Influence of Ionomer Content on Both Cell Performance and Load Cycle Durability for Polymer Electrolyte Fuel Cells Using Pt/Nb-SnO₂ Cathode Catalyst Layers

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The steady-state current-voltage performance and load cycle durability of polymer electrolyte fuel cells using Pt catalysts supported on Nb-SnO₂ cathode catalyst layers (CLs), without any carbon additive, were evaluated with various ionomer contents. The apparent mass activity at 0.80 V (MAapp @0.80 V) of the cell using Pt/Nb-SnO₂ CL improved with decreasing volume ratio of the Nafion ionomer to the support (I/S). At I/S = 0.12, surprisingly, the MAapp @0.80 V of the cell using Pt/Nb-SnO₂ CL approached 2 times higher than that using a commercial Pt catalyst supported on GCB (Pt/GCB) CL with the optimized I/S ratio. The current density at 0.60 V of the cell using Pt/Nb-SnO₂ (I/S = 0.12) CL also reached the same value of the cell using Pt/GCB CL. The electrochemically active surface area and MAapp @0.80 V of Pt/Nb-SnO₂ CLs during the load cycle durability test maintained higher values than those of Pt/GCB throughout the test, indicating that the Pt/Nb-SnO₂ CL had higher durability than the Pt/GCB CL. Evaluation by means of low acceleration voltage transmission electron microscopy proved that the Nafion ionomer covered the hydrophilic surface of the Pt/Nb-SnO₂ uniformly, whereas the ionomer did not do so on the hydrophobic surface of the Pt/GCB. The thin, uniform coverage of the Nafion ionomer, which was thus easily obtained on the Pt/Nb-SnO₂ surface, was able to lower the overpotential originating from the oxygen diffusion resistance in the Nafion ionomer, thus improving the cell performance while maintaining the high load cycle durability.

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volume ratios of Nafion ionomer (dry basis) to the support (I/S) were adjusted in steps from 0.12 to 0.67. A commercial Pt/GCB catalyst (TEC10EA30E, Pt loading amount 29 wt%, Tanaka Kikinzoku Kogyo K.K., Japan) was used as a reference for the cathode measurements. Commercial Pt/CB (TEC10E50E, Pt loading amount 46 wt%, Tanaka Kikinzoku Kogyo K.K., Japan) was utilized for all anodes of the test cells in a manner similar to that described above. The I/S values of both the reference cathode and the anode were adjusted to 0.67, previously found to be the optimal ratio. These catalyst inks were directly sprayed onto both sides of the Nafion membrane (NRE 212, 50 μm thickness, Du Pont, U.S.A.) as the anode and cathode by use of the spray-swirl-spray technique (PSS, Nordson Co., U.S.A) to prepare the catalyst-coated membranes (CCM), which were then dried at 60 °C in an electric oven. The CCMs were annealed by hot-pressing at 140 °C and 10 kgf cm−2 for 3 min, and then they were assembled with two gas diffusion layers (GDLs, 25BC, SGL Carbon Group Co., Ltd., Germany) and a single serpentine flow-channel cell (Japan Automobile Research Institute standard cell) to 0.21 mC cm−2 for all of the cathodes. The Pt loading amount of the anodes with Pt/CB was controlled at 0.55 ± 0.05 mg cm−2. The high Pt loading amount at the anode made the polarization negligibly small under all of the experimental conditions, and therefore the anodes were able to be used as a reversible hydrogen electrode (RHE) for the evaluation in single cell measurements. Pt/GCB and Pt/Nb-SnO2 CLs formed on polypropylene film were observed by use of low acceleration voltage transmission electron microscopy (low acceleration voltage TEM, HT 7700S, acceleration voltage 80 kV, Hitachi High-Technologies, Co., Japan) with a high resolution lens (EXALENS, Hitachi High-Technologies, Co., Japan). The cumulative pore volume of Pt/Nb-SnO2 CLs (I/S = 0.24 and 0.67) was estimated by the Kr gas adsorption method (BELSORP-max II, MicrotracBEL Co., Japan).

