Graphene Supported Platinum-Cobalt Nanoparticles as Anode Electrocatalyst for Direct Methanol Fuel Cell

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Abstract- In the present study the graphene supported platinum-cobalt nanoparticles were prepared via microwave synthesis. The composition of prepared catalysts was examined by Inductively Coupled Plasma Optical Emission Spectroscopy. The shape and size of catalyst particles were determined by Transmission Electron Microscopy. The electrocatalytic activity of the graphene supported platinum-cobalt nanoparticles was investigated towards the electrooxidation of methanol in an alkaline medium. It was found that the graphene supported platinum-cobalt nanoparticles having the Pt:Co molar ratio 1:7 shows highest activity towards the electro-oxidation of methanol as compared with that of catalysts with the Pt:Co molar ratios equal to 1:1 and 1:44 and the graphene supported bare Co or commercial Pt/C with 10 wt.% Pt loading.

I. Introduction

Among the supports for the Pt-based catalysts such as carbon black, graphite nanofibres and carbon nanotubes [1-3], graphene as a catalyst support has incurred an intense interest in fuel cell applications due to its unique, outstanding physicochemical properties, such as an extremely high specific surface area (2600 m^2g^{-1}), a superior electronic conductivity, a high surface to volume ratio and a high stability [4, 5]. The combination of metal nanoparticles and graphene opens up new possibilities for design of the next generation catalysts [6].

In our previous works [7, 8] it has been shown that the graphene supported platinum-cobalt catalysts prepared by means of microwave synthesis enhance electrocatalytic activity towards the oxidation of borohydride and ethanol in an alkaline medium and are promising anode materials for direct borohydride fuel cells (DBFCs) and ethanol fuel cells (DEFCs). In the present study the activity of the graphene supported platinum-cobalt nanoparticles towards the electro-oxidation of other fuel, i.e. methanol, in an alkaline medium was investigated. The composition of prepared catalysts was examined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The shape and size of catalyst particles were determined by Transmission Electron Microscopy (TEM).

II. Experimental Details

Fabrication of Catalysts

The graphene supported platinum-cobalt nanoparticles (denoted as PtCo/GR catalyst) with the different Pt:Co molar ratios were prepared by microwave heating of ethylene glycol (EG) solutions of Pt(IV) and Co(II) salts as was described in [7, 8]. Briefly: 0.25 ml of 0.096 M H_2PtCl_6 and 0.6 ml solution of different concentrations of $CoCl_2$ were mixed with 18 ml of EG. Then, pH of the solution was adjusted to 11.7 by adding dropwise a 1 M NaOH solution. 100 mg of graphene (purity of 97%, specific surface area - 60 m^2/g) was added to the mixture and sonicated for 30 min. The reduction of Pt and Co nanoparticles was carried out in the microwave reactor Monowave 300 (Anton Paar) at a temperature of 170°C for 30 min. For comparison, the graphene supported cobalt nanoparticles (denoted as Co/GR catalyst) were prepared under the same conditions. After preparation, the synthesized catalysts were washed with acetone, ultra-pure water with the resistivity of 18.2 MΩ cm^{-1}, then filtered and dried in a vacuum oven at 80°C for 2 h.

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Characterization of Catalysts

The shape and size of catalyst particles were examined using a transmission electron microscope Tecnai G2 F20 X-TWIN equipped with an EDAX spectrometer with an r-TEM detector. For microscopic examinations, 10 mg of sample were first sonicated in 1 ml of ethanol for 1 h and then deposited on Cu grid covered with a continuous carbon film.

The composition of the PtCo/GR catalysts was estimated from ICP-OES measurements. The ICP optical emission spectra were recorded using an ICP optical emission spectrometer Optima 7000DV (Perkin Elmer).

Electrochemical Measurements

The working electrode was a thin layer of Nafion-impregnated PtCo/GR, Co/GR and commercial Pt/C with 10 wt.% Pt loading catalysts cast on a glassy carbon electrode, a Pt sheet was used as a counter electrode and an Ag/AgCl/KCl (3 M KCl) electrode was used as reference. The catalyst layer was obtained according to the following steps: at first 10 mg of the PtCo/GR or Co/GR catalysts were dispersed ultrasonically for 1 hour in a solution containing 0.25 μl of 5 wt.% Nafion (D521, 1100 EW) and 0.75 μl deionized H2O, while 10 mg of Pt/C with 10 wt.% Pt loading were dispersed ultrasonically for 1 hour in a solution containing 0.25 μl of 5 wt.% Nafion and 0.75 μl 2-propanol solution, to produce a homogeneous slurry. Then 5 μl of the prepared suspension mixture was pipetted onto the polished surface of a glassy carbon electrode with a geometric area of 0.07 cm2 and dried in air for 12 h.

