Journal of Catalysis 344 (2016) 496–506

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Enhancement of ammonia oxidation activity over Y_2O_3-modified platinum surface: Promotion of $NH_{2,ad}$ dimerization process

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ARTICLE INFO

Article history:
Received 14 June 2016
Revised 23 September 2016
Accepted 23 October 2016
Available online 16 November 2016

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 $N_2H_{4,ad}$ species, which is the intermediate species of ammonia oxidation reaction, was distinctively increased, suggesting the promotion of $NH_{2,ad}$ 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 $NH_{2,ad}$ dimerization reaction, the IR band of $N_2H_{4,ad}$ 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 $NH_{2,ad}$ dimerization reaction. Furthermore, the electrocatalytic performance of Y_2O_3-modified Pt/C electrocatalyst was evaluated using the commercial AEMFC system. A twofold 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.

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 careers 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 [7–10]. 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 CO_2 in the air [7,11], the formation of those carbonate salts is suppressed in AEMs [12]. Moreover, in anion exchange membrane fuel cells (AEMFCs), OH^- generated in the cathode during the operation purges a portion of the HCO_3^- and CO_3^{2-} derived from CO_2, 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 Mauerer [15]:

$$NH_3(aq) \rightarrow NH_{3,ad} \quad \text{(Reaction 1)}$$

$$NH_{3,ad} + OH_{ad}^{\delta-} \rightarrow NH_{2,ad} + H_2O + \delta e^- \quad \text{(Reaction 2)}$$

$$NH_{2,ad} + OH_{ad}^{\delta-} \rightarrow NH_{ad} + H_2O + \delta e^- \quad \text{(Reaction 3)}$$

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http://dx.doi.org/10.1016/j.jcat.2016.10.020
0021-9517/

$$NH_{x,ad} + NH_{y,ad} \rightarrow N_2H_{x+y,ad} \quad \text{(Reaction 4)}$$

$$N_2H_{x+y,ad} + (x+y)OH_{ad}^{\delta-} \rightarrow N_2 + (x+y)H_2O + (x+y)\delta e^- \quad \text{(Reaction 5)}$$

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, $NH_{2,ad}$ 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 $N_2H_{x+y,ad}$ (x = 1 or 2, y = 1 or 2). Finally, the further dehydrogenation of $N_2H_{x+y,ad}$ 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 disadvantage of ammonia fuel. Gerischer et al. also suggested the production of atomic nitrogen adspecies (N_{ad}) via the dehydrogenation of NH_{ad} species.

$$NH_{ad} + OH_{ad}^{\delta-} \rightarrow N_{ad} + H_2O + \delta e^- \quad \text{(Reaction 6)}$$

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, $NH_{x,ad}$. This tells us that the selectivity of formation of N-dimer species ($N_2H_{x+y,ad}$) 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 clarified [23]. Moreover, electrocatalysts with superior activity for ammonia oxidation reaction were successfully developed by focusing on the OH adsorption behavior of the catalyst surface [24]. 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 $NH_{2,ad}$ 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 $NH_{2,ad}$ species forming hydrazine like $N_2H_{4,ad}$ 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 $NH_{2,ad}$ 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 solution [23]. 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 Y_2O_3 additive itself upon the $NH_{2,ad}$ dimerization process. Finally, by using direct ammonia-fueled anion exchange membrane fuel cells (AEMFCs), the performance of Y_2O_3-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 Y_2O_3 containing solution was prepared by adding the as-received Y_2O_3 (6.75 mg, Wako Pure Chemical) to ultrapure water (Millipore Milli-Q), and then ultrasonically dispersed for 2 h. The anion exchange ionomer solution (AS-4, Tokuyama Corp., diluted to 1 wt% 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 Y_2O_3-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% NH_4F solution for a minute. Then, palladium was deposited on the base plane with 1% HF–1 mM $PdCl_2$ 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 LECTROLESS Pt 100 basic solution (30 mL, Electroplating Engineering of Japan Ltd.), LECTROLESS 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 LECTROLESS Pd 1000 (30 mL, Electroplating Engineering of Japan Ltd.), LECTROLESS 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 0.5 wt% 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 elsewhere [29–32]. 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 literature [27]. 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 N_2 gas. The electrolyte solutions were prepared by mixing 28 wt% NH_3 solution (Wako Pure Chemical) with KOH (Sigma–Aldrich, >85 wt%) and ultrapure water. After deoxygenation of the electrolyte solution by purging