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CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY

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KILMONIS

Synthesis of PtM/graphene (M = W, Mo, Mn, Co, Ru) nanocomposites, their characterization and application in fuel cells

SUMMARY OF DOCTORAL DISSERTATION

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VILNIAUS UNIVERSITETAS
FIZINIŲ IR TECHNOLOGIJOS MOKSLŲ CENTRAS

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PtM/grafeno (M = W, Mo, Mn, Co,
Ru) nanokompozitų sintezė,
apibūdinimas ir taikymas kuro
elementams

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1. INTRODUCTION

Today energy production and conversion are vital to nations economy: these processes are strongly connected with nature and society. Big portion of energy is made from fossil fuel which usage induce pollution and greenhouse effect. Also polluted air causes local and global problems. One of problems solution is produced carbon dioxide reduction. This can be achieved using fuel cells (FC) which does not produce carbon dioxide and chemical energy is converted directly to electric energy. FC are effective, low emissions and does not produce waste products. Also, FC can use various fuels (e.g. sodium borohydride, hydrazine), can achieve high power, produce energy locally and globally, they are easily configured. Working FC prototypes are used from small electronic devices (e.g. mobile phones) to vehicles and even small power plants. As time passes FC price is getting lower but it is not low enough to compete with internal combustion engines. One part of FC price is platinum (used as catalyst) price. In laboratories new catalysts are created without platinum or some part of platinum is replaced with other cheaper metal.

This study is related to the preparation of efficient catalysts, their characterization and application as the anode materials for direct borohydride (DBFC) and methanol (DMFC) fuel cells with the aim to replace expensive noble metal – platinum. Simple and low-cost method has been used for preparation of catalysts. The graphene supported platinum, tungsten, molybdenum, cobalt, manganese and ruthenium nanoparticles have been synthesized using the microwave-assisted synthesis.

The aim of the work was:

Preparation of efficient catalysts, their characterization and application as the anode materials for direct borohydride and methanol fuel cells.

The main tasks of the work were as follows:

1. Preparation of PtW/GR, PtMo/GR, PtCoMn/GR, PtCoMo/GR and PtCoRu/GR catalysts using the microwave synthesis method.
2. Characterization of the surface morphology and composition of the fabricated PtW/GR, PtMo/GR, PtCoMn/GR, PtCoMo/GR and PtCoRu/GR catalysts using transmission electron microscopy and inductively coupled plasma optical emission spectroscopy.
3. Evaluation of the electrocatalytic activity of the fabricated PtW/GR, PtMo/GR, PtCoMn/GR, PtCoMo/GR and PtCoRu/GR catalysts for the oxidation reactions of sodium borohydride and methanol using cyclic voltamperometry and chronoamperometry.

Defensive statements:

1. PtM/graphene (M = W, Mo, Mn, Co, Ru) nanocomposites usable as anode materials in fuel cells can be synthesized using microwave synthesis method.
2. The prepared PtM/graphene (M = W, Mo, Mn, Co, Ru) nanocomposites have electrocatalytic activity for the electrooxidation reactions of sodium borohydride and methanol.
3. The electrocatalytic activity of the PtM/graphene (M = W, Mo, Mn, Co, Ru) nanocomposites for the oxidation of sodium borohydride and methanol is significantly higher than that of the bare graphene supported Pt, W and Mo catalysts.

Novelty and actuality of the work

European union's aim for 2030 is to reduce greenhouse gas emissions 40% (compared to 1990s data), produce 32% more energy from renewable sources and improve by 32,5% energy usage effectiveness. Fuel cells are one of the ways to achieve these aims.

Fuel cells are more effective than internal combustion engines, they operate more silently, doesn't produce carbon dioxide and have long life-span. In order to achieve wide fuel cells commercialization scientist must solve few fuel cells problems: lower production, maintenance and repair costs. Fuel cell price could be lowered if expensive platinum catalysts are replaced by other metals or lower amount of platinum is used.

In this work the graphene supported PtM (M = W, Mo, Mn, Co, Ru) catalysts were synthesized using microwave synthesis. The synthesized PtM/graphene (M = W, Mo, Mn, Co, Ru) nanocomposites catalysts show higher electrocatalytic activity for the oxidation of sodium borohydride and methanol as compared with that of the bare graphene supported Pt and M nanoparticles. Moreover, these catalysts could be successfully used as anode materials for direct sodium borohydride and methanol fuel cells.

2. EXPERIMENTAL

Chemicals. H_2PtCl_6 (99.95%), $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (99.95%), $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (99.5%), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (99.95%), $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (99.5%), RuCl_3 (99.95%), $\text{C}_2\text{H}_5\text{OH}$ (96%), HCl (35-38%), HNO_3 (65%), NaBH_4 (99%), acetone (99.8%), citric acid (99.99%), ethylene glycol (EG) (99.95%), Nafion (5%), graphene powder (97%) and NaOH (99%) were used. All chemicals were of analytical grade. Deionized water with the resistivity of $18.2 \text{ M}\Omega \text{ cm}^{-1}$ was used to prepare all the solutions.

Fabrication of catalysts. The graphene supported PtW catalysts that have different Pt:W molar ratios were prepared by means of microwave heating of H_2PtCl_6 and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ in an EG solution. Briefly, 0.25 ml of 0.0974 M H_2PtCl_6 , required amounts of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (dissolved in a minimal amount of a 10 mM citric acid solution) and 0.3 g graphene powder were mixed with 18.5 ml of EG and sonicated for 30 min. The synthesis was carried out in a microwave reactor Monowave 300 (Anton Paar) at a temperature of 150°C for 5

min. For comparison, the bare Pt/GR and W/GR were prepared in the same manner. After the preparation, the synthesized catalysts were washed with acetone and ultra-pure water, then filtered and dried in a vacuum oven at 80°C temperature for 2 h.

The graphene supported PtMo catalysts that have Pt:Mo molar ratios were prepared by means of microwave heating of H_2PtCl_6 and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ in an EG solution. All other procedures were followed exactly the same as mentioned in paragraph above.

The graphene supported PtCoM catalysts that have different Pt:Co:M (M = Mn, Mo, Ru) molar ratios were prepared by means of microwave heating of H_2PtCl_6 , $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and according salt, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ or RuCl_3 , in an EG solution. All other procedures were followed exactly the same as mentioned in paragraph above.

Characterization of catalysts. The prepared catalysts 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 a Ni grid covered with a continuous carbon film. The composition of the PtW/GR, PtMo/GR, PtCoMo/GR, PtCoMn/GR and PtCoRu/GR catalysts was estimated using an ICP optical emission spectrometer Optima 7000 DV (Perkin Elmer).

Electrochemical measurements. Borohydride and methanol oxidation measurements were performed with a Zennium electrochemical workstation (ZAHNER-Elektrik GmbH & Co. KG) and three-electrode cell. The working electrode was a glassy carbon electrode with a geometric area of 0.07 cm² and with a thin layer of Nafion-impregnated catalyst cast, the Pt sheet was used as a counter electrode and Ag/AgCl as a reference electrode. The catalyst layer was obtained by mixing the required amounts of PtW/GR, PtMo/GR, W/GR, Mo/GR, Pt/GR, PtCoMo/GR, PtCoMn/GR and PtCoRu/GR catalysts ultrasonically for 1 hour in a solution containing 0.25 µl of

Nafion and 0.75 μl of deionized H_2O to produce a homogenous slurry. The 5 μl of the prepared suspension mixture was pipetted onto the polished surface of a glassy carbon electrode and dried in air for 12 h.

The electrocatalytic activity of catalysts towards sodium borohydride oxidation was carried out by recording cyclic voltammograms (CVs) in a 0.05 M NaBH_4 + 1 M NaOH solution at a scan rate of 10 mV s^{-1} from -1.1 to 0.6 V at a temperature of 25 $^\circ\text{C}$. The electrocatalytic activity of catalysts towards methanol oxidation was carried out by recording CVs in a 1 M CH_3OH + 1 M NaOH solution at a scan rate of 50 mV s^{-1} from -0.7 to 0.5 V at a temperature of 25 $^\circ\text{C}$. The presented current densities are normalized with respect to the geometric area of catalysts. The electrochemically active surface areas (ESAs) of Pt in the prepared catalysts were determined from the CVs of the PtW/GR, PtMo/GR, Pt/GR, PtCoMo/GR, PtCoMn/GR and PtCoRu/GR catalysts recorded in a deaerated 0.5 M H_2SO_4 solution at a scan rate of 50 mV s^{-1} by calculating the charge associated with hydrogen adsorption (220 $\mu\text{C cm}^{-2}$). All solutions were deaerated by argon for 15 min prior to measurements. The chronoamperometric curves for the investigated PtW/GR, PtMo/GR, W/GR, Mo/GR, Pt/GR, PtCoMo/GR, PtCoMn/GR and PtCoRu/GR catalysts were recorded at a constant potential value of -0.9 and 0.1 V vs Ag/AgCl, respectively, for 30 min in a 0.05 M NaBH_4 + 1 M NaOH solution and 0.2 V vs Ag/AgCl for 30 min in a 1 M CH_3OH + 1 M NaOH solution. Chronopotentiometric curves were recorded at a current density of 2 mA cm^{-2} vs the geometric area of the investigated catalysts for 30 min in the same solutions.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of catalysts

The graphene supported PtW and PtMo catalysts were prepared by microwave assisted heating of Pt(IV), W(VI) and Mo(VI) salts in ethylene glycol solutions. It should be noted that the reaction mixtures contain the constant amounts of Pt, whereas the amounts of W and Mo were different. In this case, the graphene supported PtW and PtMo catalysts that have with different Pt:W and Pt:Mo molar ratios were prepared. The ICP-OES was used for determination of the Pt, W and Mo loadings in the synthesized catalysts. The data obtained are given in the Table 1 and Table 2.

