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Performance Investigation of Membrane Electrode Assemblies for Hydrogen Production by Solid Polymer Electrolyte Water Electrolysis

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The development of solid polymer electrolyte (SPE) water electrolysis requires satisfactory membrane electrode assemblies (MEAs). In this work, different types of SPE membranes and catalysts were investigated to prepare high performance MEAs via a catalyst sprayed membrane under irradiation (CSMUI) method. The water electrolysis performance and properties of the prepared MEAs were evaluated and analyzed by polarization curve, electrochemistry impedance spectroscopy (EIS) and scanning electron microscopy (SEM). The results showed that SPE type must be chosen carefully according to the specific water electrolysis system, and Pt/C catalyst with low Pt content is less suitable as cathode catalyst in water electrolysis. At a cell temperature of 80 ^{o}C and atmosphere pressure, the best performance was obtained by using 60 wt.% Pt/C and Nafion 212 membrane: the cell voltage can be as low as 1.526 V at 1 A cm^{-2} and the terminal voltage is only 1.63 V at 2 A cm^{-2}, and the performance had no obvious degradation after a primary 24 h stability test. SEM characterization revealed that the intimate contact between the catalyst layers (CLs) and the membranes, and the uniformly porous CL structure correlate positively with the MEAs prepared by CSMUI method, exhibiting high performances and good stabilities for SPE water electrolysis.

Keywords: Water electrolysis; Solid polymer electrolyte; Membrane electrode assembly; Performance; Stability

1. INTRODUCTION

Hydrogen as an energy carrier, generated from renewable energy sources, constitutes an environmental friendly solution to the world energy problem in the future. For the achievement of "Hydrogen Economy", large-scale hydrogen production without fossil consumption and various gas emissions (e.g. SO_2, NO, CO_2, etc.) is critical [1-4]. The solid polymer electrolyte (SPE) water electrolysis, firstly developed by the General Electric Company, is now considered as one of the most promising technologies for hydrogen production from solar, nuclear or other non-fossil fuel sources [5]. This technology based on a polymer electrolyte membrane (PEM), also denoted proton exchange membrane, has gained a large interest due to the absence of a hazardous electrolyte, a low temperature regime, high power density and high energy efficiency compared to conventional alkaline electrolysis technology [6-8]. At present, most works on SPE water electrolysis were focused on preparing highly active catalysts for oxygen evolution reaction (OER) [9-23], to bring down the high material costs of the electrolysis system using SPE, few works were reported on the development of the system and the preparation of membrane electrode assembly (MEA) [24-26].

MEA is the core component of SPE water electrolyzer. The performance, cost and durability of the MEA have a direct influence on the performance, cost and durability of the water electrolyzer. On the long term where hydrogen becomes the main energy carrier and where large-scale production of hydrogen take place from renewable energy sources, the energy efficiency of the electrolyser will become essential. Therefore, the development of SPE water electrolysis requires satisfactory MEAs. In our previous work, a catalyst sprayed membrane under illumination (CSMUI) method [27], was developed to prepare MEAs for SPE water electrolysis. By simultaneously evaporating the solvent under infrared light during spraying, the swelling and distorting of SPEs can be greatly reduced, then the catalyst layers (CLs) can be well contacted with membrane and a uniform porous structure of the CLs can be obtained. The resultant MEA prepared by this method showed high performance and good stability for SPE water electrolysis. In the present work, we explored the performances and stabilities of the MEAs prepared with different catalysts and membranes, in respect of membrane thickness and properties, for their suitability for SPE electrolyzers.

1.1. Literature summary of MEA performance for SPE water electrolysis

For practical devices, IrO_2 is the most commonly used anode catalyst due to the superior electrochemical stability and activity for OER [28]. A wide range of performance data have been obtained by the different research groups using significantly different approach of MEA preparation. In order to make some comparisons, some of the available results have been tabulated, as shown in Table 1.

