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The effect of Fe^{3+} contamination in feed water on proton exchange membrane electrolyzer performance

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Abstract

The effect of ferric ions on cell performance of proton exchange membrane water electrolyzer (PEM WE) was studied by injecting $Fe_2(SO_4)_3$ solution into DI water to prepare different Fe^{3+} concentrations contamination (1, 10, 100 parts per million (ppm, molar ratio)). Results showed that there was clear cell performance decay with increasing Fe^{3+} concentrations, and the cell stopped running at 100 ppm Fe^{3+} concentration in feed water. With increasing temperature, the cell performance increased for a short period. With low Fe^{3+} concentrations, cell performance decreased with increasing current density, but with 10 ppm Fe^{3+} concentration and higher current density of 2 A/cm^2, cell performance was enhanced. Therefore, both temperature and current density can make positive contributions to improve cell performance under the condition of contaminated feed water.

Key words: PEM electrolysis, ferric ion contamination, performance degradation

1. Introduction

Hydrogen, as a clean and flexible energy carrier, plays a pivotal role in the future sustainable energy arena [1]. Water electrolyzer is considered to be a promising hydrogen generator, which separates water by electricity to generate hydrogen and oxygen through an environmentally friendly electrochemical process [2, 3]. Compared with other types of water electrolyzers, PEM WE exhibits a superior performance with high hydrogen production rate, high energy conversion efficiency and high current density, low gas permeability, high gas purity(above 99.99%), compact design, rapid response and wide dynamic operation range, etc. [4-6]. However, one of the major disadvantages of PEM WE is the high capital cost caused by the high loading of noble metal (e.g., Pt, Au, Ir, Ru) electrocatalysts, bipolar plates and their coatings, and the use of perfluorinated sulfonic acid (PFSA) membranes [4, 7]. The balance of performance, durability and cost is the main factor that hinders the commercialization penetration of PEM WE for hydrogen production [8, 9]. To meet capital cost and durability targets, many studies on the components of PEM WE have been done, such as the degradation mechanism analysis and proposing mitigation strategies, noble catalyst reduction [6, 10], membrane [7, 8], bipolar plates [11, 12], manufacturing and assembly process amelioration.

In water electrolysis systems, a water purification system is typically used, but over time the quality of the circulating water may deteriorate for example due to metallic cations such as Fe^3+, Ca^{2+}, Na^+ etc. These cation ions could be originated from the fabricating process of MEA, the corrosion of components materials, such as water pipes, membranes, bipolar plates, the dissolution of electrocatalysts and other sources [13-15]. The cationic contaminants originated from feed water are another severe cause responsible for cell performance decay [5, 15-17]. These impurities migrate into the membrane and occupy ion exchange sites in the membrane and the ionomer in the catalyst layer, leading to an increase in charge transfer resistance and cell overpotential both at the cathode and anode, which will reduce the conductivity of the ionomer and electrode performance [18-20]. In addition, the external metallic cations may accumulate electrochemically on the cathode, hindering the hydrogen evolution reaction [5, 21]. Furthermore, some cation impurities may boost the generation of hydroxide radicals from hydrogen peroxide and hence enhance the membrane degradation caused by the Fenton mechanism [8, 22].

One of the common impurities, Fe^{3+} in feed water has gained much attention from researchers. The effect of Fe^{3+} on membrane conductivity, durability of cell electrode of both PEM fuel cell and water electrolyzer has been explored, and results showed that even very low ppm level (as low as 5 ppm) of Fe^{3+} contamination could cause significant performance degradation of the cell [16, 23]. This study mainly focuses on the influence of Fe^{3+} at different concentrations (0, 1, 10 ppm) in feed water on PEM WE cell performance, and how temperature and current density contribute to the cell performance in the presence of Fe^{3+}.

2. Experimental

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2.1. Single cell assembly

The active area of the membrane electrode assembly (MEA) used in the test is 2.89 cm^2 (1.7 cm × 1.7 cm). The components of the MEA from anode to cathode are Ti felt (350 µm thick, porosity of 81% , fiber diameter of 20 µm) that was employed as the anode porous transport layer, anode side catalyst IrO_2 (0.3 mg cm^{-2}), a commonly used Nafion (117) membrane, and cathode side catalyst Pt/C (0.5 mg cm^{-2}), with a carbon cloth (Sigracet 35 DC) that serves as the cathode porous transprot layer. The MEA was assembled with current collectors and end plates on both sides, and fixed with screws and nuts. The compression pressure was set to 2.61 MPa by controlling the length of the springs on the screws.