Fuel cell operation.—The cell voltage as a function of current density was measured with hydrogen and oxygen/air at 80 °C under ambient pressure (1 atm). Hydrogen gas was supplied to the anode and oxygen or air to the cathode. The flow rates of all gases were controlled by mass flow controllers. The utilization of the reactant gases were 70% for H2 and 40% for air. These gases were humidified at 80% relative humidity (RH) by purging through a hot water reservoir, controlled by a measurement system (FCE-1, Panasonic Production Technology Co., Ltd., Japan). The current-voltage (I-V) curves were galvanostatically measured under steady-state operation, after a stabilization time of 5 min, for each current by use of an electronic load (PLZ-664WA, Kikusui Electronics Co., Japan) controlled by the FCE-1. All of the potentials are referred to the hydrogen anode, which was assumed to approximate the RHE potential. The digital ac milliohmmeter (Model 356E, constant frequency 10 kHz, Tsuruga Electric, Co., Japan) was used to obtain the cell resistances of MEA using Pt/Nb-SnO2 CL. In the case of the MEA using Pt/GCB CL, a digital ac milliohmmeter (Model 3566, constant frequency 1 kHz, Tsuruga Electric, Co., Japan) was used.77

Cyclic voltammetry (CV) measurements were performed at 80 °C, 80% RH by use of a potentiostat (PGSTAT128N, Metrohm Autolab B.V., Netherlands) in order to evaluate the electrochemically active surface area (ECA) of the Pt catalyst in the cathode CLs. The cathode compartment was purged with N2 (100 mL min−1, 80% RH), while H2 gas (100 mL min−1, 80% RH) was supplied to the anode. Prior to the potential sweep, the potential was maintained at 0.075 V for 3 s to ensure that the Pt was in a reproducibly reduced state. Then, the potential was swept from 0.075 V to 1.000 V at 20 mV s−1 and reversed back to 0.075 V. The N2 flow was stopped during the entire CV measurement to avoid perturbing the H2 partial pressure.86 The values of ECA were determined from the hydrogen adsorption charge referred to 0.21 mC cm−2, the conventional value for a monolayer of adsorbed hydrogen on clean polycrystalline platinum.87

The Pt utilization (Up) value of the Pt catalyst is defined as follows:

\[
Up, \% = \frac{ECA}{S_P} \times 100
\]

The Pt loading amount on the cathode side was 0.05 g cm−2 for Pt utilization (Up) calculation. The Pt loading amount at the anode made the polarization negligibly small under all of the experimental conditions, and therefore the anodes were able to be used as a reversible hydrogen electrode (RHE) for the evaluation in single cell measurements. Pt/GCB and Pt/Nb-SnO2 CLs formed on polypropylene film were observed by use of low acceleration voltage transmission electron microscopy (low acceleration voltage TEM, HT 7700S, acceleration voltage 80 kV, Hitachi High-Technologies, Co., Japan) with a high resolution lens (EXALENS, Hitachi High-Technologies, Co., Japan). The cumulative pore volume of Pt/Nb-SnO2 CLs (I/S = 0.24 and 0.67) was estimated by the Kr gas adsorption method (BELSORP-max II, MicrotracBEL Co., Japan).

