Journal of Electroanalytical Chemistry 762 (2016) 29–36

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Electrochemical oxidation of ammonia by multi-wall-carbon-nanotube-supported Pt shell–Ir core nanoparticles synthesized by an improved Cu short circuit deposition method

Seitaro Morita [a,1], Eiji Kudo [a,2], Ryo Shirasaka [a], Minoru Yonekawa [b,3], Keiji Nagai [b], Hikaru Ota [c], Mikka N.-Gamo [c], Hidenobu Shiroishi [a,*]

[a] National Institute of Technology, Tokyo College, Kunugida 1220-2, Hachiouji, Tokyo, Japan
[b] Tokyo Institute of Technology, Nagatsuda 4259, Midori-ku, Yokohama, Kanagawa, Japan
[c] Department of Applied Chemistry, Toyo University, 2100 Kujirai, Kawagoe, Saitama 350-8585, Japan

ARTICLE INFO

Article history:
Received 28 June 2015
Received in revised form 30 November 2015
Accepted 13 December 2015
Available online 14 December 2015

Keywords:
Ammonia oxidation
Pt shell–Ir core
MWCNT
Fuel cell

ABSTRACT

Multi-wall-carbon-nanotube (MWCNT)-supported Pt shell–Ir core (Pt/Ir/MWCNT) nanoparticles were synthesized by an improved Cu short circuit deposition (ICSCD) method and were characterized by thermogravimetry (TG), transmission electron microscope (TEM), X-ray diffractometry (XRD), X-ray photon spectroscopy (XPS), and electrochemical measurements for ammonia oxidation catalysis activity. It was revealed that the overvoltage for the ammonia oxidation of Pt/Ir/MWCNT (0.52 V) at 1 μA cm^{-2}_{ECSA} is lower than those of Pt/MWCNT (0.55 V). The activation energies of the catalysis toward ammonia electrooxidation were estimated as 28.2 kJ (Pt/MWCNT), 27.8 kJ (Ir/MWCNT) and 33.6 kJ (Pt/Ir/MWCNT) at 0.60 V vs. RHE in 100 mM NH_3–0.1 M KOH. On the basis of computational kinetic analysis of the chronoamperometric curves in ammonia solution, it was revealed that the apparent rate constant of ammonia oxidation of Pt/Ir/MWCNT is higher than that of Pt/MWCNT, suggesting that the electronic property of Pt was affected by the Ir core atoms.

1. Introduction

Ammonia has attracted attention as a possible fuel for direct fuel cells and it is easily liquefied at ambient temperature under a pressure of 0.86 MPa or at −240 K under ambient pressure for easy transportation [1]. Moreover, its equilibrium potential is low as follows [2]:

$$NH_3(aq) + 3OH^- \rightleftharpoons 1/2N_2 + 3H_2O \qquad E^\circ = -0.092 \text{ V vs. RHE} \qquad (1)$$

which provides a high theoretical voltage (1.32 V) for direct ammonia fuel cells (DAmFCs). And the theoretical charge for ammonia oxidation to N_2 (4.75 Ah g^{-1}) is as high as the methanol oxidation to CO_2 (5.02 Ah g^{-1}) [2]. Furthermore, since CO_2 is not produced during power generation in DAmFCs, they are one of the most promising power sources to reduce green-house gases.

Although ammonia oxidation reaction (AOR) on various metals [2–12] and/or various alloys [2,13–26] under various conditions [27–30] at low-temperature and their mechanism [31–38] have been studied during four decades, the important issue for DAmFCs is still the development of ammonia oxidation catalysts for low temperatures. The overpotential for AOR at low temperatures with Pt catalysts, which are relatively active for AOR, are so large that ammonia-fueled fuel cells for intermediate temperatures [39,40] or high temperatures [1,41–46] have been reported rather than for low temperatures.

