**Operando X-ray Absorption Spectroscopic Study on the Effect of Ionic Liquid Coverage upon the Oxygen Reduction Reaction Activity of Pd-core Pt-shell Catalysts**

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1. **ABSTRACT**

This study provides evidence of the enhancement of the oxygen reduction reaction (ORR) activity of Pt/C and Pd-core Pt-shell catalysts upon ionic liquid modification. Under high potential at 1.15 V (vs. reversible hydrogen electrode), the lower coverage of the oxide species on the Pt surface modified with [7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD)][bis(trifluoromethylsulfonyl)imide (NTf2)] ionic liquid (IL) was confirmed by electrochemical analysis. **Operando** X-ray absorption spectra (XAS) of the ionic liquid-modified Pd-core Pt-shell catalyst displayed smaller 5d orbital vacancies than the naked catalyst. Shrinkage of Pt-Pt bond length was also displayed, indicating the suppression of oxidation. Thus, we conclude that the IL-modified systems are effective in avoiding the adsorption of oxide species on the Pt surface and improving the oxygen reduction activity.

**Keywords:** Polymer Electrolyte Membrane Fuel Cells, Oxygen Reduction Reaction, Ionic Liquid, **Operando** X-ray Absorption Spectroscopy

**Operando** X-ray Absorption Spectroscopy is a valuable tool for analyzing the electronic states and structural properties of catalysts. In this study, we used **Operando** XAS to investigate the effect of ionic liquid coverage upon the oxygen reduction reaction activity of Pd-core Pt-shell catalysts. The results showed that the IL-modified catalysts exhibited higher activity and stability compared to the naked catalyst. This study provides evidence of the enhancement of the oxygen reduction reaction (ORR) activity of Pt/C and Pd-core Pt-shell catalysts upon ionic liquid modification.

**Polymer electrolyte membrane fuel cells (PEFCs)** are considered attractive, principally because of their potential to control ORR activity on the Pt/C catalyst in both activity and stability. By systematically changing the side chain length of the imidazolium cations, ([C\(_n\)C\(_1\) im][bis(trifluoromethylsulfonyl)imide (NTf2)], n = 2, 4, 6, and 10), a clear dependence of Pt catalytic activity on ORR for side chain length was observed, with the highest activity obtained using medium chain length IL (n = 4). While the mechanism of the observed activity enhancement of IL remains elusive, the increased oxygen solubility, inhibition of Pt oxidation, and lower adsorption of nonreactive species are among the factors that enhance ORR activity. A recent study by Zhang et al. concluded that the presence of IL improved the electrochemical stability of Pt/C catalysts by suppressing the formation of oxygenated species and/or the initial oxidation of low-coordinating Pt sites. Although the addition of IL may improve the ORR activity, as described above, there are several theories regarding the cause.

**Operando** XAS is a valuable tool for analyzing the effects of changes in electronic states and local structure of the Pt alloy and core–shell catalyst, as reported in our previous papers. Currently, to the best of our knowledge, the electronic states and
local structural changes of the catalyst covered with IL have not been investigated. Improvements in ORR activity with the addition of ionic liquids have been reported in various ionic liquid systems for example; [MTBD][BETI],23,24 [CuCl] im][NTf$_2$],25 and [MTBD][NTf$_2$].30 We choose [MTBD][NTf$_2$] as one of the typical ionic liquids. In this study, to comprehensively understand the behavior of IL-modified catalytic systems, the electronic and local structures were analyzed using operando XAS. A Pd-core Pt-shell catalyst and [MTBD][NTf$_2$] was used as the model electrode and IL, respectively, to investigate the interaction between Pt and IL. The catalytic promotion effect of IL is discussed by combining the results of the electrochemical techniques and XAS.

2. Experimental

2.1 Reagents

A 30 wt% Pd/C catalyst was provided from Ishifuku Kinzoku Kogyo Co., Ltd. and a 30 wt% Pt/C catalyst (TEC10V30E) was purchased from Tanaka Kikinzoku Kogyo Co., Ltd. 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene ([MTBD]) (98 %) and lithium bis(trifluoromethylsulfonyl)imide ([NTf$_2$]) (99 %) were purchased from Sigma-Aldrich. All the chemicals were used as received without further purification.

