



Short communication

Performance of an ultra-low platinum loading membrane electrode assembly prepared by a novel catalyst-sprayed membrane technique

Hua-Neng Su, Shi-Jun Liao*, Ting Shu, Hai-Li Gao

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

ARTICLE INFO

Article history:

Received 3 July 2009

Received in revised form 15 August 2009

Accepted 17 August 2009

Available online 22 August 2009

Keywords:

High performance

Membrane electrode assembly

Nafion content

Polymer electrolyte membrane fuel cell

Ultra-low platinum loading

ABSTRACT

Membrane electrode assemblies (MEAs) with ultra-low platinum loadings are attracting significant attention as one method of reducing the quantity of precious metal in polymer electrolyte membrane fuel cells (PEMFCs) and thereby decreasing their cost, one of the key obstacles to the commercialization of PEMFCs. In the present work, high-performance MEAs with ultra-low platinum loadings are developed using a novel catalyst-sprayed membrane technique. The platinum loadings of the anode and cathode are lowered to 0.04 and 0.12 mg cm⁻², respectively, but still yield a high performance of 0.7 A cm⁻² at 0.7 V. The influence of Nafion content, cell temperature, and back pressures of the reactant gases are investigated. The optimal Nafion content in the catalyst layer is ca. 25 wt.%. This is significantly lower than for low platinum loading MEAs prepared by other methods, indicating ample interfacial contact between the catalyst layer and membrane in our prepared MEAs. Scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS) measurements reveal that our prepared MEA has very thin anode and cathode catalyst layers that come in close contact with the membrane, resulting in a MEA with low resistance and reduced mass transport limitations.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are currently considered suitable candidates to power stationary or mobile applications, including transportation vehicles, due to their high efficiency, high power density, and low operating temperature [1–3]. In recent years, PEMFC research and development has accelerated, but the cost of PEMFC systems is still too high to make them commercially viable [4].

Carbon supported platinum catalysts are still the widely used electrocatalysts in PEMFC, due to the platinum is a precious metal, the cost of catalysts accounts for about 30–45% of the whole cost of PEMFC. Thus, to prepare membrane electrode assemblies (MEAs) with lower platinum loadings is becoming one of the most important issues for PEMFC.

Ultra-low platinum loading MEAs have attracted more attention recently [5–11], as they hold the possibility of reducing precious metal use and, thereby, cost. Xiong et al. [7] prepared ultra-low platinum loading MEAs using a modified thin film method. These MEAs showed good uniformity and interfacial continuity between the membrane and the electrode, because the catalyst layer had been deposited directly onto the membrane. The best performance

was achieved at a platinum loading of 0.1 mg cm⁻², yielding a power density of 0.49 W cm⁻² at 0.65 V with hydrogen and oxygen as reactants. This method involved mixing Pt/C catalyst, a Nafion solution, and deionized water with no additional organic solvents, but required complicated processing of the MEAs. The platinum loading in MEAs can also be decreased to a very low level using advanced equipment. Saha et al. [8] prepared an MEA with a platinum loading of 0.08 mg cm⁻² using a dual ion-beam assisted deposition (dual IBAD) method. They claimed the electrode possessed a significantly different morphology, in which low-density platinum deposits (largely amorphous) were formed, had varying depths of penetration into the gas diffusion layer, and exhibited a gradual change towards an increasingly crystalline character. However, the principal shortcoming of this method is its lower power density, in the range of 0.27–0.43 W cm⁻² at 0.65 V. Other methods, such as electrodeposition [9,10] and sputter deposition [11–15], have also been developed to fabricate ultra-low platinum loading MEAs, but most of these methods are difficult to implement for real-life applications because they are expensive and involve complex procedures.

Using a novel membrane electrode assembly preparation method, developed in our lab and called catalyst-sprayed membrane under illumination (CSMUI) [16], by which the swelling and distorting of the membrane can be overcome very well and the catalyst layer can be well contacted with membrane, we prepared an MEA with very low platinum loading and very high

* Corresponding author. Tel.: +86 20 8711 3586; fax: +86 20 8711 3586.
E-mail address: chsjliao@scut.edu.cn (S.-J. Liao).

performance. We then investigated how cell performance was affected by the catalyst layer's Nafion content, as well as by certain operating conditions, namely cell temperature and the back pressures of the reactant gases. We also characterized the MEA using scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Preparation of catalyst ink and fabrication of MEAs

The catalyst ink was prepared by dispersing catalyst power into a mixture of isopropanol and Nafion solution. The catalyst used for both anode and cathode layers was Hispec 4100 Pt/C catalyst (40 wt.% Pt, Johnson Matthey); 5% Nafion solution was purchased from Du Pont, USA. The dispersion mixture was ultrasonicated for 30 min before being used.