The mechanism for AOR was well reviewed in the literature [47]. The most widely accepted mechanism for AOR on poly-Pt at low temperatures was proposed by Gerischer and Mauerer, which consists of a dehydrogenation of NH_x species, H_xNNH_y species and N–N bond formation via hydrogenated NH_x species, according to Eqs. (2)–(6) [32].

$$NH_3 + OH^- + {}^* \rightarrow NH_2^* + H_2O + e^- \qquad (2)$$

$$NH_2^* + OH^- \rightarrow NH^* + H_2O + e^- \qquad (3)$$

$$NH^* + OH^- \rightarrow N^* + H_2O + e^- \quad (>0.56 \text{ V vs. RHE}) \qquad (4)$$

$$NH_x^* + NH_y^* \rightarrow H_xNNH_y^* + {}^* \qquad (5)$$

* Corresponding author.
E-mail address: h-shiroishi@tokyo-ct.ac.jp (H. Shiroishi).
[1] Present address: Yokohama National University, 79-7 Tokiwadai, Hodogaya-ku, Yokohama 240-8501.
[2] Present address: Department of Applied Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552, Japan.
[3] Technology Research Institute of Osaka Prefecture, 7-1, Ayumino-2, Izumi, Osaka, 564-0002, Japan.

http://dx.doi.org/10.1016/j.jelechem.2015.12.017
1572-6657/

$$H_xNNH_y^* + (x+y)OH^- \rightarrow N_2 + (x+y)H_2O + (x+y)e^- + ^* \quad (6)$$

where the * indicates free surface sites or adsorbed intermediates.

Herron et al. reported that the minimum-energy pathway for Pt(111) and Ir(111) involves dimerization of adsorbed NH_2 species into hydrazine and oxidation of H_xNNH_y species such as hydrazine to form N_2 [48]. In particular, for Pt and Ir, the oxidation of $H_2NNH_2^*$ and oxidation of $HNNH_2^*$ are potential determining steps, respectively. And the catalyst becomes poisoned above 0.56 V vs. RHE by the formation of N adatoms, because the removal of N adatoms is very sluggish. It is important to control the adsorption energy of N adatoms as well as the oxidation activity of H_xNNH_y species for the development of AOR catalysts. On the other hand, Pt(100) was less affected by the N adatoms, because the adsorption energy of N adatoms on Pt(100) is lower than those on Pt(111) and Pt(110) [6].

The AOR is expected to be controlled by the physicochemical properties, which is affected by changes in the metal–metal distance and/or in the electronic state (d-vacancy character) of the catalyst surface atoms [49]. The changes were undergone by an alloying [50–55] and a synthesizing shell–core type catalyst [49,56–62]. In these reports, it is worth noting that PtIr alloy catalysts have a relatively high ammonia electrochemical oxidation activity [17].

Much attention has been paid for shell–core type catalysts in which the physicochemical properties of the shell metal may be controlled by the metal particle diameter and/or the thickness of the shell metal [61,62]. The change of physicochemical properties in the shell is considered to be caused by the ligand effect [63] and/or the strain effect [56,64]. It is suggested that the ligand effect is resulted in an interaction with a base metal, and the strain effect is considered to be the electronic state change by tenseness in the metal–metal bond length which is yielded by the core (or underlayer) metal. However, few studies have been reported on the AOR using shell–core type catalysts.

A conventional method for the preparation of shell–core type catalysts is based on their spontaneous electroless deposition by the surface replacement of less precious metal layers, followed by the immersion of the samples into a solution containing precious metal ions [65,66]. However, the above method cannot meet the requirements of large-scale synthesis.

A contact immersion process is one of the most promising method for a large-scale synthesis of a shell–core type catalyst [67,68]. X. Wang et al. developed a Pt shell–Pd core catalyst using a contact immersion process called an improved Cu short circuit deposition (ICSCD) method [67]. A large-scale synthesis of shell–core metal particle catalysts can be done by the method without a potential control.

In this study, we have reported the synthesis of multiwall carbon nanotube (MWCNT) supported Pt shell–Ir core catalyst (abbreviated as Pt/Ir/MWCNT) using an ICSCD method. The activity of oxidation of NH_3 by Pt/Ir/MWCNT, Pt/MWCNT and Ir/MWCNT has been investigated by electrochemical methods. The kinetic parameters of NH_3 electrooxidation have been also estimated on the basis of a simple mathematical model.

2. Experimental

2.1. Materials

Hexachloroplatinic(IV) acid ($H_2[PtCl_6]$, Kanto Chemicals, Japan), iridium (III) chloride trihydrate ($IrCl_3 \cdot 3H_2O$, min. 90%, Kanto), MWCNTs (20–30 nm, Wako Pure Chemical Industries, Ltd., Japan), potassium hydroxide (99.99% metal basis, semiconductor grade, Sigma-Aldrich), 5 wt.% Nafion® (Sigma-Aldrich), copper (II) sulfate (JIS special grade, Wako), potassium sulfate (JIS special grade, Wako), and ammonia (25%, for Analysis of Poisonous Metals, Wako) were used as received. Milli-Q pure water (18.2 MΩ) was used for the preparation of all solutions.

