An efficient decal transfer method using a roll-press to fabricate membrane electrode assemblies for direct methanol fuel cells

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ABSTRACT

This study has focused on the development of a roll-press based decal transfer method to fabricate membrane electrode assemblies (MEAs) for direct methanol fuel cells (DMFCs). This method exhibits an outstanding transfer rate of catalyst layers from substrates to the membrane, despite hot-pressing at a considerably lower pressure and for a much shorter duration than the flat-press based conventional decal method. The MEA produced by a roll-press (R-MEA) delivers an excellent single-cell performance with power densities more than 30% higher than that fabricated using a flat-press (F-MEA). The new method considerably improves catalyst active sites in both electrodes and renders a high cathode porosity. The superior pore structure of the cathode makes the R-MEA more efficient in terms of performance and operation stability under lower air stoichiometries. Moreover, MEAs can be prepared in a continuous mode using this new method due to the unique design of the roll-press. All these advantages demonstrate the superiority of this method over the conventional flat-press decal method and make it suitable for use in the commercial manufacturing of MEAs for direct methanol fuel cells.

1. Introduction

For more than a decade, numerous efforts have been made to improve the performance and durability of direct methanol fuel cells (DMFCs). Most of the research activities have focused on enhancement of the cell efficiency and lowering production costs to make it economically viable. A two-way research approach has been adopted, which includes the introduction of new electrolyte and electrode materials [1–3] and development of a suitable process for the fabrication of membrane electrode assemblies (MEAs) [4].

MEAs principally are of two types: a catalyst-coated substrate (CCS), and a catalyst-coated membrane (CCM). Performance and durability of the latter is usually higher than for the former due to better catalyst utilization and membrane-electrode interfacial contact [5,6]. Direct coating of catalysts onto the membrane is carried out by several methods such as spraying, casting or decal transfer, etc. In

a decal transfer process, catalyst inks are coated on the surface of inert substrate films by spraying or casting methods etc. to prepare the anode and cathode electrodes. These electrodes are then dried and placed on both sides of a polymer electrolyte membrane (PEM) and hot-pressed under high temperature and pressure conditions. As a result, both catalyst layers are transferred onto the membrane and substrate films are peeled off to form a CCM type MEA [5,7]. The decal transfer method is considered better than the others as it eliminates problems with membrane swelling and possibly can reduce catalyst losses during the MEA fabrication. These advantages make this a potential candidate for the commercial-scale production of MEAs.

According to the literature on MEA preparation using decal methods, research activities have centered on the various aspects of decal technique, such as choice of the material as a decal substrate, effect of hot-press conditions, fabrication of catalyst layers and characterization of electrodes, etc [4,7–9]. In a detailed study by Xie et al. [7], it was proven that the use of a strong hydrophobic film like Teflon as a decal substrate caused a non-uniform distribution of ionomer in the catalyst layers by forming an ionomer skin on the outer side. This resulted in a decline in cell performance due to increased mass-transport resistance. Less hydrophobic material such as Kapton film is preferable to avoid the problem of ionomer segregation. Song et al. [5] studied the structural properties of decal MEAs, particularly in terms of change in the average size of catalyst particles at different stages during the fabrication process. Getting a complete transfer of catalyst layers onto the membrane is a very crucial and challenging task in the decal process. Transfer is affected by a number of factors such as the catalyst loading amount, the surface properties of the substrate materials, the types of polymer electrolyte membranes, and hot-pressing conditions, etc. Usually, hot-pressing is carried out at a very high temperature of around ∼200 °C to achieve a good transfer rate of catalyst layers. Due to the high temperature, the membrane is converted into a Na^+ form before hot-pressing to improve its mechanical stability so that it can withstand high temperature, and then the fabricated MEA is reprotonated prior to testing in the fuel cell [10]. This process makes the decal method complicated and time-consuming, which raises questions of its feasibility for commercial-level application. Some modifications have been reported in order to obtain a good decal transfer of catalyst layers at lower hot-pressing temperatures. These modifications involve the introduction of additional layers made of different materials such as carbon or Nafion ionomer, the modification of catalyst inks, etc [8,11,12]. Such a modified process is often called a low-temperature decal technique, which is relatively simple when compared with the conventional high-temperature method.

