Group IV or V Metal Oxide Nanoparticle Catalysts for Oxygen Reduction in Polymer Electrolyte Fuel Cells

博士論文（要約）

Doctoral Dissertation

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）

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ABSTRACT

There have been many attempts to apply non-precious metal materials to polymer electrolyte fuel cells (PEFCs), especially to the cathode electrocatalysts with improved oxygen reduction reaction (ORR) activity. Since several decades, various promising electrocatalysts have been reported for the high catalytic activity. Nevertheless, their long-term stability in the typical PEFC operation condition at 80 ℃, i.e. the acidic environment, has been a big impediment to substitute for the Pt/CB catalyst which has been widely applied for the commercial PEFC systems. Hence, the group IV or V metal oxides on the periodic table have been commonly known as the stable substances in the acidic media. The metal oxides however could not be catalyzed for the electrochemical reaction such as the ORR owing to their low electroconductivity.

In this thesis, with the background, the ultrafine oxide nanoparticle catalysts based on group IV or V were studied for the ORR in PEFCs. The new approach to the oxide nanoparticles for the ORR electrocatalysts has been established largely by their strong durability in the acidic condition and by significantly improved electroconductivity originated from the particle size reduction. Here, the mainly addressed research stream will be focused on the preparation of the highly dispersed fine oxide nanoparticles below 5 nm size and their physical characteristics and electrocatalytic activity for the ORR.

Electrochemical measurements for the oxide nanoparticles were analyzed by cyclic voltammetry (CV), linear sweep voltammetry (LSV), rotating disk electrode (RDE) or rotating ring-disk electrode (RRDE) systems, and electrochemical impedance spectroscopy (EIS). Surface characterizations were performed by (scanning) transmission electron microscopy ((S)TEM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD).

The loading amounts of the electrodeposits on the carbon black (CB) were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

First, in the chapter 1, the general research background and purposes of the group IV or V metal oxide nanoparticle catalysts will be introduced for the ORR at PEFC cathodes.

In the chapter 2, the highly small TaO_x nanoparticles will be discussed on their successful preparation by an electrodeposition method in nonaqueous plating bath at room temperature. Subsequently, the various heat treatments after the electrodeposition were applied to the electrodeposited oxide nanoparticles supported on CB. The effects of the electrodeposition and heat treatment conditions were investigated for the high catalytic activity toward the ORR. It will be also exhibited their long term stability in acidic media for 1000 cycles.

Moreover, the particle size dependence on the ORR activity of the TaO_x catalysts will be addressed in the chapter 3. It will be exhibited several attempts to increase the catalyst loading on the CB elecdrodes and the preliminary single cell test with a membrane electrode assembly (MEA).

In the chapter 4, the electocatalytic study of TaO_x nanoparticles for the ORR was extended to group IV or V oxides based on their high stability in the acidic environment. The preparation conditions and the ORR activities will be compared for the electrodeposited NbO_x, ZrO_x, and TaO_x nanoparticles.

Although they showed the high activities for the ORR, there was observed the difficulty on the increase of catalyst loading by the limited electrode area. Thus, in the chapter 5, the TaO_x/CB catalysts in powder type were prepared with a new designed working cell and modified deposition parameters. With the preparation of powder typed oxide catalysts, the H_2 treatment at high temperature was applied to improved catalytic activity. Their catalytic and surface properties will be investigated in detail in the chapter. The long-term stability of the oxide powder catalysts itself will be also proved in the O_2-saturated acidic atmosphere for 10,000 cycles. Moreover, the O_2 reduction kinetics on the oxide nanoparticles will be examined in acidic media by a RRDE system.

Finally, the experiment data and discussions on the group IV or V metal oxide nanoparticles catalysts for the ORR in PEFCs will be concluded in the chapter 6.

Key words

Polymer Electrolyte Fuel Cells, Non-precious metal catalysts, Oxygen reduction reaction, Electrocatalysts, Electrodeposition, Nonaqueous plating bath, Ta-based catalysts, Nb-based catalysts, Zr-based catalysts, Ta_2O_5, Nb_2O_5, ZrO_2, TaO_x, NbO_x, ZrO_x, Oxide nanoparticles, Oxygen reduction reaction kinetics, 4 or 2-electron reduciton pathway.

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