

Synthesis, characterization and properties of the graphene supported platinum–cobalt nanocatalysts

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The graphene (GR) supported PtCo catalysts with different Pt:Co molar ratios were fabricated by means of the rapid microwave heating method. The size and shape of catalyst nanoparticles were determined by means of Transmission Electron Microscopy. Electrochemical properties of the PtCo/GR catalysts were investigated towards the electro-oxidation of methanol in an acidic medium by means of cyclic voltammetry and chronoamperometry.

The PtCo/GR catalysts with an average Pt particle size of ca. 1–3 nm were synthesized from the reaction mixture containing H_2PtCl_6 , CoCl_2 and ethylene glycol. It should be noted that the electrocatalytic activity of PtCo/GR catalysts depends on the molar ratio of Pt:Co in the catalysts. It was found that the synthesized PtCo/GR catalysts with the Pt:Co molar ratios equal to 1:3 and 1:6 exhibited an enhanced electrocatalytic activity for methanol electro-oxidation as compared with that of catalysts with the Pt:Co molar ratios equal to 1:20, 1:50 and 1:60 and 1:0.

Key words: Pt, Co, graphene, methanol oxidation

INTRODUCTION

Among different types of fuel cell technologies, direct methanol fuel cells (DMFCs) are the most suitable for mobile and portable electronic applications due to their high volumetric energy density, relatively low operating temperature and the convenience of a liquid fuel [1–3]. Especially for DMFCs Pt-based nanocomposites, in which Pt nanoparticles are incorporated into carbon black, graphite nanofibers and carbon nanotubes are used. Recently the use of a new form of carbon–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 ($2600\text{ m}^2\text{g}^{-1}$), a superior electronic conductivity, a high surface to volume ratio and a high stability [4–8]. Graphene can act as an ideal substrate for growing and anchoring various nanocrystalline Pt and Pt-based alloys for high-performance electrocatalytic devices. The combination of metal nanoparticles and graphene opens up new possibilities for design of the next generation catalysts.

On the other hand, the use of Pt has drawbacks that include the high price of Pt, as well as the propensity of Pt to be poisoned by carbon monoxide (CO), which is one of the carbonaceous species formed during the methanol dissociation

process. Alloying Pt with cheaper transition metals such as nickel, cobalt, iron, etc. allows reducing the amount of Pt (noble metal) and lowering the overall costs of catalysts [9–22]. It was found that the bimetallic Pt-M based catalysts exhibit a higher activity for the oxidation of methanol than the bare Pt catalyst [11, 12, 23–26]. The enhanced catalytic activity of Pt-based catalysts with transition metals has been attributed to the formation of PtM alloy and the change in the Pt electronic structure due to the presence of metal, Pt-Pt distance, and d-electron density in Pt [27–33].

In our previous works [34, 35], 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). Therefore, in the present study the activity of the graphene supported platinum–cobalt nanoparticles catalysts with different Pt:Co molar ratios towards the electro-oxidation of other fuel, i. e. methanol, in an acidic medium was investigated by means of cyclic voltammetry and chronoamperometry. The composition of prepared catalysts was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The shape and size of catalyst particles were determined by Transmission Electron Microscopy (TEM).

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EXPERIMENTAL

Chemicals

H_2PtCl_6 (99.9%) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (98%) were purchased from Alfa-Aesar and Sigma-Aldrich Supplies. Graphene (GR) (purity of 97%, specific surface area $60 \text{ m}^2 \text{ g}^{-1}$) was purchased from Graphene Supermarket Supply. Nafion (5 wt.%, D521, 1 100 EW) was purchased from Ion Power Inc. H_2SO_4 (96%), NaOH (98.8%), methanol, ethylene glycol (EG) and acetone were purchased from Chempur Company. All chemicals were of analytical grade. Ultra-pure water with the resistivity of $18.2 \text{ M}\Omega \text{ cm}^{-1}$ was used to prepare all the solutions.