In previous work by our group, the catalyst transfer characteristics of different types of substrates were tested using a low-temperature decal method for a DMFC using a flat hot-press. Complete transfer of the catalyst was achieved only with the Teflon substrate while Kapton exhibited the worst degree of transfer despite the introduction of an additional ionomer layer to facilitate catalyst transfer. Hot-pressing time was considerably longer compared with that of the high-temperature decal method, which usually requires 2–3 min

[5,10]. Thus, the options for substrate materials with adequate catalyst release are limited for the low-temperature decal method. To ensure a good decal transfer, hot-pressing is carried out either under very high pressure or for a longer duration. Application of such severe conditions is a drawback of the low-temperature decal method, and can cause adverse effects for MEA structure and performance. Based on both our past experience and a survey of the literature, the successful use of a low-cost Kapton substrate is rare with the low-temperature decal method to prepare MEAs for DMFC.

In the present study, we succeeded in developing a new decal process that can enable mass production of MEAs for DMFCs using a low-temperature decal method. For this method, we utilized a roll-press machine rather than the commonly used flat one for the transfer of catalyst layers from the substrate onto the membrane. Instead of expensive Teflon film, Kapton film was used as the decal substrate, and its properties regarding release of catalyst layers were examined. Kapton and Teflon decal substrates were also tested using the conventional decal method for the sake of comparison. Fuel cell performance and electrode characteristics of the decal MEAs made by the two methods were investigated using various electrochemical and physiochemical tools. Both methods were compared in terms of catalyst transfer characteristics, MEA performance and their feasibility for application to the commercial-level manufacturing of MEAs.

2. Experimental

2.1. Fabrication of MEAs

Pt black and PtRu black catalysts (Johnson-Matthey) loaded at 2.0 mg cm^{-2} and 3.0 mg cm^{-2} (based on total metal weight) were used for the cathode and anode, respectively. Catalyst inks were prepared by mixing the appropriate amounts of each catalyst, deionized water, 5 wt.% Nafion ionomer solution and isopropyl alcohol ultrasonically. Catalyst layers with the geometric area of 10.89 cm^2 were first coated on either Teflon or Kapton (Du Pont) decal substrates by direct spraying. Prior to the fabrication of catalyst layers, a thin carbon-black layer was coated onto the decal substrate. All the electrodes were kept in an oven at 60 °C for 30 min to remove solvents from the catalyst layers before hot-pressing.

Two different types of hot-press machines were used to fabricate MEAs. To prepare an MEA using the conventional decal method, a commonly used flat-press was employed. The machine was comprised of two flat metal plates connected to electric heaters and a hydraulic system. A polymer electrolyte membrane sheet was sandwiched between the two electrodes coated onto decal substrates and then the assembly was placed between the metal plates of the press, followed by pressing at a desired pressure and temperature for a certain duration of time. In the roll-press, two cylindrical rollers rotated on one another and a control panel was used to control the rolling speed and the roller temperature. A schematic diagram of the roll-press is shown in Fig. 1, which demonstrates its design and function. The rolling speed could be varied in units of mm min^{-1} and this determined the hot-pressing time. The two electrodes on the decal substrates
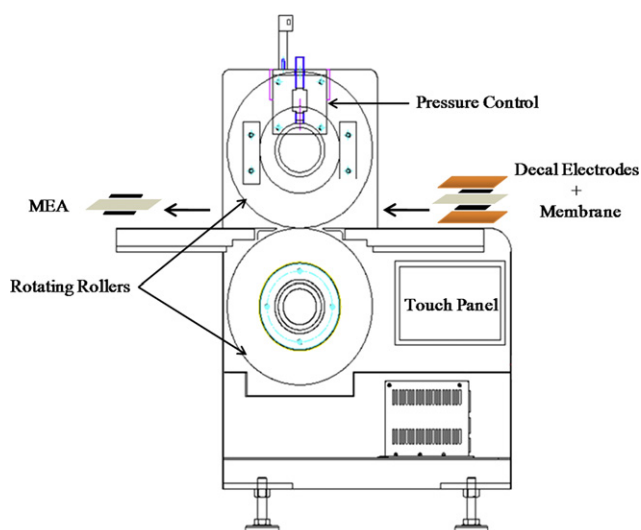
Fig. 1 — Schematic diagram of a roll-press machine.

were placed on either side of the membrane and were inserted between the two rotating rollers on the front side, and the resultant MEA was collected from the back side after hot-pressing.

The conventional decal method using a flat-press was employed to prepare MEA by hot-pressing the two electrodes coated on Teflon films on both sides of a Nafion 115 membrane (H$^+$ form). Hot-pressing was carried out at a temperature of 150 °C under 8 MPa for 8 min. The hot-pressing conditions used for the conventional decal method had already been optimized in our lab. This MEA was designated F-MEA. Kapton film was also tried as a decal substrate in the conventional decal technique, but the degree of catalyst transfer was only about 50% for both anode and cathode even under optimal hot-pressing conditions, so it could not be used to prepare an MEA with intact electrodes.