2.2. Test bench set-up and contamination procedure

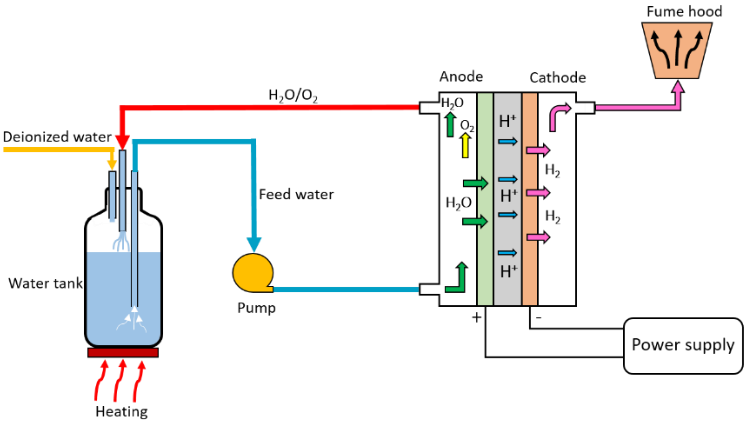

Fig. 1 Schematic of the test bench

Fig. 1 illustrates the test setup used in the experiment. It's a two-electrode set-up, of which the anode acted as the working electrode and cathode was the reference electrode. A Gamry Reference 3000 potentiostat/galvanostat was emplyed as the power supply. The water tank was heated by a heater, and then the cell was heated by feed water to keep a constant temperature. The water flow rate was 270mL min^{-1}. For contamination test, 3 bottles of $Fe_2(SO_4)_3$ solution with different Fe^{3+} ion concentrations (1, 10, 100 ppm) were prepared in advance. The pH of the ferric solution was set to 2 in order to prevent the hydrolysis of Fe^{3+}. The water tank was replaced after each test point with a solution containing the Fe^{3+} concentration of the successive test point, and during each test stage, the ion concentration is assumed constant, neglecting the amount of ions adsorbed on the membrane and pipes, which is deemed plausible as the time scale of the tests was relatively short. Detailed test procedure can be found in Figure S1 in the supplementary material**.**

3. Results and discussion

3.1. Polarization curve analysis

Fig. 2 shows the effect of different Fe^{3+} concentrations in feed water on cell performance. As can be seen from Fig. 2 (a), the cell voltage increased with time both at 60 ^{0}C and 80 ^{0}C, but 4 hours after the feed water temperature was increased to 80 ^{0}C, the cell voltage decreased to even lower than the initial value. Similar cell performance variation trend can be seen at 1 ppm and 10 ppm Fe^{3+} contamination in Fig. 2 (b) and (c), respectively. However, with increasing Fe^{3+} concentrations, the effect of temperature became weaker, the cell voltage for 10 ppm Fe^{3+} concentration decreased but was not better than the initial value when increasing the temperature to 80 ^{0}C. When Fe^{3+} concentration of feed water was 100 ppm, the plot of cell voltage was distorted as shown in Fig. 2 (d) and the effects on the cell were so detrimental that the channels were blocked after 2 h. Therefore,the effects of 100 ppm Fe^{3+} concentration will be not discussed further. Fig. 2 (d) and (e) shows the effect of different Fe^{3+} concentrations on cell performance at constant temperature. As can be seen both in (d) and (e) , in the presence of Fe^{3+}, the cell voltage increased both with time and when increasing Fe^{3+} concentration from 0 ppm (DI water) to 10 ppm. The big gaps between the two ion concentration test points can be attributed to the Fe^{3+} contamination in feed water.

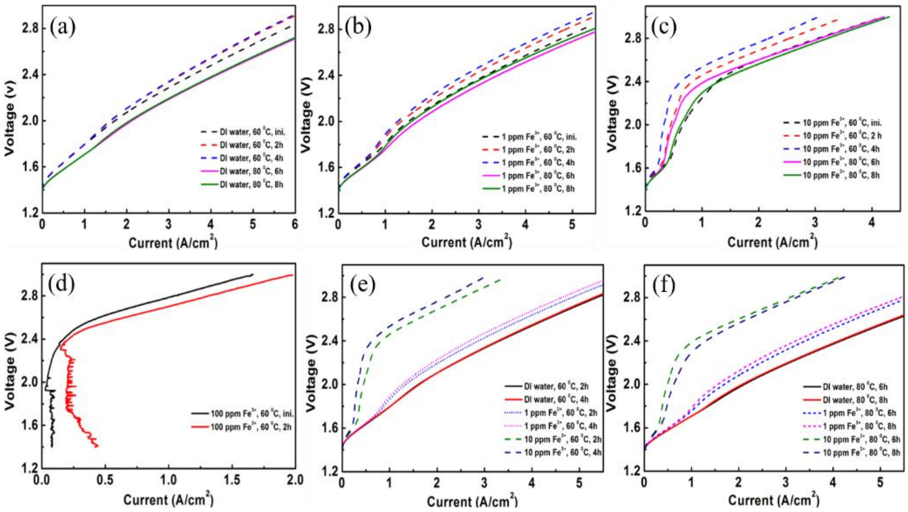

Fig. 2 Polarization curves of electrolyzer with different ferric ion concentrations at different temperatue, (a) DI water, (b) 1 ppm Fe^{3+} solution, (c) 10 ppm Fe^{3+} solution, (d) 100 ppm Fe^{3+} solution, (e) at 60 ^{0}C, (f) at 80 ^{0}C.