Typically the cell potential at 1 A cm^{-2} and 80 ^{o}C ranges between 1.60~1.72 V by using Nafion 115 membrane, and noble metal loadings from 2.0 to 4.5 mg cm^{-2}. A cell voltage obtained by Yamaguchi et al. [33] at 1.53 V is by far the best performance reported. However, this does not necessarily indicate that the best preparation technique has been obtained when considering the thin membrane (51 μm), gold- and Pt-plated current collectors and a relatively high noble metal loading of totally 6.44 mg cm^{-2}.

Therefore, reaching stable cell potentials of less than 1.6 V at 1 A cm^{-2} and 80 ^{o}C using Nafion 115 membrane, or ~1.53 V for thinner membranes (e.g. Nafion 212) is considered as a significant achievement.

Table 1. Summary of literature MEA performances for SPE water electrolysis

Reference	SPE (thickness)	Anode, Cathode	Noble metal loading (mg cm–2)	Ecell (V)
Marshall et al. [15-17]	Nafion 115 (127 µm)	IrO2, 20 wt.% Pt/C	2.12	~1.64
Siracusano et al. [29]	Nafion 115 (127 µm)	IrO2, 30 wt.% Pt/C	2.65	~1.70
Cruz et al. [30]	Nafion 115 (127 µm)	IrO2, 30 wt.% Pt/C	3.18	~1.70
Siracusano et al. [31]	Nafion 115 (127 µm)	IrO2, 30 wt.% Pt/C	3.18	~1.72
Zhang et al. [26]	Nafion 115 (127 µm)	IrO2, Pt black	4.5	~1.60
Ma et al. [32]	Nafion 112 (50 µm)	Ir black, Pt black	2.5	~1.70
Xu et al. [25]	Nafion 212 (51 µm)	Ir-Sn oxide, 40 wt.% Pt/C	1.8	~1.58
Yamaguch et al. [33]	B2-type (51 µm)	IrO2, Pt black	6.44	~1.53
Ecell: Cell voltage at 1 A cm−2, 80 oC and atmosphere pressure.				

2. EXPERIMENTAL

2.1. MEA Preparation

Three types of proton exchange membranes (PEMs): Nafion 115 membrane (thickness ~127 µm, Du Pont, USA), Nafion 212 membrane (thickness ~51 µm, Du Pont, USA) and Nafion 211 membrane (thickness ~25 µm, Du Pont, USA), were used as the polymer electrolyte membrane for MEA preparation. Before use, the membranes were pretreated in hydrogen peroxide solution (5 wt.%) at 80 ^{o}C for approximately 1 h; after being flushed with deionized water, it was transferred into a 0.5 M sulfuric acid solution and boiled at 80 ^{o}C for an additional 1 h, then washed with deionized water.

The catalyst inks were prepared by dispersing catalysts powder into a mixture of isopropanol and Nafion solution. The catalysts used for anode and cathode layers were IrO_2 (99.9%, Johnson Matthey) and Hispec Pt/C (20 wt.% Pt, 40 wt.% Pt, 60 wt.% Pt and Pt black , Johnson Matthey), respectively; 5% Nafion solution was purchased from Sigma Aldrich. The mixture was ultrasonically dispersed for 30 min before being used.

All MEAs used in this study were prepared using the catalyst sprayed membrane method. A more detailed description regarding the preparation of the MEA has been given previously [27]. The catalyst loadings were calculated from the difference between the dried membrane weight and the weight of the membrane with the catalyst ink dried under the same conditions. Unless specified, the catalyst loadings for all the cathodes and the anodes were 0.5 mg cm^{-2} of Pt and 3 mg cm^{-2} of IrO_2, respectively. The active area of the prepared MEAs was 4 cm^{2}.

2.2. Fabrication of diffusion backing layers

The diffusion backing layer for cathode was prepared by the following procedures. First, TGP-H-060 carbon paper (Toray, Japan) was hydrophobically treated by impregnating the paper with a Teflon dispersion and calcining at 330 ^{o}C for 30 min; then, a slurry of carbon black and Teflon, with a composition of 85 wt.% carbon powder (Vulcan XC72, Cabot, USA) and 15 wt.% polytetrafluoroethylene (PTFE) (60%, Aldrich, USA), was sprayed onto the pretreated carbon paper, followed by calcining at 350 ^{o}C for 30 min in air. The diffusion backing layer for anode was Ti fibre (Bekenit, Japan; thickness 0.3 mm, 60% porosity).

