Experiment study on sodium chloride diffusion in membrane electrode of proton exchange membrane fuel cell

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Abstract: The sodium chloride poisoning of proton exchange membrane fuel cell (PEMFC) has important influence on performance. The concentration diffusion of NaCl on a PEM fuel cell membrane electrode (MEA) was investigated. The MEA was soaked in five NaCl solutions with different concentrations (0mg/L, 50mg/L, 100 mg/L, 300 mg/L, 500 mg/L), and the surface morphology was observed by scanning electron microscope, and the element content was quantitatively analyzed by energy dispersive spectrometer. The results show that with the increase of pollution concentration, the number and size of sodium chloride square crystal on the gas diffusion layer also show a positive correlation. At the same time, the analysis of the determination results of the energy dispersive spectrometer shows that the closer to the proton exchange membrane region of the membrane electrode, the percentage of sodium atom content also presents a positive correlation.

1. Introduction
At present, the shipping industry is under increasing pressure to cope with greenhouse gas emission reduction, and needs to find alternative energy sources to reduce emissions of CO\textsubscript{2} and other exhaust pollutants\textsuperscript{1}. Ammonia and hydrogen are the most promising zero-carbon fuels for the shipping industry, according to the report, The Potential of Zero-carbon Fuels for Ships in Developing Countries. China's carbon peak and carbon neutral targets put forward clear requirements for the transformation of carbon reduction in the field of transportation, and the voice of "hydrogen on board" is gradually rising. As a key carrier for converting hydrogen energy into electric energy, hydrogen fuel cell has been one of the hot issues in the global development of clean energy technology in recent years\textsuperscript{2-3}. Proton exchange membrane fuel cell (PEMFC) not only has high energy conversion efficiency and little environmental pollution, but also has simple structure and stable operation, which has great advantages in energy conservation, emission reduction and improvement of Marine environment\textsuperscript{4}. Hydrogen fuel cell is a green ship energy with broad prospects. However, Marine environment which is different from terrestrial environment should be considered when PEMFC technology is applied to ship. The salt spray content in the Marine environment is about 10~20 times that in the land\textsuperscript{5}. Under the influence of the Marine atmospheric environment, the air into the cathode of the Marine proton exchange membrane fuel cell inevitably contains sodium chloride impurity.

At the beginning of 21st century, domestic and foreign scholars began to study and report the problem of sodium chloride poisoning in PEMFC. In 2006, Mikkola and Rockward et al.\textsuperscript{6} of Los Alamos National Laboratory proved through cyclic voltammetry and resistance compensation that Cl\textsuperscript{−} had little effect on the electrochemical reaction of fuel cells in low current density regions. The concept of "sodium chloride poisoning" was first proposed, and they found that NaCl became a potential long-
term source of sodium chloride after initial exposure. Yan et al. [7] pointed out that the hydrogen pumped into the cathode of fuel cell contained sodium chloride impurity, which would lead to the reduction of toxic performance and service life of the battery. Wang [8] and Huan Guang [9] et al. respectively studied the toxicity mechanism of Mg$^+$ and Na$^+$ on fuel cells, and believed that metal impurity ions on fuel cells mainly affected the performance of fuel cells by obstructing proton transport in the membrane, and the obstruction of proton transport by impurity ions was also the main reason for the increase of resistance of PEMFC. Wang Leilei et al. [10] prepared cationic impurity solution for immersion experiment by simulating water generated by PEM fuel cell, and studied the influence of metal cationic impurities on the performance of PEMFC by changing the experiment time. It was found that the performance of PEMFC decreased with the increase of immersion time. Zhu Jingyu et al. [11] studied the immersion of proton exchange membrane in cationic solutions with different MgSO$_4$ concentrations. Through analysis and IEC determination, XRD, TGA and ATR-FT-IR experimental results, it was confirmed that the foreign Mg$^{2+}$ pollutant would reduce IEC of Nafion membrane, and make the proton conduction capacity of the membrane worse. The chemical structure of the membrane is damaged, the crystallization and thermal stability of the membrane are deteriorated, and the performance of the proton exchange membrane is affected.

