1. Introduction

Hydrogen has been increasingly developed as a source of energy to achieve both sustainable development of industry and reduction of greenhouse gas emissions, as well as to ensure the stable supply of energy \(^1\).\(^-\)\(^3\). Fuel cells with high energy conversion efficiency and zero-emission characteristics have been developed as key devices for the utilization of hydrogen energy, and have gradually been introduced in society as power generation systems for vehicles and households \(^1\),\(^4\),\(^5\). However, fuel cells are expensive compared to conventional power generation devices such as internal combustion engines. Therefore, costs must be reduced for the widespread use of fuel cells.

Proton exchange membrane fuel cells (PEMFCs), which are currently in practical use in vehicles and households, have highly acidic internal environments \(^1\). Consequently, inexpensive base metals are not suitable for the catalyst materials, because they generally lose activity due to corrosion and leaching. In contrast, anion exchange membrane fuel cells (AEMFCs) have a low corrosive internal environment due to the conductance of hydroxide ions in the membranes \(^6\). Therefore, various materials including base metals can be used for catalysts and other structures inside the cell. In addition, the kinetics of the oxygen reduction reaction (ORR) on the cathode is enhanced under basic conditions compared to acidic conditions. In fact, various base-metal catalysts have been applied to the ORR under basic conditions, and their activity was comparable to that of platinum catalysts \(^7\)-\(^9\). Recent developments in AEMFCs, especially in anode catalysts and membranes, have significantly improved cell performance. In fact, the performance of the AEMFC is now comparable to or even better than PEMFCs, although pure hydrogen and pure oxygen are required \(^10\).

One of the problems of AEMFCs is the low activity of the hydrogen oxidation reaction (HOR) at the anode \(^6\),\(^11\). HOR rate under basic conditions in AEMFCs is two orders of magnitude slower than that under acidic conditions \(^11\),\(^12\). Another problem of AEMFCs is the durability of the membrane. Air supplied to the cathode side also introduces CO\(_2\) which reacts with OH\(^-\) to produce carbonic acid species (CO\(_3^{2-}\), HCO\(_3^-\)) in the membrane thus lowering the membrane conductivity and degrading the cell performance \(^6\),\(^13\),\(^14\). Therefore, AEMFCs have not yet been used as widely as PEMFCs. However, the AEMFC performance has been drastically improved in recent years \(^10\),\(^15\),\(^16\). Consequently, the AEMFC is likely to be a future option for the use of hydrogen as the main energy source. Here, our recent studies on AEMFC anode catalysts are reviewed to describe the catalyst factors controlling the HOR on the anode.
2. Ru Nanoparticles

2.1. Screening of Metal Nanoparticle Catalysts

Figure 1 shows the schematic diagram of the AEMFC. The ORR proceeds on the cathode to produce OH⁻ from O₂ and H₂O. The resulting OH⁻ passes through the AEM to the anode, where the HOR proceeds to produce H₂O from H₂ and OH⁻. During this process, electrons flow from the anode to the cathode, thus generating an electrical current. In this study, carbon supported metal nanoparticle catalysts were prepared using various metal species and applied to AEMFC anodes. AEM (A201, Tokuyama Corp.) was used as the electrolyte, and carbon supported platinum nanoparticle catalyst (TEC10E50E, Tanaka Precious Metals Corp.) was used as the cathode catalyst.

Figure 2 shows the AEMFC cell performance using different metal catalysts on the anode. The cell performance was strongly dependent on the anode catalysts, and the highest cell performance was obtained with ruthenium nanoparticles. HOR activity changes in a volcano-like relationship with the hydrogen binding energy of the metal species, in accordance with Sabatier’s law. Thus, metal species with moderate hydrogen binding energy, i.e., neither too large nor too small, are most effective for the HOR. The change in performance shown in Fig. 2 is consistent with Sabatier’s law. Therefore, the changes in cell performance in Fig. 2 are considered to result from the metal-hydrogen binding energy of the anode catalysts. In addition, the high performance of Ru/C is explained by the moderate hydrogen binding energy of Ru.

