



Carbon nano-fiber interlayer that provides high catalyst utilization in direct methanol fuel cell

Masataka Okada, Yuri Konta, Nobuyoshi Nakagawa*

Department of Biological and Chemical Engineering, Gunma University, 1-5-1 Tenjin-cho, Kiryu, Gunma 376-8515, Japan

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ABSTRACT

The introduction of a carbon nano-fiber (CNF) interlayer to the interface between the carbon paper and the catalyst layer was investigated for providing a highly active catalyst layer with PtRu nano-particles on it for the direct methanol fuel cell (DMFC) anode. A precipitation method was used for applying the CNF layer and the catalyst layer. The effects of the loadings of the CNF and the catalyst on the DMFC power generation were evaluated. The CNF interlayer covered the large openings of the carbon paper resulting in a dense and smooth surface. The PtRu black catalyst prepared on the surface of the CNF layer provided a higher power density of DMFC than that obtained by using carbon black, suggesting that the dense and crackless surface of the CNF layer reduced the catalyst loss that leaks into the crack and increases the active reaction sites on the anode surface.

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1. Introduction

The direct methanol fuel cell (DMFC) is expected to be a promising power source with a high energy density and a compact volume that is suitable for portable and mobile use. However, the power output of the conventional DMFC is still unsatisfactory because of the methanol crossover [1] and the large electrode overvoltage. To reduce the overvoltage at the electrode, not only the catalyst activity itself, but also the morphology and the structure of the catalyst layer are important factors for the catalyst utilization [2] and the mass transport [3,4]. In the case of a polymer electrolyte fuel cell, there are some standard fabrication methods for the preparation of the catalyst layer on the polymer electrolyte. One of the general methods begins with the catalyst layer preparation by coating a catalyst ink on the supporting layer of a porous gas diffusion layer (GDL) like carbon paper [5] and carbon cloth. As a catalyst of the DMFC anode, unsupported PtRu exhibits a higher performance with a lower overvoltage in relation to the carbon-supported catalyst [6]. The noncatalyzed carbon particle layer, sometimes called a microporous layer (MPL), is often introduced between the catalyst layer and the gas diffusion layer, [7–11] in order to reduce the loss of the catalyst that leaks into the large pores of the GDL and increases the contact of the catalyst to the membrane by preparing a thin and dense backing surface for the catalyst layer. MPL is also used to con-

trol the water and methanol transport at the electrode in the PEFC [8–11] and DMFC [7]. For this purpose, the effect of the carbon particle size and the PTFE content have been reported [11]. However, many cracks appear on the MPL and part of the catalyst leaks into these cracks that reduces the catalyst utilization. A carbon nano-fiber (CNF) which has a smaller diameter and shorter length than that of the carbon fiber used for the carbon paper and carbon cloth would be appropriate for preparing a thin and dense surface on the backing diffusion layer.

In this study, we used a carbon nano-fiber with a several hundred nanometers diameter and several micron length as the material for the interlayer between the PtRu black catalyst layer and the carbon paper to increase the catalyst utilization in the DMFC. CNF is expected to provide an interlayer with a thin and dense surface on the carbon paper with large openings by covering them. The DMFC performance with the CNF interlayer was compared to that with a carbon black interlayer.

2. Experimental

2.1. MEA preparation

The carbon nano-fiber layer, a support layer of the catalyst nanoparticles, was prepared on carbon paper (CP) (TGP-H-060, Toray Co., Ltd.) by a precipitation method. The CNF used in this study was supplied from Gun Ei Chemical Industry Co., Ltd., and was produced from phenol resins by a polymer blend spinning method [12]. A fiber of the CNF having about a 200–500 nm diameter and several

* Corresponding author. Tel.: +81 277 30 1458; fax: +81 277 30 1457.
E-mail address: nakagawa@bce.gunma-u.ac.jp (N. Nakagawa).

