marine salt spray environment on the catalyst layer cannot be ignored. From the perspective of the influencing mechanism, cations usually occupy the active sites within the ionomer in the catalyst layer, reducing the rate of ORR. Anions represented by Cl^- first block the electrochemical active sites due to their adsorption on Pt catalysts. Moreover, due to its ability to react with Pt to form chlorides, the dissolution of Pt catalyst further reduces the electrochemical active area of the catalyst layer. In addition, it may also cause the growth and aggregation of the Pt catalyst, thereby affecting their performance. In view of the above effects of the marine salt spray environment on the catalyst layer, strategies such as developing new catalysts and optimizing the structure of catalysts, ionomers, and pores, or increasing the number of three phase boundaries can be used to improve the electrochemical reaction efficiency of the catalyst layer and reduce its degradation.

2.4. Impact on the Proton Exchange Membrane

The perfluorinated sulfonic acid membrane is widely used as the membrane, and its chemical structure is consistent with the ionomer used in the catalyst layer [48–50]. It is a material with ion selective permeability, which can efficiently conduct protons while limiting the direct migration of electrons, thus affecting the electrochemical reactions of the fuel cell [51].

Current studies indicate that the proton exchange membrane generally has high sensitivity to metal cations in marine salt spray environments. These metal cations undergo ion exchange with functional groups in the proton exchange membrane, which may cause changes in the ion distribution and equilibrium state, thereby altering the structure of the proton exchange membrane [52,53]. Specifically, the perfluorinated sulfonic acid membrane typically contains sulfonic acid groups ($-SO_3H$), which dissociate into protons (H^+) and sulfonic acid ions ($-SO_3^-$) in water. The conduction of protons in proton exchange membranes mainly occurs through the hopping of hydrated hydrogen ions (H_3O^+) between sulfonic acid groups. Due to the stronger affinity between most metal cations and sulfonic acid sites, when metal cations are present, these cations will replace protons and combine with sulfonic acid ions to form new sulfonic acid salts. This process can cause protons in the membrane to be replaced by other metal cations, thereby reducing the available number of protons and affecting proton conductivity, resulting in the "cation effect of proton exchange membrane" [54].

Wen et al. [33] studied the elemental distribution of the membrane electrodes tested by the 500 mg/L Na^+ mass concentration in a salt spray environment. The results indicate that sodium ions penetrate into the proton exchange membrane, as shown in Figure 7. Zhu et al. [55] conducted EDS analysis and SEM characterization on the cross-section of the membrane electrode, and the results showed that Mg^{2+} mainly appeared in the proton exchange membrane. It also found that the longer the contamination time and the higher the concentration, the higher the Mg^{2+} content in the proton exchange membrane.

