Short communication

Significant improvement in cathode performance for proton exchange membrane fuel cell by a novel double catalyst layer design

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ABSTRACT

Conventional double catalyst layer (DCL) structures show no obvious improvement in cathode performance, due to the contradiction between improving mass transfer and maintaining good platinum (Pt) utilization. To decrease this conflict, a novel DCL cathode is prepared using catalysts with two different amounts of Pt; the catalyst with higher Pt content is used in the inner layer to concentrate the Pt, and the catalyst containing less Pt is used in the outer layer to maintain a suitable layer thickness. Polarization characteristics of cathodes with this novel DCL, a conventional DCL, and a single catalyst layer (SCL) are evaluated at ambient pressure in an H_2/air PEMFC. The results show a significant increase in performance with the novel DCL cathode. Compared with the SCL cathode, the current density of the novel DCL cathode at 0.6 V increases by 35.9%, while that of the conventional DCL cathode increases by just 8.8%.

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1. Introduction

Despite enormous improvements, major voltage losses still occur in proton exchange membrane fuel cells (PEMFCs) due to the poor kinetics of the oxygen reduction reaction (ORR) [1] and the transport limitations of protons and reactants in cathode catalyst layers [2]. The characteristics of the cathode catalyst layer in a PEMFC therefore have a significant influence on the overall cell performance.

Many studies have been conducted to improve cathode performance by optimizing electrode structure [2–15], including optimization of ionomer content [3,4], introduction of pore former [5], and fabrication of a multi-catalyst-layer structure [6–14]. Among these, fabricating a multi-catalyst-layer structure (typically a double catalyst layer (DCL)) has proved effective in enhancing cathode performance [6,7] because this structure facilitates mass transport, such as oxygen supply and water removal, and has no significant effect on proton migration since the electrochemical reaction occurs mainly in the inner catalyst layer (close to the membrane), which contains sufficient Nafion ionomer. In general, a catalyst layer with a graded distribution of ionomer, in which Nafion content is higher toward the catalyst layer/membrane interface and lower toward the catalyst layer/gas diffusion layer (GDL) interface, should exhibit higher performance in a PEMFC. How-

ever, some studies show that prepared DCL cathodes achieve only slightly higher (and sometimes worse) performance than normal single catalyst layer (SCL) cathodes [6–10]. These findings are probably related to platinum utilization and mass transfer in the catalyst layer. Studies demonstrate that increasing the thickness of the catalyst layer that contains a low amount of Nafion may reduce mass transport problems to some extent [3,15]. According to the theoretical modeling of Wang et al. [6], a DCL cathode exhibits better performance when the thickness of the outer layer is very similar to that of the inner catalyst layer. To achieve this, approximately the same amounts of Pt (or other catalyst) should be used in both layers, since only one type of catalyst is being employed. However, it is widely recognized that Pt is better utilized when concentrated near the catalyst layer/membrane interface [16]. Thus, in conventional DCL cathodes containing only one catalyst, there is a conflict between improving mass transfer and maintaining effective Pt utilization. This may explain the limited potential for improvement in conventional DCL cathodes.

In this work, we fabricated a novel DCL cathode using catalysts with two different amounts of Pt; the catalyst with higher Pt content was used in the inner layer to concentrate the Pt, and the catalyst containing less Pt was used in the outer layer to maintain a suitable layer thickness. Much better performance was achieved than with a conventional DCL cathode or an SCL cathode. We also investigated the performance effects of (1) Pt distribution in the outer and inner layers, and (2) the ratio of inner to outer layer thicknesses.

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Table 1
Specifications of five novel DCL cathodes.

Novel DCL cathode	NDCL-1	NDCL-2	NDCL-3	NDCL-4	NDCL-5
Pt distribution (inner:outer)	9:1	8:2	7:3	6:4	5:5
L_{out}/L_{in} (estimated value)[a]	0.44	1	1.71	2.78	3.91

[a] L_{out}: the thickness of outer catalyst layer, L_{in}: the thickness of inner catalyst layer.