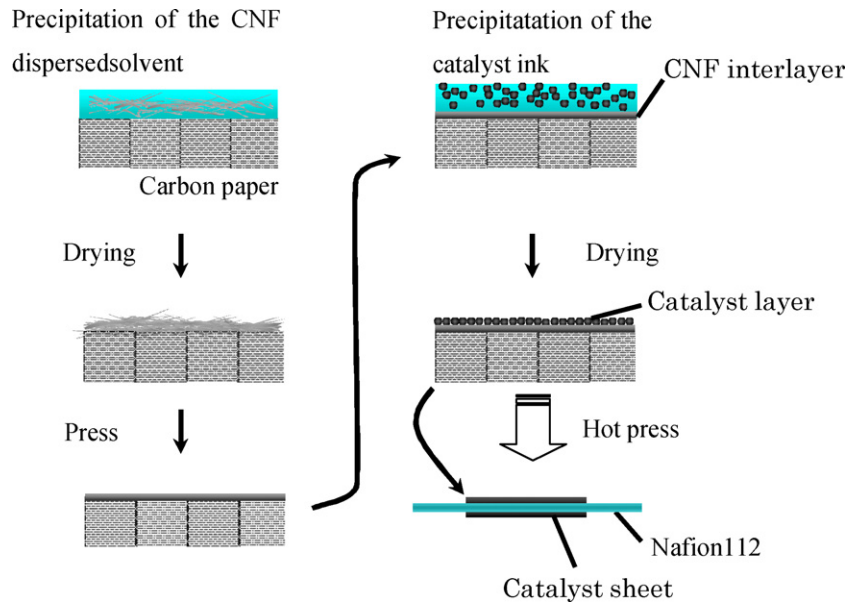


Fig. 1. Schematic procedure of the sedimentation method for the preparing of CNF interlayer on the carbon paper.

hundred micrometer length, was produced as small bundles with many nano-fibers. Hence, the bundles were milled with a mortar and then used. The ground CNF was dispersed in 2-propanol to form a 10 wt% dispersion by treating it in a bath with an ultrasonic generator for 30 min. A certain amount of the dispersed solvent was uniformly dropped on the surface of the carbon paper, then it was dried at room temperature and next at 370 K in an oven to form the CNF interlayer. Since the dried CNF layer was very bulky, then it was pressed at 33 kgf cm^{-2} , resulting in a dense CNF layer. Magnitude of the pressure to the surface smoothness of the CNF layer was not sensitive between 33 kgf cm^{-2} and 150 kgf cm^{-2} , and then 33 kgf cm^{-2} was used as a smallest one. The procedure for the CNF layer preparation followed by the application of the catalyst is illustrated in Fig. 1.

As a reference, a layer of carbon black, CB, that is similar to MPL, was also prepared by the screen printing method using an ink with homogenized carbon black (Ketjen black EC) and 5.0 wt% Nafion solution (Wako Pure Chemical Industries, Ltd.), 2.4 ml mg^{-1} -C, and 2-propanol, 20 ml mg^{-1} -C. In contrast to the CNF layer, the CB layer was not pressed excepting the hot press for MEA preparation mentioned later, because the prepared CB layer looked already dense.

The catalyst ink was prepared by the dispersion of PtRu black (HiSPEC 6000, Johnson Matthey Fuel Cells) in a mixture of 5.0 wt% Nafion solution (Wako Pure Chemical Industries, Ltd.) 2.4 ml mg^{-1} -cat, distilled water 1.2 ml mg^{-1} -cat and 2-propanol 1.2 ml mg^{-1} -cat in an ultrasonic generator for 15 min. The catalyst layer was applied by uniformly dropping the ink on the CNF layer in a manner similar to the preparation of the CNF layer. The sheet of catalyst/CNF/CP was then used the anode.

Nafion 112 (Dupont) was used as the polymer electrolyte in this experiment. The polymer membrane was sandwiched between the anode and Pt(1 mg cm^{-2})/C electrode (Electro Chem, Inc.) after spraying the 5.0 wt% Nafion solution on the surface of their catalyst layers, then it was hot pressed at 408 K, and 50 kgf cm^{-2} for 3 min to form the MEA.

The thickness of the CNF layer and the catalyst layer was measured with a micrometer. For observation of the surface morphology, a SEM observation of the surfaces of the CNF layer and the catalyst layer with JSM-5310 (JOEL) at 20 kV was conducted.

