



Preparation and evaluation of a highly stable palladium yttrium platinum core–shell–shell structure catalyst for oxygen reduction reactions



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ABSTRACT

A core–shell–shell structure Pd–Y–Pt/C catalyst was prepared using a controlled surface reaction method. The structure was confirmed by X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray (EDX) techniques. Nano-scale yttrium was formed as a shell located as the middle layer of the catalyst. Electrochemical evaluation of the Pd–Y–Pt/C with less than 7% of Pt showed an improved performance toward oxygen reduction reaction (ORR) compared to Pt/C (20 wt.% Pt). Accelerated degradation tests (ADT) indicated that the addition of Y improved catalyst stability compared to Pt/C and Pd–Pt/C core–shell catalysts under various experimental conditions. This was due to the Y middle layer created approximate half-filled metal–metal d bond between Pt (or Pd) and Y. This catalyst utilized the core–shell–shell structure to minimize the Pt usage, and Y middle shell to improve stability.

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1. Introduction

Catalyst is the most important factor which governs the performance of polymer electrolyte membrane fuel cells (PEMFCs). It has been extensively studied in the past decades in terms of increasing the catalyst durability and reducing the cost. Carbon supported Pt nano-particle catalyst is recognized as the best candidate for oxygen reduction reactions (ORRs). It has been reported that the fuel cell suffers from power loss after a certain period running due to the degradation of the cathode catalyst [1–3]. This degradation of catalyst is caused by sintering of the Pt particles [4,5] and corrosion of the carbon support [6,7]. In terms of increasing the activity and durability on cathode side, Pt based alloys were widely studied. Among the Pt–M bimetallic catalysts, Jeon et al. [8] found that Pt–Y/C has 20% higher mass activity and 65% higher specific activity than comparable Pt/C catalyst. Greeley et al. [9] reported that Pt alloyed with early transition metals such as Sc or Y ORR catalysts are the most stable Pt based binary alloys using density functional theory calculations, their electrochemical measurements showed that the activity of polycrystalline Pt₃–Sc and Pt₃–Y electrodes is enhanced relative to pure Pt by a factor of 1.5–1.8 and 6–10,

respectively, in the range of 0.9–0.87 V. Researchers also found that Pd based alloys can be a good candidate to replace Pt for the purpose of cost reduction as well as retain a comparable activity to Pt/C catalysts [10–12]. Both Greeley et al. [9] and Seo et al. [13] found that Pd₃–Y/C showed increased ORR activity and stability than Pt/C catalyst.

Core–shell structure nanoparticle catalyst has recently become the research trend, because it reduces the usage of the noble metal when used as shell material as well as retains similar or prior catalytic activity compared to bulk alloy catalysts. Zhang et al. [12] and Sasaki et al. [14] prepared Pd–Pt core–shell structure catalyst using different preparation methods, and both catalysts showed an increased ORR activity, durability and mass activity comparing with Pt/C commercial catalysts. A controlled surface reaction (CSR) method for core–shell catalysts preparation was previously reported by Crabb et al. [15,16], this method utilizes the reaction between an organometallic compound and the core metal surface in a hydrogen environment, and the surface composition was well controlled. It also has the advantage of forming an uniform shell of the second metal on the surface of the core material.

In this present work, Pd–Y–Pt/C core–shell–shell structure catalysts were synthesized using yttrium(III) acetylacetonate hydrate and platinum(II) acetylacetonate in a hydrogen environment to produce Pd as the core, Y as the middle shell on Pd particles and Pt as the outer shell. Meanwhile, a Pd–Pt/C core–shell structure catalyst was also included as comparison.

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2. Experimental

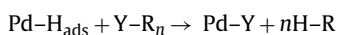
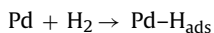
2.1. Materials and chemicals

Vulcan XC-72R carbon powder was purchased from Cabot Corporation (USA). All other chemicals, *ca.*, ammonium tetrachloropalladate(II) ((NH₄)₂PdCl₄), yttrium(III) acetylacetonate hydrate (Y(acac)₃), platinum(II) acetylacetonate (Pt(acac)₂); Nafion 117 solution (5%), sulfuric acid (98%), potassium hydroxide (85%), hydrogen peroxide (30%), sodium hydroxide (97%) and ethanol (99.8%) were purchased from Sigma–Aldrich. Millipore water with 18 MU cm resistivity was used in the experiments.

2.2. Preparation of carbon supported Pt–Y–Pd/C catalyst

The core–shell–shell structure Pd–Y–Pt/C catalyst was prepared in two steps. Firstly, we prepared a 20 wt.% loading of Pd supported on carbon catalyst using polyol method. 500 mg of Vulcan XC-72R carbon powder was dispersed in 150 ml of ethanol in a two neck round flask and the mixture was ultrasonically mixed for 30 min then stirred using a magnetic bar under nitrogen atmosphere for 1 h. 334.0 mg of (NH₄)₂PdCl₄ was dissolved in 50 ml de-ionized water and added drop wisely to the mixture. After 1 h stirring, the pH value of this mixture was measured with a Jenway 3310 pH meter and adjusted to 11 by drop wise addition of 2 M NaOH solution. The mixture was refluxed at 75 °C for 12 h under a nitrogen atmosphere. The resultant Pd/C catalyst was washed several times with ethanol and de-ionized water and then dried at 80 °C in a hot air oven.

