



Size-controlled platinum nanoparticles prepared by modified-version atomic layer deposition for ethanol oxidation



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HIGHLIGHTS

- This study uses a modified atomic layer deposition (ALD) to prepare Pt particles.
- The pulse period of MeCpPtMe₃ serves as a key factor in tuning the particle size.
- The growth rate depends on surface adsorption, diffusion, and lateral interaction.
- The small-sized Pt catalysts offer better activity and excellent stability.
- The modified ALD method exhibits a great potential for tuning the Pt particle size.

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ABSTRACT

This study adopts a modified atomic layer deposition (ALD) process to prepare size-controlled Pt nanoparticles on the surface of carbon black, showing superior catalytic activity toward ethanol oxidation. Two types of ALD precursors, (methylcyclopentadienyl) trimethyl platinum (MeCpPtMe₃) and oxygen (O₂), were used to grow Pt deposits at 250 °C. For 30 ALD cycles, the pulse period of MeCpPtMe₃ serves as a key factor in controlling the particle size and the weight loading of Pt deposits. The Pt growth rates over the carbon support can be attributed to the surface coverage of Pt–O* sites, diffusion rate of MeCpPtMe₃, and lateral interaction between each active site. Since the MeCpPtMe₃ dose strongly affects the Pt particle size and the deposit density, the growth of ALD–Pt can be assumed as being diffusion-limited. Because of the surface-catalyzed reaction steps, the small-sized ALD–Pt catalysts offer better catalytic activity, CO tolerance, and long-term stability as compared with the large-sized ones. On the basis of the results, the modified ALD technique exhibits a great potential for tuning the Pt particle size and weight loading onto the carbon support for fuel cell application.

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1. Introduction

Atomic layer deposition (ALD) is one modified version of thin-film growth technique, exhibiting an excellent conformal and uniform growth with precision control over both thickness and composition [1]. In principle, the ALD process relies on the self-limiting chemistry of precursors and the interaction between substrates and precursor molecules [2,3]. Thus, the conformal growth can be ascribed to the atomic level control of thin-film growth using sequential and self-limiting surface reactions.

Recently, the ALD of metallic Pt nanoparticles has been explored to deposit Pt onto various complex supports such as carbon aerogels [2], graphene oxide (GO) sheets [4], carbon nanotubes (CNTs) [5,6], and GO/CNT hybrid [7]. The ALD–Pt catalysts onto various carbon supports can serve as electrochemical catalysts, which show superior catalytic activities toward hydrogen oxidation [5] and formic acid oxidation [4,6].

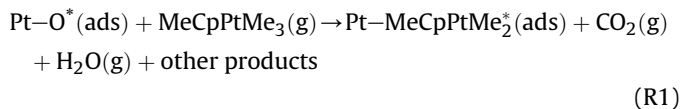
Pioneering studies have reported that a linear relationship between Pt deposit loading and ALD cycle number confirms the presence of self-limiting reaction steps [6,7]. The surface-limiting reactions would occur when a reaction is limited to the top layer of a deposit and stops when the surface is completely covered [8]. So far, (Methylcyclopentadienyl) trimethyl platinum (MeCpPtMe₃)

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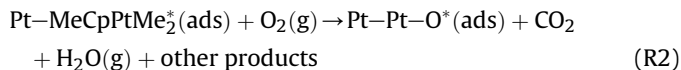
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and oxygen are frequently used precursors for ALD–Pt process. Basically, one ALD cycle consists of four steps: (i) MeCpPtMe₃ pulse, (ii) system purge, (iii) oxygen pulse, and (iv) system purge. The ALD cycle, thus, involves two self-limiting steps [1,9], which are described as.

The 1st half cycle:



The 2nd half cycle:



where “*” represents active surface species and Pt–O* represents chemically adsorbed oxygen on the platinum surface. Theoretically, the above self-limiting steps are established when adsorption saturation occurs. However, the ALD cycling operation usually takes a long time, especially for >100 cycles, which are capable of growing the Pt nanoparticles with an average size of 3–5 nm. Accordingly, one strategy to resolve the above problem is shortening the pulse period of precursor, and thus developing a modified ALD route.

The present work applied an improved ALD approach to grow Pt nanoparticles onto commercial carbon black (CB) powders. The MeCpPtMe₃ pulse period is chosen as a crucial factor in controlling the particle size and surface density of Pt deposits over the CB powders. The ALD cycle was fixed at 30 cycles, which is much less than previous studies [5]. To examine the catalytic performance, the ALD–Pt catalyst electrodes are characterized through the measurement of ethanol oxidation. The merit of the present study is that it shed some light on (i) applying the pulse period to control the morphology of ALD–Pt deposits and (ii) examining the catalytic activity of Pt nanoparticles for ethanol oxidation.

