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Effect of Nafion Loading in the Oxygen Electrode on Performance of the PEM-type Water Electrolyzer

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Abstract: *The electrocatalyst layers of the oxygen electrode with various Nafion loading for water electrolyzer with polymer electrolyte membrane (PEM-type) were prepared, and the relationship between Nafion loading in the oxygen electrode and the performance of PEM-type water electrolyzer were examined by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and Steady-state galvanostatic polarization (GP). It is found that the appropriate Nafion loading in the oxygen electrode (i.e., 0.5 and 1.0 mg/cm^2) can increase the electrochemically active area and decrease resistance of electrocatalyst layer. The decrease in working voltage for water electrolyzer with 0.5 and 1.0 mg/cm^2 Nafion loading was 0.23 and 0.19 V at a current density of 1A/cm^2, compared with that of water electrolyzer without Nafion loading (2.25V).*

Keywords: Nafion loading, water electrolysis, oxygen electrode

1. INTRODUCTION

The utilization of hydrogen as an energy carrier is believed to be an ideal energy system because of its high conversion efficiency, regenerative and zero-emission properties [1]. Renewable energy sources, like the sun and wind, can't produce energy all the time. But they could, for example, produce electric energy and hydrogen, which can be stored until needed. Hydrogen can also be transported (like electricity) to locations where it is needed.

Water electrolysis may also play an essential role in making the transition to increased hydrogen use. Hydrogen production by water electrolysis is a clean and simple way of storing energy from sources such as solar, wind and hydroelectric power. Water electrolysis is traditionally carried out in alkaline media with many commercial electrolysers available on the market. The benefits of PEM based electrolysers over alkaline systems is that there is much higher current densities (1-3 A/cm^2 compared with 0.2 A/cm^2 [2,3]), no circulating liquid electrolyte, wide range of power loadings, conversion efficiencies about 90% and very rapid power-up/power-down rates.

Generally, the majority of performance loss for water electrolyser system is attributed to oxygen electrode (anode) overpotential and the cell resistance [4]. Most of the polarization is caused by the oxygen evolution reaction (OER) during water electrolysis. Therefore, the development of anodic catalysts and anode catalyst layer structures for the oxygen evolution reaction is quite important for improving the efficiency of water electrolysis. The Nafion ionomer incorporated with the catalysts in PEM-type fuel cell, enables the porous catalysts to be integrated into the electrolyte by extending the reaction zone [5,6]. Although the influence of Nafion loading in catalyst layer for polymer electrolyte fuel cell (PEFC) or unitized regenerative fuel cell (URFC) has been widely investigated [7-12], the influence of Nafion loading in catalyst layer for PEM-type water electrolyzer has never been discussed in details.

The aim of this work is to gain more information on the effect of Nafion loading on the oxygen evolution performance of anode of PEM-type water electrolyzer by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and Steady-state galvanostatic polarization (GP). It is found that the electrode containing 0.5-1.0 mg/cm^2 Nafion showed good performance. This loading was found to correspond to a minimum in the resistance of electrocatalyst layer and in the oxygen evolution overpotential and a maximum in the electrochemical active area.

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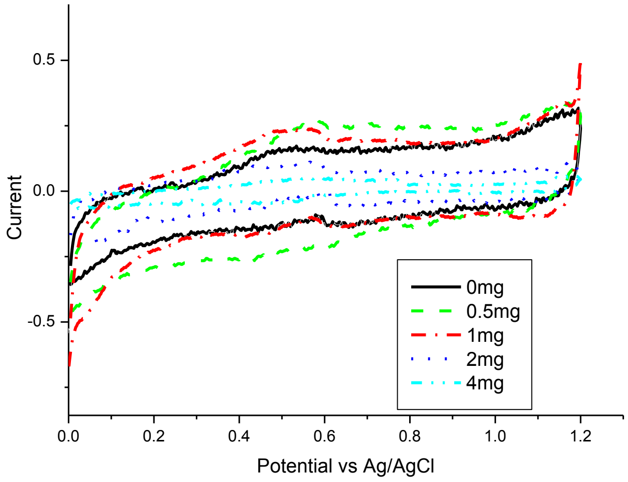

