Fabrication and evaluation of membrane electrode assemblies by low-temperature decal methods for direct methanol fuel cells

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ABSTRACT

In this study, a low-temperature decal transfer method is used to fabricate membrane electrode assemblies (MEAs) and the MEAs are tested for application in a direct methanol fuel cell (DMFC). The low-temperature decal transfer uses a carbon-layered decal substrate with a structure of ionomer/catalyst/carbon/substrate to facilitate the transfer of catalyst layers from the decal substrates to the membranes at a temperature as low as 140 °C, and also to prevent the formation of ionomer skin layer that is known to be formed on the surface of the transferred catalyst layer. The DMFC performance of the MEA (with carbon layer) fabricated by the low-temperature decal transfer method is higher than those of MEAs fabricated by the same method without a carbon layer, a conventional high-temperature decal method, and a direct spray-coating method. The improved DMFC performance of the MEA fabricated with carbon layer by the low-temperature decal transfer method can be attributed to the absence of an ionomer skin on the catalyst layer, which can streamline the diffusion of reactants. Furthermore, the intrinsic properties of the MEA fabricated by the low-temperature decal transfer method are elucidated by field-emission scanning electron microscopy (FESEM), electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) techniques, and cathode CO_2 analysis.

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1. Introduction

Direct methanol fuel cells (DMFCs), as promising power sources for portable electronic devices and small-scale vehicles, generate electricity through the electrochemical reactions of methanol oxidation and oxygen reduction. The DMFC is very compact, exhibits high energy density, and the fuel methanol has a superior chemical stability [1,2]. Nevertheless, factors such as the sluggishness of the methanol oxidation reaction, methanol crossover to the cathode, un-optimized structure of membrane electrode assembly (MEA) and high fabrication cost are obstacles to the commercialization of DMFCs. Hence, the importance of MEA fabrication, which determines mainly the performance and cost of the cell, has been highly emphasized in the literature [3,4]. In order to improve MEA performance, various strategies such as different MEA fabrication methods, modification of the MEA structure and operating conditions have been adopted [5–12]. Although the issues of slow kinetics of methanol oxidation reaction and methanol crossover to the cathode can be addressed through the use of a high surface-area PtRu catalyst and development of new types of polymer electrolyte membranes, fabrication of an optimized structure of the MEA can also mitigate these issues. Many attempts have been made to improve the fabrication process and structural parameters of the MEA to enhance its DMFC performance.

Conventional methods to fabricate MEAs are divided into two groups [5,9,13–16]. One is the catalyst-coated substrate (CCS) method and the other is the catalyst-coated membrane (CCM) method. In the CCS approach, catalysts are coated on the gas-diffusion layer (GDL), which is made from carbon paper, felt or cloth, and then hot-pressed with the membrane electrolyte to form the MEA. This method is suitable for the fabrication of large-scale MEAs and for mass production. In the CCM method the catalysts are directly coated on the membrane and subsequently hot-pressed with the GDL. The MEA made by CCM method has an improved catalyst|membrane interface [16], better utilization of catalysts [9]
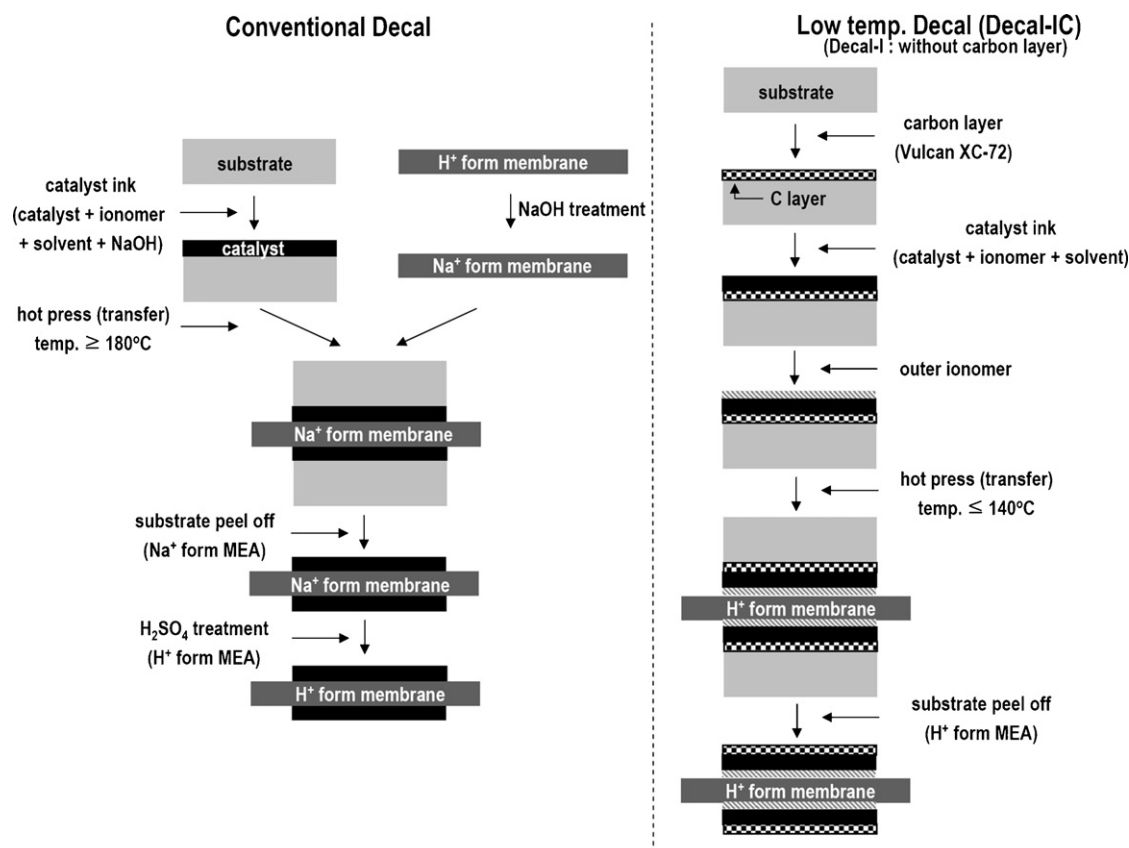
Fig. 1. Schematic diagram of conventional high-temperature decal process and low-temperature decal method. Decal-IC refers to right-side low-temperature decal process, where I and C mean outer ionomer and carbon layer, respectively. Decal-I corresponds to same method as Decal-IC except for the carbon layer coating.

and superior formation of the ionomer network [9], which are all beneficial in improving the performance and long-term durability of the MEA.