Nafion 212 membrane (Du Pont, USA) was used as the polymer electrolyte membrane. Before use, the membrane was pretreated in hydrogen peroxide solution (5 wt.%) at 80 °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 °C for an additional 1 h, then washed with deionized water.

Under an infrared light, the catalyst ink was sprayed on the pretreated membrane with a spray gun (atomization style, nozzle caliber: 0.2 mm), which made the resultant catalyst distribution very uniform [16]. The active area of the prepared MEA was 5 cm². Fig. 1 shows the prepared MEA without a gas diffusion layer (GDL).

It can be seen that no distortion occurred during the fabrication process. The catalyst loadings were calculated by weighing the MEAs before applying the catalyst ink, and then after application and oven drying. Unless specified, the platinum loadings for the cathode and anode were 0.12 and 0.04 mg cm⁻², respectively, much lower than for conventional MEAs, and almost the lowest loadings for catalyst coated membrane (CCM)-type MEAs that we have found in the literature [17,18].

The GDLs for anode and cathode were 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 °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 °C for 30 min in air.

2.2. Evaluation of MEAs in a single cell

The MEAs were evaluated in a single cell, using a Fuel Cell Testing System (Arbin Instruments, USA). Pure hydrogen and air were fed to the anode and the cathode, respectively, at flow rates of 300 cm³ min⁻¹ (hydrogen) and 1000 cm³ min⁻¹ (air). The cell temperature was 60 °C, and the humidifying temperature of hydrogen and air was 65 °C for most of the tests.

Generally, the MEAs were activated at 70 °C and discharge mode for 3 h under 100% humidified conditions before measurements were taken. The back pressure of both hydrogen and air was 30 psi.

2.3. Characterization of MEAs with ultra-low platinum loadings

The MEAs were characterized using EIS with a Zahner IM6e electrochemistry station (Zahner, Germany), at different cell working statuses. The resistances and other kinetic characteristics of the MEAs were obtained by calculation and simulation with IM6e software. The measurements were carried out at a cell potential of 0.8 V with an amplitude of 5 mV, and in the frequency range of 0.1–1000 Hz.

A SEM (JSM-6380LA, JEOL, Japan) was used to observe the membrane's porous structure, a cross-section of the MEA, the thickness of the anode and cathode catalyst layers, and the contact between a catalyst layer and the membrane of the prepared MEA.

3. Results and discussion

3.1. Performances of MEAs with different platinum loadings

Through gradual decreasing of the platinum loadings on both anode and cathode sides, a series of MEAs with very low platinum loadings were successfully prepared by using the CSMUI method and optimizing the catalyst layers' composition. Fig. 2 shows the performances of four MEAs with various platinum loadings. The loadings on the cathode and anode sides, respectively, were: (1) 0.3 mg cm⁻² and 0.2 mg cm⁻²; (2) 0.2 mg cm⁻² and 0.08 mg cm⁻²;

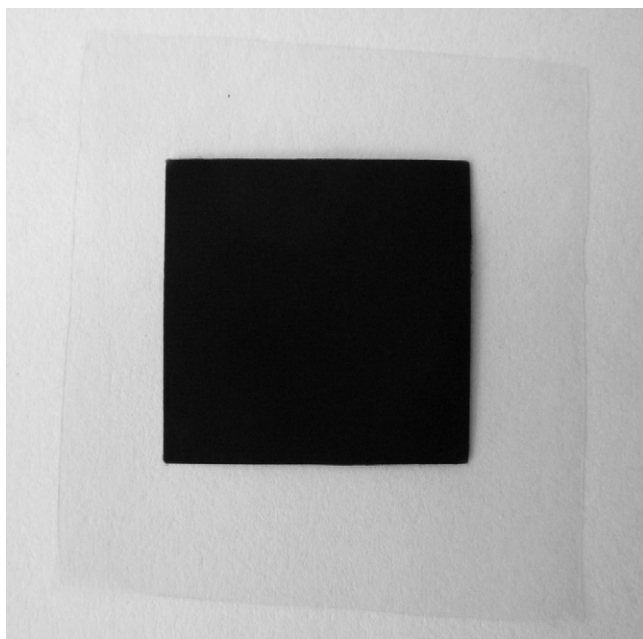


Fig. 1. Photograph of an MEA prepared using the CSMUI approach.