Fabrication of catalysts by microwave synthesis

The PtCo/GR catalysts were prepared by microwave heating of ethylene glycol solutions of Pt(IV) and Co(II) salts as was described in details in Ref. [34]. A typical preparation consists of the following steps: 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 was added to the mixture and sonicated for 30 min. The reaction mixture obtained was put into a Monowave 300 microwave reactor (Anton Paar). The synthesis of PtCo/GR was carried out at a temperature of $170 \text{ }^\circ\text{C}$ for 30 min. For comparison, the graphene supported Pt catalyst was also prepared at $170 \text{ }^\circ\text{C}$ for 30 s. The duration of Pt/GR preparation was shortened to 30 s with the aim to compare the obtained PtCo/GR and Pt/GR catalysts having approximately a similar size of Pt particles in the created catalysts. After the preparation, the synthesized catalysts were washed with acetone, then filtered and dried in a vacuum oven at $80 \text{ }^\circ\text{C}$ for 2 h.

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 the sample was first sonicated in 1 ml of ethanol for 1 h and then deposited on the Cu grid covered with a continuous carbon film.

The Pt and Co metal loadings were estimated from ICP-OES measurements. The ICP optical emission spectra were recorded using an ICP optical emission spectrometer Optima700DV (Perkin Elmer).

Electrochemical measurements

A three-electrode electrochemical cell was used for electrochemical measurements. The working electrode was a thin layer of Nafion-impregnated PtCo/GR catalysts deposited on a glassy carbon electrode. The Pt sheet was used as a counter electrode and Ag/AgCl as a reference electrode. The catalyst layer was obtained according to the following steps: at first

the required amounts of PtCo/GR or Pt/GR catalysts were dispersed ultrasonically for 1 hour in a solution containing $0.25 \mu\text{l}$ of 5 wt.% Nafion and $0.75 \mu\text{l}$ deionized H_2O to produce a homogeneous slurry. Then $5 \mu\text{l}$ of the prepared suspension mixture was pipetted onto the polished surface of a glassy carbon electrode with a geometric area of 0.07 cm^2 and dried in air for 24 h.

All electrochemical measurements were performed with a Zennium electrochemical workstation (ZAHNER-Elektrik GmbH & Co.KG). Steady-state linear sweep voltammograms were recorded in a deaerated 1 M CH_3OH + 0.5 M H_2SO_4 solution at a linear potential sweep rate of 50 mV s^{-1} from 0 to 1.2 V at a temperature of $25 \text{ }^\circ\text{C}$. 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 electrochemically active surface areas (ESAs) of the prepared catalysts were determined from the cyclic voltammograms (CVs) of the Pt/GR and PtCo/GR catalysts recorded in a deaerated 0.5 M H_2SO_4 solution at a sweep rate of 50 mV s^{-1} by calculating the charge associated with hydrogen adsorption ($220 \mu\text{C cm}^{-2}$) [36].

RESULTS AND DISCUSSIONS

The graphene supported PtCo catalysts having the Pt:Co molar ratios equal to 1:3, 1:6, 1:20, 1:50 and 1:60 (denoted as PtCo(1:3)/GR, PtCo(1:6)/GR, PtCo(1:20)/GR, PtCo(1:50)/GR, and PtCo(1:60)/GR) were prepared by means of rapid microwave heating in the same manner as described in Ref. [34]. As seen from the TEM images of catalysts in Fig. 1, the PtCo catalysts with the Pt:Co molar ratios equal to 1:3 (a), 1:6 (b) and 1:50 (c) were well dispersed on the surface of graphene. The size of PtCo nanoparticles was found to be ca. 1–3 nm. For comparison, the Pt/GR catalyst synthesized in the same way has the size of Pt nanoparticles of ca. 4–5 [34].

