# The electrochemical sensor for methanol detection using silicon epoxy coated platinum nanoparticles

Deog-Su Park [a], Mi-Sook Won [b], Rajendra N. Goyal [c], Yoon-Bo Shim [a,d,∗]

[a] Institute of BioPhysio Sensor Technology, Pusan National University, Busan 609-735, South Korea
[b] Busan Center, Korea Basic Science Institute, Busan 609-735, South Korea
[c] Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, India
[d] Department of Chemistry, Pusan National University, Busan 609-735, South Korea

## ABSTRACT

A platinum (Pt) nanoparticle-based electrochemical sensor has been applied for the detection of methanol in methanol fuel cells. The platinum nanoparticles were electrodeposited on glassy carbon (GC) in HCl containing hydrogen hexachloroplatinate using cyclic voltammetry. The size and distribution of the nanoparticles were found to be dependent on the deposition parameters, such as the concentration of platinum ions, scan rate, and number of cycles. The deposited platinum nanoparticles were spin-coated with silicone epoxy (SE), and scanning electron microscopy (SEM) confirmed the deposition. The concentration of methanol was determined by a double potential step chronoamperometric method using the SE/Pt/GC electrode at the oxidation potential of +0.60 V *vs.* Ag/AgCl electrode. The sensor exhibited a long-term stability for 40 h repeat using and has an advantage that adsorption of CO was eliminated by use of SE film. The dynamic range of the analytical method was determined to be from $2.5 \times 10^{-4}$ to $10.0$ M in two slopes with a detection limit of $1.0 \times 10^{-4}$ M.

## 1. Introduction

Methanol, the simplest alcohol, has attracted considerable attention in the last decade due to its use in fuel cells. Direct methanol fuel cells have been found useful in portable electronic devices due to their high energy and a small molecular weight [1,2]. These cells use methanol as fuel at an anode and oxygen or air at the cathode. As the concentration of methanol fluctuates during electrochemical reactions, it affects the cell performance [3,4]. A review on methanol cross over in direct methanol fuel cells highlighting the importance of methanol concentration has also appeared in the literature [5]. The effects of temperature and methanol concentration on the performance of methanol fuel cells have been studied, and the concentration of methanol used increased the power density of cell [6]. The cell performance of air breathing fuel cells has been enhanced by using higher feeding concentration of methanol [7,8]. Thus, it is necessary to develop a robust, reliable, and sensitive in an *in situ* method to determine the methanol concentration. Several analytical methods have described the determination of

methanol among which chromatography [9], surface plasmon resonance (SPR) [10] and FT-IR [11] are more common. These methods have disadvantages that they are expensive and far from the on-site where the analysis is actually needed.

As the concentration of methanol plays a vital role and affects the performance and durability of the fuel cell, several attempts have been made to develop a liquid methanol concentration sensor [12–14]. A review on methanol concentrations sensors for liquid fed direct methanol fuel cells has also appeared in publications [15]. Sensor-less control of methanol concentration based on methanol consumption rate has also been proposed [16]. The weakness of most of these methods is poisoning of the electrode due to strong adsorption of CO species formed as the product of methanol oxidation, which decreases the stability and sensitivity of the electrode. In addition, the slow response due to diffusion limitations also poses problems in many cases.

In the present study, we describe a robust method based on platinum nanoparticles modified electrode coated with silicon epoxy film (SE/Pt/GC) for the determination of methanol concentration in an alkaline solution. The Pt nanoparticles can be formed by chemical methods using a seed-mediated growth method [17,18] or electrochemical method [19]. In these studies, the electrochemical method is used for the deposition of Pt nanoparticles at the surface of glassy carbon. The final sensor treated with the silicon epoxy layer was examined for poisoning of the electrode by the CO gas

∗ Corresponding author at: Department of Chemistry and Institute of BioPhysio Sensor Technology, Pusan National University, Busan 609-735, South Korea.
Tel.: +82 51 510 2244; fax: +82 51 514 2122.
*E-mail address:* ybshim@pusan.ac.kr (Y.-B. Shim).

adsorption, the stability, and reproducibility of the sensor where it was evaluated in the methanol fuel cell environment.

## 2. Experimental

### 2.1. Materials and equipment

Commercially available HCl (35%, Osaka, Japan), $H_2PtCl_6$ (99.995%, Aldrich, USA), $KH_2PO_4$, NaOH (Junsei Chemical, Japan), silicon epoxy {poly(dimethylsiloxane)} (3140 liquid RTV, Dowconing, Korea), alumina (Breher, USA), tetrahydrofuran (99.5%, Kanto Chemical, Japan), glassy carbon (Tokai, Japan), methanol (99.97%, SK Chemical, Korea) and ethanol (99.9%, SK Chemical, Korea) were used in the study.

The electrode surface was cleaned with an ultrasonicator (Powersonic 405, Hwashin Technology Co., Korea). Distilled water was obtained using a Milli-Q water purification system (18 MΩ cm). Electrochemical measurements were carried out using a Kosentech model KST-P2 (S. Korea) potentiostat/galvanostat. Scanning electron microscopic (SEM) images were obtained using a Hitachi S-4200 SEM.