Although both CCS and CCM methods have been widely adopted to fabricate MEAs, they have their own limitations. In the CCS method, the catalyst layers coated on the GDL cannot be effectively transferred to the membrane during the course of hot-pressing the MEA. In the case of the CCM method, generally, the membrane undergoes serious swelling when spraying/applying the catalyst ink directly on the membrane. In the light of these problems, the CCS and CCM methods cannot be followed for the large-scale MEA production required for commercialization of the DMFC. An alternative approach for large-scale production of MEA is the decal process, in which catalyst layers primarily formed over the Teflon decal substrates are subsequently transferred to a dry membrane during hot-pressing of the MEA [17,18].

The procedure of the conventional, high-temperature decal method is illustrated in Fig. 1. Basically, catalyst layers preliminarily formed on a foreign substrate are transferred to the membrane by hot-pressing at the temperature of 160–210 °C [19–24]. All the H$^+$ form of Nafion membrane and ionomer are converted to other cationic forms such as Na$^+$, K$^+$ and TBA$^+$ by treatment with sodium hydroxide (NaOH), potassium hydroxide (KOH), or tetrabutylammonium hydroxide (TBAOH) to give more mechanical strength. Subsequent re-protonation by boiling the MEA in sulfuric acid solution is also required [19–25]. This conventional decal process appears to be more complex and laborious and, additionally, the temperature used to hot-press the MEA is too high. There is also the possibility of sintering of the catalytic particles and the formation of oxides of Pt that are generally deleterious for the electrochemical

reactions. Furthermore, it has been reported [21] that an ionomer segregation (a skin-like structure) is likely to occur on the outside of the catalyst layer (especially, when a Teflon blank is used as the decal substrate); and this catalyst layer with an ionomer skin, which faces the GDL during the cell assembly, is believed to hinder mass transfer, thereby causing enormous flooding in the cathode side of a cell [21].

Therefore, in order to make the decal process very simple and to avoid the formation of an ionomer skin in the catalyst layer, we have developed a low-temperature decal transfer method which enables the complete transfer at a temperature as low as 140 °C without material modification or performance deterioration. In this method, as shown in Fig. 1, a thin layer of carbon is first applied over the decal substrate and this is followed by addition of the catalyst and ionomer layers, in such a way that the catalyst layer is sandwiched in between the inner thin carbon and outer ionomer layers on the Teflon decal substrate. Subsequently, the MEA is fabricated by completely transferring the whole structure, consisting of carbon, catalyst and ionomer layers, to the dried Nafion membrane at the temperature as low as 140 °C. In the final MEA structure, the ionomer layer exists between the membrane and the catalyst layer while carbon layer is located on the outer side of the MEA.

Recently, Park et al. [26] have modified the conventional decal method for the polymer electrolyte membrane fuel cell (PEMFC). In their work, a 'breaking layer' composed of carbon powder and Nafion ionomer was coated on a decal substrate to facilitate the transfer of a catalyst layer from the decal substrate to a membrane. The Nafion ionomer present in the carbon layer can, however, introduce an additional resistance to mass transport.

The performance of a DMFC using the MEA fabricated by our method is compared with MEAs made by various other methods such as the conventional high-temperature decal and direct spray-coating methods. The intrinsic properties of MEAs are analyzed by field-emission scanning electron microscope (FESEM), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). Carbon dioxide in the cathode exhaust gas from single cell is also measured to assess methanol crossover rates through the MEAs.

2. Experimental

2.1. Fabrication of MEAs

Four different routes were applied to fabricate MEAs, namely: direct spray-coating of the catalysts on the membrane, conventional high-temperature decal method, low-temperature decal method using an outer ionomer [27] (denoted as Decal-I), and low-temperature decal method using an outer ionomer and carbon layer (denoted as Decal-IC). In all methods, Nafion® 115 membrane (Du Pont) was used as the membrane electrolyte. Membranes were cleaned several times with de-ionized (DI) water, hydrogen peroxide solution, and sulfuric acid.

In the direct-coating method, the catalyst ink slurry was made by dispersing catalyst (PtRu black for anode and Pt black for cathode, Johnson Matthey Co.) with a mixture of 5 wt.% Nafion ionomer solution (Du Pont), isopropyl alcohol (IPA), and DI water. Then the ink solutions were sprayed on each side of the membrane and the amounts of catalysts were $3\,\mathrm{mg\,cm^{-2}}$ for each electrode. The catalyst-coated membrane was subsequently pressed with a gas-diffusion layer (carbon paper, E-TEK) at 8 MPa pressure and 140 °C. $0.6\,\mathrm{g\,cm^{-2}}$ of a microporous layer composed of Vulcan XC-72R carbon, IPA and PTFE (polytetrafluoroethylene) were sprayed on the cathode side of the GDL prior to hot-pressing.

The detailed procedure for conventional high-temperature decal is illustrated in Fig. 1. In this route, a Na⁺ form of membrane was used instead of the H⁺ form by immersing the membrane in 1 M NaOH solution at 80 °C for 1 h. Appropriate amounts of NaOH were added to the catalyst ink solutions (both anode and cathode) to convert the H⁺ form of ionomer to the Na⁺ form. These ink solutions were then sprayed on separate Teflon sheets that subsequently served as the decal substrates. After drying, the catalyst-coated Teflon sheets were hot-pressed on both sides of the Na⁺ form of membrane at 8 MPa pressure and 180 °C to make the MEA. The substrates were then removed. The prepared MEA was treated in 1 M H_2SO_4 solution to replace Na⁺ ions present in the membrane and in the ionomers with H⁺ ions. A detailed description of the experimental conditions has been reported elsewhere [19–25].

