

Modification of Pt/C with various metal oxides improving catalytic activity for alkaline hydrogen oxidation

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Abstract: Modification of Pt/C with metal oxides improves catalytic activity for hydrogen oxidation reaction (HOR) in alkaline electrolyte. In particular, Ru/Pt/C and Mo/Pt/C exhibits the excellent HOR activity, which is twice higher than unmodified Pt/C. The activity of the Ru oxides modified Pt/C is superior to that of the alloy Pt-Ru/C which has been reported as one of the most active catalysts for HOR.

Keywords: alkaline fuel cell, hydrogen oxidation reaction, Platinum.

1. Introduction

Anion exchange membrane fuel cells (AEMFCs) have the possibility of using nonprecious metals as catalysts. However, the cell performance of AEMFCs has been lower than that of conventional proton exchange membrane fuel cells. One of the reasons is the low hydrogen oxidation reaction (HOR) rate on the anode. In the previous study, it was reported that modifying the surface of platinum single crystal with Ni(OH)₂ improved the HOR activity.¹ In this study, we aimed to improve the HOR activity by modifying commercial Pt/C with various metal oxides.

2. Experimental

Various metal oxide modified catalysts M/Pt/C (M = Ti, V, Ni, Zr, Nb, Mo, Ru, W) were prepared by impregnation method. Commercial Pt/C (46.7 wt%, TEC10E50E) purchased from Tanaka Kikinokogyo was impregnated with an aqueous solution containing each metal precursor, and then the solvent was evaporated. The modification amount was set at 7.7 at% of Pt. Also, Ru/Pt/C was prepared at different Ru modification amounts (Ru/(Pt+Ru) = 2.0, 4.0, 7.7, 11.1, 14.3 at%). The Ru/Pt/C catalysts are denoted as Ru/Pt/C (at%). All metal oxide modified catalysts were treated for 30 minutes at 573 K under H₂ flow before activity test. Pt/C (46.7 wt%, TEC10E50E) and Pt-Ru/C (Pt: 32.4 wt%, Ru: 16.8 wt%, TEC61E54) purchased from Tanaka Kikinokogyo were used as control catalysts.

The HOR activity was evaluated by linear sweep voltammetry (H₂ saturated 0.1 M NaOH, 298 K, 10 mV/s, 2500 rpm, iR free) using the rotating disc electrode method. The HOR activity was determined from the linear gradient in the micropolarization region (-10-10 mV) of the HOR curve using the approximate Butler-Volmer equation. Electrochemical specific surface area was calculated from Cu stripping charge (N₂ saturated 0.1 M H₂SO₄ including 0.005 M CuSO₄, 298 K, 10 mV/s). The surface composition ratio was also calculated by Cu stripping charge by utilizing the different stripping potentials on Pt (0.30-0.90 V) and Ru (0.30-0.50 V). Reversible hydrogen electrode (RHE) was used as the reference electrode. Nafion was used for binder, and the catalyst was applied on the disk electrode at 10 μg_{Pt}/cm_{disk}².

3. Results and discussion

Figure 1 shows the Pt-mass normalized activity (mass activity) of M/Pt/C (M = Ti, V, Ni, Zr, Nb, Mo, Ru, W) for HOR. All M/Pt/C exhibited higher the HOR activity than Pt/C, indicating that the activity of Pt/C was improved by modification of the metal oxides. In particular, Mo/Pt/C and Ru/Pt/C showed high specific activity, more than twice higher than Pt/C.

The modification amount of Ru/Pt/C was changed. Fig. 2 shows the mass activity and the surface-area-normalized activity (specific activity) of Ru/Pt/C, Pt/C, and Pt-Ru/C. Ru/Pt/C (7.7) was the highest activity and showed three times higher specific activity than Pt/C. Moreover, Ru/Pt/C (7.7) exhibited higher

activity than Pt-Ru alloy catalyst which was known as one of the most active catalysts in HOR under alkaline conditions¹.