The Pt loading in the synthesized catalysts was determined by ICP-OES. It was found that the Pt loadings were near $0.1 \text{ mg Pt cm}^{-2}$ in all catalysts. The electrochemically active surface areas of Pt in the synthesized catalysts were determined from the CVs of the Pt/GR and PtCo/GR catalysts recorded in a deaerated 0.5 M H_2SO_4 solution at a sweep rate of 50 mV s^{-1} by calculating the charge associated with hydrogen adsorption ($220 \mu\text{C cm}^{-2}$) (Fig. 2). The determined values of ESA are 0.7 cm^2 for Pt/GR and 5.2, 2.9, 1.6, 1.0 and 0.5 cm^2 for the catalysts with the Pt:Co molar ratios equal to 1:3, 1:6, 1:20, 1:50 and 1:60, respectively. These results show that the ESA values are ca. 1.4, 2.3, 4.1 and 7.4 times higher at the PtCo/GR catalysts with the Pt:Co molar ratios equal to 1:50, 1:20, 1:6 and 1:3 than those of the Pt/GR catalyst.

The electrocatalytic properties of the Pt/GR and different PtCo/GR catalysts were investigated towards methanol oxidation reaction in an acidic medium by means of cyclic voltammetry and are presented in Fig. 3. As shown in

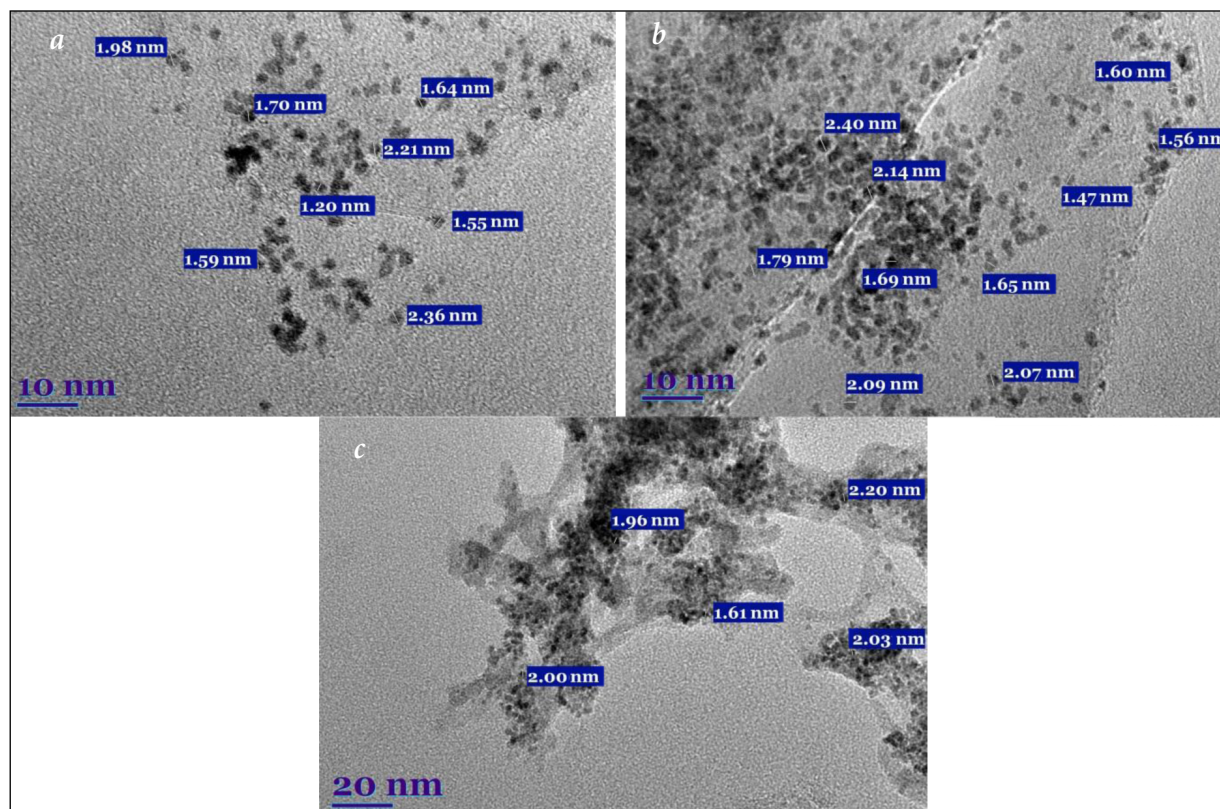


Fig. 1. HRTEM images of PtCo/GR with different Pt:Co molar ratios: (a) PtCo(1:3), (b) PtCo(1:6) and (c) PtCo(1:50)

