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Direct methanol fuel cells: The effect of electrode fabrication procedure on MEAs structural properties and cell performance

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Abstract

In the present paper, the effect of electrode preparation procedure on the structural properties of *membrane electrode assembly* (MEA) and consequently on the performance of *direct methanol fuel cells* (DMFCs) was investigated. Commercial PtRu black anode catalyst and Pt black cathode catalyst were characterized by XRD in their initial form and in their intermediate and final states after each step involved in catalyst-coated membrane electrode preparation procedure by a *decal transfer method* (DTM). XRD results demonstrated that the DTM process has a significant effect on the catalyst structural properties, especially on the particle size of Pt black cathode catalyst. It is also discussed that among all the steps involved in the electrode fabrication procedure, catalyst ink preparation and high temperature transfer process are key factors affecting the particle size of Pt black catalyst. Furthermore, it was found that the maximum power density of the single DMFC using a MEA fabricated by the DTM, when air is used as oxidant, is more than two times greater than that of the cell using conventionally prepared MEA, and more than three times greater when pure oxygen is used as oxidant. This could be attributed to the easier mass transportation due to the thinner catalyst layer and the better contact between the catalyst layer and the electrolyte membrane in the former case, even if, according to in situ CO stripping voltammetry results in the fuel cell anode environment, the surface composition of PtRu anode has been changed.

Keywords: Direct methanol fuel cell; MEA preparation; Decal transfer method

1. Introduction

Direct methanol fuel cells are regarded as promising electrochemical systems for directly converting the chemical energy of a fuel and an oxidant into electric energy in a wide range of the portable and transportation applications. A short list of their advantages may include, interalia, their suitability for applications where mass and volume constraints are stringent, the compatibility of liquid methanol for handling and storage in the existed gasoline infrastructure, and their ability for quick start-up and immediate response to consumer needs [1–3]. Membrane electrode assembly is the heart of DMFCs where the electrochemical reactions take place to generate electrical power. MEAs development stands central in bringing fuel cell from the laboratory and prototype stages into the marketplace [4]. Minimization of the noble metal electrocatalyst loadings without affecting the cell efficiency is the objective target of numerous ongoing efforts aiming at the economic competitiveness of DMFCs. At the same time, a key parameter for the successful control of these loading efficiency compromises is the quality of the contact which is achieved between the catalyst layer and the electrolyte membrane during MEA fabrication process. In order

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to optimize MEAs performance, a full understanding of the impact of each component on the performance is mandatory. The activity of anode and cathode electrocatalysts is one of the main factors affecting the cell performance. The procedure and method for the preparation of the electrocatalysts play an important role in their particle size, surface morphology, composition and electrocatalytic activity with direct consequences to the fuel cell performance [5–8]. Significant research efforts have been addressed to the investigation of novel preparation procedures for MEA preparation [9,10]. But up to now, there is no report about the effect of electrode preparation process on the electrocatalysts. The electrode fabrication process, especially for the decal transfer fabrication technology, which involves several intermediate processing steps, should also have an obvious effect on the physical characteristics of electrocatalysts, and accordingly on their electrochemical activity.

In the present paper, the decal transfer method is used to apply thin-film catalyst layers onto Nafion® membranes. The characterization of the commercial unsupported PtRu and Pt electrocatalysts (Johnson Matthey Corp.) and as well as of those resulting from each step of the electrode fabrication procedure has been accomplished by XRD. The technique of CO stripping voltammetry was applied to in situ probe the sample surface composition of PtRu catalysts in the fuel cell anode environment. The single DMFC tests were performed to evaluate the feasibility and advantage of the decal transfer method with respect to the conventional electrode preparation method.

