

Highly sensitive nanostructured platinum electrocatalysts for CO oxidation: Implications for CO sensing and fuel cell performance

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Abstract

Synthesis and electrochemical characterization of tailor-made nanostructured platinum catalysts efficient to oxidize dissolved carbon monoxide has been demonstrated in this work. Chemically modified electrodes using nanostructured (18 ± 0.5 nm size) platinum prepared by the electrodeposition from 0.25 M chloroplatinic acid on glassy carbon (GC) electrode shows interesting CO sensing behavior. Electrochemical oxidation of CO on this modified electrode surface has been investigated by cyclic voltammetry and stripping techniques preceded and followed by morphological and chemical characterization using scanning electron microscopy, transmission electron microscopy, and X-ray diffraction. Clear evidence for CO adsorption on these Pt nanoparticles is obtained from the combined analysis of energy-dispersive and X-ray photoelectron spectroscopy data, suggesting the nature of improvement in sensitivity due to nanostructured Pt particles. Enhancement in Pt 4f binding energy (ca. 1.5 eV) suggests interesting charge transfer features, which will help to unravel the mechanism of CO sensing by these electrochemical devices. Preliminary experiments using a prototype device show excellent sensitivity (i.e. within 20–25 s in the form of an increase in current from 0.01 to 3.8 μ A), and selectivity using and without a filter upon the introduction of 100 parts per million of CO in nitrogen.

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1. Introduction

Carbon monoxide, one of the most deleterious and toxic gaseous pollutants, is released in our environment from a variety of anthropogenic means. Being a colorless and odorless gas capable of causing serious health hazards like headache, disorientation, nausea, and death, its accurate detection is a daunting requirement. For this gas, Environmental Protection Agency recommends the threshold of 9 ppm or lower as an ambient air quality goal averaged over 8 h and 35 ppm or higher over 1 h exposure as a dangerous limit [1–4]. More significantly, this increased demand for portable monitoring of CO pollution has motivated researchers worldwide to develop smaller, cheaper

and low power consuming devices to replace the currently existing CO sensors [5–10]. Electrochemical sensors have many advantages over other types of CO sensors in terms of their linear output, low power requirements, and good resolution although their cross-sensitivity needs significant improvement [11,12].

One of the major approaches towards developing improved electrochemical sensors is the effective utilization of exciting properties of metal nanoparticles due to their high surface area with an objective of fabricating miniaturized devices [13,14]. This necessitates the development of many new electrocatalyst materials with better performance, specially applicable for solid-state electrochemical CO sensors, which in turn requires a fundamental understanding of its reactivity towards electrochemical CO oxidation and its relationship to the electrocatalyst's morphology [15,16]. In addition, the importance of such fundamental studies becomes evident from two other perspectives, the first arising from the necessity to mitigate the problem of irreversible binding of CO to Pt catalysts in PEM-

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FCs by CO in the reformed hydrogen [17,18]. More interesting is the second perspective where, the development of good catalysts for the water–gas shift reaction to generate hydrogen with low CO content, offering a valuable solution to the aforementioned problem of CO poisoning in PEMFCs.

Since platinum is the widely employed electrocatalyst for CO oxidation due to its chemical inertness in the acidic environment of PEMFCs, ensuring also a wide potential window, it would be attractive to explore any size and shape dependence to achieve better CO tolerance by tuning the size and morphology of these electrocatalysts. In this regard, designing a nanostructured platinum electrocatalyst has several benefits. First, since one of the imperative tasks of nanotechnology is to solve the kinetic limitations of existing materials, this approach can in principle, help to design better electrocatalysts especially because, nanoparticles exhibit unique chemical, physical and electronic properties that are different from those of their bulk materials. For example, the dependence of electrocatalytic activity on the surface structure and shape of the nanoparticles has been demonstrated [19,20], recently by a comparison of a nanoparticle-modified electrode with a macroelectrode, attributing their high effectiveness to enhanced surface area, mass transport, catalysis and control over confined microenvironment [21]. Similarly, Hall et al. have performed a comparative study of electrochemical detection of hydrogen peroxide at a bulk platinum electrode and modified platinum nanoparticle film electrode, in which the response of hydrogen peroxide on bulk platinum has been shown to be inferior owing to kinetic and diffusional limitations and complications arising from competitive adsorption of dioxygen to their electroactive sites and protonation of the adsorbed hydrogen peroxide complex. Secondly, an electrode modified by platinum nanoparticle film should have enhanced mass transport characteristics as demonstrated recently towards the detection of hydrogen peroxide due to its increased surface area [22,23]. More significantly, since reactivity of these nanoparticles varies strongly with size especially below a critical threshold, it is possible to tune selectivity by using monodispersed particles.