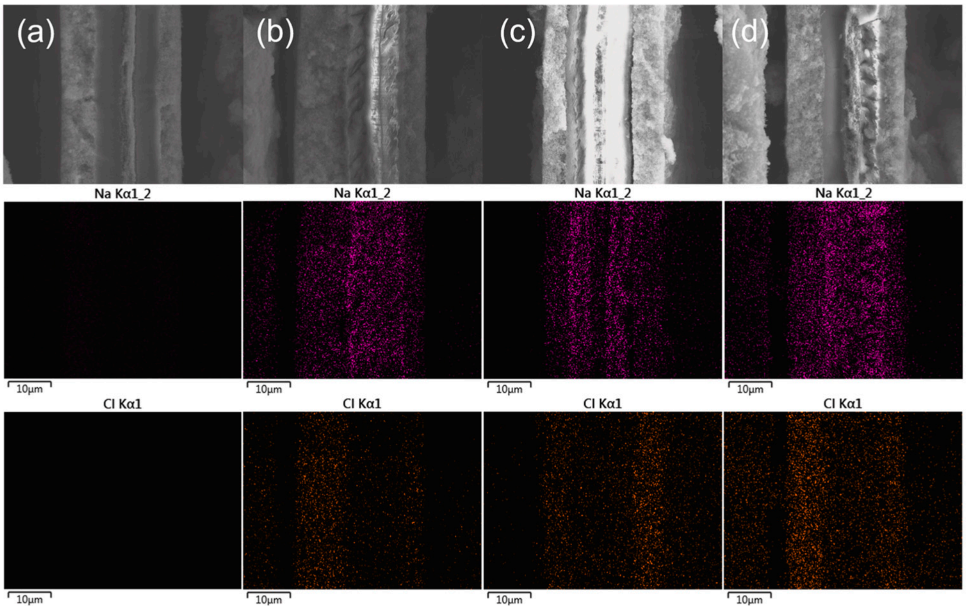

Figure 7. Element distribution of membrane electrode under 500 mg/L Na^+ contamination: (**a**) original membrane electrode; (**b**) membrane electrode tested for 24 h; (**c**) membrane electrode tested for 144 h; (**d**) membrane electrode tested for 288 h [33].

Ma et al. [56] investigated the effect of Na^+, Ca^{2+} contaminants on the performance of PEMFC by injecting cationic salt solutions. They speculated that the mechanism behind the degradation of PEMFC performance might be due to the entry of these cations into the proton exchange membrane and their interaction with the protons in the sulfonic acid groups of the membrane, resulting in ion exchange reactions that replace hydrogen ions and form new sulfonic acid salt structures, thereby increasing the resistance of the proton exchange membrane. Additionally, Qi et al. [57] also concluded that the metal cations including K^+ and Ca^{2+} had a stronger affinity for the sulfonic acid groups in the proton exchange membrane, and various metal cations could occupy proton exchange sites. Some researchers have also found that different cations have different affinities for the sulfonic acid groups on the proton exchange membrane. Zhang et al. [58,59] not only found that sulfonic acid groups have a stronger affinity for K^+, Mg^{2+}, Na^+, and Ca^{2+}, but the results showed that cations significantly reduced the diffusion coefficients of hydronium ions and water molecules, disrupting the connectivity of water clusters. At the same time, they also found that compared to K^+ and Na^+, Ca^{2+} and Mg^{2+} had more severe effects on the above-mentioned aspects. Li et al. [60] conducted molecular dynamics studies and concluded that Ca^{2+} was more likely to attract sulfonic acid groups than Mg^{2+}. There are also some studies on the impact of anions on proton exchange membranes in marine salt spray environments. Matsuoka et al. [39] found partial Pt dissolution and deposition in the membrane only in the inlet side of the membrane electrode assembly. The partial loss of Pt led to concentration of the current density and degradation of the cell performance.

The above studies have shown that cations in the marine salt spray environment, as the main source of contamination, penetrate directly into the proton exchange membrane. Anions will promote the dissolution of the catalyst, and the dissolved Pt species will deposit in the proton exchange membrane, thus affecting the structure of the membrane. For cations, due to the ease of displacement of hydrogen ions in proton exchange membranes by cations, stronger affinity-induced ion exchange directly affects the ion conductivity of the membrane while changing the membrane structure. In addition, some cations also have a significant catalyst effect on the chemical degradation of the proton exchange membrane [61]. Under the contamination of cations, the degradation of the proton exchange membrane can be reflected through the release of fluorides [62,63]. Madhav et al. [64] studied the effect of NaCl concentration on membrane degradation and found that the quality of the membrane increased at high NaCl concentrations. It was speculated that the change in membrane quality is related to the substitution of H^+ in carboxyl groups by Na^+, and the fluoride ion concentration in the test solution increases continuously over time and decomposes from the membrane at a constant rate. Kundu et al. [65] established a membrane degradation model and found that after contaminated testing, the fluoride content on the membrane near the cathode side significantly decreased, indicating that a large amount of fluoride was released. The results were consistent with the findings of Lim et al. [66], who also discovered that membrane degradation primarily occurs on the cathode side. It was analyzed that the reason for this phenomenon was due to the production of byproduct hydrogen peroxide (H_2O_2) in the reaction. In the presence of cations, H_2O_2 would decompose into $HO_2\cdot$, $HO\cdot$, and other hydroxyl radicals, which would attack the proton exchange membrane. The generated HO2· and HO· is prone to attack these structures, manifested as the sulfonic acid group (-SO3H) decomposes after being attacked by hydroxyl radicals, resulting in a decrease in membrane conductivity. The main chain C-F bonds and side chain C-S and C-O bonds are broken after being attacked, resulting in thinning or even rupture of the proton exchange membrane.