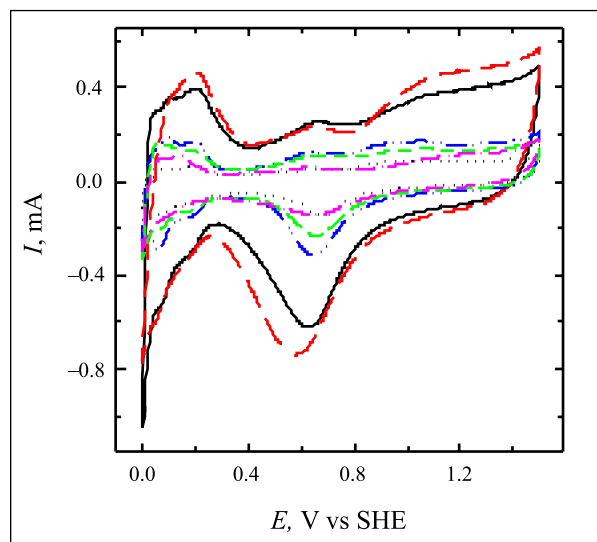


Fig. 2. CVs of the PtCo(1:3)/GR (solid line), PtCo(1:6)/GR (long dashed line), PtCo(1:20)/GR (dash-dot-dotted line), PtCo(1:50)/GR (short dashed line), PtCo(1:60)/GR (dash-dotted line) and Pt/GR (dotted line) catalysts recorded in 0.5 M H_2SO_4 at 50 mV s^{-1} ; 25°C

Fig. 3a, all CV curves show similar oxidation current peaks I in the forward scans and peaks II in the reverse scans. Peak I in the forward scan is related to the oxidation of freshly chemisorbed species issued from methanol adsorption, whereas peak II may be related to the removal of carbonaceous species incompletely oxidized in the forward scan [37]. It

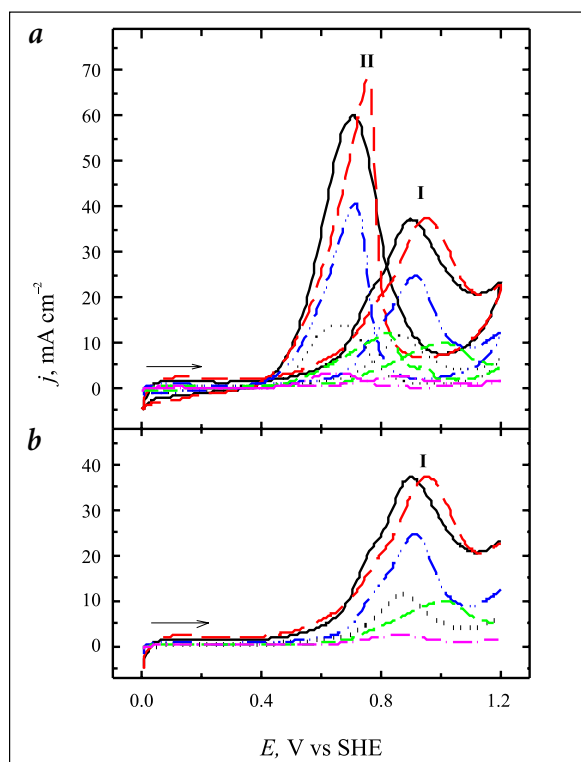


Fig. 3. (a) CVs of the PtCo(1:3)/GR (solid line), PtCo(1:6)/GR (long dashed line), PtCo(1:20)/GR (dash-dot-dotted line), PtCo(1:50)/GR (short dashed line), PtCo(1:60)/GR (dash-dotted line) and Pt/GR (dotted line) catalysts recorded in 1 M CH_3OH + 0.5 M H_2SO_4 at 50 mV s^{-1} ; 25°C . (b) Positive-potential going scans of the same catalysts