The second step was to synthesize approximately 1.5 monolayer (ML) equivalence of Y and Pt core–shell–shell Pd–Y–Pt/C catalyst using a controlled surface reaction method [16]. The dispersion of Pd/C was 18.0% which was calculated from the electrochemical surface area (ECSA) in half cell electrochemical testing detailed in Section 2.4, and confirmed with the average particle size (from TEM) and dispersion relationship [17,18]. 1.5 ML coverage was employed to provide a reservoir large enough to enable the Y and Pt formation of particles in which a greater fraction of each particle will consist of the Pd–Y–Pt trimetallic catalyst, *i.e.* yielding particles with a smaller Pd core. Briefly, 500 mg of 20 wt.% Pd/C was reduced with H₂ at 200 °C for 30 min in a three neck round flask reactor. 65.3 mg of Y(acac)₃ was dissolved in 100 ml toluene and loaded into a dropping funnel, connected to the reactor. After purging with N₂ gas, the solution was transferred into the reactor at room temperature. After mixing for 2 h the temperature was increased up to 90 °C and maintained for 24 h under pure H₂. This experimental condition allows H₂ to adsorb onto the Pd surface to form Pd–H_{ads}, ideally each H₂ occupies 2 Pd atoms. Y(acac)₃ reacts with Pd–H_{ads} by forming Pd–Y and releasing the C₅H₈O₂. Then the surface of Pd particles is homogeneously covered by Y. The mechanism of controlled surface reaction can be explained in the following formulas [19]:



Then the content was cooled down to room temperature under N₂. 66.5 mg of Pt(acac)₂ was dissolved in 100 ml toluene and loaded into the dropping funnel, then added into the same reactor after purging with N₂ at room temperature. The content then, again, heated up to 90 °C and the reaction was carried out under H₂ for 4 h to allow Pt deposit onto the Y surface. The contents of the reactor were filtered, washed, dried and reduced again with H₂ at 250 °C for 2 h, a small amount of this catalyst was heat treated at 350 °C for 2 h to check the function of Y against the heat

treatment condition. NaOH solution was added to the filtrates in terms of checking any unreacted Y or Pt precursors. The resulting trimetallic catalyst had a composition of 18.1 wt.% Pd, 3.0 wt.% Y and 6.6 wt.% Pt. A 20% Pt/C catalyst was also prepared using the same polyol method from chloroplatinic acid as comparison.

2.3. Characterizations

X-ray photoelectron spectroscopy (XPS) analysis was used to elucidate the electronic structures and composition of the Pd–Y–Pt/C and Pd–Pt/C nanoparticles. XPS analysis was performed with a Kratos Axis Nova spectrometer. The catalyst was fixed on the support using a copper double-sided adhesive conducting tape and then evacuated at room temperature. The spectra were excited by the monochromatized Al K α source (1486.6 eV) run at 15 kV and 10 mA. For the individual peak regions a pass energy of 20 eV was used. Survey spectrum was measured at 160 eV pass energy. Analyses of the peaks were performed with the CasaXPS software after Shirley background subtraction. The peaks were fitted using an asymmetric Gaussian–Lorentzian sum function with the constraint that all the peaks display the same asymmetry and Gaussian/Lorentzian ratio. The binding energies were lined up with respect to the C 1s peak at 284.6 eV. High resolution transmission electron microscopy (HRTEM) was employed to determine the morphology of the catalysts, energy dispersive X-ray (EDX) fitted in HRTEM was used to analyze the structure of core–shell–shell nanoparticles, both line and mapping scans was performed to identify the structure of Pt, Y and Pd elements. The HRTEM/EDX analysis was performed at Leeds Electron Microscopy and Spectroscopy (LEMAS) Center. The instrument was FEI Tecnai TF20 FEGTEM Field emission gun TEM/STEM fitted with HAADF detector, and Oxford Instruments INCA 350 EDX system/80 mm X-Max SDD detector and Gatan Orius SC600A CCD camera.

2.4. Electrochemical evaluation

Half cell electrochemical evaluations were conducted using a BASi RRDE-3A package which consists of a rotating ring disk electrode (RRDE) apparatus, a glass cell vial (100 ml), an Ag/AgCl reference electrode, a 7.5 cm long Pt wire with 0.5 mm diameter and RRDE tip. The RRDE tip consisted of a glassy carbon disk with a surface area of 0.1256 cm² and platinum ring surface area of 0.1884 cm². The data were recorded using an AutoLab PGSTAT30 potentiostat/galvanostat with GPES software. The potential reported in this study are referred to the reference hydrogen electrode (RHE). The loading of catalyst deposited on the GC disk was 0.5 mg cm⁻². The ink was prepared by ultrasonically mixing the catalysts and 5.0 wt.% Nafion ionomer in ethanol. A required amount of the catalyst slurry was carefully dropped on glassy carbon surface and allowed to dry at room temperature for 15 min to obtain a uniform catalyst film. The cyclic voltammograms (CV) were recorded at 0.2 V s⁻¹ between 0 and 1.2 V vs. RHE, the ECSA of reduction peak which is between potential 1.0–0.4 V vs. RHE at cathodic sweep was considered as the active surface area of the catalysts. The charge related to a monolayer of double banded oxygen pieces reduction was 420 $\mu\text{C cm}^{-2}$. The dispersion value of Pd–C catalyst (for preparation of Pd–Y–Pt/C catalyst) was calculated using this method to find out the active amount of Pd atoms out of the total Pd atoms in certain amount of Pd/C catalyst. After the initial measurement, the electrodes were scanned 20,000 times under the same condition as ADT test. The electrolytes were 0.5 M H₂SO₄ solution saturated with N₂ for the CV and potential cycling ADT test. ORR profile was analyzed using the same electrode in O₂ saturated 0.5 M H₂SO₄, linear scan voltammetry (LSV) was recorded from 1.0 to 0.5 V vs. RHE against the increasing rotation speeds—400, 900, 1600 and 2500 rpm. RRDE study was carried

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