The roll-press method was used to test the catalyst release for electrodes coated onto a Kapton substrate by hot-pressing on both sides of a Nafion 115 membrane (H$^+$ form). The hot-pressing temperature was 150 °C, and the pressure was 3 MPa with a rolling speed of 50 mm min^{-1}. The MEA thus obtained was designated R-MEA.

2.2. Electrochemical and morphological characterization

The single-cell performance of MEAs made by the roll-press and conventional decal methods (using a Teflon substrate) was tested at 60 °C by supplying 0.5 and 1.0 M methanol to the anode and dry air to the cathode. The stoichiometries of the methanol and air were 6 and 9, respectively, unless otherwise mentioned. Anode polarization curves were measured by replacing dry air at the cathode with humidified hydrogen at 100 sccm while other conditions remained the same as that of single-cell testing. Electrochemical impedance spectroscopic (EIS) analysis of the MEAs was carried out in galvanostatic mode at 1 A current in a frequency range of 0.1–1000 Hz. The anode was fed with 1.0 M methanol at 1 ml min^{-1} and the cathode with dry air at 100 sccm. Cyclic voltammetry (CV) was used to estimate the electrochemically active surface areas (ECSAs) of the anodes and cathodes by following the procedures provided in Ref. [13]. The morphologies and thicknesses of the electrodes were analyzed using cross-sectional images of the MEAs by field emission scanning electron microscope (FESEM, NOVA NANO SEM 200, Philips). The pore structures of the cathode catalyst layers were determined by using a mercury porosimeter (AutoPore IV, Micromeritics).

3. Results and discussion

To investigate the degree of decal transfer of electrodes and the possibility of using Kapton film as a decal substrate, hot-pressing was carried out with flat and roll-press machines. Hot-pressing conditions and photographs of the decal substrates and MEAs after hot-pressing are shown in Fig. 2. The flat-press machine gave a fairly good transfer of both catalyst layers in the case of the Teflon substrate, but use of

Type of press machine	Decal substrate	Hot-pressing conditions	Anode	Cathode	MEA
Flat-press	Teflon	150 °C, 8 MPa, 8 min			
Flat-press	Kapton	150 °C, 8 MPa, 8 min			
Roll-press	Kapton	150 °C, 3 MPa, 50 mm min^{-1}			

Fig. 2 — Hot-pressing conditions and photographs of decal substrates and MEAs after hot-pressing.

the Kapton film failed to prepare an MEA for a DMFC under the same optimized conditions leaving about 50% of electrode layers unreleased. However, both catalyst layers coated onto Kapton films were completely transferred onto the membrane using a roll-press, even with a pressure value of 3/8 and a pressing duration of 1/12 those of the conventional process using a flat-press. This indicates excellent transfer characteristics for the roll-press machine. These results imply that the new decal method provides an easy and quick fabrication of MEAs using the Kapton film, which is a preferable material as a substrate because of its adequate chemical and mechanical properties as well as its low cost. Apart from that, MEAs can only be prepared in separate batches using a flat-press, which places certain limits on geometric dimensions and mass production of MEAs. A roll-press allows the fabrication of large-scale MEAs in a continuous-production mode due to its unique design. These advantages make the roll-press decal method suitable for the commercial-level manufacturing of MEAs.

A precise inspection reveals that Teflon film undergoes dimensional changes during the hot-pressing step, which can affect the geometric area of an MEA. The F-MEA (where Teflon was employed as decal substrate) suffered elongation in both directions, (width and length) as shown in Fig. 3. The original length of each side of a sprayed electrode was 3.3 cm (total geometric area is 3.3*3.3 cm^2) before decal transfer, but the resultant F-MEA had dimensions of 3.4 and 3.45 cm (total geometric area is 3.4*3.45 cm^2), showing 3.03 and 4.55% expansion in the respective dimensions. The deformation of the membrane and electrode by the flat-press process made it very difficult to control the dimensions of the resultant MEAs and can also damage the structural integrity of the MEAs. This is another setback of a Teflon substrate besides having a strong hydrophobic nature, which makes it inappropriate for use as a substrate material. A good substitute is the successful application of Kapton film through the roll-press method where no such instability issues have been observed, and the geometric area of the R-MEA (where Kapton was employed as a decal substrate) is exactly the same as that of the original size of the electrodes formed on the substrate. These results indicate that the roll-press method offers high decal transfer yield with Kapton films under moderate conditions, and also that the resultant MEAs encounter no dimensional changes.