In the low-temperature decal method employed in this study, which is denoted as Decal-I and Decal-IC in Fig. 1, the H⁺ forms of the membrane and the ionomer were used as such and not replaced by Na⁺ ions. With respect to the decal substrate, a series of different materials was tested to select a proper substrate, namely, Teflon, PDMS (polydimethylsiloxane), Kapton and Al foil. The same catalyst ink solutions used in the direct-coating method were sprayed
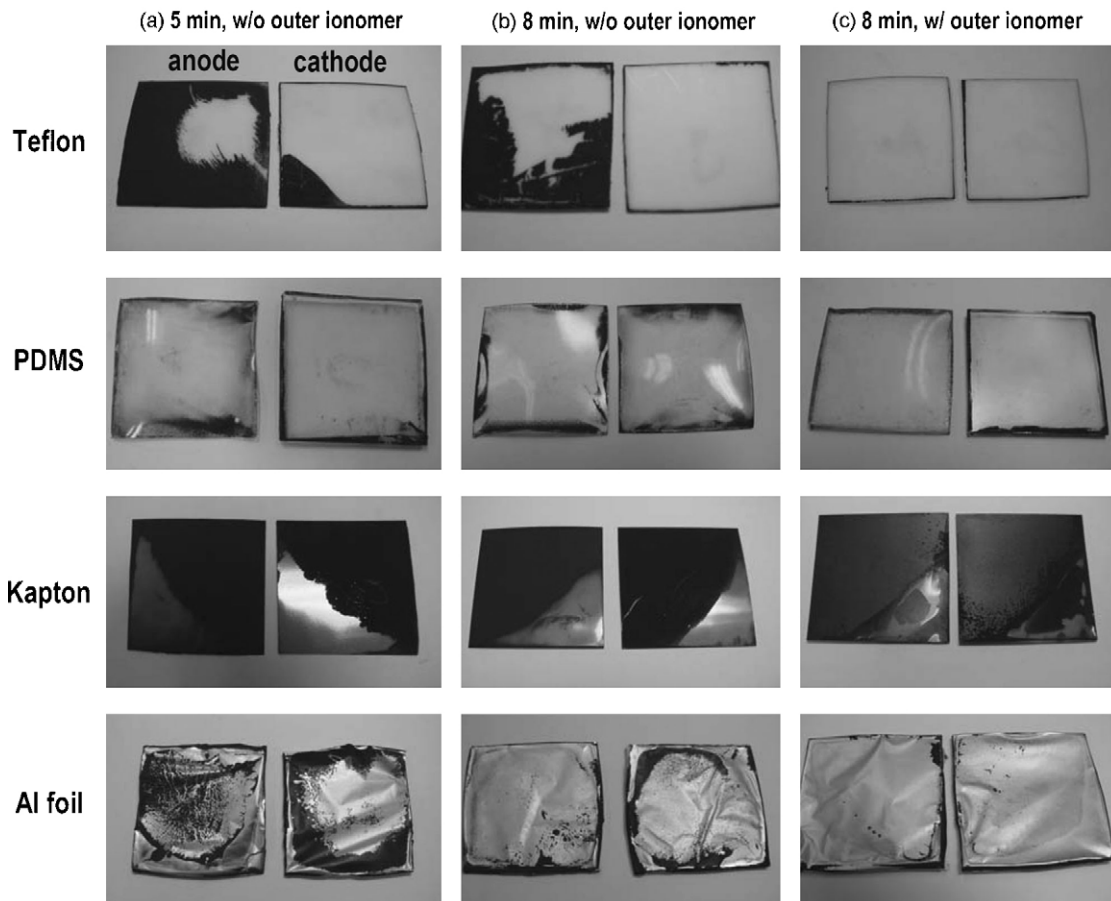
Fig. 2. Photographs of residual surfaces of various decal substrates after decal transfer: (a) hot-pressing for 5 min without outer ionomer coating; (b) hot-pressing for 8 min without outer ionomer coating; (c) hot-pressing for 8 min with outer ionomer coating (Decal-I). Four different substrates were used; Teflon, PDMS, Kapton, and Al foil. Left-side and right-side substrates in each photograph correspond to anode and cathode substrates, respectively.
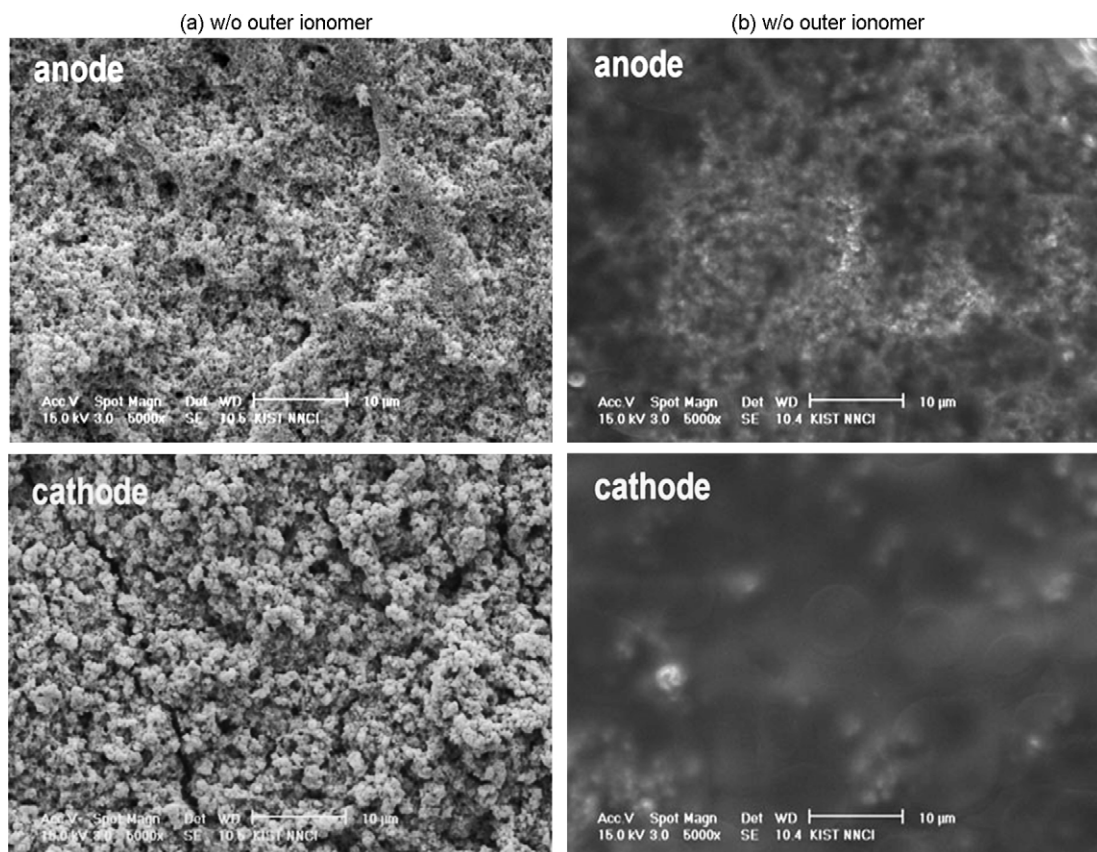
(a) w/o outer ionomer

(b) w/o outer ionomer

Fig. 3. Surface FESEM images of catalyst layers on Teflon substrates: (a) before and (b) after outer ionomer coating.

on each substrate. An additional layer of Nafion ionomer was then sprayed on the coated catalyst layer [27] with at an amount of 0.1 g cm^{-2}. This is denoted as the outer ionomer in Fig. 1 and acts as an adhesion layer in the subsequent transferring of the catalyst layer to the membrane. The prepared multi-layer substrates (outer ionomer/catalyst/substrate) were then hot-pressed on both sides of the H$^+$ form of membrane at 8 MPa pressure and 140 °C to form the MEA (Decal-I). The primary aim in selecting the substrate is to ensure the complete transfer of catalyst layer to the membrane. The effects of outer ionomer and hot-pressing time on the catalyst transferring process were also observed. The selected substrate was further used in the development of Decal-IC method denoted in Fig. 1. The purpose of developing the Decal-IC method is to prevent the formation of an ionomer skin layer outside the catalyst after decal transfer [21]; this is explained in detail in a later section. The experimental procedure of Decal-IC is basically the same as that of Decal-I, except for applying the carbon layer on the decal substrate prior to the catalyst spraying. A mixture of Vulcan XC-72 carbon and IPA was prepared and heated at 65 °C for 1 h. The mixture was sprayed on the decal substrate to achieve 0.1 g cm^{-2} amounts. After applying the carbon layer, the other steps mentioned in the procedure of Decal-I were repeated as such. The geometric active area of all the MEAs was 10 cm^2.

