Microscopic characterizations of membrane electrode assemblies prepared under different hot-pressing conditions

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Received 1 June 2007; received in revised form 18 July 2007; accepted 31 July 2007
Available online 6 August 2007

Abstract

The durability of the membrane electrode assembly (MEA) for direct methanol fuel cells (DMFCs) is one of the most critical issues to be addressed before widespread commercialization of the DMFC technology. In this work, we investigated the effect of the hot-pressing duration on the performance and durability of the MEA prepared by hot-pressing technique. It was found that the 60-min hot pressing at 135 °C under the pressure of 4.0 MPa yielded a significantly improved MEA durability than did the 3-min hot pressing (a typical duration in practice) under the same condition, but no substantial difference was found in the cell performance of the MEAs prepared with the two different hot-pressing durations. The reason why the hot-pressing duration had no significant effect on cell performance is explained based on X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FT-IR) characterizations of the changes in the physiochemical properties of MEAs and their constituent components, including the anode, cathode and Nafion membrane, before and after hot pressing with different durations.

Keywords: Membrane electrode assembly (MEA); Durability; Delamination; Hot-pressing; Direct methanol fuel cell (DMFC)

1. Introduction

Over the last decade, the polymer electrolyte membrane fuel cell (PEMFC) has attracted enormous interest as a promising power candidate for stationary and mobile applications [1,2]. Although this type of fuel cell offers the promise of high power density and high energy-conversion efficiency, there are a number of challenging technical problems to be resolved before its widespread commercialization, in which the durability has been recognized as one of the most critical issues [3–5]. An irreversible loss of performance is generally encountered after a PEMFC operates for a certain time. Although the mechanism leading to the performance loss has not been well understood yet, it is believed that this irreversible loss is related, at least, to the following issues: (i) the loss in the electrochemical active surface area (triple phase boundaries) of the electrode caused by the catalyst nanoparticle growth/agglomeration [3,4,6–10], the catalyst dissolution/loss [7,11], and the electrolyte degradation/loss [7,11]; (ii) the degradation of electrolyte membrane [4,6,11,12]; (iii) the interfacial delamination between the electrode and the electrolyte membrane [8,9,13–15]. The decreased electrochemical active surface area will lead to an increased kinetics polarization loss. Xie et al. [7] found that the irreversible performance loss can be attributed to the platinum nanoparticles agglomeration and loss in the electrode after tested PEMFC operated for 500 h. This problem can be relaxed by employing a more stable catalyst and/or improved design of electrodes. For example, recently, Zhang et al. [16] found that the platinum nanoparticles could be stabilized against dissolution by depositing gold clusters on the surface, which did not affect significantly the catalytic activity to oxygen reduction reaction. Their results suggested that the stability be achieved by the larger platinum oxidation potential conferred by the gold clusters. Another critical problem that leads to the irreversible loss is the degradation of the Nafion membrane. It was reported that Nafion could be attacked by the peroxide intermediates or the radicals formed during the oxygen reduction reaction at the cathode [4,5,12]. The decomposition of the Nafion membrane will lead to a lower proton conductivity, which may give a rise in the ohmic polarization of the fuel cell performance [4,5]. More seriously, the
formation of pinhole due to the membrane degradation can result in a larger fuel crossover, which, in turn, will cause the so-called short-circuit of fuel cell [4,5]. Tanuma et al. [12] proposed that a suitable heat treatment of the catalyst could suppress the degradation of the Nafion membrane by the removal of functional groups (including hydroxyl groups and carboxyl groups) on the surface of the catalyst particles. The lifetime of the PEM was greatly improved with the catalyst that was heat-treated at 700–900 °C for 15 min.

The membrane electrode assembly (MEA) delamination has been observed both at the anode and at the cathode interfaces of the MEA for PEMFC [8,9,13–15]. Yan et al. [13] reported that the hydrogen-fed PEMFC performance seriously decayed in a few cycles’ operation at −15 °C, which was attributed primarily to the interfacial delamination of the MEA. This delamination problem may become more serious in the case of using liquid methanol (or ethanol) as a fuel in a direct methanol (or ethanol) fuel cell (DMFC or DEFC), because of the serious swelling of the PEM in methanol (or ethanol) solution, which can greatly affect the intimate contact between the polymer electrolyte membrane (PEM) and the electrodes in MEAs [8,9,14,15]. The delamination of the electrode from the membrane will lead to an increase in the resistance of proton transfer at the electrode–membrane interface, which may lead to the operation failure of the fuel cells [15]. Therefore, achieving a better interfacial contact between an electrode and a Nafion membrane is the subject of great interest, especially for the long-term operation of the DMFC (or DEFC). Wang et al. [17] applied a Nafion® layer between the PEM and the electrodes, resulting in an improved interfacial contact at the electrode–membrane interface. The addition of a Nafion® layer could roughen the surface of the PEM, leading to an improved interfacial contact between the PEM and the electrodes in the MEA. In our previous work [14], a glue method was developed by introducing a binding agent – Nafion dispersion between the PEM and the electrodes during the hot-pressing process. With this method, a MEA with a satisfactory interfacial binding force was obtained even at a much lower hot-pressing temperature.