The cross-sectional SEM images of the two MEAs are shown in Fig. 4. There was good adhesion between the catalyst layers and the membrane for both MEAs, as shown in Fig. 4a and b. Their electrodes were thin and the average thicknesses had no noticeable differences. The average thickness for each type of anode was 8–9 μm, and it was 5–6 μm for the cathodes. This indicates that despite a much shorter hot-pressing time and a lower pressure, it is possible to obtain thin catalyst layers with a R-MEA. Magnified images of the cathodes from the cross-sectional view are shown in Fig. 4c and d. These images apparently depict a similar cathode morphology for both types of MEAs.

The single-cell performance of the F-MEA (made with Teflon substrate) was compared with that of the R-MEA (made with Kapton substrate) at 60 °C using 0.5 and 1.0 M methanol solutions, as shown in Fig. 5a and b, respectively. The R-MEA generated a maximum power density (P_{max}) of 87 mW cm^{-2} using a 0.5 M methanol solution, which was 32% higher than the F-MEA with a P_{max} value of 66 mW cm^{-2}. For a 1.0 M methanol concentration, the corresponding P_{max} values for the F and R-MEAs were 86 and 110 mW cm^{-2}, respectively, hence showing a 28% increase for the R-MEA. At a cell voltage of 0.4 V, the current density of the R-MEA ($\sim$195 mA cm^{-2}) was about 70% higher than that of the F-MEA ($\sim$115 mA cm^{-2}). This superior performance of the R-MEA over the F-MEA for both methanol concentrations demonstrated the usefulness of the new decal process. Use of the roll-press has proven very handy in the improvement of the decal technique in terms of catalyst transfer rates, as well as for single-cell performance.

The EIS spectra of the complete cells were measured under the galvanostatic mode, as shown in Fig. 6. The two types of MEAs possessed similar ohmic resistances as shown by the real axis intercept of the EIS curves. Values of 0.460 Ω cm^2 and 0.499 Ω cm^2 that corresponded to the R- and F-MEAs, respectively, imply that the new decal method provided an adequate interfacial contact of the electrodes with the membrane despite the mild hot-pressing conditions. Two semi-circles appeared in the EIS curves of both the R-MEA and the F-MEA with smaller diameters for the R-MEA, which pointed out its superior reaction kinetics. Total charge transfer resistance of
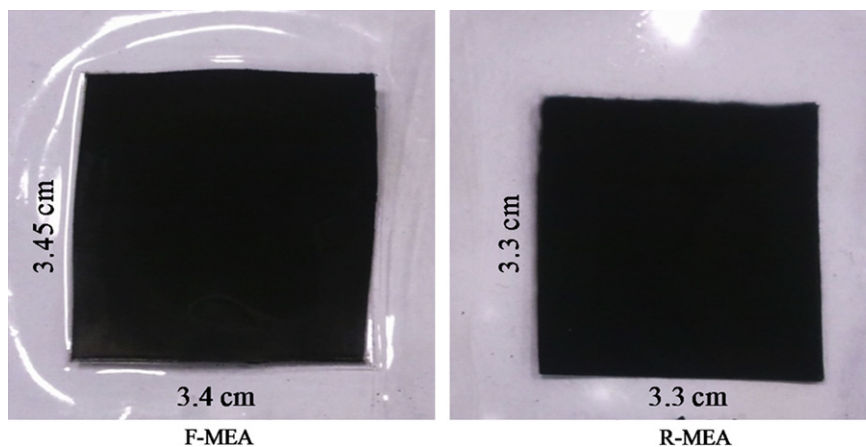