2.3. Single cell assembly and performance evaluation

A SPE water electrolysis cell was used to evaluate the performance of the prepared MEAs. Details of the cell can be found elsewhere [27]. The cell was produced by the CSIR (Pretoria, South Africa) consisting of a stainless steel body with two porous titanium sinters (thickness 1 mm, 30% porosity) covering the flow fields. The MEA was mounted between the two porous titanium sinters. The SPE electrolyzer performance was evaluated at atmosphere pressure and 80 ^{o}C. Preheated deionised water (18.3 MΩ cm), which was circulated by a peristaltic pump at a flow rate of 50 mL min^{-1}, was supplied to the anode compartment. The water temperature was maintained at 5 ^{o}C higher than the cell temperature. Total cell polarization curves were recorded galvanostatically between 1 mA cm^{-2} and 2 A cm^{-2} using a Neware battery testing system (Neware Technology Ltd, China).

2.4. SEM and electrochemical measurement

An ultra-high resolution field-emission SEM (Nova$^{™}$ NanoSEM 230, FEI, USA) was employed to observe the surfaces and cross-sections of the MEAs. The cross sections for SEM analysis were prepared by freezing the samples in liquid nitrogen and cutting the samples with a razor. Samples prepared by this method are reported to yield higher quality cross sections than other methods [34].

Electrochemical impedance spectroscopy (EIS) was carried out by an Autolab PGSTAT 30 Potentiostat/Galvanostat (Metrohm) equipped with a 10 A booster and a FRA. Because cathode polarization is negligible against to anode polarization during water electrolysis operation, so the cathode can be used as the counter electrode and reference electrode. The measurements were carried out at a cell potential of 1.5 V with an amplitude of 5 mV, and in the frequency range of 10 mHz to 10 kHz. The impedance data were obtained by calculation and simulation with Autolab Nova software.

3. RESULTS AND DISCUSSION

3.1. Water electrolysis performances of the MEAs with different membranes

Fig. 1 shows the polarization curves of the SPE water electrolysis cell with the three MEAs using different membranes, in which it is clear that the MEAs based on Nafion membranes (i.e., Nafion 115, Nafion 212 and Nafion 211) showed high performances for SPE water electrolysis. At the current density of 1 A cm^{-2}, the cell voltages of the MEAs with Nafion 115, Nafion 212 and Nafion 211 were 1.585 V, 1.534 V and 1.523 V, respectively, which are amongst the best results yet reported for SPE water electrolysis with IrO_2 catalyst. It is understandable that the performance of Nafion 115 MEA was inferior to that of Nafion 212 and Nafion 211 MEAs due to the decreased proton conductivity caused by increased membrane thickness (~127 μm). However, the increased membrane thickness is favorable to reduce gases (H_2 and O_2) cross-permeation and increase the strength of the membrane, which might be important when operating SPE electrolyzer at high pressure for hydrogen production.