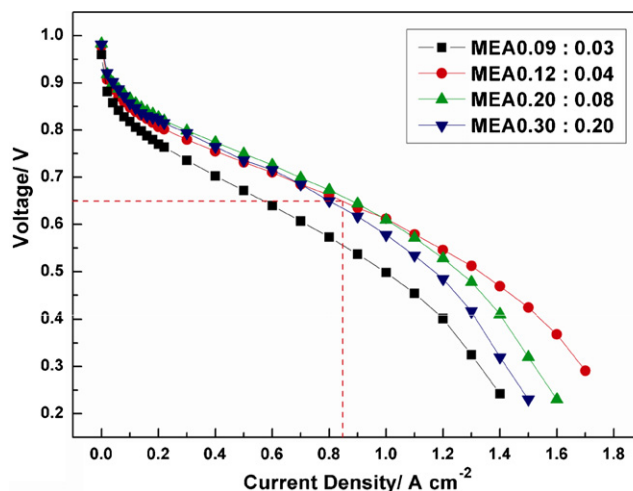


Fig. 2. Performances of MEAs with various platinum loadings at cathode and anode, evaluated at a cell temperature of 60 °C; humidifying temperature for hydrogen and air: 65 °C; back pressure of both hydrogen and air: 30 psi.

Table 1
Resistances of single cells with various MEAs.

MEA	MEA 0.09:0.03	MEA 0.12:0.04	MEA 0.20:0.08	MEA 0.30:0.20
R_{Ω} ($\Omega \text{ cm}^2$)	0.206	0.158	0.149	0.155
R_{ct} ($\Omega \text{ cm}^2$)	0.489	0.293	0.326	0.335

(3) 0.12 mg cm⁻² and 0.04 mg cm⁻²; and (4) 0.09 mg cm⁻² and 0.03 mg cm⁻². The four MEAs were denoted in abbreviated form as MEA 0.30:0.20, MEA 0.20:0.08, MEA 0.12:0.04, and MEA 0.09:0.03.

It is important and interesting that even when the platinum loadings were decreased from 0.3:0.2 to 0.12:0.04, the MEA performance did not noticeably decline. At 0.65 V, the performance of MEA 0.12:0.04 was higher than that of MEA 0.30:0.20, and just a little bit lower than that of MEA 0.20:0.08. The current density was as high as 850 mA cm⁻², which is higher than that of commercial MEAs, suggesting that there was no serious difference in the cell performance at low and medium current densities (<0.9 A cm⁻²) for those three MEAs. But when the platinum loadings were decreased from 0.12:0.04 to 0.09:0.03, the performance of MEA 0.09:0.03 observably decreased, as shown in Fig. 2. This result indicates that MEA 0.12:0.04 carried the minimum platinum loadings for the best performance.

It is well known that the linear decrease region of the polarization curve of a PEMFC is due to ohmic cell resistance, which originates from ionic flow through the electrolyte membrane, and from electron flow through the electrode layers, flow field plates, and current collectors. As Fig. 2 shows, three of the MEAs (MEA 0.12:0.04, MEA 0.20:0.08, and MEA 0.30:0.20) present almost the same decreasing slopes in the linear region, which implies that they had similar ohmic cell resistances. Furthermore, similar performance of the three MEAs in this region means that the ultra-low platinum loading MEA, MEA 0.12:0.04, has ample three-phase reaction boundaries and a higher platinum utilization, since its platinum loading was much lower than the loadings in the other two MEAs.

It should be pointed out that the performance of MEA 0.12:0.04 surpassed that of MEA 0.3:0.2 and of MEA 0.2:0.08 in the high current density region (>0.9 A cm⁻²), and the surplus performance increased with increasing current density, indicating that our ultra-low platinum loading MEA has excellent performance at high current densities. Generally, a voltage drop at a high current density is due to mass transport limitations occurring in the electrodes and the membrane. So, the higher performance of the ultra-low platinum loading MEA in the high current density region can be explained by postulating fewer mass transport limitations, due to much thinner catalyst layers. It is reasonable that the larger the current density, the more obvious the advantages of MEA 0.12:0.04, because thinner catalyst layers would promote the diffusion and transportation of fuel and oxidant gases, especially at high current densities.

Fig. 3 shows the *in situ* impedance curves of the four MEAs at a cell voltage of 0.8 V. Only one semicircular loop can be observed in the Nyquist plot, as the electrode process is dominated at low current densities by the oxygen reduction reaction (ORR) [19]. The high-frequency intercept on the real axis represents the total ohmic resistance of the single cell, as mentioned above, and the diameter of the arc is a measure of the charge transfer resistance of the ORR [19].

Through simulation with an RC equivalent circuit, the cell resistances (R_{Ω}) and charge transfer resistances (R_{ct}) of the four MEAs can be calculated, as listed in Table 1.

It can be seen that MEA 0.09:0.03 had the largest cell resistance and charge transfer resistance, due to the poor ORR kinetics resulting from insufficient catalyst.