2.2. Characterization of MEA

A field-emission scanning electron microscope (Hitachi S-400) was utilized to observe (i) the catalyst surface after spraying on the decal substrate and (ii) the cross-sectional configuration of the MEAs according to the fabrication methods. The residue on the Teflon substrate after Decal-IC was examined with energy disper-

sive X-ray spectroscopy (EDX) to confirm a complete transfer of the catalyst.

The performance of the MEAs fabricated via the different routes was measured by assembling single cells with gaskets, separators and end-plates. Serpentine-type graphite separators with a channel dimension of 1.0 mm × 1.0 mm (depth × width) were employed. The anode and the cathode were fed at 0.5 M methanol and dry air, respectively, at a stoichiometry of 6. Also a higher concentration of 1.0 M methanol was used to observe the rate of methanol crossover through the MEAs. The cells were operated at 80 °C, ambient pressure, and the current–voltage (I–V) characteristics were measured with a commercial test station (SMART-II, WonA Tech, Korea). Methanol crossover was measured by converting the amount of CO$_2$ at cathode outlet using a catalytic burner and CO$_2$ analyzer (MI70, Vaisala). Methanol crossover measurements were carried out at open-circuit voltage (OCV) and at a loading current of 1 A for 30 and 60 min, respectively. Operating parameters, such as reactant concentration, feed rate and temperature, were maintained constant while measuring the performance of a cell and the rate of methanol crossover.

The electrochemical behaviour of MEAs made via different methods was monitored with EIS and CV. The impedance was galvanostatically measured at 1 A using an Autolab potentiostat (Eco Chemie) over the frequency range of 0.1–1000 Hz. 0.5 M methanol and dry air at a stoichiometry of 6 were fed to the cell and the temperature was maintained at 80 °C. For CV analysis, 100 sccm of fully humidified hydrogen was supplied to the anode to serve as a reference electrode and 1 sccm of water was fed to the cathode as a working electrode. The current was measured with a IM-6 potentiostat (Zahner) over a range of 0–1.23 V (vs. hydrogen electrode) at scan rate of 50 mV s^{-1}.

3. Results and discussion

First, various types of inert thin films were tested as substrates for the decal process. In these experiments, the transfer conditions were also varied to find ways and means under which the catalyst layer can be completely transferred to the polymer electrolyte membrane. For instance, the hot-pressing timing was maintained at 5 and 8 min to transfer completely the catalyst layer from the substrate to the membrane and an additional ionomer layer on the outer surface of the catalyst layer was introduced to facilitate complete transfer of the catalyst layer to the membrane. Photographs of decal substrates after catalyst layers were transferred to the membranes are given in Fig. 2. It is obvious that the complete transfer of the catalyst layer depends on the type of substrate, the presence of the outer ionomer, and the time of hot-pressing. In all cases, the catalyst ink solutions were directly sprayed on each substrate and the hot-pressing temperature was fixed at 140 °C. As shown in Fig. 2(a), the samples without an outer ionomer layer and hot-pressed for 5 min exhibit incomplete transfer regardless of substrate used. In the case of Teflon, the degree of transfer of the Pt–Ru catalyst layer (anode side) is less than 50%, but much lesser amounts of Pt (cathode side) remain un-transferred. Incomplete transfer is also found in the case of Kapton and Al foil, while with PDMS film as a substrate only a trace amount of catalyst remained on the substrate for both catalysts. Although there is no significant difference in the degree of transfer in using Pt and Pt–Ru catalysts, the former

catalyst layer appears to be more easily transferred than the latter. Longer hot-pressing (8 min) appears to improve the transfer. In the case of Teflon, complete transfer has been achieved with Pt catalyst. The different behaviour at both electrode sides is due partially to the different material characteristics of the catalyst, i.e., Pt–Ru vs. Pt. While a slight improvement in the transfer rate is also observed in the case of Al foil, the other two substrates of PDMS and Kapton exhibit no noticeable change. When an additional outer ionomer layer [27] is applied on the catalyst surface prior to the hot-pressing (Decal-I, see Fig. 1), the transfer rate is greatly improved in all cases, except for Kapton. Particularly, on using the Teflon substrates, a complete transfer of both the catalysts can be achieved. The PDMS and Al foil also exhibit better transfer, though some of the catalyst still remains at the edges. Kapton film is proven to be inadequate as a substrate for this low-temperature decal transfer under any of the conditions tested in this study. The great improvement in transferring the catalyst layer after applying the outer ionomer suggests that the outer ionomer layer can act as a binding agent between the Nafion membrane and the catalyst layer.

Based on the above results, Teflon film was chosen as a decal substrate in the following experiments and hence all data related to the decal transfer method in this study were obtained by using Teflon substrate. Hot-pressing conditions of 140 °C for 8 min and applying an outer ionomer were also taken as standard procedure of the low-temperature decal process and denoted as the Decal-I method.
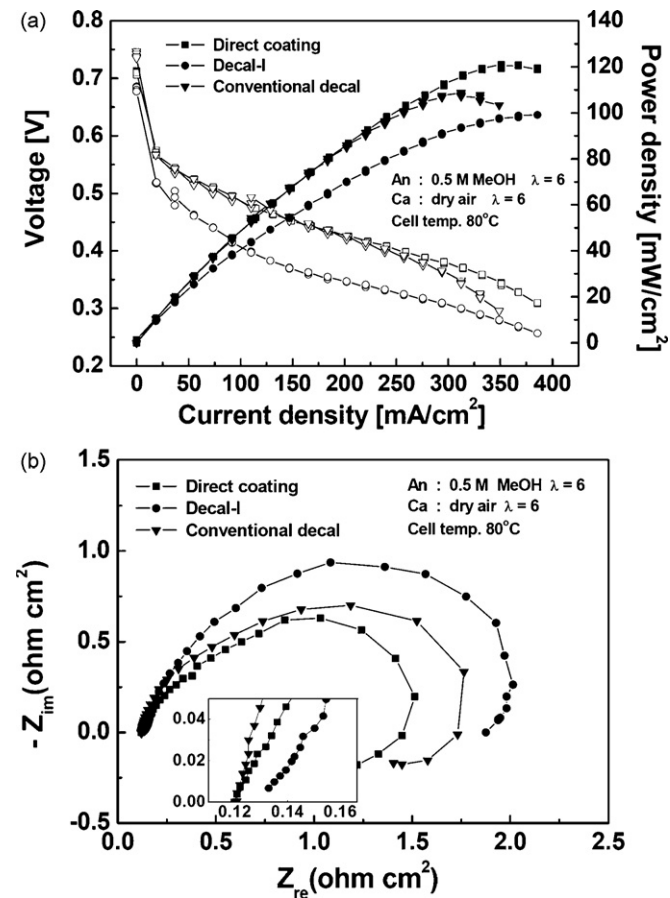