The MEA delamination can be suppressed by optimizing the MEA preparation conditions, such as hot-pressing temperature, pressure, and duration. However, little work has been reported in this aspect, although a lot of work has been carried out to optimize the MEA preparation conditions to improve the DMFC performance [18–20]. Typically, a MEA is formed by hot pressing at 120–140 °C for 1.5–3 min under the pressure of 4.0–15.0 MPa [3–15,19–20]. The hot-pressing temperature is selected between the glass transition temperature ($T_g = 115 °C$) and the decomposition temperature ($T_d > 280 °C$) of the Nafion 1100 series membranes [21]. Only at temperatures above $T_g$, the Nafion membrane is softened and can be attached to the electrodes under a high pressure. At temperatures much higher than $T_g$, the Nafion membrane will undergo a micro-structural change and an irreversible water uptake loss, which leads to a lower proton conductivity [22]. Therefore, the hot-pressing temperature generally ranges between 120 °C and 140 °C. In addition to temperature, the hot-pressing pressure is another key parameter. A too small pressure will not provide enough binding force between the electrodes and the Nafion membrane, but a too high pressure will lead to a serious deformation of the electrode, which, in turn, leads to a porosity loss and thus a larger oxygen transfer resistance in the cathode catalyst layer [23]. With respect to the hot-pressing duration, typically, 1.5–3 min has been proved to be sufficient to form the MEA for DMFC that enables satisfactory performance in the short-term operation. However, for the long-term operation, the 3-minute hot-pressing may not be able to produce a sufficiently large interfacial binding force to avoid the delamination problem. In this work, we investigated the effect of the hot-pressing duration on the MEA durability at 135 °C under a moderate pressure of 4.0 MPa. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FT-IR) were employed to characterize the change in physico-chemical properties of the MEA components, including the commercial E-TEK electrodes (ELAT) and Nafion membrane as the result of hot-pressing for different conditions.

2. Experimental

2.1. The preparation of the MEAs

The commercial Nafion® 115 membranes (Electrochem. Inc.) were pretreated according to the membrane cleaning procedure detailed elsewhere [24]. Briefly, the Nafion® 115 membranes were boiled at 80 °C for 1 h in 3% H2O2 solution, DI water, 0.5 M H2SO4 solution and again in D.I. water. The ELAT electrodes were employed both in the anode (PtRu black with 4 mg cm$^{-2}$) and in the cathode (Pt black with 4 mg cm$^{-2}$) with a Nafion® loading of 0.8 mg cm$^{-2}$ on the surface of each electrode. The MEAs with an active area of 1.0 cm$^2$ were fabricated by sandwiching the Nafion® 115 membrane between the anode and cathode; and hot-pressing them at 135 °C under the pressure of 4.0 MPa for 3, 30, and 60 min. To investigate the hot-pressing effect on the components of MEAs, each membrane and ELAT electrode were also hot pressed at 135 °C or 160 °C under the pressure of 4.0 MPa for 3, 30, and 60 min. The behavior of the catalyst in the electrodes during the hot-pressing process was characterized by XRD, while the surface of the Nafion membrane was characterized by XPS and FT-IR.