2.2. Size Effect of Ru Nanoparticles

The size effect of Ru nanoparticle catalysts was investigated using 2-7 nm Ru/C. The size of Ru/C was controlled by changing the temperature during liquid phase reduction of Ru precursor by sodium borohydride. In addition, heat treatment was performed after the preparation. AEMFC performance was evaluated using Ru/C with various particle sizes on the anode. Figure 3 shows the AEMFC performance varied with the particle size of Ru/C and was highest at 3 nm. To accurately evaluate the catalytic activity of Ru/C, the HOR was performed in an alkaline electrolyte (0.1 M sodium hydroxide solution) using a rotating disk electrode system. Figure 4 shows the dependence of HOR activity on the size of Ru/C. HOR activity was evaluated in terms of activity per electrically active surface area (specific activity) as well as activity per metal weight (mass activity). Figure 4 shows volcano-shaped dependence was observed with maximum specific and mass activities at about 3 nm. To accurately evaluate the catalytic activity of Ru/C, the HOR was performed in an alkaline electrolyte (0.1 M sodium hydroxide solution) using a rotating disk electrode system. Figure 4 shows the dependence of HOR activity on the size of Ru/C. HOR activity was evaluated in terms of activity per electrically active surface area (specific activity) as well as activity per metal weight (mass activity). Figure 4 shows volcano-shaped dependence was observed with maximum specific and mass activities at about 3 nm. Furthermore, activities using 3 nm Ru/C were higher than those of Pt/C (TEC10E50E). Therefore, particle size control of Ru/C is effective to improve the HOR activity.

The cause of the size-specific high activity of Ru/C at 3 nm was investigated at the atomic scale using a high-resolution transmission electron microscope (TEM). TEM found well-defined lattice fringes and
surfaces for 7 nm Ru/C, but less crystallinity and disordered surfaces for 3 nm Ru/C. Structural analysis of Ru/C using X-ray absorption spectroscopy suggested that 2 nm Ru/C is present in the oxide state and ≥3 nm Ru/C in the metallic state. Based on these results, the size-specific high activity of Ru/C is derived from the disordered Ru metal surface. Therefore, the size of Ru/C affects the crystallinity and surface order/disorder, which strongly affect the catalytic performance.

3. Ru–Ir Nanoparticles

3.1. Alloying

Alloy formation of two or more metals can change the adsorption of reactants and products, and so modify the catalytic performance. Formation of Ru alloy with different metals may change the adsorption of hydrogen, and possibly improve the HOR activity. Therefore, Ru alloys with various metals including Ni, Cu, Ag, and Ir were prepared. Ru alloys with Ni, Cu, and Ag did not improve the catalytic activity compared to Ru metal, whereas Ru alloy with Ir greatly improved the HOR activity.

Ru-Ir alloy catalysts were prepared by the liquid-phase reduction method at 20 °C and 60 °C, which were denoted as Ru-Ir/C-20 and Ru-Ir/C-60, respectively. The HOR activities of the Ru-Ir catalysts are presented in Fig. 5. Catalytic activity depended on the preparation temperature, as Ru-Ir/C-20 was more active than Ru-Ir/C-60. To investigate this effect, the catalyst structure was analyzed by X-ray diffraction and TEM. Ru-Ir/C-20 had a random alloy nanoparticle structure with well mixed Ru and Ir in each particle, whereas Ru-Ir/C-60 consisted of segregated Ru and Ir nanoparticles. Therefore, the atomic-level mixing of Ru and Ir is the key to improve the HOR activity.

Ru-Pt alloy catalyst was also evaluated using a commercially available catalyst (TEC61E54, Tanaka Precious Metals Corp.). Figure 5 shows Ru-Pt alloy improved the HOR activity. The effect of the alloying on the hydrogen binding energy was evaluated to investigate mechanism of the enhanced HOR activity. Hydrogen binding energy was decreased and resulted in higher HOR activity as shown in Fig. 6. These results indicate that HOR activity is improved by alloying through lower hydrogen binding energy.

3.2. Surface Pair site

The effect of the composition of Ru-Ir alloy nanoparticles on the catalytic performance was investigated with Ru-Ir alloy nanoparticles containing Ru/Ir ratios from 3/1 to 1/3. The HOR activity depended on the Ru/Ir ratio, and maximum activity was obtained in the middle range of the Ru/Ir ratio. The Ru/Ir ratio on the catalyst surface, i.e., the Ru/Ir surface composition, was evaluated by underpotential deposition of Cu2+ ions on surface Ru and Ir. Figure 7 shows the dependence of the HOR activity on the Ru/Ir surface composition.
Maximum activity occurred at surface Ru/Ir ratio of 0.5. This improvement in HOR activity can be explained by the increase of Ru-Ir pair site probability (Fig. 7). Therefore, Ru-Ir pair sites are the highly active species in Ru-Ir alloy nanoparticles.