In summary, the current relevant literature focuses on the performance change rule of PEM fuel cell after cation pollution. There are few reports on the pollution of PEM fuel cell membrane electrode by sodium chloride in Marine environment. This paper is based on the existing experimental methods for studying cations. The concentration diffusion experiment of sodium chloride on PEM fuel cell membrane electrode soaked in sodium chloride solution was investigated.

2. Experiment

2.1 Experiment Scheme
PEMFC membrane electrode is the core component of the battery. Taking MEA as the research object, five groups of membrane electrodes soaked in NaCl contaminated solution with different concentrations were designed to investigate the NaCl diffusion experiment on PEMFC membrane electrode. The surface morphology and element content of MEA were measured by scanning electron microscope and energy dispersive spectrometer, and the NaCl diffusion effect on PEMFC membrane electrode was directly presented from the microscopic morphology and quantitative element content.

2.2 Reagents and Instruments
The membrane electrode (as shown in Fig. 1) consists of carbon paper gas diffusion layer, Pt/C electrode catalytic layer with Pt loading of 0.48 mg/cm$^2$ and Nafion 211 proton exchange membrane, with an effective area of 25 cm$^2$, produced by Wuhan New Energy Co., LTD. Sodium chloride: 99% pure, produced by Tianjin Zhiyuan Chemical Reagent Co., LTD. Deionized water is provided by Shaoxing Zhihuan Trading Co., LTD. Hh-2 constant temperature water bath and DZF-6020 vacuum drying oven are provided by Shanghai Li Chen Bang Xi Instrument Technology Co., LTD. Germany Zeiss Field emission scanning electron microscope SIGMA 300 (as shown in Fig. 2).
2.3 Configuration of Contaminated Solution
Configuration of sodium chloride solution: NaCl powder with a purity of 99% is dissolved in deionized water with an impedance of 18 Ω, and four NaCl solutions with different concentrations (50 mg/L, 100 mg/L, 300 mg/L, 500 mg/L) are prepared. In the control experiment, deionized water without NaCl powder was used as the solution.

2.4 Experimental Process
Preparation of fouling film electrode assembly: First, the weighed 5 film samples were put into a vacuum drying oven at 80 ℃ for 8 h, and then the weight of the samples was weighed again. Secondly, the five dried film electrode components were placed in five beakers with different NaCl concentrations in the digital display constant temperature water bath, which were filled with 0 mg/L, 50 mg/L, 100 mg/L, 300 mg/L and 500 mg/L NaCl respectively. During the experiment, the beakers were placed in the digital display constant temperature water bath at 80 ℃ for 20 h, and then vacuum dried to a constant weight. The experiment was repeated three times to verify the consistency of the results.

3. Experimental Results and Discussion
3.1 SEM and EDS Experiments
In order to study the concentration diffusion effect of NaCl on PEMFC membrane electrode assembly, SEM and EDS were used to analyze the morphology and elemental analysis of membrane electrodes contaminated with different concentrations of NaCl. First, the PEMFC membrane electrode assembly contaminated with five concentrations was placed in a vacuum drying oven, during which the sample was kept in an incubator at 80 ℃ until the constant quantity was taken out. Secondly, the membrane electrode assembly was interrupted by liquid nitrogen embrittlement to obtain a consistent flat section, as shown in Fig. 3. Finally, 1 cm×1 cm samples were made according to the testing requirements of SEM and EDS equipment, and sealed in a new zipper bag for SEM and EDS experiments. According to the actual operation requirements, the sample was cut into 8 mm×8 mm, and the surface of the membrane electrode was sprayed with gold. The electron microscope parameters were 3 kv voltage and 300 times magnification. The energy spectrum parameter is, the voltage is 15 kv, the amplification is 1000 times.
3.2 Analysis of Morphology Experiment Results

In order to study the concentration diffusion effect of sodium chloride on PEMFC membrane electrode, the surface morphology changes of membrane electrode contaminated with 0 mg/L, 50 mg/L, 100 mg/L, 300 mg/L and 500 mg/L sodium chloride for 20 h were observed, and the results are shown in Fig. 4. The diffusion residue of sodium chloride was analyzed by scanning electron microscope at the same magnification of 300 X. Fig. 4 (a) As the control group, the electron microscope junction was used as the reference sample for the analysis of the experimental results.

