

Synthesis and electrochemical analysis of Pt-loaded, polypyrrole-decorated, graphene-composite electrodes

Jiyoung Park and Seok Kim*

Department of Chemical and Biochemical Engineering, Pusan National University, Busan 609-735, Korea

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*Corresponding Author

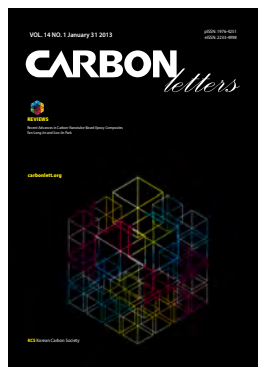
E-mail: seokkim@pusan.ac.kr

Tel: +82-51-510-3874

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Abstract

In this study, an electro-catalyst of Pt nanoparticles supported by polypyrrole-functionalized graphene (Pt/PPy-reduced graphene oxide [RGO]) is reported. The Pt nanoparticles are deposited on the PPy-RGO composite by chemical reduction of H₂PtCl₆ using NaBH₄. The presence of graphene (RGO) caused higher activity. This might have been due to increased electro-chemically accessible surface areas, increased electronic conductivity, and easier charge-transfer at polymer-electrolyte interfaces, allowing higher dispersion and utilization of the deposited Pt nano-particles. Microstructure, morphology and crystallinity of the synthesized materials were investigated using X-ray diffraction and transmission electron microscopy. The results showed successful deposition of Pt nano-particles, with crystallite size of about 2.7 nm, on the PPy-RGO support film. Catalytic activity for methanol electro-oxidation in fuel cells was investigated using cyclic voltammetry. The fundamental electro-chemical test results indicated that the electro-catalytic activity, for methanol oxidation, of the Pt/PPy-RGO combination was much better than for commercial catalyst.

Key words: Pt/PPy, graphene, direct methanol fuel cell

1. Introduction

The direct methanol fuel cell (DMFC) is an extremely promising power source for portable applications due to its simple handling and processing of fuel. DMFCs have several advantages (e.g., high energy-conversion efficiency, simple design, and environmental friendliness) compared with hydrogen, for applications involving transportation and portable electronic systems. Such fuel cells can provide a clean power source with high theoretical energy density and low cost, without requiring a separate hydrogen generation system [1]. Despite many efforts devoted to development of the DMFC, there still remain difficulties to be overcome in terms of efficiency and power density. Commercialization of these fuel cells has been facing serious difficulty due to kinetic constraints on the methanol oxidation reaction. To this end, Pt-based electro-catalysts for the methanol electro-oxidation reaction in acid solution has been widely studied in recent years, but high cost and limited quantities have prevented Pt from being used at commercial levels [2]. In addition, the Pt electro-catalyst is poisoned by intermediate products of methanol oxidation (e.g., CO_{ads}). Since the mid-1970s, modification of the catalyst surface has been made by the addition of a second, less expensive metal to the platinum to selectively direct methanol electro-oxidation to the platinum particles [3]. The electro-catalytic activity of Pt-based catalysts can be substantially enhanced by incorporation of other metals or oxides to form binary-alloy catalysts (i.e., PtRu, PtSn, PtFe, and PtCo) [4-6]. Conductive polymers, with highly accessible surface areas and high stability, have also been used to improve the activity of the graphene support layer and to enhance dispersal of the metal [7]. With this in mind, we developed a facile and efficient way to deposit Pt nano-particles using polypyrrole, on reduced graphene oxide (RGO) functionalized with conducting polymer. All the results demonstrated that, with

high electronic conductivity and easier charge transfer, this Pt/PPy-RGO combination exhibited the higher activity and stability than widely used commercial catalysts.

2. Experimental

Graphite oxide was synthesized from natural graphite (SP-1, Bay carbon) by a modification of Hummer's method [8]. The graphite powder was added to a mixture of sulfuric acid, sodium nitrate, potassium permanganate for the acid treatment. The oxidized and treated solution was filtered and washed with HCl (10%); then subjected to centrifugation (3600 rpm, 5 min) to remove residual graphite. The product of synthesis of PPy-RGO composites from 35 mg of graphene and 20 mg of pyrrole, was homogeneously dispersed in ethanol-water solution (1:1), then excess $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was slowly added to the suspension, which was stirred continuously at 0-5°C for 8 h. Finally, the resulting PPy-graphene powder was filtered and rinsed, first with water; then with ethanol, until the filtrate was colorless. The black powder so obtained was freeze-dried overnight. The product of synthesis of the Pt/PPy-RGO composites, using Pt/PPy-RGO at 20 wt% Pt loading, was then used as seeds. The PPy-functionalized RGO (0.1 g) was mixed ultrasonically with $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in ethylene glycol, after which the pH was adjusted to 10-11 by adding NaOH (1.0 M). The solution was subjected to ultrasonication for 10 min, and N_2 bubbling for 20 min; then stirred for 4 h at 120°C. After reaction, the resulting solid, black product was isolated by centrifugation, washed with distilled water and ethanol to remove any remaining ions in the final products, and then freeze-dried overnight. This final product is called PPy-RGO supported, Pt nano-particles.