2.2. Electrochemical measurement

A single DMFC cell was constructed by fixing the MEA in a cell holder with flow channels at both the anode and cathode (FC-005-01SP, Electro Chem Co., Ltd.). 2 M methanol was fed to the anode at 4.8 ml min^{-1} and oxygen at atmospheric pressure was fed from a cylinder to the cathode at 1.0 L min^{-1} . The current–voltage curve and cell impedance were then measured at 353 K using an electrochemical measurement system (HZ-3000, Hokuto Co., Ltd.). The impedance measurement was conducted by applying a 10 mV sinusoidal voltage at a frequency ranging from 20 kHz to 1 mHz, and used to obtain the ohmic resistance of the cell from the Cole–Cole plot that cut the real axis on the high frequency side.

3. Results and discussion

3.1. Morphology of the CNF layer

Fig. 2 shows SEM photographs of the surface of the CNF layer prepared on the carbon paper with different amounts. It includes the surface of the carbon paper, Fig. 2(a), as a reference. It could be seen that the nano-fibers covered the openings of the surface of the carbon paper and closed the openings thus reducing the size down from several hundreds to several tens of micrometers or smaller. When the CNF amount was 0.9 mg cm^{-2} , small holes with several tens of micrometers were still observed on the surface. This is because the bundles of CNF remained in the layer. The grinding of CNF was not sufficient in this case. However, when the amount was increased to 2.1 mg cm^{-2} or more, the entire surface was covered with the nano-fibers and the large holes disappeared from the surface. Once the entire surface was covered by it, the surface morphology was similar to each other even if the amount was further increased. It was confirmed that the CNF was quite effective to cover and close the large openings of the surface of the carbon paper and provide a thin and dense layer on the carbon paper. The density of the CNF interlayer was calculated to be 0.40 g cm^{-3} based on the increase in the thickness after the addition of a certain amount of the interlayer.

Fig. 3 shows the SEM photographs of the catalyst layer with different catalyst amounts prepared on the 2.6 mg cm^{-2} CNF layer. It