Interestingly, MEA 0.12:0.04, MEA 0.20:0.08, and MEA 0.30:0.20 had almost the same ohmic resistance, but MEA 0.12:0.04 had the lowest charge transfer resistance. The R_{ct} order of the four MEAs is certainly consistent with their performances showed in Fig. 2; the lower the charge transfer resistance, the higher the MEA performance. These results suggest that the ultra-low platinum loading MEA yielded a more efficient electrochemically active layer than did the MEA 0.2:0.08 or the MEA 0.30:0.20.

3.2. Effect of Nafion content in the catalyst layer on the performance of ultra-low platinum loading MEAs

Nafion ionomer is an important component in catalyst layers, helping to increase three-phase reaction boundaries and boost platinum utilization in the electrode. It also aids in retaining moisture and preventing membrane dehydration, especially at high current densities. Nafion ionomer content in the electrode simultaneously affects gas permeability, catalytic activity, and ionic resistance. Therefore, Nafion content in the catalyst layer needs to be optimized using precise control mechanisms, in order to achieve the best balance among these influencing factors and thereby obtain high-performance MEAs [20–22].

We found that the catalyst layer's Nafion content strongly affected the performance of MEAs with ultra-low platinum loadings. Fig. 4(a) presents polarization curves for a series of MEAs having different Nafion content in the anode and cathode catalyst layers. The platinum loadings at anode and cathode for all of these MEAs were 0.04 and 0.12 mg cm⁻², respectively; the Nafion content is expressed as wt.%, which is the weight of dry Nafion divided by the sum of the weights of dry Nafion and catalyst. For comparison purposes, we plotted the current densities of MEAs at 0.7 V with various Nafion contents, as shown in Fig. 4(b).

It is evident from Fig. 4(b) that MEA performance was strongly affected by Nafion content; when the Nafion content in the catalyst layer increased from 15 wt.% to 25 wt.%, MEA performance increased by more than 100%, and the current density at 0.7 V increased from 300 mA cm⁻² to 650 mA cm⁻². This can be explained by the rising conductivity of the catalyst layers as Nafion content increases. However, when the Nafion content went from 25 wt.% to 35 wt.%, the performance decreased sharply. This event may be related to a high overall resistance in the MEA (and in particular, a high mass transport resistance) due to the large amount of Nafion blocking the electrode pores and reducing gas permeability. Some catalyst sites covered by a thick layer of Nafion may also

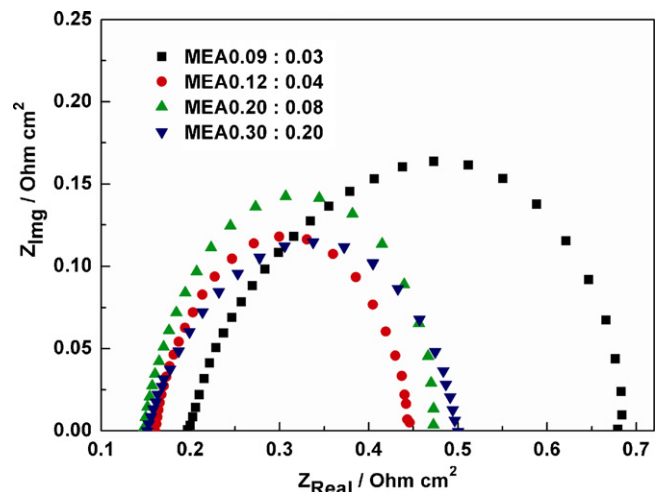


Fig. 3. *In situ* impedance curves of MEAs with various platinum loadings at anode and cathode, at a cell voltage of 0.8 V.