### 2.2. Preparation of probe electrode

Glassy carbon (GC) electrode was polished with 0.30 and 0.05 μm alumina slurries, rinsed with deionized water and sonicated for 10 min in distilled water followed by electrochemical precleaning in a 0.1 M $H_2SO_4$ solution. Platinum nanoparticles were electrodeposited on the surface of glassy carbon electrode by potential cycling between +0.05 and −0.35 V (vs. Ag/AgCl) from an aqueous solution of hydrogen hexachloroplatinate at a scan rate of 50 mV s$^{-1}$. Hydrochloric acid was used as a supporting electrolyte, and its concentration was 0.1 M in all solutions. The electrodeposition was carried out with 30 potential cycles. The silicone epoxy film on Pt/GC electrode was prepared by spin coating using a 0.5 μL of 1% tetrahydrofuran (THF) solution of silicone epoxy at room temperature. Three times spins were used at 30 min interval using a spin coater. The rotation speed was 1000 rpm. The coated silicon film was dried at room temperature for 12 h and thus a SE/Pt/GC electrode was ready to use. The thickness of the silicone epoxy layer was approximately 300 nm using SEM studies as shown in Fig. 1.

### 2.3. Determination of methanol

The redox potential of methanol was measured by using cyclic voltammetry (CV) between −0.1 and +1.0 V (vs. Ag/AgCl) at a scan
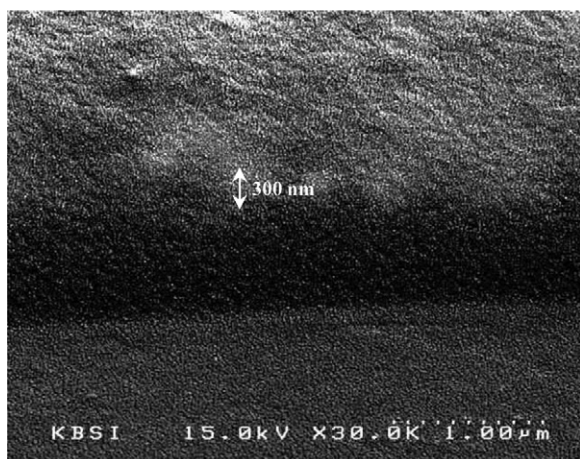


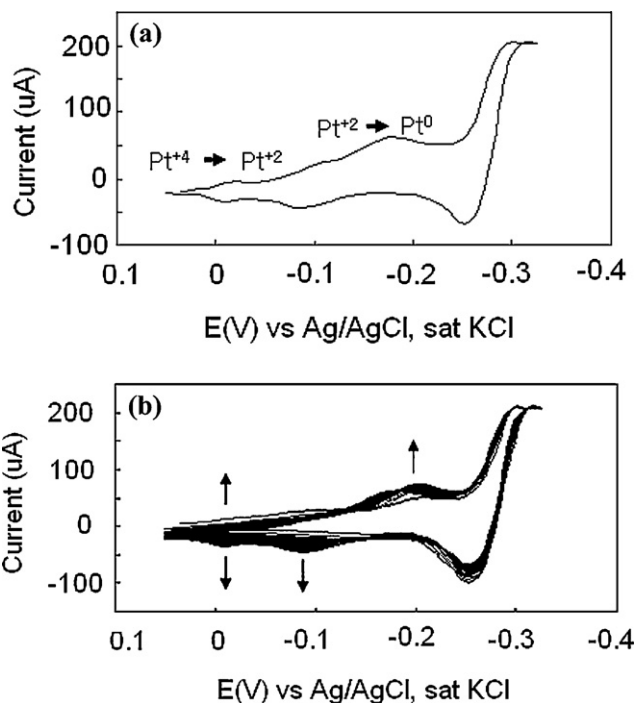Fig. 1. SEM micrograph of SE/Pt/GC surface depicting the thickness of the SE layer.



Fig. 2. CVs of electrodeposition of platinum on the GC surface with (a) 1 and (b) 30 cycles.

rate of 50.0 mV s$^{-1}$ and an equilibrium time was 15 s. A double potential step chronoamperometry was employed for the determination of methanol with the initial potential ($E_i$) of −0.10 V for 100.0 s, and a step potential ($E_s$) of +0.60 V for 100.0 s. The standard methanol solution was prepared by mixing a pH 10.0 of buffer solution (0.1 M NaOH + $KH_2PO_4$) and the appropriate amount of methanol in the range from $1.0 \times 10^{-4}$ to 10.0 M. A SE/Pt/GC or GC electrode, a saturated Ag/AgCl electrode and a spiral platinum wire were used as working, reference and auxiliary electrodes, respectively.

## 3. Results and discussion

### 3.1. Electrodeposition of platinum nanoparticles on a glassy carbon electrode

Electrodeposition of platinum from a hydrogen hexachloroplatinate solution involves the following steps [20,21]

$$PtCl_6^{2-} + 2e^- \rightarrow PtCl_4^{2-} + 2Cl^- \qquad (1)$$

$$PtCl_4^{2-} + 2e^- \rightarrow Pt + 4Cl^- \qquad (2)$$

Or overall reaction

$$PtCl_6^{2-} + 4e^- \rightarrow Pt + 6Cl^- \qquad (3)$$

The CVs recorded for electrodeposition of platinum in a 0.1 M HCl solution containing 3.0 mM hydrogen hexachloroplatinate is shown in Fig. 2. In this case, the potential scan started from 0.05 V and ended at 0.05 V through −0.35 V to complete a cycle at a scan rate of 50.0 mV s$^{-1}$. A peak at around −0.02 V appeared in the forward scan, which is due to the reduction of Pt(IV) to Pt(II) according to Eq. (1). On the other hand, the second peak at around −0.18 V associated to the reduction of Pt(IV) and/or Pt(II) to Pt(0) following Eqs. (2) and (3), respectively [22,23]. The evolution of hydrogen starts on the already-deposited platinum at the potential of approximately −0.25 V as shown in Fig. 2(a). In the reverse scan, a sharp peak is observed at −0.25 V, which is