

Short communication

# NaBH<sub>4</sub>-assisted ethylene glycol reduction for preparation of carbon-supported Pt catalyst for methanol electro-oxidation

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## Abstract

A carbon-supported Pt catalyst (40 wt.% loading) is prepared by a modified ethylene glycol reduction method (Pt–EG-complex). In this procedure, a complex produced by reacting ethylene glycol with sodium borohydride (NaBH<sub>4</sub>), serves as a reducing agent for the Pt precursor and as a stabilizer for preventing the growth of Pt particles. For purposes of comparison, two types of carbon-supported Pt catalyst (40 wt.% loading) are also prepared by a NaBH<sub>4</sub> reduction method, in which the Pt precursor is reduced in a ethylene glycol solution (Pt–EG–NaBH<sub>4</sub>) and in de-ionized water (Pt–H<sub>2</sub>O–NaBH<sub>4</sub>). Analysis by X-ray diffraction and transmission electron microscopy reveal that the Pt–EG-complex catalyst is comprised of highly-dispersed Pt nanoparticles with a uniform size (2.9–3.1 nm) on the carbon support, while large Pt particles are observed in the Pt–EG–NaBH<sub>4</sub> (3.3–3.6 nm) and Pt–H<sub>2</sub>O–NaBH<sub>4</sub> (5.7–6.2 nm) catalysts. The Pt–EG-complex catalyst has the highest electrochemical surface area and shows the highest catalytic performance for methanol electro-oxidation.

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**Keywords:** Carbon-supported platinum catalyst; Ethylene glycol reduction; Methanol electro-oxidation; Sodium borohydride; Nanoparticles

## 1. Introduction

One of the major problems in the polymer electrolyte fuel cell (PEMFC) systems is the use of expensive Pt-based noble metals as electro catalysts. Although several strategies have been proposed for cost reduction [1–3], the preparation of a supported Pt catalyst with a high Pt surface area is an attainable and feasible route to reducing the cost without decreasing the performance of the membrane-electrode assembly (MEA). Carbon-supported catalysts with high Pt loadings (above 20 wt.%) are typically used in MEA fabrication because of their many advantages over counterparts with low Pt loadings [4]. Due to the limited surface area of the carbon support, however, the preparation of a carbon-supported Pt catalyst with both high Pt loading and fine Pt dispersion is a challenging task.

Several methods, such as impregnation [5], chemical reduction [6] and electrodeposition [7] have been used for the deposition of Pt nanoparticles on carbon supports. Among these methods, the chemical reduction method, which involves the reduction of metal ions by a chemical agent such as ethylene glycol or NaBH<sub>4</sub>, has been widely used due to its relative simplicity for obtaining a carbon-supported Pt catalyst with a high Pt loading [8,9].

It has been reported that a partially-oxidized species, which is thought to originate from a reducing agent such as ethylene glycol, serves as an efficient stabilizer in the formation of a finely dispersed carbon-supported Pt catalyst with a narrow particle-size distribution [10–12]. Therefore, this method is generally considered to be attractive in that an additional stabilizer is not required to prevent metal growth and to disperse the reduced metal particles. In addition, considerable attention has also been paid to controlling the process parameters, such as the homogeneous heating of the synthesis mixture [12,13].

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It should be noted, however, that it is difficult to control synthesis conditions in a large-scale batch reactor without the use of an additional process such as microwave irradiation. The reproducibility of this method is strongly affected by the synthesis conditions.

This study presents a modified ethylene glycol reduction method for the preparation of highly dispersed, carbon-supported Pt catalysts. Specifically, a complex that is produced by reacting ethylene glycol with sodium borohydride ( $\text{NaBH}_4$ ), serves as a reducing agent for the Pt precursor and, simultaneously, as a stabilizer for the dispersion of Pt nanoparticles. Since the entire preparation process can be conducted at room temperature, the method promises to be an efficient and reproducible procedure for preparing carbon-supported Pt catalysts with a high Pt dispersion.