Fig. 4. (a) MEA performance and (b) corresponding impedance analysis according to MEA fabrication method: direct coating, Decal-I, and conventional high-temperature decal. 0.5 M MeOH and dry air at a stoichiometry of 6 fed to anode and cathode, respectively. Cell temperature = 80 °C. Impedance measured galvanostatically at 1 A.
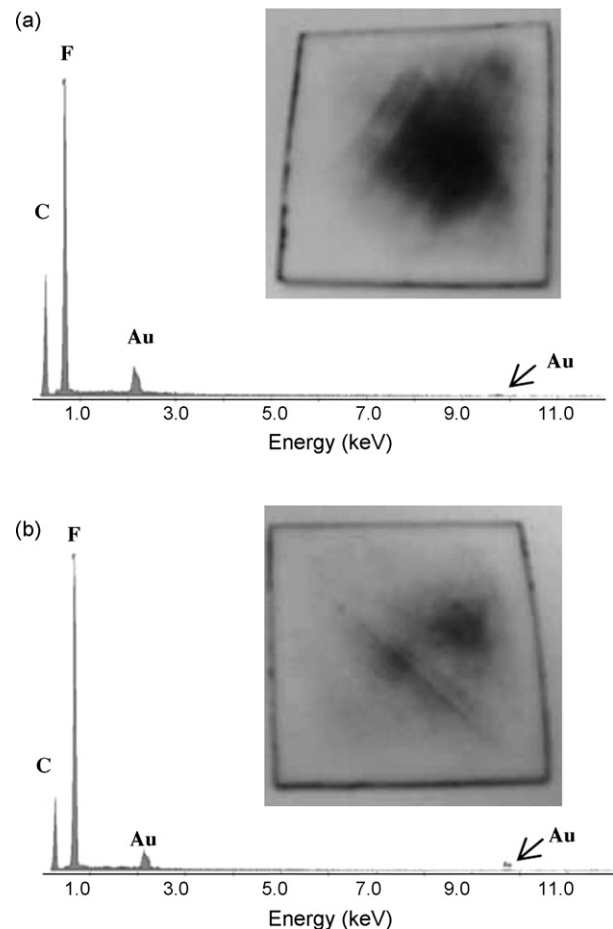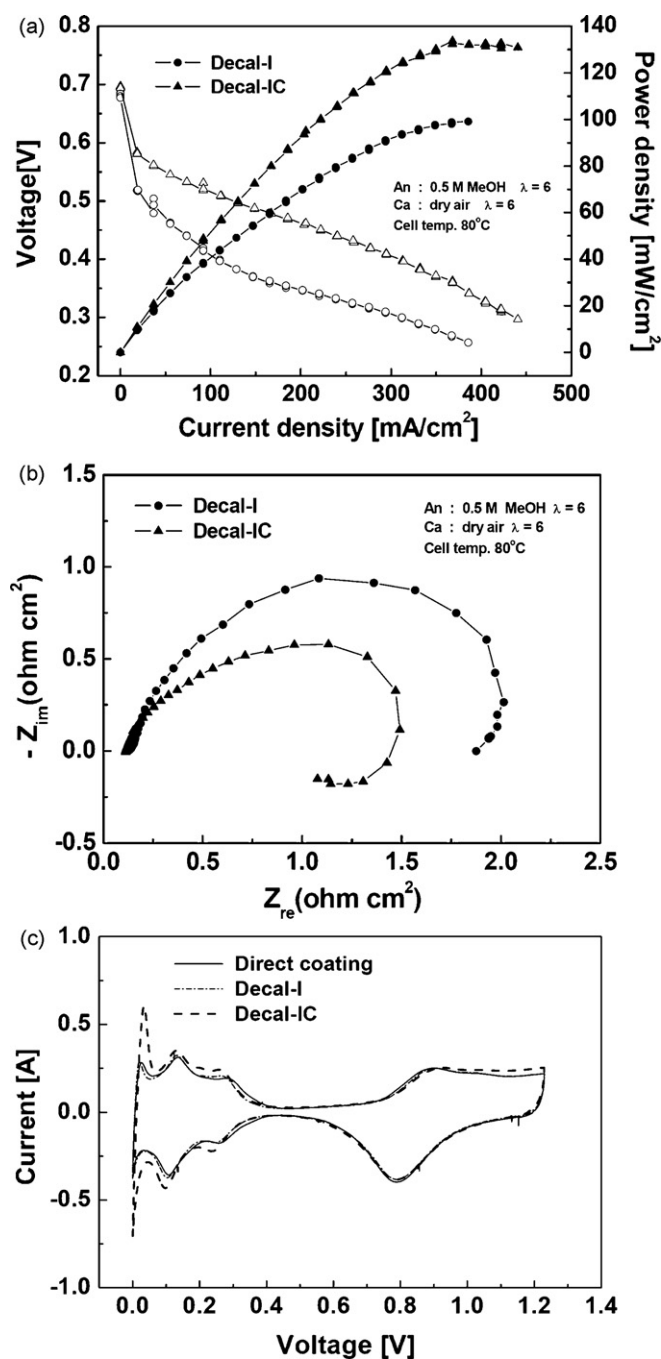

Fig. 5. EDX analysis of residual surface of Teflon substrates after decal transfer with Decal-IC method: (a) anode and (b) cathode. Box images are corresponding pictures of Teflon substrates after transfer.

Fig. 6. Comparisons of (a) MEA performance, (b) impedance analysis and (c) cyclic voltammogram according to MEA fabrication method. 0.5 M MeOH and dry air at a stoichiometry of 6 fed to anode and cathode at cell temperature of 80 °C for (a) and (b). Impedance was measured galvanostatically at 1 A. For CV analysis, 100 sccm of fully humidified hydrogen was supplied to anode as reference electrode and 1 sccm water was fed to cathode as working electrode. Scan range was from 0 to 1.23 V vs. hydrogen electrode.