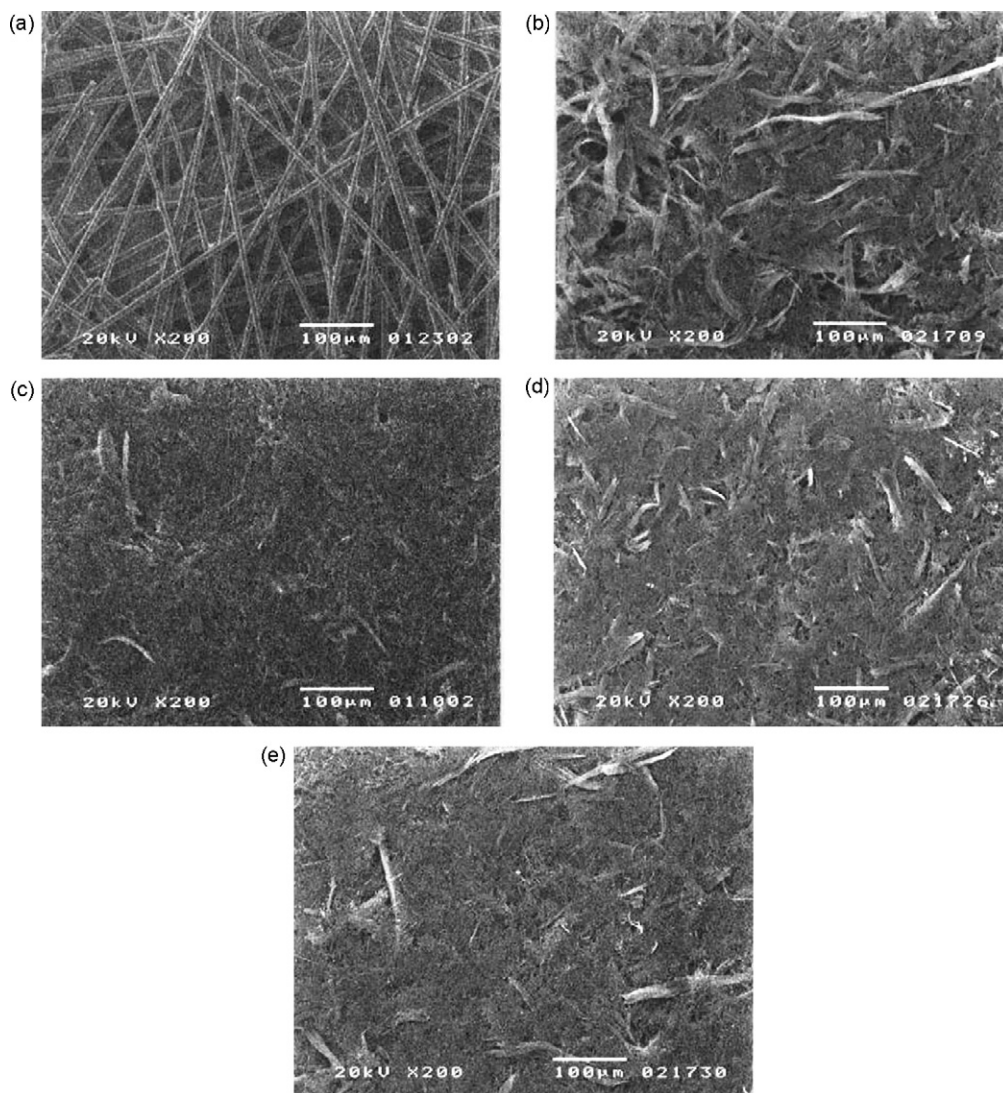


Fig. 2. SEM photographs taken of the surface of the carbon paper, (a) and that of the CNF interlayer with different amounts: (b) 0.9 mg-CNF cm⁻², (c) 2.1 mg-CNF cm⁻², (d) 2.6 mg-CNF cm⁻², and (e) 3.0 mg-CNF cm⁻².

was found that the PtRu nano-particles formed agglomerates with a few micrometer diameter as shown in the figure as white dots. When the catalyst loadings were 1.0 mg cm⁻² and 1.8 mg cm⁻², the amount of the catalyst was not sufficient to cover the entire surface, and the uncovered CNF layer could be seen in this figure. The agglomerates of the catalyst tended to gather at the hollow part like besides the bundles of the CNF. When the loading was increased to 3.7 mg cm⁻², almost the entire surface was covered with the catalyst agglomerates. The catalyst agglomerates accumulated and formed a deep layer on the surface, when the loading was further increased to 6.0 mg cm⁻².

3.2. DMFC performance

Fig. 4 shows the current–voltage curves of the DMFC with different CNF loadings at a constant catalyst loading. It was found that the CNF loading affected the current density depending on the range of the cell voltage, i.e., the high voltage range and low voltage range. Current densities at the high cell voltages, over 0.35 V, were similar to each other irrespective of the CNF loading as shown in Fig. 5. On the other hand, the current densities at the low cell voltages, below 0.35 V, were significantly affected by the CNF loading, and showed

a maximum at a 2.6 mg cm⁻² CNF loading as shown in the figure. The current density at the high cell voltages, i.e., at low current densities, is dominated by the electrode reaction, and that at the low cell voltages, i.e., at high current densities, is usually controlled by the mass transport resistance. It was then postulated that the CNF loading had an effect on the mass transport, but little effect on the activity of the electrode reaction. This was quite understandable from the surface morphology of the CNF layer that was similar to each other, i.e., thin and dense, with the different amounts as shown in Fig. 2. The surface morphology is sensitive to the electrode activity because the reaction site is formed at the interface between the membrane and the catalyst layer. A similar morphology would provide a similar electrode activity. On the other hand, the increase in the loading of the CNF caused an increase in the thickness of the CNF layer resulting in the increased mass transport resistance. When the CNF loading was below 2.1 mg cm⁻², the current density increased with the increasing CNF loading at the low voltage region. This may be due to reduction of the methanol crossover controlled by the dense CNF layer. The decrease in the current density at 3.0 mg cm⁻² would be due to methanol depletion by late limiting of the methanol supply to the anode. The optimum loading of the CNF was around 2.6 mg cm⁻² in this experiment.