Figure 1. Voltammetric curves of oxygen electrode with various Nafion loadings at $20 mVs^{-1}$ in 1.0M H_2SO_4

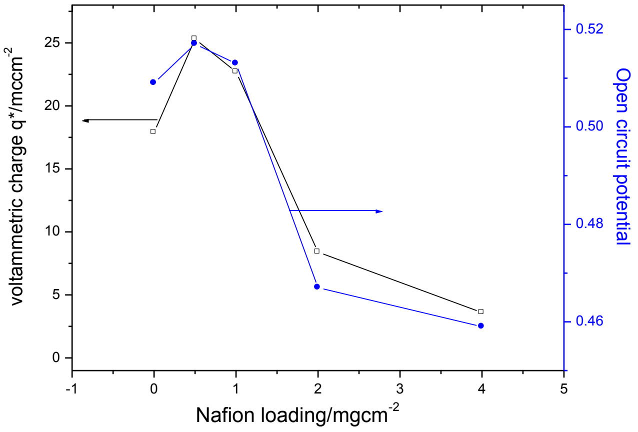

Figure 2. Dependence of voltammetric charge and open-circuit potential of samples on Nafion loading

2. MATERIALS AND METHODS

Nafion membrane and Nafion solution were purchased from Du Pont. 40wt% Pt/C (cathodal catalyst) and RuO_2 (anodic catalyst) were made in self. All the water used was tapped from a Milli-Q Ultra Pure Water system with a water resistivity of 18.2 MΩcm.

2.1. Preparation of MEAs

The anodic and cathodal electrodes were prepared by a brushing procedure using catalysts, carbon powder (Vulcan XC-72, Cabot), a carbon paper substrate, a polytetrafluoroethylene (PTFE) suspension (Teflon 306A, Du Pont) and a 5wt% Nafion solution (Aldrich).

A homogeneous suspension composed of PTFE and carbon powder was brushed onto the carbon paper (geometric area of 9 cm^2) to form the diffusion layer (thickness about 100 μm) of the electrodes [13,14]. The composite structure was then dried at 120℃ for 30 min, followed by thermal treatment at 350℃ for 30 min to remove the dispersion agent contained in PTFE. The amount of PTFE in the diffusion layer is 20 wt%.

To prepare the catalyst layer, a homogeneous suspension was made from the RuO_2 or 40 wt% Pt/C catalyst and the Nafion solution with isopropanol as solvent. The resulting ink was deposited onto the composite diffusion layer of the electrode by a brushing procedure to produce the catalyst layer. RuO_2 and platinum loadings are 10 and 0.4 mg/cm^2 in slurry, respectively. After pretreatment of the Nafion membrane with H_2O_2/H_2SO_4, electrodes and membrane are hot-pressed (4 MPa, 120℃) for 3 min.

The single SPE cell body was made of gilded Ti with flow fields machined into the Ti plates. Gilded Ti-net functioned as backings and was pressed by the Ti-plates against the MEAs.

2.2. Electrochemical measurements

Applying a three electrodes cell with one reference electrode is extremely difficult for the investigation of electrochemical systems with solid electrolytes, furthermore Marshall et al [15] also reported that oxide catalysts have similarly behavior in aqueous and PEM cell.

Thus, cyclic voltammetry (CV) studies were performed with a PAR 273A potentiostat/galvanostat in a three-electrode configuration using a platinum plate counterelectrode and a saturated silver-chloride reference electrode. The working electrode was prepared by mixing the active material with various Nafion loadings in ethanol solvent, which was made into slurry. A small drop of the slurry was added onto the mirror polished glassy-carbon substrate. The electrolyte was 1.0 M H_2SO_4 and the scan rate was 20 mV/s with the voltage range from 0 to 1.2 V referred to the saturated silver-chloride electrode. The voltammetric charges (q*) corresponding to active surface area was determined by integrating the area of the cyclic curve.