The surface morphologies of catalyst layers coated on top of the Teflon substrates were observed by means of FESEM and the results are shown in Fig. 3. The catalyst layers without an outer ionomer layer (Fig. 3(a)) are very rough and some cracks are even found on the Pt layer (cathode). The poor wetting property of the catalyst ink solution to the hydrophobic substrate [21] might be the reason for the aggregation of catalyst particles that causes the rough surface and cracks. The outer ionomer layer dispersed on the catalyst layer (Fig. 3(b)) prevents the direct exposure of the rough catalyst surface

to the membrane. The strong affinity between the ionomer binder in the catalyst layer, the outer ionomer and the Nafion membrane may help to bind one layer to the next and thus promote the transfer of the catalyst layer from the substrate to the membrane, as in the case of the Teflon substrate in Fig. 2(c).

The performance and EIS results for MEAs fabricated by the various methods (i.e., direct coating, Decal-I and conventional high-temperature decal) are presented in Fig. 4. In this performance testing, 0.5 M methanol and air with a stoichiometry of 6 were fed to the anode and the cathode, respectively. All the measurements and analyses were undertaken at a cell temperature of 80 °C. As shown in Fig. 4(a), the MEA made by the direct-coating method delivers a maximum power of 122 mW cm^{-2} at a current density of 350 mA cm^{-2}. On the other hand, the MEA fabricated by the conventional high-temperature decal method shows a slightly lower performance, namely, 110 mW cm^{-2} at 310 mA cm^{-2}. As discussed earlier, the conventional decal method has the drawback of ionomer skin formation that acts as a barrier to mass transport [21]. A similar inference is possible from our results, as the performance of the conventional decal MEA rapidly decreases in the higher current density region, i.e., over 310 mA cm^{-2}, compared with that of the direct-coating MEA, which implies that the supply of reactant has been retarded by the ionomer skin layer. It might also increase the electrical contact resistance between the catalyst layer and the GDL. Among the MEAs from the three fabrication methods, the MEA made by the low-temperature decal method with an outer ionomer coating procedure (Decal-I) exhibits the worst performance, as shown in Fig. 4. The poor performance may be ascribed to the presence of the outer ionomer layer which is now sandwiched between the membrane and the catalyst layer. The intervening ionomer layer could increase the ohmic resistance and also increase the mass-transport resistance because part of the ionomer penetrates into the pores of the catalyst layer and thus hinders access of the reactants to the catalyst particles. In addition to this, the ionomer skin layer peculiar to MEAs obtained from the decal transfer method could also increase the resistive components, as described earlier.

The EIS results of the corresponding MEAs are presented in Fig. 4(b). All the circles have the typical shape of Nyquist plots for DMFCs and the resistance of the MEAs exhibits the same tendency as the corresponding cell performance in Fig. 4(a), that is, Decal-I has the highest resistance and direct coating has the lowest one. As mentioned above, the higher resistances for the decal MEAs are presumably due to the formation of the ionomer skin layer that increases both the ohmic and mass-transfer resistances. The resistances could be further amplified by applying the outer ionomer. For example, the ohmic resistance shown in the inset of Fig. 4(b) follows the order of direct coating < conventional decal < Decal-I. It is unclear whether the increased semicircle diameter of the conventional decal MEA in the low-frequency region is related to mass-transfer hindrance by the ionomer skin layer. But from the fact that the deterioration in the performance of the conventional decal MEA occurs only in the high current region when compared with the direct-coating MEA (Fig. 4(a)), it can be reasonably assumed that the ionomer skin inhibits mass transfer of reactants and thereby causes an increase in the impedance as shown in Fig. 4(b). An excess amount of ionomer in the catalyst layer by applying the outer ionomer appears to increase both the ohmic resistance and the mass-transfer resistance as indicated by an overall increase in the circle size of the Decal-I MEA.

Xie et al. [21] have explained the formation of the ionomer skin in terms of a hydrophobic interaction between the ionomer in the catalyst layer and the Teflon substrate and have suggested the use of a less hydrophobic substrate such as Kapton film as one of the solutions that could prevent skin formation. As discussed in the previous section, however, Kapton is not a good material as a substrate

for the transfer of the DMFC catalyst layer from the substrate to the polymer electrolyte membrane by a low-temperature decal transfer process.

In order to improve the performance of MEAs made by the low-temperature decal method, the formation of ionomer skin layer should be avoided during the decal process. There are several probable reasons for the skin formation, such as hydrophobic interaction [21], interfacial energy differences between the air|ionomer and Teflon|ionomer interfaces, or hydrogen bonding between the fluorine and hydrogen atoms of the ionomer and Teflon.

In fact, we have tried various types of substrate material and also optimized the conditions of the decal transfer method to find a decal process that can effectively prevent formation of the ionomer skin and ensure complete transfer of the catalyst layer at lower temperatures to obtain maximum cell performance. In this investigation, we have adopted a strategy of applying a thin carbon layer on the Teflon substrate prior to depositing a catalyst layer. We have used the same carbon powder (Vulcan XC-72) that is employed in the microporous layer deposited on the GDL and thereby it will have no negative impact on the MEA performance though the layer still exists outside of the catalyst layer after transfer.

In using the carbon-coated Teflon substrate, the transfer of catalyst layers from the substrate to the Nafion membrane seems to be incomplete when compared with that of a substrate without carbon (Fig. 5 vs. Fig. 2). After transferring the catalyst layer, a black residue remains on the substrates; in fact, it has been analyzed to check whether the residues on the substrate are catalytic particles or carbon powders (coated on the substrates). Fig. 5 presents photographs and compositions of the residues on the Teflon substrates via EDX analysis (both anode (a) and cathode (b) sides) after decal transfer of catalyst layers using substrates with a thin carbon layer (Decal-IC). The corresponding EDX spectra reveal that the residues are composed of C from both Teflon and the carbon layer and F from Teflon. Also, Au signals appear in the spectrum and originate from the Au coating used to prepare the samples for EDX analysis. Although it is known that Pt and Au signals can partially overlap in the EDX spectrum, the Ru peak does not appear at the anode side. This indicates that no PtRu particles remain on the residue present on the surface of the substrate and the peak around 2.2 keV corresponds to Au. The same situation almost holds for the cathode side (note that the amount of the residue at the cathode side is much less than that at the anode). Therefore, in the Decal-IC method the catalyst layers are completely transferred and only trace amounts of carbon residue are left on the Teflon substrates regardless of the type of catalyst (Pt or Pt–Ru).

