Enhancement of Ammonia Oxidation Activity over Y₂O₃-Modified Platinum Surface: Promotion of NH_{2,ad} Dimerization Process

*Yu Katayama, Takeou Okanishi, Hiroki Muroyama, Toshiaki Matsui, Koichi Eguchi**

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto
University, Kyoto 615-8510, Japan

KEYWORDS: Ammonia oxidation, Electrocatalyst, Yttrium oxide, *in situ* ATR-IR
spectroscopy, Alkaline electrolyte

ABSTRACT

In recent years, increasing attention has been focused on the utilization of ammonia as a fuel for anion exchange membrane fuel cells (AEMFCs) due to the significant development of anion exchange membranes (AEMs). Although the improvement in catalytic activity for ammonia oxidation reaction was achieved for some Pt-based electrocatalysts, no effective methods were established to enhance the tolerance toward the catalyst poisoning, which is known as the major issue for the utilization of ammonia as a fuel. In this paper, first, the additive effect of Y_2O_3 was intensely investigated by *in situ* ATR-IR spectroscopy. For the Y_2O_3 -modified Pt surface, the IR band area of $\text{N}_2\text{H}_{4,\text{ad}}$ species, which is the intermediate species of ammonia oxidation reaction, was distinctively increased, suggesting the promotion of $\text{NH}_{2,\text{ad}}$ dimerization process. This effect of Y_2O_3 was then accurately clarified by applying the Y_2O_3 modification for Pd surface. Despite that Pd was inactive for the $\text{NH}_{2,\text{ad}}$ dimerization reaction, the IR band of $\text{N}_2\text{H}_{4,\text{ad}}$ species was clearly detected only in the case of Y_2O_3 -modified Pd surface. This is the strong evidence that the Y_2O_3 additive itself promotes the $\text{NH}_{2,\text{ad}}$ dimerization reaction. Furthermore, the electrocatalytic performance of Y_2O_3 -modified Pt/C electrocatalyst was evaluated using the commercial AEMFC system. A two-fold increase in both maximum power density and tolerance toward the catalyst poisoning was confirmed as compared to the cell with the conventional Pt/C electrocatalyst. These results clearly show the applicability of our catalyst design strategy to improve the performance of the real-world electrocatalyst for the ammonia oxidation reaction.

TEXT

1. Introduction

Hydrogen is now generally accepted as the typical fuel for fuel cells, but its physical property has limited the popularization of fuel cells in many cases. To overcome this problem, many hydrogen carriers have been proposed as alternative fuels^{1 2}. Among the hydrogen carriers, ammonia is one of the promising candidates due to its low production cost, ease in liquefaction at ambient temperatures, high volumetric energy density, and no carbon content^{3 4}. However, in fuel cells operated under acidic conditions, such as polymer electrolyte fuel cells (PEFCs), ammonia cannot be used as a fuel because the cell performance significantly deteriorated even with a trace amount of ammonia in an anode fuel^{5 6}. In contrast, ammonia can be electrochemically oxidized in an alkaline electrolyte. Moreover, the oxygen reduction reaction (ORR), which is known as a cathode reaction in fuel cell systems, can proceed over nonprecious metal catalysts in alkaline electrolytes^{7 8 9 10}. The performance of alkaline anion exchange membranes (AEMs) has improved significantly in recent years, which has gained the potential and the importance of ammonia as a fuel. Unlike KOH-based electrolytes, which suffer from the decrease in conductivity caused by the formation of carbonate salts via the chemical reaction between KOH and CO₂ in the air^{7 11}, the formation of those carbonate salts is suppressed in AEMs¹². Moreover, in anion exchange membrane fuel cells (AEMFCs), OH⁻ generated in the cathode during the operation purges a portion of the HCO₃⁻ and CO₃²⁻ derived from CO₂, leading to the enhancement of cell performance^{13 14}. Therefore, AEMs are promising electrolytes for direct ammonia fuel cells.

The most widely accepted reaction mechanism for ammonia oxidation over Pt electrode was proposed by Gerischer and Mauerer¹⁵;

where $x = 1$ or 2 and $y = 1$ or 2 .

This reaction mechanism has been supported by the coulometric experiment ¹⁶, differential electrochemical mass spectroscopy (DEMS) ^{17 18}, surface enhanced Raman spectroscopy (SERS) ^{19 20}, and *in situ* attenuated total reflection infrared (ATR-IR) spectroscopy. ²¹ According to this mechanism, $\text{NH}_{2,ad}$ and NH_{ad} species are produced on the Pt electrode by the sequential ammonia dehydrogenation with the aid of OH_{ad} species, and subsequently combined each other through the catalytic reaction to form $\text{N}_2\text{H}_{x+y,ad}$ ($x = 1$ or 2 , $y = 1$ or 2). Finally, the further dehydrogenation of $\text{N}_2\text{H}_{x+y,ad}$ leads to the formation of N_2 . Unfortunately, it is known that the formation of poisonous species proceeds in parallel with the N_2 formation reaction, which is the major disadvantages of ammonia fuel. Gerischer *et al.* also suggested the production of atomic nitrogen adspecies (N_{ad}) via the dehydrogenation of NH_{ad} species.

Although this N_{ad} species has expected to be a surface poisoning species on Pt electrode, no experimental evidences have been reported yet. On the other hand, the formation of NO and NO_2 species was suggested in several studies ^{17 16 22}. These species remained on the surface once it has been formed, even in the high potential region. In any cases, the important thing is that the

poisonous species should be generated via the oxidation of the N-monomer species, $\text{NH}_{x,\text{ad}}$. This tells us that the selectivity of formation of N-dimer species ($\text{N}_2\text{H}_{x+y,\text{ad}}$) is the key factor to promote the ammonia oxidation reaction over Pt electrode. Recently, the contribution of the OH_{ad} species to ammonia oxidation was clarified²³. Moreover, electrocatalysts with superior activity for ammonia oxidation reaction were successfully developed by focusing on the OH adsorption behavior of the catalyst surface²⁴. The emphasis here is that the superior electrocatalytic activity was derived from the oxide additives, which were used as surface modifiers of electrodes. At the current state, however, no effective methods have been established to prevent or reduce the formation of the poisonous species.