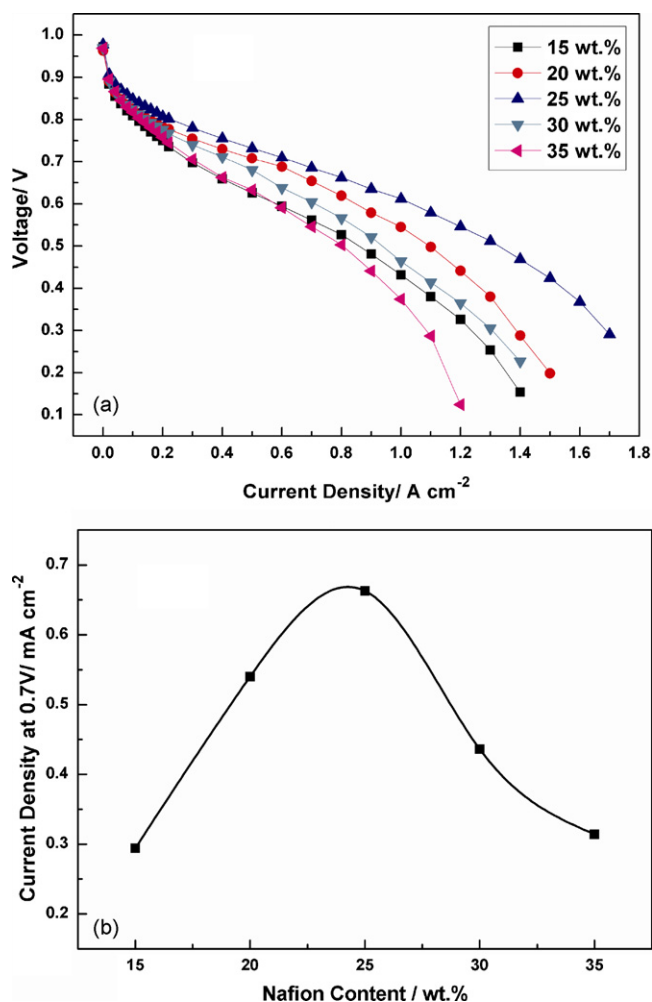


Fig. 4. The performances of MEAs with various levels of Nafion in their catalyst layers. (a) Polarization curves corresponding to MEAs with different Nafion content. (b) Current density versus Nafion content at 0.7 V. All data were collected at a cell temperature of 60 °C, with both hydrogen and air back pressures at 30 psi.

have been inactive. In other words, this mass transport limitation resulted from an increase in the distance through which the gas had to permeate, diffuse, or migrate. We concluded that the MEA with 25 wt.% Nafion content in the catalyst layer showed the best performance (0.663 A cm⁻² at 0.7 V) by minimizing ohmic, charge transfer, and mass transport limitations.

In addition, the optimum Nafion content (25 wt.%) for our ultra-low platinum loading MEA was just half of that reported by Sasikumar (50 wt.%) [20,21] on electrodes prepared using ink processes and having a platinum loading of 0.1 mg cm⁻². This result suggests much better interfacial contact between the catalyst layer and the membrane in our CSMUI prepared electrodes than in electrodes prepared by ink processes.

3.3. The effect of hydrogen and air back pressure on the performance of ultra-low platinum loading MEAs

It is widely recognised that major voltage losses occur in PEMFC cathodes due to poor ORR kinetics and limitations on the transportation of oxygen or air. Therefore, elevated cathodic pressure is necessary for better cell performance.

Fig. 5(a) and (b) shows MEA performances with ultra-low platinum loading (MEA 0.12:0.04) and with normal platinum loading (MEA 0.30:0.20) at different air back pressures. It can be seen that

air back pressure has a clear influence on cell performance in the two MEAs.

To compare the performances of two MEAs at various air back pressures, we plotted the current density at 0.7 V and different air back pressures for both MEAs, as shown in Fig. 5(c). For MEA 0.30:0.20, the current density was almost linear to the air back pres-