2. Experimental

2.1. Preparation of DCL cathode and membrane electrode assembly (MEA)

All MEAs were prepared using the catalyst-sprayed membrane method [17]. Hispec 4100 Pt/C (40 wt% Pt, Johnson Matthey (JM)) and lab-made 10 wt% Pt/C were used in the novel DCL cathodes. Catalyst inks were prepared by dispersing catalyst powder into a mixture of isopropanol and 5 wt% Nafion ionomer solution (DuPont, USA). Ink with JM 40 wt% Pt/C was sprayed on Nafion 212 membrane (DuPont, USA) to form the inner catalyst layer. Then, ink with 10 wt% Pt/C was sprayed on the surface of this inner layer to form the outer catalyst layer. In this work, five different novel DCL cathodes were prepared and named NDCL-1 to NDCL-5, as shown in Table 1.

The Pt loadings at the anode and cathode were controlled and calculated using a combination of two methods. First, the catalyst amounts for the anode and cathode were precisely weighed. To take into account the loss during the fabrication process, we generally used 10% more catalyst than the calculated amount. Second, we weighed the Nafion membrane, the coated anode membrane, and the coated anode and cathode membranes, and calculated the individual Pt loadings for the anode and cathode, respectively, to ensure that these loadings conformed to our design.

Each novel DCL cathode has a different Pt distribution in the catalyst layer. The ratio of outer to inner layer thicknesses (L_{out}/L_{in}) can be estimated based on the Pt distribution values in the DCL. In this work, the Nafion contents in the inner and outer layers were 33 wt% and 20 wt%, respectively. Of the five novel DCL cathodes, NDCL-2 was our target because the thicknesses of the outer and inner catalyst layers were similar and sufficient Pt was concentrated in the inner layer.

For comparison, an SCL cathode and a conventional DCL cathode were also prepared using JM 40 wt% Pt/C on its own. The Nafion content of the SCL cathode was 33 wt%, equal to that of the inner layers in the novel DCL cathodes. The Pt distribution and Nafion content in the conventional DCL cathode were the same as in the NDCL-2. The Pt loading for all of these cathodes was 0.2 mg cm^{-2}.

All of the anodes were prepared using JM 40 wt% Pt/C. The Pt loading was ca. 0.1 mg cm^{-2}, which our previous experiments have shown to be sufficient [17].

The anode and cathode GDLs were prepared according to the following procedure. First, TGP-H-060 carbon paper (Toray, Japan) was hydrophobically treated by impregnating the paper with a Teflon dispersion and calcining at 330 °C for 30 min; then, a slurry of carbon black and Teflon, with a composition of 85 wt% carbon powder (Vulcan XC72, Cabot, USA) and 15 wt% PTFE (60 wt%, Aldrich, USA), was sprayed onto the pre-treated carbon paper, followed by calcining at 350 °C for 30 min in air.

2.2. Single cell test and electrochemical measurements

The MEAs were evaluated in a single testing cell, using a Fuel Cell Testing System (Arbin Instruments, USA). Pure hydrogen and air were fed to the anode and cathode, respectively, at flow rates of 300 cm^3 min^{-1} (hydrogen) and 1000 cm^3 min^{-1} (air) under ambient pressure. The cell temperature was 60 °C, and the humidifying temperature of hydrogen and air was 65 °C. The active area of the MEA was 5 cm^2.

Scanning electron microscopy (SEM) (JSM-6380LA, JEOL, Japan) using secondary electron imaging (SEI) was employed to observe cross-sections of the MEAs and gauge the thicknesses of the anode and cathode catalyst layers. The cross-sections were prepared by freezing the sample in liquid nitrogen, then cutting it with a blade.

Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were performed using a Zahner IM6e electrochemistry station (Zahner, Germany). The resistances and other kinetic characteristics of the MEAs were obtained by calculation and simulation with IM6e software. These measurements were carried out at a cell potential of 0.8 V with an amplitude of 5 mV, and in the frequency range of 0.1–1000 Hz. Voltammetric measurements, undertaken to study the electrochemical active surface area (EASA), were conducted using humidified N$_2$ at the cathode (working electrode) and humidified H$_2$ at the anode (counter electrode). Cyclic voltammograms were recorded from 1.2 V to 0.05 V at a scan rate of 0.05 V s^{-1}.