In this paper, then, the Pt-based catalysts with high tolerance toward poisonous species during ammonia oxidation reaction were developed by focusing on the enhancement of $\text{NH}_{2,\text{ad}}$ dimerization step. Many researches including a combined first-principles molecular dynamics/density functional theory study have suggested that the rate determining step of the electrochemical oxidation of ammonia is the catalytic dimerization of $\text{NH}_{2,\text{ad}}$ species forming hydrazine like $\text{N}_2\text{H}_{4,\text{ad}}$ species^{25 26}. Therefore, to improve both activity and poisoning resistance of electrocatalysts, a totally new concept must be realized. In this study, we applied an electrode surface modification approach to introduce the secondary functional sites specifically for the promotion of the catalytic $\text{NH}_{2,\text{ad}}$ dimerization process. In our previous study, the Y_2O_3 -modified Pt electrocatalyst showed the distinct tolerance toward the catalyst poisoning in an alkaline aqueous solution²³. Therefore, Y_2O_3 was selected as an additive species, and its additive effect on the catalytic activity of Pt was investigated. First we conducted *in situ* ATR-FTIR spectroscopy to clarify the additive effect of Y_2O_3 through the observation of surface adsorbed species on the Pt surface. Moreover, the Pd substrate known as an inactive material for the

NH_{2,ad} dimerization was applied, and *in situ* ATR-FTIR measurement was conducted to accurately clarify the effect of Y₂O₃ additive itself upon the NH_{2,ad} dimerization process. Finally, by using direct ammonia-fueled anion exchange membrane fuel cells (AEMFCs), the performance of Y₂O₃-modified Pt/C anode was compared to that of the conventional Pt/C anode in order to emphasize the validity of our catalyst design strategy.

2. Experimental

2.1. Additive Preparation

The aqueous dispersant of Y₂O₃ containing solution was prepared by adding the as-received Y₂O₃ (6.75 mg, Wako Pure Chemical) to ultrapure water (Milipore MiliQ), and then ultrasonically dispersed for 2 h. The anion exchange ionomer solution (AS-4, Tokuyama Corp., diluted to 1wt% solution with ethanol, 0.7 mL) was added to the resultant dispersion liquid (0.75 mL) and ultrasonically dispersed for 1 h to obtain the Y₂O₃-containing ionomer solution.

2.2. Electrocatalyst Preparation

The Pt working electrode used for *in situ* ATR-IR measurement was a thin film (ca. 50 nm) formed on the total reflecting plane of a hemispherical Si prism (radius 22 mm) by the electroless deposition method^{27 28}. First of all, the base plane of the Si prism was etched by contacting with 40% NH₄F solution for a minute. Then, palladium was deposited on the base plane with 1% HF–1 mM PdCl₂ for 5 min at room temperature. After rinsing with water, platinum or palladium deposition was carried out by contacting with the Pt or Pd plating solution at 55°C for 12 min.

The Pt plating solution was prepared by mixing ELECTROLESS Pt 100 basic solution (30 mL, Electroplating Engineering of Japan Ltd.), ELECTROLESS Pt 100 reducing solution (0.6 mL), 28% NH_3 solution (Wako Pure Chemical), and ultrapure water. The Pd plating solution was prepared by mixing ELECTROLESS Pd 1000 (30 mL, Electroplating Engineering of Japan Ltd.), ELECTROLESS Pd 2000S (0.6 mL), and ultrapure water. For ionomer-coated and Y_2O_3 -modified Pt or Pd prisms, the ionomer solution (AS-4, Tokuyama Corp., diluted to 0.5wt% solution with ethanol and ultrapure water, 50 μL) and the obtained Y_2O_3 -containing ionomer solution (50 μL) were dropped onto the Pt or Pd prism, respectively.

Two types of Pt electrocatalysts were used for fuel cell tests. For the conventional Pt electrocatalyst, the commercially available Pt/C catalyst (Tanaka Kikinzoku Kogyo, TEC10E50E, 46.1 wt% Pt on Ketjen Black) was used. Y_2O_3 -modified Pt/C was prepared by simply mixing the as-received Y_2O_3 powder with the above mentioned Pt/C catalyst. In this case, the weight ratio of Pt/C to Y_2O_3 was controlled to be 2.0.

2.3. In situ ATR-IR Measurement

Details of ATR-IR spectroscopy were described in elsewhere^{29 30 31 32}. For *in situ* ATR-IR measurements, ionomer-coated Pt, Y_2O_3 -modified Pt, ionomer-coated Pd, and Y_2O_3 -modified Pd prisms were used. The prism was mounted in a spectro-electrochemical three electrode cell with an Ag/AgCl reference electrode and a platinum wire counter electrode. The cell was then placed in a self-made reflection optics at an incident angle of 70° as shown in the literature²⁷. A Fourier transform infrared spectrometer equipped with a MCT detector (NICOLET8700, Thermo Fisher Scientific) was employed for *in situ* ATR-IR measurements. The optical path was fully replaced

with N₂ gas. The electrolyte solutions were prepared by mixing 28wt% NH₃ solution (Wako Pure Chemical) with KOH (Sigma–Aldrich, >85 wt%) and ultrapure water. After deoxygenation of the electrolyte solution by purging Ar, the prism surface was cleaned by cycling the potential between 0.05 and 0.90 V *vs.* reversible hydrogen electrode (RHE). For electrochemical measurements, cyclic voltammetry, linear sweep voltammetry, and chronoamperometry were conducted at room temperature by using HSV-100 (Hokuto Denko). All potentials in this paper were converted to the potential versus RHE. The electrochemical surface area (ECSA) for Pt-based electrocatalysts was calculated from cyclic voltammograms recorded in the Ar purged electrolyte by integrating the charge in the hydrogen adsorption/desorption region, in the range of 0.05–0.45 V *vs.* RHE. For Pd-based electrocatalysts, the ECSA was calculated from cyclic voltammograms recorded in the Ar purged electrolyte by integrating the charge from PdO reduction³³. The current density expressed was normalized by ECSA (expressed as A cm⁻²_{ECSA}). All spectra are shown in the absorbance units defined as $\log(I_0/I)$, where I_0 and I represent the intensities of the spectra at reference and sample potentials, respectively. The reference spectrum I_0 was measured at 0.05 V in the blank KOH solution. The ATR-IR spectra below 1200 cm⁻¹ had poor signal-to-noise ratio (S/N) due to the strong IR absorption by the Si prism and thus the results above 1200 cm⁻¹ were reported.

