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One-pot synthesis of graphene supported platinum–cobalt nanoparticles as electrocatalysts for methanol oxidation

V. Kepenienė [a, *], L. Tamašauskaitė-Tamašiūnaitė [a], J. Jablonskienė [a], M. Semaško [a], J. Vaičiūnienė [a], R. Vaitkus [b], E. Norkus [a]

[a] Department of Catalysis, Center for Physical Sciences and Technology, Vilnius LT 01108, Lithuania
[b] Faculty of Chemistry, Vilnius University, Vilnius LT 03225, Lithuania

HIGHLIGHTS

- Preparation of graphene supported Pt-Co nanoparticles by microwave synthesis.
- Electrocatalysts for oxidation of methanol.
- Higher activity of PtCo/graphene towards methanol oxidation.

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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 electro-oxidation of methanol in an alkaline medium. It has been found that the graphene supported platinum–cobalt nanoparticles having the Pt:Co molar ratio 1:7 show the highest activity towards the electro-oxidation of methanol among the catalysts with the Pt:Co molar ratios equal to 1:1 and 1:44, graphene supported bare Co and Pt/C catalysts.

1. Introduction

One of the renewable energy sources is alkaline polymer membrane fuel cells, in which alcohols are used as a fuel. The alkaline polymer membrane fuel cells have several advantages as compared to hydrogen fuel cells: alcohols can be used without any modification nor purification, they are easily transported, stored, and what is more, their production infrastructure has already been created and industrialized [1,2]. Moreover, the kinetics of alcohol oxidation and oxygen reduction is more rapid in the alkaline medium compared to the acidic one, the components of fuel cells almost do not corrode, and therefore reasonably priced materials can be used for their production. Pt is one of the best catalysts for hydrogen oxidation and dehydrogenation for electro-oxidation reactions of organic species [3–9], but its application for practical purposes is not promising because of its high price. The strategy of search for new catalysts is based on the creation of alternative, more effective materials with reduced amount of noble metal in the catalyst, thus with increased activity.

Well-known that the addition of transition metals such as Ni, Co, Fe etc., to the Pt-based catalysts allow to create an effective catalysts and to reduce amount of Pt in the catalysts. The PtM catalysts show enhanced electrocatalytic activity towards borohydride oxidation [10–17], methanol oxidation [18–27] and oxygen reduction [26–40] as compared with that of pure Pt. The catalytic enhancement of Pt with transition metals has been attributed to the PtM alloy formation and the Pt electronic structure change due to the presence of metal, Pt–Pt distance, and d-electron density in Pt [41–45]. Also deposition of nanoparticles of Pt with other metals makes it possible to diminish the quantity of Pt used in the catalyst as well as to increase the activity of the catalyst.

Recently graphene has been used as a substrate for deposition of various metal nanoparticles with the aim to increase the catalytic properties of catalysts. Graphene has great surface area

* Corresponding author.
E-mail address: virginalisk@gmail.com (V. Kepenienė).

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(2600 m^2g^{-1}), a superior electronic conductivity and a high surface to volume ratio and a high stability [46,47]. An important feature is to develop simple and cost-effective technologies for fabrication of catalysts. The microwave heating method is a modern fast and simple method, which allows preparing catalysts with small particles uniformly distributed on the substrate and with tailored properties. The microwave synthesis has recently been intensively used for the synthesis of various substances. The application of microwave synthesis markedly shortens the reaction time as compared to the traditional heating used for preparation of catalysts.

In this study we investigated the graphene supported platinum–cobalt nanoparticles catalysts (denoted as PtCo/GR) with different Pt:Co molar ratios for their methanol oxidation performance, whereas in our previous study those catalysts were identified as good catalysts for the electro-oxidation of borohydride and ethanol [17,48]. The PtCo/GR catalysts were prepared by means of microwave synthesis. The catalysts obtained were characterized by Transmission Electron Microscopy (TEM) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The activity of catalysts was investigated with respect to the oxidation of methanol in an alkaline medium by means of cyclic voltammetry (CV) and chrono-techniques.

2. Experimental

2.1. Chemicals

Reagents needed for research were purchased from Alfa-Aesar Supply: $H_2PtCl_6{\cdot}6H_2O$ (99.9%), $CoCl_2{\cdot}6H_2O$ (98%), $HAuCl_4{\cdot}3H_2O$ (99.99%) and carbon (99.99%). Graphene (purity of 97%, specific surface area - 60 m^2/g) was purchased from Graphene Supermarket Supply. Nafion (5 wt.%, D521, 1100 EW) was purchased from Ion Power Inc. Supply. H_2SO_4, NaOH, 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 MΩ cm^{-1} was used to prepare all the solutions.