2.2 Synthesis of [MTBD][NTf$_2$] IL

[MTBD][NTf$_2$] IL was synthesized following a procedure from the literature.30 Equal quantities of [MTBD] (33.9 mmol) and Li[NTf$_2$] (33.9 mmol) were individually dissolved in water at 0 °C. Then, 10.6 M HNO$_3$ was slowly added dropwise to the [MTBD] solution to form [MTBD][NO$_3$] until a neutral pH was obtained. Next, the Li[NTf$_2$] solution was slowly added to the [MTBD][NO$_3$] solution and [MTBD][NTf$_2$] IL was precipitated. The detailed scheme was illustrated in Fig. S1 in supporting information. The IL was washed several times with ultrapure water and then placed in a rotary evaporator at 60 °C for one day to remove residual water. The IL was further dried under high vacuum.

2.3 Preparation of the Pd-core Pt-shell catalyst by underpotential deposition of Cu (Cu-UPD)

Our previously reported method was used for producing the Pd-core Pt-shell catalyst. The Pd/C catalyst ink consisted of water-2-propanol (99.99%, Wako) in 2 : 3 ratio, and the loading of Pd/C was adjusted to 5 µg Pd cm$^{-2}$ by dropping 5 µL of the ink on a glassy carbon rotating disk electrode (GC RDE) (HOKUTO DENKO, area = 0.196 cm$^2$). The RDE was dried at 700rpm at 25 °C. Then, 5 wt% Nafion solution (Sigma-Aldrich) was casted at a thickness of 200 nm. A Pd-core Pt-shell catalyst (denoted as Pt/Pd/C) was prepared by depositing Pt through the galvanic displacement of the Cu monolayer. Under-potential deposition (UPD) measurements were carried out in a three-electrode cell. A Pt counter electrode and reference electrode, respectively. Next, the deposition of Cu was conducted under 10 mM CuSO$_4$ in a 0.1 M HClO$_4$ solution, and RDE was rinsed with N$_2$-saturated water and soaked with a N$_2$ saturated 5.0 mM K$_2$PtCl$_4$. Figure S2 of the Supporting Information shows that the cyclic voltammogram (CV) during underpotential deposition was typical for the underpotential deposition of Cu on Pd.35 After completely replacing Cu with Pt in 8 min, the RDE was rinsed again with N$_2$-saturated water. A commercial available Pt/C catalyst (TEC10V30E, Tanaka Kikinzoku Kogyo) was used as a reference. Finally, the synthesized [MTBD][NTf$_2$] IL (1 µL) was drop-casted onto the electrode. For Pt/C and IL-modified Pt/Pd/C, the electrochemical surface area was calculated from hydrogen underpotential deposition region from 0.05 to 0.40 V (vs. RHE). For Pt/Pd/C and IL-modified Pt/Pd/C, the hydrogen deposition potential from 0.1 to 0.4 V (vs. RHE) was used for estimation of the electrochemical surface area because the hydrogen storage occurs under 0.1 V (vs. RHE).

2.4 Transmission Electron Microscopy (TEM) observations

Transmission electron microscope (TEM), scanning transmission electron microscope and elemental mapping images was obtained by using JEM-F200 and SDD (Silicon drift detector, JEOL Ltd.) at 200 kV.

2.5 Electrochemical measurement

ORR activity measurements were carried out in a three-electrode cell at 25 °C. The counter electrode was a Pt mesh, and the reference electrode was RHE. Prior to the catalyst activity measurements, the potential was cycled 50 times between 0.02 and 1.0 V (vs. RHE) at 200 mV s$^{-1}$ to obtain a stable cyclic voltammogram (CV) in N$_2$-saturated 0.1 M HClO$_4$. The final CV was obtained at 50 mV s$^{-1}$. After the CV measurements, the electrolyte was saturated in O$_2$. Then, hydrodynamic voltammograms were recorded between 0.2 and 1.2 V vs. RHE at 10 mV s$^{-1}$ at rotation speeds ranging from 100 rpm to 2500 rpm. The data regarding oxygen reduction for all materials were analyzed using the Koutechy-Levich (K-L) equation at 0.9 V (vs. RHE).

2.6 Operando XAS (X-ray absorption spectra) measurement

Operando XAS measurements for Pt $L_{III}$-edge of Pt/C and Pd-core Pt-shell catalysts were performed using a home-made operando cell at BL37XU and BL14B2 of SPring-8, Hyogo, Japan. A Si 111 monochromator and a Pt or Rh mirror were used to obtain collimated and monochromatic X-rays. Prior to the experiments, the samples were electrochemically cleaned by CV in the range from 0.0 to 1.1 V (vs. RHE). Data processing was analyzed using ATHENA and ARTEMIS, a suite of IFEFFIT software programs.36

3. Results and Discussions

3.1 TEM observations

The high-resolution TEM images of the prepared catalysts are shown in Fig. 1. Energy-dispersive X-ray (EDX) mapping of Pd and Pt (Fig. 1a) confirmed the successful formation of the Pd-core Pt-shell structure through Cu-UPD. According to Fig. 1b, the Pt nanoparticles were highly dispersed on the carbon support. The black arrow in Fig. 1c shows the IL covering the surface of the catalyst. The thickness of IL covering the catalyst was about 3 nm. Figure S3a indicates the scanning transmission electron microscope image. The particle size distribution (Fig. S3b) was made by counting 200 particles from the Fig. 3a and the average particle size of Pt/Pd/C was estimated to 2.7 nm.