2.2. X-ray diffraction

The X-ray diffraction (XRD) measurement was carried out by using a Philips PW 1830 diffractometer using a Cu Kα radiation source operated at 40 keV and at a scan rate of 0.05° s$^{-1}$. The catalyst particle average diameter can be calculated from the broadening of the Pt (2 2 0) diffraction peaks in the XRD patterns using Scherrer’s equation:

$$L = \frac{0.94 \lambda K_{\text{Cu}}}{B(2\theta) \cos \theta}$$

where $L$ is the diameter of the particle, $\lambda$ is the wavelength of the radiation and $B$ is the line broadening which is measured from the full-width at half-maximum (FWHM).
2.3. X-ray photoelectron spectroscopy

The X-ray photoelectron spectroscopy (XPS) measurement of the Nafion membrane was carried out with a Physical Electronics PHI 5600 multi-technique system using an Al monochromatic X-ray at a power of 350 W. The XPS provides the elemental information of the surface in the nanometer scale. The content ratio of sulfur to fluorine was used to characterize the surface change of the Nafion membrane during the hot-pressing process. The XPS peak intensities after normalized by the sensitivity factors can be used to calculate the surface composition sensitivity factors can be used to calculate the surface composition.

\[ C_i = \frac{I_i}{S_i} \sum_{j} \frac{I_j}{S_j} \]  
\[ \]  
\[ \text{where } C_i \text{ is the concentration of an element, } i \text{ and } m \text{ are the number of elements in the sample, } I_i \text{ and } S_i \text{ are the peak area and the sensitivity factor of the element } i, \text{ respectively.} \]

2.4. Fourier transform infrared spectroscopy

The Fourier transform infrared spectra (FT-IR) were collected in the attenuated total reflection (ATR) mode (with ZnSe) due to the saturated absorption of C–F groups in the Nafion® membrane under the transmission mode. The detection depth of ATR, which is generally in the range of micron, can be calculated from:

\[ d_p = \frac{\lambda_1}{2\pi[sin^2 \alpha - (n_2/n_1)^2]^{1/2}} \]  
\[ \]  
\[ \text{where } \alpha \text{ is the incident angle of the light, } \lambda_1 \text{ is the wave length of the light in ZnSe, } n_1 \text{ is refractive index of the ZnSe, and } n_2 \text{ is refractive index of the Nafion membrane.} \]

2.5. Surface roughness

The surface roughness of the ELAT electrode was measured using an optical phase-shifting and white light vertical scanning interferometer (WYKO NT3300). The roughness average (R\text{a}) can be obtained from the topography of the electrode surface.

2.6. Anode polarization

The anode polarization experiment was conducted by connecting, respectively, the cathode of the cell to the working electrode and the anode to the reference and counter electrodes of the potentiostat. During the course of the experiment, the cathode was fed with D.I. water (N\text{2} was purged to D.I. water for about 30 min before it was fed to the cathode) at 1.0 ml min\text{−1} and anode was fed with the hydrogen gas at 20.0 ml min\text{−1}. The CV curves for the cathode were recorded by applying the potential between −0.05 and 1.0 V at a scan rate of 20 mV s\text{−1}. The electrochemical active surface area can be calculated from:

\[ S = \frac{Q \times 100}{vcL_{\text{Pt}}} \]  
\[ \]  
\[ \text{where } S \text{ is the electrochemical active surface area, } Q \text{ (mV A) is integrated average area of the hydrogen adsorption/desorption peak, } v \text{ (mV s\text{−1}) is the scan rate, } c \text{ is } 0.210 \text{ mC cm}\text{−2} \text{ and } L_{\text{Pt}} \text{ (mg) is the platinum loading.} \]

2.8. DMFC performance test

The DMFC performance test was conducted at 75.0 ± 0.2 °C by feeding 1.0 M methanol at a flow rate of 1.0 ml min\text{−1} using a high-pressure piston pump (Model Series III, Scientific Systems Inc.) and by feeding dry oxygen gas into the cathode at a flow rate of 20 ml min\text{−1} at ambient pressure by fixing the load current, which was controlled with an electric load system (BT2000, Arbin Instrument Inc.). A stable DMFC performance was collected after a 24-h activation process with methanol solution.

2.9. MEA delamination test

The life-time test of DMFC is a time-consuming process, which generally needs at least several hundred hours. In this work, we only focused on examining the cell performance degradation caused by the MEA delamination in the DMFC. An accelerated delamination test can be achieved by immersing the MEAs first in pure methanol (which enables Nafion membranes to swell to a great extent) for expansion, and then in D.I. water for contraction. As such, the MEAs will be delaminated at the electrode–membrane interface as the result of the residual stress caused by the difference in swelling degree between the membrane and electrode. The details of the off-cell delamination test are as follows: the MEA was taken off from the cell and immersed in pure methanol for 5 min and then in D.I. water for 2 min. This process was repeated for several cycles for each MEA. DMFC performance was collected after each cycle of the delamination test.