## 2. Experimental

### 2.1. Preparation of carbon-supported Pt catalyst

Vulcan XC-72 (Cabot, BET surface area of  $230 \text{ m}^2 \text{ g}^{-1}$ ) and  $\text{H}_2\text{PtCl}_6$  (Acros) were used as the carbon support and platinum precursor, respectively. The carbon support (100 mg) was dispersed with known amounts of Pt precursor in ethylene glycol. To the mixed solution, a solution prepared by reacting ethylene glycol with sodium borohydride (Aldrich) (molar ratio of ethylene glycol: $\text{NaBH}_4 = 10:1$ ) was slowly added with vigorous stirring. After stirring for 4 h at room temperature, an aqueous solution of HCl was added to deposit the Pt nanoparticles on the carbon support. The black precipitate was isolated on a filter, washed with de-ionized water and then dried at  $120^\circ\text{C}$  overnight to give a carbon-supported Pt catalyst (Pt-EG-complex). For purposes of comparison, two types of carbon-supported Pt catalyst were prepared by reducing the Pt precursor with  $\text{NaBH}_4$  in ethylene glycol solution and in de-ionized water, respectively. In each preparation, the carbon support and the Pt precursor were homogeneously mixed using a magnetic stirrer, followed by the reduction of the Pt precursor with an excess of  $\text{NaBH}_4$  (0.2 M). Pt-EG- $\text{NaBH}_4$  (prepared in ethylene glycol solution) and Pt- $\text{H}_2\text{O}$ - $\text{NaBH}_4$  (prepared in de-ionized water) catalysts were obtained after washing the corresponding filtered black precipitates with de-ionized water, followed by drying at  $120^\circ\text{C}$  overnight. FE-SEM-EDX analyses showed that Pt was successfully loaded on the carbon support in all catalysts.

### 2.2. Methanol electro-oxidation

Methanol electro-oxidation was carried out in a conventional three-electrode system that was equipped with a saturated calomel reference electrode and a platinum counter electrode. The working electrode was prepared by coating a small amount of catalyst ink on a glassy carbon disc. Cyclic voltammograms and galvanostatic current-potential curves were obtained at room temperature in a 0.5 M  $\text{H}_2\text{SO}_4$  solution that contained 2 M  $\text{CH}_3\text{OH}$  (EG & G 263A Potentiostat/Galvanostat).

## 3. Results and discussion

### 3.1. Characterization of carbon-supported Pt catalyst

The XRD patterns of Pt-EG-complex, Pt-EG- $\text{NaBH}_4$ , Pt- $\text{H}_2\text{O}$ - $\text{NaBH}_4$  and commercial Pt/C catalysts with 40 wt.% Pt loadings are shown in Fig. 1. All of the catalysts exhibit the typical diffraction peaks corresponding to Pt (1 1 1), Pt (2 0 0), and Pt (2 2 0). This is consistent with a face centred cubic phase of Pt nanoparticles. By applying Scherrer's equation to the Pt (2 2 0) diffraction peak, the average size of the Pt crystallites are found to be 2.9, 3.3, 5.7 and 3.6 nm for the Pt-EG-complex, Pt-EG- $\text{NaBH}_4$ , Pt- $\text{H}_2\text{O}$ - $\text{NaBH}_4$  and commercial Pt/C catalysts, respectively. The metal surface area was calculated using the following equation [14]:  $S = 6000/\rho d$ , where  $d$  is the average crystallite size (nm),  $S$  is the surface area ( $\text{m}^2 \text{ g}^{-1}$ ), and  $\rho$  is the density of Pt ( $21.4 \text{ g cm}^{-3}$ ). The metal surface areas of the Pt-EG-complex, Pt-EG- $\text{NaBH}_4$ , Pt- $\text{H}_2\text{O}$ - $\text{NaBH}_4$ , and commercial Pt/C catalysts are determined to be 97, 85, 49, and  $77 \text{ m}^2 \text{ g}^{-1}$ , respectively. These results demonstrate that the Pt-EG-complex is the most efficient catalyst in terms of Pt particle size and Pt surface area.

Transmission electron micrographs of the carbon-supported Pt catalysts are presented in Fig. 2. Compared with the Pt particles in the commercial catalyst (3.9 nm), the Pt-EG-complex and Pt-EG- $\text{NaBH}_4$  catalysts contained regular and highly-dispersed Pt nanoparticles on the carbon support (3.1 and 3.6 nm for Pt-EG-complex and Pt-EG- $\text{NaBH}_4$ , respectively). On the other hand, the Pt- $\text{H}_2\text{O}$ - $\text{NaBH}_4$  catalyst has the largest Pt particles (6.2 nm), with broad particle-size distribution.