3. Results and Discussion

The morphology of the Pt/PPy-RGO product and the deposition of the Pt nano-particles were characterized by transmission electron microscopy (TEM). In Fig. 1a, sheet-like graphene with crumple can be observed. In Fig. 1b, these PPy-assisted, graphene nano-sheets were exfoliated from graphite, and exhibited a smooth, paper-like structure. TEM images of Pt/RGO and Pt/PPy-RGO are shown in Figs. 1c and d, respectively. In Fig. 1c, the Pt/GO combination is shown condensed with other platinum nano-particles, which caused an increase in particle diameters and subsequent decrease in the activity at the Pt nano-particle sites, compared with those of the Pt/PPy-RGO combination.

The X-ray diffraction (XRD) patterns of the Pt/RGO (a) and Pt/PPy-RGO (b) in Fig. 2 revealed distinguishing diffraction peaks. The graphite showed (002) a diffraction peak at $2\theta = 26.5^\circ$ [9], but for Pt/PPy-RGO, the diffraction peaks of C (002) plane-shifted negatively. These peaks appeared at 24.8° and 24.1° , corresponding to an interlayer space of 0.337 nm, and implied successful preparation of the PPy-RGO. The diffraction peaks at $2\theta = 40.2^\circ$, 46.4° and 68.2° could be attributed to the (111), (200) and (220) crystalline planes of the face-centered cubic structure, respectively, of the Pt [10]. The Pt (220) peaks can be used to calculate the average Pt particle size according to the Scherrer equation [11]:

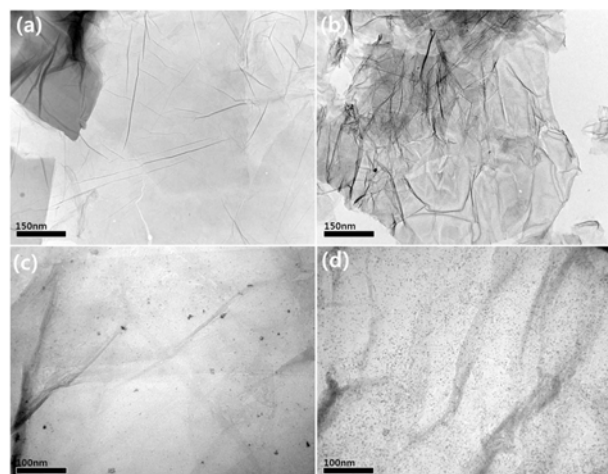


Fig. 1. Transmission electron microscopy images of (a) graphene, (b) PPy-graphene, (c) Pt/RGO and (d) Pt/PPy-RGO. RGO: reduced graphene oxide.

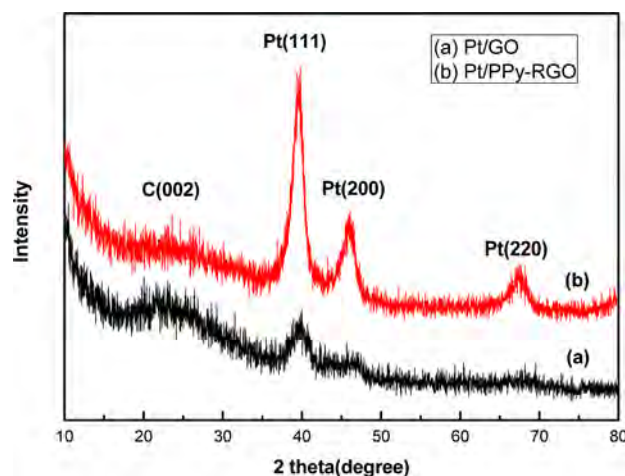


Fig. 2. X-ray diffraction patterns of (a) Pt/RGO and (b) Pt/PPy-RGO. RGO: reduced graphene oxide.

$$d = \frac{0.9\lambda}{B_{2\theta} \cos \theta_{\max}} \quad (1)$$

Where d is the average particle size (nm), λ is the wavelength of the X-ray used (0.15406 nm), $B_{2\theta}$ is the width of the diffraction peak at half height in radians, and θ_{\max} is the angle at the position of the peak maximum. The calculated mean sizes of Pt particles were found to be 2.7 and 2.4 nm for the Pt/RGO and Pt/PPy-RGO electro-catalysts, respectively.

Fig. 3 shows the CV of Pt/RGO and Pt/PPy-RGO in 0.5 M H_2SO_4 solution at 20 mV/S in a potential window of -0.2 to 1.0 V vs. SCE. Well-defined hydrogen desorption and adsorption peaks in the potential range of -0.05 to +0.3 V, and irreversible pre-oxidation and reduction peaks in the potential range of +0.5 to +1.0 V were observed. The electrochemically active surface area (EAS) was determined by assuming that a monolayer of adsorbed hydrogen requires 210 $\mu\text{C}/\text{cm}^2$ for its oxidation [12]. The EAS was then calculated using the following equation [13].