3. Results and discussion

3.1. Hot-pressing effect on each component of MEAs

3.1.1. Electrodes

Fig. 1 shows the XRD patterns of the ELAT anode and cathode before and after hot pressing for 3, 30 and 60 min at 135 °C. The catalyst particle size calculated by Eq. (1) is listed in Table 1. It can be observed that the cathode catalyst particle size increased...
Fig. 1. XRD patterns of the ELAT electrodes before and after hot pressing for 3, 30, and 60 min at 135°C; (a) anode, (b) cathode.

from 7.2 nm to 8.1 nm after the 60-min hot pressing procedure, whereas the anode catalyst particle size remained almost the same before and after hot pressing. The growth of cathode catalyst particles can be attributed to the decrease in the overall surface energy as the result of the decreased specific surface area associated with hot pressing [25]. The reason why the change in the anode catalyst particle size is insensitive to hot pressing can be explained as follows. The anode of the DMFC generally contains more Nafion than does the cathode. The Nafion resin surrounding the catalyst particles can function as the stabilizer that prevents the catalyst particles from growing. Additionally, since the catalyst is Pt–Ru at the anode, rather than Pt only at the cathode, the presence of Ru oxide may tend to stabilize the change in the anode catalyst particle size associated with hot pressing.

Table 2 shows the change in electrode thickness after hot pressing. It can be observed that the anode became significantly thinner with increasing the hot-pressing duration, whereas the change in cathode thickness was rather small. The different deformations of the two electrodes as the result of hot pressing may be attributed to different compositions of the electrodes (not provided by E-TEK). Table 2 also shows the compression ratio, which is calculated from:

\[
\text{compression ratio} = \frac{L_t - L_0}{L_0} \times 100\% \tag{5}\]

where \(L_t\) is the thickness of the electrode after hot pressing for \(t\) time and \(L_0\) is the thickness of the original electrode (before hot pressing). The compression ratio can be an index representing the change in the electrode porosity [23]. The measured compression ratio shown in Table 2 indicates that the change in the cathode porosity was rather small, but the anode porosity decreased significantly with the hot-pressing duration. This result implies that the effect of hot pressing on oxygen transfer in the cathode is insignificant, but hot pressing may increase the mass transfer resistance of methanol from the flow field to the anode catalyst sites, as discussed later.

3.1.2. Membranes

Fig. 2 shows the XPS spectra of the Nafion membranes before and after hot pressing for 3, 10 and 30 min at 135 and 160°C. The relative content ratio of sulfur to fluorine can be quantified with Eq. (2) and is presented in Fig. 3. Compared with the original Nafion membrane (before hot pressing), the content ratio of sulfur to fluorine decreased with increasing the hot-pressing temperature. And the ratio exhibited a decline trend with increasing the hot-pressing duration at each treatment temperature. The decrease in the ratio (S/F) can be attributed to the decomposition of the side chain (sulfonic acid group) at high temperatures. This is consistent with the measurement of the in-plane proton conductivity of the heat-treated Nafion membrane [22], in
which it was found that the proton conductivity of the membrane decreased by about two times after heat treatment at 120 °C. This decrease was attributed to the lowered water uptake and the microstructure change of the treated Nafion membrane [22].

It should be noted that the decomposition of the side chain of the membrane is also related to the decrease in the in-plane proton conductivity. Generally, the sulfonic acid group decomposition at the surface of the membrane should be avoided because the

Fig. 2. XPS spectra of the Nafion membranes before and after hot pressing for 3, 10 and 30 min at 135 and 160 °C: (a) original Nafion membrane, (b) Nafion membrane hot-pressed for 3 min at 135 °C, (c) Nafion membrane hot-pressed for 10 min at 135 °C, (d) Nafion membrane hot-pressed for 30 min at 135 °C, (e) Nafion membrane hot-pressed for 3 min at 160 °C, (f) Nafion membrane hot-pressed for 10 min at 160 °C, (g) Nafion membrane hot-pressed for 30 min at 160 °C.
decomposition will lead to an increase in the resistance of proton transport at the electrode–membrane interface. However, it should be recognized that the decrease in the ratio (S/F) provided by the XPS characterization is limited to the surface change in the nanometer scale as the result of hot pressing the bare membrane. As will be shown later, the decrease in the sulfonic acid group concentration occurring in the nano-meter surface of the bare membrane when hot pressed does not necessarily mean that the sulfonic acid group concentration also decreases in the micron range of the MEA prepared by hot pressing.

