Electrochemical Characterization of Pt Catalysts Supported on Nb-$SnO_{2-\delta}$ and Sb-$SnO_{2-\delta}$ with Aggregated Structure in Membrane Electrode Assembly Measurements

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Platinum-based catalysts supported on carbon have been widely applied as the cathode catalysts for PEFC s. It is well known that the carbon support degrades under the operating condition in high potential regions. In order to improve the durability of the support, several oxides (e.g., TiO_x, SnO_2) have been proposed as alternatives to carbon.[1,2] We reported the electrochemical performance and durability of Pt catalysts supported on nanometer-sized $SnO_{2-\delta}$ particles (Pt/$SnO_{2-\delta}$) with an aggregate structure similar to that of carbon black (CB) by using a rotating disk electrode (RDE).[3] In this research, we investigated the electrochemical performance of Pt supported on nanometer-sized Nb-doped $SnO_{2-\delta}$ (Pt/Nb-$SnO_{2-\delta}$) and Sb-doped $SnO_{2-\delta}$ (Pt/Sb-$SnO_{2-\delta}$) in a single cell (as the membrane-electrode assembly, MEA).

The Nb-$SnO_{2-\delta}$ (BET, 37 $m^2\ g^{-1}$) and Sb-$SnO_{2-\delta}$ (BET, 33 $m^2\ g^{-1}$) supports, with a CB-like aggregated structure were synthesized by the flame combustion method and were loaded with Pt by the colloidal method. A catalyst paste was prepared by mixing each catalyst and 5 wt.% Nafion® solution (Aldrich Co.) in a ball-mill. The resulting catalyst paste was directly sprayed onto the gas diffusion layer (GDL, 25BCH, SGL Carbon Group Co., Ltd.) by the pulse-swirl-spray technique to prepare the gas diffusion cathode. The loading amount of Pt was 0.2 mg cm^{-2}. In a similar manner, anodes for the fuel cell tests were prepared using commercial Pt/CB (TEC10E50E, Tanaka Kikinzoku Kogyo K.K.), and the loading amount of Pt was 0.5 mg cm^{-2}. The geometric electrode area was 3.8 cm^2. Cells were operated at 80°C; the flow rates of reactant gases (anode, H_2; cathode, O_2 or air) were constant at 200 mL min^{-1}.

TEM images of Pt/Nb-$SnO_{2-\delta}$ (Pt loading 13.0 wt.%) are shown in Fig. 1. It is clear that the Pt catalyst particles were well-dispersed on the oxide support with aggregated structure. A similar image was observed for Pt/Sb-$SnO_{2-\delta}$ (Pt loading 12.3 wt.%). The average sizes of the Pt particles were 2.8 ± 0.4 nm (Pt/Nb-$SnO_{2-\delta}$) and 2.7 ± 0.5 nm (Pt/Sb-$SnO_{2-\delta}$).

Figure 2 shows the I–E curves and the ohmic resistances of the cells (R_{cell}). The cells were operated between 0.3 V and 1.0 V at an operating temperature of 80°C with 30% RH. The I–E performances of the cells with Pt/Nb-$SnO_{2-\delta}$ and Pt/Sb-$SnO_{2-\delta}$ cathodes were superior to that of a cell with a Pt/CB cathode. The ohmic resistance of the electrolyte membrane (R_{PEM}) was found to be dominant for the R_{cell} of Pt/CB cell. The values of R_{cell} of cells with Pt/Nb-$SnO_{2-\delta}$ and Pt/Sb-$SnO_{2-\delta}$ were slightly lower than that of Pt/CB cell. Therefore, it was considered that hydrophilic oxide supports of Nb-$SnO_{2-\delta}$ and Sb-$SnO_{2-\delta}$ certainly adsorbed water generated at the cathode and contributed to decrease the R_{PEM}. As shown in Fig. 3, the O_2-gains of the Pt/Nb-$SnO_{2-\delta}$ and Pt/Sb-$SnO_{2-\delta}$ cathodes under low relative humidity (RH) were smaller than that of Pt/CB cathode. This indicates higher O_2-gas diffusivities and/or higher effectiveness of Pt in the Pt/Nb-$SnO_{2-\delta}$ and Pt/Sb-$SnO_{2-\delta}$ catalyst layers. One of the reasons for such a superior performance at low RH is a high effectiveness of Pt due to adsorbed water by these oxide supports. We conclude that these are promising alternative cathode catalysts for PEFCs.

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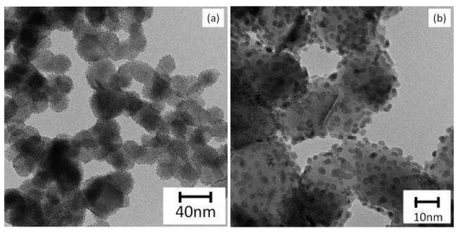

Fig. 1 TEM images of Pt/Nb-$SnO_{2-\delta}$ (a) low magnification (b) high magnification.

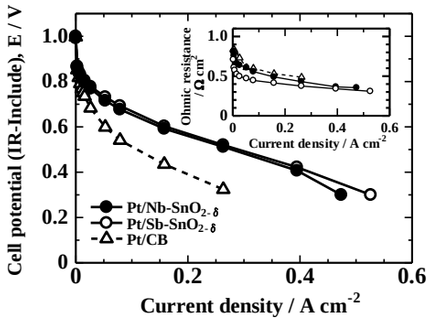

Fig. 2 I-E characteristics of MEAs using Pt/Nb-$SnO_{2-\delta}$ and Pt/Sb-$SnO_{2-\delta}$ as cathode catalysts at 80°C, 30% RH, Air/H_2, in comparison with that of a commercial Pt/CB cathode (inset shows the ohmic resistances of the cells).

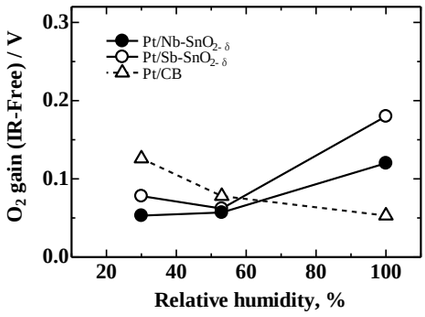

Fig. 3 Humidity dependence of O_2 gains of Pt/Nb-$SnO_{2-\delta}$ and Pt/Sb-$SnO_{2-\delta}$ cathodes at 0.2 A cm^{-2}, in comparison with that of a Pt/CB cathode.

References

1. T. Ioroi, Z. Siroma, N. Fujiwara, S. Yamazaki, K. Yasuda, Electrochem. Commun. **7**, 183 (2005).
2. A. Masao, S. Noda, F. Takasaki, K. Ito, K. Sasaki, Electrochem. Solid-State Lett., **12**, B119 (2009).
3. K. Kakinuma, M. Uchida, T. Kamino, H. Uchida, M. Watanabe, Electrochim. Acta, **56**, 2881 (2011).