

論文の内容の要旨

論文題目 Group IV or V Metal Oxide Nanoparticle Catalysts for Oxygen Reduction in
Polymer Electrolyte Fuel Cells
(PEFCの酸素還元のためのIV、V族金属酸化物ナノ粒子触媒)

氏 名 徐 貞淑 (ソ ジョンスク)

In order to reduce the high cost for Pt or Pt-based catalysts which have been absolutely employed in polymer electrolyte fuel cell (PEFC) electrodes, there have been addressed many promising non-precious electrocatalysts. The Fe- and Co-based materials with N-coordinated geometries as one of non-noble metal candidates have been reported to be effective electrocatalysts for the oxygen reduction reaction (ORR). However, these compounds have been known susceptible to dissolution in acidic media, i.e. a typical PEFC cathode condition.

Another challenging substitute is group IV and V compounds in the periodic table. The elements such as Ti, Zr, Nb, and Ta have been proved chemically very stable under the acidic and oxidizing environment. Several compounds based on these elements have also been reported as the ORR electrocatalysts. Most attempted compounds were focused on the improvement of their electrocatalytic activities by doping another heterogeneous atom such as N or/and C or by various heat treatments. Despite many attempts, the oxides, nitrides, carbides, and their mixtures based on Ta, Nb, and Zr have shown yet the limited catalytic activity and poor long-term stability for fuel cell applications. Especially, the nitrides with N doping basically have displayed excellent ORR activity and but, a very poor stability because they tend to turn into the most stable state, i.e. oxides in acidic solutions.

In fact, the oxides are the most stable substance in the acidic atmosphere. Nevertheless, they have highly low electric conductivity due to typically an insulator in bulk, indicating the definitely low ORR activity. Furthermore, there has been a significant difficulty to control the particle size of oxide catalysts by conventional methods such as an impregnation.

In this thesis, with this background, highly small nanoscale oxide catalysts without any doping in both electrode and powder type were first attempted to design the best electrode structure and to improve the electric conductivity for the high ORR activity. In experimental, the potentiostatic electrodeposition facilitated the preparation of ultrafine oxide nanoparticles well deposited on carbon black (CB) at room temperature. In particular, group IV-V metal precursors are not soluble in aqueous solutions at room temperature because they form oxide or hydroxide precipitates by the

reaction with H_2O . By the reason, the ethanol-based metal plating baths were selected for the electrodeposition. Here, based on the chemical stability in acidic media, the group IV and V oxide nanoparticle catalysts prepared by different deposition conditions and subsequent heat treatments were studied on the basis of their physical characteristics and electrocatalytic activity for the ORR. The electrodeposited oxide nanoparticles will be denoted as TaO_x , NbO_x , and ZrO_x in this article simply according to the XPS analysis results.

In the **chapter 1**, the general research background and purposes of the group IV or V metal oxide nanoparticle catalysts were introduced towards the ORR at PEFC cathodes.

In the **chapter 2**, the highly small TaO_x nanoparticles on CB electrodes were discussed on their successful preparation by the electrodeposition and the subsequent various heat treatments. The effects of the electrodeposition and heat treatment conditions were mainly investigated for the high catalytic activity toward the ORR. Ta species in the ethanol-based 20 mM $\text{Ta}(\text{OEt})_5$ plating bath were directly electrodeposited onto the prepared bare CB electrode by applying different potentials -0.3, -0.5, -0.7, and -1.0 $\text{V}_{\text{Ag}/\text{AgCl}}$ for 10 s. It was clearly observed that the electrodeposited TaO_x electrodes only after the electrodeposition at -0.5 $\text{V}_{\text{Ag}/\text{AgCl}}$ for 10 s exhibited some catalytic activity with an onset potential of 0.87 V_{RHE} at $-2 \mu\text{A cm}^{-2}$ for the ORR. However, it still showed low ORR current density measured at 0.6 ~ 0.7 V_{RHE} , within the reasonable voltage output ranges for PEFCs. The ORR performance on the all oxide catalysts was largely enhanced by applying the H_2 heat treatment at 523 K for 30 min. The current density at 0.6 V_{RHE} for the H_2 -treated catalyst prepared in the same potential was increased about six times of that for untreated catalyst and the ORR onset potential was also shifted to more positive side of 0.92 V_{RHE} at $-2 \mu\text{A cm}^{-2}$. Moreover, the physical analyses were carried out to identify the reasons why the TaO_x catalysts fabricated by electrodeposition show high ORR activity. According to the scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDS) analyses, it was revealed that the TaO_x species in the average size of 1~2 nm were uniformly deposited on CB. The results explain that the electrodeposition could produce highly small TaO_x catalysts and the ultrafine size of oxide particles was an origin of the high ORR activity that might not be observed in bulk oxides.