Fig. 4 shows the relative absorbance ratio of two functional groups of the membranes: \(-\text{SO}_3\text{H} (\nu_s = 1060 \text{ cm}^{-1})/\text{CF}_2– (\nu_s = 1145 \text{ cm}^{-1})\), calculated from the IR-ATR results, before and after hot pressing for 3, 30, and 60 min at 135 and 160 °C. It can be observed that the relative absorbance of the two functional groups increased after hot pressing. At each temperature, the ratio increased with the hot-pressing duration. And the ratio at the high temperature (160 °C) is larger than that at the lower temperature (135 °C). The absorbance of the vibration peaks is proportional to the functional group concentration, which can be observed from the Lambert–Beer law:

\[
A = \lg \left( \frac{1}{T} \right) = Kbc
\]

where \(A\) is absorbance, \(K\) is absorbance coefficient, \(b\) is the thickness of the sample and \(c\) is concentration. Accordingly, the absorbance ratio of \(-\text{SO}_3\text{H}\) to \(-\text{CF}_2–\) can be used to quantify the relative concentration of the two groups in the micron-depth surface of the membrane. As mentioned above, \(-\text{CF}_2–\) group is much more stable than the \(-\text{SO}_3\text{H}\) group and the \(-\text{CF}_2–\) group concentration can be regarded as constant during hot pressing. Therefore, the change in the ratio virtually means the change in the concentration of sulfonic acid group. The IR-ATR characterization indicates that the sulfonic acid group at the surface of the membrane is enriched after hot pressing. The result is consistent with that reported elsewhere [21], in which it was found that the side chain exhibited a tendency to move from the
bulk to the surface of the Nafion membrane in the heat treatment process. And this segmental movement of side chains could be kinetically accelerated at higher temperatures.

In summary, hot pressing the bare membrane can lead to a slight decrease in sulfonic acid group concentration near the membrane surface in the range of nanometer scale, as reflected by the XPS characterization. However, the sulfonic acid group concentration in the bulk region of the membrane in the range of micrometer scale actually increased after hot pressing, as indicated by the IR-ATR characterization. In hot pressing the electrode onto the membrane, it was observed that the catalyst aggregates intruded into the membrane [7]. The intrusion depth depends upon the roughness of the electrode. The average roughness of the ELAT electrode is found to be the order of several microns ($R_a = 2.1 \mu m$), as seen from Fig. 5. This means that during the formation of the MEA, the original surface of the bare membrane will be distorted by the rough electrode and the interfaces between the catalyst and Nafion will be virtually located in the range of micrometer scale, where the sulfonic acid group concentration gets increased after hot pressing. Therefore, it can be concluded that hot pressing will lead to improved MEA performance in terms of proton transport, although hot pressing the bare membrane can cause a slight decrease in sulfonic acid group concentration near the membrane surface in the range of nanometer scale.

3.2. Electrochemical characterization of the MEAs prepared for different hot-pressing durations

3.2.1. Cathode cyclic voltammetry

Fig. 6 shows the cathode cyclic voltammetry of the MEAs hot-pressed for 3, 30, and 60 min. The calculated ECSA of the MEA corresponding to each hot-pressing duration is 11.0, 8.5, and 7.9 m² g⁻¹, respectively. The electrochemical active surface area decreased with increasing hot-pressing duration. This decrease can be attributed to the increased platinum particle size during the longer hot-pressing process, as reflected by the XRD characterization. The decreased cathode ECSA as the result of longer hot-pressing durations may have some adverse effect on the performance of the MEAs.

3.2.2. Anode polarization

Fig. 7 shows the anode polarization curves of the MEAs hot-pressed for 3, 30, and 60 min. In general, the anode performance seems similar for all the MEAs prepared for different hot-pressing durations. The performance of the MEA formed at 3 min is found slightly inferior to that of the other two MEAs at current densities lower than 250 mA cm⁻², but the trend reversed at higher current densities. The better performance of the MEA prepared with a longer hot-pressing process at lower current densities may be related to the better interfacial contact between the anode and the membrane, which results in a lower barrier of the proton conduction at the interface. With increasing current density, the anode polarization associated with the mass transport resistance of methanol from the flow field to the catalyst layer becomes more dominated than the ohmic resistance. As discussed earlier, longer hot-pressing durations, such as 30 and 60 min, may lead to a decrease in anode porosity. Therefore, the MEAs formed with longer hot pressing durations (30 and...
60 min) may exhibit a larger methanol transfer resistance, and thus lower performance at higher current densities.

