PEFC Electrode Catalysts Supported on Nanocrystalline Semiconducting Oxides

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Polymer electrolyte fuel cells (PEFCs) are environmentally compatible energy conversion systems. As electrode supports, the use of semiconducting oxides instead of carbon-based materials is of technological interest because of the possibility to control their electronic properties. However, their electronic conductivity is relativity low in general, so that an increase in electronic conductivity is essential. Therefore, in this study, the effect of doping on electrode catalyst performance is examined by using TiO_2, In_2O_3 and SnO_2 as model semiconducting oxide catalyst supports.

TiO_2 powders doped with Al^{3+} as an acceptor and with Nb^{5+} as a donor were prepared via sol-gel method. In_2O_3 doped with Sn^{4+} as donor was prepared via ammonia coprecipitation method, and SnO_2 doped Sb^{5+} as a donor from commercial sol. Calcination temperature was determined after DTA-TG measurements. BET surface area and XRD crystallite size were measured after calcination. For conductivity measurements, sintered bulk samples were used. Electrical conductivity was measured by four-probe method during cooling from 900°C with a cooling rate of 4°C/min, in air. Pt catalysts were deposited on oxides via conventional impregnation processes. Redox activity was evaluated by CV measurements. Glassy carbon electrode was used for the CV measurements, and 0.1M $HClO_4$ (pH =1.4) was used as electrolytic solution.

The potential(vs. SHE)-pH diagram of Ti-H_2O system calculated is shown in Fig.1. TiO_2 is, at least, stable in the potential range of 0.04V-1.1V at pH≈1. Fuel cells with these catalysts were prepared, I-V characteristics were measured, and the current-interrupt method was applied to separate ohmic and nonohmic polarizations. Flow rate of O_2 and H_2 gases were 100ml/min. Pt loading was 0.6mg/cm^2.

Electrical conductivity of various oxides is shown in Fig.2. Doping TiO_2 with Nb^{5+} enhanced electrical conductivity in 5 orders of magnitude. On the contrary, it could be confirmed that electrical conductivity decreased by the acceptor doping. The conductivity of Sn-In_2O_3 was much higher than that of Nb-doped TiO_2. I-V characteristics of fuel cells with pure and doped TiO_2 as electrode supports were measured. Pt/C electrode catalysts were added where a weight ratio of oxide-to-carbon was 1-to-1. The results are shown in Fig.3. Cell voltage increased with increasing electrical conductivity of TiO_2. Ohmic polarization, determined by the current-interrupt technique, has also a similar relationship. These results indicate that the increase in electrical conductivity leads to a decrease in ohmic polarization and thus an increase in cell voltage. CV measurements revealed that effective surface area of Pt catalysts also increased with increasing electrical conductivity.

Other oxide semiconductors exhibiting higher conductivity were also used for cathodes, and electrochemical characteristics were evaluated. Their I-V characteristics are shown in Fig.4. Whereas Sn-In_2O_3 showed a high electrical conductivity, I-V characteristics were lower than those with TiO_2. Crystallite size of Pt on TiO_2 was 9nm, much smaller than that on SnO_2 and In_2O_3, which may be one of the reasons explaining poor I-V characteristics for cells with doped In_2O_3 and SnO_2. These results mentioned above indicate that high electrical conductivity and smaller grain size are, at least, essential in order to apply semiconducting oxides as catalyst supports for PEFC electrodes.

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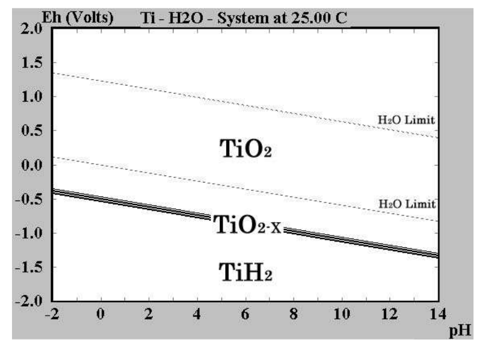

Fig.1: Potential (vs. SHE) -pH diagram of Ti-H_2O at 25℃

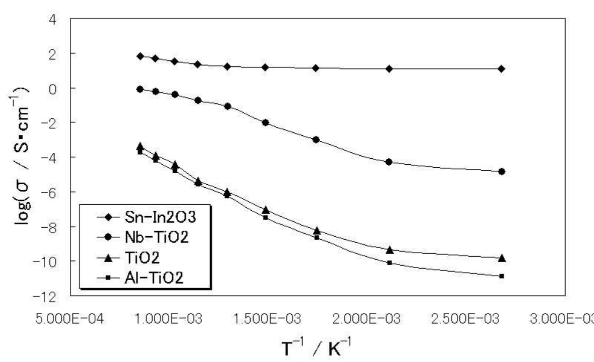

Fig. 2: Electrical conductivity of various metal oxides

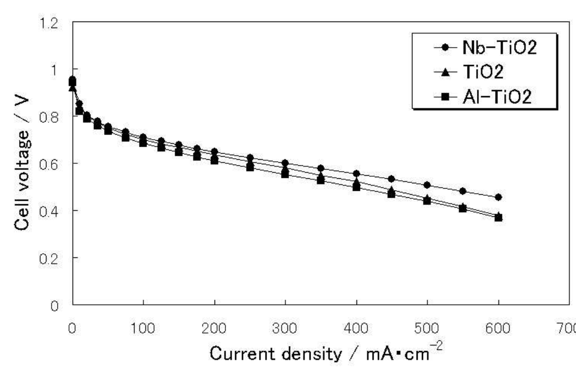

Fig. 3: Current-voltage characteristics of fuel cells with cathodes containing doped and undoped TiO_2

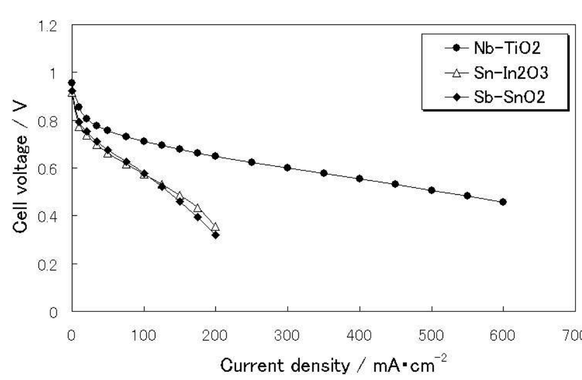

Fig. 4: Current-voltage characteristics of fuel cells with cathodes containing various metal oxides