The change in hydrogen binding energy may be the cause of the enhanced activity by formation of Ru-Ir pair sites. However, the hydrogen binding energy did not exhibit strong correlation with the HOR activity, suggesting that other factors are involved at the Ru-Ir pair sites. Recently, a bifunctional mechanism involving reaction of surface OH species has been proposed for the HOR mechanism, in which the catalyst surface has two functions, hydrogen adsorption and formation of reactive surface OH species. According to the bifunctional mechanism, the HOR activity changes with both reactivity of the hydrogen adsorption site and surface OH site, and with the positional relationship of these two types of sites, i.e., the presence or absence of pairing. In other words, such pair sites promote the reaction between adsorbed hydrogen and OH species, which increases the HOR rate. Thus, the bifunctional mechanism is considered to explain the high activity of the Ru-Ir pair site. Since Ru is more easily oxidized than Ir, Ru is considered to form the active site for formation of OH species and Ir forms the hydrogen adsorption sites.

4. Surface Modified Metal Nanoparticle Catalysts

4.1. Addition of Different OH Species to the Catalyst Surface

The study of Ru-Ir alloy nanoparticles suggested that the HOR activity in alkaline conditions is affected by both hydrogen binding energy and the surface OH species characteristics. Consequently, introduction of different OH species on metal nanoparticle surface may improve the HOR activity. Therefore, Pt nanoparticles were modified with fifteen metals and the HOR activity evaluated as shown in Fig. 8. HOR activity was changed by the modifying metal species. The highest specific activity was obtained with Pt nanoparticles modified with Co and Ru, at about two times higher than that of Pt nanoparticles without the surface modification. More importantly, the HOR activity of the various modified Pt nanoparticles showed volcano-type dependence on the standard oxidation potential of the modifying metal species as presented in Fig. 8. The standard oxidation potential of the modifying metal species is a descriptor of the surface OH species introduced. Therefore, the volcano-type dependence in Fig. 8 indicates that the HOR activity is enhanced by the introduction of OH species with appropriate reactivity onto the surface of metal nanoparticles.

4.2. Removal of Catalyst Surface Poisoning

The HOR activity of Pt catalysts under alkaline conditions is two orders of magnitude lower than that under acidic conditions as described in the introduction. This difference in activity partly depends on the change in hydrogen binding energy with pH. In addition, adsorption of OH species or other substances under alkaline conditions can cause lower hydrogen adsorption, which is also detrimental to the HOR and so reduces power generation in AEMFCs. Such surface catalyst poisoning might be removed by surface modification with other metal species. Therefore, we investigated whether surface modification can ameliorate surface poisoning or increase hydrogen adsorption. In-situ Pt L3 edge X-ray absorption spectral analysis was conducted to evaluate hydrogen adsorption on modified Pt nanoparticles during electrochemical measurement.
Surface modification of the Pt nanoparticles with other metal species increased the electrochemically active Pt surface area in alkaline media. In other words, surface modification reduced poisoning of the Pt nanoparticle surface. Therefore, surface modification can improve the HOR activity by both introduction of active OH species and reduction of poisoning of hydrogen adsorption sites in alkaline conditions.

5. Conclusions

The performance of anode catalysts for AEMFCs has been improved by identifying Ru nanoparticle catalysts, particle size control, and alloying with Ir, as the improved HOR activity is dependent on the hydrogen binding energy and the bifunctional mechanism. In addition, surface modification of metal nanoparticles further improved the HOR activity based on the bifunctional mechanism. Such surface modification can form reactive OH species and remove surface poisoning of the hydrogen adsorption sites. The present results are important for the recent development of AEMFCs as the next generation of fuel cells. The next challenge will be development of non-precious metal catalysts for the cell anode.

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要  旨

ルテニウム系ナノ粒子触媒の開発によるアニオン交換膜形燃料電池の水素酸化反応の向上

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プロトン交換膜形燃料電池（PEMFC）に代わる燃料電池としてアニオン交換膜形燃料電池（AEMFC）が注目されている。AEMFCの課題の一つとして、燃料極（アノード）側での水素酸化反応（HOR）が遅いことが挙げられる。これに対し、筆者らは、金属ナノ粒子触媒の探索を行い、ルテニウム系触媒がHORに対して高い活性を示すことを見出した。さらに、HORの速度を向上させるために、ルテニウムナノ粒子のサイズ制御、ルテニウムとイリジウムの合金化、金属ナノ粒子の表面修飾などによる触媒開発を行ってきた。これらにより触媒表面の水素結合エネルギーを変化させ、さらに表面の酸素基の反応性を操作することで触媒活性を向上させてきた。ここでは、筆者らのAEMFC用アノード触媒の開発について紹介する。