The proton exchange membrane has a stronger affinity for metal ions than H^+, resulting in metal cations easily binding with sulfonic acid groups and existing inside the proton exchange membrane. It greatly affects the ion conductivity, stability, and other properties of the proton exchange membrane. Some cations can also promote the chemical degradation of the proton exchange membrane. Anions can easily cause the Pt in the catalyst layer to redeposit in the proton exchange membrane after dissolution, affecting the structure of the membrane. Therefore, while striving to minimize the contamination caused by salt ions in marine salt spray during PEMFC operation, optimizing proton exchange membrane materials and developing proton exchange membranes with greater chemical stability also require attention from more researchers.

From the above studies, it can be seen that the marine salt spray environment has a significant impact on the bipolar plate, gas diffusion layer, catalyst layer, and proton exchange membrane of PEMFC, which will result in a loss of the output performance of PEMFC. Table 2 summarizes the degradation mechanisms of components in PEMFC under salt.

Table 2. Degradation mechanisms and feasible improvements under the salt spray environment.

Components	Degradation Mechanisms	Proposed Improvements
Bipolar plate	Surface corrosion caused by Cl^- and F^-	Coating technology and surface modification
Gas diffusion layer	Salt deposits on carbon fibers, thereby reducing hydrophobicity	Application of corrosion-resistant materials, coating technology, structural gradient design
Catalyst layer	Cations occupy the active sites of ionomers in the catalytic layer; anions strongly adsorb onto Pt catalysts, which can easily lead to complexation reactions and cause redeposition of Pt catalysts	Developing new catalysts and optimizing the structure, increasing the number of three phase boundaries
Proton exchange membrane	Cations undergo ion exchange reactions with sulfonic acid groups, reducing conductivity and potentially promoting membrane degradation, while anions can cause changes in membrane structure	Utilizing a proton exchange membrane with high chemical stability and mechanical strength

2.5. Impact on PEMFC Performance

The polarization curve is one of the key indicators for evaluating the performance of PEMFC, which reflects the voltage variation of the fuel cell at different current densities, and thus reflects the overall operation status of PEMFC [67]. The salt ions in the marine salt spray environment, including the types and concentrations, have a significant impact on the polarization curve of PEMFC. Therefore, exploring the specific impact of these ions on the polarization curve of PEMFC is an important area worthy of in-depth study.

In general, the polarization curve of PEMFC includes an activated polarization region at low current density, an ohmic polarization region at medium current density, and a concentration polarization region at high current density [68]. The rate of the cathodic redox reaction caused by the catalyst performance has a significant impact on the polarization loss in the activated polarization region. The main reason for voltage loss in the Ohmic polarization region is the increase in resistance caused by the ion conductivity of the proton exchange membrane and the electron conductivity in the electrode. The voltage loss in the concentration polarization region is mainly attributed to the mass transfer effect of the reaction gas through the gas diffusion layer and electrocatalyst layer [69].