2. Experimental

2.1. Preparation of catalyst-coated membrane

The detailed procedure of the catalyst-coated membrane prepared through the decal transfer method (DTM) is schematically represented in Fig. 1, in comparison with

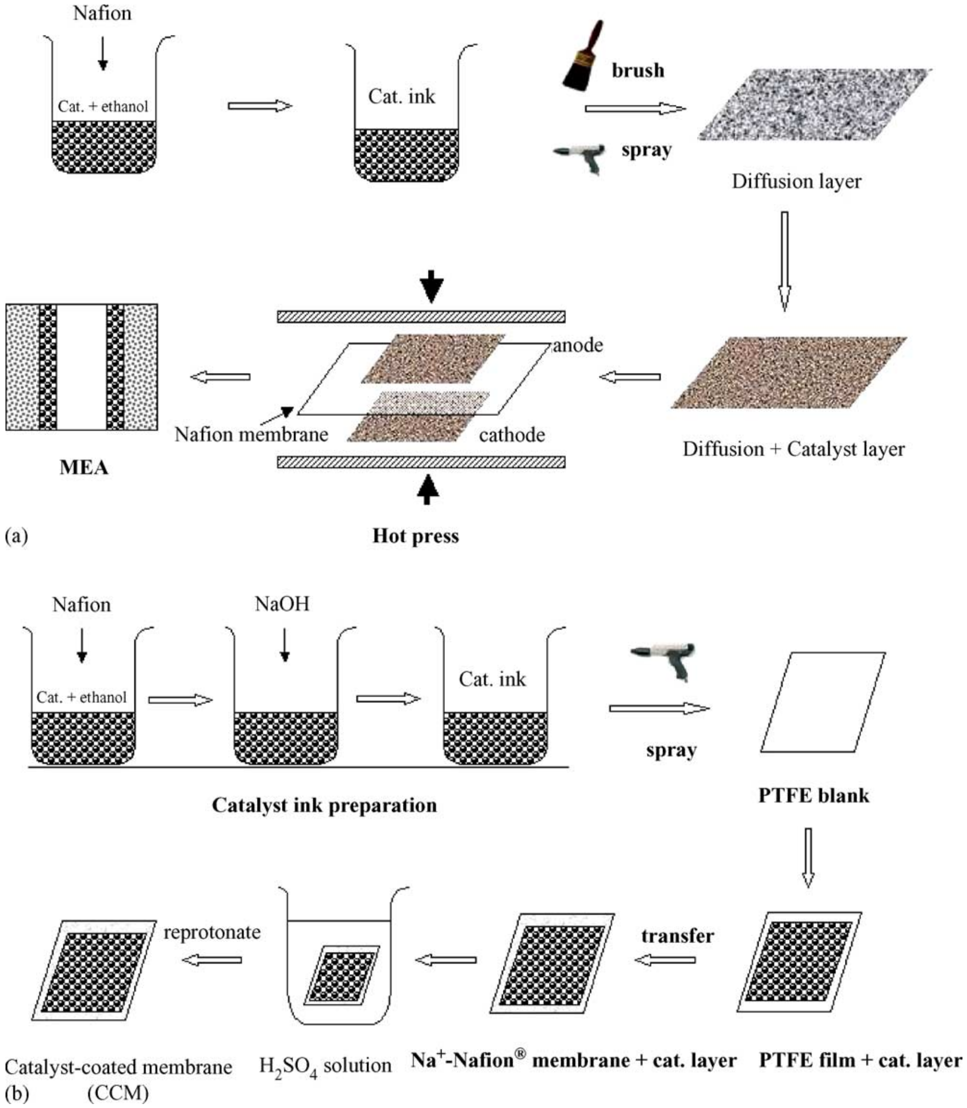

Fig. 1. The schematically detailed electrode preparation procedure of the conventional method and the typical decal transfer method.