2.4. Fuel cell operation

The basic properties of the AEM (A201, Tokuyama) used in this study have been already described³⁴. A commercially available Pt/C catalyst described in section 2.2 was applied to the cathode in all cases, while the anode was composed of either a Pt/C or a Y₂O₃-modified Pt/C

catalyst. A catalyst slurry was prepared by mixing each catalyst with the anion exchange ionomer solution such that the weight ratio of the ionomer content to carbon was 0.8 for both anode and cathode. The slurry was directly screen-printed on the membrane. The geometric electrode area was 1.0 cm^2 ($1.0\text{ cm} \times 1.0\text{ cm}$), and the Pt loadings were set at 0.5 mg cm^{-2} for both electrodes. A membrane electrode assembly (MEA) was constructed by sandwiching the catalyst-coated membrane between two microporous gas diffusion layers (24BC, SGL). The MEA was mounted in a single-cell holder composed of two carbon separator plates with ribbed single serpentine flow channels. The cells were operated at 50°C and ambient pressure under high humidity conditions (95% relative humidity (RH) for both electrodes). Humidified H_2 or humidified 50% NH_3 –50% N_2 was fed to the anode, and O_2 to the cathode. The flow rate for all of the feed gases was 100 mL min^{-1} . The obtained current–voltage characteristics were measured at a scanning rate of 10 mV s^{-1} using a Solartron 1470E potentiostat.

3. Results and discussion

3.1. Characterization of electrocatalysts

In the beginning, cyclic voltammograms (CVs) of ionomer-coated and Y_2O_3 -modified Pt/Si electrodes in 1 M KOH were compared (Figure 1). As reported previously³⁵, the hydrogen adsorption/desorption was observed in the potential range of 0.05–0.45 V vs. RHE for the Pt surface. The voltammetric responses of both ionomer-coated and Y_2O_3 -modified Pt/Si electrodes were almost the same, indicating that the bond strength and/or adsorption enthalpy of Pt-H_{ad} were not affected by the Y_2O_3 modification. After the double-layer capacitance appeared in the potential range of 0.45–0.70 V, a small pseudocapacitance ascribable to the OH adsorption was

observed at 0.70–0.85 V. As is the case of hydrogen desorption, the change in Pt-OH_{ad} energy by the addition of Y₂O₃ can be negligible.

Figure 2 displays the time resolved IR spectra of the Y₂O₃-modified Pt surface acquired simultaneously with the linear sweep voltammogram (LSV) in 1 M KOH. The negative-going bands at 1616 cm⁻¹ and 1226 cm⁻¹ can be assigned to the bending mode of H-O-H^{36 27} from interfacial water and the stretching mode of Si-O-Si^{37 38} from Si prism, respectively. Note that these assignments and adsorption behavior of the surface adsorbed species were not affected by the Y₂O₃ modification (see Fig. S1).

3.2. Effect of Y₂O₃ additive on ammonia oxidation behavior

In situ ATR-IR spectroscopy was conducted in the presence of 0.1 M NH₃ in 1 M KOH to clarify the effect of Y₂O₃ modification on ammonia oxidation behavior. In Fig. 3, the peak current density increased for Y₂O₃-modified Pt/Si compared with ionomer-coated Pt/Si, indicating the enhancement in activity for electrochemical ammonia oxidation. For the time-resolved IR spectra of Y₂O₃-modified Pt surface in the presence of NH₃, five distinctive bands can be observed (Figure 4). The potential dependencies of these bands were consistent with those in the previous report, and their assignment has been already clarified^{21 24}. Therefore, the bands at *ca.* 1670 cm⁻¹, *ca.* 1510 cm⁻¹, and *ca.* 1270 cm⁻¹ can be ascribable to the vibrational modes of NH_{3,ad}, NO_{ad}, and N₂H_{4,ad} species, respectively. It is important to point out that the bands observed over the Y₂O₃-modified Pt surface were almost the same as those of the ionomer-coated Pt surface, suggesting that the ammonia oxidation mechanism itself remained unchanged even in the case of Y₂O₃ modified surface (see Fig. S2).

The potential dependence of the band area clearly indicated the effect of Y_2O_3 additive on ammonia oxidation reaction (Fig. 5). The band area shown in Fig. 5 was normalized by the same method used in our previous study²⁴. For the simplification, two factors ((i) the amount of the adsorbed species and (ii) the degree of surface enhancement effect of each prism) were considered to normalize the band area of two prisms. The procedure used in this study was briefly summarized as follows; first, the amount of CO_{ad} over each prism was calculated by using the CO stripping voltammetry. According to the previous studies, IR band area and surface coverage exhibit the linear relationship³⁹⁻⁴⁰. Therefore, by combining the calculated CO_{ad} amount and the CO_{ad} band area taken simultaneously with the CO stripping voltammetry, a coefficient reflecting the degree of surface enhancement effect of each prism can be obtained. The band area data shown in Fig. 5 were normalized by using the resultant coefficient. Although this calculation is a simple approach, it is still enough to clarify the phenomena over these prisms. To make sure the validity of this calculation, the band area for $\text{NH}_{3,\text{ad}}$ at 0.05 V, which is closely related to the amount of H_{ad} species in the KOH solution, was compared to the ECSA for each prism¹⁸. The ratio of the ECSA for Y_2O_3 -modified Pt/Si to ionomer coated Pt/Si was $9.63 \text{ cm}^2/7.10 \text{ cm}^2 = 1.35$, which matched well with the ratio of the normalized band area of $\text{NH}_{3,\text{ad}}$ for Y_2O_3 -modified Pt/Si to ionomer-coated Pt/Si, $1.39/1.04=1.34$. In addition, the potential dependencies of $\text{NH}_{3,\text{ad}}$, $\text{N}_2\text{H}_{4,\text{ad}}$, and NO_{ad} for ionomer-coated Pt/Si corresponded well with those in the previous studies (Fig. 5 (a))²¹⁻²⁴. That is, the ammonia oxidation began with the adsorption of NH_3 , followed by the sequential dehydrogenation to form N_2H_4 intermediate, which was accompanied by a reduction in the amount of absorbed NH_3 . When the potential reached to *ca.* 0.45 V or more, the oxidation reaction of $\text{NH}_{3,\text{ad}}$ and $\text{N}_2\text{H}_{4,\text{ad}}$ species was initiated. In the case of Y_2O_3 -modified Pt/Si, the band area of $\text{N}_2\text{H}_{4,\text{ad}}$ increased significantly though the

potential dependency was similar to that of ionomer-coated Pt/Si . To be more precise, the band area of $\text{N}_2\text{H}_{4,\text{ad}}$ increased by a factor of 2.4, while the band area of NO_{ad} was only a 1.4-fold increase. This distinct increment of the $\text{N}_2\text{H}_{4,\text{ad}}$ amount over Y_2O_3 -modified Pt/Si suggested the promotion of $\text{NH}_{2,\text{ad}}$ dimerization process (Reaction 4) by the Y_2O_3 additive.