The result of Fig. 2 illuastrates that increasing the feed water temperature to some degree (from 60 ^{0}C to 80 ^{0}C in this study) can enhance the cell performance, because high temperature could improve the electrocatalytic reaction rates both at the anode and cathode and thus reduce the charge transfer resistance, which increased cell efficiency [23, 24]. Nevertheless, when introducing high concentration ferric ions, the cell performance deteriorates. This may be attributed to the higher affinities of Fe^{3+} than protons for the sulfonic acid groups in Nafion [18], which leads to their adsorptions on the Nafion membrane and the ionomer in the catalyst layer thereby occupying ion exchange sites, decreasing the proton conductivity of the membrane and the ionomer [20], and thus lower the cell efficiency. Besides, with increasing Fe^{3+} concentration, the slopes of low current density and high current density increased markedly, which indicates bigger kinetic and ohmic losses. This is reasonable because high concentration will lead to Fe^{3+} acumulation both on the membrane and the catalytic layer, leading to increased ohmic and charge transfer resistace. Also, the existance of Fe^{3+} can promote Fenton reaction [8], which may result in membrane attack , causing cell failure as depicted in Fig. 1 (d).

3.2. EIS test analysis

To further illustrate the performance decay of the cell, EIS tests were carried out, results are shown in Fig. 3. The equivalent circuit model as shown in Figure S2 in the suplimentary material were employed to simulate the EIS data. The obtained resistance values are listed in Table 1.

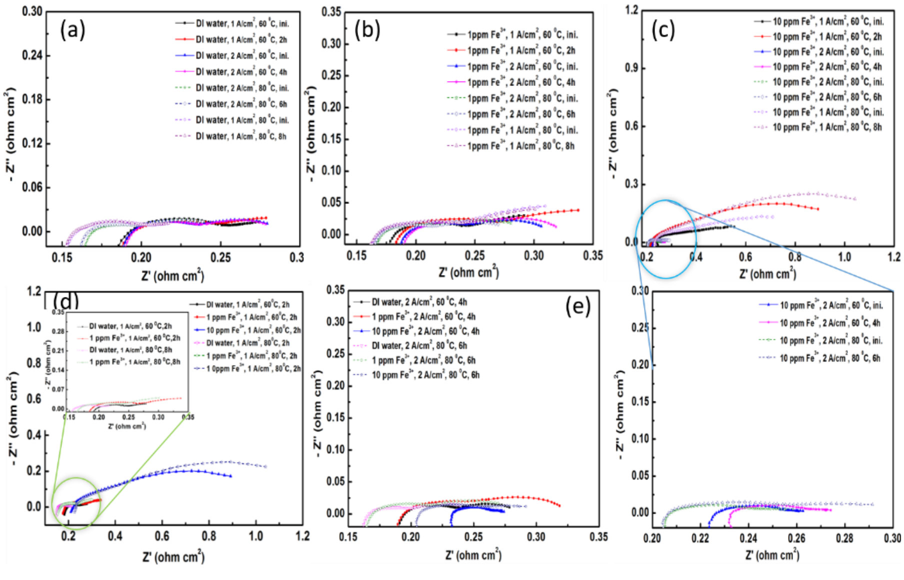

Fig. 3 EIS spectras at test conditions of current density of 1 A/cm^2 and 2 A/cm^2, temperature of 60 ^{0}C, and 80 ^{0}C, (a) DI water; (b) 1 ppm Fe^{3+} solution; (c) 10 ppm Fe^{3+} solution, EIS at (d) 1 A/cm^2, (e) at 2 A/cm^2.

