Electro-oxidation of methanol and formic acid on platinum nanoparticles with different oxidation levels

Chien-Te Hsieh [a],[*], Han-Tsung Hsiao [a], Dong-Ying Tzou [a], Po-Yuan Yu [a], Po-Yen Chen [b], Bi-Sheng Jang [b]

[a] Department of Chemical Engineering and Materials Science, Yuan Ze University, Taoyuan 320, Taiwan
[b] Materials and Electro-Optics Research Division, National Chung-Shan Institute of Science & Technology, Taoyuan 325, Taiwan

HIGHLIGHTS

- This study adopts atomic layer deposition (ALD) to grow metallic Pt nanoparticles.
- The Pt catalysts show catalytic activity toward methanol and formic acid oxidation.
- The reduction treatment induces a decrease in amount of Pt oxide (Pt—O) species.
- The Pt—O species creates a number of active sites to strip the CO-adsorbed sites.
- A stepwise reaction step concerning the promoted catalytic activity is proposed.

ARTICLE INFO

ABSTRACT

Herein reported is an atomic layer deposition (ALD) process of platinum (Pt) from (methyl-cyclopentadienyl) trimethylplatinum ($MeCpPtMe_3$) and oxygen (O_2) for synthesizing the Pt electro-catalysts toward methanol and formic acid oxidation. The as-synthesized Pt catalysts are thermally reduced in 5 vol% H_2 within temperature window of 150—450 °C. The reduction treatment induces a decrease in amount of Pt oxide (Pt—O) species, e.g., PtO and PtO_2. The presence of Pt—O species not only enhances catalytic activity but also improves anti-poisoning ability toward the oxidation of methanol and formic acid. The improved activity originates from the fact that the Pt—O species, formed by the ALD route, creates a large number of active sites (e.g., Pt—O_{ads} and Pt—$(OH)_{ads}$) to strip the CO-adsorbed sites, leading to a high-level of CO tolerance. This work also proposes a stepwise reaction steps to shed some lights on how the Pt—O species promote the catalytic activity.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Atomic layer deposition (ALD) is a thin film growth technique in which at least two types of gaseous precursors are introduced over a solid support based on the use of surface-limiting reactions [1–3]. The surface-limiting reactions take place when a reaction is limited to the top layer of a deposit and stop when the surface is completely covered [4]. Essentially, the ALD process starts with a nucleation stage, and then after a sequence number of cycles which is governed by the precursor—surface interaction, the deposited island tends to grow and coalesce into a continuous film. Recently, ALD of metals or alloys has been investigated to grow a variety of nanostructures with precise control onto complex supports such as Pt layers onto metallic cores and stabilized zirconia substrate [5], Pt—Pd core—shell nanostructures [6], and TiO_2 in mesoporous silica thin films [7]. Of noticed, ALD of Pt nanoparticles exhibits superior catalytic activity for fuel cell applications due to its well dispersion and precious size control on different types of carbon supports, e.g., carbon aerogels [8], graphene oxide (GO) sheets [9], carbon nanotubes (CNTs) [10,11], and GO/CNT hybrid [12].

The growth mechanism of noble metal ALD has been observed and examined by pioneering studies [13–15]. (Methyl-cyclopentadienyl) trimethylplatinum ($MeCpPtMe_3$) and oxygen have emerged as the most commonly used precursors for ALD—Pt process. In this ALD system, the organometallic precursor (i.e., $MeCpPtMe_3$) reacts with the oxygen atoms present in the metal's top monolayer. These O atoms are capable of combusting a large amount of the $MeCpPtMe_3$ precursor ligands at appropriate temperature [13]. The remaining ligands could be combusted through

the subsequent oxygen pulse upon the dissociative chemisorption of O_2, creating the saturated O atomic coverage. According to this model, the saturation of the ALD reaction is mainly limited by the supply of surface oxide species from the O_2 pulse [15]. The oxide skin layer exists over the surface of Pt nanoparticles due to the self-limiting reactions. However, how do the oxide layers affect the electrocatalytic activity of ALD−Pt is still unclear, and this issue is rarely discussed in literature.

In this report, one strategy for removing the Pt−O skin layer from the Pt surface by thermal reduction of the ALD−Pt nanoparticles in H_2-containing atmosphere was adopted. Three reduction temperatures (i.e., 150, 300, and 450 °C) were adopted to treat the resulting ALD−Pt nanoparticles onto commercial carbon black (i.e., XC-72). The relationship between the atomic O fraction and the reduction temperature was clarified using X-ray photoelectron spectroscopy (XPS). To inspect the catalytic activity, methanol and formic acid were electrochemically oxidized on ALD−Pt nanoparticles. The merit of the present work is to shed some light on how the Pt−O layer plays an important role in determining the catalytic performance of ALD−Pt nanoparticles for fuel cell applications.