should be noted that the exact potential values of peaks I (e. g. at ca 0.4 V) differ (Fig. 3b) for different catalysts investigated and this difference could reach about 0.1 V. Methanol oxidation current density values (peak I) are ca. 2.1–3.2 times higher at the PtCo(1:3)/GR, PtCo(1:6)/GR and PtCo(1:20)/GR catalysts than those at the Pt/GR catalyst. The highest electrocatalytic activity towards the electro-oxidation of methanol shows the graphene supported PtCo catalyst with the Pt:Co molar ratios equal to 1:3 and 1:6 as compared with those at the catalysts with the Pt:Co molar ratios equal to 1:20, 1:50 and 1:60 and the Pt/GR catalyst (Fig. 3a). It should be noted that increase in the Pt:Co molar ratios from 1:20 up to 1:60 in the PtCo/GR catalysts decreases the activity of those catalysts towards methanol oxidation (Fig. 3a).

Additionally, it is worth to note that the onset potential of methanol oxidation on the 1:3 and 1:6 catalysts are lower than that of other investigated catalysts, indicating a higher activity towards methanol oxidation. As described in literature [1, 39–41], the onset potential is related to the breaking of C-H bonds and the subsequent removal of intermediates by oxidation with OH_{ads} . A lower onset potential indicates that the overpotential of methanol oxidation is lower and the electrocatalytic methanol oxidation occurs more easily on the electrode.

To evaluate the electrocatalytic activity of catalysts the methanol oxidation current density values under the potential values of peak I were normalized by the Pt loadings and electrochemically active surface areas for each catalyst to represent the mass activity (Fig. 4a) and specific activity (Fig. 4b) of catalysts. As seen from the data in Fig. 4a, the highest Pt mass activity shows the PtCo/GR catalyst with the Pt:Co molar ratio equal to 1:6. However, assuming ca. 7.4, 4.1, 2.3 and 1.4 times higher active surface area of the PtCo/GR catalysts with the Pt:Co molar ratios equal to 1:3, 1:6, 1:20 and 1:50 compared to the bare Pt/GR catalyst, the surface area normalized methanol oxidation current densities are ca. 2.3, 1.3, 1.1 and 1.7, respectively, times higher on Pt/GR (Fig. 4b).

The catalytic stability of the PtCo/GR and Pt/GR catalysts were examined using chronoamperometry. Figure 5 shows the chronoamperometric curves recorded at the different PtCo/GR catalysts and Pt/GR in a 1 M CH_3OH + 0.5 M H_2SO_4 solution at a fixed potential value of 0.9 V. As evident from the data in Fig. 5a, all the catalysts show a current decay for methanol oxidation, which might be due to the formation of intermediate species, such as CO_{ads} , CHO_{ads} etc., during the methanol oxidation reaction [38]. At the end of the experimental period ($t = 300$ s) the current density values of the PtCo/GR catalysts with the Pt:Co molar ratios equal to 1:50, 1:20, 1:6 and 1:3 are ca. 2–5 times higher than those of Pt/GR, indicating a higher electrocatalytic activity and stability of the prepared PtCo/GR catalysts towards the oxidation of methanol (Fig. 5a). Figure 5 b, c shows the methanol oxidation current densities normalized by the Pt load-