the conventional electrode preparation method (CON)) [11]. For the sake of simplicity, the MEAs prepared by the DTM and CON are denoted as MEA-DTM and MEA-CON, respectively. Pre-treatment of Nafion®-115 membrane was accomplished by successively boiling the membranes in 3–5% H_2O_2, deionized water, 0.5 mol L^{-1} H_2SO_4, and then deionized water again, for 1 h each step [12]. The H^+-Nafion®-115 membranes were converted into the Na^+ form by slightly boiling them in 0.5 mol L^{-1} NaOH aqueous solution, deionized water and then deionized water again for 1 h each step. PtRu black of 1:1 nominal atomic ratio and Pt black purchased from Johnson Matthey Corporation were used as the anode and cathode catalysts, respectively. Catalyst inks were prepared by adding 5% Nafion solution (1100 equivalent weight) to the water pre-wetted and ethanol well-dispersed catalyst inks. The soluble Nafion was converted into the Na^+ form by adding an appropriate amount of NaOH aqueous solution. The weight ratios of un-supported catalyst, Nafion and NaOH were 85:15:15 for the anode and 90:10:10 for the cathode, respectively. The desirable well-dispersed catalyst inks were obtained by mechanically and continuously stirring them in an ultrasonic bath for at least 10 min. The appropriate amounts of anode and cathode inks were uniformly sprayed by a spray gun to Teflon decal blanks with a given area to give a metal loading of about 3.0 mg cm^{-2} both for the anode and for the cathode. The *catalyst-coated membrane* (CCM) was obtained by transferring the catalyst films from the Teflon films to the Na^+ form Nafion®-115 membrane by pre-heating at 160–200 °C for 1 min to remove the water from the electrolyte membrane and by hot pressing at 160–200 °C and 100 kg cm^{-2} for another 1.5 min. The complete re-protonation of CCM was obtained by immersing the CCM in 0.5 mol L^{-1} H_2SO_4 aqueous solution for 2 h and then rinsed in deionized water for 1 h in 80 °C water bath. The CCM was sandwiched between two 2 cm × 2 cm diffusion layers and then this assembly was inserted into the fuel cell hardware, which has been previously described in details [13].

2.2. XRD characterization

The XRD patterns of the commercial PtRu black and Pt black (from Johnson Matthey Corporation) as well as the patterns of the catalysts in each step involved in the CCM preparation procedure were all obtained with a Rigaku X-3000 X-ray powder diffractometer using Cu Kα radiation with a Ni filter. The tube voltage was maintained at 40 kV, and the tube current was kept equal to 100 mA. The angular resolution in the 2θ-scans was 0.05° for the wide-angle 2θ-scans. The scan range was from 10° to 85°, and the scan rate was 5° min^{-1}. It is noted that the range from 60° to 75° was finely scanned at a rate of 1.0° min^{-1} to get fine Pt (2 2 0) reflection peaks of the catalysts.

2.3. CO stripping voltammetry [14]

The in situ electrochemical surface areas of the PtRu anode catalysts were measured by using an EG&G PAR 273A potentiostat/galvanostat. Cyclic voltammetry (CV) of the PtRu anode catalysts was performed at 30 °C using the single fuel cell apparatus with a 2 cm × 2 cm active electrode area. The anode compartment was supplied with humidified high-purity Ar, or CO plus Ar (5% CO), serving as working electrode and humidified H_2 was fed to the Pt black cathode with a flow rate of 40 mL min^{-1} at atmospheric pressure, acting both as the counter electrode and as a *dynamic hydrogen electrode* (DHE). The humidification temperature was 15 °C higher than that of the fuel cell. CO was adsorbed onto the PtRu black catalysts by supplying 5% CO in Ar at a flow rate of 40 mL min^{-1} at atmospheric pressure to the anode for 20 min, while keeping the PtRu catalyst electrode potential at 0.1 V (versus DHE). The gas was then switched for 30 min to high-purity Ar at a flow rate of 40 mL min^{-1}, with the potential still held at 0.1 V (versus DHE), to remove any CO from the gas phase. The potential was scanned from the adsorption potential to 0.75 V (versus DHE) at 5 mV s^{-1}, to record the CO stripping voltammograms.

2.4. Single fuel cell tests

The single fuel cell test was carried out in an in-house made fuel cell test apparatus previously described in details [13]. Electrical heaters were placed in the middle of the bipolar plates with parallel flow field in order to obtain the desired cell temperature monitored by the thermocouple placed in the bipolar plates. Methanol aqueous solution (1.0 mol L^{-1}) was fed to the anode compartment of the DMFC by a peristaltic pump at a flow rate of 1.0 mL min^{-1} and the effluent from the anode in-flowed to the recovery reservoir where the produced CO_2 was released to the atmosphere. In parallel, un-humidified oxygen was supplied to the cathode compartment from the cylinder at ambient temperature and a backpressure regulator controlled the desired gas pressure without duty-cycle operation. The polarization curves were obtained using a Fuel Cell Test System (Arbin Instrument Corporation) in a galvanodynamic polarization mode.

