

## Electrochemical Properties of Pt Catalysts Supported on Nb-Doped SnO<sub>2</sub> with Network Structure

Y. Senoo,<sup>a,b</sup> Y. Chino,<sup>a</sup> K. Kakinuma,<sup>c</sup> M. Uchida,<sup>c</sup>  
H. Uchida,<sup>c,d</sup> S. Deki,<sup>c</sup> and M. Watanabe<sup>c</sup>

<sup>a</sup> Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, 6-43 Miyamae, Kofu, 400-0021, Japan.

<sup>b</sup> Corporate R and D Center, Mitsui Mining and Smelting Co., Ltd., 1333-2 Haraichi, Ageo, 362-0021, Japan

<sup>c</sup> Fuel Cell Nanomaterials Center, University of Yamanashi, 6-43 Miyamae, Kofu, 400-0021, Japan.

<sup>d</sup> Clean Energy Research Center, University of Yamanashi, 4-3 Takeda, Kofu 400-8511, Japan

The polymer electrolyte fuel cell (PEFC) is one of the most attractive power generation systems for fuel cell vehicles. Platinum-based catalysts supported on carbon are typical cathode catalysts for PEFCs, but the degradation of the carbon support in the high potential region is a problem to be solved. Tin oxide (SnO<sub>2-δ</sub>) is stable in the high potential region and becomes a good candidate for use as a non-carbon support if it possesses a high electrical conductivity.<sup>1</sup> Meeting such an expectation, we have succeeded synthesis of a Nb-doped tin oxide (Nb-SnO<sub>2-δ</sub>) support with a network structure, like carbon black (CB), by a flame oxide-forming method.<sup>2</sup> In this research, we evaluate the electrical conductivity of the Nb-SnO<sub>2-δ</sub> with such unique morphology, and the electrochemical properties of Pt catalysts supported on the Nb-SnO<sub>2-δ</sub>.

The obtained particles (crystallite size, 10-20 nm; specific surface area, 40-100 m<sup>2</sup>/g) were necked with nearest neighbors and formed a network structure (Fig. 1). We proposed two parameters to evaluate the degree of such a structure formation. One is "SSA ratio", and the other is "primary pore volume". The SSA ratio is defined as the ratio of measured specific surface area (BET) to the geometric surface area estimated from the spherically approximated crystallite size. The SSA ratio for the separated particles is unity. It decreases with the increase of necking degree among the primary particles. The second parameter is defined as the open space volume formed by their non-linear aggregation.<sup>3</sup> The Nb-SnO<sub>2-δ</sub> support had a similar pore size and volume to that of CB.<sup>4</sup> Increase of primary pore volume could be due to a ramification of the aggregates, which would contribute to the improvement of the electron conducting paths.

We investigated the relationship between the network structure and the electrical conductivity by using these parameters mentioned above. The SSA ratio varied from 0.67 to 0.91 depending on synthetic conditions. With decreasing the SSA ratio, the apparent electrical conductivity  $\sigma_{app}$  of the support increased (Fig. 2, dotted line), which is ascribed to the decrease of contact resistance accompanied by development of the necking among the particles. Some particles exhibited a deviation from the simple correlation curve to higher conduction values even though the SSA ratios were nearly the same (0.82~0.85). The corresponding conductivities are increased with increasing their primary pore volumes as shown in Fig. 3. This suggests that increase in the apparent electrical conductivity further increases with increasing the open space in the network structure.

Pt was loaded on the Nb-SnO<sub>2-δ</sub> by a colloidal method (17 wt%, Pt particle size, 3.0 nm). The electrochemical activity of each sample was measured by the rotating disk electrode (RDE) technique. The kinetically controlled current density ( $j_k$ ) for the oxygen reduction reaction (ORR) at 0.85 V increased with increasing the  $\sigma_{app}$  of the support. The maximum  $j_k$  value reached 0.84 mA/cm<sup>2</sup> for the catalyst with the maximum  $\sigma_{app}$  ( $2.0 \times 10^{-4}$  S/cm), which is superior to that of commercial Pt/CB (0.65 mA/cm<sup>2</sup>, TEC10E50E, Tanaka Kikinzo Kogyo Co.).<sup>5</sup> We considered that the network structure and necking of the support particles affected the electrochemical activity for the ORR of the Pt catalyst.

This work was supported by funds for the "HiPer-FC Project" of NEDO, Japan.

## References

1. A. Masao, S. Noda, F. Takasaki, K. Ito, K. Sasaki, *Electrochem. Solid-State Lett.*, **12**, B119 (2009).
2. K. Kakinuma, M. Uchida, T. Kamino, H. Uchida, M. Watanabe, *Electrochim. Acta*, **56**, 2881(2011).
3. M. Watanabe, M. Tomikawa, S. Motto, *J. Electroanal.Chem.*, **195**, 81 (1985).
4. K. Kakinuma, Y. Chino, Y. Senoo, M. Uchida, M. Uchida, H. Uchida, S. Deki, M. Watanabe, submitted.
5. H. Yano, T. Akiyama, P. Bele, H. Uchida, M. Watanabe, *Phys.Chem. Chem. Phys.*, **12**, 3806 (2010).

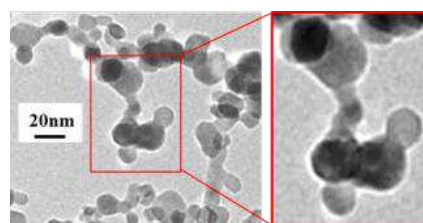


Fig. 1. TEM image of Nb-SnO<sub>2-δ</sub> support synthesized by the flame oxide-forming method.

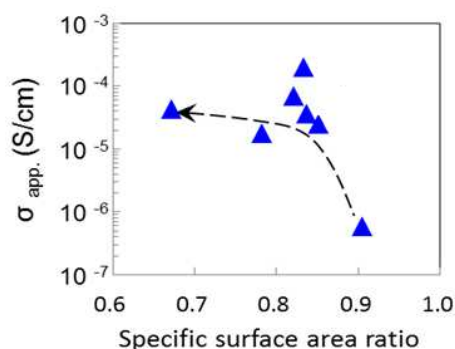


Fig. 2. Relationship between SSA ratio and apparent electrical conductivity ( $\sigma_{app}$ ) of Nb-SnO<sub>2-δ</sub>.

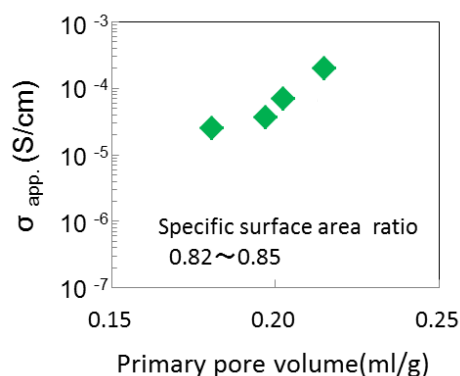


Fig. 3. Relationship between primary pore volume and apparent electrical conductivity ( $\sigma_{app}$ ) of Nb-SnO<sub>2-δ</sub>.