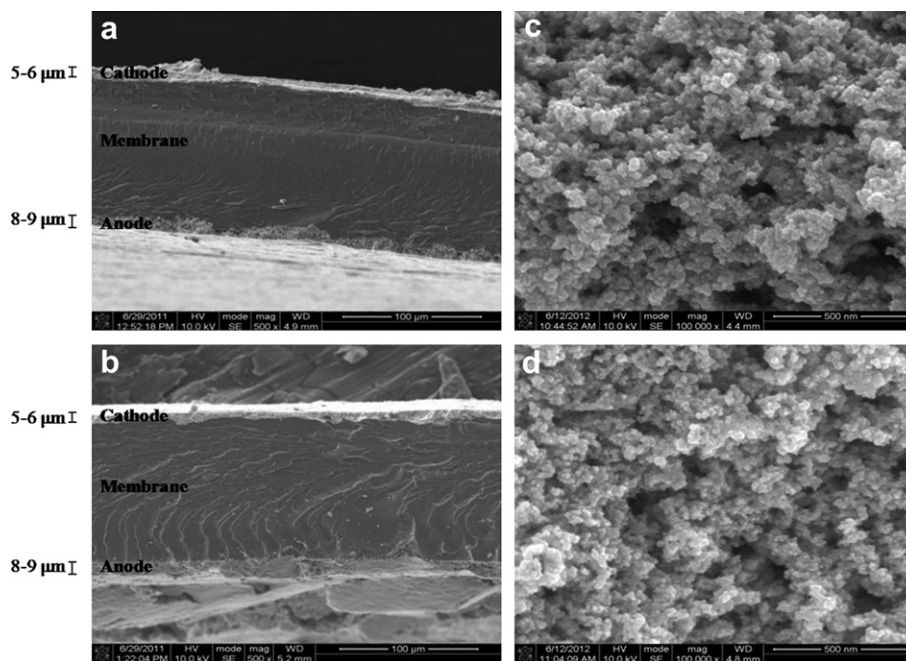Fig. 3 – Photographs of two types of MEAs presenting changes in geometric dimensions.

Fig. 4 — Cross-sectional SEM images of (a) F-MEA, and (b) R-MEA. Their magnified cathode images from a cross-sectional view are presented in (c) and (d), respectively.
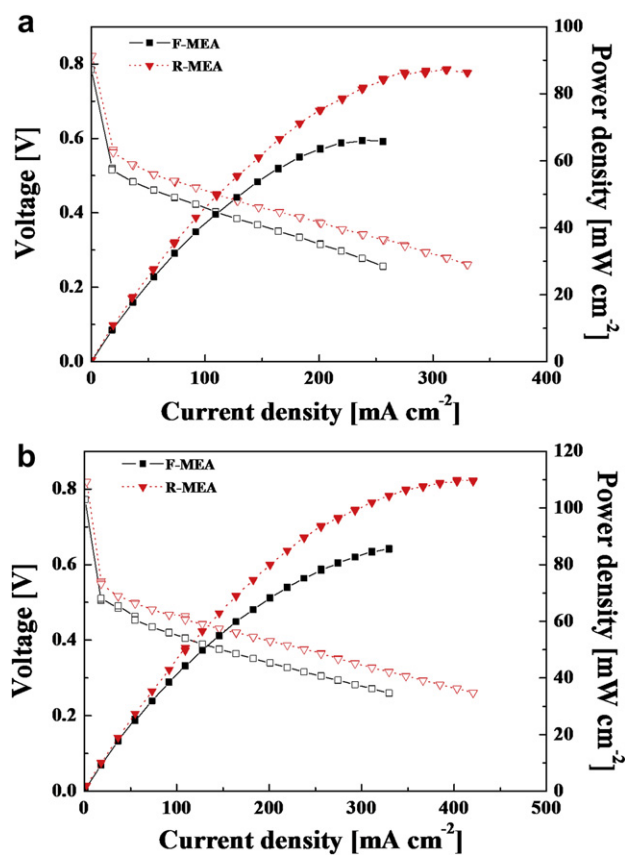

Fig. 5 — Comparison of the single-cell performance of two MEAs at 60 °C using (a) 0.5, and (b) 1.0 M methanol solutions.

the R-MEA (1.23 Ω cm^2) was considerably lower than that for the F-MEA (1.38 Ω cm^2), which shows that the catalyst active sites were well exposed for electrochemical reactions in the R-MEA, and that reactant accessibility to the reaction region was better compared with that of the F-MEA [11].

The measurement of individual electrode potentials under the single-cell test conditions is useful to delineate their contributions to MEA performance [14]. Fig. 7 compares the anode and cathode polarizations for the two types of MEAs. R-MEA exhibited better anodic activity for both 0.5 and 1.0 M methanol concentrations. The anode overpotential loss was lower for the R-MEA than it was for the F-MEA, particularly in a current density range of more than 100 mA cm^{-2} as shown in Fig. 7a and b. The R-MEA also possessed superior cathode performance with a potential loss that was
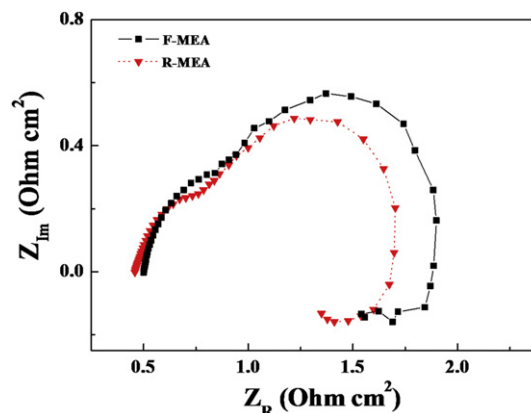