3. Results and discussion

3.1. XRD results

The as-received unsupported samples of PtRu black (for the anode) and Pt black (for the cathode) and those resulting from each step of the electrode preparation procedures were characterized by XRD and the results are shown in Figs. 2 and 3. As it can be seen from Fig. 2 the XRD patterns of all PtRu black samples clearly and only demonstrated the characteristic peaks of the Pt fcc structure. The Pt (2 2 0) reflections are used to calculate the average particle size according to the Scherrer formula [15]. The particle size and lattice parameters of catalysts obtained from XRD are summarized in Table 1. From Fig. 2 jointly Table 1, it can be seen that there is almost no change in the particle size of PtRu

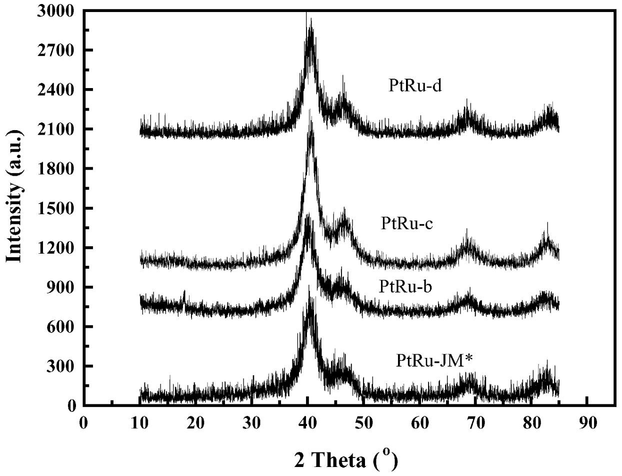

Fig. 2. X-ray diffraction patterns of PtRu black of the as-received (Johnson Matthey Corporation) as well as of the PtRu black involved in each step during the anode fabrication process JM, b, c and d shown in the figure have the same meanings as described in Table. 1.

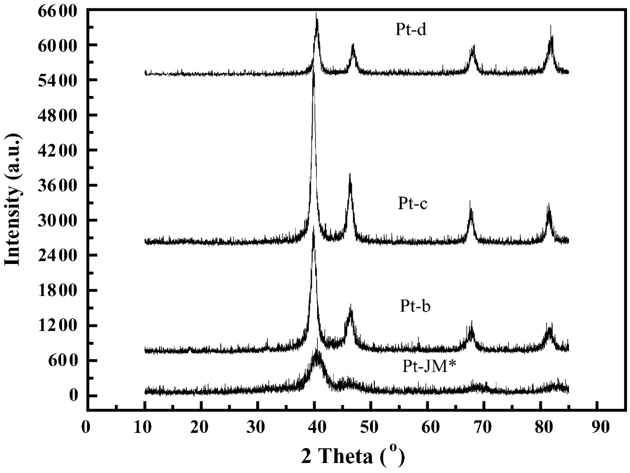

Fig. 3. X-ray diffraction patterns of Pt black of the as-received (Johnson Matthey Corporation) and of the Pt black involved in each step during the cathode fabrication process JM, b, c and d shown in the figure have the same meanings as described in Table. 1.

black even if there are a series of processing steps during electrode fabrication. However, there is an about 0.01° 2θ shift during the electrode fabrication process. The fact that it was not observed a similar behavior (size increment in Pt black described in the following part) in the PtRu is probably due to the presence of oxides, forming during the electrode procedure, as it is also shown by the following in situ CO stripping voltammetry results. The oxides can be served as a dispersion agent, consequently, help to prevent the catalysts from agglomerating during the processing procedures mentioned above. However, there is no obvious peak for metal oxides in the XRD spectra shown in Fig. 2, which is probably due to their amorphous state.