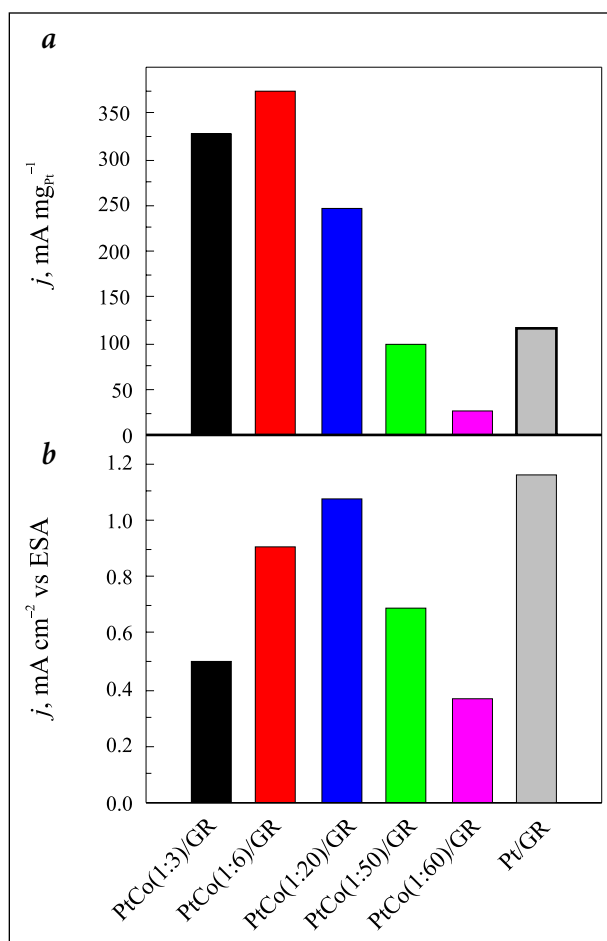


Fig. 4. Methanol oxidation current densities under the potential values of peak I recorded in 1 M CH_3OH + 0.5 M H_2SO_4 at 50 mV s^{-1} and normalized by the Pt loadings (a) and electrochemically active surface areas (b) for each catalyst

ings (b) and electrochemically active surface areas (c) for each catalyst at the end of the experimental period (300 s). As evident, the current densities normalized by the Pt loadings for each catalyst are also ca. 2–5 times higher at the catalysts with the Pt:Co molar ratios equal to 1:50, 1:20, 1:6 and 1:3 as compared with Pt/GR (Fig. 5b). The highest Pt mass activity also shows the PtCo/GR catalysts with lower Pt:Co molar ratios, e. g. 1:3 and 1:6. The fabricated graphene supported PtCo catalysts have a higher catalytic activity and a better stability for methanol oxidation than the graphene supported Pt. This result is in agreement with the results of cyclic voltammetry curves. Notably, the methanol oxidation current densities normalized by the ESAs values for each catalyst are highest at the PtCo/GR with the Pt:Co molar ratio equal to 1:50 (Fig. 5b).

It can be noted that in some cases the values of the data obtained by means of CV and CA and normalized by ESA values differ. The explanation of this phenomenon could be related to the electrode potential values, since in the case of CA they were fixed and equal to 0.9 V, whereas in the CV measurements the peak values which differ at different potentials were used for calculations (see above).