3.2 Electrochemical measurements

The electrochemical properties of the Pt/C and Pt/Pd/C catalyst [MTBD][NTf$_2$] IL-modified systems were studied and compared with those without IL. Figures 2a and 2b show CV curves for Pt/C and Pt/Pd/C at 25 °C in a 0.1 M N$_2$-saturated HClO$_4$ solution. Both catalysts showed the characteristic features of H adsorption on Pt in the potential region from 0.05 to 0.4 V (vs. RHE) and the formation of Pt oxide species over 0.6 V (vs. RHE). Comparing the CVs of Pt/C and Pt/Pd/C with/without IL, the H adsorption peaks for the IL-modified system were slightly suppressed, and the peaks shifted to a lower potential range, which agreed with previous reports.23,37 These results suggest that the presence of IL suppresses the access of H on the Pt surface by reducing the bonding strength of Pt and H through a ligand effect35,38 and/or the occupation of certain Pt sites by IL molecules.28 Figures 2a and 2b also show the smaller coverage of the oxide species on Pt when modified with [MTBD][NTf$_2$] IL, confirming that the IL-modified system suppressed the oxidation of Pt. It is well known that an excessively strong Pt-O bonding strength
saturated 0.1 M HClO₄ at 25 °C. Therefore, the weakened Pt-O interaction is expected to improve the ORR kinetics when modified with IL. The influence of IL modification on the ORR specific activity is compared in Fig. 3 and Table S1 shows the electrochemical surface area and the specific activity for each catalyst. For Pt/C, the estimated electrochemical surface area was decreased 21% while the specific activity was increased 207%. For Pt/Pd/C, the estimated electrochemical surface area was decreased about 6% while the specific activity was increased 131%. Therefore, the increase in ORR activity is not due to the underestimation of the electrochemical surface area but due to the IL addition effect, which indicates that the intrinsic ORR activity is actually improved. Linear sweep voltammograms (LSVs) at 1600 rpm for Pt/C and Pt/Pd/C are also illustrated in Figs. S4a and S4b of the Supporting Information, and their voltammograms clearly indicate the positive shifts upon modification with the IL. As the IL-modified Pt/Pd/C catalyst have a better oxygen reduction reaction activity, the onset potential showed the more positive shift than Pt/Pd/C. This result was also supported by the cyclic voltammogram in Fig. 2 since the oxidation peak at 0.8 V (vs. RHE) was suppressed by IL modification. The reason of this activity improvement is discussed on operando X-ray absorption spectroscopy section. The Tafel plots and slopes of Pt/C and Pt/Pd/C were shown in Fig. S5. They showed about 60 mV/dec and 120 mV/dec respectively for low and high current density region, which was characteristic to Pt-based catalysts. As there were no obvious differences in Tafel slope between Pt/C and Pt/Pd/C regardless of IL, the reaction mechanism was not changed by IL modification, which was also identical to the previous report. The impact of IL on ORR activity was different between Pt/C and Pt/Pd/C. The cause was not determined; however, these results may be partially due to the greater quantity of free active sites on the IL-modified system and the resulting accelerated ORR kinetics.

Figure 3. Specific activities of Pt/C and Pt/Pd/C with/without [MTBD][NTf₂] IL in O₂-saturated 0.1 M HClO₄ at 10 mV s⁻¹. Specific activities were estimated using the Koutechy-Levich (K-L) equation at 0.9 V (vs. RHE).

Figure 1. TEM images and EDX mapping for (a, b) Pd-core Pt-shell catalyst and (c) IL-modified Pd-core Pt-shell catalyst; The black arrow indicates the IL covering the surface of the catalyst.

Figure 2. Cyclic Voltammograms (CVs) for (a) Pt/C and (b) Pt/Pd/C (black line) covered with [MTBD][NTf₂] IL (red line) in N₂-saturated 0.1 M HClO₄ at 25 °C.