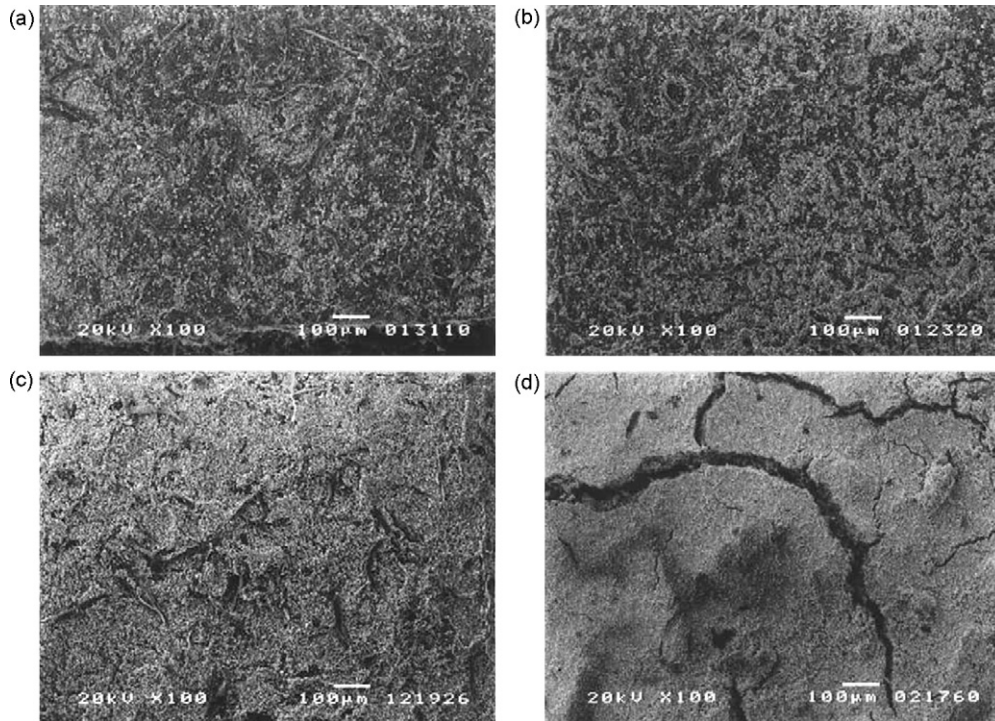


Fig. 3. SEM photographs taken for the surface of the PtRu black catalyst layer with different amounts, (a) $1.0 \text{ mg-PtRu cm}^{-2}$, (b) $1.8 \text{ mg-PtRu cm}^{-2}$, (c) $3.7 \text{ mg-PtRu cm}^{-2}$, and (d) $6.0 \text{ mg-PtRu cm}^{-2}$, on the CNF (2.6 mg cm^{-2}) interlayer.

The effect of the catalyst loading on the current–voltage curve was measured at the constant CNF loading, of 2.6 mg cm^{-2} , as shown in Fig. 6. In contrast to the effect of the CNF loading shown in Fig. 4, the current density was affected by the loading both at the high cell voltages around 0.45 V and at the low cell voltages around 0.15 V as shown in Fig. 7. At the high cell voltage, the current density increased with the increasing catalyst loading up to 3.7 mg cm^{-2} and it was almost similar to that at 6.0 mg cm^{-2} . This suggested that the active reaction sites provided at the interface between the membrane and the catalyst layer increased with the increasing catalyst loading until the entire surface was covered with

the catalyst. The SEM photos shown in Fig. 3 supported the result that the whole surface was covered by the catalyst at 3.7 mg cm^{-2} , and it was saturated over this loading. At the low cell voltage, the current density decreased when the catalyst loading increased from 3.7 mg cm^{-2} to 6.0 mg cm^{-2} . This decrease would be caused by the increase in the mass transport resistance through the catalyst layer because the catalyst layer became thick as shown in Fig. 3. Based on the above investigations, the catalyst with a 3.7 mg cm^{-2} loading was the optimum in this experiment. At the optimum loading, the maximum value of the power density, the product of the cell voltage and the current density, was obtained as 133 mW cm^{-2} at 0.25 V . This is relatively high comparing with that of other DMFCs with similar catalyst loadings [13] suggesting that the catalyst layer with the CNF interlayer showed a high anode activity.