All electrochemical measurements were performed with a Zennium electrochemical workstation (ZAHNERElektrik GmbH & Co.KG). Steady state linear sweep voltammograms were recorded in a 1 M CH3OH + 0.5 M NaOH solution at a linear potential sweep rate of 50 mV s–1 from -0.5 to 0.3 V at a temperature of 25 oC. The electrode potential is quoted *versus* the standard hydrogen electrode (SHE). The presented current densities are normalized with respect to the geometric area of catalysts.

The chronoamperometric curves for the investigated Pt/C and PtCo/GR catalysts were recorded in a 1 M CH3OH + 0.5 M NaOH solution at a constant potential value of 0 V vs. SHE for 5 min. All solutions were deaerated by argon for 15 min prior to measurements.

III. Results and Discussion

In the study presented herein a rapid microwave heating method was used to prepare the graphene supported platinum-cobalt nanoparticles with the different Pt:Co molar ratios. The composition of the prepared catalysts was determined by ICP-OES. It was found that the graphene supported platinum-cobalt catalysts with the Pt:Co molar ratios equal to 1:1, 1:7 and 1:44 (denoted as PtCo(1:1)/GR, PtCo(1:7)/GR and PtCo(1:44)/GR) were synthesized by means of rapid microwave heating.

Fig. 1 shows HRTEM images and corresponded EDX spectra of the Pt/C (a, e) and graphene supported PtCo nanoparticles with the Pt:Co molar ratios equal to 1:1 (b, f), 1:7 (c, g) [7] and 1:44 (d, h) [7]. According to the data of TEM analysis of the graphene supported PtCo and Pt/C catalysts, the Pt nanoparticles of ca. 1-3 nm in size were deposited on the surfaces of graphene and carbon. Pt nanoparticles were uniform and well dispersed on the surfaces of graphene and carbon.

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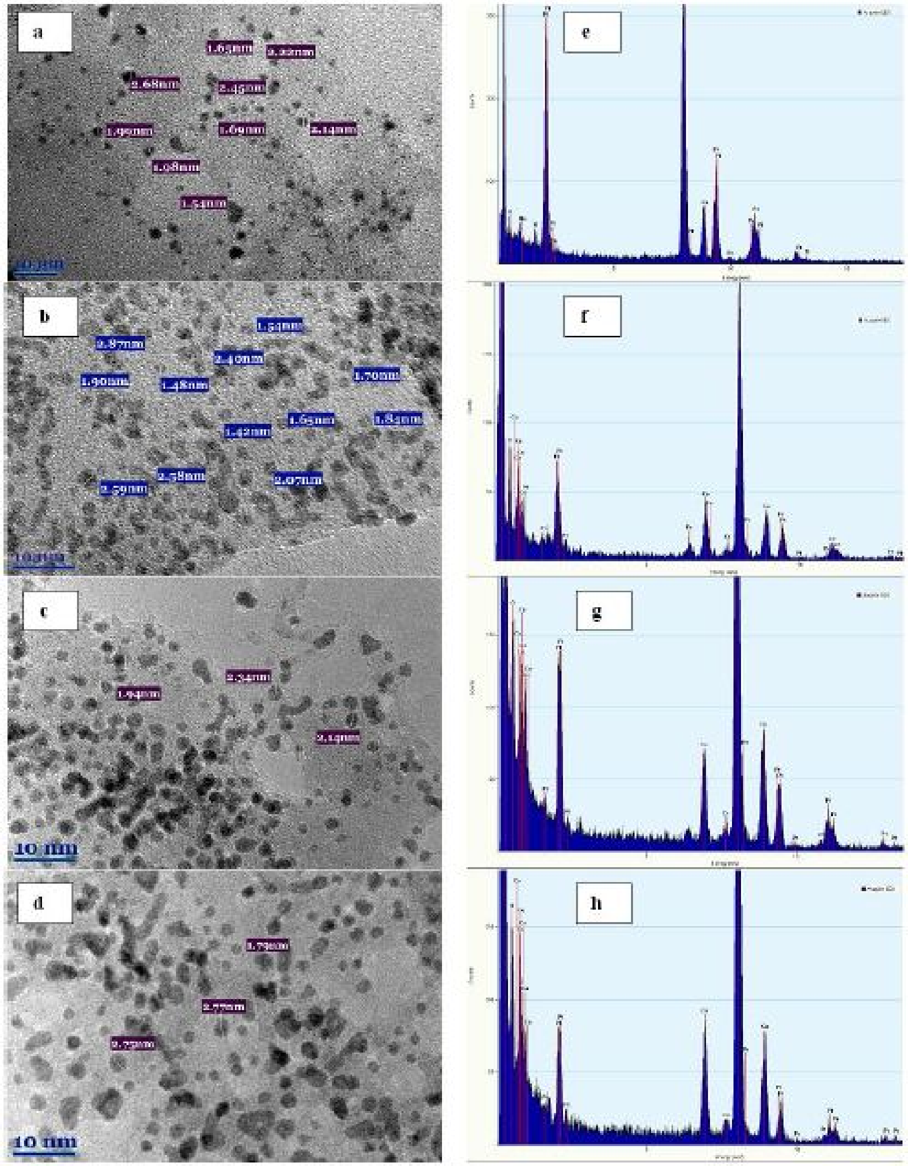