3.3. Role of Y_2O_3 additive on $\text{NH}_{2,\text{ad}}$ dimerization reaction

To further clarify the role of Y_2O_3 additive on $\text{NH}_{2,\text{ad}}$ dimerization process, *in situ* ATR-IR measurements were conducted for both ionomer-coated and Y_2O_3 -modified Pd surfaces. Here, Pd was selected because many previous papers claimed that Pd itself did not have the catalytic activity toward the $\text{NH}_{2,\text{ad}}$ dimerization process^{41 19 42 18}. In addition, recent first principle study revealed that the Pd surface has the significantly higher $\text{N}_2\text{H}_{4,\text{ad}}$ formation barrier than the Pt surface despite the binding characteristics of $\text{N}_2\text{H}_{4,\text{ad}}$ species are similar²⁶. Therefore, by using Pd as a substrate, the role of Y_2O_3 additive on $\text{NH}_{2,\text{ad}}$ dimerization process can be accurately evaluated. Figure 6 shows linear sweep voltammograms (LSVs) of ionomer-coated Pd/Si and Y_2O_3 -modified Pd/Si electrodes. There was no obvious change in the voltammogram waveform for the Y_2O_3 -modified electrode in 1 M KOH electrolyte. This result suggests that the Y_2O_3 additive did not affect the bond strength and/or the adsorption enthalpy of Pd- H_{ad} and Pd- OH_{ad} , as was the case in the Pt surface. However, in 1 M KOH–0.1 M NH_3 , the new oxidation peak appeared at *ca.* 0.3 V by the Y_2O_3 modification, suggesting the contribution of Y_2O_3 additive on the reaction in the presence of NH_3 . Figure 7 represents the ATR-IR spectra taken simultaneously with LSV in 1 M KOH (Fig. 6(a)). According to the previous study, the bands at 1220 cm^{-1} and 1621 cm^{-1} observed in Fig. 7 were ascribable to Si-O-Si and $\text{H}_2\text{O}_{\text{ad}}$ species,

respectively ⁴³. As compared to the result for Pt surface (Fig. 2), the $\text{H}_2\text{O}_{\text{ad}}$ peak was shifted only 5 cm^{-1} , which suggested that the assignment for Pt surface can be directly applicable to that for Pd surface. Based on this assumption, the band assignment of IR spectra of the Pd surface in 1 M KOH–0.1 M NH_3 was determined (Fig. 8). The bands at *ca.* 1670 cm^{-1} and *ca.* 1520 cm^{-1} were corresponded to $\text{NH}_{3,\text{ad}}$ and NO_{ad} , respectively. It should be noted here that no band was observed at around 1270 cm^{-1} , where the band corresponds to the $\text{N}_2\text{H}_{4,\text{ad}}$ species expected to appear. It is difficult to consider that only the $\text{N}_2\text{H}_{4,\text{ad}}$ band shows a large band shift on Pd surface as compared to Pt surface. Therefore, this result indicates that in the case of Pd surface, no $\text{N}_2\text{H}_{4,\text{ad}}$ species was produced during the ammonia oxidation reaction. In addition, this conclusion matches well with the results of many aforementioned previous studies. In the case of the Y_2O_3 -modified Pd surface, the resultant band positions of Si-O-Si, $\text{H}_2\text{O}_{\text{ad}}$, $\text{NH}_{3,\text{ad}}$, and NO_{ad} were almost the same to those over Pd surface (Fig. 9). Moreover, the new band appeared at *ca.* 1270 cm^{-1} , where the $\text{N}_2\text{H}_{4,\text{ad}}$ band was observed for Pt surface. Because the Y_2O_3 modification did not affect the wavenumber, this band can be ascribable to the $\text{N}_2\text{H}_{4,\text{ad}}$ band. Comparing the results shown in Figs. 8 and 9, it was obvious that Y_2O_3 additive itself had the activity toward the $\text{NH}_{2,\text{ad}}$ dimerization reaction.

The characteristic change in catalytic behavior by the Y_2O_3 modification can also be confirmed by comparing the potential dependence of the band area of $\text{NH}_{3,\text{ad}}$, $\text{N}_2\text{H}_{4,\text{ad}}$, and NO_{ad} for both ionomer-coated and Y_2O_3 -modified Pd surfaces (Fig. 10). For the ionomer-coated Pd surface, the band area of $\text{N}_2\text{H}_{4,\text{ad}}$ was almost zero in the entire potential range studied. On the other hand, the band area of both $\text{NH}_{3,\text{ad}}$ and NO_{ad} slightly increased as the potential rose. The potential dependence of the NO_{ad} band area was similar to that of the Pt surface, while that of the $\text{NH}_{3,\text{ad}}$ band area was quite different. For the Pt surface, as described in section 3.2., the $\text{NH}_{3,\text{ad}}$

species was consumed mainly due to the $\text{NH}_{2,\text{ad}}$ dimerization reaction to form the $\text{N}_2\text{H}_{4,\text{ad}}$ species. In the case of the Pd surface, however, the $\text{NH}_{2,\text{ad}}$ dimerization reaction did not occur, which meant that the $\text{NH}_{3,\text{ad}}$ species simply accumulated on the Pd surface. According to this hypothesis, $\text{NH}_{3,\text{ad}}$ band area will be the index of the reaction activity for the $\text{NH}_{2,\text{ad}}$ dimerization. In fact, for the Pd surface, the $\text{NH}_{3,\text{ad}}$ band area increased monotonously with a rise in applied potential. As expected, the potential dependence of the band area for the Y_2O_3 -modified Pd surface was significantly different from the result for the ionomer-coated Pd surface. First, the increase in $\text{N}_2\text{H}_{4,\text{ad}}$ band area was clearly observed for the Y_2O_3 -modified Pd surface, indicating the progress of $\text{NH}_{2,\text{ad}}$ dimerization reaction. In addition, the $\text{NH}_{3,\text{ad}}$ band area decreased in response to the increase in $\text{N}_2\text{H}_{4,\text{ad}}$ band area. This behavior supports our hypothesis that the $\text{NH}_{3,\text{ad}}$ band area reflects the progress of the $\text{NH}_{2,\text{ad}}$ dimerization reaction. Moreover, the suppression of NO_{ad} formation was also observed for the Y_2O_3 -modified Pd surface. At the current state, it is difficult to identify whether the Y_2O_3 additive itself directly suppresses the $\text{NH}_{3,\text{ad}}$ oxidation reaction to form the NO_{ad} species or not. This suppression of NO_{ad} formation was possibly due to the second-order effects: (i) The consumption of N-monomer species ($\text{NH}_{x,\text{ad}}$, most likely the $\text{NH}_{3,\text{ad}}$), proposed as the starting material of NO_{ad} ^{44 45}, through the $\text{NH}_{x,\text{ad}}$ dimerization reaction. (ii) A decrease in the number of vacant Pd active sites for the NO_{ad} formation due to the accumulation of $\text{N}_2\text{H}_{4,\text{ad}}$ species.