Next, the particle size dependence on the ORR activity of the TaO_x catalysts was addressed in the **chapter 3**. It was also discussed the preliminary single cell test with a membrane electrode assembly (MEA). The ORR properties of the different sized TaO_x electrocatalysts deposited on the CB electrodes in an average of 1.0, 2.6, 4.6, and 13.5 nm were investigated in a 0.1 M H_2SO_4 solution. It was discussed the mass specific ORR currents at 0.6 V_{RHE} and the onset potentials at $-2 \mu\text{A cm}^{-2}$. The negative shift of onset potential with increasing particle size was only 0.13 V, however, the current density was drastically decreased. It was reached to almost zero current on the largest TaO_x nanoparticles in 13.5 nm size, indicating that they must be absolutely useless to be electrocatalyst. The mass activities on the TaO_x electrodes were largely increased with their size decrease.

Electrochemically, the relationship between the particle size of metallic catalysts such as Pt, Pd and their activity has been discussed in an electrochemical surface area (ECSA). However, in the case of the TaO_x electrocatalysts, the advantage of the ultrafine particle size is regarded mainly as the electroconductivity of particles.

In the **chapter 4**, the electrocatalytic study on the TaO_x nanoparticles as the ORR electrocatalyst was extended to group IV or V oxides based on their high stability in the acidic environment. The preparation conditions and the ORR activities were compared for the electrodeposited ultrafine NbO_x, ZrO_x, and TaO_x particle catalysts. It was focused on the ORR activities for NbO_x, ZrO_x, and TaO_x electrodes electrodeposited under optimal conditions. NbO_x, ZrO_x, and TaO_x were electrodeposited on CB at -0.4, -0.5, and -0.5 V_{Ag/AgCl} for 10 s, and then treated under H₂ at 553, 473, and 523 K for 30 min, respectively. The prepared oxide nanoparticles showed high onset potential for the ORR comparable to the Pt/CB catalyst although the current densities were lower. The ZrO_x catalysts showed the highest onset potentials and were followed by NbO_x and TaO_x, in that order. This trend in onset potential can be understood along with the intrinsic activity of a number of active sites for the ORR. However, the amount of Zr deposition was smaller than those for group V metals, so that the current at 0.7 V_{RHE} was also smaller. Fine tuning the preparation conditions and selecting the appropriate Zr complexes for the deposition bath might yield more highly loaded ZrO_x electrodes.

Although the oxide nanoparticles obviously showed the high activities for the ORR, there was observed the difficulty on the increase of catalyst loading by the limited electrode areas. Thus, in the **chapter 5**, the TaO_x/CB catalysts in powder type were prepared with a new designed working cell and a modified deposition parameters. With the preparation of powder typed oxide catalysts, the H₂ treatment at high temperature could be applied to improved catalytic activity. Their catalytic and surface properties were investigated in the chapter. Also, by a RRDE system, the O₂ reduction kinetics on the oxide nanoparticles was examined in acidic media. The ORR polarization curves with different rotation rates for the electrodeposited TaO_x/CB catalysts were measured in the O₂-saturated 0.1 M H₂SO₄ aqueous solution at 298 K. The transferred electron number per an oxygen molecule on the catalyst surface could be estimated by *Koutechy-Levich* plots. The plots for the oxide catalysts suggested a linearity between I^1 and $\omega^{-1/2}$ at the applied potentials, indicating that the O₂ reduction kinetics are exactly the first-order reaction relied on the concentration of dissolved oxygen in solution. Moreover, the slopes of straight lines for the catalysts were referenced by the two theoretical lines calculated with 4-electron and 2-electron transfer pathways. The slopes for the electrodeposited TaO_x/CB catalysts at the calculated potential regions were paralleled almost to the 4-electron baseline. It means that the ORR process on the electrodeposited oxide nanoparticles was dominated by a 4-electron transfer pathway.

The experiment results and discussion on the group IV or V metal oxide nanoparticle catalysts as

the ORR electrocatalysts in PEFCs were summarized in the **chapter 6**. The group IV and V oxide nanoparticle catalysts in the average size of 1-2 nm, which were successfully prepared by cathodic electrodeposition in ethanol-based metal plating solutions and followed by H₂ heat treatment, exhibited excellent catalytic activities with high onset potentials of 0.93 V_{RHE} (TaO_x), 0.96 V_{RHE} (NbO_x), and 1.02 V_{RHE} (ZrO_x) at -2 μA cm⁻² for the ORR under the optimized conditions, respectively. Also, the ORR kinetics on the catalysts was determined to the 4-electron transfer pathway, resulting in the high catalytic activity. Therefore, based on the ORR activity comparable to that of the commercial Pt/CB catalyst and the strong long-term stability in the acidic solution, the group IV and V oxide nanoparticles prepared by electrodeposition are proposed as potential candidates for non-precious metal cathode catalysts in PEFCs.