Figure 1. HRTEM images and corresponded EDX spectra of Pt/C (a, e), PtCo(1:1)/GR (b, f), PtCo(1:7)/GR (c, g) and PtCo(1:44)/GR (d, h).

The EDX spectra confirm the presence of Pt and Co nanoparticles in the investigated PtCo(1:1)/GR, PtCo(1:7)/GR and PtCo(1:44)/GR catalysts (Fig. 1 (f-h)).

Data of XRD analysis of the investigated catalysts described in Refs. [8] confirm that the crystallites of Pt in the synthesized graphene supported PtCo catalysts are very small, whereas the metallic Co crystallites of ca. 12 nm in size with an increased hexagonal crystal lattice (a = 0.25083 nm, c = 0.40824 nm) are predominant in the PtCo/GR catalysts. It should be noted that the increase in a lattice parameter could be caused by formation of platinum solid solution in cobalt.

The electrocatalytic activity of the graphene supported PtCo catalysts with the different Pt:Co molar ratios towards the electro-oxidation of methanol in an alkaline medium was compared with that of the commercial Pt/C catalyst with 10 wt.% Pt loading. The Pt/C, PtCo(1:1)/GR, PtCo(1:7)/GR and PtCo(1:44) catalysts with the Pt loadings of 0.385, 0.160, 0.165 and 0.125 mg Pt cm–2, respectively, were used for

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methanol electro-oxidation measurements by means of cyclic voltammetry. Fig. 2 shows long-term cyclic voltammograms for the Pt/C (the inset a'), PtCo(1:44)/GR (a), PtCo(1:7)/GR (b), PtCo(1:1)/GR (c) and Co/GR (a-c) catalysts recorded in a 1 M CH3OH + 0.5 M NaOH solution at a sweep rate of 50 mV s–1. In the forward sweep, anodic peaks **I** related with the direct oxidation of methanol in an alkaline medium are observed at ca. 0.1 V for the investigated Pt/C, PtCo(1:1)/GR, PtCo(1:7)/GR and PtCo(1:44)/GR catalysts (Fig. 2). In the reverse sweep, anodic peaks **II** attributed to the removal of the incompletely oxidized carbonaceous species formed in the forward sweep were detected at ca. -0.04 V for the all investigated catalysts. In all cases the reverse anodic peaks **II** recorded on the investigated catalysts are lower as compared to direct methanol oxidation peaks **I** (Fig. 2).

During long-term cycling the methanol electro-oxidation current density values (anodic peak **I**) recorded at the all investigated catalysts are slightly decreased and then are stabilized. As seen from the data in Fig. 2, the obtained stabilized methanol oxidation current densities (10th cycles) are greater at the PtCo(1:44)/GR (a), PtCo(1:7)/GR (b) and PtCo(1:1)/GR (c) catalysts as compared to those at the Pt/C catalyst (the inset a'). Furthermore, methanol oxidation current densities are ca. 4.8, 6.4 and 11.2 times higher at the PtCo(1:44)/GR, PtCo(1:1)/GR and PtCo(1:7)/GR catalysts than those at the bare Pt/C catalyst. The graphene supported PtCo catalyst with the Pt:Co molar ratio equal to 1:7 shows highest activity towards the electro-oxidation of methanol. Ca. 1.7 and 2.3 times greater methanol oxidation current densities are obtained at the latter catalyst as compared to those at the PtCo(1:1)/GR and PtCo(1:44)/GR catalysts, respectively.