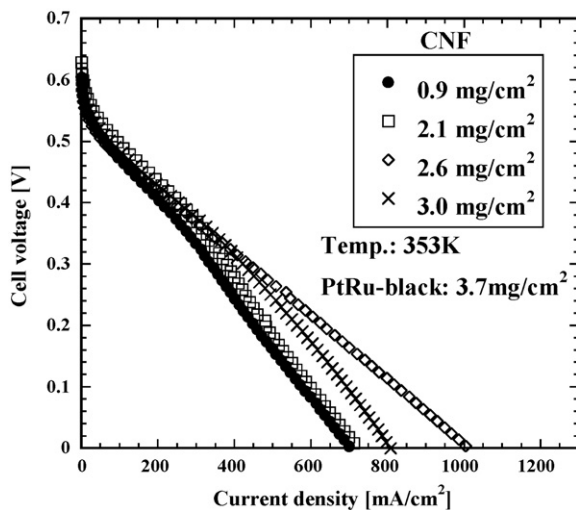


Fig. 4. Current–voltage curves for the DMFC with different amounts of CNF in the interlayer, but with the same catalyst amount, $3.7 \text{ mg-PtRu cm}^{-2}$ for the anode. Their cathodes were similar to each other and the performance was obtained with 2 M methanol (4.8 ml min^{-1}) and oxygen (1 L min^{-1}) at 353 K .

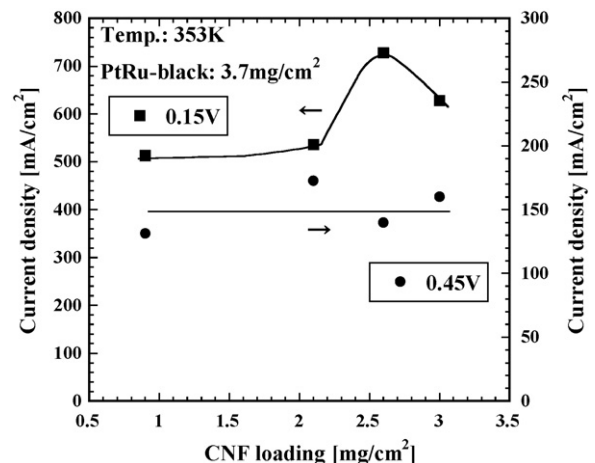


Fig. 5. Effect of the amount of CNF for anode interlayer on the current density of DMFC at high, 0.45 V , and low, 0.15 V , cell voltages.

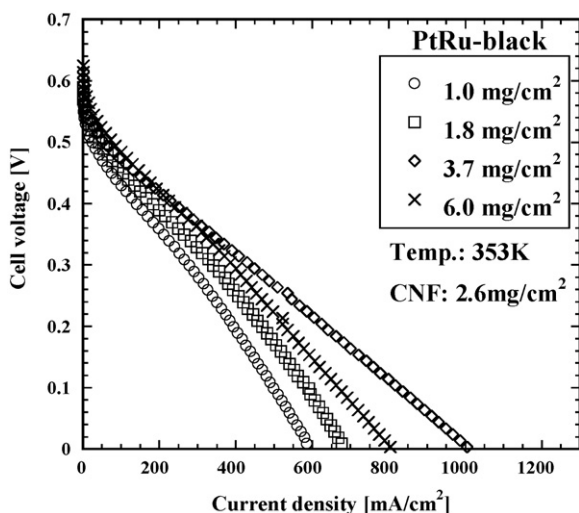


Fig. 6. Current–voltage curves for the DMFC with different amounts of PtRu black catalyst on the CNF (2.6 mg cm^{-2}) interlayer. Their cathodes were similar to each other and the performance was obtained with 2 M methanol (4.8 ml min^{-1}) and oxygen (1 L min^{-1}) at 353 K.