Impedance measurements were also performed with a PAR 273A potentiostat/galvanostat in above three-electrode configuration and were carried out using an EG&G-PARC model 5210 lock-in amplifier. The frequencies were scanned from 100 mHz to 100 KHz using the “single-sine” method. The experimental impedance data was fitted to an equivalent circuit using Wuhan University’s EvolCRT software (version 6.0).

The polarization test of electrodes was measured in PEM electrolyzer at galvanostatic condition up to 1.1A cm^{-2} at room temperature.

3. RESULTS AND DISCUSSION

The cyclic voltammetry is also a powerful tool to investigate the effect of Nafion loading on the extension of active region. Cyclic voltammograms of electrodes with various Nafion loadings are shown in Fig.1. The irreversible peaks occurring around +0.5V *vs* Ag/AgCl are attributed to the valence state change of Ru from 3+ to 4+ in RuO_2[16]. According to the investigation of some researchers [17,18], the voltammetric charge q* obtained from integration of the j–E curve is proportional to the number of surface active sites when sweep rate *v* is lower. The change of q* values of samples with various Nafion loadings are shown in Fig.2. It is found that the q* values of the electrodes with 0.5 and 1.0 mg/cm^2 Nafion loadings are higher than others.

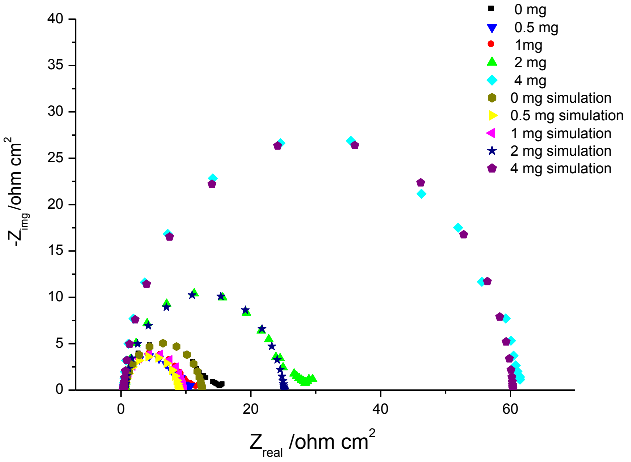

Figure 3. Complex plane plots of RuO_2 catalysts as a function of Nafion loadings, measured at 1.4 VAg/AgCl, at room temperature

Generally, the potential of oxide electrodes rest with the solid state redox equilibrium of the electrodes surface at the steady state open-circuit [19.20], such as the potential of in IrO_2 [21] or IrO_2+SnO_2 [22] electrode is corresponding to the surface redox equilibrium of Ir^{3+}/Ir^{4+}:

$$2IrO_2 + 2H^+ + 2e \leftrightarrow Ir_2O_3 + H_2O \qquad (1)$$

$$E_{eq}=E^o - 1.059pH + 0.029\log(\alpha 1/\alpha 2) \qquad (2)$$

$\alpha 1$:IrO_2 activity $\alpha 2$: Ir_2O_3 activity

Moreover, the potential of electrodes for the $RuTiCeO_2$ [20] and $RuTiPtO_2$ [23] is corresponding to surface redox equilibrium of Ru^{3+}/Ru^{4+}:,

$$2RuO_2 + 2H^+ + 2e \leftrightarrow Ru_2O_3 + H_2O \qquad (3)$$

$$E_{eq}=E^o - 1.059pH + 0.029\log(\alpha 1/\alpha 2) \qquad (4)$$

$\alpha 1$: RuO_2 activity $\alpha 2$: Ru_2O_3 activity

Thus, we consider that open-circuit potential (E_{oc}) of the oxygen electrodes with various Nafion loadings is corresponding to the surface active sites of the electrodes. The open-circuit potential of the electrodes with various Nafion loadings is also shown in Fig.2. It is found that the sequence of open-circuit potential for the electrodes with various Nafion loadings is 0.5 mg/cm^2>1.0 mg/cm^2>0 mg/cm^2>2.0 mg/cm^2>4.0 mg/cm^2. This result is in good agreement with the Nafion loading dependence of the voltammetric charge q*.