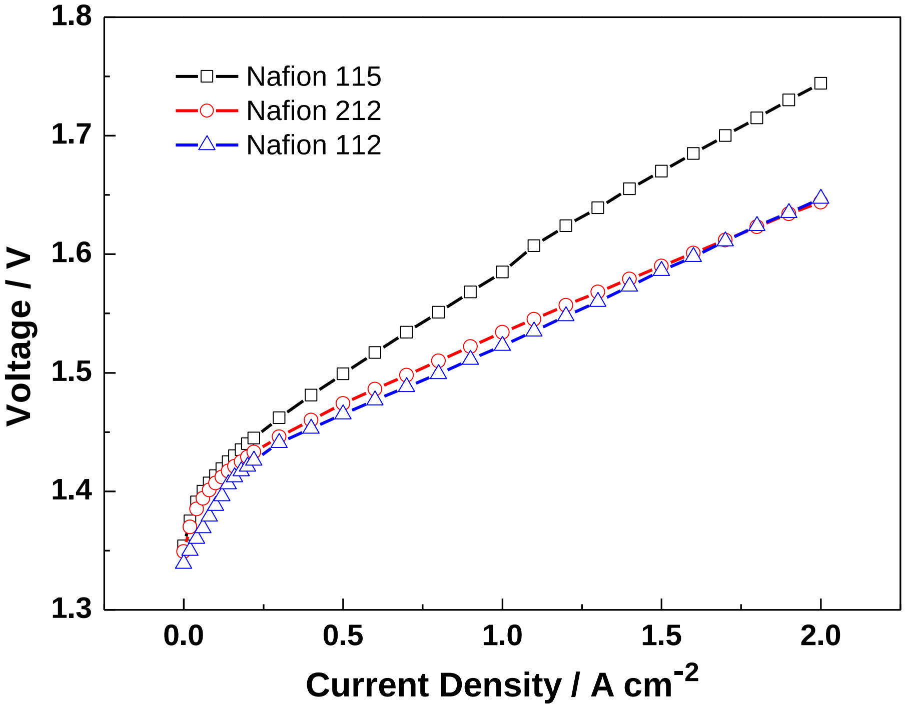

Figure 1. Polarization curves of the SPE water electrolysis cell with the MEAs prepared by Nafion 115, Nafion 212 and Nafion 211, operated at atmosphere pressure and 80 °C. Anode IrO_2 loading: 3.0 mg cm^{-2}; cathode Pt loading: 0.5 mg cm^{-2}.

It is noteworthy that Nafion 211 MEA showed almost the same performance as Nafion 212 MEA, although its proton conductance is higher than that of the latter. This could be attributable to increased H_2 crossover due to the reduced membrane thickness, which offset the advantage on higher proton conductance, especially at high current densities (> 1.5 A cm^{-2}, as shown in Fig.1). According to Yoshida et al. [35], gas permeation of different membrane types is determined by the thickness of the membrane and that the permeation is inversely proportional to its thickness. Lowering the membrane thickness (25 μm) reduces the membrane strength, which increases the chance for the MEAs to fail during the water electrolysis operation. This occurred frequently in our tests, probably the reason why Nafion 211 membrane is seldom used in SPE water electrolysis.

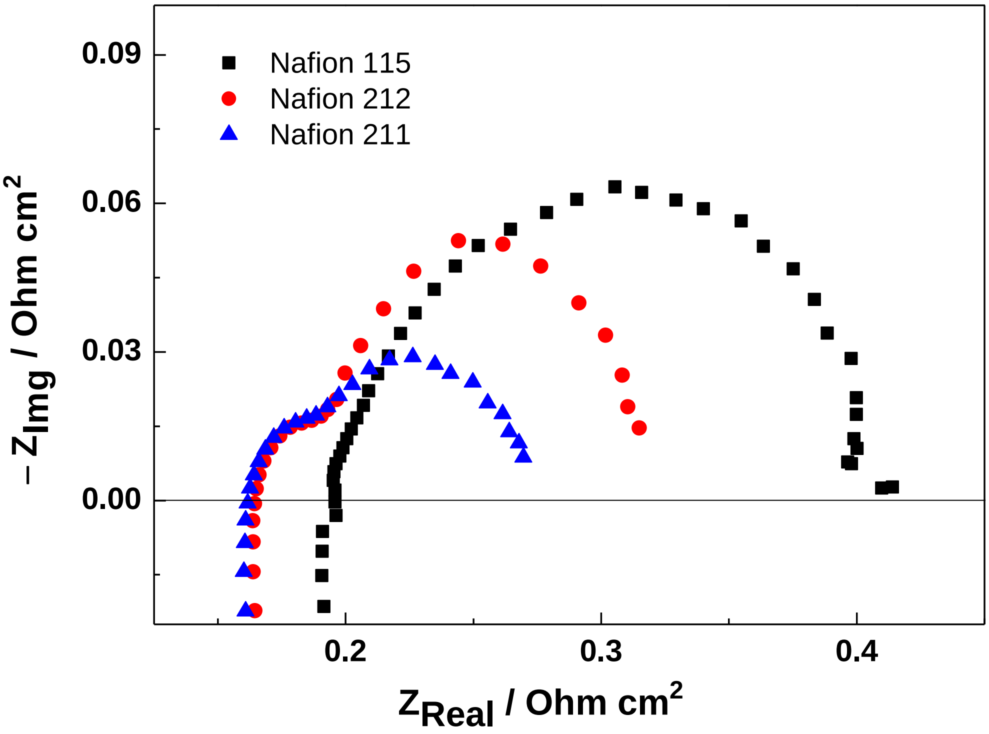

Figure 2. *In situ* impedance curves of the SPE water electrolysis cells with the MEAs prepared by Nafion 115, Nafion 212 and Nafion 211 membranes at 80 °C and 1.50 V.