3. Results and discussion

To reveal the different thicknesses of the cathodes' layer structures, cross-sections of three MEAs with an SCL cathode, a conventional DCL cathode, and the NDCL-2 cathode, respectively, were observed using SEM. As shown in Fig. 1, the thickness of the SCL cathode (Fig. 1a) is 6.25 μm, similar to that of the conventional DCL cathode (6.14 μm, Fig. 1b), which is reasonable because the amount of catalyst in both cathodes is almost the same. However, the thickness of the NDCL-2 (Fig. 1c) is 11.8 μm because a catalyst with low Pt content (10 wt% Pt/C) was used in the outer catalyst layer. Although the interface between the two layers cannot be clearly observed in Fig. 1 due to the limitations of SEI, comparison of the first two images allows a rough determination that the thicknesses of the outer and inner layers are similar, and thus meet the design requirements.

Fig. 2 shows a performance comparison of the three MEAs, in which it is clear that the MEA with the novel DCL cathode (NDCL-2) yields much better performance than the MEA with the SCL cathode or the MEA with the conventional DCL cathode, especially at high current density. At 0.6 V, the current density of the MEA with NDCL-2 improves to 1.04 A cm^{-2}, 35.9% higher than that of the MEA with the SCL cathode (0.765 A cm^{-2}), and 24.8% higher than that of the MEA with the conventional DCL cathode (0.833 A cm^{-2}). Generally, this enhancement at high current density is primarily attributable to reduced mass transport limitations. An outer layer with low Pt catalyst content and low Nafion content is beneficial for oxygen diffusion and water removal.

To understand why the NDCL-2 cathode achieves such excellent performance, electrochemical impedance was used to investigate the three different MEAs. As presented in Fig. 3, the MEAs show no significant difference in ohmic resistance. The ohmic resistance of the MEA with the NDCL-2 cathode (0.162 Ω cm^2) is just slightly lower than that of the MEAs with the SCL cathode (0.182 Ω cm^2) and the conventional DCL cathode (0.187 Ω cm^2). However, the charge transfer resistance of the NDCL-2 MEA is much smaller than that of the other two, which suggests that the NDCL-2 cathode yields a more efficient electrochemical active layer than the others.

Fig. 4 shows cyclic voltammograms of the three different MEAs. The corresponding EASAs were calculated from the H$_2$ desorption peak of each voltammogram and the results are summarized in Fig. 4. The EASA of NDCL-2 is about 81.4 m^2 g^{-1}, which is smaller than that of the SCL cathode. Generally, the EASA depends on the amount of Nafion in the catalyst layer: increasing the Nafion content helps to increase the EASA [15,18], but inhibits access to
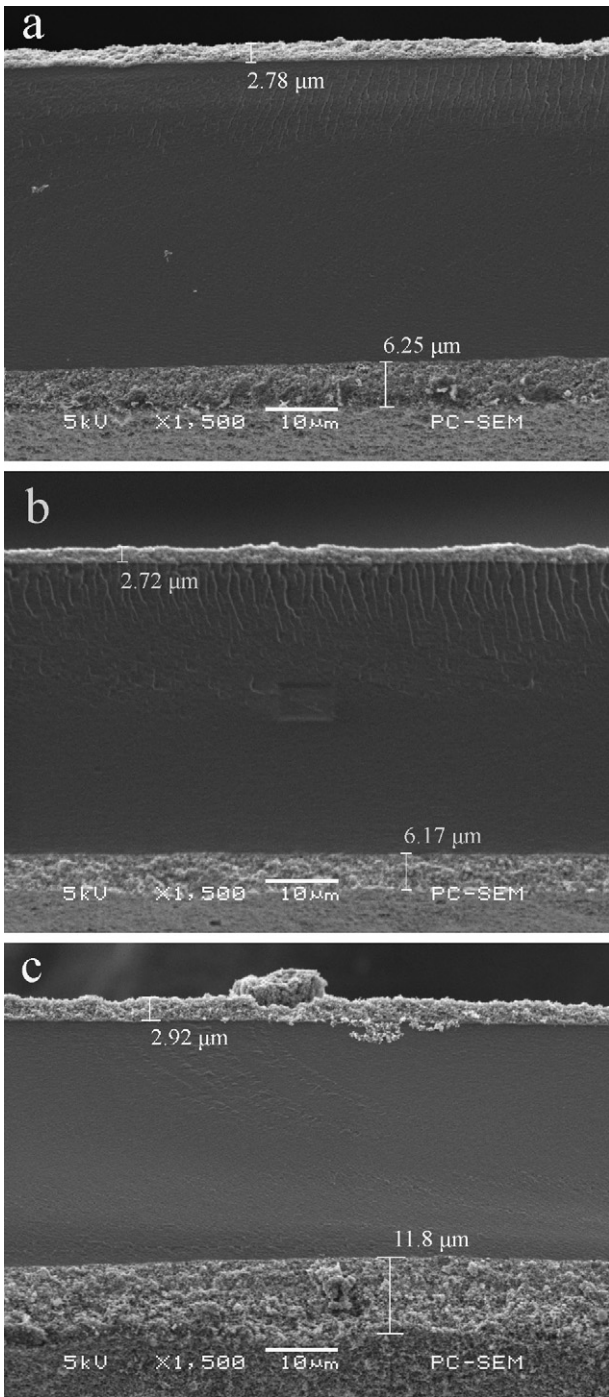
Fig. 1. SEM images of cross-sectional views of MEAs with SCL cathode (a), conventional DCL cathode (b), and NDCL-2 (c).