Yan et al. [32] found that as the current density increases, the effect of the chloride concentration on the PEMFC performance becomes more significant. The declination rate is 1.082 mV h^{-1} for the NaCl/air fuel gas mixture and 3.446 mV h^{-1} for the $CaCl_2$/air fuel gas mixture. Uddin et al. [44] investigated the impacts of hydrochloric acid and chloride salts on the performance of PEMFC. With the start of contaminant injection, the rate of voltage loss increased for all cases. HCl affected the cell faster than the other contaminants. Significant performance decay was observed for HCl in less than 24 h of contamination. Zhu et al. [55] found that there was no significant difference in the effect of concentrations of Mg^{2+} on the performance of PEMFC within 4 h of contamination. However, there was a significant difference at 20 h, as shown in Figure 8. It was observed that performance degradation mainly occurred in the ohmic polarization region and concentration polarization region. Wang et al. [70] found that the presence of Ca^{2+} ions not only led to a significant decrease in performance, but also significantly reduced the open circuit voltage at high concentrations. It was speculated that the decrease in open circuit voltage might be caused by membrane degradation. It is found that high current density (1 A/cm^2) combining with high concentrations of Ca^{2+} (5 ppm and 10 ppm) results in significant performance loss as well as membrane degradation. In contrast, the cells tested at 1 A/cm^2 with 2 ppm Ca^{2+} and 0.6 A/cm^2 with 5 ppm Ca^{2+} only show slight performance decay. The highest voltage degradation is 253.9 mv. Sasank et al. [71] investigated the impact of salt spray on PEMFC performance in marine environments. It was found that the longer the time of contamination, the greater the damage to the performance of PEMFC, and the performance decreased by more than 60% after 48 h of operation, as shown in Figure 9.

Lamard et al. [72] introduced NaCl contamination and tested for 120 h operation time. While the longer the time of contamination, the greater the damage, the performance degradation was greatly affected by the concentration of NaCl contamination. Mikkola et al. [73] injected NaCl solution from the cathode into PEMFC and maintained a constant voltage of 0.6 V to obtain a current time response graph. It was found that the performance of fuel cells decreased significantly at high concentrations and flow rates of sodium chloride solution, with a current density decrease of about 30% within 100 h. This was due to the proton conductivity decrease caused by Na^+ replacing H^+. Yoo et al. [74] systematically studied the effect of the flow field type on the electrochemical performance of PEMFC humidified with NaCl solution. The author found that after 20 h of contamination testing, the ohmic resistance of the parallel flow field increased by 14.5%, and the ohmic resistance of the serpentine flow field increased by 96.09%. The parallel flow field performance decreased by 30.91%, and the serpentine flow field performance decreased by 84.51%. Table 3 summarizes the comparison of the effects of marine salt spray contaminants on the PEMFC performance.