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surface of the Pt/Nb-SnO₂ and Pt/GCB agglomerates and were stable, without any discernable changes occurring during the TEM observation. These thin layers were determined to consist of Nafion ionomer and were found to cover the Pt/Nb-SnO₂ surface uniformly (Figs. 2a, 2b). In the case of Pt/GCB, the ionomer coverage was partial and non-uniform (Fig. 2c). In the case of Nb-SnO₂, the surface can include oxygen vacancies and dangling bonds, which would bind to hydroxyl groups originating from water, due to its intrinsic hydrophilicity. The hydrophilic surface of the Nb-SnO₂ support has adsorbed hydroxide groups originating from water, due to its intrinsic hydrophilicity. The oxygen vacancies and dangling bonds, which would bind to hydroxyl groups with negative charge, which would interact with the positive charge of the sulfonic acid groups in the ionomer. The electrostatic interaction between the two groups would assist in constructing the uniform coverage of the ionomer on Pt/Nb-SnO₂. The proton-conducting pathways are easily constructed on the Pt/Nb-SnO₂ and enhance the Pt utilization compared with that on Pt/GCB. The modification of the hydrophobic surface of a carbon nanotube support to a hydrophilic state was shown to enhance the Pt catalytic activity by improving the coverage of the Nafion binder.

The uniform ionomer coverage also has a beneficial effect in maintaining wide pores in the CLs. The cumulative pore volume in the primary pore region of Pt/Nb-SnO₂ CLs with I/S = 0.24, estimated by the Kr gas adsorption method (Fig. 2d), was higher than that with I/S = 0.67. The cumulative pore volume per gram of Pt/GCB with Nafion ionomer (I/S = 0.67) was found in previous work to be of the same order as that of Pt/Nb-SnO₂ (I/S = 0.67). We conclude that the gas diffusion pathways were better developed in the CLs with I/S = 0.24 in comparison with I/S = 0.67.

The low acceleration voltage TEM images of the Pt/Nb-SnO₂ also indicate that, in the case of the image with I/S = 0.24, most of the tops of the Pt particles were covered with extremely thin ionomer layers on top. In contrast, in the case of I/S = 0.67, all of the Pt particles were buried in the ionomer. In the case of uniform ionomer coverage on the support, I/S is estimated from the Eq. 3:

\[ I = \frac{S_d d_i}{\frac{4}{3} \pi r_s^3} = \frac{3d_i}{r_s} \]

where \( S \) is the surface area of the Nb-SnO₂ support (4\( \pi r_s^2 \), radius of Nb-SnO₂ support) and \( d_i \) is the estimated thickness of the ionomer on the Nb-SnO₂ support. From Eq. 3, the estimated ionomer thickness (\( d_i \)) is shown below:

\[ d_i = \frac{r_s}{3} \left( \frac{I}{S} \right) \]

Fig. 3 shows the relationship between \( d_i \) and I/S as a function of the radius of the Nb-SnO₂ support particles. When I/S is 0.24 and the size of the Nb-SnO₂ particles is 30 nm, \( d_i \) is ca. 1.2 nm. All of the Pt particles were hemispheres, as shown in Figs. 2a and 2b. The distance from the top of the Pt nanoparticles to the interface between Pt and Nb-SnO₂ approached half the Pt particle size (ca. 1.5 nm), so that the tops of the Pt catalyst particles would be exposed to the gas phase, without a covering of ionomer. The low acceleration voltage TEM images of the Pt/Nb-SnO₂ of I/S = 0.24 (Fig. 2a) substantiated this absence of ionomer covering on the tops of the Pt nanoparticles and the construction of three-phase boundaries of gas phase/Pt/ ionomer, which would lead to the reduction of the overpotential due to gas diffusion in the ionomer.