Fig. 2. Performance comparison of MEAs with different cathode structures at ambient pressure.
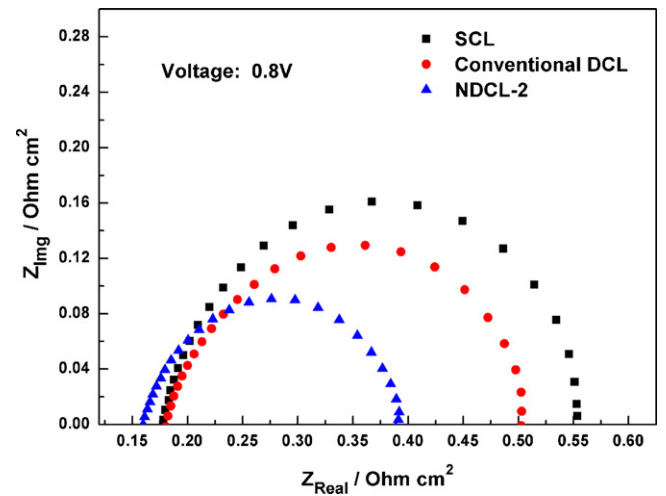
Fig. 3. *In situ* impedance curves of MEAs with different cathode structures.

Fig. 4. Cyclic voltammograms using MEAs with different cathode structures.

reactant molecules on the reactive sites. Therefore, based on these EASA results we think that the high performance of NDCL-2, which has a lower EASA, is mainly attributable to the ease with which oxygen diffuses through the catalyst layer.

