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The dynamic-state effects of sodium ion contamination on the solid polymer electrolyte water electrolysis



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HIGHLIGHTS

• The dynamic-state effect of Na⁺ on the SPE water electrolysis is studied.

• Operation conditions significantly affect the degradation.

• Anode poisoning causes more severe degradation than cathode poisoning.

• The degradation is mainly attributes to the increase in cathode overpotential.

• The reaction $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ takes place at cathode.

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ABSTRACT

Na⁺ is a likely intrinsic impurity in water and is a potential cation impurity in the solid polymer electrolyte water electrolysis. In this paper, the dynamic-state effect of low concentration of Na⁺ is studied by adding Na⁺ into the deionized water fed in the SPE water electrolyser. The dynamic variation of cell voltage results show that the cell performance degraded more severely in the presence of Na⁺ impurity by anode poisoning than by cathode poisoning. The severity and poisoning rate of the cell depend on the Na⁺ concentration, water flow rate and cell temperature. However, the current density does not impact the extent of the cell voltage increase. In the meantime, an external reference electrode is used to measure the anode and cathode poisoning. EIS measurements show that the performance difference primarily comes from the kinetics loss rather than the ohmic loss. The decrease of available protons in the three phase boundaries may lead to the increase in charge transfer resistance. The electron probe microanalysis tests show that Na⁺ remains in CCM even recovered with deionized water, which results in only partially recovered cell performance.

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1. Introduction

Hydrogen is an efficient and clean energy source and will be widely used in the future [1]. The solid polymer electrolyte (SPE) water electrolysis is considered to be a very promising technology of producing hydrogen from renewable energy source [2,3]. And it possesses significant advantages compared with the conventional alkaline electrolyte water electrolysis, including greater operating safety, higher product purity and energy efficiency [4–9].

During water electrolysis operation, cationic contaminations originating from stack component materials and feed water can cause serious performance degradation of electrolyser. The impurities will produce a progressive increase of cell voltage or a decrease of current density [6,10], because these cations have higher affinity than protons for the sulfonic acid group sites and replace protons in accord with normal ion exchange processes in the ionomer phase [11–14]. The cationic impurity could significantly reduce the conductivity of the membrane and reduce water content in the fully hydrated membranes by replacement of protons [11,15]. Furthermore, platinum is the best electrocatalyst for hydrogen evolution in acid media and it is extremely sensitive to poisoning by under potential deposition (UPD) of monolayer of other metals. NiSO₄ in the feed water resulted in a strong decrease in current density because the platinum surface was covered by nickel deposition and proton discharge took place on nickel with a



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much higher cathodic overvoltage than on bare platinum [4]. It was found that the UPD of Cu monolayer produced an overpotential increase of 160 mV at 100 mA cm⁻² during hydrogen evolution for platinum electrode [10]. Moreover, Kotz and Stucki [16] demonstrated that the poisoning of platinum in the presence of Cd^{2+} or Cu^{2+} ions occurred immediately, causing steep overpotential increase during hydrogen evolution in acid media.

Sodium ion is a common impurity in the feed water. It has very negative Nernst potential and cannot be reduced at the cathode. Only a few researches about the influence of Na⁺ on fuel cells were reported. The in situ contamination results showed that Na⁺ impurities could exchange with protons in the cathode catalyst layer, which resulted in the dramatic decrease of the fuel cell voltage mainly due to the cathode overpotential increase [13]. In addition, Na⁺ in the air stream at the cathode side severely affected the performance of a proton exchange membrane fuel cell, which is primarily caused by ohmic losses due to the displacement of protons by Na⁺ [17,18]. In the aspect of modeling, the simulation showed that the cationic contaminants will always be more concentrated on the cathode side, and decrease the exchange current density and the limiting current by decreasing the available protons in the cathode catalyst layer [19]. In our previous work, the influence of high concentration of Na^+ (0.05 mol L⁻¹) on the SPE water electrolysis was studied [20]. Base on previous study results, high concentration of Na⁺ causes serious performance degradation to SPE water electrolyser, which mainly resulted from the cathodic overpotential increase. Additionally, it was found that and the pH of cathode outlet water increased to above 11.0 due to the reaction of $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$. From a practical point of view, the concentration of contaminant is extremely low in the feed water. Accordingly, it is important to study the influence of low concentration of Na⁺ for the application of SPE water electrolysis.

In this work, the dynamic-state effect of low concentration of Na^+ on the SPE water electrolysis was investigated. The influence of different operating conditions were also investigated, including Na^+ concentrations, feed water flow rates, cell temperatures and current densities.

2. Experimental

2.1. Materials and fabrication

Ir black (HiSPEC 16000, Johnson Matthey) and Pt/C catalyst (70 wt.%, HiSPEC 13100, Johnson Matthey) were used as anode and cathode electrocatalysts, respectively. To prepare the catalyst coated membrane (CCM), a homogeneous ink consisting of catalyst, Nafion solution (5 wt.%, DuPont) and isopropanol was sprayed onto each side of a Nafion 115 membrane. The resulting loading of Ir black and Pt/C was 2 mg cm⁻² and 1 mg cm⁻², respectively. The Nafion content was 25 wt.% for both sides. The platinum-plated porous titanium plate and carbon paper (Toray H-060) were used as anode and cathode current collector, respectively. The membrane electrode assembly (MEA) was fabricated by hot pressing the CCM and carbon paper together at 140 °C under a pressure of 1 MPa for 2 min. The effective area of the MEA was about 5 cm⁻².

2.2. Single cell tests and electrode potential measurements

The single cell tests were carried out with a SPE water electrolyser (Fig. 1a). The end plate was made of stainless steel. The porous titanium plate and stainless steel mesh were used as anode current collector and cathode flow field, respectively.



Fig. 1. (a) Sketch of the single SPE cell; (b) Sketch of the single cell test stand of water electrolysis.

The cell was operated galvanostatically at 500 mA cm⁻² and the cell temperature was kept at 60 °C with deionized water feeding to anode and cathode. In the anode poisoning, the contaminant was fed to the anode with deionized water containing Na_2SO_4 , and the concentration of Na^+ impurity was varied as 0.001, 0.002, 0.005 mol L^{-1} . Similarly, the cathode poisoning study was followed by the same procedure. The pH values of the anode and cathode outlet water were monitored by basic pH meter PB-10 (Sartorius AG) during the whole experiment.

To investigate the dynamic-state effect of Na⁺ and the poisoning mechanism, the anode and cathode electrode potentials should be measured separately. An external reference electrode was introduced, as mentioned in Refs. [13,14,21]. The anode and cathode electrode potentials were measured against a saturation calomel electrode (SCE, E = 0.242 V vs. RHE). As shown in Fig. 1, the extending part of Nafion membrane in the MEA was immersed in 0.5 mol L⁻¹ H₂SO₄ solution. The end of the reference electrode (SCE) was positioned close to the Nafion sheet to reduce solution ohmic potential drops. Using this method, the ionic contact was assured through forming a bridge between the MEA and H₂SO₄ solution [13]. The anode and cathode potential was measured separately by a multimeter, from which one of the leads was connected to the anode or cathode and the other was connected to the reference electrode. The electrode potentials

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