



# The influence of Ferric ion contamination on the solid polymer electrolyte water electrolysis performance



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## ABSTRACT

Fe<sup>3+</sup> is a sort of common metal ion contaminant for the solid polymer electrolyte (SPE) water electrolyser. In this paper, the effect of Fe<sup>3+</sup> on the performance of SPE water electrolyser has been investigated by both in-situ and ex-situ characterizations. The electron probe microanalysis and ultraviolet test results showed that Fe<sup>3+</sup> could migrate from the anode to the cathode and mostly be reduced to Fe<sup>2+</sup> in the cathode rather than occurred underpotential deposition as described in the previous report. The in-situ dynamic contamination test showed that the anode voltage increased sharply as soon as the Fe<sup>3+</sup> was fed into the anode, while the cathode voltage kept constant until the contamination time was over 30 minutes, indicating the higher tolerance of the cathode than the anode for the Fe<sup>3+</sup> contamination. The calculation results based on the electrochemistry impedance spectroscopy test results revealed that the striking increase of the electrolysis voltage was mainly attributed to the ohmic overpotential, which was due to the replacement of H<sup>+</sup> by Fe<sup>3+</sup> in the Nafion resin. Interestingly, the voltage lagged behind the current for several minutes in the multi-current-step test for the contaminated electrolyser, which phenomenon may be used for judging whether the SPE water electrolyser performance degradation is due to the metal ions contamination. Furthermore, recovery strategy has been developed, and it was found that the contaminated electrolyser could be mostly recovered by 0.5 M H<sub>2</sub>SO<sub>4</sub> solution treatment for 13 h.

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## 1. Introduction

Solid polymer electrolyte (SPE) water electrolysis provides a promising method to produce hydrogen from renewable but intermittent energy sources [1–5]. Compared with the conventional alkaline water electrolyser, SPE water electrolyser possesses the advantages of higher safety, simplicity, greater energy efficiency, higher specific production capacity and lower maintenance [2–4,6–8]. However, during water electrolysis process, the membrane electrode assembly is susceptible to cation impurities, including Na<sup>+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup> and Fe<sup>3+</sup>, originating from the fabrication of the MEA, the impurity of feedwater, the corrosion of water pipes and stack component materials, and other sources [9–13]. The cations may affect the electrolysis performance by exchanging with protons in the Nafion electrolyte and depositing at the cathode.

The replacement of protons by metal ions significantly impacts the ionic conductivity of the Nafion electrolyte [14–17]. This is because that most of the metal ions possess higher affinities than protons for the sulfonic acid groups in Nafion, and that the mobility of the metal ions in Nafion electrolyte is quite lower than that of protons [18]. Moreover, the replacement of protons by metal ions impacts water transportation in Nafion electrolyte, for the much faster diffusion of H<sub>3</sub>O<sup>+</sup> than that of the complex metal ion - water clusters [M-(H<sub>2</sub>O)<sub>m</sub>]<sup>n+</sup> [14,19].

The exchanged metal ions, driven by the cell voltage and concentration difference, will transfer across the Nafion membrane to the cathode. Some metal ions, such as Cu<sup>2+</sup>, have positive reversible potential compared with the standard hydrogen electrode (SHE), thus bulk deposition of these metal ions can occur at the cathode of the water electrolyser. Some metal ions, e.g. Sn<sup>2+</sup>, possess negative reversible potential versus SHE, can occur underpotential deposition of monolayer on the surface of the catalyst [20]. Some other metal cations, such as Ca<sup>2+</sup>, have too negative Nernst potential and can not deposit on the cathode catalyst. But they could precipitate as hydroxides at the interface

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between the Nafion membrane and the cathode catalyst layer, thus decrease the conductivity of the MEA.

The metal ions contamination is a slowly accumulative process during SPE water electrolysis. Therefore, it is necessary to take detail study on the dynamic process of the metal ions contamination to the electrolyser. However, there are limited reports about this study [10,20–22]. Kötzt et al. [20] discovered that RuO<sub>2</sub> cathodes were insensitive to metal ions contamination for the underpotential deposition phenomenon did not occur on RuO<sub>2</sub>. Wei et al. [10] provided evidence for the accumulation of metal ions in the feed-water during electrolysis. The influence of Na<sup>+</sup> on the SPE water electrolysis was studied in our previous work [21,22]. It was found that 0.05 M Na<sup>+</sup> caused serious performance degradation to the electrolyser, which mainly resulted from the cathodic overpotential increase for the reaction of  $2\text{H}_2\text{O} + 2\text{e}^- = \text{H}_2 + 2\text{OH}^-$ .

Fe<sup>3+</sup> is a sort of common metal ion contaminant for the SPE water electrolyser. It can originate from the impurities of feed-water, the corrosion of water pipes and stack component materials. Understanding how and to what extent Fe<sup>3+</sup> affects the SPE water electrolyser can help to choose proper feed-water purity standards and component materials with acceptable corrosion rates, develop analytic methods and recovery statics for the poisoned electrolyser. Herein, the effect of Fe<sup>3+</sup> on the SPE water electrolyser performance was investigated by both in-situ contamination test and ex-situ characterization, the recovery strategy was also developed.