2. Experimental section

2.1. Synthesis of Pt on carbon supports by ALD

First, commercial carbon black (CB, Vulcan XC-72) was chemically oxidized by citric acid treatment. This chemical oxidation allowed the implantation of oxygen functionalities including carboxyl (O−C=O), carbonyl (C=O), and ether (C−O) groups [11],

onto the CB surface. In this oxidation process, 2.0 g of CB powders was mixed with 2.0 g of citric acid (99.5%) and 50 ml distilled water with the aid of ultrasonic vibration for 1 h. The CB slurry was placed in a muffle furnace and then heated at 300 °C for 0.5 h. Second, the oxidized CB powders (10 mg) were well mixed with 25 ml acetone (95%) in an ultrasonic bath for 0.5 h. This ultrasonic shaking process would induce a homogenous suspension of CB ink. The CB ink was carefully painted onto carbon paper substrate (SGL 10 BC, Sigracet, Germany) with an area of 4×4 cm^2 by using a spray coater. Afterward, the treated carbon paper was 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 at 250 °C onto the CB-coated carbon paper (area: 4×4 cm^2) in a home-made ALD reactor, which has been published previously [12]. The deposition chamber was evacuated by a turbo-molecular pump, capable of providing a base pressure of ~10^{-6} Torr. Herein MeCpPtMe$_3$ (99%) and high-purity oxygen (99.9995%) served as ALD precursors, and ultra-high-purity N_2 (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 metal and O_2 pulses. The regular ALD cycle consisted of a 2.5-sec exposure to MeCpPtMe$_3$, a 20-sec N_2 purge, a 5-sec pumping, a 2.5-sec exposure to O_2, a 20-sec N_2 purge and a 5-sec pumping. The schematic procedure for the first and the second cycles has been proposed and illustrated in Fig. 1a and b, similar to our previous study [11,12]. To obtain ultralow loading and well dispersion of Pt nanoparticles, the ALD cycle was set at 30 cycles. After the ALD process, the Pt/CB samples were placed into horizontal furnace and then heated to
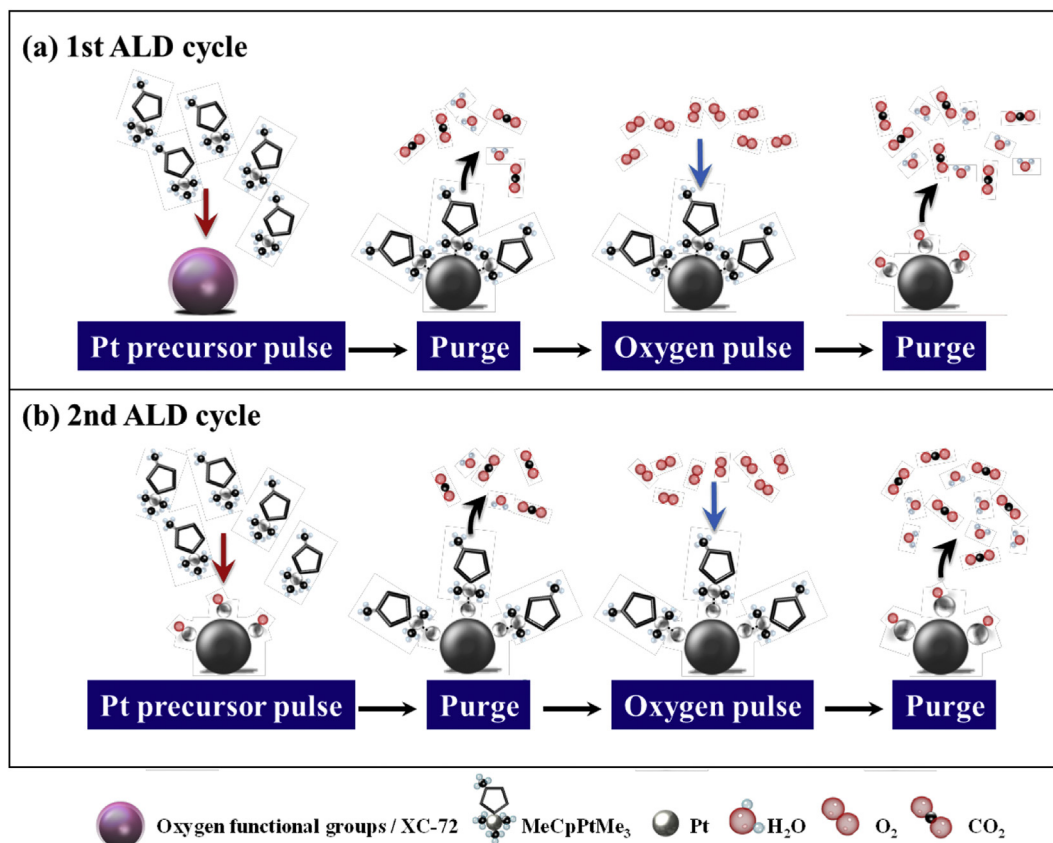

Fig. 1. Schematic diagram for the ALD growth mechanism of Pt onto CB powders: (a) the first and (b) the second cycles.