Fig. 6 — EIS spectra of the complete cell at 0.4 V for two types of MEAs.
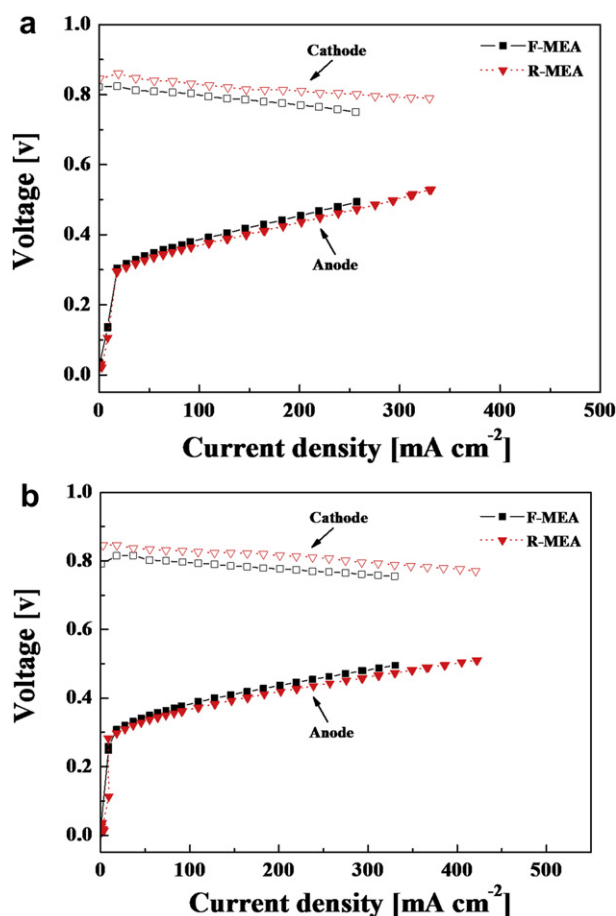
Fig. 7 – Comparison of electrode polarization curves of two MEAs at 60 °C using (a) 0.5, and (b) 1.0 M methanol solutions.

Fig. 8 – Cyclic voltammetric curves for (a) anodes, and (b) cathodes of the F-MEA and the R-MEA.

substantially smaller than that of the F-MEA over the entire current density range. The extent of improvement in the R-cathode was even larger than that of the anode. For instance, at a current density of 300 mA cm^{-2}, the improvements in the anode and cathode of the R-MEA were 21 and 33 mV, respectively, by comparison with the corresponding electrodes of the F-MEA. This implies that the roll-press method provides a more favorable electrode structure and improves reaction kinetics by lowering the overpotential losses. The improved kinetics might originate from better catalyst utilization of the electrodes, which was further analyzed by cyclic voltammetry.