## 2. Experimental

### 2.1. Preparation of MEA

The CCM was prepared by spraying 5 wt.% of Nafion solution (0.6 mg cm<sup>-2</sup>) and isopropanol onto each side of Nafion membrane (Dupont 115), followed by spraying catalyst layers. Iridium black (Johnson Matthey) and Pt/C (70 wt.%, Johnson Matthey) were used as the anode and cathode catalyst, respectively. Homogeneous ink consisting of catalyst (Iridium black or Pt/C), Nafion solution (5 wt.%, Du Pont) and isopropanol was sprayed onto the Nafion membrane with Nafion layers to form the catalyst layers. The catalyst loading of the CCM was about 2.0 mg cm<sup>-2</sup> for iridium black and 1.0 mg cm<sup>-2</sup> for Pt/C. Porous titanium (Pt plated, 0.7 mm in thickness) and wet-proof carbon paper (Toray, TGP-H-60) served as the anode and cathode diffusion layer, respectively. The MEA was fabricated by hot pressing the CCM and the carbon paper together.

### 2.2. Single cell test and ferric contamination

A home-made electrolysis test stand was employed to evaluate the performance of the CCM. The SPE water electrolyser performance was evaluated at atmosphere pressure and 80 °C. After the electrolyser operating galvanostatically at 500 mA cm<sup>-2</sup> for 30 min with deionized water fed to the anode side at the flow rate of 10 mL min<sup>-1</sup>, 500 mL solution containing 0.005 mol L<sup>-1</sup> Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and 0.01 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> was continuously delivered to the anode side. The add of sulphuric acid was to avoid the hydrolysis of Fe<sup>3+</sup>. The water from the cathode was exported into a water tank containing 500 mL deionized water. The pH changes of the anode feed water and cathode water were measured by immersing the basic pH meter PB-10 (Sartorius AG) into the anode water tank and cathode water tank, respectively.

The single electrode potentials were measured against a saturation mercury electrode (SCE,  $E = 0.242\text{ V vs. SHE}$ ) and finally calibrated against SHE. As schematically shown in Fig. 1, the SCE was placed in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution, then an ionic contact can be formed by immersing the piece of Nafion membrane extending from the MEA in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution [21–24].

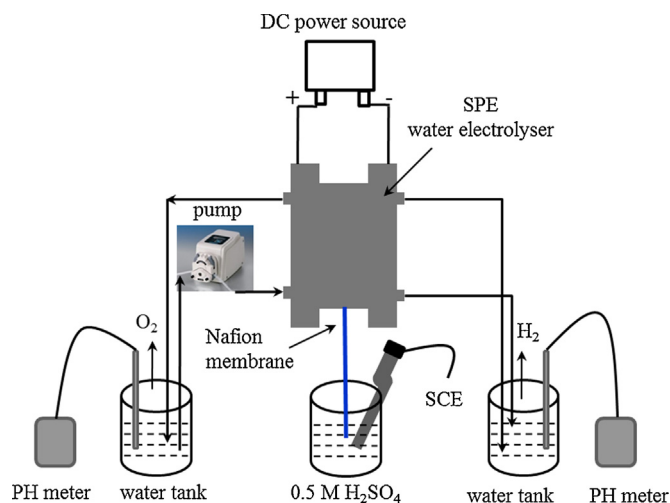


Fig. 1. Schematic illustration for the single cell test stand of water electrolysis.

Electrochemistry impedance spectroscopy (EIS) was carried out at 1.45 V vs. SHE by Solartron 1287 Electrochemical Interface in conjunction with Solartron 1260 Frequency Response Analyzer [25].

### 2.3. Physical characterizations

The iron element distribution on the cross-section of the contaminated CCM was investigated by electron probe microanalysis (EPMA, SHIMADZU EPMA-1600).

The changes in weight percentage of iron element in the cathode water were determined by inductively coupled plasma (ICP, Optima, 2000DV) analysis.

The valence of iron element in the cathode water was determined by phenanthroline spectrophotometry method [26] on a UV-vis spectrophotometer (SHIMADZU, UV-2550). All the chemicals used were of analytical grade. The test solution for determining the total iron content in cathode water was prepared by putting 10 mL cathode water into a 100 mL volumetric flask, then sequentially adding 50 mL deionized water, HCl solution to adjust the pH to 2, 2.5 mL ascorbic acid (20 g L<sup>-1</sup>) solution to reduce Fe<sup>3+</sup> to Fe<sup>2+</sup>, 10 mL acetic acid-sodium acetate buffer solution (pH = 5), 5 mL phenanthroline solution (2 g L<sup>-1</sup>), and finally diluting to the mark with deionized water. The test solution for determining the Fe<sup>2+</sup> content in cathode water was prepared with the above procedure except that ascorbic acid solution was not used. The absorbance was measured at 510 nm and the Fe<sup>2+</sup> concentration was read from the standard concentration curve. The Fe<sup>3+</sup> concentration could be determined by difference.

## 3. Results and discussion

Fig. 2 showed the effects of 0.01 M Fe<sup>3+</sup> on the electrolysis performance. As shown in Fig. 2a, the anode voltage severely increased initially until reaching a maximum, then slowly dropped and finally became steady. According to the previous reports [15,27,28], the mobility of Fe<sup>3+</sup> in the Nafion membrane was between  $2.6 \times 10^{-9} - 7.1 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ , so it only needs no more than 5 s for Fe<sup>3+</sup> to transfer from anode surface to cathode when the thickness of Nafion 115 membrane and anode catalyst layer is about 125 μm and 10 μm, respectively. What's more, the ICP analysis (Fig. 4) also showed that Fe element appeared in the cathode water when the electrolyser was contaminated for 5 min, which further verified that the Fe<sup>3+</sup> reached the cathode catalyst layer. However, the cathode voltage was not influenced until when

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