2. Experimental Section

A citric acid treatment was used to chemically oxidize commercial CB powders (Vulcan XC-72), implanting oxygen functionalities such as carboxyl (O–C=O), carbonyl (C=O), and ether (C–O) groups on the carbon surface [10]. The CB powders (2 g) were added to citric acid-containing aqueous solution (i.e., 2 g citric acid + 50 ml distilled water), and the CB slurry was then put in an ultrasonic bath for 1 h. After filtration, the wetted CB powders were heated in a furnace at 300 °C for 0.5 h. The oxidized CB powders (10 mg) were impregnated in 25 ml acetone in an ultrasonic bath for 0.5 h, inducing well-dispersed CB ink. A spray coating technique was capable of painting CB ink onto carbon paper (SGL 10 BC, Sigracet, Germany) with an area of 4 × 4 cm². The CB-coated carbon papers were then heated to 105 °C in an oven overnight. The weight loading of CB powders onto the carbon paper was set at approximately 0.6 mg cm⁻².

The Pt nanoparticles were deposited onto the CB-coated carbon paper at 250 °C by using home-made ALD reactor [7]. The deposition chamber was evacuated by a turbo-molecular pump, capable of providing a base pressure of ~10⁻⁶ Torr. In the ALD process, MeCpPtMe₃ (99%) and high-purity oxygen (99.9995%) were adopted as ALD precursors, and ultra-high-purity N₂ (99.9995%) was used as a carrier and a purging gas. The precursors were vapor-drawn into the ALD chamber through a stainless steel gas line heated to 110 °C. The pressure in the chamber was increased to 700 mTorr during the Pt precursor and O₂ pulses. Five different

MeCpPtMe₃ pulse periods (4, 6, 8, 10, and 20 s) were used in our study. After the MeCpPtMe₃ exposure, the next steps were N₂ purge (20 s), pumping (10 s), exposure to O₂ (10 s), N₂ purge (10 s) and pumping (10 s). The modified ALD process was carried out at 250 °C for 30 ALD cycles. After that, the ALD–Pt samples were placed at ambient temperature and assembled to catalyst electrodes without any further heat treatment.

Field-emission scanning electron microscope (FE-SEM, JEOL 2010F) and transmission electron microscope (TEM, JEOL, JEM-2100) were utilized to examine the dispersion and particle size distribution of as-prepared Pt catalysts over the CB surface. A thermogravimetric analyzer (TGA, Perkin Elmer TA7) was used to analyze the weight percentage of Pt catalysts on the CB support. The TGA analysis was performed under an air atmosphere at a heating rate of 10 °C min⁻¹ with the temperature range of 30–900 °C. The crystalline structure of the Pt catalysts was characterized by X-ray diffraction (XRD) with Cu-Kα radiation, using an automated X-ray diffractometer (Shimadzu Labx XRD-6000).

To examine catalytic activity, cyclic voltammetry (CV) measurement on ALD–Pt electrodes was conducted using 0.5 M H₂SO₄ as electrolyte with the potential range of –0.2 and 0.8 V vs. Ag/AgCl at sweep rates of 10–50 mV s⁻¹. The potential window employed here was based on our preliminary studies, indicating that the current collector (stainless foils) was electrochemically stable in sulfuric acid. In the three-electrode configuration, Pt wire and Ag/AgCl electrode served as counter and reference electrodes, respectively. The area (2 × 1 cm²) of the working electrode (i.e., Pt dispersed onto CB support) was the geometric area exposed to the electrolyte. First, the working electrodes were constructed by pressing the Pt/CB composites onto stainless steel foil, which served as current collector. The fresh stainless foils were electrochemically stable in 0.5 M H₂SO₄ within the potential range, confirmed by CV measurements. One crucial index, electrochemical surface area (ESA) value, based on the specific charge transfer, contributed from the Pt-based catalysts (Q_{cat}), could be determined

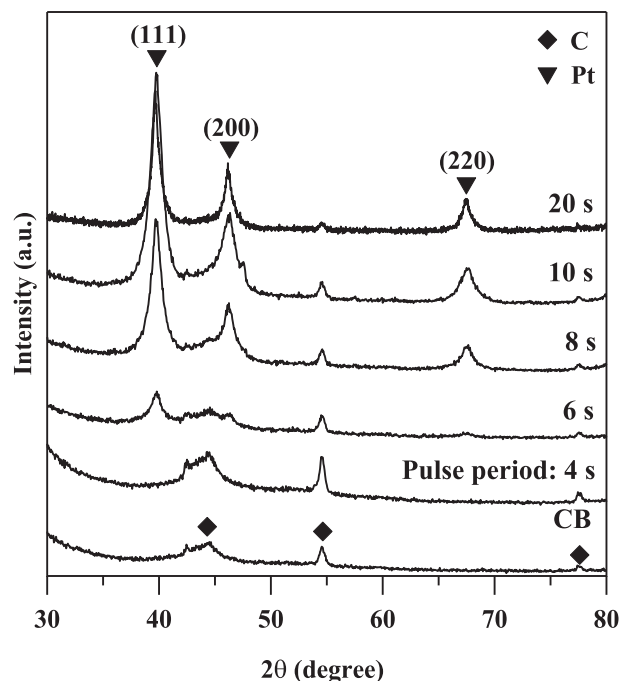


Fig. 1. Typical XRD pattern of ALD–Pt nanoparticles onto the surface of CB powders, prepared from the modified-version ALD route with different pulse periods of MeCpPtMe₃.

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