Table 1. Composition of Pt/GR and PtW/GR by ICP-OES and ESA values of Pt in the catalysts determined from CVs recorded in 0.5 M H₂SO₄.

Catalyst	M loading, $\mu\text{g cm}^{-2}$		Pt:W molar ratio	ESA, cm^2	ESA, $\text{m}^2 \text{g}^{-1}$
	Pt	W			
PtW/GR	24.7	14.4	1.6:1	2.3	134.0
PtW/GR	54.6	21.9	2.3:1	3.2	84.5
PtW/GR	41.4	5.5	7.1:1	3.6	125.7
Pt/GR	73.0	-	1.0:0	5.2	102.5

Table 2. Composition of PtMo/GR by ICP-OES and ESA values of Pt in the catalysts determined from CVs recorded in 0.5 M H₂SO₄.

Catalyst	M loading, $\mu\text{g cm}^{-2}$		Pt:Mo molar ratio	ESA, cm^2	ESA, $\text{m}^2 \text{g}^{-1}$
	Pt	Mo			
PtMo/GR	69.4	0.80	43:1	1.2	24.9
PtMo/GR	34.7	2.40	7:1	1.5	60.9
PtMo/GR	41.3	7.01	3:1	4.0	140.0
Pt/GR	73.0	-	1:0	5.2	102.5

After the microwave heating of the reaction mixture at 150 °C for 5 min, the graphene supported PtW catalysts were prepared that have the Pt:W molar ratios equal to 1.6:1, 2.3:1 and 7.1:1 (Table 1). The catalysts were denoted as PtW(1.6:1)/GR, PtW(2.3:1)/GR and PtW(7.1:1)/GR. The Pt loadings determined by means of ICP-OES analysis were 73 $\mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ in the Pt/GR, 24.7, 54.6, and 41.4 $\mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ in the synthesized PtW (1.6:1)/GR, PtW(2.3:1)/GR and PtW(7.1:1)/GR catalysts, respectively.

As seen from the data in Table 2, PtMo/GR catalysts that have Pt:Mo molar ratios equal to 43:1, 7:1 and 3:1 were synthesized. The Pt loadings determined by means of ICP-OES analysis were 69.4, 34.7 and 41.3 $\mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ in the synthesized PtMo (43:1)/GR, PtMo(7:1)/GR and PtMo(3:1)/GR catalysts, respectively.

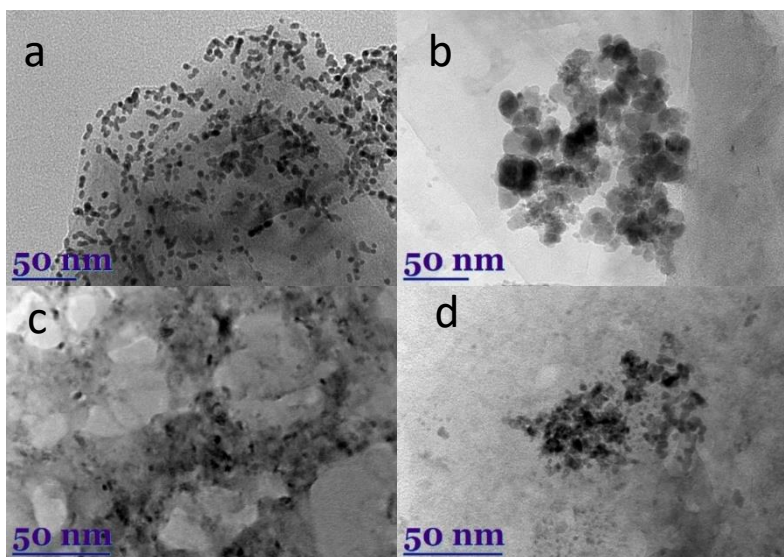


Figure 1. TEM views of Pt/GR (a), PtW(1.6:1)/GR (b), PtW(2.3:1)/GR (c), and PtW(7.1:1)/GR (d) prepared by microwave synthesis.

As evident from the data in Fig. 1a, the Pt/GR catalyst with an average Pt nanoparticle size of ca. 3 nm was synthesized. In the case of the PtW/GR catalysts, the Pt nanoparticles were found to be ca. 5–20 nm (Fig. 1b–d). Pt nanoparticles were uniform and well dispersed on the surfaces of graphene. Figure 2 shows the TEM views of the synthesized PtMo/GR catalysts.

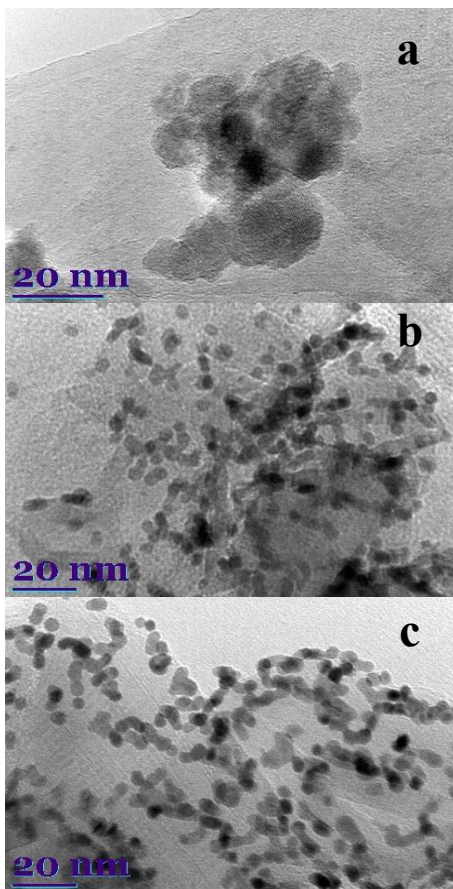


Figure 2. TEM views of PtMo(43:1)/GR (a), PtMo(7:1)/GR (b) and PtMo(3:1)/GR (c) prepared by microwave synthesis.

In the case of the PtMo(7:1)/GR and PtMo(3:1)/GR catalysts, the PtMo nanoparticles were found to be ca. 3 nm (Fig. 2 b–c) and in PtMo(43:1)/GR catalyst PtMo particles were 10 nm size (Fig. 2a).

The electrochemically active surface areas of Pt in the synthesized catalysts were determined from the cyclic voltammograms of the Pt/GR, PtW/GR and PtMo/GR catalysts recorded in a deaerated 0.5 M H₂SO₄ solution at a sweep rate of 50 mV s⁻¹ by calculating the charge associated with hydrogen adsorption (220 μC cm⁻²) (Fig. 3).

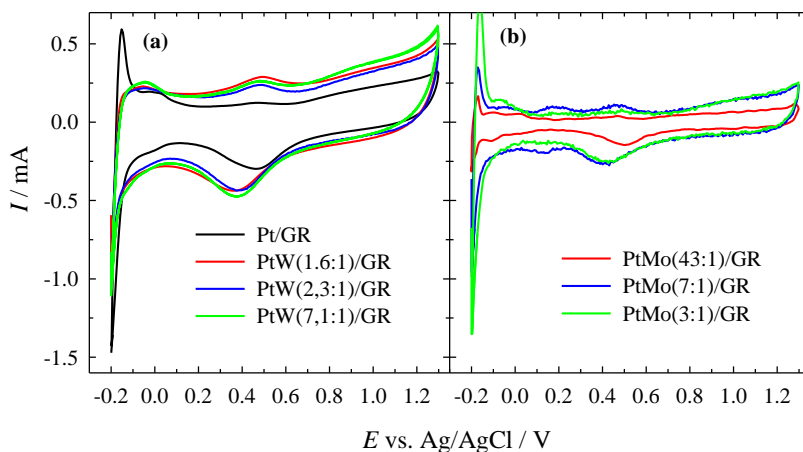


Figure 3. CVs of the Pt/GR, PtW/GR and PtMo/GR catalysts recorded in 0.5 M H₂SO₄ at 50 mV s⁻¹; 25 °C

The data obtained are also given in the Table 1 and Table 2. The ESA values are ca. 2.3, 1.6 and 1.4 times higher at the Pt/GR catalyst than those of the PtW(1.6:1)/GR, PtW(2.3:1)/GR and PtW(7.1:1)/GR, respectively. The ESA values are ca. 4.3, 3.5 and 1.3 times higher at the Pt/GR catalyst than those of the PtMo(43:1)/GR, PtMo(7:1)/GR and PtMo(3:1)/GR, respectively.