As shown in Fig. 3 (a) and (b), the variation trends for DI water and 1 ppm Fe^{3+} solution were similar, where R_{ohm} and R_{HF} decreased with increase in temperature from 60 ^{0}C to 80 ^{0}C, however, when current density increased from 1 A/cm^2 to 2 A/cm^2, R_{ohm} increased but R_{HF} decreased. When comparing the initial values to the final values, the effect of time under every test condition was not outstanding, indicating there was no significant performance degradation with DI water and low Fe^{3+} concentration contamination (1 ppm) in short time period (2 h in this test). The R$_{ohm}$ and R$_{HF}$ values in Table 1 well confirmed the results of Fig. 3 (a) and (b). While the variation trend of 10 ppm Fe^{3+} solution was a little complex, though the degradation effect was obvious. As shown in Fig. 3 (c), when the current density changed from 1 A/cm^2 to 2 A/cm^2 at 60 ^{0}C, R$_{Ohm}$ increased, however R$_{HF}$ decreased greatly. This could be due to the high current density promoting the reaction processes and thus lowering the charge thansfer resistance, while gas production increase with higher current density will cause gas crossover phonomenon [25]. When the current density was 2 A/cm^2, R$_{ohm}$ decreased with increasing temperature from 60 ^{0}C to 80 ^{0}C, but R$_{HF}$ increased. Nevertheless, when reduceing the current density from 2 A/cm^2 to 1 A/cm^2 at 80 ^{0}C, the cell performance didn’t get better as Fig. 3 (a) and (b) show. Similarly, at 1 A/cm^2 higher temperature of 80 ^{0}C didn’t contribute to a better cell performance compared with the same current density at 60 ^{0}C. From Fig. 3 (d) and (e), one can see that R$_{ohm}$ increases markedly with increase in Fe^{3+} concentration, corresponding to the result presented in Table 1. With 10 ppm Fe^{3+} contamination, the cell shows the largest R$_{HF}$ and R$_{IF}$ value at the end of the test stages, representing the worst charge and mass transfer performance. This is reasonable because with increasing Fe^{3+} concentration, more and more Fe^{3+} will acumulate not only on the membrane occupying or even blocking the proton and gas transfer channels resulting in gas crossover phenomenon, but also will agglormerate on the catalyst layers, lowering the reaction kinetics and leading to increased R$_{ohm}$, R$_{HF}$ and R$_{IF}$ values. The results also show that the effect of severe Fe^{3+} contamination on cell performance is unrecoverable and cannot be compensated by changing temperature and current density.

Table 1 Impedance values obtained by fitting the experiment datas to the equivalent circuir

Test condition	R$_{ohm}$ /(ohm*cm^2)	R$_{HF}$ /(ohm*cm^2)	R$_{IF}$ /(ohm*cm^2)
DI water, 1A/cm^2, 60 ^{0}C, 2h.	0.173	0.058	0.063
DI water, 2A/cm^2, 60 ^{0}C, 4h.	0.182	0.054	0.057
DI water, 2A/cm^2, 80 ^{0}C, 6h.	0.156	0.041	0.06
DI water, 1A/cm^2, 80 ^{0}C, 8h.	0.153	0.05	0.041
1ppm Fe^{3+}, 1A/cm^2, 60 ^{0}C, 2h	0.177	0.091	0.142
1ppm Fe^{3+}, 2A/cm^2, 60 ^{0}C, 4h	0.183	0.06	0.091
1ppm Fe^{3+}, 2A/cm^2, 80 ^{0}C, 6h	0.159	0.055	0.075
1ppm Fe^{3+}, 1A/cm^2, 80 ^{0}C, 8h	0.154	0.076	0.152
10ppm Fe^{3+}, 1A/cm^2, 60 ^{0}C, 2h	0.228	0.145	0.28
10ppm Fe^{3+}, 2A/cm^2, 60 ^{0}C, 4h	0.232	0.037	0.014
10ppm Fe^{3+}, 2A/cm^2, 80 ^{0}C, 6h	0.201	0.051	0.049
10ppm Fe^{3+}, 1A/cm^2, 80 ^{0}C, 8h	0.218	0.197	0.934

Drawing on the research experience of fuel cells, multivalent cation ions such as Al^{3+}, Fe^{3+}, Mg^{2+} in feed water have stronger affinity for sulfonic acid groups in Nafion than protons and substitute protons in the ion exchange process [26, 27]. In this study, some degree of side-chains occupation effect of Fe^{3+} in the ionomer is suspected and the decrease in cell performance with increasing Fe^{3+} may be connected to it.

4. Conclusion

The influence of Fe^{3+} cotamination on cell performance was investigated by introducing different concentrations of Fe^{3+} in the circulating water. Results of porlarization and EIS tests showed that the cell perfomance degrades severely with Fe^{3+} concentration increase in feed water. The Fe^{3+} ions adsorbed on Nafion membrane and catalyst layers, resulting in the increase of membrane ohmic resistance and charge transfer resistance on both electrodes. High temperature and low current density can contribute to improve cell performance at low Fe^{3+} concentration. The values obtained through fitting the experiment data with equivalent circuit model were used to better describe the results. Long time degradation test of PEM water electrolysis with Fe^{3+} contamination are necessary to fully understand the mechanisms of how Fe^{3+} ions contribute to the cell performance decay and components corrosion.

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