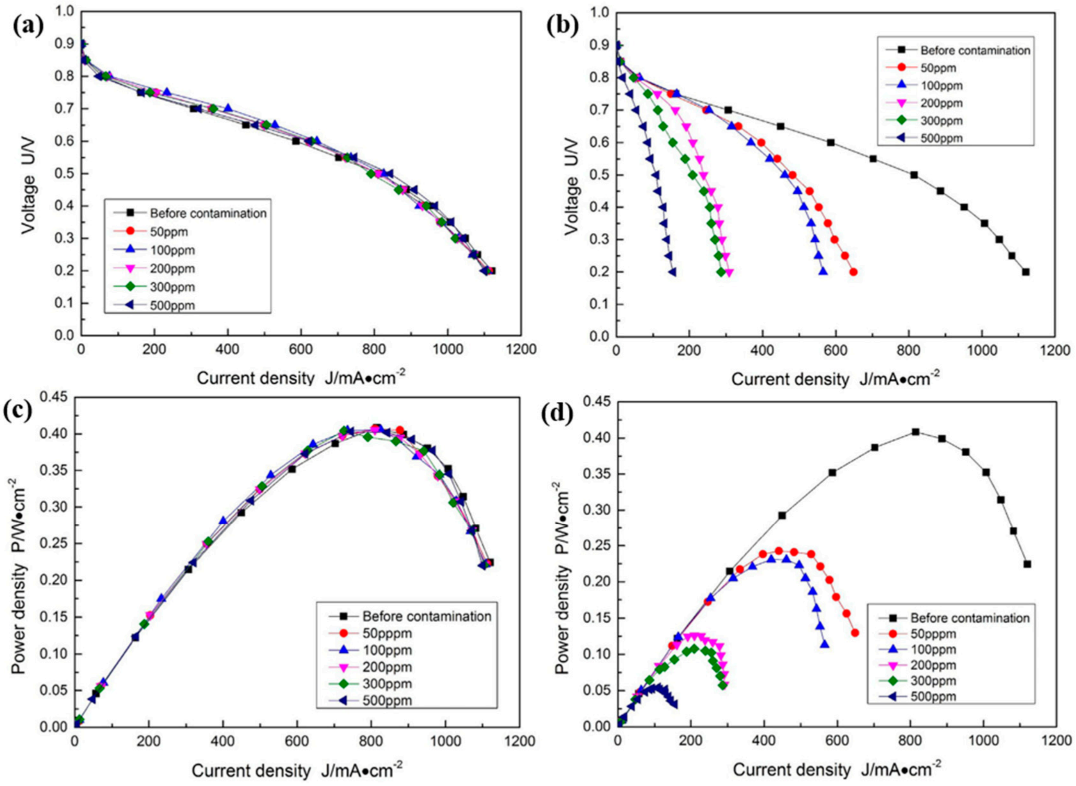

Figure 8. Polarization curves and power density curves of PEMFC under Mg^{2+} contaminations at four different concentrations: (**a**) the polarization curve after 4 h of contamination; (**b**) the polarization curve after 20 h of contamination; (**c**) the power density curve after 4 h of contamination; (**d**) the power density curve after 20 h of contamination [55].

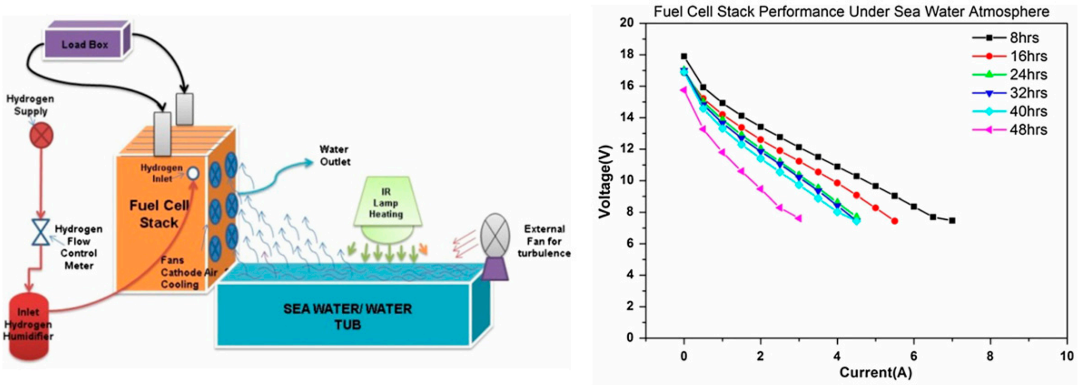

Figure 9. Performance of PEMFC stack on sea water environment [71].

Various salt ion contaminants present in the salt spray can affect the electrochemical reactions inside the PEMFC, resulting in significant degradation of PEMFC performance. The studies have shown that the concentration of salt ion contaminants and the duration of contamination are two key factors affecting PEMFC performance. As the concentrations of salt ion contaminants increase and the duration of contamination extends, the downward trend in PEMFC performance becomes increasingly evident.

Table 3. Comparison of the effects of marine salt spray contaminants on the PEMFC performance.