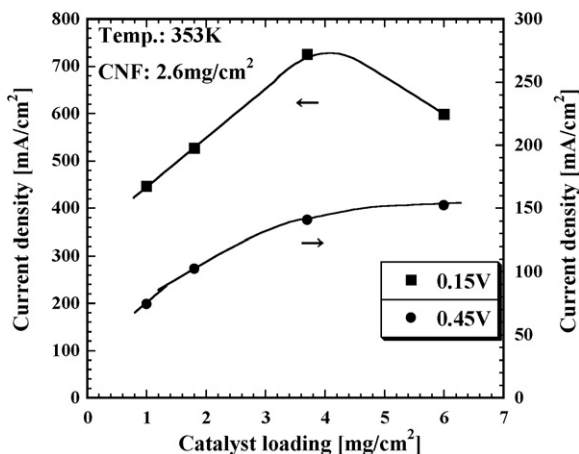


Fig. 7. Effect of the amount of PtRu black catalyst for anode on the current density of the DMFC at high, 0.45 V, and low, 0.15 V, cell voltages.

3.3. Comparison with CB backing layer

Fig. 8 shows a comparison in the current–voltage curve of the DMFCs with the different interlayers, i.e., CNF and carbon black (CB). The electrode with the CNF interlayer showed higher current den-

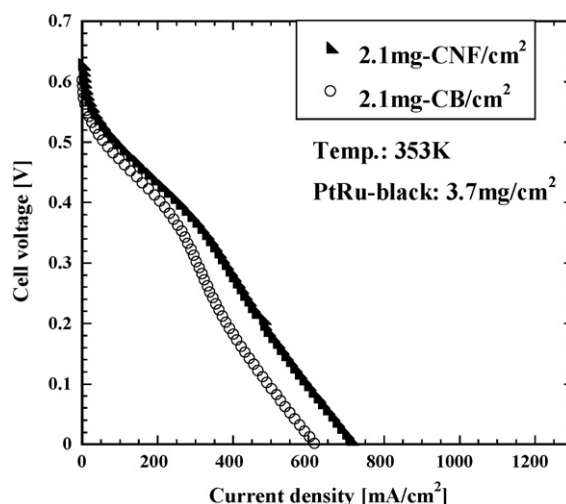


Fig. 8. Current–voltage curves for the DMFC with PtRu black (3.7 mg cm^{-2}) catalyst prepared on the different interlayers: CNF (2.1 mg cm^{-2}) interlayer and CB (2.1 mg cm^{-2}) interlayer. Their cathodes were similar to each other and the performance was obtained with 2 M methanol (4.8 ml min^{-1}) and oxygen (1 L min^{-1}) at 353 K.

sities at all the measured voltages cell compared to that with the CB interlayer. When we observed the surface of the catalyst layer on the CB interlayer, it was not a smooth surface and had many cracks as shown in Fig. 9. A part of the catalyst prepared on the CB interlayer would leak through the crack and be lost. Actually, some catalysts that got into the cracks were observed in the SEM observation. It was shown that the CNF layer provided a smooth and crackless surface that is necessary for the preparation of a thin and uniform catalyst layer for the nano-particulate catalyst on the bulky carbon paper. The calculated apparent density of the CB interlayer based on the increase in the thickness and the loading of the CB was 0.19 g cm^{-3} that is almost half that of the CNF interlayer. This also confirmed that the CNF interlayer was denser and crackless compared to the CB interlayer.

3.4. Catalyst utilization at the anode

The anode activity, defined that the maximum power densities calculated from the I–V curve for the DMFC at a certain condition divided by the mass of PtRu loading for anode, were plotted versus the loading of the PtRu black for the anode in Fig. 10. Not only for the DMFCs with the CNF interlayer but also for that with the CB interlayer were plotted in the figure for comparison. Since the DMFCs used in the figure had the same cathode and the same membrane but the different anode, i.e., the interlayer, CNF or CB, and the load-