The cyclic voltammograms of the anodes and cathodes of the two MEAs are compared in Fig. 8. Anodic scans are presented in Fig. 8a, and the relative ECSAs of the anodes were estimated from their H$_2$ desorption peaks in the low potential range, as reported in Ref. [15]. The anode ECSA of the R-MEA (5.25 mA V cm^{-2}) was 16.2% larger than that of the F-MEA (4.52 mA V cm^{-2}). The catalyst utilization and ECSAs of Pt black cathodes were calculated from the corresponding CV curves given in Fig. 8b. An ECSA of 16.5 m^2 g^{-1} was obtained for the cathode of the R-MEA, which was 8.3% higher than the cathode of the F-MEA (15.3 m^2 g^{-1}). By considering a BET surface area of 28.6 m^2 g^{-1} for Pt black, HiSPEC 1000 (Johnson-
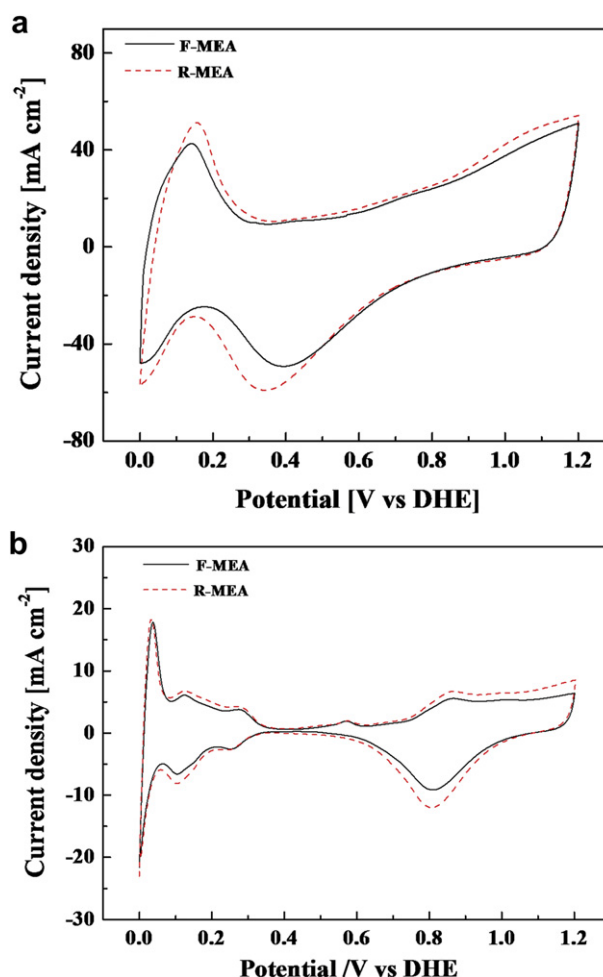
Matthey) [16] catalyst utilization for the cathode of the R-MEA was 57.8% compared with 53.4% for the F-MEA. The higher-electrode ECSAs of the R-MEA can be attributed to the mild hot-pressing conditions of the roll-press method. The conventional decal method uses a two-fold higher pressure with a more than twelve-fold longer hot-pressing period for a complete transfer of catalyst layers. Various studies have shown that hot-pressing of an MEA for long duration or at very high temperature and pressure conditions decreases catalyst utilization by blocking some of the active catalyst sites, and leads to poor cell performance [14,17−19]. Apart from that, possible ionomer segregation due to the strong hydrophobicity of the Teflon substrate may lead to its non-uniform distribution in the catalyst layers of the F-MEA [7]. This can adversely affect the catalyst utilization and porosity of the electrodes.

Cathode porosity plays a vital role in regulating the diffusion of reactant gases to active sites and the drainage of product water out of the cell. An improper pore structure can cause cathode flooding due to the excessive accumulation of water, which limits air diffusion and causes a decline in cell performance [20]. Therefore, the pore volume and pore size distribution of the cathode catalyst layer has

a central role in determining the MEA performance. Fig. 9 shows a comparison of the pore size distribution of the two types of cathode catalyst layers. Compared with that of the F-MEA, the R-MEA had a substantially higher volume of micro pores in the diameter range below 0.01 μm. This was probably due to the very short hot-pressing duration of the R-MEA under a quite low pressure. The superior cathode porosity of the R-MEA decreased resistance to the mass transport of air to the three-phase reaction region and thus improved the oxygen reduction reaction [9,21]. Micro pores have a higher capillary pressure because of the smaller diameters, which makes them more efficient in discarding water and avoiding flooding [20,22]. This allows an effective diffusion of the reactant gases and enhances cell performance.

When a DFMC operation is carried out under low air supply, the performance difference between a R-MEA and its counterpart is expected to be even larger as a F-MEA is more prone to water accumulation at its cathode due to a fewer number of micro pores [23]. This was confirmed by testing the two MEAs under an air stoichiometry of 3 (49.8 sccm A^{-1}). The P$_{max}$ of R-MEA showed an enhancement of 37% over that of the F-MEA under low air supply conditions, as shown in Fig. 10a. The improvement was 32% with an air stoichiometry of 9 (Fig. 5a). The stability of both MEAs was compared in a continuous DMFC test for 1500 min at a current density of 100 mA cm^{-2}. As shown in Fig. 10b, the R-MEA not only sustained a higher performance but also exhibited improved stability. The initial cell voltage of the F-MEA was 0.410 V, which gradually decreased to 0.360 V. This means that the F-MEA suffered a voltage loss of 12.2% over 1500 min. However, the initial cell voltage of the R-MEA was 0.450 V and the final voltage was 0.417 V, which represented a voltage loss of 7.3%. These voltage losses were predominantly caused by cathode flooding under a limited air supply. Other factors contributing to the performance decline were almost negligible for such a short testing time. This implies that the superior cathode structure of the R-MEA not only contributed to performance enhancement but it also improved stability under a lower air supply.
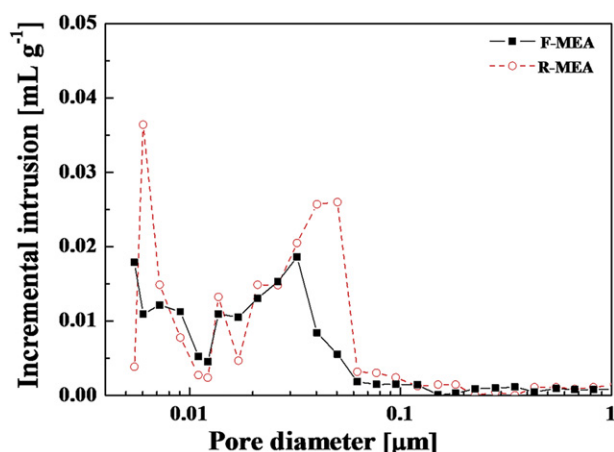