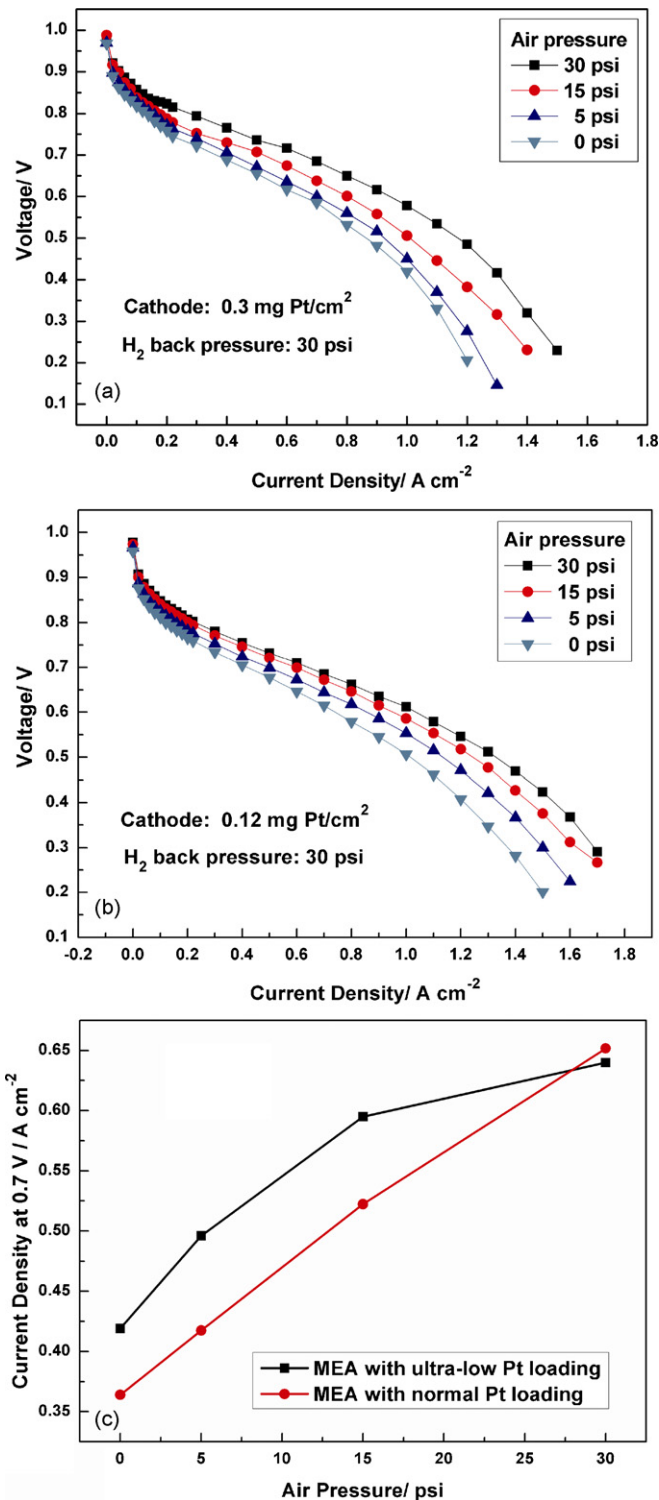


Fig. 5. The performance of an ultra-low platinum loading MEA (a) and a normal platinum loading MEA (b) at various air back pressures, and (c) a comparison of current density at 0.7 V of both MEAs at various back pressures. All data were collected at a cell temperature of 60 °C.

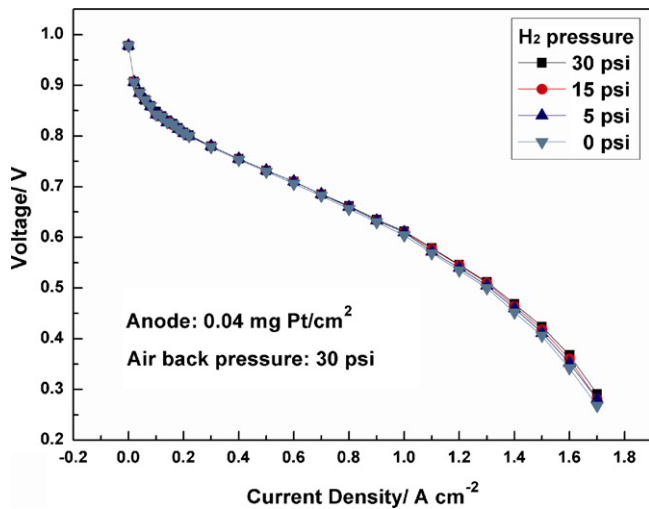


Fig. 6. Effect of hydrogen back pressure on the performance of an ultra-low platinum loading MEA. Data collected at a cell temperature of 60 °C.

sure in the range of 0–30 psi. Compared with MEA 0.30:0.20, MEA 0.12:0.04 exhibited the excellent characteristics of a thin catalyst layer, showing better performance for a lower air back pressure (0–15 psi) than a normal MEA. Its performance increased with the increase in back pressure more sharply than that of a normal MEA in this back pressure region. When back pressure was increased from 15 to 30 psi, the performance increased only slightly. At an air back pressure of 15 psi, the performance of MEA 0.12:0.04 was almost 20% higher than that of MEA 0.30:0.20; but at 30 psi, the performance of MEA 0.30:0.20 was only slightly higher than that of MEA 0.12:0.04. All of these findings imply that the MEA with ultra-low platinum loadings had excellent low back pressure performance due to its thinner catalyst layer and decreased mass transport limitations. These results indicate that the ultra-low platinum loading MEA has an efficient electrochemically active layer and reduced mass transfer limitations.

We also investigated the effect of hydrogen back pressure on the performance of this MEA with ultra-low platinum loadings. As shown in Fig. 6, the hydrogen back pressure had almost no effect on the MEA performance, which is a reasonable result for two reasons: (1) no transfer limitation problems occurred in the anode because the anode layer was very thin; (2) oxidation of hydrogen at the anode occurred very easily because the electrochemical reaction at the anode is much faster than at the cathode. These results correspond to the experimental results previously reported by our group [16].