Fig. 2 shows the *in situ* impedance curves of the three MEAs at a cell voltage of 1.5 V. Only one semicircular loop can be observed in the Nyquist plot, as the electrode process is dominated at low current densities by the OER [36]. The high-frequency intercept on the real axis, R_{Ω}, represents the total ohmic resistance of the single cell, which is the sum of the ohmic resistances of each component (i.e. the membrane, CLs, backing layers and bipolar plates) and the interfacial contact resistances between them. The diameter of the arc is a measure of the charge transfer resistance of the OER, which is designated as R_{ct}. And the diameter of the arc is a measure of the charge transfer resistance of the OER [36].

Table 2. Resistances of single cells with various MEAs

MEA	Nafion 115 MEA	Nafion 212 MEA	Nafion 211 MEA
R_{Ω} (Ω cm^2)	0.197	0.172	0.159
R_{ct} (Ω cm^2)	0.194	0.146	0.112

Through simulation with RC equivalent circuit, the cell resistances (R_{Ω}) and charge transfer resistances (R_{ct}) of the three MEAs can be calculated, as listed in Table 2. It can be seen that the cell resistances and the charge transfer resistances of these MEAs increased with the decrease of membrane conductance, which is certainly consistent with their performances showed in Fig. 1.

3.2. Stability tests

From the viewpoint of practical application, the stability and durability studies of the MEAs in water electrolysis are of significance while the number of reports on this subject is very limited [37-39]. For this reason, primary ~24 h water electrolysis operation tests under atmosphere pressure for the three MEAs (Nafion 115 MEA, Nafion 212 MEA and Nafion 211 MEA) at 80 °C and 1 A cm^{-2} were conducted and the results are shown in Fig. 3. It is clear that the MEAs with Nafion 212 and Nafion 115 membranes have good stability for SPE water electrolysis: the cell voltages of the two MEA remains at 1.55 V and 1.61 V respectively, without obvious deterioration after ~24 h operation at a usual working current density of 1 A cm^{-2} and 80 °C.