In the preparation of the carbon-supported Pt catalyst, ethylene glycol first reacts with  $\text{NaBH}_4$  to form a complex of  $\text{Na}^+\text{B}^-(\text{OCH}_2\text{CH}_2\text{OH})_4$  which then serves as a reducing agent for the Pt precursor and as a stabilizer for the dispersion of Pt nanoparticles. The reducing strength of this complex is stronger than that of ethylene glycol, and as a result, the Pt precursor

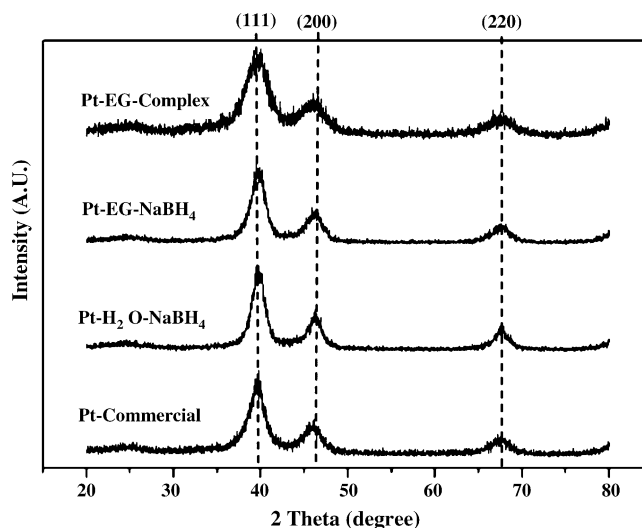


Fig. 1. X-ray diffraction patterns of carbon-supported Pt catalysts (40 wt.% loading).