3.2. Sodium borohydride oxidation on PtW/GR and PtMo/GR catalysts

The activity of the graphene supported PtW and PtMo catalysts that have different Pt:W and Pt:Mo molar ratios with respect to the oxidation of sodium borohydride was investigated by cyclic voltammetry. Figure 4 presents CVs for the PtW/GR catalysts that have Pt:W molar ratios equal to 1.6:1 (a), 2.3:1 (b), and 7.1:1 (c) recorded in 0.05 M NaBH₄ + 1 M NaOH at a scan rate of 10 mV s⁻¹. For comparison purposes, CVs of W/GR catalyst are also presented. During long-term cycling, two anodic peaks A0 and A are seen in the CVs plots for different PtW/GR and PtMo/GR catalysts (Figs. 4, 5). The mentioned catalysts show a typical electrochemical behaviour towards sodium borohydride oxidation as on a pure Pt electrode. The anodic peak A0 at lower potential values may be related with the oxidation of H₂ generated by catalytic hydrolysis of BH₄⁻, and the peak A at more positive potential values may be corresponded to the direct oxidation of BH₄⁻ ions. In the reverse potential sweep, the peak B observed at about -0.3 V can be assigned to the oxidation of absorbed intermediate oxidation products of BH₃OH⁻ on the partially oxidized Pt surface.

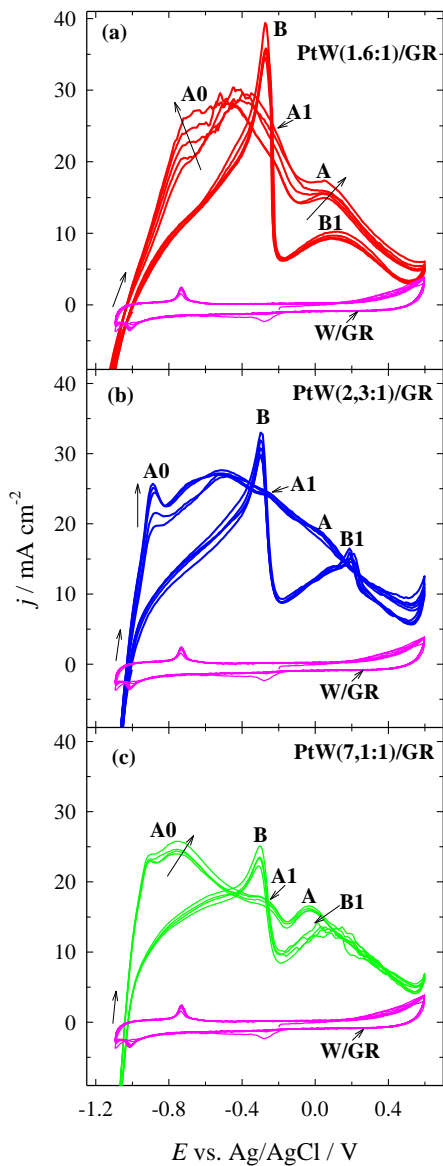


Figure 4. CVs for PtW(1.6:1)/GR (a), PtW(2.3:1)/GR (b) and PtW(7:1)/GR (c) recorded in 0.05 M NaBH_4 + 1 M NaOH at 10 mV s^{-1} ; $25 \text{ }^\circ\text{C}$.

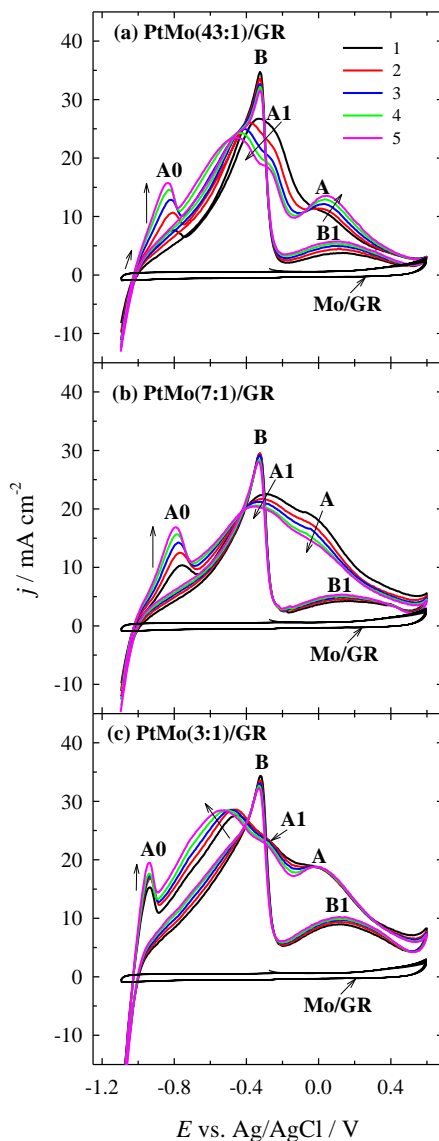


Figure 5. CVs for PtMo(43:1)/GR (a), PtMo(7:1)/GR (b) and PtMo(3:1)/GR (c) recorded in 0.05 M NaBH₄ + 1 M NaOH at 10 mV s⁻¹; 25 °C.

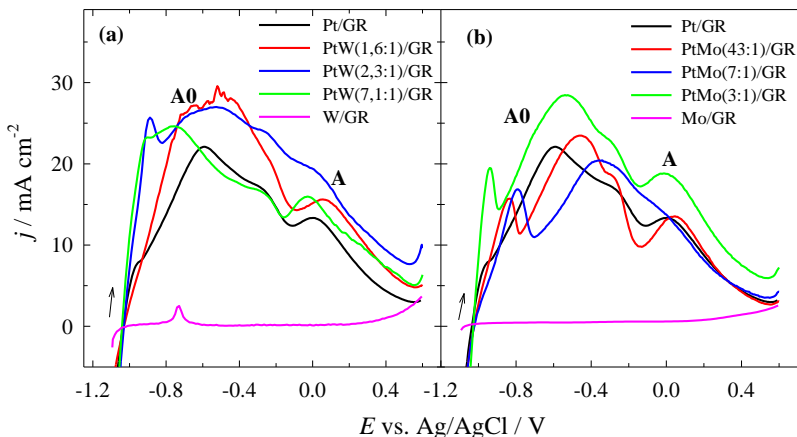


Figure 6. Positive-potential going scans of Pt/GR, W/GR, PtW/GR (a) and Pt/GR, Mo/GR, PtMo/GR (b) catalysts recorded in 0.05 M NaBH₄ + 1 M NaOH at 10 mV s⁻¹; 25 °C.

Figure 6 presents the comparison of positive-potential going scans of oxidation of BH₄⁻ ions recorded on Pt/GR, W/GR, Mo/GR, PtW/GR and PtMo/GR catalysts that have different Pt:W and Pt:Mo molar ratios in a 0.05 M NaBH₄ + 1 M NaOH solution at a potential scan rate of 10 mV s⁻¹. The potential values of the anodic peak A0 are shifted to the negative potential values at the PtW/GR catalysts that has the Pt:W molar ratios equal to 2.3:1 and 7.1:1 as compared with those at Pt/GR and PtW/GR that has the Pt:W molar ratio equal to 1.6:1, indicating a higher activity of those catalysts. The PtMo/GR catalyst that has the Pt:Mo molar ratio 3:1 outperformed Pt/GR catalyst. The current densities of the peak A0 recorded on the PtW(1.6:1)/GR, PtW(2.3:1)/GR and PtW(7.1:1)/GR catalysts are ca. 1.3, 1.1 and 1.2 times higher than those on Pt/GR. The current densities under the peak A are also ca. 1.2–1.4 times higher as compared to those of Pt/GR. It should be noted that the prepared PtW/GR catalysts that have different Pt:W molar ratios and bare Pt/GR significantly outperformed the bare W/GR catalyst. Since the

borohydride oxidation current densities recorded at the W/GR catalyst (Fig. 6) are negligible as compared to those of different PtW/GR and Pt/GR catalysts, the enhanced electrocatalytic activity of the synthesized PtW/GR catalysts may be ascribed to the Pt electronic structure change due to the presence of W. In order to evaluate the specific and mass activities of the prepared catalysts, the sodium borohydride oxidation current densities were normalized by the electrochemically active surface areas of Pt and Pt loadings for each catalyst. The data obtained are given in Figs. 7 and 8. As seen from the data in Fig. 7, the PtW/GR catalysts outperformed the bare Pt/GR catalyst. Assuming ca. 2.3, 1.6 and 1.4 times higher active surface areas of Pt/GR compared to those of the PtW(1.6:1)/GR, PtW(2.3:1)/GR and PtW(7.1:1)/GR catalysts, respectively, surface area normalized borohydride oxidation current densities under the peaks A0 and A are ca. 3.0, 1.8, 1.8 and 2.7, 2.0, 2.1, respectively, times higher on the latter catalysts (Fig. 7a, b). Mass activity of the different PtW/GR catalysts is ca. 3.9, 1.5 and 2.2 (peak A0), and 3.5, 1.6 and 2.5 (peak A) times higher than that at Pt/GR (Fig. 7c, d).