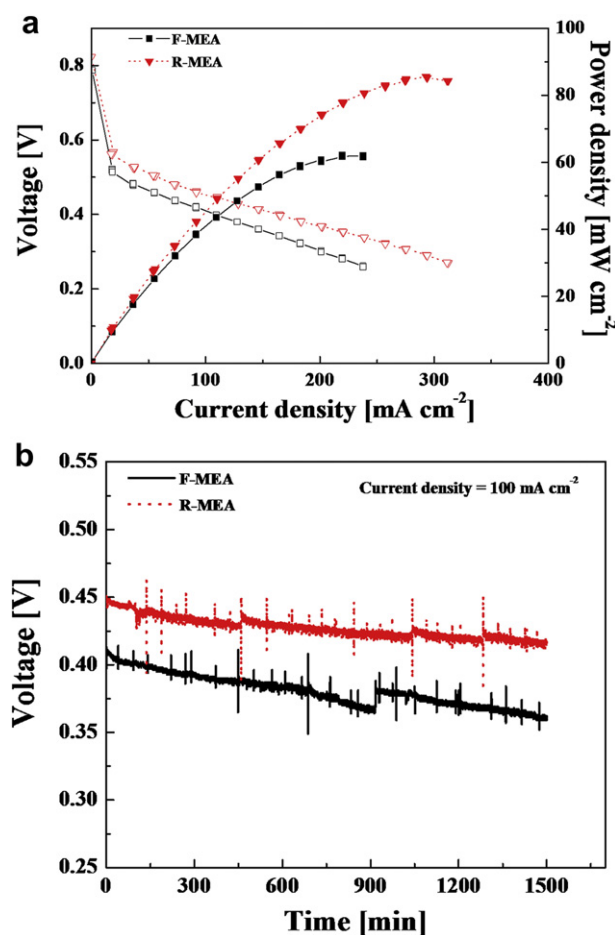**Fig. 9 — Comparison of the pore size distribution of cathode catalyst layers made by two different decal methods.**

Fig. 10 — (a) Single-cell performance under low air stoichiometry (λ = 3) at 60 °C using a 0.5 M methanol solution, and (b) voltage stability curves for two MEAs.

4.   Conclusions

This is the first report of the application of the decal technique involving a roll-press machine to fabricate MEAs for DMFCs. This method ensured an excellent transfer yield of catalyst layers even at quite lower pressure and with a much shorter hot-pressing time, which demonstrated its superiority over the conventional flat-press decal method. The electrode layers of the R-MEA were uniformly affixed with the membrane and their average thickness was the same as that of the F-MEA, despite relatively gentle hot-pressing conditions. The single-cell performance of the R-MEA in a DMFC delivered almost 30% higher maximum power density than that of the F-MEA at 60 °C, which was ascribed to the improvement in electrode kinetics. The new method considerably extended the three-phase reaction zone for both electrodes, which was mainly attributed to the moderate hot-pressing conditions, and, to some extent, to a uniform ionomer distribution due to the Kapton substrate. The R-MEA exhibited better and more stable DMFC operation under lower air stoichiometries compared with that of the F-MEA because of the enhanced cathode porosity. These results exploited the usefulness of the roll-press decal technique, which not only facilitated catalyst

transfer, but also markedly improved the performance. This process is believed to be adequate for commercial-level manufacturing of MEAs due to its continuous production mode and excellent catalyst transfer yield.

Acknowledgment

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