Hereafter, the results of Y_2O_3 -modified Pd and Pt surfaces were compared to clarify the influence of metal substrates. The most notable difference was the potential dependency of $\text{N}_2\text{H}_{4,\text{ad}}$ band area above 0.45 V. In this potential range, the $\text{N}_2\text{H}_{4,\text{ad}}$ species begins to be oxidized into N_2 in the case of the Pt surface, which causes the decline in the band area. However, for the Y_2O_3 -modified Pd surface, the $\text{N}_2\text{H}_{4,\text{ad}}$ band area simply increased with a rise in potential. This

result clearly indicates that on the Pd surface, no further oxidation of $\text{N}_2\text{H}_{4,\text{ad}}$ species occurred, and the $\text{N}_2\text{H}_{4,\text{ad}}$ species existed stably. This behavior was unexpected because in the previous study, Pd was reported to be active toward the oxidation of hydrazine even at the low potential region such as $<0.2 \text{ V vs. RHE}$ ^{46 47}. In the case of Pd, therefore, the $\text{N}_2\text{H}_{4,\text{ad}}$ species produced as an intermediate species of ammonia oxidation has a quite different characteristic and is somehow stabilized as compared to hydrazine.

Finally, a correlation between the electrochemical response and the IR response was elucidated. As described above, the $\text{NH}_{2,\text{ad}}$ dimerization reaction is a catalytic process, not an electrochemical process. However, as clearly seen in Figs. 5 and 10, the formation of $\text{N}_2\text{H}_{4,\text{ad}}$ species was initiated at around 0.2 V and 0.3 V for Pt and Y_2O_3 -modified Pd surfaces, respectively. Moreover, no $\text{N}_2\text{H}_{4,\text{ad}}$ species was observed during the potentiostatic operation at 0.1 V (not shown). From these findings, it was suggested that there should be a potential dependent step which triggers the subsequent $\text{NH}_{2,\text{ad}}$ dimerization reaction. To reveal the details of this "trigger step" for the $\text{NH}_{2,\text{ad}}$ dimerization, the potential dependence of the current and the peak wavenumber for the $\text{NH}_{3,\text{ad}}$ band of both ionomer-coated and Y_2O_3 -modified Pd/Si prisms were investigated (Fig. 11(a)). The peak wavenumber of $\text{NH}_{3,\text{ad}}$ band was slightly shifted to a higher wavenumber region only in the case of Y_2O_3 -modified Pd surface, which has been revealed to be active for the $\text{NH}_{2,\text{ad}}$ dimerization reaction. Moreover, concomitant with the appearance of the shift in wavenumber, the small oxidation peak has newly emerged at *ca.* 0.3 V, indicating that this oxidation peak strongly related to the $\text{NH}_{3,\text{ad}}$ band shift. This oxidation peak should be different from that observed for ionomer-coated Pd/Si at *ca.* 0.4 V, which is related to the oxidation of NH_3 to NO. The wavenumber shift strongly indicates the change in the nature of N-H bond; the shortening of the N-H bond distance or the change of a molecular stereoscopic

structure of $\text{NH}_{3,\text{ad}}$ species. The voltammetric response suggested this process includes the electrochemical reaction. Both the change in the wavenumber and the voltammetric response probably indicate the “trigger step” for the $\text{NH}_{2,\text{ad}}$ dimerization reaction over the Y_2O_3 -modified Pd surface. On the other hand, ionomer-coated Pd showed neither wavenumber shift nor oxidation peak at *ca.* 0.3 V. Thus, Pd itself did not have the catalytic and/or the electrocatalytic activity toward the “trigger step”, which resulted in no formation of $\text{N}_2\text{H}_{4,\text{ad}}$ species that was considered as the essential intermediate chemicals to produce N_2 ⁴⁸. Note that this wavenumber shift of the $\text{NH}_{3,\text{ad}}$ band is deeply related to the $\text{NH}_{2,\text{ad}}$ dimerization reaction activity of the electrocatalyst, as well as the enhancement of $\text{NH}_{2,\text{ad}}$ dimerization reaction by the Y_2O_3 additive. From obtained results, it can be said that the Y_2O_3 additive itself promotes the “trigger step” and activated the $\text{NH}_{2,\text{ad}}$ dimerization reaction over the Pd surface.

This shift in wavenumber of $\text{NH}_{3,\text{ad}}$ band was also observed for both ionomer-coated and Y_2O_3 -modified Pt surfaces. Since Pt itself has activity towards the $\text{NH}_{2,\text{ad}}$ dimerization reaction, the difference in the wavenumber of $\text{NH}_{3,\text{ad}}$ band between ionomer-coated and Y_2O_3 -modified Pt surfaces was relatively small compared to that of Pd. However, examining the wavenumber shift in detail, especially focused on the change observable in the potential between 0.2 V to 0.4 V, the difference can be realized in those two surfaces (Figure 11(b)). In both cases, the peak wavenumber at 0.05 V was almost the same, which was *ca.* 1655 cm^{-1} . On the other hand, the amount of wavenumber shift at the potential of 0.4 V was quite different; for the ionomer-coated Pt surface, it was only around 10 cm^{-1} , while that for the Y_2O_3 -modified Pt surface was more than 20 cm^{-1} . As with the discussion in the Pd surfaces, this increment of the amount of $\text{NH}_{3,\text{ad}}$ band shift should be related to the acceleration of the “trigger step” by the Y_2O_3 additive.