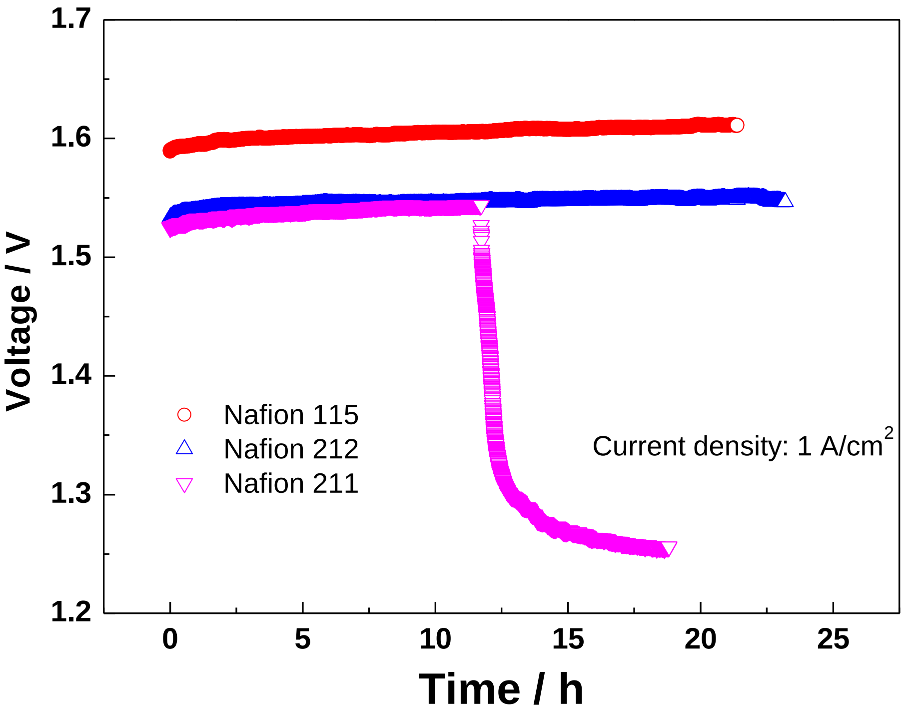

Figure 3. The stability tests of SPE cells with the MEAs indicated, operated at 80 °C and 1 A cm^{-2}.

However, it can be seen that Nafion 211 MEA failed during the stability test. The cell voltage suddenly dropped after approximately 11 hours test, indicating that a short circuit occurred. It mainly caused by the breakage of the membrane due to the insufficient strength for the impact of heat, pressure and gases during the long time operation. Based on this result, we think that Nafion 211 membrane is not suitable for SPE water electrolysis.

Altogether, membrane type must be chosen carefully according to the specific water electrolysis system. Gas permeation and risk of membrane destruction must also be taken into account. It is evident that the thickness of the membrane plays a major role in the durability of the MEA, pointing towards the necessity of a detailed study on the durability of the MEAs with different membrane thickness. A lower conductivity of the membrane can be accepted if the long-term stability is significantly better for thicker membranes.

3.3. Effect of cathode catalyst on the water electrolysis

At present, IrO_2 was widely used as anode catalyst for practical SPE electrolyzers or stacks due to the excellent stability and satisfactory activity for OER. However, cathode catalyst in SPE electrolysis is considered to be of less importance compared to the anode catalyst due to very low overvoltage of hydrogen evolution reaction (HER) [6]. Actually, the type of cathode catalysts has certain influence on the structure and electrical conductivity of the catalyst layer, which are important limitations of the electrolysis system using polymer membrane as electrolyte [20]. Therefore, the performance characteristics of the cathode layer in SPE water electrolysis with Nafion 212 MEA, with respect to different type of catalysts was investigated in this work, and the results are shown in Fig. 4.