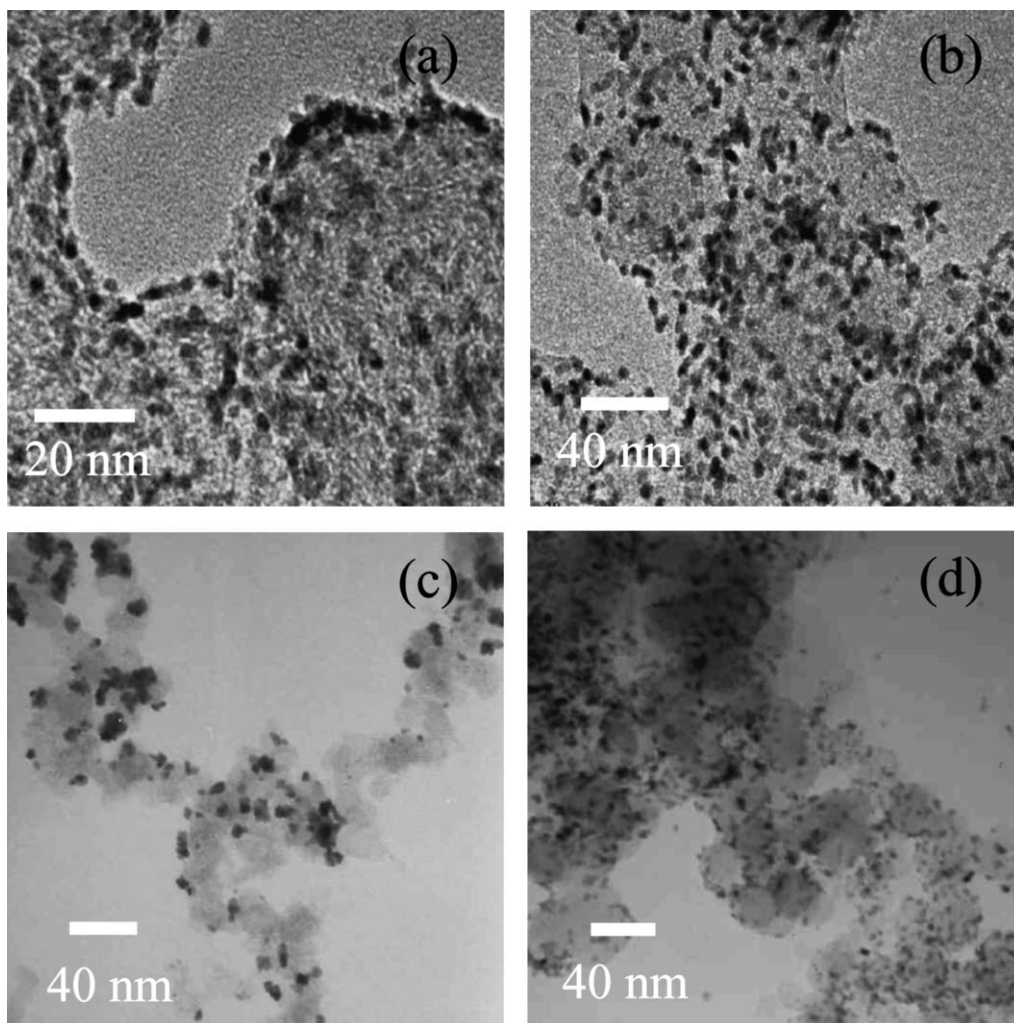


Fig. 2. Transmission electron micrographs of carbon-supported Pt catalysts (40 wt.% loading): (a) Pt-EG-complex, (b) Pt-EG-NaBH<sub>4</sub>, (c) Pt-H<sub>2</sub>O-NaBH<sub>4</sub>, (d) Pt-commercial.

is completely reduced at room temperature. Furthermore, this complex, as a stabilizer, has bulky characteristics and a strong affinity for Pt nanoparticles. Therefore, small Pt nanoparticles with a narrow particle-size distribution are formed in the Pt-EG-complex catalyst. When the Pt precursor is reduced directly with NaBH<sub>4</sub> in ethylene glycol (Pt-EG-NaBH<sub>4</sub>) a similar type of stabilizer might be also formed, and thus finely-dispersed Pt nanoparticles are expected in the Pt-EG-NaBH<sub>4</sub> catalyst. Compared with the Pt-EG-complex, however, the Pt precursor is reduced immediately by NaBH<sub>4</sub> in the Pt-EG-NaBH<sub>4</sub> catalyst and this results in the development of rather large Pt nanoparticles. On the other hand, when the entire process is conducted in water (Pt-H<sub>2</sub>O-NaBH<sub>4</sub>), this type of stabilizer is not formed and the resulting Pt-H<sub>2</sub>O-NaBH<sub>4</sub> catalyst contains very large Pt nanoparticles.

### 3.2. Electrochemical performance and methanol electro-oxidation

In order to estimate the electrochemical surface area (EAS), cyclic voltammograms (CVs) were obtained in a solution of

0.5 M H<sub>2</sub>SO<sub>4</sub>. The CVs (not shown here) of all the catalysts exhibit typical electro-adsorption/desorption of hydrogen at Pt sites. The electrochemical surface area (EAS) is calculated from the mean value of the coulombic charge exchanged during the electro-adsorption/desorption of hydrogen [14]. The Pt-EG-complex (83 m<sup>2</sup> g<sup>-1</sup>) and Pt-EG-NaBH<sub>4</sub> (70 m<sup>2</sup> g<sup>-1</sup>) catalysts exhibit higher EASs than the commercial Pt catalyst (65 m<sup>2</sup> g<sup>-1</sup>). The lowest EAS (38 m<sup>2</sup> g<sup>-1</sup>) is observed for the Pt-H<sub>2</sub>O-NaBH<sub>4</sub> catalyst.

Cyclic voltammograms are shown in Fig. 3(a) for methanol electro-oxidation on the carbon-supported Pt catalysts in a 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte containing 2 M CH<sub>3</sub>OH at room temperature. All the catalysts display maximum current peaks at 0.6–0.7 V versus SCE in the forward scan and these result from the electro-oxidation of methanol. Compared with the commercial catalyst, the Pt-EG-complex and Pt-EG-NaBH<sub>4</sub> catalysts exhibit a high maximum peak current, which demonstrates the superior catalytic performance of these catalysts. In particular, the Pt-EG-complex that shows the highest peak current exhibits a 1.5 times higher catalytic performance than the commercial catalyst. The Pt-H<sub>2</sub>O-NaBH<sub>4</sub> catalyst gives the lowest catalytic performance.