Rosca *et al.* also suggested the existence of the “trigger step” to initiate the $\text{NH}_{2,\text{ad}}$ dimerization reaction⁴⁹. From their electrochemical results and DFT calculations, they assumed that the surface coverage of the $\text{NH}_{2,\text{ad}}$ species need to exceed the threshold value to trigger the $\text{NH}_{2,\text{ad}}$ dimerization reaction. In conclusion, they pointed out the importance of the stabilization of the $\text{NH}_{2,\text{ad}}$ species in order to proceed the $\text{NH}_{2,\text{ad}}$ dimerization reaction. We believe this is also the case in our Y_2O_3 -modified electrocatalysts; the Y_2O_3 additive stabilizes the $\text{NH}_{2,\text{ad}}$ species and increases the surface coverage of the $\text{NH}_{2,\text{ad}}$ species to the sufficient amount to trigger/promote the $\text{NH}_{2,\text{ad}}$ dimerization reaction. The shift of the wavenumber of $\text{NH}_{3,\text{ad}}$ band discussed above probably tied to this stabilization of $\text{NH}_{2,\text{ad}}$ species by the Y_2O_3 additive.

3.4. Effect of Y_2O_3 modification on fuel cell performance

The results so far clearly showed the positive effect of Y_2O_3 modification on ammonia oxidation reaction by means of the acceleration of $\text{NH}_{2,\text{ad}}$ dimerization process in an alkaline aqueous environment. Therefore, to demonstrate the applicability of this positive effect of Y_2O_3 modification for commercial anion exchange membrane fuel cells (AEMFCs), the cell performance was compared between two different MEAs employing Y_2O_3 -modified Pt/C or conventional Pt/C electrocatalysts as anodes. Figure 12 shows voltage–current density and power density–current density plots of single cells with a supply of either hydrogen or ammonia as a fuel. As shown in Fig. 12(a), the open circuit voltage (OCV) under the hydrogen supply was independent of the anode electrocatalyst and exhibited the value of *ca.* 0.96 V. As have been pointed out in the previous studies, this value was lower than the theoretical value of 1.23V, partially due to the permeation of the reactant hydrogen and oxygen gases across the AEM⁵⁰. The performance of the cell with the Y_2O_3 -modified Pt/C electrocatalyst became lower than that with the Pt/C electrocatalyst. As we discussed previously, Y_2O_3 additive is only active towards

the $\text{NH}_{2,\text{ad}}$ dimerization process. This means Y_2O_3 additive is simply a spectator species for the hydrogen oxidation reaction. . Therefore, one possible explanation for this negative effect on cell performance by using the Y_2O_3 -modified Pt/C electrocatalyst is that the decrease in the ECSA and/or the electrical conductivity of the anode. On the other hand, under the supply of ammonia as a fuel, the performance of the cell with the Y_2O_3 -modified Pt/C electrocatalyst improved notably as compared to that with the conventional Pt/C anode. More specifically, the maximum power density for the Y_2O_3 -modified Pt/C anode doubled in comparison with that for the conventional Pt/C anode. However, the obtained OCV value of *ca.* 0.4 V was significantly lower than the theoretical value of 1.17 V. The same behavior was also reported in the previous studies^{51 34}, and following possible reasons were given; the high overpotential for ammonia oxidation and/or the permeation of the ammonia fuel throughout the AEM.^{34 52} Aside from the low OCV, the cell with the Y_2O_3 -modified Pt/C anode clearly achieved a higher current density compared to that for the Pt/C anode under ammonia-fueled conditions. This result corresponds to the fact that the Y_2O_3 additive promoted the ammonia oxidation reaction in alkaline aqueous solutions, as discussed above.

To further confirm the validity of our catalyst design strategy, the current degradation behavior was compared between AEMFCs employing Y_2O_3 -modified Pt/C and conventional Pt/C electrocatalysts as anodes. As shown in Fig. 13, Y_2O_3 -modified Pt/C showed more gradual current degradation than the conventional Pt/C, indicating Y_2O_3 -modified Pt/C had higher tolerance to the catalyst poisoning. This result has come up to our expectations, because the acceleration of $\text{NH}_{2,\text{ad}}$ dimerization process by the Y_2O_3 modification caused a reduction in the amount of N-monomer species, which was considered as the starting material for poisonous species such as N_{ad} species. By combining the results shown in Figs. 12 and 13, therefore, it was

successfully demonstrated that our catalyst design strategy was valid in the ammonia-fueled AEMFCs.

4. Conclusion

In this work, the effect of Y_2O_3 on the activity of ammonia oxidation reaction was studied in detail. By comparing the result of *in situ* ATR-IR spectroscopy for both ionomer-coated and Y_2O_3 -modified Pt surfaces, it was revealed that the band area of $\text{N}_2\text{H}_{4,\text{ad}}$ species was selectively increased in the latter case, indicating the Y_2O_3 additive accelerated $\text{NH}_{2,\text{ad}}$ dimerization process which is considered as the rate determining step of the ammonia oxidation reaction. To distinguish and evaluate the effect of the Y_2O_3 on the $\text{NH}_{2,\text{ad}}$ dimerization process, the same measurement was carried out for ionomer-coated and Y_2O_3 -modified Pd surfaces, since the Pd was known to have no catalytic activity toward the $\text{NH}_{2,\text{ad}}$ dimerization. Predictably, for the ionomer-coated Pd surface, no band related to the $\text{N}_2\text{H}_{4,\text{ad}}$ species was observed throughout the experiment. In the case of Y_2O_3 -modified Pd surface, however, the $\text{N}_2\text{H}_{4,\text{ad}}$ band was clearly emerged above 0.3 V. This results strongly indicated that Y_2O_3 itself promoted the $\text{NH}_{2,\text{ad}}$ dimerization. Finally, to confirm this effect of the Y_2O_3 additive on ammonia oxidation activity was applicable in real-world conditions, the cell performance was evaluated by using commercial AEMFCs. As a result, both maximum power density and catalyst poisoning resistance for Y_2O_3 -modified Pt/C achieved a 2-fold increase as compared to that of the conventional Pt/C. These results clearly indicate the validity of our catalyst design strategy in commercial AEMFC operating conditions, as well as the impact of the $\text{NH}_{2,\text{ad}}$ dimerization process on overall ammonia oxidation activity. Furthermore, this work proposed a fundamentally

new approach to improve the ammonia oxidation reaction, that is, the acceleration of the catalytic dimerization process included in the reaction pathway. Because this method can be combined with various electrocatalysts available, our approach was found to be a promising way to further enhance the ammonia oxidation activity.