To investigate the cell performance effects of Pt distribution and the corresponding thickness of the outer layer, the other four novel DCL cathodes were also tested and compared with the SCL cathode. As shown in Fig. 5, the performances of NDCL-1 and NDCL-3 are moderately better. The inner catalyst layer composition of NDCL-1 is similar to that of the SCL cathode, while its outer catalyst layer is very thin and therefore has no significant effect on performance. NDCL-3 has a comparatively thick outer layer, which possibly has
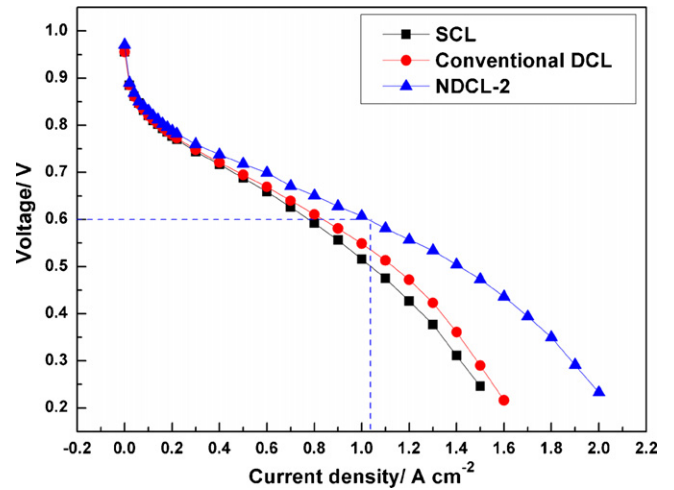
a negative effect on the charge transfer efficiency; hence, the performance does not significantly increase. In the cases of NDCL-4 and NDCL-5, the outer layers are about 3–4 times thicker than the inner layers (Table 1), and the Pt content of the inner layers is very
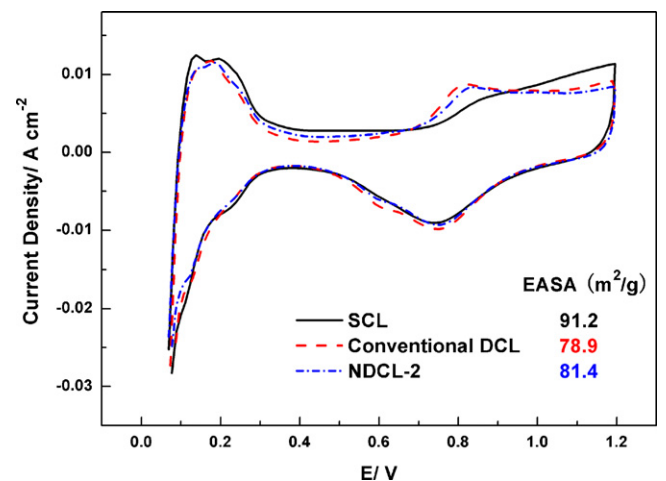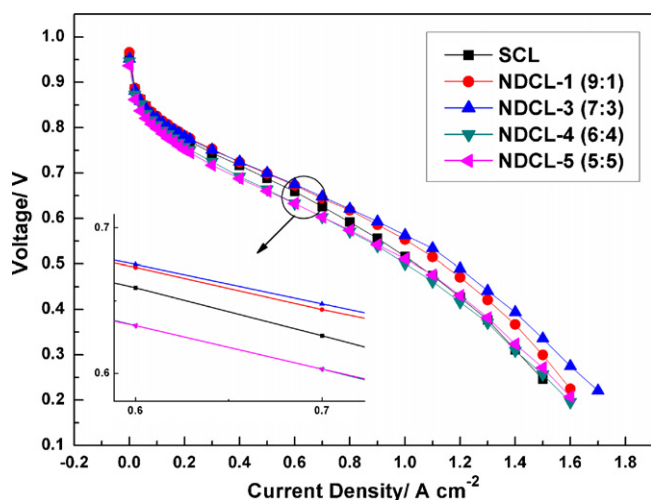
Fig. 5. Performance comparison of MEAs with SCL cathode and novel DCL cathodes. with various platinum distributions.

low, which limits performance improvement. These results agree with the fact that increasing the thickness of the catalyst layer with low Nafion content may reduce the mass transport problems to some extent, but the increase beyond a certain tipping point can reduce the effective charge transfer in the catalyst layer [3,15]. We therefore conclude that the significant enhancement in cell performance exhibited in the MEA containing NDCL-2 is attributable to this novel DCL cathode, which simultaneously possesses the advantages of better Pt distribution and appropriate thickness in the outer catalyst layer.

4. Conclusion

A novel DCL cathode was prepared using two catalysts with different levels of Pt. The new cathode effectively eliminates the conflict between Pt utilization and mass transfer, and achieves excellent performance. Pt distribution in the DCL and the corresponding thickness of the outer catalyst layer are found to have an important influence on the performance of the novel cathode. The best performance is obtained when the thicknesses of the inner and outer layers are equal. We conclude that better Pt utilization and mass transfer can be realized by designing an appropriate cathode structure, resulting in superior performance.

Acknowledgments

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