As seen from the data in Fig. 8, the PtMo/GR catalysts outperformed the bare Pt/GR catalyst. Assuming ca. 4.3, 3.5 and 1.3 times higher active surface areas of Pt/GR compared to those of the PtMo(43:1)/GR, PtMo(7:1)/GR and PtMo(3:1)/GR catalysts, respectively, surface area normalized borohydride oxidation current densities under the peaks A0 and A are ca. 4.6, 3.2, 1.6 and 4.4, 3.7, 1.8, respectively, times higher on the latter catalysts (Fig. 8a, b). Mass activity of different PtMo/GR catalysts is ca. 1.1, 1.9 and 2.8 (peak A0), and 1.1, 2.2 and 2.5 (peak A) times higher than that at Pt/GR (Fig. 8c, d).

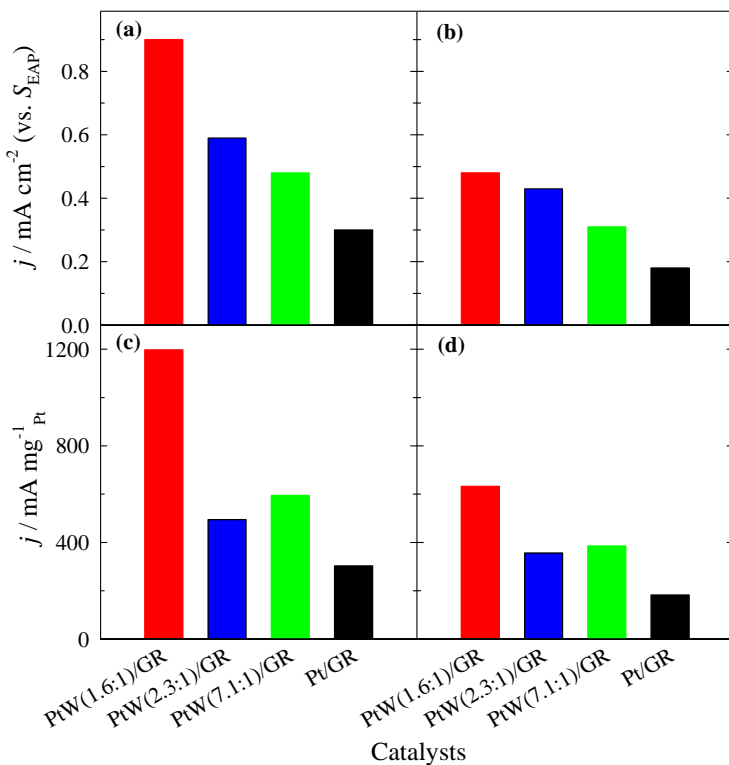


Figure 7. Comparison of specific activity (a, b) and mass activity (c, d) of different PtW/GR catalysts under values of peak A0 (a, c) and peak A (b, d).

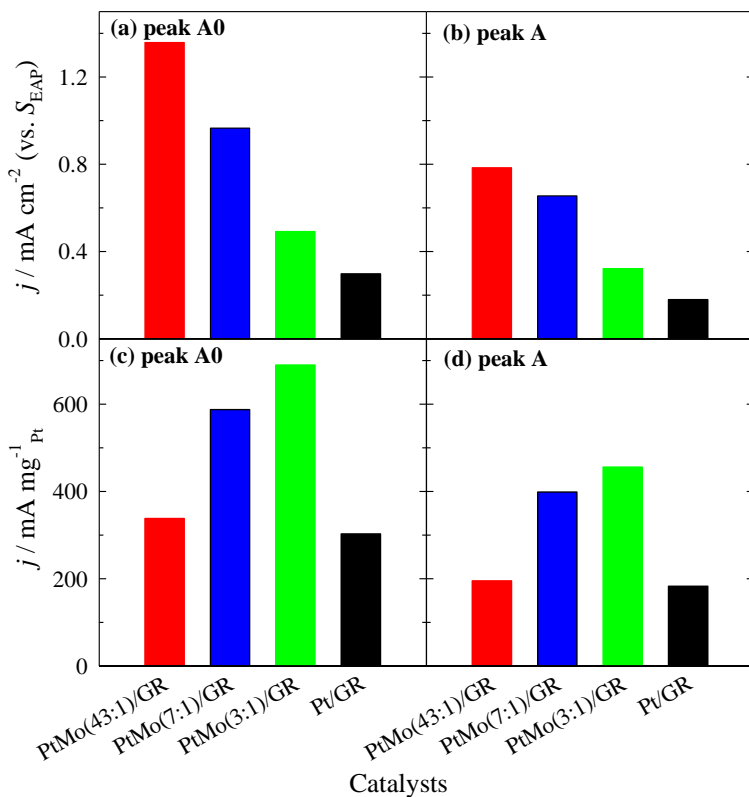


Figure 8. Comparison of specific activity (a, b) and mass activity (c, d) of different PtMo/GR catalysts under values of peak A0 (a, c) and peak A (b, d).

Stability of catalysts for the oxidation of H_2 generated by catalytic hydrolysis of BH_4^- (peak A0) and oxidation of BH_4^- ions (peak A) was investigated under chronoamperometric conditions. Figure 9 presents the chronoamperometric curves obtained at the Pt/GR, W/GR and PtW/GR catalysts in 0.05 M NaBH_4 + 1 M NaOH at constant potential values of -0.9 (a) and 0.1 (b) V, respectively, for 1800 s.

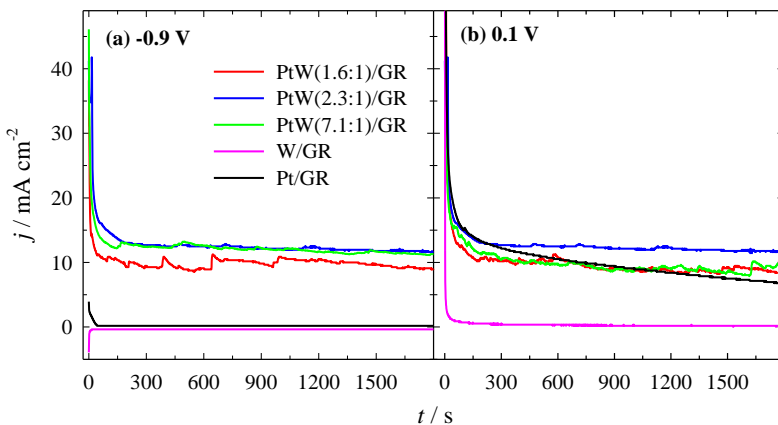


Figure 9. Chronoamperometric data of the Pt/GR and PtW/GR catalysts recorded in $0.05 \text{ M NaBH}_4 + 1 \text{ M NaOH}$ at -0.9 (a) and 0.1 (b) V, respectively, for 1800 s.

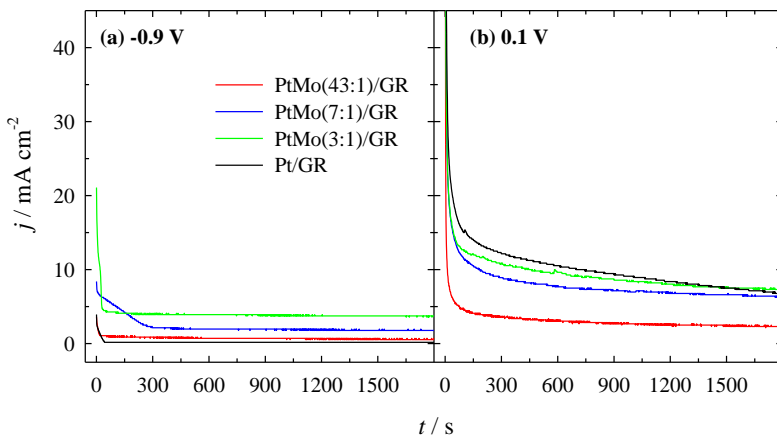


Figure 10. Chronoamperometric data of the Pt/GR and PtMo/GR catalysts recorded in $0.05 \text{ M NaBH}_4 + 1 \text{ M NaOH}$ at -0.9 (a) and 0.1 (b) V, respectively, for 1800 s.

All the catalysts show a current decay for both reactions. It is worth to note that at -0.9 V , the current densities obtained for all

synthesized PtW/GR catalysts are much higher than those for Pt/GR and W/GR. The current densities of the peak A0 recorded at the PtW(1.6:1)/GR, PtW(2.3:1)/GR and PtW(7.1:1)/GR catalysts are ca. 51, 65 and 62 times higher as compared to those at Pt/GR (Fig. 9a). The current densities of the peak A recorded at the PtW(1.6:1)/GR, PtW(2.3:1)/GR and PtW(7.1:1)/GR catalysts at 0.1 V are ca. 1.3, 1.2 and 1.4 times greater than those at Pt/GR (Fig. 9b). PtMo/GR catalysts shows similar tendencies (Fig. 10a, b).