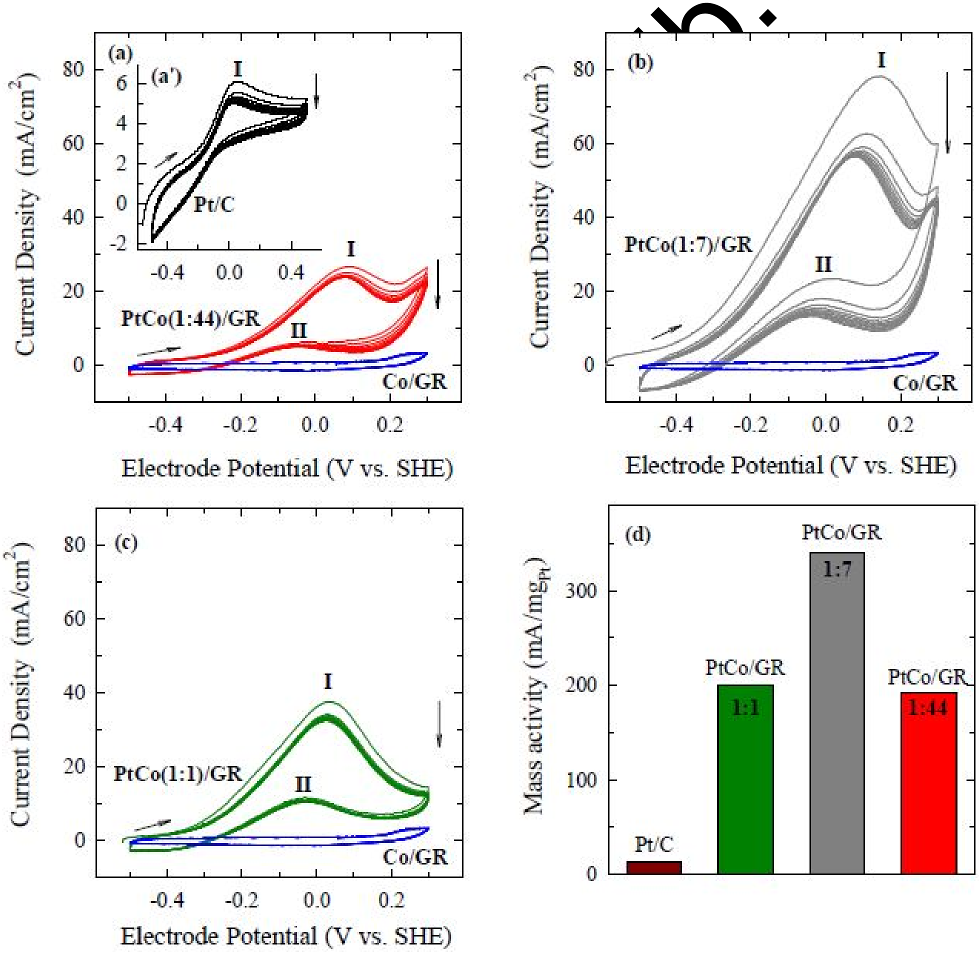

Figure 2. Cyclic voltammograms of the PtCo(1:44)/GR (a), PtCo(1:7)/GR (b), PtCo(1:1)/GR (c) and Co/GR (a-c) catalysts recorded in 1 M CH3OH + 0.5 M NaOH at a sweep rate of 50 mVs–1; 25 oC. The inset (a') represents the CVs of Pt/C in the same solution. (d) Bar columns of methanol oxidation current densities, normalized by the Pt loadings for the Pt/C and PtCo/GR catalysts, at a potential values of peak I.

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It should be noted that the investigated PtCo(1:1)/GR, PtCo(1:7)/GR and PtCo(1:44)/GR catalysts outperformed the bare Co/GR catalyst. Since the Co/GR catalyst exhibits significantly lower anodic currents as compared to those of the graphene supported PtCo catalysts with the different Pt:Co molar ratios, the enhanced electrocatalytic activity of the synthesized PtCo/GR catalysts may be ascribed to PtCo alloy formation and Pt electronic structure change due to the presence of Co [9-12].

To represent the mass activity of the Pt/C and graphene supported PtCo catalysts, methanol oxidation current densities were normalized by the Pt loadings for each catalyst. Figure 2d shows bar columns of methanol oxidation mass activities for the investigated catalysts at a the potential values of peak **I**. Methanol oxidation current densities normalized by the Pt loadings are ca. 14.8, 15.4 and 26.2 times higher at the PtCo(1:44)/GR, PtCo(1:1)/GR and PtCo(1:7)/GR catalysts as compared to those at Pt/C (Fig. 2d). It has been found that the graphene supported PtCo catalysts with the Pt:Co molar ratios equal to 1:1, 1:7 and 1:44 show an enhanced electrocatalytic activity towards the electro-oxidation of methanol in an alkaline medium as compared with that of the bare Pt/C catalyst.