FIGURE CAPTIONS

Figure 1 Cyclic voltammograms of ionomer-coated and Y₂O₃-modified Pt/Si electrodes in 1 M KOH at 25°C with a scanning rate of 20 mV s⁻¹.

Figure 2 Time-resolved IR spectra of the Y₂O₃-modified Pt surface acquired simultaneously with the linear sweep voltammogram in 1 M KOH at 25°C with a scanning rate of 20 mV s⁻¹.

Figure 3 Linear sweep voltammograms of ionomer-coated Pt and Y₂O₃-modified Pt nanofilm electrode in 1 M KOH–0.1 M NH₃ at 25°C with a scanning rate of 20 mV s⁻¹.

Figure 4 Time-resolved IR spectra of the Y₂O₃-modified Pt surface acquired simultaneously with the linear sweep voltammogram in 1 M KOH–0.1 M NH₃ at 25°C with a scanning rate of 20 mV s⁻¹.

Figure 5 Potential dependence of the current and the normalized band area of NH_{3,ad}, N₂H_{4,ad}, and NO_{ad} of (a) ionomer-coated and (b) Y₂O₃-modified Pt/Si electrodes.

Figure 6 Linear sweep voltammograms of ionomer-coated and Y₂O₃-modified Pd/Si electrodes in (a) 1 M KOH and (b) 1 M KOH–0.1 M NH₃ at 25°C with a scanning rate of 20 mV s⁻¹.

Figure 7 Time-resolved IR spectra of the ionomer-coated Pd surface acquired simultaneously with LSV in Fig. 6 (a).

Figure 8 Time-resolved IR spectra of the ionomer-coated Pd surface acquired simultaneously with LSV in 1 M KOH–0.1 M NH₃.

Figure 9 Time-resolved IR spectra of the Y₂O₃-modified Pd surface acquired simultaneously with LSV in 1 M KOH–0.1 M NH₃.

Figure 10 Potential dependence of the current and the band area of NH_{3,ad}, N₂H_{4,ad}, and NO_{ad} of (a) ionomer-coated and (b) Y₂O₃-modified Pd/Si electrodes.

Figure 11 Potential dependence of the current and the peak wavenumber for NH_{3,ad} band of the ionomer-coated and the Y₂O₃-modified (a) Pd/Si and (b) Pt/Si electrodes.

Figure 12 Voltage–current density and power–current density plots for anion exchange membrane fuel cell in the supply of (a) H₂ and (b) NH₃ to the anode and O₂ to the cathode at 50 °C. Pt/C and Y₂O₃-modified Pt/C were used as anodes.

Figure 13 Time dependence of the current degradation for anion exchange membrane fuel cell in the supply of NH₃ to the anode and O₂ to the cathode at 50 °C with a terminal voltage of 0.2 V. Pt/C and Y₂O₃-modified Pt/C were used as anode catalysts.

AUTHOR INFORMATION

Corresponding Author

*Corresponding author. Tel.: +81-75-383-2519; fax: +81-75-383-2520

E-mail address: eguchi@scl.kyoto-u.ac.jp (K. Eguchi).

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

This work was supported by Council for Science, Technology and Innovation (CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), “energy carrier” (Funding agency: JST). We thank Tokuyama Corporation for the supply of anion exchange membrane (A201) and anion exchange ionomer (AS-4).

REFERENCES

1. Kordesch, K.; Hacker, V.; Gsellmann, J.; Cifrain, M.; Faleschini, G.; Enzinger, P.; Fankhauser, R.; Ortner, M.; Muhr, M.; Aronson, R. R., *J. Power Sources*, **2000**, *86*, 162-165.
2. Liu, H.; Song, C.; Zhang, L.; Zhang, J.; Wang, H.; Wilkinson, D. P., *J. Power Sources*, **2006**, *155*, 95-110.
3. Cairns, E. J.; Simons, E. L.; Tevebaugh, A. D., *Nature*, **1968**, *217*, 780-781.
4. Christensen, C. H.; Johannessen, T.; Sorensen, R. Z.; Norskov, J. K., *Catal. Today*, **2006**, *111*, 140-144.
5. Uribe, F. A.; Gottesfeld, S.; Zawodzinski, T. A., *J. Electrochem. Soc.*, **2002**, *149*, A293.
6. Halseid, R.; Vie, P. J. S.; Tunold, R., *J. Power Sources*, **2006**, *154*, 343-350.
7. McLean, G. F.; Niet, T.; Prince-Richard, S.; Djilali, N., *Int. J. Hydrogen Energy*, **2002**, *27*, 507-526.
8. Spendelow, J. S.; Wieckowski, A., *Phys. Chem. Chem. Phys.*, **2007**, *9*, 2654-2675.
9. Holewinski, A.; Idrobo, J. C.; Linic, S., *Nat. Chem.*, **2014**, *6*, 828-834.
10. Markovic, N. M.; Schmidt, T. J.; Stamenkovic, V.; Ross, P. N., *Fuel Cells*, **2001**, 105-116.
11. Tewari, A.; Sambhy, V.; Urquidi Macdonald, M.; Sen, A., *Journal of Power Sources*, **2006**, *153*, 1-10.
12. Adams, L. A.; Poynton, S. D.; Tamain, C.; Slade, R. C.; Varcoe, J. R., *ChemSusChem*, **2008**, *1*, 79-81.
13. Yanagi, H.; Fukuta, K., *ECS trans.*, **2008**, *16*, 257-282.
14. Fukuta, K.; Inoue, H.; Watanabe, S.; Yanagi, H., *ECS trans.*, **2009**, *19*, 23-27.
15. Gerischer, H.; Mauerner, A., *J. Electroanal. Chem.*, **1970**, 421-433.