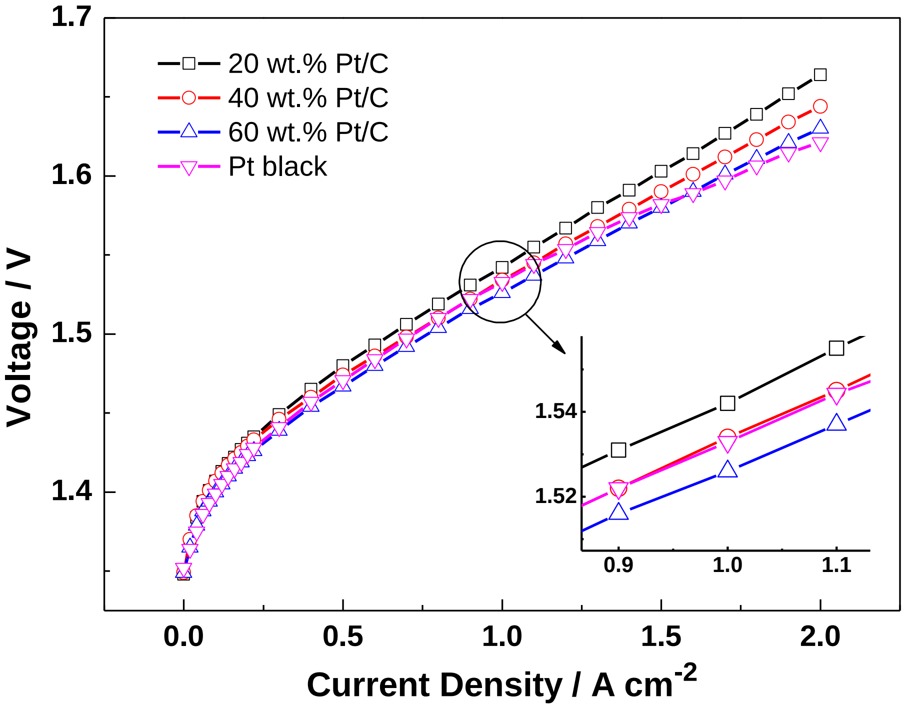

Figure 4. Polarization curves of the MEAs with J.M. 20 wt.% Pt/C, 40 wt.% Pt/C, 60 wt.% Pt/C and Pt black anode catalysts, using Nafion 212 membrane, operated at atmosphere pressure and 80 °C. Anode IrO_2 loading: 3.0 mg cm^{-2}; cathode Pt loading: 0.5 mg cm^{-2}.

It can be seen that all these MEAs showed high performance for SPE water electrolysis. At the current density of 1 A cm^{-2}, the cell voltages were between 1.52~1.54 V and the best performance was obtained by using 60 wt % Pt/C catalyst (see the insert in Fig.4). Interestingly, the performances of the MEAs with Pt supported catalyst are in order of 60 wt.% Pt/C > 40 wt.% Pt/C > 20 wt.% Pt/C, which suggests that Pt supported catalysts with low Pt contents are less suitable as cathode catalyst in water electrolysis. As the thickness of the catalyst layer increases with decreasing the Pt content on the catalysts, an increase in mass transport- and electronic- resistance is expected. Better performance can be obtained by using high Pt content catalysts, which possess better electrical conductivities and lower mass transfer limitations at similar total noble metal loadings.

It should be pointed out that Pt black served as a better hydrogen catalyst at higher current densities (> 1.5 A cm^{-2}), possibly caused by a more densely packed catalytic layer and a higher electrical conductivity. As shown in Fig.4, the cell voltage of the MEA with Pt black catalyst can be as low as 1.621 V at 2 A cm^{-2}, 43 mV lower than that of the MEA with 20 wt.% Pt/C (1.664 V). For low current densities (< 1 A cm^{-2}), the Pt black catalyst was less active than the 60 wt.% Pt/C catalyst, probably due to the latter possesses a much higher dispersion of Pt on the carbon support. Further improvements of the MEA performance can possibly be achieved by using smaller particles of the support and/or support particles of higher electrical conductivity.

3.4. The morphology of the MEA

The performance of MEAs can be influenced by the structure of the CLs and the interface contact between CLs and membrane.