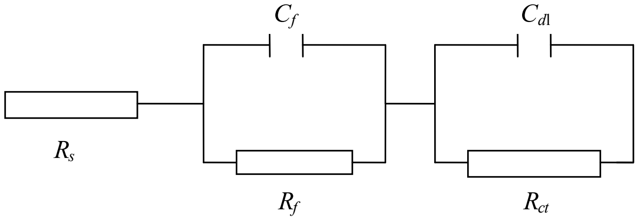

Figure 4. Equivalent circuits (EC) used in the analysis of the experimental EIS data

These results indicate that the addition of appropriate Nafion can elevate the ionic conductivity of the catalyst layers and increase catalyst utilization efficiency. However, as more Nafion is added the porosity of the catalyst layers decreases and limits mass transfer, which retarding the access of reactant to the active sites or gas-diffusion.

Electrochemical impedance spectroscopy (EIS) at constant potential 1.4 V (oxygen evolution region) was used. The complex plane (-Zimage vs. Zreal) at a given potential 1.4 V for various samples is shown in Fig.3. Nyquist plots show that the diameter of the low frequency arc, which should be a measure of the polarization resistance (is mostly charge transfer resistance for oxygen evolution) and thereby of the catalytic activity of the electrode. While the impedance behavior observed at low frequencies can be attributed to the oxide/electrolyte interface, the impedance behavior observed in high frequency domain may be related to the intrinsic properties of these materials. Similar impedance spectras have been observed for thermally prepared RuO_2-based electrodes [24-28]. The equivalent circuit model in Fig.4 was used to analyze the EIS data. In Fig.4, this circuit the parallel (R_fC_f) combination corresponds with the properties of the film, while the parallel ($R_{ct}C_{dl}$) combination is associated with the OER. R_s, R_f and R_{ct} represent solution resistance, oxide film resistance and charge transfer resistance for oxygen evolution, respectively. The parameters obtained by simulation are also summarized in Table 1.

It is found from Table 1 that R_s values have little change between 0.4 and 0.55 Ω cm^{-2}. The film resistance (R_f) has a minor value when Nafion loading of the electrode is 0.5 and 1.0 mg/cm^2. Charge transfer resistance (R_{ct}) as apparent activity has similarly a minor value when Nafion loading of the electrode is 0.5 and 1.0 mg/cm^2, which indicates the Nafion loading of 0.5 and 1.0 mg/cm^2 is the most

Table 1. Impedance parameters for the double layer potential region and the oxygen evolution region obtained by fitting the experimental data to the equivalent circuit R_s (R_fC_f) C_{dl} and R_s (R_fC_f) ($R_{ct}C_{dl}$).

Nafion loadings (mg/cm^2)	R_s (Ωcm^{-2})	R_f(Ωcm^{-2})	R_{ct} (Ωcm^{-2})	C_f(mFcm^{-2})	C_{dl} (mFcm^{-2})
0	0.53	0.084	11.88	39.2	63.6
0.5	0.43	0.028	8.39	60.3	85.8
1.0	0.48	0.07	9.09	48.1	81.5
2.0	0.54	0.14	24.47	34.2	57.2
4.0	0.41	0.559	59.44	15.7	50.4