Single cell performance of MEAs using Pt/Nb-SnO₂ with varying ionomer content.—The ohmic loss (IR) included I-V curves and cell resistances of the cells using Pt/Nb-SnO₂ cathode CLs (Pt amount; 0.05 mg cm⁻²) at 80°C with ambient pressure air humidified at 80% RH and hydrogen are shown in Fig. 4a. In previous literature, Pt loadings have been in the 0.2–0.5 mg/cm² range, which is the present standard. However, the Nb-SnO₂ support discussed here is compatible with much lower Pt loadings (1/10 reduction of present Pt loadings).
The apparent mass activity (MA_app, at 0.80 V) of the cell using each of the Pt/Nb-SnO2 cathode CLs at BOT (Fig. 4b) increased with decreasing I/S and reached a maximum value of 305 A gPt⁻¹ at I/S = 0.12, which was 2 times higher than that using the Pt/GCB cathode CL with the optimized I/S ratio 0.67. The current density at 0.60 V of the cells using Pt/Nb-SnO2 cathode CLs at BOT also increased with decreasing I/S and reached the value of the cell using a Pt/GCB CL with the optimized I/S ratio 0.67. The Tafel plots for each cell using Pt/Nb-SnO2 CLs at BOT are shown in the inset of Fig. 4a. The plot of the cell using Pt/GCB CL at BOT (open circles) is also shown as a reference. Each of the Tafel plots exhibited a linear portion at potentials greater than 0.70 V; the Tafel slopes at BOT (inset of Fig. 4b) for the Pt/Nb-SnO2 CLs with greater than I/S = 0.24 maintained values of the same order as that of Pt/GCB CL (89.8 mV decade⁻¹). In the case of I/S = 0.12, the Tafel slope for the Pt/Nb-SnO2 CL at BOT decreased to 80 mV decade⁻¹. From the observation of low acceleration voltage TEM images and the estimation of ionomer thickness (Figs. 2a–2b and Fig. 3), the tops of the Pt nanoparticles would be left uncovered, and the three-phase boundary of gas phase/Pt/ionomer would be better constructed at I/S = 0.12. Part of the cathode overpotential is known to originate from the oxygen diffusion in the ionomer. An optimized three-phase boundary would reduce the gas diffusion overpotential in the ionomer and thus enhance the cell performance.

Single cell performance of MEA using Pt/Nb-SnO2 with varying ionomer content at the end of testing. The IR-included I-V curves and cell resistances of the cells using Pt/Nb-SnO2 cathode CLs at the end of testing (EOT: 50000 cycles) are shown in Fig. 5a. The I-V curve of the cell using a Pt/GCB cathode CL with the optimized I/S ratio 0.67 at EOT is also shown as a reference in the same figure. The current density at each voltage improved with decreasing I/S and exceeded that of commercial Pt/GCB at I/S = 0.24 and or less. The significant increase in cell resistance for I/S values higher than 0.24 after the load cycle test is an important issue for the Pt/Nb-SnO2 CLs. The Tafel plots at EOT showed that, for I/S greater than 0.36, the slope increased up to 200 mV decade⁻¹, indicating that either the oxygen diffusion or the proton conductance in the Nafion binder might have degraded during the load cycle test. Pt catalyst nanoparticles can easily dissolve at high Nafion binder content, even though a Pt band did not appear in the membrane. We need further investigation to elucidate the reasons for the resistivity increase, but we consider that soluble Pt cations might interrupt the proton conductivity in the Nafion ionomer and thus increase the cell resistivity. The MA_app values at 0.80 V of the cells using each of the Pt/Nb-SnO2 cathode CLs at EOT (Fig. 5b) were also 2 times higher than that using Pt/GCB with I/S = 0.67. The current density at 0.60 V of the cell using Pt/Nb-SnO2 at EOT (Fig. 5b) also increased with decreasing I/S and approached the value obtained using Pt/GCB with I/S = 0.67.