Authors	Contaminants	Main Conclusions	Performance Degradation
Yan et al. [32]	Na^+, Ca^{2+}	The declination rate is 1.082 mV h^{-1} for NaCl/air fuel gas mixture and 3.446 mV h^{-1} for $CaCl_2$/air fuel gas mixture	About 2.2% for Na^+ and 7.5% for Ca^{2+} contained after 12 h
Uddin et al. [44]	H^+/ Chloride salt	With the start of contaminant injection, the rate of voltage loss increased for all cases; HCl affected the cell faster than the other contaminants; Significant performance decay was observed for HCl in less than 24 h of contamination	About 80 mv decrease for HCl contained after 48 h, other chloride salt less than this value
Zhu et al. [55]	Mg^{2+}	After contaminated by 50 ppm Mg^{2+}, the maximum power density of the fuel cell decreased	For 4, 9, 16, and 20 h, the performance decreased by 1%, 21.9%, 31.7%, and 41.4%
Wang et al. [70]	Ca^{2+}	The presence of Ca^{2+} ions not only led to a significant decrease in performance, but also significantly reduced the open circuit voltage at high concentrations	The highest voltage degradation is 253.9 mv in all cases
Sasank et al. [71]	Salt spray	Performance decreased by simulating salt spray environment	Performance decreased by more than 60% after 48 h of operation
Lamard et al. [72]	NaCl	NaCl mist reduces PEMFC lifetime, especially when operated discontinuously	The voltage degradation of the fuel cell stack is about 0.012 mv/h
Mikkola et al. [73]	NaCl	At high concentrations and flow rates of sodium chloride solution, PEMFC performance deteriorates rapidly	The decrease in current density is about 30% within 100 h
Yoo et al. [74]	NaCl	The influence of NaCl solution on the serpentine flow field is more severe than that on the parallel flow field	After 20 h of pollution testing, the parallel flow field performance decreased by 30.91%, and the serpentine flow field performance decreased by 84.51%

3. Recovery Strategies for PEMFC After Marine Salt Spray Contamination

Due to the frequent long-distance maritime operations of ships, PEMFC has difficulty maintaining stable operation for extended periods under the harsh condition of the marine salt spray environment, which can easily lead to the performance degradation of PEMFC [75]. Nowadays, some scholars have studied protective measures for PEMFC, such as anti-corrosion coatings or coatings on the shell of PEMFC to improve its corrosion resistance, and installing air filters and other purification devices at the inlet of PEMFC to remove salt and other corrosive substances from the air [76,77]. Although these protective measures mitigate the impact of salt ions in marine salt spray on PEMFC performance to some extent, they cannot completely prevent the intrusion of these contaminants. Therefore, it becomes crucial to perform regular recovery operations on PEMFC operating on ships. Common restoration methods include flushing with deionized water, dilute sulfuric acid solution, or other specialized cleaning agents. These cleaning agents can dissolve and remove contaminants, restoring the clean state inside the PEMFC. In addition, the electrochemical restoration method is also an effective method. By controlling the voltage and current applied to PEMFC, it can promote the redistribution or direct removal of internal salt ion pollutants, thereby mitigating performance loss.

Li et al. [40] conducted two recovery tests using pure water at the same rate by injecting HCl of different concentrations into the anode at different current densities. The performance of the PEMFC could not be restored at a high Cl^- concentration of 20 ppm but could be partially restored at a low Cl^- concentration of 4 ppm. Park et al. [45] found that by adjusting the voltage to an appropriate range, the performance of PEMFC after NaCl contamination could be fully restored. If the applied potential was too low, Cl^- would not be oxidized, while if it was too high, CO_2 formed due to carbon corrosion would increase. The recovery mechanism could be distinguished by the Cl^- adsorbed on the catalyst surface, where Cl^- ions could be oxidized and removed in the form of Cl_2 gas. As shown in Figure 10, it was speculated that the phenomenon of the performance not being restored under the same concentration of NaCl contamination at a working voltage of 0.9 V was due to the irreversible dissolution of Pt.