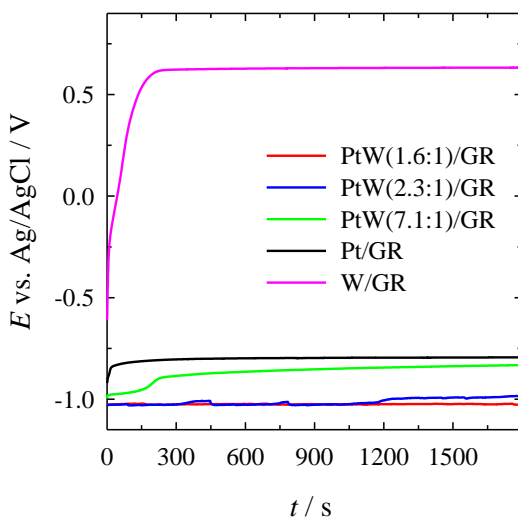


Figure 11. Chronopotentiometric data of the Pt/GR, W/GR and PtW/GR catalysts recorded in 0.05 M NaBH₄ + 1 M NaOH at 2 mA cm⁻² for 1800 s.

Chronopotentiometry measurements were carried out to screen the catalyst performance under the conditions of constant current operation of the fuel cell anode. Following a rest period of 10 s at open circuit, a current density step of 2 mA cm⁻² was applied to the investigated catalysts for 1800 s. Figure 11 shows the anode potentials (including the open circuit values between -0.612, -0.920, -0.996, -1.028 and -1.027 V vs Ag/AgCl) for the catalysts operating at 2 mA

cm^{-2} . Notably, the open-circuit potential values are by ca. 0.3–0.4 V more negative than those of W/GR. After 1800 s, the operating potentials for Pt/GR and PtW/GR are by approximately 1.4–1.6 V more negative than those for W/GR, which demonstrates that the overpotentials for the oxidation of BH_4^- ions on the Pt/GR and PtW/GR catalysts are lower than those for W/GR. The difference between the steady-state operating anode potential and the one at open circuit was the smallest one on the PtW(1.6:1)/GR and was equal to ca. 0.007 V, followed by the PtW(2.3:1)/GR, Pt/GR and PtW(7.1:1)/GR catalyst, where they reached ca. 0.044, 0.126 and 0.164 V, respectively, and finally, W/GR where it reached ca. 1.245 V.

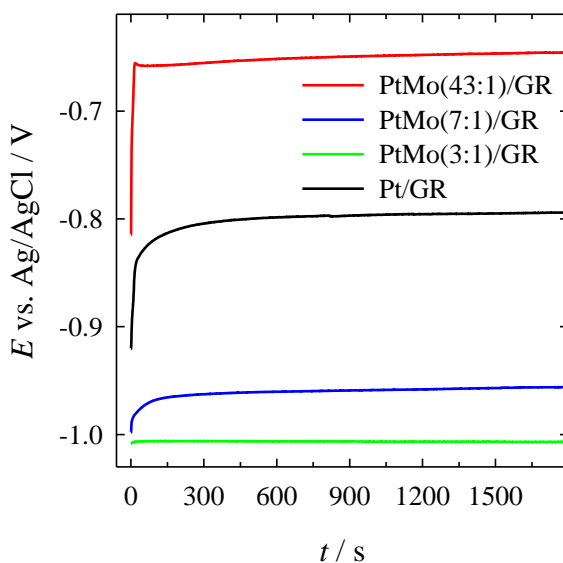


Figure 12. Chronopotentiometric data of the Pt/GR and PtMo/GR catalysts recorded in 0.05 M NaBH_4 + 1 M NaOH at 2 mA cm^{-2} for 1800 s.

Figure 12 shows the anode potentials for the PtMo/GR catalysts operating at 2 mA cm^{-2} . The difference between the steady-state

operating anode potential and the one at open circuit was the smallest one on the PtMo(3:1)/GR and was equal to ca. 0.0017 V, followed by the PtMo(7:1)/GR, Pt/GR and PtMo(43:1)/GR catalyst, where they reached ca. 0.0421, 0.1263 and 0.1691 V, respectively.

3.3. Methanol oxidation on PtW/GR catalyst

The electrochemical properties of the GR supported PtW catalysts that have different Pt:W molar ratios were investigated with respect to the oxidation of methanol in an alkaline media by means of cyclic voltammetry. Figure 13 shows CVs for the W/GR (a), Pt/GR (b) and PtW/GR catalysts that have Pt:W molar ratios equal to 1.6:1 (c), 2.3:1 (d), and 7.1:1 (e) recorded in 1 M CH₃OH + 1 M NaOH at a scan rate of 50 mV s⁻¹. For the sake of simplicity, in Fig. 13f only positive potential going scans of stabilized CVs of all the catalysts are presented. As evident from the obtained data in Fig. 13, all CV plots exhibit two typical anodic peaks in the forward and reverse scans (labelled as A and B), which are well-known to reflect the electrooxidation of alcohols and the intermediate carbonaceous species, respectively. The first anodic current peak A in the forward scan is related to the oxidation of methanol on the catalyst, whereas the second anodic peak B on the reverse scan may be related to the oxidation of intermediate products generated during the forward scan. During the long-term cycling, the current density values on the W/GR catalyst (Fig. 13a) significantly decrease, immediately after the first potential scan, to a rather low current value of ca. 7.8 mA cm⁻².

Meanwhile, the methanol oxidation current values recorded on the Pt/GR (Fig. 13b) or PtW/GR (Fig. 13c–e) catalysts increase with the scan number and depend on the Pt:W molar ratio in the catalyst.

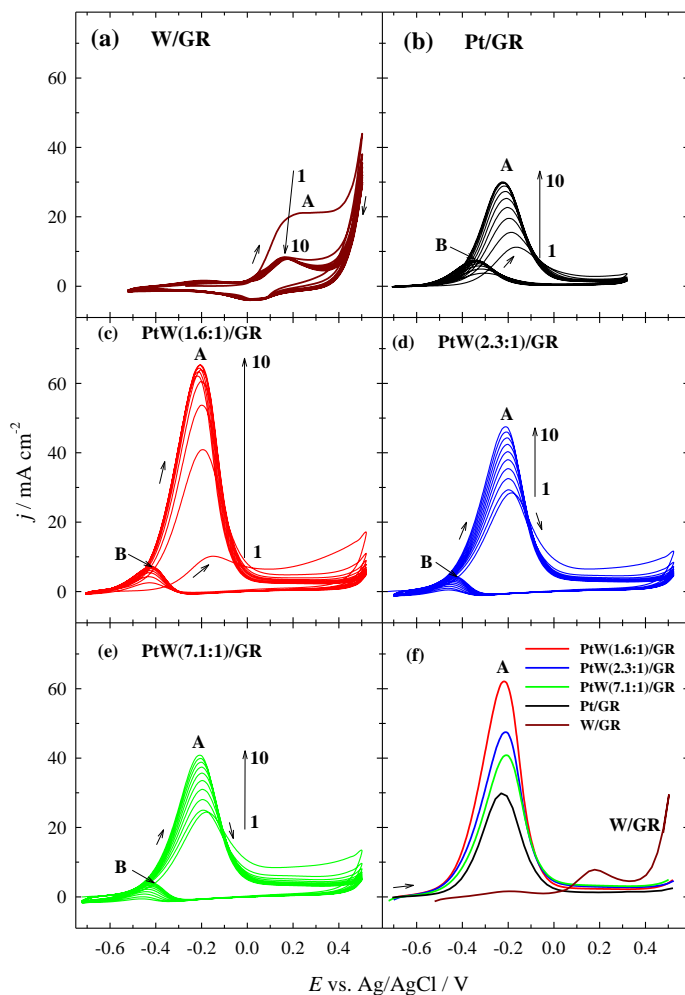


Figure 13. CVs recorded at W/GR (a), Pt/GR (b), PtW(1.6:1)/GR (c), PtW(2.3:1)/GR (d), PtW(7.1:1)/GR (e) and stabilized positive potential-going scans (f) for the same catalysts in 1 M CH_3OH + 1 M NaOH at 50 mV s^{-1} .

Moreover, the onset potential of methanol oxidation at the W/GR catalyst is obtained in a rather positive potential region at a

potential value of ca. 0.057 V that is almost ca. 0.5 V more positive than those observed for Pt/GR or PtW/GR (ca. -0.45 V) (Fig. 13f).

A lower onset potential suggests that the overpotential for methanol oxidation is lower and the electrocatalytic methanol oxidation occurs more easily on Pt/GR or PtW/GR. Therefore, the Pt/GR or PtW/GR catalysts that have different Pt:W molar ratios are considered to be of a higher activity towards methanol oxidation compared to that of W/GR.

The stabilized CVs of the investigated catalysts presented in Fig. 13f show that the highest current density is obtained at the PtW/GR catalyst that has the lowest Pt loading of $24.7 \mu\text{g Pt cm}^{-2}$ and containing the Pt:W molar ratio equal to 1.6:1. The current densities of peak A recorded on the PtW(1.6:1)/GR, PtW(2.3:1)/GR and PtW(7.1:1)/GR catalysts are ca. 2.1, 1.6 and 1.4 times higher than those on Pt/GR and, considerably more, i.e. ca. 7.8, 6.0 and 5.2 times higher compared to those obtained on the W/GR catalyst. The enhanced electrocatalytic activity of the synthesized PtW/GR catalysts may be attributed to the Pt electronic structure change due to the presence of W.