A performance comparison between MEAs made by Decal-I and Decal-IC methods is given in Fig. 6(a). The low performance of 100 mW cm^{-2} in the case of Decal-I MEA is greatly improved to 134 mW cm^{-2} by adopting carbon-coated substrates (Decal-IC), a performance is even higher than that obtained from a direct-coating MEA by 10 mW cm^{-2}. The cell resistance exhibited in Fig. 6(b) is also greatly reduced in the case of Decal-IC and the overall size and shape of the circle are very similar to those of a direct-coating MEA, which is important evidence of prevention of the ionomer skin layer by the interaction of carbon layer.

Cyclic voltammetry for hydrogen adsorption and desorption was also performed and the results are given in Fig. 6(c). The Decal-IC MEA has the larger electrochemically active area than direct coating or Decal-I MEAs. Since the ionomer skin formation is accompanied by segregation of the ionomer in the catalyst layer, it could result in subsequent non-uniform distribution and deficiency of ionomer throughout the catalyst layer. Therefore, prevention of the ionomer skin enables the catalyst layer to maintain the content and distribution of the ionomer compared with the Decal-I MEA, thus leading to superior MEA performance. The Decal-IC MEA is also believed to have a better catalyst–ionomer network structure than the direct-coating MEA, since it has a more compact catalyst layer compared with the direct coating MEA (thickness of 7–10 μm vs. 15–16 μm, see Fig. 8).

Fig. 7 is a schematic representation of ionomer skin formation (left) and its prevention by the carbon layer (right). In the conventional decal processes where bare Teflon films are used as substrates, the Nafion ionomer in the catalyst layer migrates and forms a skin layer of ionomer at the surface of Teflon substrate due to hydrophobic interaction between ionomer and Teflon [21]. However, the applied carbon layer in this study might act as a barrier for the chemical/physical attraction between them and prevent skin formation. Moreover, with its porous nature, the carbon layer might inhibit the formation of a dense ionomer film by being percolated with ionomer. The resulting MEAs show better performance than those made by the conventional decal processes, as shown in Fig. 6.

Cross-sectional FESEM images of MEAs made with different fabrication methods are shown in Fig. 8. The thickness of the catalyst layer in the case of the direct-coating MEA (Fig. 8(a)) is around 15–16 μm while the other two MEAs fabricated by Decal-I (Fig. 8(b)) and Decal-IC (Fig. 8(c)) have thicknesses of 7–10 μm. In the MEA made by direct coating, the catalyst layers normally experience a cushion effect offered by the GDL during hot-pressing of the MEA. In the decal method, however, the catalyst layers are directly pressed
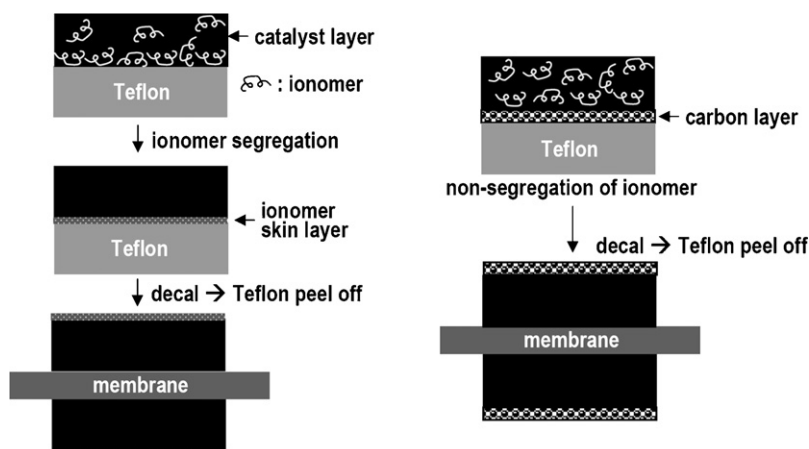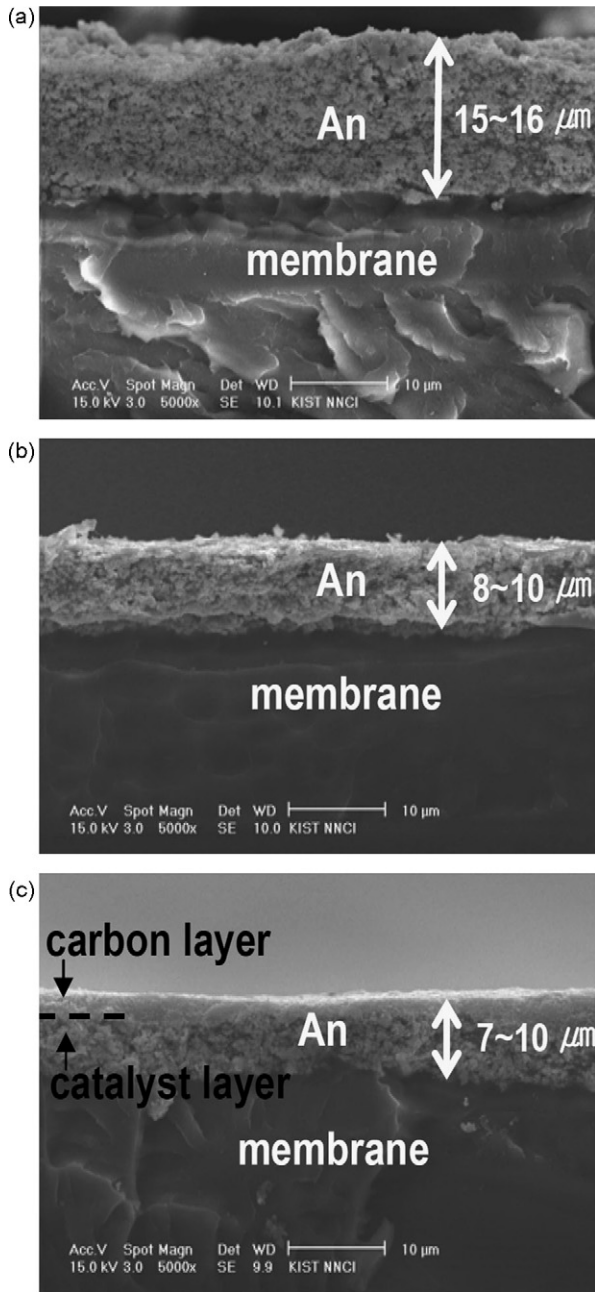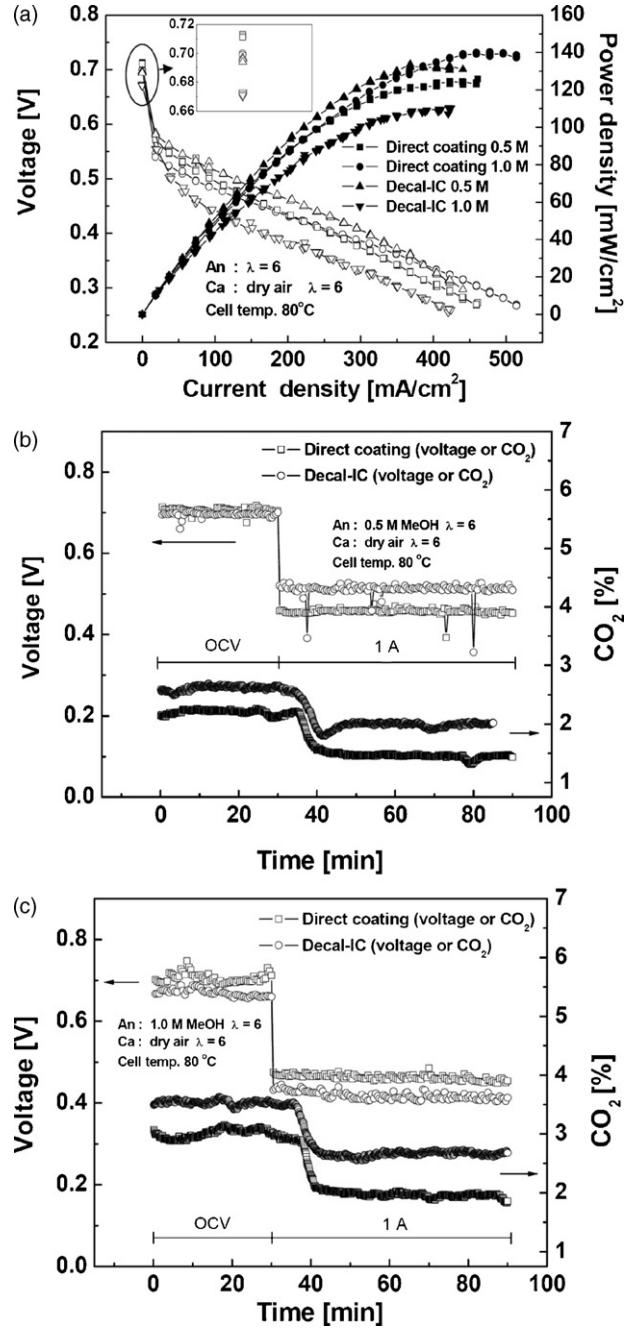