It can be distinguished from Fig. 3 and Table 1 that the average particle size of Pt black gets obviously bigger, almost three times larger than that of the as-received catalysts after their application onto the electrolyte membrane by a series of processing steps for CCM preparation. It can be clearly seen from Fig. 3 that the diffraction peaks of Pt in its initial form is widened with respect to those of Pt black in other states, which results from the smaller particle size of Pt in its initial form. The larger particle size could have a serious effect on the cathode performance. This may be attributed to two different reasons: The first one is that when Pt acts as oxygen reduction electrocatalyst, the smaller Pt particles are less affected by the presence of methanol since the specific activity for the methanol oxidation decreases with a decrease in the Pt particle size [16]. The potential loss induced by the presence of methanol will be smaller when the Pt particle size decreases due to the fact that in oxygen-free electrolyte the methanol oxidation peak is sifted to a more negative potential [17]. This seems very important because, up to date, the methanol crossover from the anode to the Pt-based oxygen cathode through the electrolyte membrane is still one of the major practical problems limiting the DMFC performances and retarding the DMFCs commercialization. The second reason is that for oxygen electro-reduction, the specific activity decreases with the decrease of the Pt particle size, while specific activity for large particles (d >5 nm) is approximately the same as for smooth platinum [18]. Furthermore, the mass activity versus particle size plots for oxygen reduction in sulfuric and phosphoric acid electrolyte exhibit an obvious maximum at $d \approx 3.5$ nm [18]. In the present case, the Pt particle size is 7.3 nm just after being applied to the membrane through a series of processing steps for CCM preparation, thus showing a lower activity to oxygen electro-reduction, and consequently, exhibiting relatively poorer cathode performance compared to a smaller Pt particle size. From Table 1, it can also be clearly seen that among all the steps involved in the electrode fabrication procedure, catalyst ink preparation and transfer process are key factors for the particle size increment. This may be attributed to the fact that during the catalyst ink preparation process, ul-

Table 1
Summary of particle size and lattice parameter of electrocatalysts for DMFC during CCM fabrication procedure

Electrocatalysts	Anode				Cathode			
	PtRu JM[a]	PtRu step-b	PtRu step-c	PR step-d	Pt JM*	Pt step-b	Pt step-c	Pt step-d
Average particle size (nm)	2.4	2.6	2.5	2.4	2.4	5.2	7.6	7.3

Step-b, step-c and step-d denote the preparation steps involved in the decal transfer electrode preparation. Step-b: catalyst ink application onto Teflon blank film. Step-c: the transfer of the thin film catalyst layers from Teflon film to Na^+-Nafion® membrane. Step-c: the transformation of Na^+-CCM into H^+-CCM.

[a] JM stands for the catalysts in as received form from the Johnson Matthey Corporation.

Table 2
Summary of CO stripping data: CO stripping peak potential (E_p), CO stripping peak current density (J_p) and CO stripping charge density (q_{CO}) at 30 °C over PtRu-MEA-DTM and PtRu-MEA-CON respectively. Anode catalyst: PtRu black (Johnson Matthey Corp.), the metal loading: 3.0 mg cm^{-2}. Cathode catalyst: Pt black (Johnson Matthey Corp.), the metal loading: 3.0 mg cm^{-2}. Electrolyte: Nafion®-115 membrane

	PtRu-MEA-DTM	PtRu-MEA-CON
E_p/mV vs. DHE	460	470
J_p (mA cm^{-2})	6	50
q_{co} (μQ cm^{-2})	300	790

trasonic dispersion led to making the ink hot during mixing, which may make Pt black in soft-aggregation state aggregate again, leading to a bigger Pt particle size. On the other hand, during the transfer process, the higher transfer temperature for the desired transfer of the thin film catalyst layers from Teflon films to Nafion® membrane may be just the main reason resulting in the increased Pt particle size.

It is important to avoid the growth of the particle size of electrocatalysts during the electrode fabrication procedure. It was reported [19] that the high cell performance is obtained by the co-precipitation of perfluorosulfonate-ionomer (PFSI) solution, e.g. Nafion and simultaneous cross-linkage of PFSI covered on Pt/C. Yang et al. [20] investigated the effect of various organic solvents for catalyst ink preparation on the performance of polymer electrolyte membrane fuel cell's electrode. They found that the electrode prepared by using ethylene glycol as the solvent showed a better performance than that prepared by using the other solvents. They attributed this to the higher dielectric constant of ethylene glycol. Another probable reason is that ethylene glycol serves not only as a dispersion agent but also as a protective agent to prevent the growth of the Pt particle size during the electrode preparation process.