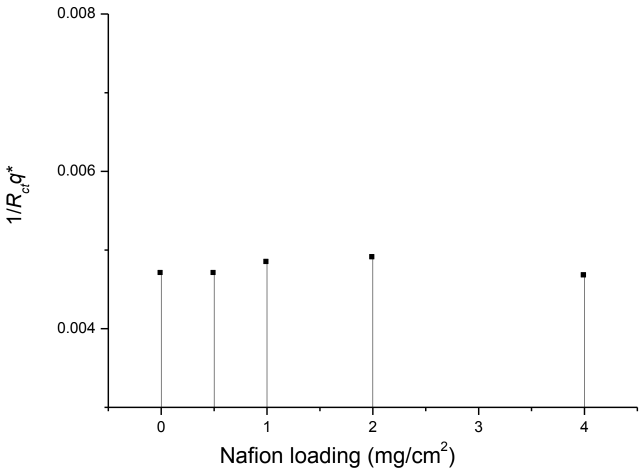

Figure 5. Site activity,1/$R_{ct}q^*$, as a function of Nafion loadings. E=1.4 VAg/AgCl

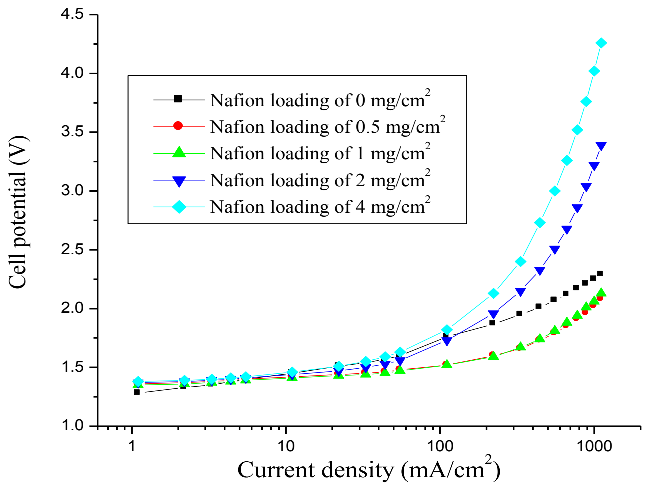

Figure 6. Steady state cell polarization curves of RuO_2 electrodes with various Nafion loadings during oxygen evolution

efficient for the OER. This observation is in agreement with the behavior of Cf and Cdl (see Table 1) as a function of Nafion loading, as evidenced by E_{OC} and CV.

In fact, R_{ct} is proportional to the product of active site number and site activity [29]. Thus, to obtain information with respect to the real electrocatalytic activity of the several materials, R_{ct} values must be normalized for morphological effects. According to some authors [30,31], this can be done dividing 1/R_{ct} (apparent activity) by the number of active sites (q*) or 1/R_{ct}q* [30,31]. The 1/R_{ct}q* data shows site activity almost is a constant for all samples (see Fig.5). This behavior of 1/R_{ct}q* (as a funtion of Nafion loading) reveals that the doped Nafion maintains the continuity of reactants-active sites-products and doesn't change intrinsic activity of catalyst.

Steady state polarization curves of samples with various Nafion loadings are shown in Fig.6. The potentials are not corrected for IR drops. At low current densities the several samples exhibit the similar catalytic properties for OER. At high current densities (i.e., above 50 mA/cm^2), the potential of OER for samples with Nafion loading of 0, 2.0 and 4.0 mg/cm^2 are higher than that of samples with Nafion loading of 0.5 and 1.0 mg/cm^2. These results show that the catalytic properties of the material govern the potential for OER at low current densities, whereas the active sites of catalyst layer and resistance of the catalyst layer (R_f) determines the potential for OER at high current densities. This means that Nafion loading of 0.5 and 1.0 mg/cm^2 are the most efficient for the OER at where the total anodic potential in the high current densities range of 0.05-1.0A /cm^2 is the lowest.

4. CONCLUSION

The relations between the Nafion loading in catalyst layer and the performance of PEM electrolyzer were examined. The PEM electrolyzer performance significantly depended on the Nafion loading in catalyst layer. The anodic electrode containing 0.5–1.0 mg/cm^2 Nafion is appropriate for the PEM electrolyzer. This trend correlated well with the decrease in charge transfer resistance and increase in the electrochemically active surface area. This work shows that the doped Nadion play an important role to extend the three-dimensional reaction zone and to minimize ohmic and mass transport overpotentials within the electrode.

5. ACKNOWLEDGEMENTS

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