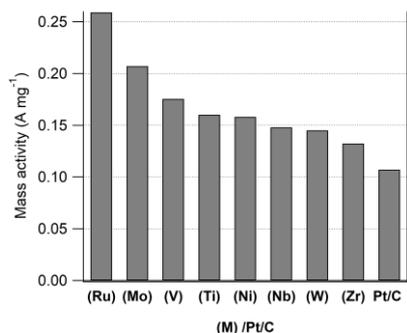


Figure 1. Mass activity of various metal oxide modified catalysts.

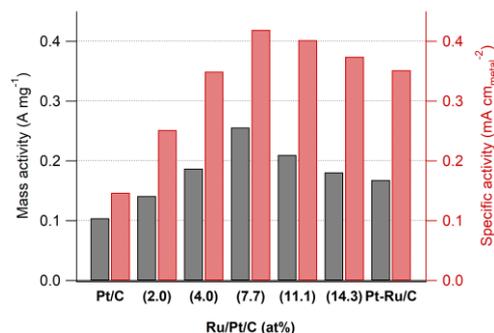


Figure 2. Mass activity and specific activity of Ru/Pt/C with various Ru modification amounts.

When Ru/Pt/C (7.7) was observed by TEM-EDS analysis (Fig. 3), Ru did not aggregate and was dispersed on Pt. From the XRD patterns (Fig. 4), no peak shift due to alloying or a peak derived from Ru was observed.

The difference in specific activity of Ru/Pt/C (Fig. 5) could be explained by the Ru/Pt surface composition ratio. Fig. 5 exhibits the correlation between the specific activity and the surface composition. The volcano-shaped correlation suggests that surface Pt-Ru pair sites cause enhanced the HOR activity, since surface Pt-Ru pair sites increases with the Ru modification amount, but decrease with too much Ru modification. According to the previous studies, the HOR kinetics in alkaline conditions was limited by the Volmer step $M-H_{ad} + OH^- \rightarrow M + H_2O + e^-$, where the reactive hydroxyl species (OH_{ad}) could promote this step.² Thus, Ru is considered to have a role of supplying reactive OH_{ad} to $M-H_{ad}$.²

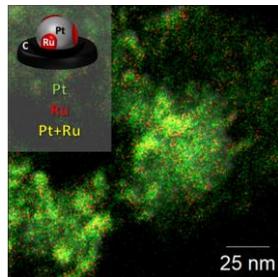


Figure 3. EDS mapping image of Ru/Pt/C (7.7).

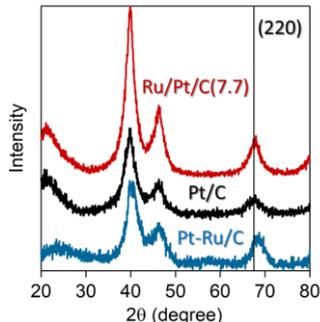


Figure 4. XRD patterns of Ru/Pt/C (7.7) and Pt/C, Pt-Ru/C.

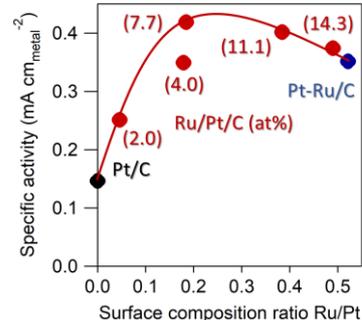


Figure 5. Specific activity of Ru/Pt/C and Pt/C, Pt-Ru/C

4. Conclusions

Various metal oxide modified catalysts M/Pt/C (M = Ti, V, Ni, Zr, Nb, Mo, Ru, W) were prepared by impregnation method. As a result of HOR activity test, it was suggested that all M/Pt/C exhibited higher activity than Pt/C, and the HOR activity of Pt/C was improved by modification of the metal oxides. When the modification amount of Ru was changed, the correlation was found between the HOR activity and the Ru/Pt surface composition. It was suggested that the HOR activity depends on the surface Pt-Ru pair sites.

References

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