3.2. *CO stripping voltammetry results*

CO stripping voltammetry can be used as a tool for the in situ study of the surface of the dispersed PtRu anode catalysts [14]. The CO stripping peak potential can provide the information on the composition of the surface metal alloy domains in the fuel cell anode environment. The CO stripping peak charge provides information of such active metal alloy surface sites as well as information on the activity that such a catalyst exhibits in the key step of the process of anodic methanol oxidation, i.e. anodic stripping of adsorbed CO [14]. Fig. 4 shows the adsorbed CO stripping voltammograms measured at 30 °C for the PtRu anode in the MEA-DTM and the MEA-CON, respectively. From Fig. 4, it can be clearly seen that the peak potential of CO stripping on PtRu-MEA-DTM occurs at a similar potential ($E_p = 460$ mV versus DHE) to that for PtRu-MEA-CON, suggesting a similar surface composition for the active part of the surface of these two catalysts (Table 2). From Table 2 it can also be seen that in the case of the MEA-DTM, the peak current density of CO stripping is about 6 mA cm^{-2}, while the respective value for the MEA-CON is about 50 mA cm^{-2}, and that is 8 times lower at the same scan rate and temperature. The much smaller peak current density and CO stripping charge for PtRu-MEA-DTM indicates that there are fewer surface sites, which are prerequisite for CO adsorption and electro-oxidation. The excess metal oxides that are present in this sample may reduce the surface sites mentioned above and the oxidation process probably occurs during the electrode preparation procedure by the decal transfer method involving a series of intermediate steps. On the other hand, it is probably the existence of metal oxide that prevents the PtRu catalyst particle from getting bigger in the multi-step processing procedures involved in DTM electrode preparation, as it can be seen from Fig. 2 and Table 1.

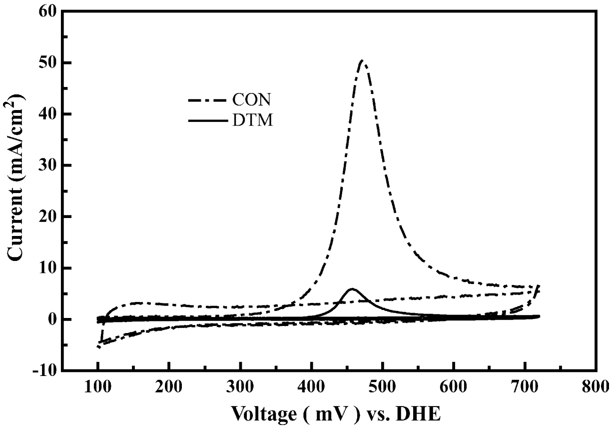

Fig. 4. CO stripping voltammetries of PtRu black in the anode of MEAs prepared by using the decal transfer method and the conventional method at 30 °C, respectively. Shown are first and next cyclic voltammograms at 5 mV s^{-1} in high purity Ar atmosphere. Adsorption from 5% CO in Ar occurred at 0.1 V vs. DHE for 30 min. Anode catalyst: PtRu black (Johnson Matthey Corp.), the metal loading: 3.0 mg cm^{-2}. Cathode catalyst: Pt black (Johnson Matthey Corp.), the metal loading: 3.0 mg cm^{-2}. Electrolyte: Nafion®-115 membrane.

3.3. *Single fuel cell test results*

Fig. 5 compares the cell performance of DMFCs with different MEAs prepared by using the decal transfer method and the conventional method respectively, at 90 °C with 2 atm oxygen or air as oxidants. In Fig. 5(a), it can be clearly seen that, in the case of the MEA-DTM, the single DMFC has higher discharge ability with the maximum current densities of 800 and 650 mA cm^{-2} for oxygen and air as the oxidant, respectively, while the corresponding values for the MEA-CON are about 440 and 380 mA cm^{-2}. From Fig. 5(b), one can distinguish that the cell with the MEA-DTM exhibits the peak power densities of 225 mW cm^{-2} at 680 mA cm^{-2} and 140 mW cm^{-2} at 480 mA cm^{-2} with 2 atm oxygen or air supplied to the cathode at 90 °C. From the same figure it can also be observed that, when the MEA-CON was used, the highest power densities are about 70 mW cm^{-2} at 350 mA cm^{-2} and 60 mW cm^{-2} at 250 mA cm^{-2} with oxy-