3.2.3. DMFC performance

Fig. 8 compares the cell performance of the MEAs hot-pressed for 3, 30, and 60 min. It can be seen that the three MEAs yielded almost the same cell performance, implying that the hot-pressing duration has almost no effect on the cell performance. This result can be explained based on the effect of hot-pressing duration on both the anode and cathode. The anode-potential characterization discussed earlier indicated that a longer hot-pressing duration would result in an improved anode performance (see Fig. 7). However, the study of the hot-pressing effect on the cathode revealed that a longer hot-pressing duration would lead to an increase in the cathode catalyst particle size (see Table 1), lowering the cathode potential. As a result, the balanced favorable effect on the anode potential and adverse effect on the cathode potential associated with the longer hot-pressing durations make the overall cell performance insensitive to the change in the hot-pressing duration.

3.2.4. Delamination test of the MEAs

Following the off-cell delamination test procedure described in Experimental Section, we found that the MEA hot-pressed for 3 min delaminated completely after one cycle test. However, for the MEAs hot-pressed for 30 and 60 min, no obvious delamination could be identified even after testing for 10 cycles. To examine the possible effect of the MEA durability on the cell performance, we tested the DMFC performance of the MEA hot pressed for 60 min after different numbers of delamination-test cycles. Fig. 9 shows the DMFC performance after the MEA experienced 2, 6, and 10 cycles of the delamination test. It is interesting to notice that the cell performance did not decline even after the 10-cycle delamination test, but somewhat improved to a certain extent. The results of the performance tested shown in Fig. 9 indicates that the MEA hot pressed for 60 min did not delaminate even after 10 cycles of the delamination test. Hence, it can be concluded that a longer hot-pressing duration generally tends to improve the MEA durability. The improved cell performance after delamination tests can be attributed to the decreased cell resistance of the MEA, as shown in Fig. 10, where the cell resistance of the MEA was measured after the 2, 6, and 10-cycle delamination tests by the current-interruption method. Clearly, the cell resistance gradually decreased from 0.48 Ω cm$^{-2}$ to 0.35 Ω cm$^{-2}$ after the 10-cycle delamination test. The cell resistance mainly arises from the resistance of proton transport through the membrane. Therefore, the decrease in cell resistance should result from the increased proton conductivity of the membrane as the result of the delamination tests. The continuous increase in the proton conductivity during the delamination tests can be explained as follows. During the cell performance test, the hydrophobic cath-
ode was fed with dry oxygen, which led to a certain degree of dehydration of the membrane near the cathode. For this partially hydrated membrane, the resistance of proton transport was relatively high. During the delamination test, the entire MEA was repeatedly immerser in pure methanol and water, and thus the membrane could be gradually hydrated. As a result, a continuous increase in the proton conductivity of the membrane associated with the delamination tests can be observed.

In summary, the MEA delamination tests showed that an adequately longer hot-pressing duration is essential to ensure a better interfacial binding between the electrodes and membrane. As a result, the MEA durability associated with the delamination problem can be greatly improved.

4. Conclusions

The problem of the catalyst layer delamination from the membrane due to the residual stress caused by the different swelling degrees between the membrane and electrode is one of the most serious issues that affect the durability of the DMFC. In this work, the effect of the hot-pressing duration on the performance and durability of the MEA for the DMFC was investigated. It was found that longer hot-pressing duration, such as 60 min, yielded a significantly improved MEA durability than did shorter one, such as 3 min, which is a typical duration in practice. The improved MEA durability can be attributed to the fact that longer hot pressing will result in a stronger interfacial binding between the electrodes and membrane, which suppresses the problem of the catalyst layer delamination from the membrane. The cell characterization indicated that the MEA prepared with the longer hot-pressing duration exhibited almost the same performance as that prepared with the shorter duration. The reason why the hot-pressing duration had no significant effect on cell performance is explained based on the changes in the physicochemical properties of the Nafion membrane and electrodes characterized by IR-ATR and XRD. The IR-ATR characterization revealed that a longer hot-pressing duration induced the enrichment of sulfonic acid groups at the electrode-Nafion membrane interface, improving the cell performance in terms of the interfacial proton transport. However, the XRD characterization showed that catalyst particle size of the cathode increased with increasing the hot-pressing duration, resulting in a decreased electrochemical active surface area, and thus lowering the cathode performance. The combination of the favorable and adverse effects of hot pressing on the MEA preparation determines that the hot-pressing duration does not exert significant effects on the cell performance. In summary, the results revealed in this work suggest that an adequately longer hot-pressing duration during the preparation process is essential to ensure the MEA durability.

Acknowledgements

The work described in this paper was fully supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. 622706).

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