3.3 Operando XAS measurement
To understand the behavior of IL-modified catalytic systems, the electronic state of Pt was analyzed by operando XAS. Pt L₃-edge X-ray absorption near-edge spectra (XANES) for Pt/Pd/C and IL-modified Pt/Pd/C at 0.50, 0.85, and 1.15 V (vs. RHE) are shown in Figs. 4a and 4c. This provides a different insight into the reaction mechanism through electronic structural changes induced by Pt oxidation. In addition, the difference spectra from 0.5 V (vs. RHE) are shown in Figs. 4b and 4d. The clear increase in the white line of Pt/Pd/C (Fig. 4a) suggested an increase in unoccupied Pt 5d states due to charge transfer from Pt to the adsorbed oxygen species. In contrast, the IL-modified Pt/Pd/C (Fig. 4c) shows suppression of oxidation when compared with Pt/Pd/C. These results are in agreement with those of the electrochemical measurement described above. The oxygen species adsorbed on the Pt were analyzed based on the difference spectra (Δdiff XANES), as shown in Figs. 4b and 4d. There was not much difference in peak position between Pt/Pd/C and IL-modified Pt/Pd/C probably because the adsorbed species
Figure 4. Pt LIII-edge XANES of Pt/Pd/C at 0.50, 0.85 and 1.15 V (vs. RHE) in O2-saturated 0.1 M HClO4 (a) without and (c) with IL. Panels (b) and (d) indicate the difference spectra from 0.5 V (vs. RHE) respectively for without and with IL. (e) The potential dependence of 5d orbital vacancy of Pt/Pd/C without (○) and with (●) IL.

were nearly the same regardless of the presence of IL. Figure 4e shows 5d orbital vacancies evaluated by using Mansour’s method, which is a quantitative technique for determining the number of unoccupied 5d electron states in Pt. In Pt/Pd/C, the 5d orbital increased with potential and reached a value of 0.42 and 0.33, respectively, for without and with IL. Density functional theory studies have predicted that the quantity of charge transfer from Pt to oxygen species was 0.37 when atomic oxygen was adsorbed at face-centered cubic (fcc) hollow sites with full coverage. The 5d orbital vacancy of Pt/Pd/C was slightly larger than DFT calculation, which might be because of the further oxidation of Pt such as formation of Pt oxides. On the other hand, IL-modified Pt/Pd/C showed a lower value than Pt/Pd/C because of the lower coverage of oxide species.

The local structure around Pt in Pt/Pd/C was investigated through extended X-ray absorption spectra (EXAFS). The non-phase-shift-corrected Fourier-transformed EXAFS at 0.50, 0.85, and 1.15 V (vs. RHE) are shown in Figs. 5a and 5b. The features at 0.50 V indicated the typical Pd core Pt-shell structure reported elsewhere regardless of the IL. At 0.85 V, the peak at 1.44 Å, corresponding to the Pt-O bond, was observed for Pt/Pd/C without IL, and the peak intensity of the Pt-O bond was further increased at 1.15 V, indicating that the coverage of the oxygen species increased (Fig. 5a). In contrast, the Pt-O bond could not be observed until 1.15 V for the IL-modified system (Fig. 5b). These results also suggested that the adsorption of oxygen species in Pt/Pd/C was suppressed by the coverage of the IL, as expected from the XANES and electrochemical measurements. In addition, the estimated Pt-Pt distance (Fig. 5c) of IL-modified Pt/Pd/C was relatively smaller than that of naked Pt/Pd/C at any potential. This shrinkage might be caused by adsorption of IL on the Pt surface and charge transfer from IL to Pt, the so-called ligand effect, and this compressive Pt-Pt bond-induced structure had an advantage for the ORR kinetics. In other words, our results provide clear evidence that IL suppresses the adsorption of oxygen species on the Pt surface and improves the ORR activity.

4. Conclusion

This study provides evidence that the activity of Pt/C and Pt/Pd/C catalysts for ORR can be greatly enhanced by [MTBD][NTf2] IL modification. Electrochemical analysis revealed lower coverage of the oxide species on the Pt surface when modified with [MTBD][NTf2] IL. This suggests that the IL-modified system suppressed the oxidation of Pt. According to operando XAS of Pt/Pd/C, the increase in unoccupied Pt 5d states at higher potentials due to charge transfer from Pt to adsorbed oxygen species and the IL-modified Pt/Pd/C showed suppression of oxidation. These results provide clear evidence that IL suppresses the oxidation of Pt and improves the ORR activity. Thus, we anticipate that IL-modified systems are highly promising for future fuel cell applications.
5. The potential dependence of Pt 1L3-edge Fourier-transformed EXAFS (Δk range: 3.0–12.5 Å⁻¹) for Pt/Pd/C (a) without and (b) with IL, and (c) Pt-Pt bond distance of Pt/Pd/C without (○) and with (●) IL.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.20-00122.

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