2.2. Fabrication of catalysts

The graphene supported platinum–cobalt nanoparticles with different Pt:Co molar ratios were synthesized by polyol method using microwave-assisted heating previously reported in Refs. [46,47]. Briefly: the reaction mixture, containing 0.25 ml of 0.096 M H_2PtCl_6 and 0.6 ml solution of different concentrations of $CoCl_2$, 18 ml of EG and 100 mg (pH 11.7), was put into the microwave reactor Monowave 300 (Anton Paar). The Pt and Co nanoparticles were deposited on the surface of graphene at a temperature of 170 °C for 30 min. The graphene supported cobalt nanoparticles (denoted as Co/GR) and Pt/C catalysts were prepared under the same conditions, except that the duration of Pt/C preparation was shortened to 30 s with the aim to compare the obtained PtCo/GR and Pt/C catalysts having approximately the similar size of Pt particles in the created catalysts. For comparison, the AuCo/GR catalyst having the Au:Co molar ratio equal to 1:40 was synthesized. The reaction mixture contained 0.25 ml of 0.05 M $HAuCl_4$ and required amount of 0.5 M $CoCl_2$, 18 ml of EG and 100 mg of graphene. Synthesis was carried out at 150 °C for 30 min. The Au loading was 103 μg cm^{-2} in the synthesized catalyst.

After preparation, the synthesized catalysts were washed with acetone, ultra-pure water, then filtered and dried in a vacuum oven at 80 °C for 2 h.

2.3. Characterization of catalysts

A transmission electron microscope Tecnai G2 F20 X-TWIN equipped with an EDAX spectrometer with an r-TEM detector was used for detection of the size and shape of Pt nanoparticles deposited on the surface of graphene and carbon. For microscopic examinations, 10 mg of sample were first sonicated in 1 ml of ethanol for 1 h and then deposited on a Cu grid covered with a continuous carbon film.

The composition of synthesized catalysts was determined by using ICP optical emission spectrometer Optima 7000DV (Perkin Elmer).

2.4. Electrochemical measurements

For methanol electro-oxidation experiments three-electrode electrochemical cell was used. The working electrode was a thin layer of the prepared PtCo/GR, Co/GR and Pt/C catalysts deposited on a glassy carbon electrode with a geometric area of 0.07 cm^2, 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 as described in Refs. [17,48]: 5 μl of the catalyst mixture was pipetted onto the polished surface of a glassy carbon electrodeanddried in air for 12 h. The catalysts mixture was prepared by mixing ultrasonically 10 mg of the PtCo/GR or Co/GR catalysts, 0.25 μl of Nafion and 0.75 μl of deionized H_2O.

Electrochemical analyses were performed with a Zennium electrochemical workstation (ZAHNER-Elektrik GmbH & Co.KG) by recording cyclic voltammograms in a 1 M CH_3OH + 0.5 M NaOH solution at a linear potential sweep rate of 50 mV s^{-1} under the potential region from −0.5 to 0.3 V at a temperature of 25 °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 chronoamperometric measurements were carried outin a 1 M CH_3OH + 0.5 M NaOH solution at a constant potential value of 0 V vs. SHE for 5 min. Chronopotentiometric curves were recorded at a current density of 2 mA cm^{-2} vs. the geometric area of the investigated catalysts for 5 min.

All solutions were deaerated by argon for 15 min prior to measurements.

3. Results and discussion

Over the last few decades, material synthesis techniques based on microwave chemistry have received considerable attention as a new promising method for the one-pot synthesis of metallic nanostructures in solutions. In the study presented herein a rapid microwave heating method was used to prepare the graphene supported platinum–cobalt nanoparticles having different Pt:Co molar ratios. To obtain the catalysts with the different Pt:Co molar ratios, required amounts of graphene, H_2PtCl_6 and ethylene glycol were kept constant, whereas amounts of $CoCl_2$ and NaOH were changed. The synthesis was carried out at 170 °C for 30 min in the microwave reactor. The composition of catalysts was detected by

Table 1
Data of composition and electrochemically active surface areas of the Pt/C and PtCo/GR catalysts.

Catalysts	Pt loading, mg cm^{-2}	ESA, cm^2
Pt/C	0.128	1.8
PtCo(1:1)/GR	0.160	7.3
PtCo(1:7)/GR	0.165	4.8
PtCo(1:44)/GR	0.125	3.9