In addition, it is well known that the ratio of forward anodic peak current (j_F) to the backward anodic peak (j_B), j_F/j_B , is an index of the catalysts tolerance to the poisoning species accumulated on the surface of the electrode. The ratios j_F/j_B were 8.7, 10.9, 9.8 and 4.1 for the PtW(1.6:1)/GR, PtW(2.3:1)/GR, PtW(7.1:1)/GR and Pt/GR catalysts, respectively. A higher j_F/j_B ratio indicates an efficient oxidation of methanol during the forward scan, with a little accumulation of carbonaceous residues. Notably, the ratio j_F/j_B was ca. 2 times higher for the all PtW/GR catalysts as compared with that for the pure Pt/GR catalysts, indicating a greater efficiency of the PtW/GR catalysts towards the electro-oxidation of methanol in an alkaline medium.

In order to evaluate the electrocatalytic activity of the catalysts, the methanol oxidation current density values under the potential

region of peak A were normalized by the electrochemically active surface areas of Pt and the Pt loadings for each catalyst to represent the specific and mass activity of the catalysts. Figure 14 presents the calculated specific (a) and mass (b) activity values of the prepared catalysts. As seen from the data in Fig. 14, all the PtW/GR catalysts that have different Pt:W molar ratios outperformed the bare Pt/GR catalyst in respect to both specific activity and mass activity.

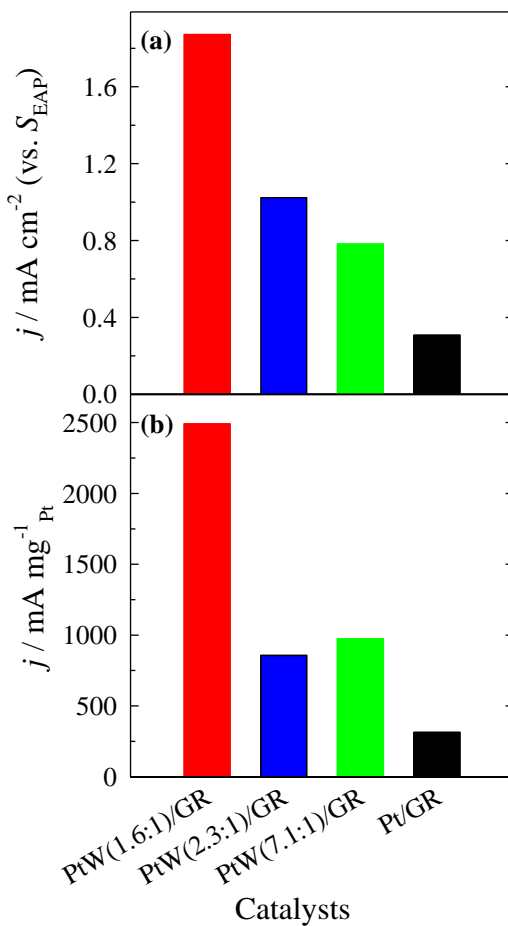


Figure 14. Current densities normalized by ESA (a) and Pt loadings (b) for Pt/GR, PtW(1.6:1)/GR, PtW(2.3:1)/GR and PtW(7:1)/GR catalysts in 1 M CH₃OH + 1 M NaOH at 50 mV s⁻¹.

Assuming ca. 2.3, 1.6 and 1.4 times higher active surface area of the Pt/GR catalyst compared to those of the PtW(1.6:1)/GR, PtW(2.3:1)/GR and PtW(7.1:1)/GR catalysts, respectively, the surface area normalized methanol oxidation current densities under peak A, on the contrary, are ca. 4.6, 2.6 and 2.0 times higher on the latter catalysts (Fig. 14a). Similarly, the mass activities of the same PtW(1.6:1)/GR, PtW(2.3:1)/GR and PtW(7.1:1)/GR catalysts are ca. 6.1, 2.1 and 2.4 times higher than that at Pt/GR (Fig. 14b).

The catalytic stability of the synthesized catalysts for the oxidation of methanol was further investigated under chronoamperometric conditions. Figure 15 presents the chronoamperometric curves obtained at the Pt/GR, W/GR and PtW/GR catalysts in a 1 M CH₃OH + 1 M NaOH solution at a fixed potential value of -0.2 V for 1800 s. All the catalysts show a current decay for the methanol oxidation reaction. Such behaviour might be explained by the formation of intermediate species, such as CO_{ads}, CHO_{ads}, etc., during the methanol oxidation reaction. The current densities obtained at a fixed potential value of -0.2 V for all synthesized PtW/GR catalysts are higher than those for the bare Pt/GR and W/GR. After exposing the catalysts at the mentioned potential for a time period equal to 1800 s, the current density values of methanol oxidation at the PtW/GR catalysts that have Pt:W molar ratios of 1.6:1, 2.3:1 and 7.1:1 were found to be ca. 2.0, 2.4 and 1.3 times, respectively, higher than those at Pt/GR. This indicates a higher electrocatalytic activity and stability of the prepared PtW/GR catalysts towards the oxidation of methanol (Fig. 15).

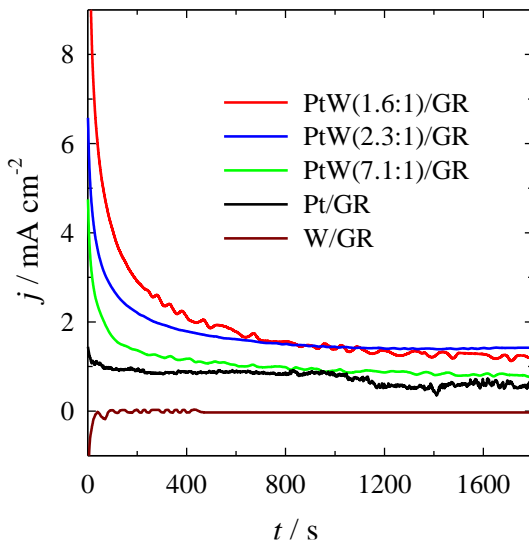


Figure 15. Chronoamperometric data recorded for W/GR, Pt/GR PtW(1.6:1)/GR, PtW(2.3:1)/GR and PtW(7:1)/GR catalysts in 1 M CH₃OH + 1 M NaOH at $E = -0.2$ V for 1800 s.

The voltammetric and chronoamperometric measurements confirm that the PtW(1.6:1)/GR, PtW(2.3:1)/GR and PtW(7.1:1) catalysts, which were prepared via a simple and rapid microwave heating method, exhibit a higher electrocatalytic activity and a better stability towards the oxidation of methanol in an alkaline medium than that of Pt/GR and W/GR catalysts.

3.4 Methanol oxidation on PtCoMn/GR, PtCoRu/GR and PtCoMo/GR catalysts

The graphene supported PtCoM (M = Mn, Ru, Mo) catalysts were prepared by microwave assisted heating of Pt(IV), Co(II), Mn(II), Ru(III) and Mo(VI) salts in ethylene glycol solutions. It should be noted that the reaction mixtures contain the constant amounts of Pt

and Co, whereas the amounts of Mn, Ru and Mo were different. In this case, the graphene supported catalysts that have different Pt:Co:Mn, Pt:Co:Ru and Pt:Co:Mo molar ratios were prepared. The ICP-OES was used for the determination of the Pt, Co, Mn, Ru and Mo loadings in the synthesized catalysts. The data obtained are given in the Table 3.

Table 3. The composition of PtCoMn/GR, PtCoRu/GR and PtCoMo/GR catalysts by ICP-OES and ESA values of Pt in the catalysts determined from CVs recorded in 0.5 M H₂SO₄ solution.

Catalyst	Pt:Co:M molar ratio	Pt loading, $\mu\text{g cm}^{-2}$	ESA, cm^2	ESA, $\text{m}^2 \text{g}^{-1}$
PtCoMn/GR	1:3:1	103.8	11.6	160.0
PtCoRu/GR	1:2:2	183.2	3.9	31.9
PtCoMo/GR	7:2:1	83.8	3.8	64.5
Pt/GR	1:0:0	73.0	5.2	102.5

It was found that Pt:Co:Mn, Pt:Co:Ru and Pt:Co:Mo molar ratios in the prepared PtCoMn/GR, PtCoRu/GR and PtCoMo/GR catalysts are 1:3:1, 1:2:2 and 7:2:1 respectively. Figure 1 presents TEM views of the graphene supported PtCoMn (a), PtCoRu (b) and PtCoMo (c) catalysts. All the catalysts are well dispersed on the surface of graphene (Fig. 1). The Pt nanoparticle size in the catalysts was found to be 1-3 nm. It was determined that Pt loadings in the PtCoMn/GR, PtCoRu/GR and PtCoMo/GR catalysts were 103.8, 183.2 and 83.8 $\mu\text{g cm}^{-2}$ respectively.