In Fig. 4 (b), a small number of speckle structures were found in the gas diffusion layer (GDL) structure of the membrane electrode after being contaminated with 50 mg/L NaCl for 20 h, which could not be determined as square crystals. In Fig. 4 (c), after 20 h of 100 mg/L NaCl pollution, NaCl square crystal structure was found to be attached to the surface of tubular carbon fiber in GDL structure. With the increase of NaCl concentration, the attachment of NaCl on GDL could be observed obviously. In Fig. 4 (d), NaCl square crystals were found in the GDL structure after 20 h of 300 mg/L NaCl contamination, not only on the surface of the carbon fiber tubular structure, but also at the bonding point. The crystal structure was larger than that of 50 mg/L and 100 mg/L. In Fig. 4 (e), in the GDL structure of the membrane electrode contaminated with 500 mg/L NaCl for 20 h, more NaCl square crystals with larger crystal sizes were observed in the same field of vision. Therefore, it can be seen from Fig. 4 (a) ~ (e) that with the increase of NaCl concentration, the number of NaCl square crystals on the GDL structure of the membrane electrode increased, and the attachment mode expanded from the tubular surface of carbon fiber to the bonding place of the network structure. Secondly, with the increase of NaCl concentration, GDL microscopic characterization can observe the serious damage of carbon fiber interwoven bonding.
3.3 Experimental Results and Analysis of Elemental Analysis

In order to study the concentration diffusion of NaCl contamination on PEMFC membrane electrode, SEM-EDS experiments were performed on PEMFC membrane electrode assembly after being contaminated with 500 mg/L NaCl for 20 h. Fig. 5 shows the cross-section image of PEMFC membrane electrode contaminated with 500 mg/L sodium chloride under electron microscope. In Fig. 5, MEA is divided into five regions. The middle part of the picture is divided into proton exchange membrane with deep color. The left and right sides of the region are the catalytic layer structure, the anodic gas diffusion microporous layer of the membrane electrode assembly is on the far left, and the cathode gas diffusion
microporous layer of the membrane electrode assembly is on the right. Points A, B, C, D and E marked in Fig. 5 respectively represent the locations of dots on the proton exchange membrane, anode and cathode catalytic layer, anode and cathode gas diffusion layer during the EDS experiment.

![Fig. 5 Cross-section image of MEA under scanning electron microscope](image)

Fig. 5 Cross-section image of MEA under scanning electron microscope

Fig. 6 shows the experimental results of EDS for points A, B, C and D. According to the energy spectrum results, NaCl was found in the proton exchange membrane (point A in Fig. 6), the anode catalytic layer (point B in Fig. 6), the anode gas diffusion layer (point D in Fig. 6) and the cathode gas diffusion layer (point C in Fig. 6). Compared with sodium, the content of chlorine is relatively small, and the percentage of atomic content of chlorine in the experimental dot area is less than 0.14 %. The percentage of atomic content of sodium in the four dot experiment results of A, B, C and D is 8.55 %, 8.88 %, 5.88 % and 6.69 %, respectively. After being contaminated with 500 mg/L NaCl for 20 h, the diffusion of sodium chloride concentration in PEM fuel cell membrane electrode is roughly the same, and the percentage of elements near the middle region is slightly higher.

![Fig. 6 EDS dot experiment results of 500 mg/L sodium chloride polluted membrane electrode assembly](image)

Fig. 6 EDS dot experiment results of 500 mg/L sodium chloride polluted membrane electrode assembly
4. Conclusion
The morphology and concentration diffusion of NaCl on the membrane electrode assembly soaked in NaCl solution can be obviously observed. Through the observation of apparent morphology, a small number of sodium chloride crystals were observed on the gas diffusion layer of the membrane electrode soaked with low concentration (less than 100 mg/L) of sodium chloride solution. With the increase of sodium chloride concentration, a large number of sodium chloride cube crystals were observed on the gas diffusion layer of the membrane electrode. According to the energy spectrum experiment results, after 20 h of 500 mg/L NaCl contamination, the diffusion in PEMFC membrane electrode structure is roughly the same, without breaking through the concentration diffusion, but the percentage of atomic content near the middle region is slightly higher than that at the edge. Considering the influence of the length of the experiment, high concentration and long period experiments were considered to further reveal the concentration diffusion effect of sodium chloride on the membrane electrode.

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