2.2. Preparation of Pt/MWCNT and Ir/MWCNT

Ir/MWCNT and Pt/MWCNT were prepared by a selective reductive deposition method [69] followed by a microwave polyol process [70]. 40 mL of 2.0 mM H_2PtCl_6 was adjusted to pH 5.6 by addition of 1 M KOH at room temperature with stirring. 35.0 mg of multi-walled carbon nanotube was dispersed into the solution with ultrasonication for 15 min, the suspension was refluxed at 100 °C for 48 h for the adsorption of Pt precursor, then it was evaporated to dryness as a catalyst precursor. After the catalyst precursor was suspended in 25 mL ethylene glycol–20 mL Milli-Q water with ultrasonic dispersion for 15 min, it was irradiated with a microwave (500 W) for 150 s. Then, Pt(IV) complexes were reduced to Pt(0). The final product was washed by decantation with ethanol, water and acetone sequentially, and drying in a vacuum.

Similarly, the synthesis of Ir/MWCNT was carried out using an $IrCl_3$ aqueous solution adjusted at pH 6.4 instead of H_2PtCl_6, and the amount of MWCNT was 28.3 mg.

2.3. Preparation of Pt/Ir/MWCNT

Pt/Ir/MWCNT catalysts were prepared by an ICSCD method as follows [67]: Cu mesh was immersed in the suspension of 3.16 mg of Ir/MWCNT–20 mL of 5 mM $CuSO_4$–0.1 M H_2SO_4 aqueous solution for 25 h with stirring under N_2 atmosphere (Fig. 1(a)). Cu atoms on Ir particles were replaced with Pt atoms by the addition of 1.1 mL of 10 mM K_2PtCl_4–0.1 M K_2SO_4 aqueous solution deaerated by N_2, followed by stirring for 90 min (Fig. 1(b)). The final product was washed by decantation with Milli-Q water, and drying in a vacuum.

2.4. Characterization by TGA, XRD, TEM and XPS

The metal loadings and thermal durability of the catalysts were analyzed by TG/DTA measurements (EXSTAR TG/DTA 6000, SII) at heating rates of 10 °C/min below 257 °C and 2.5 °C/min above the temperature under air atmosphere. X-ray diffraction powder patterns of all synthesized catalysts were collected using a Bruker AXS D8 Advance system with Cu-*Kα* radiation (λ = 0.154 nm) between 10° to 80° at a step of 0.02°. TEM observations were performed on a JEM-2100 (JEOL). Particle size distributions from TEM images were obtained by "ImageJ" [71]. X-ray photoelectron spectroscopy (PHI Model ESCA 5700) measurements were used to characterize the catalysts. The X-ray source was Al-*Kα* at 400 W. The binding-energy scale was calibrated with Au 4f at 84.0 eV.

2.5. Electrochemical measurements

Each 10 μL of catalyst suspension (2.0 mg mL^{-1} in 0.1 wt.% Nafion–methanol) was cast onto a glassy carbon (GC) disk electrode and the solvent was dried for 1 h. Electrochemical measurements were carried out with a conventional three electrode system equipped with the modified disk electrode, an Au wire counter electrode and a reversible hydrogen reference electrode (RHE) at 22 °C in 0.1 M $HClO_4$ or 0.1 M NH_3–0.1 M KOH aqueous solution (pH 12.95) saturated with N_2 gas. Cyclic voltammetric measurements were performed in the presence and absence of ammonia at the scan rates of 50 mV s^{-1} between 0.05 and 0.9 V vs. RHE, and linear sweep voltammetric measurements for the ammonia electrooxidation were performed at the scan rates of 5 mV s^{-1}. In addition, chronoamperometric measurements for ammonia oxidation were also conducted at 0.65 V vs. RHE to estimate apparent rate constants for AOR. The electrode potential was held at 0.4 V for 5 min prior to each polarization. The electrochemically active surface areas (ECSAs) of the catalysts were measured from the charge of hydrogen desorption region (so-called H-UPD charge) in 0.1 M $HClO_4$ with values of 210(Pt) and 218(Ir) μC cm^{-2} [72]. In order to rule out other effects due to different cleaning protocols, any cleaning protocols such