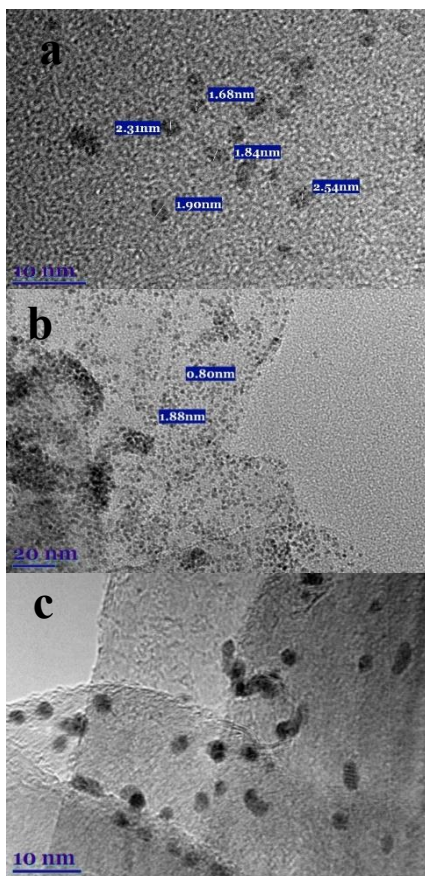


Figure. 16. TEM views of PtCoMn/GR (a), PtCoRu/GR (b) and PtCoMo/GR (c) prepared by microwave synthesis.

The electrochemically active surface areas of Pt in the synthesized catalysts were determined from the cyclic voltammograms of the PtCoMn/GR, PtCoRu/GR and PtCoMo/GR catalysts recorded in a deaerated 0.5 M H_2SO_4 solution at a sweep rate of 50 mV s^{-1} and by calculating the charge associated with hydrogen

adsorption ($220 \mu\text{C cm}^{-2}$) (Fig. 17). The summarized data are given in Table 1. These results show that the highest ESA values was obtained for the PtCoMn/GR catalyst. ESA of Pt is 2.2, 2.9 and 3.1 times higher at PtCoMn/GR than those at Pt/GR, PtCoRu/GR and PtCoMo/GR catalysts, respectively (Table 3).

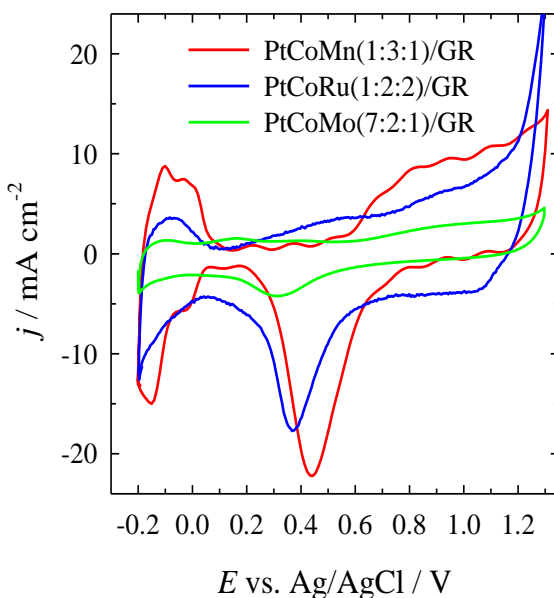


Figure. 17. CVs of the PtCoMn/GR, PtCoRu/GR and PtCoMo/GR catalysts recorded in $0.5 \text{ M H}_2\text{SO}_4$ at 50 mV s^{-1} ; 25°C .

The electrochemical properties of the GR supported PtCoM (M = Mn, Ru, Mo) catalysts that have different metals molar ratios were investigated with respect to the oxidation of methanol in an alkaline media by means of cyclic voltammetry. Figure 18 shows CVs for the PtCoMn(1:3:1)/GR (a), PtCoRu(1:2:2)/GR (b), and PtCoMo(7:2:1)/GR catalysts recorded in $1 \text{ M CH}_3\text{OH} + 1 \text{ M NaOH}$ solution at a scan rate of 50 mV s^{-1} . For the sake of simplicity, in Fig.

18d only positive potential going scans of stabilized CVs of all the catalysts are presented.

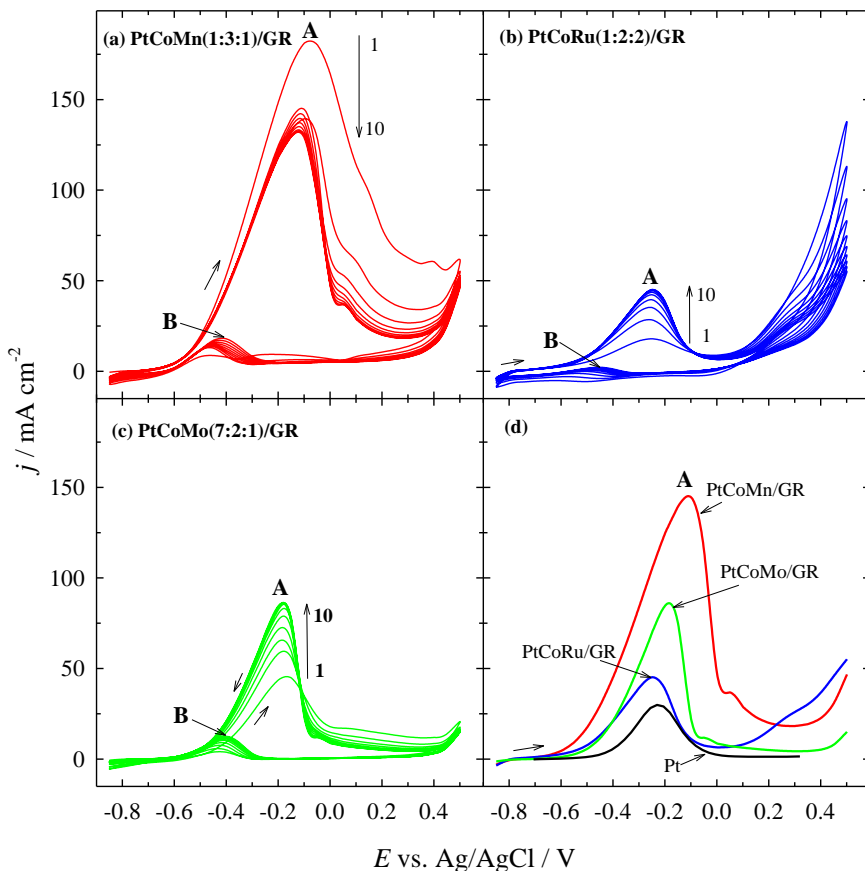


Figure 18. CVs recorded at PtCoMn(1:3:1)/GR (a), PtCoRu(1:2:2)/GR (b), PtCoMo(7:2:1)/GR. (d) Stabilized positive potential-going scans for the same catalysts in 1 M CH_3OH + 1 M NaOH at 50 mV s^{-1} .

As evident from the obtained data in Fig. 18, all CV plots exhibit two typical anodic peaks in the forward and reverse scans

(labelled as A and B), which are well-known to reflect the electrooxidation of alcohols and the intermediate carbonaceous species, respectively. The first anodic current peak A in the forward scan is related to the oxidation of methanol on the catalyst, whereas the second anodic peak B on the reverse scan may be related to the oxidation of intermediate products generated during the forward scan.

During long-term cycling, the methanol electro-oxidation current density values (anodic peak A) recorded at the investigated PtCoMn(1:3:1)/GR catalyst at first slightly are decreased and then stabilized (Fig. 18a). The other way is for PtCoRu(1:2:2)/GR and PtCoMo(7:2:1)/GR catalysts (Fig. 18b, c). During long-term cycling, current density values are rising and then stabilized. The highest electrocatalytic activity for methanol oxidation reaction is noted for PtCoMn(1:3:1)/GR catalyst (Fig. 18d). Furthermore, methanol oxidation current densities are ca. 4.8, 1.5 and 2.8 times higher at ternary PtCoMn(1:3:1)/GR, PtCoRu(1:2:2)/GR and PtCoMo(7:2:1)/GR catalysts than those at the bare Pt/GR catalyst.

Figure 19 shows the calculated methanol oxidation current density values normalized by the ESAs of Pt in the catalysts (a) and Pt loadings (b) for each catalyst.

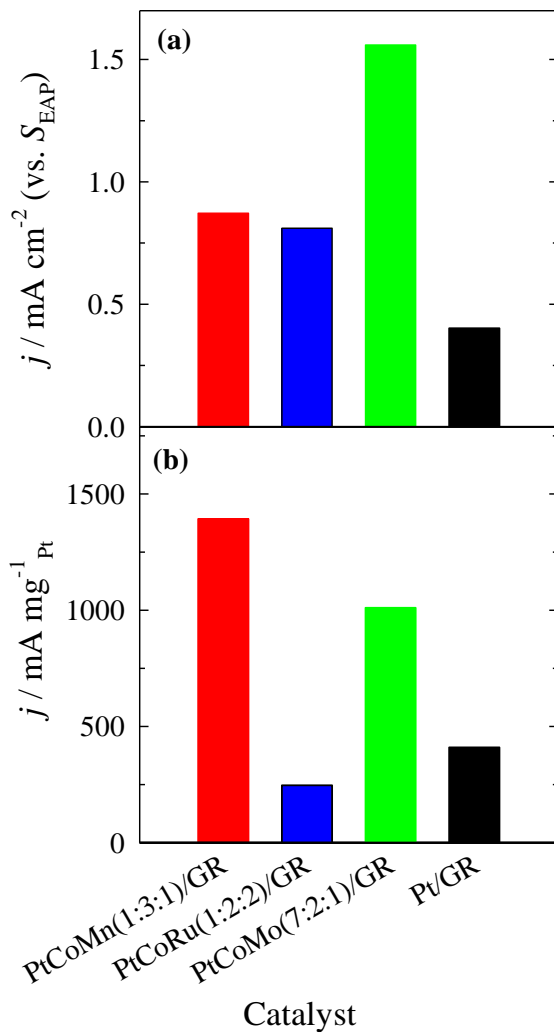


Figure 19. Columns of Pt/GR, PtCoMn/GR, PtCoRu/GR and PtCoMo/GR catalysts recorded in 1 M CH_3OH + 1 NaOH and normalized by the Pt loadings (a) and electrochemically surface areas (b).