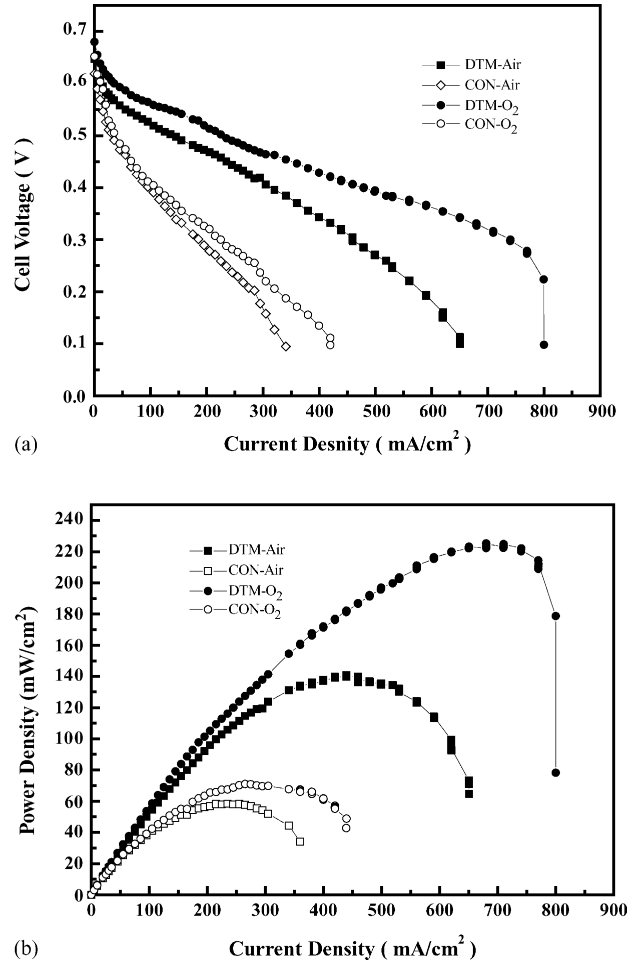

Fig. 5. Single DMFC cell performance comparison of membrane electrode assemblies prepared by using the decal transfer method (DTM) and the conventional method (CON). $T_{\text{cell}} = 90\,^{\circ}\text{C}$. Anode: $C_{\text{methanol}} = 1.0\,\text{mol L}^{-1}$, flow rate: $1.0\,\text{mL min}^{-1}$, anode catalyst: PtRu black (Johnson Matthey Corp.), the metal loading: $3.0\,\text{mg cm}^{-2}$. Cathode: $P_{\text{O}_2\,\&\,\text{air}} = 2$ atm., cathode catalyst: Pt black (Johnson Matthey Corp.), the metal loading: $3.0\,\text{mg cm}^{-2}$. Electrolyte: Nafion®-115 membrane.

gen and air as oxidant at 90 °C, respectively. The former is more than 3 times greater than the latter in the case of oxygen as oxidant and more than 2 times greater when air is used as oxidant. The bigger difference between these two cases when air, is used as oxidant, could be caused by the easier mass transportation due to the thinner catalyst layer resulting from the intrinsic advantage of the DTM over the CON. By comparing these two cases, one can conclude that in the case of the MEA-DTM, even with air as oxidant, DMFC still presents better performance than that with the MEA-CON with pure oxygen as oxidant. The peak power density of the former is twice higher than that of the latter. Based on the above experimental results, it suggested that a higher DMFC performance can be obtained when the MEA-DTM is used. This fact implies the suitability of the DTM for electrode preparation despite its serious effect on the structure of the electrocatalysts, which was described above. The improved cell performance of the MEA-DTM may be attributed to a better contact between the catalyst layer and the electrolyte membrane, which facilitates the transportation of protons and electrons in the electrodes and reduces the cell internal resistance. On the other hand, as observed in Fig. 4, PtRu anode catalysts in the MEA-CON has an optimum surface composition for methanol electro-oxidation, while in this case DMFC shows inferior cell performance compared to that with the MEA-DTM. This may be attributed to the lower catalyst utilization except the poor contact between the catalyst layer and the electrolyte membrane.