The CV curves of the Pt/Nb-SnO2 cathode CLs obtained at BOT are presented in Fig. 6. Peaks of both the adsorption/desorption of hydrogen and the oxidation of the platinum surface are clearly observed in these CVs. The initial values of ECA and U_Pt of Pt/Nb-SnO2 (I/S = 0.12, 0.24, 0.36, 0.45, 0.67) were more than 50 m² g⁻¹ and 50%, respectively, significantly greater than those of Pt/GCB (22 m² g⁻¹, 27%). All Pt catalyst nanoparticles were located on the outer surface of the Nb-SnO2 support, due to the lack of nanopores, and the ionomer covered uniformly the surface of the Pt/Nb-SnO2 cathode CLs at EOT (Fig. 5b). However, in the case of Pt/GCB, 30% of the Pt nanoparticles on GCB were located in the interiors of nanopores of the GCB, which would lead to difficult in making contact to the ionomer. Also, the Nafion ionomer itself did not cover the Pt/GCB surface uniformly, as shown in the low acceleration voltage TEM image (Fig. 2c). The higher ECA and U_Pt values obtained for Pt/Nb-SnO2 in comparison with those of Pt/GCB originates from the uniform coverage of the ionomer and the high dispersion of Pt on the outer surface of the Nb-SnO2 support particles. The CV curves of the Pt/Nb-SnO2 cathode CLs at EOT are also shown in Fig. 6. The electric double layer current at EOT was maintained at nearly the same values as that of BOT, indicating that the current density of the single cell using Pt/Nb-SnO2 CLs was less than 0.2 Ω cm⁻², which was lower than that using commercial Pt/GCB CLs.

The microstructure of both Pt/Nb-SnO2 and Pt/GCB CLs. The data were obtained at the development over the next decade in Japan. Thus, we have unified the Pt i.e., 0.05 mg/cm²), which are the target for the future fuel cell stack development over the next decade in Japan. Thus, we have unified the Pt dispersion of Pt on the outer surface of the Nb-SnO2 support.

Figure 4. Cell voltage (IR included) and cell resistivity vs. current density in the cells using Pt/Nb-SnO2 and Pt/GCB as cathode catalyst at 80 °C, 80%RH, supplied air/H₂ at BOT (a). The inset shows the Tafel plots of the cells using Pt/Nb-SnO2 and Pt/GCB as cathode catalyst. The apparent mass activity at 0.80 V (MA_app @0.80 V) and current density @0.60 V of Pt/Nb-SnO2 as a function of volume ratio of Nafion ionomer and support, I/S (b). The open circles and open squares are the MA_app @0.80 V and current density @0.60 V of Pt/GCB. The inset shows the Tafel slope as a function of I/S.
the Nb-SnO₂ support did not degrade during the load cycles. These adsorption/desorption currents for hydrogen and those for the oxidation/reduction of the platinum were smaller than those at BOT. The changes of ECA for Pt/Nb-SnO₂ and Pt/GCB during the load cycles are summarized in Fig. 7. For example, the ECA of Pt/Nb-SnO₂ (I/S = 0.12) and that of Pt/Nb-SnO₂ (I/S = 0.67) at EOT were 30.8 m² g⁻¹ and 28.0 m² g⁻¹, which were about 51.0% and 55.2% of the values at BOT, respectively. The ECA of Pt/GCB (I/S = 0.67) at EOT was 11.2 m² g⁻¹, which was about 46.6% of the value at BOT. Figs. 8a–8c show the TEM images of Pt/Nb-SnO₂ (I/S = 0.12), Pt/Nb-SnO₂ (I/S = 0.67) and Pt/GCB (I/S = 0.67) at EOT. The mean Pt particle size of Pt/Nb-SnO₂ at EOT was 8.9 nm (I/S = 0.12) and 4.7 nm (I/S = 0.67). The Pt catalyst particles undergo enlargement due to Ostwald ripening during the load cycling, and diminution due to the dissolution of Pt. The particle size of Pt/GCB at EOT was 8.5 nm, which was rather larger than that at Pt/Nb-SnO₂ (I/S = 0.67). The decrease rates of the ECA of Pt/Nb-SnO₂ and Pt/GCB during the load cycling were similar, but the ECA values of Pt/Nb-SnO₂ were always higher than those of Pt/GCB. The MA_app @0.80 V of Pt/Nb-SnO₂ at BOT with I/S = 0.24 was higher than that of Pt/GCB (Fig. 4c).