Fig. 7. Illustration of formation of ionomer skin layer in absence of carbon layer (left side) and prevention of it in case of carbon layer coating (right side).

Fig. 8. Cross-sectional FESEM images of MEAs according to fabrication method: (a) direct coating, (b) Decal–I, and (c) Decal-IC.

Fig. 9. (a) Comparison of performance between direct-coating MEA and Decal-IC MEA according to methanol concentrations: 0.5 and 1.0 M. Other conditions denoted in the figure. (b) and (c) Changes of voltage and CO_2 generation at cathode side according to MEA fabrication method (direct coating vs. Decal-IC) and methanol concentrations (0.5 M (b) vs. 1.0 M (c)). MEAs were maintained at OCV for 30 min followed by 1 A load for 60 min.

and subsequently have good contact with the membrane and this results in a thinner thickness than the MEA made by direct coating. The thinner catalyst layers generally have the attributes of lower ohmic and mass-transport resistances due to the shorter passage, and also a larger active area of catalyst due to the better contact between the catalyst particles as well as between the catalyst particles and the ionomer.

On considering the methanol crossover effect, the thinner catalyst layer is not always beneficial to the performance, as depicted in Fig. 9. The methanol concentration effects on MEA performance in Fig. 9(a) show that an increase in methanol concentration from 0.5 to 1.0 M deteriorates the performance of the Decal-IC MEA by 22 mW cm^{-2} in terms of the maximum power density, while it enhances the performance of the direct-coating MEA by 15 mW cm^{-2}. The open-circuit voltage shown in the inset, a

direct indicator of methanol crossover, also decreases from 0.696 to 0.672 V by increasing the methanol concentration in the case of the Decal-IC MEA. Only half of that decrease in OCV is observed (0.712–0.700 V) in the case of the direct-coating MEA. The OCV values themselves also indicate higher methanol crossover in the Decal-IC MEA.

For more a precise understanding of methanol crossover, the concentrations of CO_2 produced from the crossovered methanol by the catalytic burner at the air exhaust out of the cathode outlet were measured using a CO_2 analyzer and taken as a measure

of the methanol crossover rates. The CO_2 concentrations in terms of volumetric percentage in the air were monitored at the OCV for 30 min and then at 1 A for 60 min according to the methanol concentrations. In the case of 0.5 M methanol shown in Fig. 9(b), the CO_2 concentration of the Decal-IC MEA at the OCV is about 2.55%, which is slightly higher than 2.21% for the direct-coating MEA. As an electric load of 1 A is applied to the cell, the CO_2 concentrations gradually decrease in both cases during the next 10 min due to the decrease in the concentration of un-reacted methanol at the anode side that is available for crossover. The concentrations of CO_2 at 1 A are 1.97% and 1.45% for the Decal-IC MEA and the direct-coating MEA, respectively. These values indicate a slightly higher methanol crossover rate in the case of the Decal-IC MEA; but its voltage is still higher than that of the direct-coating MEA. In the case of 1.0 M methanol, the direct-coating MEA shows higher voltages and lower CO_2 concentrations than Decal-IC MEA over the entire range of load including OCV because of the lower methanol crossover rates due to the thicker catalyst layers in the MEA.

These experimental results indicate that the Decal-IC MEA has higher electrode activities than the direct-coating MEAs, but is vulnerable to methanol crossover. Therefore, a combination of the Decal-IC method with a low methanol permeable hydrocarbon membrane [28–30] may yield much better results.

4. Conclusions

In this study, a low-temperature decal transfer method has been developed to fabricate MEAs for application in DMFCs. The MEA is fabricated by transferring three layers consisting of carbon, catalyst and ionomer primarily applied on the Teflon decal substrate to a dry Nafion membrane at a temperature as low as 140 °C. In the low-temperature decal transfer method, the use of a multi-layer substrate enables 100% transfer of the catalyst layer from the decal substrate to the membrane and also prevents the formation of an ionomer skin on the surface of the transferred catalysts layer. MEAs fabricated with a carbon layer by the low-temperature decal transfer method give a relatively higher performance when compared with other types of MEA prepared by Decal-I, conventional high-temperature decal and direct-coating methods. The improved DMFC performance of the MEAs fabricated via the low-temperature decal transfer method can be attributed to absence of an ionomer skin in the catalyst layer, which can streamline the diffusion of reactants and provide good interfacial contact. Thus, the introduction of a carbon layer in the low-temperature decal transfer method is beneficial in enhancing the performance of MEAs in DMFC. The vulnerability of low-temperature decal MEA to methanol crossover is expected to be circumvented by combination with hydrocarbon membranes that have lower methanol permeability.

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