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Electrochemical behavior of hydrophobic ionic liquids layer modified Pt/C catalyst

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Abstract

We examined to improve oxygen reduction reaction (ORR) activity of platinum carbon catalyst (Pt/C) used in polymer electrolyte fuel cells by surface modification with ionic liquids (ILs). Aprotic ILs with quaternary phosphonium cations were used. In addition, a mixture of the ILs and an acid with the same anion of the ILs were also examined. In this presentation, we will report the effect of protons on ORR at ILs modified Pt/catalyst surface.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are expected as one of the clean energy conversion systems, to achieve a sustainable society. Pt nanoparticles on carbon supports (Pt/C) are commonly used as a cathode catalyst for PEFCs, because of their high activity on oxygen reduction reaction (ORR). However, its durability during long term driving and high mass activity (MA) for ORR has not been sufficiently fulfilled at the present. It is required to improve the ORR activity and durability toward realizing a low-carbon hydrogen-based society. Pt/C-Solid catalysis with an ionic liquids layer (SCILL) catalysts has recently attracted much attention for their higher activity to enhance the bare catalyst [1)]. In our recent study [2)], we found that Pt/C-SCILL containing trace amounts of aprotic phosphonium ionic liquids (ILs) enhanced the ORR activity. However, Pt/C-SCILL with the excess amount of the ILs had lower ORR activity than the bare Pt/C but higher durability. In this presentation, we will report not only hydrophobicity and oxygen permeation rate for ILs but also proton conduction are important factors for ORR activity on Pt/C-SCILL catalysts.

2. Experiment

Quaternary phosphonium based ILs, tributyldodecylphosphonium bis(trifluoromethanesulfonyl)imide (P444(12)TFSA), were used for Pt/C-SCILL modified electrodes. 30wt% Pt/C catalysts were purchased from TKK. Pt/C-SCILL modified electrodes were prepared by dropping the ultrasonicated Pt/C catalyst suspension with ILs on mirror polished glassy carbon disk electrodes. Moreover, a mixtures of the ILs and bis(trifluoromethanesulfonyl)-imide (HTFSA) were also examined. The thickness of the ILs layer was calculated relative to the surface area of the carbon support. A Pt wire and a reversible hydrogen electrode (RHE) were used as counter and reference electrodes, respectively. Cyclic Voltammetry (CV) and linea sweep voltammetry (LSV) were carried out in 0.1 M $HClO_4$ solution under Ar (CV) or O_2 (LSV) atmosphere, respectively.

3. Results and discussion

Fig. 1 shows polarization curves at the Pt/C-SCILL modified electrodes. Broadened PtOx formation peaks observed in high potential region of the cyclic voltammograms (CVs) (inset) at both with (red line) and without (blue line) H^+ Pt/C-SCILL modified electrodes. The PtO reduction peak were observed in the high potential region was shifted to the high potential side compared to that of Pt/C modified electrodes without ILs. These results indicate that ILs improve hydrophobicity, which is not affected by the presence of protons in the ILs. In contrast, linear sweep voltammograms (LSVs) at Pt/C-SCILL modified electrodes showed different behavior with and without protons in ILs. LSVs at ILs with H^+ Pt/C-SCILL modified electrodes (red line) shifted toward higher potentials than at Pt/C modified electrodes (black lien), whereas modified with ILs without protons, the LSV (blue line) shifted to the lower potential side. Interestingly, different behaviors were also observed in the limiting current region around 0.4 V vs. RHE. ILs with H^+ Pt/C-SCILL modified electrodes obtained similar diffusion-limiting currents as those of bare Pt/C modified electrodes. However, for the ILs without H^+ Pt/C-SCILL modified electrodes, a somewhat smaller wave was observed. These results indicate that there is an influence of ILs on the transport of chemical species involved in ORR. Hydrophobicity and oxygen permeability do not significantly change between with and without H^+ in the ILs. Therefore, we consider that proton transport is the rate-determining step.

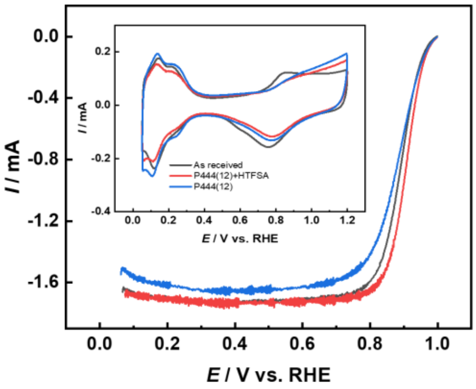

Fig. 1 Linear sweep voltammograms and (inset) cyclic voltammograms at (black) Pt/C modified and (red) P444(12)TFSA with HTFSA and (blue) P444(12)TFSA Pt/C-SCILL modified electrodes for ORR.

4. Conclusions

In this study, we show that ORR activity of Pt/C catalysts modified with hydrophobic ILs is improved by the presence of protons in ILs. Hydrophobic ILs interfered oxide formation on Pt surface. Pt/C catalyst modified with a mixture of ILs with protons source, such as acid, significantly increased ORR activity over ionic liquid unmodified catalysts. On the other hand, Pt/C modified only with ILs showed a decrease in ORR activity compared to the commercial catalyst. A decrease in diffusion limiting current was also observed at the same time. It is likely that proton transport, rather than O_2 transport, was the rate-determining factor. Optimization of proton transports in ILs was found to be necessary to enhance ORR activity for Pt/C-SCILL catalyst.

Acknowledgments

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References

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