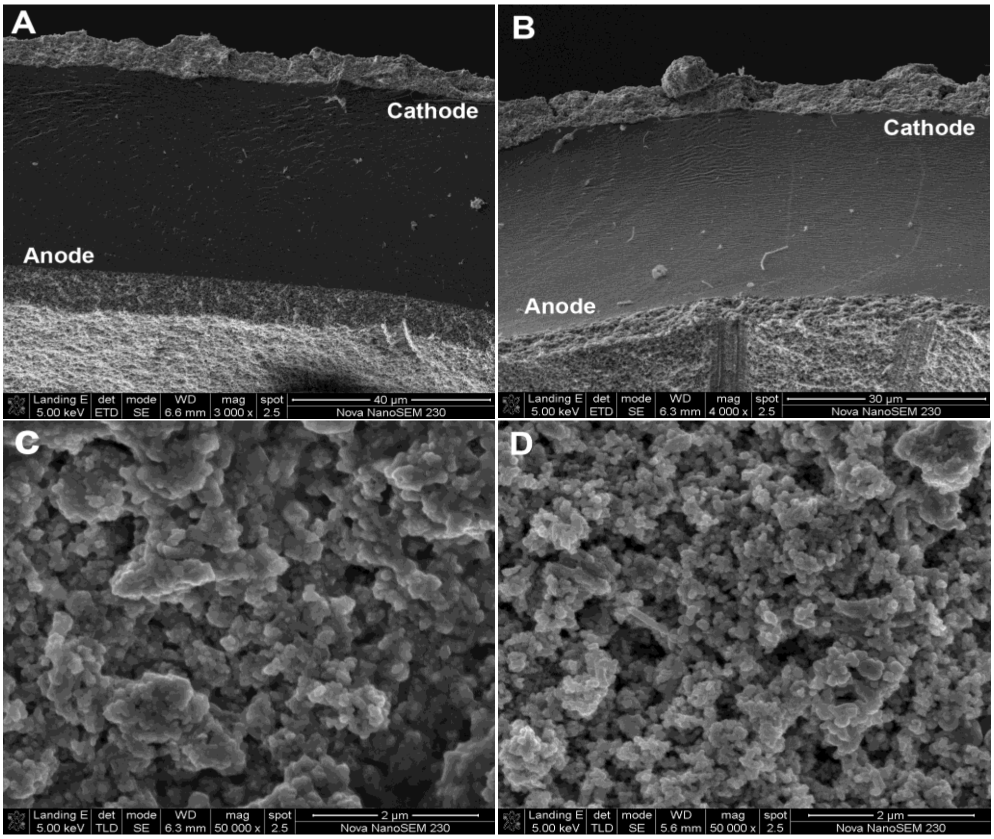

Figure 5. SEM micrographs showing the cross-sections of a fresh Nafion 212 MEA (A) and the MEA after stability test (B), the surface morphologies of the anode CL (C) and the cathode CL (D) of the MEA after stability test.

In this work, all the MEAs were prepared by the CSMUI method, and showed good performances and stabilities for SPE water electrolysis. With the case of Nafion 212 MEA, the surfaces and cross-sections of the MEA were observed by SEM to understand the structural characteristics of these MEAs, as shown in Fig. 5.

It can be observed that the CLs adhered closely to the Nafion membrane in the fresh MEA (Fig. 5(A)). In addition, no part of the electrode peeled off from the electrolyte membrane (see Fig. 5(B)) after 24 h stability test at high current density (1 A cm^{-2}), which suggests that the CLs remain bonded to the electrolyte membrane strongly during electrolysis and confirms the interest of CSMUI method used for the preparation of the MEAs for SPE water electrolysis. Moreover, no obvious cracks can be observed from the surfaces of the anode CLs of the MEA after 24 h of electrolysis (see Fig. 5(B), the two imprints on the anode CL may be caused by Ti fibre backing). Also, the SEM images in Fig. 5(C) and Fig. 5(D) show the uniform porous structure of both CLs. It may be concluded that during electrolysis, gas evolution occurs preferentially through the pore structure and that the electrodes work homogeneously: the porosity of the CLs is sufficient to allow gas departure. From these observations, it can be inferred that intimate contact between the CL and the membrane, and uniformly porous CL structure are the main reasons that the MEAs prepared by CSMUI method exhibited high performance and good stability for SPE water electrolysis, which are consistent with our previous research results [27].

4. CONCLUSIONS

The performances of SPE water electrolysis with different MEAs prepared by CSMUI method were evaluated in this work. The influences of electrolyte and cathode catalyst on MEA performance were investigated. The best performance with current density over 1.5 A cm^{-2} was obtained using Pt black and Nafion 212 while the best performing MEA operating below 1.5 A cm^{-2} was obtained by using 60 wt.% Pt/C and Nafion 212 membrane: the cell voltage can be as low as 1.526 V at 1 A cm^{-2} and the terminal voltage is only 1.63 V at 2 A cm^{-2}, which are the best results yet reported for SPE water electrolysis with IrO_2 catalyst. EIS results further revealed that the higher performance of the prepared MEA resulted from its smaller charge transfer resistance and ohmic resistance. It is found that Pt supported catalysts with low Pt contents are less suitable as cathode catalyst in water electrolysis. Better performance can be obtained by using high Pt content catalysts, which possesses better electrical conductivity. The stability test showed that the MEAs using Nafion 212 and Nafion 115 membranes have good stabilities for SPE water electrolysis: the performances had no obvious degradation after a primary 24 h of testing at 80 ^{o}C and 1 A cm^{-2}. However, Nafion 211 membrane was found to be unsuitable for SPE water electrolysis due to the decrease strength and the increased gas crossover. SEM observation revealed that the intimate contact between the CL and the membrane, and the uniformly porous CL structure are the main reasons that the MEAs prepared by CSMUI method exhibited high performances and good stabilities for SPE water electrolysis.

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