The electrochemical stability of catalysts for methanol electro-oxidation was investigated by means of chronoamperometry. Fig. 3 shows the data obtained at the PtCo(1:1)/GR, PtCo(1:7)/GR, PtCo(1:44)/GR and Pt/C catalysts recorded at a constant potential of 0 V in a 1 M CH3OH + 0.5 M NaOH solution at 25 oC at the end of experimental period (*t* = 5 min). As evident from Fig. 3a, at the end of experimental period (*t* = 5 min), the current densities recorded at the PtCo(1:44)/GR, PtCo(1:1)/GR and PtCo(1:7)/GR catalysts are ca. 3.1, 4.8 and 7.9, respectively, are greater as compared to those at Pt/C, whereas ca. 1.6 and 2.6 times higher current densities are obtained at PtCo(1:7)/GR than those at PtCo(1:1)/GR and PtCo(1:44)/GR, respectively.

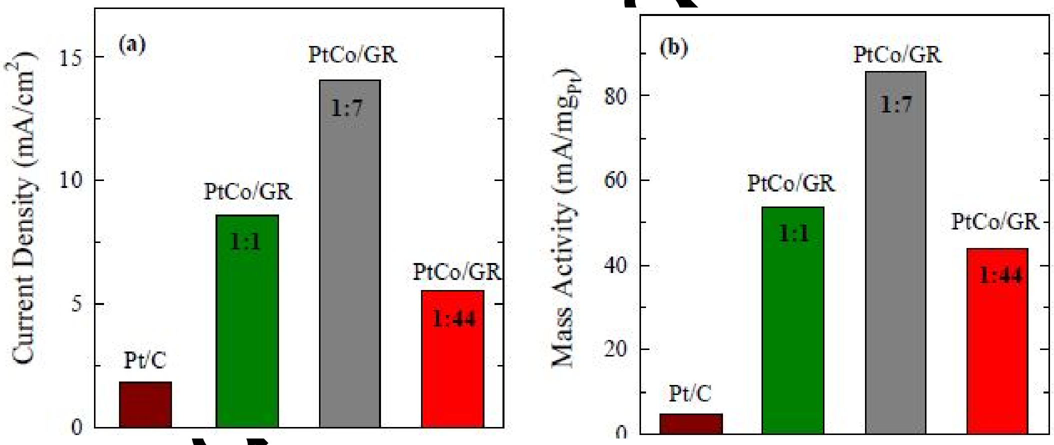

Figure 3. Bar columns of methanol oxidation current densities (a) and those normalized by the Pt loadings for each catalyst (b) obtained at the end of experimental period of 5 min, recorded at 0 V vs. SHE in 1 M CH3OH + 0.5 M NaOH at 25 oC.

The Pt mass current values for the electro-oxidation of methanol, recorded on the PtCo(1:7)/GR catalyst, are also ca. 1.6 and 1.9 times greater than those on the PtCo(1:1)/GR and PtCo(1:44)/GR catalysts, respectively (Fig. 3b). It should be noted that the investigated PtCo(1:1)/GR, PtCo(1:7)/GR and PtCo(1:44)/GR catalysts outperformed the bare Pt/C catalyst, i.e., the Pt mass current values are ca. 9.5, 11.6 and 18.4 times higher at PtCo(1:44)/GR, PtCo(1:1)/GR and PtCo(1:7)/GR than those at Pt/C. These data confirm the data obtained by cyclic voltammetry.

IV. Conclusions

The graphene supported platinum-cobalt catalysts with the Pt:Co molar ratios equal to 1:1, 1:7 and 1:44, with Pt nanoparticles of ca. 1-3 nm in size, were prepared by microwave synthesis. Highest electrocatalytic

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activity towards the electro-oxidation of methanol shows the graphene supported PtCo catalyst with a Pt:Co molar ratio equal to 1:7 as compared with those at the graphene supported PtCo catalyst with the Pt:Co molar ratios equal to 1:1 and 1:44 and bare Co catalysts and the commercial Pt/C catalyst with 10 wt.% Pt loading. The graphene supported PtCo catalysts synthesized by means of rapid microwave synthesis seem to be a promising anode material for direct methanol fuel cells.

Acknowledgments

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