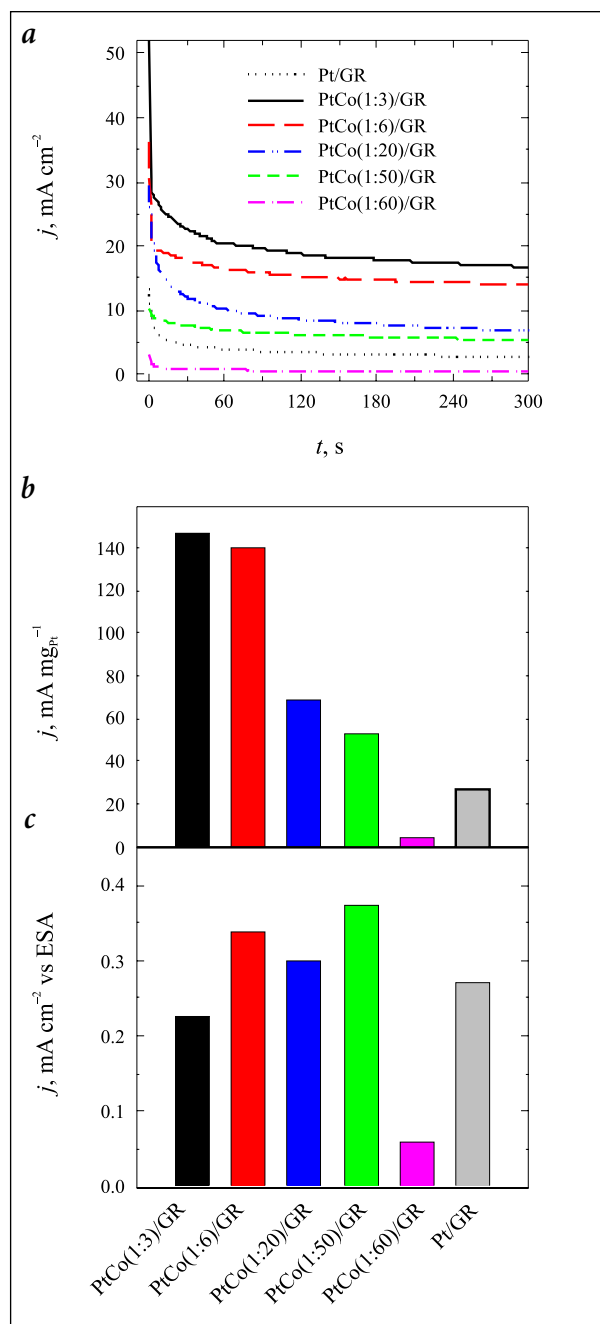


Fig. 5. (a) Chronoamperometric data of PtCo(1:3)/GR (solid line), PtCo(1:6)/GR (long dashed line), PtCo(1:20)/GR (dash-dot-dotted line), PtCo(1:50)/GR (short dashed line), PtCo(1:60)/GR (dash-dotted line) and Pt/GR (dotted line) recorded in 1 M CH₃OH + 0.5 M H₂SO₄ at 0.9 V vs SHE for 300 s. Bar columns represent the same data normalized by the Pt loadings (b) and electrochemically active surface areas (c) for each catalyst at the end of the experimental period (300 s)

It is worth to note that the catalytic activity of graphene PtCo catalysts towards methanol oxidation differs depending on the reaction medium – in acidic solutions the catalysts with a lower amount of cobalt are more active (this work), whereas in alkaline solutions it was found that the highest catalytic activity exhibits PtCo catalyst with the molar ratio of Pt:Co equal to 1:7 [42].

CONCLUSIONS

A simple approach to prepare the graphene supported PtCo catalysts with different Pt and Co molar ratios by means of microwave synthesis is presented. The graphene supported PtCo catalysts were prepared having the Pt and Co molar ratios equal to 1:3, 1:6, 1:20, 1:50 and 1:60, and Pt nanoparticles in a size of ca. 1–3 nm. It has been determined that the composition of the prepared graphene supported PtCo catalysts influences the activity of those catalysts towards the electro-oxidation of methanol. The graphene supported PtCo catalysts with the Pt:Co molar ratios equal to 1:3 and 1:6 exhibit the highest electrocatalytic activity towards methanol electro-oxidation as compared with that of the catalysts with the Pt:Co molar ratios equal to 1:20, 1:50, 1:60 and 1:0.

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**PLATINOS-KOBALTO NANOKATALIZATORIŲ
GRAFENO PAGRINDU SINTEZĖ,
CHARAKTERIZAVIMAS IR SAVYBĖS**

S a n t r a u k a

Darbe pristatomi ant grafeno pagrindo (GR) mikrobangų sintezės metodu sintetinti PtCo/GR katalizatoriai, turintys skirtingus Pt ir Co molinius santykius. Katalizatorių forma ir dydis nustatyti elektronų peršvietimo mikroskopu. Gautųjų PtCo/GR katalizatorių elektrocheminės savybės buvo įvertinamos tiriant metanolio elektrooksidaciją rūgštinėje terpėje, taikant ciklinę voltamperometriją ir chronoamperometriją.

Naudojant reakcijos mišinį, susidedantį iš H_2PtCl_6 , $CoCl_2$ ir etilenglikolio, buvo suformuoti PtCo/GR katalizatoriai, kuriuose Pt nanodalelių dydis yra 1–3 nm. Pastebėta, kad elektrokatalizinis PtCo/GR katalizatorių aktyvumas priklauso nuo Pt:Co molinio santykio. Nustatyta, kad PtCo/GR katalizatoriai, esant Pt:Co moliniams santykiams 1:3 ir 1:6, pasižymi geresnėmis elektrokatalizinėmis savybėmis metanolio oksidacijos reakcijai, palyginti su Pt:Co katalizatoriais, kurių moliniai santykiai yra 1:20, 1:50, 1:60 ir 1:0.