16. Gootzen, J. F. E.; Eonders, A. H.; Visscher, W.; van Santen, R. A.; van Veen, J. A. R., *Electrochim. Acta*, **1998**, *43*.
17. Vidal-Iglesias, F. J.; Solla-Gullón, J.; Feliu, J. M.; Baltruschat, H.; Aldaz, A., *J. Electroanal. Chem.*, **2006**, *588*, 331-338.
18. de Vooy, A. C. A.; Koper, M. T. M.; van Santen, R. A.; van Veen, J. A. R., *J. Electroanal. Chem.*, **2001**, *506*, 127-137.
19. de Vooy, A. C. A.; Mrozek, M. F.; Koper, M. T. M.; van Santen, R. A.; van Veen, J. A. R.; Weaver, M. J., *Electrochem. Commun.*, **2001**, 293-298.
20. Vidal-Iglesias, F. J.; Solla-Gullón, J.; Pérez, J. M.; Aldaz, A., *Electrochem. Comm.*, **2006**, *8*, 102-106.
21. Matsui, T.; Suzuki, S.; Katayama, Y.; Yamauchi, K.; Okanishi, T.; Muroyama, H.; Eguchi, K., *Langmuir*, **2015**, *31*, 11717-11723.
22. Wasmus, S.; Vasini, E. J.; Krausa, M.; Mishima, H. T.; Vielstich, W., *Electrochim. Acta*, **1994**, *39*, 23-31.
23. Katayama, Y.; Okanishi, T.; Muroyama, H.; Matsui, T.; Eguchi, K., *J. Phys. Chem. C*, **2015**, 9134-9141.
24. Katayama, Y.; Okanishi, T.; Muroyama, H.; Matsui, T.; Eguchi, K., *ACS Catal.*, **2016**, *6*, 2026-2034.
25. Skachkov, D.; Venkateswara Rao, C.; Ishikawa, Y., *J. Phys. Chem. C*, **2013**, *117*, 25451-25466.
26. Herron, J. A.; Ferrin, P.; Mavrikakis, M., *J. Phys. Chem. C*, **2015**, *119*, 14692-14701.
27. Miki, A.; Ye, S.; Osawa, M., *Chem. Comm.*, **2002**, 1500-1501.
28. Miki, A.; Ye, S.; Senzaki, T.; Osawa, M., *J. Electroanal. Chem.*, **2004**, *563*, 23-31.
29. Osawa, M.; Yoshii, K.; Ataka, K.-i.; Yotsuyanagi, T., *Langmuir*, **1994**, 640-642.
30. Chen, Y. X.; Miki, A.; Ye, S.; Sakai, H.; Osawa, M., *J. Am. Chem. Soc.*, **2003**, 3680-3681.
31. Kunimatsu, K.; Senzaki, T.; Tsushima, M.; Osawa, M., *Chem. Phys. Lett.*, **2005**, *401*, 451-454.
32. Ataka, K.; Yotsuyanagi, T.; Osawa, M., *J. Phys. Chem.*, **1996**, 10664-10672.
33. Henning, S.; Herranz, J.; Gasteiger, H. A., *Journal of the Electrochemical Society*, **2014**, *162*, F178-F189.
34. Suzuki, S.; Muroyama, H.; Matsui, T.; Eguchi, K., *J. Power Sources*, **2012**, *208*, 257-262.
35. Markovic, N. M.; Ross, P. N., *Surf. Sci. Rep.*, **2002**, *45*, 117-229.
36. Samjeské, G.; Komatsu, K.; Osawa, M., *J. Phys. Chem. C*, **2009**, *113*, 10222.
37. Müller, C. M.; Molinelli, A.; Karlowatz, M.; Aleksandrov, A.; Orlando, T.; Mizaikoff, B., *J. Phys. Chem. C*, **2012**, *116*, 37-43.
38. Miyazaki, S.; Nishimura, H.; Fukuda, M.; Ley, L.; Ristein, J., *Appl. Surf. Sci.*, **1997**, *113-114*, 585-589.
39. Kunimatsu, K., *J. Electroanal. Chem.*, **1986**, *213*, 149-157.
40. Leung, L. W. H.; Wieckowski, A.; Weaver, M. J., *J. Phys. Chem.*, **1988**, *92*, 6985-6990.
41. Bunce, N. J.; Bejan, D., *Electrochim. Acta*, **2011**, *56*, 8085-8093.
42. Vidal-Iglesias, F. J.; Solla-Gullón, J.; Montiel, V.; Feliu, J. M.; Aldaz, A., *J. Power Sources*, **2007**, *171*, 448-456.
43. Yang, Y.-Y.; Ren, J.; Li, Q.-X.; Zhou, Z.-Y.; Sun, S.-G.; Cai, W.-B., *ACS Catal.*, **2014**, *4*, 798-803.

44. Katsounaros, I.; Chen, T.; Gewirth, A. A.; Markovic, N. M.; Koper, M. T., *J. Phys. Chem. Lett.*, **2016**, 7, 387-92.
45. Finkelstein, D. A.; Bertin, E.; Garbarino, S.; Guay, D., *J. Phys. Chem. C*, **2015**, 119, 9860-9878.
46. Maleki, N.; Safavi, A.; Farjami, E.; Tajabadi, F., *Anal. Chim. Acta.*, **2008**, 611, 151-5.
47. Serov, A.; Kwak, C., *Appl. Catal. B*, **2010**, 98, 1-9.
48. Petek, M.; Bruckenstein, S., *Electroanal. Chem. and Interfacial Electrochem.*, **1973**, 47, 329-333.
49. Rosca, V.; Koper, M. T., *Phys Chem Chem Phys*, **2006**, 8, 2513-24.
50. Varcoe, J. R.; Atanassov, P.; Dekel, D. R.; Herring, A. M.; Hickner, M. A.; Kohl, P. A.; Kucernak, A. R.; Mustain, W. E.; Nijmeijer, K.; Scott, K.; Xu, T.; Zhuang, L., *Energy Environ. Sci.*, **2014**, 7, 3135-3191.
51. Okanishi, T.; Katayama, Y.; Muroyama, H.; Matsui, T.; Eguchi, K., *Electrochimica Acta*, **2015**, 173, 364-369.
52. Lan, R.; Tao, S., *Electrochem. Solid-State Lett.*, **2010**, 13, B83.

Figure 1 (Y. Katayama *et al.*)

Figure 2 (Y. Katayama *et al.*)

Figure 3 (Y. Katayama *et al.*)

Figure 4 (Y. Katayama *et al.*)

Figure 5 (Y. Katayama *et al.*)

Figure 6 (Y. Katayama *et al.*)

Figure 7 (Y. Katayama *et al.*)

Figure 8 (Y. Katayama *et al.*)

Figure 9 (Y. Katayama *et al.*)

Figure 10 (Y. Katayama *et al.*)

Figure 11 (Y. Katayama *et al.*)

Figure 12 (Y. Katayama *et al.*)

Figure 13 (Y. Katayama *et al.*)

Graphical abstract