We conclude that the Pt/Nb-SnO₂ (I/S <0.24) had higher load cycle durability in comparison with that of Pt/GCB. Some of the Pt particles on GCB aggregated partially with nearest neighbor Pt particles, and the number of the Pt particles on Pt/GCB was less than that on Pt/Nb-SnO₂. The cross-sectional Z contrast images of the MEAs using Pt/Nb-SnO₂ and Pt/GCB at EOT are also shown in Figs. 9a–9c. Very few Pt particles existed in the membranes of the MEAs using Pt/Nb-SnO₂ CLs in low I/S (Fig. 9a), whereas large numbers (white small particles, Pt bands) were detected in the membrane of the MEA using Pt/GCB (Fig. 9c). We concluded that the Pt/Nb-SnO₂ CLs has an ability to diminish the deposition of Pt band in the membrane. The dissolution of Pt was clearly diminished on the Nb-SnO₂ support in comparison with that on GCB from the observation of TEM images of the catalysts of EOT (Figs. 8a–8c). The hydrophilic surface of the Nb-SnO₂ support has a negative charge, which would be expected to enhance the electrostatic attraction of dissolved Pt cations. Although further investigation of the Pt/Nb-SnO₂ surface at the EOT is necessary for a deeper understanding, the present results clearly suggest that the low I/S can help to diminish the dissolution of Pt, and the electrostatic attraction of the support surface can help to prevent the diffusion of Pt cations into the membrane.
The steady-state I-V performance and load cycle durability of PEFC using Pt/Nb-SnO₂ cathode CLs with varying I/S values were evaluated at 80 °C, 80%RH. The MA_{app} values at 0.80 V (I/S > 0.20) were at the same level as that using Pt/GCB CLs with an optimized I/S ratio, and increased up to 2 times higher at I/S = 0.12 in comparison with that using the Pt/GCB CL. The current density at 0.60 V of the PEFC using Pt/Nb-SnO₂ cathode CLs with varying I/S values were evaluated at 80 °C, 80%RH. The MA_{app} values at 0.80 V (I/S > 0.20) clearly have desirable characteristics that lead to decreased oxygen diffusion overpotentials, and thus to improved cell performance.

The ECA values of Pt/Nb-SnO₂ for all I/S were higher than that of Pt/GCB at each cycle number during the load cycle durability evaluation, which indicates that the Pt/Nb-SnO₂ catalyst had high durability in comparison with that of Pt/GCB. Essentially, no Pt band was observed in the MEAs using Pt/Nb-SnO₂ CLs after the load cycle durability evaluation. The thin, uniform coverage of the Nafion ionomer on the Pt/Nb-SnO₂ surface appears to increase the Pt utilization and mitigate the degradation of the Pt catalyst.

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Conclusions
The steady-state I-V performance and load cycle durability of PEFC using Pt/Nb-SnO₂ cathode CLs with varying I/S values were evaluated at 80 °C, 80%RH. The MA_{app} values at 0.80 V (I/S > 0.20) were at the same level as that using Pt/GCB CLs with an optimized I/S ratio, and increased up to 2 times higher at I/S = 0.12 in comparison with that using the Pt/GCB CL. The current density at 0.60 V of the Pt/Nb-SnO₂ CL (I/S = 0.12) also reached the same value as that of the Pt/GCB CL. From the observation of low acceleration voltage TEM, it was confirmed that the Nafion ionomer covered the hydrophilic surface of Nb-SnO₂ uniformly in the CLs, and that the tops of the Pt nanoparticles were left uncovered, so that an effective three-phase boundary of gas phase/Pt/ionomer was constructed. The hydrophilic surface of the GCB was not covered uniformly by the ionomer, and the Pt particles on GCB were either not covered or were deeply buried under the ionomer. The three-phase boundary of the cathode using Pt/Nb-SnO₂ (I/S < 0.20) clearly has desirable characteristics that lead to decreased oxygen diffusion overpotentials, and thus to improved cell performance.

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