In this regard, we report here the synthesis and characterization of nanostructured Pt electrocatalysts capable of oxidizing dissolved CO at ambient temperatures. The unique feature of this material is its high sensitivity for detecting low parts per million of CO coupled with attractive characteristics such as good selectivity, rapid response, remarkable reproducibility and excellent stability in acidic medium. X-ray photoelectron spectroscopy and electron dispersive spectroscopy results suggest reasons for their improved performance, thereby demonstrating its applicability as electrocatalysts in solid-state CO sensors, PEMFCs and water–gas shift reaction employed in hydrogen reforming.

2. Experimental

2.1. Chemicals

Chloroplatinic acid (99.9%), lead acetate (99%), sodium borohydride (NaBH_4) and Nafion were purchased from Aldrich Chemicals while AR grade acetonitrile, ethanol, isopropyl alcohol and acetone were purchased from Merck. The PTFE-PM28Y

(thickness: 177 μm ; pore size: 3 μm ; porosity: 40 %) membrane for the fabrication of the sensor was purchased from POREX Corporation UK (MuporTM). Carbon monoxide (1% with nitrogen) was purchased from Deluxe Trading Co., India. All reagents were used without further purification and deionized water (16 M Ω) from Milli-Q system was used in all experiments.

2.2. Synthesis of platinum nanoparticles

Platinum black catalyst was synthesized by conventional electrodeposition using a two electrode system in which the platinum foil was used as anode while GC electrode (0.5 mm diameter) was used as a cathode in an aqueous solution of chloroplatinic acid (2.5 mM) containing 0.02% lead acetate for uniform deposition [24]. A GC electrode (3 mm diameter) was polished to mirror-finish with a 0.05 μm alumina powder prior to each experiment before passing a constant current of 0.1 mA/cm² for 15 min. A similar procedure was carried out using a platinum foil working electrode for collecting large amount for characterization. Since the size of the platinum particle depends on the concentration and temperature of the reaction conditions, lower concentration (mM) and 0 °C temperature were maintained through out the deposition to get smaller size distribution. The particles were washed repeatedly (three to four times) using deionized water and finally with acetone to remove chloride ions and other impurities. The resultant platinum nanoparticles showed an average particle size of 18 ± 0.5 nm.

3. Material characterization

The structure and morphology of these platinum particles were characterized using a scanning electron microscope (SEM) equipped with energy-dispersive X-ray analysis (EDS) attachment (A Leica Stereoscan 440 model SEM with a Kevex model EDAX system), X-ray diffractometer (XRD, Philips 1730 machine) and a transmission electron microscope (TEM, Philips CM200 FEG microscope). X-ray photoelectron spectroscopic (XPS) measurements were carried out on a VG MicroTech ESCA 3000 instrument at a pressure of $>1 \times 10^{-9}$ Torr (pass energy of 50 eV, electron takeoff angle 60°, and overall resolution ~ 1 eV). The spectra were fitted using a combined polynomial and Shirley type background function. Cyclic voltammograms (CV) were recorded on an Autolab PGSTAT30 (ECO CHEMIE) instrument using a standard three electrode cell comprising of Pt black modified GC disc as working electrode, Pt foil as counter electrode and Hg–Hg₂SO₄ as reference electrode in 0.5 M H₂SO₄ at room temperature.

4. Sensor fabrication

The electrodes were fabricated on PTFE–PM28Y membrane pretreated by placing the membrane in 50% isopropyl alcohol for 24 h before applying catalytic ink consisting of a homogeneous paste of platinum nanoparticles, Nafion and aqueous isopropyl alcohol. The binder was selected to acquire good adhesion of electrode material to the membrane improving the

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