4. Conclusion

Based on the above experimental results, the process of the decal transfer electrode preparation has an obvious effect on the structural properties of both the PtRu anode catalyst and the Pt cathode catalyst. There is a significant increase in metal particle size for Pt cathode electrocatalysts during the electrode preparation procedure, especially in the steps of catalyst ink preparation and the transfer of the thin film catalyst layer from Teflon film to Na^+-Nafion® membrane. In the case of PtRu anode catalysts, the PtRu particle size remains almost the same, while the surface states of the catalyst changes with higher metal oxides content. Both the bigger Pt particle size and the changed PtRu surface composition with higher metal oxides content will have a negative effect on the single DMFC performance. Nevertheless, compared to the conventional electrode preparation method, the decal transfer method still provides MEAs with a higher single DMFC performance, as it resorts to a better contact between the catalyst layer and the electrolyte membrane, and reduces the protonic and electronic resistance of the electrodes. Moreover, the decal transfer method can provide MEAs with the thinner catalyst layers, leading to a desirable mass transportation, which is especially important when air is used as oxidant. In order to maximize the fuel cell performance in the case of the decal transfer electrode preparation method, it is necessary and important to identify an appropriate dispersion agent for catalyst ink preparation and to find a solution to protect catalyst from being affected by the processing steps involved in the decal transfer electrode fabrication method.

Acknowledgements

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References

[1] R. Dillon, S. Srinivasan, A.S. Aricò, A. Antonucci, J. Power Sources 127 (1/2) (2003) 112.

[2] X. Ren, P. Zelenay, S. Thomas, J. Davey, S. Gottesfeld, J. Power Sources 86 (1/2) (2000) 111.

[3] C. Lim, C.Y. Wang, J. Power Sources 113 (2003) 145.

[4] G. Hoogers, Fuel Cell Technology Handbook, CRC Press, 2003, P 4-1.

[5] L. Dubau, F. Hahn, C. Coutanceau, J.M. Léger, C. Lamy, J. Electroanal. Chem. 554/555 (2003) 407.

[6] Z. Jusys, J. Kaiser, R.J. Behm, Electrochim. Acta 47 (22/23) (2002) 3693.

[7] U.A. Paulus, U. Endruschat, G.J. Feldmeyer, T.J. Schmidt, H. Bönnemann, R.J. Behm, J. Catal. 195 (2) (2000) 383.

[8] W.J. Zhou, B. Zhou, W.Z. Li, Z.H. Zhou, S.Q. Song, G.Q. Sun, Q. Xin, S. Douvartzides, M. Goula, P. Tsiakaras, J. Power Sources 126 (1/2) (2004) 16.

[9] X. Ren, S. Mahlon Wilson, S. Gottesfeld, J. Electrochem. Soc. 143 (1) (1996) L12.

[10] M. Uchida, Y. Aoyama, N. Eda, A. Ohta, J. Electrochem. Soc. 142 (1995) 463.

[11] M. Uchida, Y. Fukuoka, Y. Sugawara, H. Ohara, A. Ohta, J. Electrochem. Soc. 145 (1998) 3708–3713.

[12] K. Scott, W.M. Taama, P. Argyropoulous, J. Power Sources 79 (1) (1999) 43.

[13] Z.B. Wei, S.L. Wang, B.L. Yi, J.G. Liu, L.K. Chen, W.J. Zhou, W.Z. Li, Q. Xin, J. Power Sources 106 (2002) 364.

[14] H.N. Dinh, X. Ren, F.H. Garzon, P. Zelenay, S. Gottesfelf, J. Electroanal. Chem. 49 (2000) 222.

[15] V. Radmilovic, H.A. Gasteiger, P.N. Ross, J. Catal. 154 (1995) 98.

[16] Y. Takasu, T. Iwazaki, W. Sugimoto, Y. Murakami, Electrochem. Commun. 2 (9) (2000) 671.

[17] F. Maillard, M. Martin, F. Gloaguen, J.-M. Léger, Electrochim. Acta 47 (2002) 3431.

[18] K. Kinoshita, J. Electrochem. Soc. 137 (1990) 845.

[19] M. Uchida, Y. Aoyama, N. Eda, A. Ohta, J. Electrochem. Soc. 142 (1995) 463.

[20] T.-H. Yang, Y.-G. Yoon, G.-G. Park, W.-Y. Lee, C.-S. Kim, J. Power Sources 127 (2004) 230.