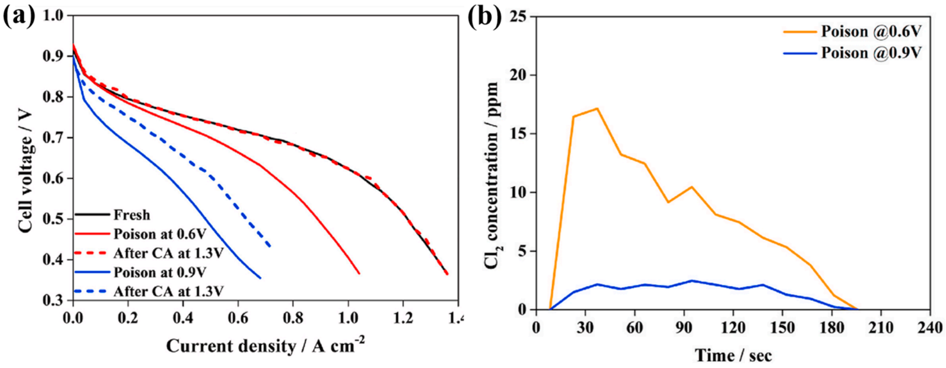

Figure 10. (**a**) Polarization curve of NaCl poisoning under different voltages and polarization curve changes after recovery; (**b**) the concentration of Cl^- oxidized to Cl_2 under different voltages [45].

Qi et al. [57] conducted recovery tests on PEMFC injected with four types of cations and found that when switching back to supersaturated air, there was a tendency to recover some of the lost performance. Sasank et al. [71] independently designed an open-cathode PEMFC to simulate the damage caused by salt spray in the marine environment. After about 48 h of salt spray damage, the author rinsed the cathode with clean water. As the cleaning progressed, the performance gradually recovered with the cleaning time. Finally, the maximum performance recovery of PEMFC could reach 93.3%. Lamard et al. [72] found that most PEMFC contaminated with NaCl for a short period of time has good regeneration effects. Washing the cathode with nitrogen and clean water could generally restore performance, but there was still a small amount of activation loss. Yoo et al. [74] investigated the stability test of PEMFC contaminated with NaCl solution after 20 h, and restored the PEMFC with deionized water at a constant voltage of 0.4 V. The performance of the fuel cell with the serpentine flow field recovered more effectively (+52.96%) than that of the fuel cell with the parallel flow field (+1.22%) after regeneration. Unnikrishnan et al. [78] investigated the impact of non-humidified chlorine on the recovery of fuel cell performance. After entering, Cl_2 would dissociate and adsorb on the Pt catalyst surface in the form of Cl^-, which affected the performance. The recovery of PEMFC performance was achieved by operating at a voltage of 0.1 V. The higher the concentration of contamination, the longer the time required for complete recovery. Reshetenko et al. [79] found that due to the strong adsorption of Pt, the performance cannot be restored even after being placed in pure air for 70 h. However, after H_2/N_2 purging of the anode/cathode, the polarization curve showed almost complete recovery of cell performance. The final loss of approximately 50 mV was due to an increase in activation overpotential. Table 4 summarizes the research conducted by researchers on recovery strategies for salt ions contamination in marine salt spray. In the next-to-last column of the table, reversible refers to the ability to fully restore the operational performance to its uncontaminated state, while partially reversible indicates the presence of irreversible factors such as dissolution of the catalyst, corrosion under high-concentration contamination, etc., which can only partially restore the performance of PEMFC. Existing research indicates that in most cases, recovery operations are partially reversible.

Table 4. Recovery strategies for PEMFC after salt ion contamination from the marine salt spray.