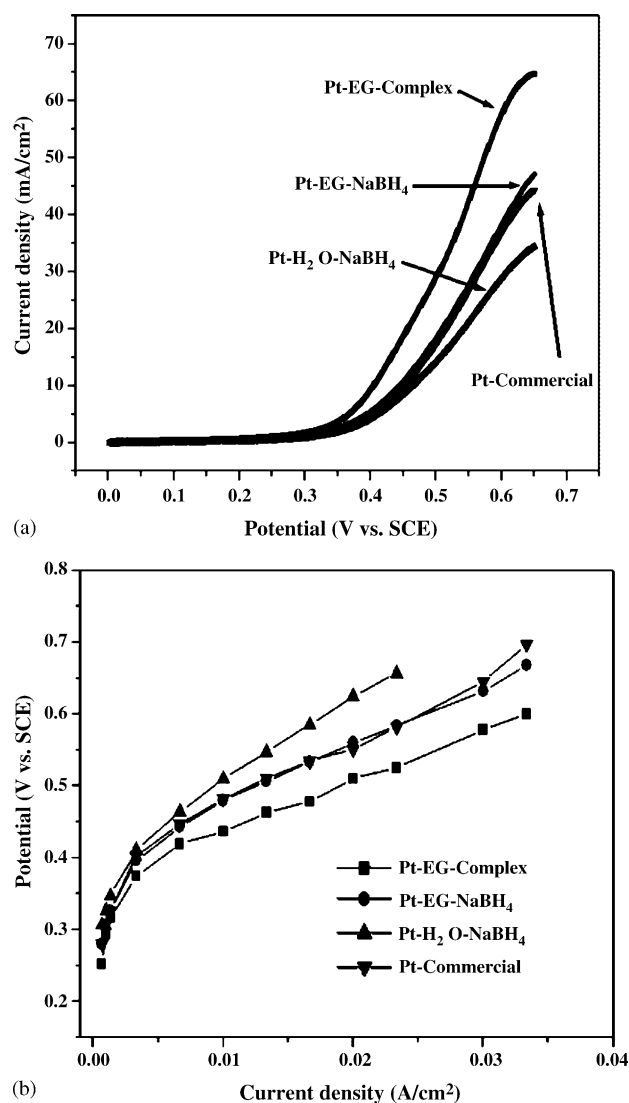


Fig. 3. (a) Cyclic voltammograms and (b) galvanostatic current-potential curves for a carbon-supported Pt catalysts (40 wt.% loading) on a glassy carbon disc electrode (working electrode) in H<sub>2</sub>SO<sub>4</sub> (0.5 M) containing CH<sub>3</sub>OH (2 M).

The catalytic activities are further confirmed by galvanostatic polarization measurements in a methanol solution. As shown in Fig. 3(b), the Pt-EG-complex catalyst has the lowest polarization performance over the entire range of current density, and this indicates that it has the highest catalytic activity for methanol electro-oxidation. The catalytic performance decreases in the order of Pt-EG-complex > Pt-EG-NaBH<sub>4</sub> ≥ Pt-commercial > Pt-H<sub>2</sub>O-NaBH<sub>4</sub>. It is concluded that the enhanced catalytic performance of the Pt-EG-complex catalyst results from a high EAS and a small particle size.

#### 4. Conclusions

Carbon-supported Pt catalysts have been prepared by the reduction of a Pt precursor in either ethylene glycol solution or de-ionized water using a NaBH<sub>4</sub> reducing agent (Pt-EG-NaBH<sub>4</sub> and Pt-H<sub>2</sub>O-NaBH<sub>4</sub>, respectively). A complex (Pt-EG-complex) catalyst has also been produced by reacting ethylene glycol with NaBH<sub>4</sub> which serves as both an efficient stabilizer and a reducing agent. There are uniform-sized Pt particles with a high Pt dispersion in the Pt-EG-complex. On the other hand, no stabilizing effect is observed for the Pt-H<sub>2</sub>O-NaBH<sub>4</sub> catalyst which has large Pt particles for methanol electro-oxidation, the Pt-EG-complex catalyst with the highest EAS (electrochemical surface area) exhibits the highest catalytic activity. The behaviour of a carbon-supported Pt catalyst is closely related to its EAS value.

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