3.4. The effect of cell temperature on the performance of ultra-low platinum loading MEAs

Fig. 7(a) shows the performance of our ultra-low platinum loading MEA (MEA 0.12:0.04) at different temperatures. It can be seen that the performance increased with cell temperature over the entire current density range. At a cell temperature of 70 °C, the maximum power density reached 0.71 W cm^{-2} and the current density reached 0.7 A cm^{-2} at 0.7 V, which were among the best results yet reported for similar low platinum loading MEAs and operated using air. At 0.7 V, the current density and maximum power density increased almost linearly with cell temperature in the range of 35–70 °C (see Fig. 7(b)). Generally, the effect of temperature can be explained by the more facile reaction kinetics at higher temperatures for both cathode and anode, but especially for the cathode.

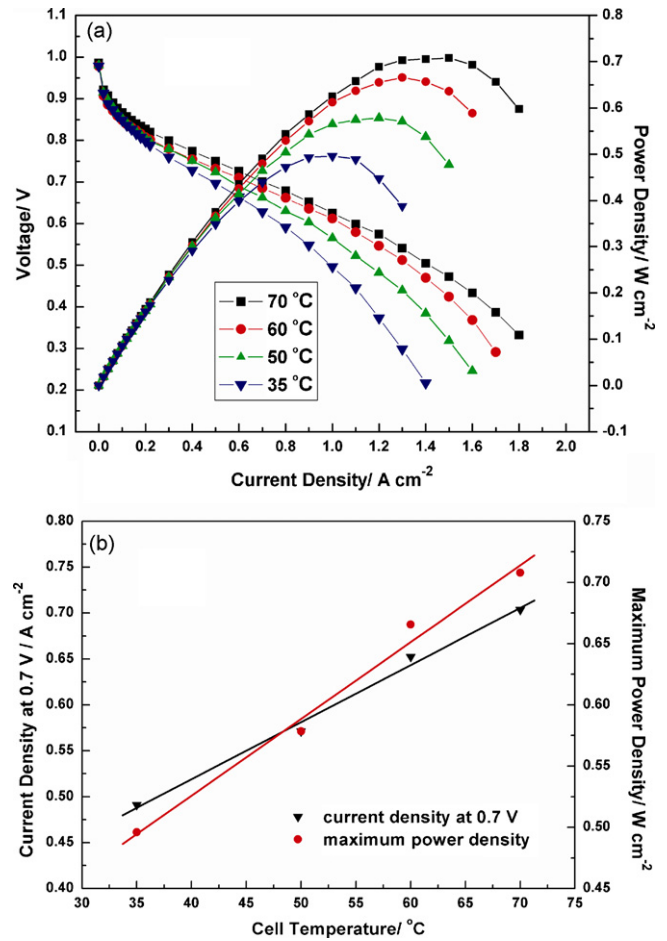


Fig. 7. Effect of cell temperature on cell performance: (a) polarization curves at different cell temperatures; (b) current density at 0.7 V and maximum power density versus cell temperature. All data were collected with the back pressures of hydrogen and air at 30 psi.

3.5. The morphology of the ultra-low platinum loading MEA

Fig. 8 shows the cross-sectional morphology of the MEA with ultra-low platinum loading. Evidently, the anode and cathode catalyst layers were about $1.1 \mu\text{m}$ and $3.8 \mu\text{m}$ thick, respectively. Such

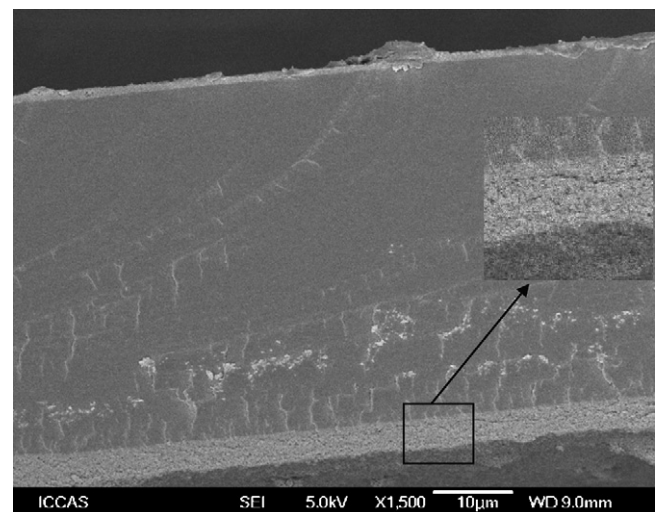


Fig. 8. SEM image of a cross-sectional view of the prepared MEA with ultra-low platinum loading.

thin catalyst layers may have led to small charge transfer resistance and mass transport resistance, which would further reinforce the results in Figs. 2 and 3. In addition, it can be observed that the catalyst layers adhered closely to the Nafion membrane—one of the possible reasons that our ultra-low platinum loading MEA still achieved excellent performance.