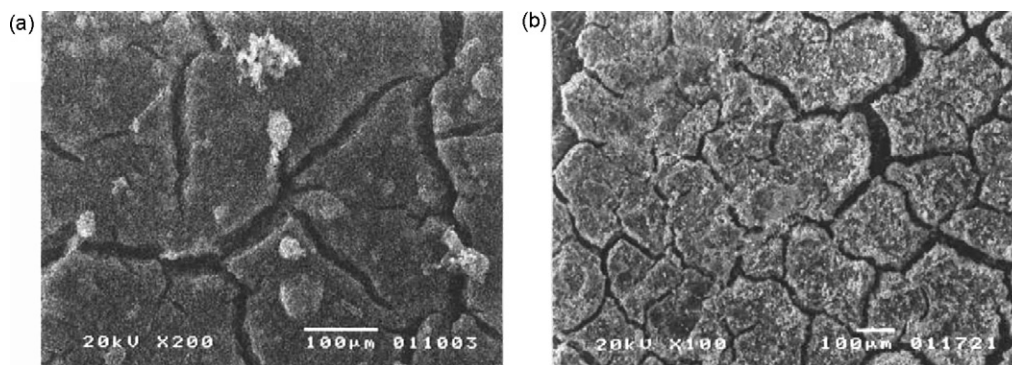


Fig. 9. SEM photographs taken of the surface of the CB (2.1 mg cm^{-2}) interlayer (a) and that of the PtRu black (3.7 mg cm^{-2}) on it (b).

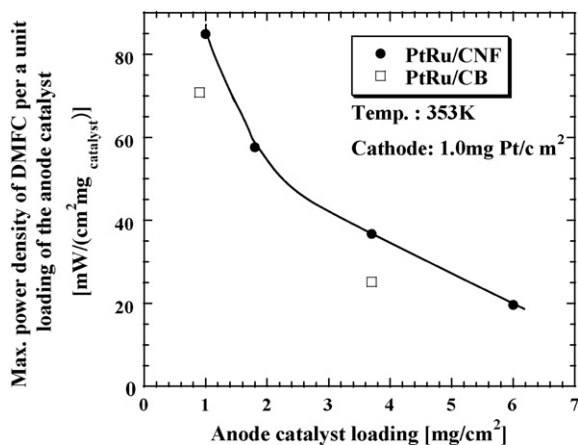


Fig. 10. Effect of PtRu black loading, for anode, prepared on the CNF interlayer and the CB interlayer on the maximum power density calculated as the anode activity.

ing of the catalyst on it, the difference in the power density was due to the anode catalyst layer including the interlayer. Then the anode activity includes the effect of the catalyst utilization and the mass transport resistance through the layers. The anode activity decreased with the increase in the PtRu black loading suggesting that the catalyst utilization decreased with the increasing catalyst loading. This means that the inside of the agglomerates of the PtRu black catalyst were less active compared to its outside, and the increase in the size of the agglomerates of the nano-particle catalyst and the multi-layer structure of the agglomerates reduced the anode activity. As shown in Fig. 3, the catalyst particles tend to gather at the hollow points formed between the thick CNF bundles especially when the catalyst loading was low. The detachment of the CNF from the bundle in this experiment was not enough. To provide a flatter and smoother surface and reduce the size of the catalyst agglomeration, such hollow points should be reduced from the surface by completely detaching the CNF from the bundle. We need to uniformly disperse the fine particle catalyst on the surface of the CNF interlayer to further increase the utilization and reduce the catalyst amount. In this figure, we could confirm that the anode activity for the CNF interlayer was higher than that of the CB interlayer at the different anode catalyst loadings, suggesting that the catalyst utilization with the CNF interlayer was superior to that with the CB interlayer.

4. Conclusions

A thin and dense CNF interlayer was introduced between the carbon paper and the catalyst layer of the PtRu black by the precipitation method, and its effect on the anode performance of the DMFC was investigated. The CNF interlayer provided a crackless and smooth surface on the carbon paper, and it was quite appropriate for the catalyst layer of the PtRu black with a high catalyst utilization to reduce catalyst loss from a leak into the crack or openings of the carbon paper. For the catalyst layer of PtRu black on the CNF interlayer, there was an optimum loading for each layer. The CNF loading affected the current densities at low cell voltages suggesting that the mass transport was affected by it. The optimum loading of the catalyst was that required for covering the entire CNF surface. The optimized catalyst layer had a power density as high as 130 mW cm^{-2} at 353 K for a DMFC. The anode activity defined by the DMFC power density divided by the amount of used PtRu was higher than that obtained by the CB interlayer.

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