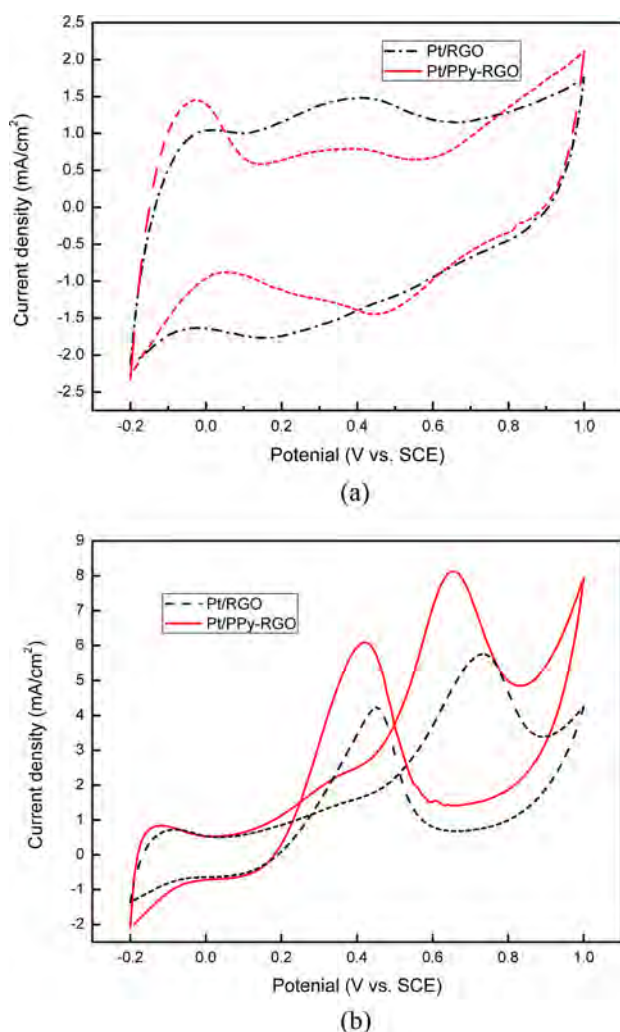


Fig. 3. (a) Cyclic voltammety (CV) of Pt/RGO and Pt/PPy-RGO in 0.5 M H_2SO_4 solution at a scan rate of 50 mVs⁻¹ between -0.2 and 1.0 V vs. SCE, (b) CV of Pt/RGO and Pt/PPy-RGO in 0.5 M H_2SO_4 and 1 M CH_3OH solutions, respectively, at a scan rate of 50 mVs⁻¹ between -0.2 V and 1.0 V vs. SCE: saturated calomel electrode.

$$\text{EAS} = Q/SI \quad (2)$$

Where 'S' is the proportionality constant used to relate charge with area and 'I' is the catalyst loading in 'g.' The EAS evaluated from the hydrogen adsorption and desorption peaks was calculated to be 61 and 35 m^2/g for the Pt/EDTA-GO and Pt/GO catalysts, respectively. The higher EAS of Pt/PPy-RGO was most likely due to the smaller size, and much better dispersion, of the Pt nano-particles on the polypyrrole-functionalized graphene. Fig. 4 shows the cyclic voltammety (CV) for methanol electro-oxidation, performed in a solution of 0.5 M H_2SO_4 and 1 M CH_3OH at room temperature. It is well known that the ratio of the forward anodic peak current (I_f) to the backward anodic peak current (I_b), I_f/I_b , is an index of the tolerance of the catalyst to the poisonous species accumulated on the surface of an electrode [14]. The higher I_f/I_b ratio indicates that much more methanol is oxidized as carbon dioxide and that intermediate species on the Pt particles are relatively less. Table 1 shows the values of I_f and

Table 1. The cyclic voltammety results for Pt/RGO synthesized by different mechanisms

Sample	ESA (m^2/g)	I_f (mA/cm^2)	I_b (mA/cm^2)	I_f/I_b ratio
Pt/RGO	35	4.0	5.7	0.7017
Pt/PPy-RGO	61	6.0	8.1	0.7407

EAS: electrochemically active surface area, RGO: reduced graphene oxide, I_f : the forward anodic peak current, I_b : the backward anodic peak current.

The higher anodic current of Pt/PPy-RGO indicated that the electric conductivity of graphene was higher than the commercial carbon, a result consistent with previous reports [15]. All of the above data reveal that the Pt/PPy-RGO combination exhibits enhanced catalytic activity for methanol oxidation.

4. Conclusions

In summary, a convenient and green approach was used to synthesize Pt nano-particles on polypyrrole-assisted graphene for methanol oxidation. XRD and TEM were used to characterize the morphology and structure of the catalysts. The electro-catalytic activities were measured by CV. In comparison with graphene as the support for the catalyst, the polypyrrole-assisted graphene can effectively enhance the electro-catalytic activity of the Pt nanoparticles for the oxidation of methanol. This was due to an increase in the conductivity of the graphene, by the insertion of polypyrrole. All the results indicated that the Pt/PPy-RGO combination is the more promising catalyst for fuel cell applications.

Acknowledgments

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