The SEM image insert also shows the uniform porous structure of the cathode catalyst layer. The combination of thin catalyst layer, intimate contact between the catalyst layer and the membrane, and uniformly porous catalyst layer structure may be the main reason that our ultra-low platinum loading MEA exhibited high performance and other excellent characteristics.

4. Conclusions

A high-performance MEA with ultra-low platinum loading has been prepared by a novel catalyst-sprayed membrane approach. The optimal Nafion content for the MEA was 25 wt.%, with platinum loadings of 0.12 mg cm^{-2} and 0.04 mg cm^{-2} in the cathode and anode, respectively. These values were significantly lower than those for similar MEAs with low platinum loadings prepared by other methods, and suggested ample interfacial contact between the catalyst layer and the membrane. Compared with normal platinum loading MEAs, our ultra-low platinum loading MEA showed excellent low-pressure performance and high current density performance, perhaps due to its thin catalyst layer and reduced mass transfer limitations. At a cell temperature of 70°C and an air back pressure of 30 psi, the maximum power density reached 0.71 W cm^{-2} , and the current density at 0.7 V was up to 0.7 A cm^{-2} , which is comparable to the best results previously reported for similar MEAs with such a low platinum loading, operating in air. We suggest that the thinness of the catalyst layer, the intimate contact between catalyst layer and membrane, and the uniform porous structure of the catalyst layers may be the crucial factors yield-

ing the high performance and other excellent characteristics of our ultra-low platinum loading MEA.

Acknowledgements

We would like to thank the National Scientific Foundation of China (NSFC Project Nos. 20673040, 20876062) and the Guangdong Provincial Scientific Foundation (Project No. 36055) for financial support of this work.

References

- [1] M.C. Williams, J.P. Strakey, W.A. Surdoyal, J. Power Sources 143 (2005) 191–196.
- [2] Y. Wang, S. Choi, E. Lee, Int. J. Hydrogen Energy 34 (2009) 2340–2349.
- [3] P. Costamagna, S. Srinivasan, J. Power Sources 102 (2001) 242–252.
- [4] K. Sopian, W.R.W. Daud, Renewable Energy 31 (2006) 719–727.
- [5] K. Karan, Electrochem. Commun. 9 (2007) 747–753.
- [6] Z. Qi, A. Kaufman, J. Power Sources 113 (2003) 37–43.
- [7] L. Xiong, A. Manthiram, Electrochim. Acta 50 (2005) 3200–3204.
- [8] M.S. Saha, A.F. Gulláb, R.J. Allenb, S. Mukerjee, Electrochim. Acta 51 (2006) 4680–4692.
- [9] H. Kim, N.P. Subramanian, B.N. Popov, J. Power Sources 138 (2004) 14–24.
- [10] Z.D. Wei, S.H. Chan, L.L. Li, H.F. Cai, Z.T. Xia, C.X. Sun, Electrochim. Acta 50 (2005) 2279–2287.
- [11] R. O'Hayre, S.J. Lee, S.W. Cha, F.B. Prinz, J. Power Sources 109 (2002) 483–493.
- [12] D. Gruber, N. Ponath, J. Müller, F. Lindstaedt, J. Power Sources 150 (2005) 67–72.
- [13] C.H. Wan, M.T. Lin, Q.H. Zhuang, C.H. Lin, Surf. Coat. Technol. 201 (2006) 214–222.
- [14] K. Sasaki, J.X. Wang, M. Balasubramanian, J. McBreen, F. Uribe, R.R. Adzic, Electrochim. Acta 49 (2004) 3873–3877.
- [15] J.H. Wee, K.Y. Lee, S.H. Kim, J. Power Sources 165 (2007) 667–677.
- [16] L.M. Xu, S.J. Liao, L.J. Yang, Z.X. Liang, Fuel Cells 9 (2009) 101–105.
- [17] L. Sun, R. Ran, G. Wang, Z. Shao, Solid State Ionics 179 (2008) 960–965.
- [18] S.G. Yan, J.C. Doyle, US Patent US 0163920 (2005).
- [19] X. Yuan, H. Wang, J.C. Sun, J. Zhang, Int. J. Hydrogen Energy 32 (2007) 4365–4380.
- [20] G. Sasikumar, J.W. Ihm, H. Ryu, Electrochim. Acta 50 (2004) 601–605.
- [21] G. Sasikumar, J.W. Ihm, H. Ryu, J. Power Sources 132 (2004) 11–17.
- [22] A. Caillard, C. Charles, D. Ramdutt, R. Boswell, P. Brault, J. Phys. D: Appl. Phys. 42 (2009), 045207 (9pp) <http://www.iop.org/EJ/abstract/0022-3727/42/4/045207>.