Authors	Experimental Methods	Recovery Method	Reversibility or Not	Performance Recovery
Li et al. [40]	HCl cathode or anode injection	H_2O introduced to the cathode or anode	Irreversible at high concentrations, partially reversible at low concentrations	A slight decrease than initial state at 4 ppm contamination
Park et al. [45]	NaCl cathode atomization injection	Apply an external voltage of 1.3 V to the cathode	The initial working voltage is reversible at 0.6 V and partially reversible at 0.9 V	Recovery degree 100% at 0.6 V, only partially recover at 0.9 V
Qi et al. [57]	Cations contaminations cathode atomization injection	Air introduced to the cathode	Partially reversible	Only a slight increase in voltage in all cases
Sasank et al. [71]	Marine salt spray cathode injection	H_2O introduced to the cathode	Partially reversible	The maximum performance recovery of PEMFC could reach 93.3%
Lamard et al. [72]	NaCl cathode atomization injection	N_2, H_2O introduced to the cathode	Partially reversible under short-term contamination, while irreversible under long-term contamination	Under less than 50 h of contamination, the performance can be restored by about 80%
Yoo et al. [74]	NaCl cathode atomization injection	H_2O introduced to the cathode	Partially reversible	The serpentine flow field recovered 52.96%, the parallel flow field 1.22%
Unnikrishnan et al. [78]	Cl_2 cathode and anode injection	Apply an external voltage of 0.1 V to the cathode	Reversible	Performance recovery 100%
Reshetenko et al. [79]	Cathodic injection of Br^--containing solution	Air, N_2 introduced to the cathode	Air purging is irreversible, while N_2 purging is reversible	Performance recovery only 50 mv

When PEMFC works in the marine salt spray environment, although filters and other devices can provide certain protection, the impact of salt ions in marine salt spray on PEMFC is difficult to avoid due to factors such as long working hours. Although commonly used recovery methods can achieve the goal of PEMFC performance recovery to a certain extent, they also have certain limitations. Solvents such as deionized water have high surface tension and limited water solubility, making it difficult to fully remove these salt spray ions. Meanwhile, electrochemical methods also have the risk of causing local overheating and structural changes such as catalyst porosity and curvature. To improve the lifespan of PEMFC, reduce replacement costs, and maintain high efficiency during operation, more targeted and feasible recovery strategies are needed, such as self-healing materials or advanced coatings, etc.

4. Conclusions

This study provides an overview of the impact of salt ions in the marine salt spray environment on the performance of PEMFC, and delves into the mechanisms of its effects on the components of PEMFC, focusing on the bipolar plate, gas diffusion layer, catalyst layer, and proton exchange membrane.

For the bipolar plate, the impact of marine salt spray is primarily manifested in the corrosion of the bipolar plate. This corrosion is mainly due to the pitting corrosion induced by anions, such as Cl^- and F^-. The higher the concentration of Cl^- and F^- is, the lower the corrosion resistance of the bipolar plate.

For the gas diffusion layer, white sediment will appear, composed of salt substances formed by metal cations, such as Na^+ and Ca^{2+}. These salts predominantly deposit on the carbon fibers as white precipitates, reducing the hydrophobicity and increasing the mass transfer resistance of the gas diffusion layer.

For the catalyst layer, the cations can affect the oxygen reduction reaction. Anions, represented by Cl^-, can adsorb on the surface of Pt catalyst, blocking the active sites of Pt. Additionally, Cl^- can react with Pt to form chloride complexes, which facilitate the dissolution of the Pt catalyst. The phenomena of Pt growth and aggregation may also occur. These processes can lead to the decrease in the electrochemical active area and the increase in charge and mass transfer resistances.

For the proton exchange membrane, the sulfonic acid group in the commonly used perfluorinated sulfonic acid proton exchange membrane has a stronger affinity for cations in marine salt spray and is prone to ion exchange with H^+ on the sulfonic acid group. The newly formed sulfonic acid structure reduces the proton conductivity of the proton exchange membrane.

The higher the concentration of contaminants and the longer the duration of contamination, the more pronounced the performance decline of PEMFC is. For the recovery strategies, applying an appropriate voltage, or purging with air, N_2, H_2O, and other specific cleaning agents, can restore the performance of contaminated PEMFC. Due to irreversible factors such as corrosion and Pt catalyst dissolution caused by high-concentration salt ion contamination, recovery measures in most cases are only partially reversible. This review seeks to identify solutions for mitigating the impact of marine salt spray on PEMFC performance and to establish a theoretical basis for guiding the development of corrosion-resistant, high-performance PEMFC suitable for the marine salt spray environment.

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