As seen from the data obtained, the highest specific activity has PtCoMo(7:2:1)/GR. Ca. 1.8, 1.9 and 3.9 times higher methanol oxidation current densities are obtained at the PtCoMo(7:2:1)/GR catalyst as compared with those at PtCoMn(1:3:1)/GR, PtCoRu(1:2:2)/GR and Pt/GR, respectively (Fig. 19a). The highest mass activity for methanol oxidation has the PtCoMn(1:3:1)/GR and PtCoMo(7:2:1)/GR catalysts (Fig. 19b).

The catalytic stability of the synthesized catalysts for the oxidation of methanol was further investigated under chronoamperometric conditions. Figure 20 presents the chronoamperometric curves obtained at the Pt/GR, PtCoMn(1:3:1)/GR, PtCoRu(1:2:2)/GR, and PtCoMo(7:2:1)/GR catalysts in a 1 M CH₃OH + 1 M NaOH solution at a fixed potential value of -0.2 V for 1800 s.

All the catalysts show a current decay for the methanol oxidation reaction. Such behaviour might be explained by the formation of intermediate species, such as CO_{ads}, CHO_{ads}, etc., during the methanol oxidation reaction. The current densities obtained at a fixed potential value of -0.2 V for PtCoMn(1:3:1)/GR and PtCoMo(7:2:1)/GR catalysts are higher than those for the bare Pt/GR. At the end of the experimental period ($t = 1800$ s), the current densities recorded at the PtCoMn(1:3:1)/GR catalyst are ca. 7.8, 1.7 and 2.6, respectively, greater as compared to those at PtCoRu(1:2:2)/GR, PtCoMo(7:2:1)/GR and Pt/GR. These data confirm the results obtained by cyclic voltammetry.

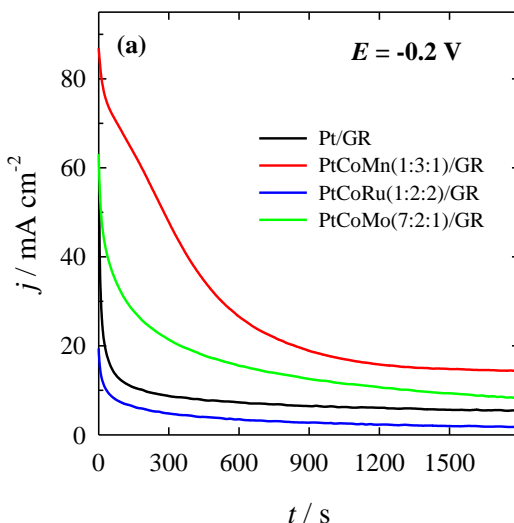


Figure 20. Chronoamperometric data recorded for Pt/GR, PtCoMn(1:3:1)/GR, PtCoRu(1:2:2)/GR, PtCoMo(7:2:1)/GR catalysts in 1 M CH₃OH + 1 M NaOH at $E = -0.2$ V for 1800 s.

The specific and mass activities for methanol oxidation on the investigated Pt/GR, PtCoMn(1:3:1)/GR, PtCoRu(1:2:2)/GR and PtCoMo(7:2:1)/GR catalysts at the end of experimental period ($t = 1800$ s) are given in Fig. 21. It is clearly seen that the highest specific activity towards methanol oxidation (Fig. 21a) has the PtCoMo(7:2:1)/GR catalyst, whereas, the highest mass activity for the oxidation of methanol has PtCoMn(1:3:1)/GR catalyst (Fig. 21b). Specific activity values are ca. 1.8, 2.1 and 4.6 times higher on the PtCoMo(7:2:1)/GR catalyst than those on the PtCoMn(1:3:1)/GR, Pt/GR and PtCoRu(1:2:2)/GR catalysts, respectively (Fig. 21a). The mass current density values are ca. 1.4, 1.8 and 13.7 times higher at PtCoMn(1:3:1)/GR than those at PtCoMo(7:2:1)/GR, Pt/GR and PtCoRu(1:2:2)/GR catalysts, respectively (Fig. 21b).

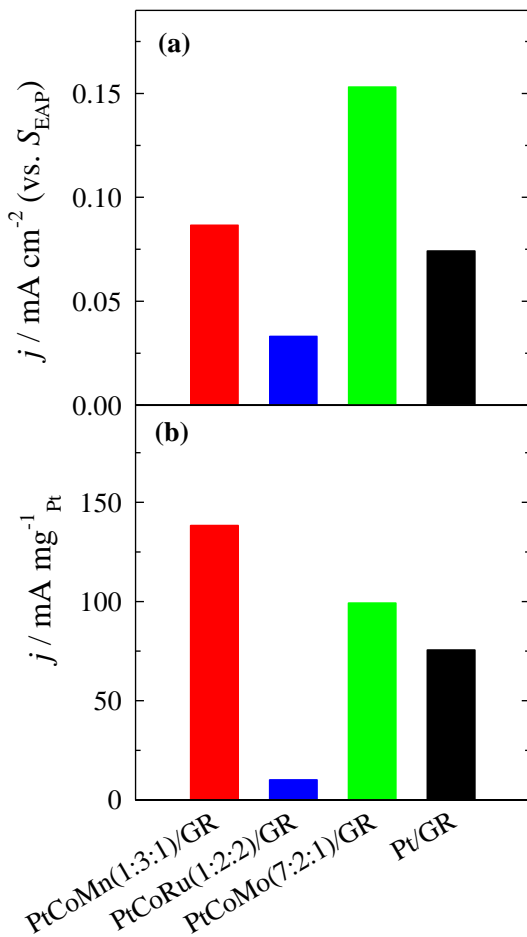


Figure 21. Bar columns represent PtCoMn/GR, PtCoRu/GR ir PtCoMo/GR catalysts specific (a) and mass (b) activity values in 1 M CH_3OH + 1 M NaOH solution, at $E = -0,2 \text{ V}$, $t = 1800 \text{ s}$.

CONCLUSIONS

1. In this study, the graphene supported PtW catalysts that have Pt:W molar ratios equal to 1.6:1, 2.3:1 and 7.1:1 and graphene supported PtMo catalysts that have Pt:Mo molar ratios equal to 43:1, 7:1 and 3:1 have been prepared by microwave-assisted heating. The ternary PtCoMn/graphene, PtCoRu/graphene and PtCoMo/graphene catalysts that have Pt:Co:Mn, Pt:Co:Ru and Pt:Co:Mo molar ratios equal to 1:3:1, 1:2:2 and 7:2:1, respectively, have also been fabricated. The catalysts were synthesized with nanoparticles in size of ca. 1-3 nm.
2. Synthesized PtW/graphene catalysts that have the Pt:W molar ratio equal to 1.6:1, 2.3:1 and 7.1:1, and PtMo/graphene catalysts that have the Pt:Mo molar ratio equal to 43:1, 7:1 and 3:1 show higher electrocatalytic activity for sodium borohydride and methanol oxidation reactions than pure W/graphene and Mo/graphene catalysts. Moreover, sodium borohydride oxidation current density values are 1.2-1.5 and ~81.2-101.1 times higher on different PtW/graphene catalysts compared with those on the Pt/graphene and W/graphene catalysts, respectively. In the case of PtMo/graphene catalysts, sodium borohydride oxidation current density values are 22.7-31.9 times higher at PtMo/graphene than those on the Mo/graphene catalyst. Highest mass activity for sodium borohydride oxidation reaction has been found on PtW/graphene and PtMo/graphene catalysts that have the Pt:W and Pt:Mo molar ratio equal to 1.6:1 and 3:1, respectively.
3. Highest electrocatalytic activity for methanol oxidation reaction showed the PtW/graphene catalyst that has the Pt:W molar ratio equal to 1.6:1. Methanol oxidation current density values recorded on the PtW(1.6:1)/graphene,

PtW(2.3:1)/graphene and PtW(7.1:1)/graphene catalysts are ca. 2.1, 1.6 and 1.4 times higher compared with those on the Pt/graphene catalyst and much higher e.g. 7.8, 6.0 and 5.2 times compared with those on the W/graphene catalyst.

4. It was found that the highest electrocatalytic activity for methanol oxidation showed PtCoMn/graphene catalyst that has the Pt:Co:Mn molar ratio equal to 1:3:1 compared with that of PtCoRu(1:2:2)/graphene, PtCoMo(7:2:1)/graphene and Pt/graphene catalysts.
5. Synthesized PtW/graphene, PtMo/graphene, PtCoMn/graphene, PtCoRu/graphene and PtCoMo/graphene catalysts are promising anode materials for low temperature fuel cells.

SUMMARY IN LITHUANIAN

Šiame darbe buvo kuriamos naujos medžiagos, kurios gali būti panaudojamos kaip katalizatoriai tiesioginiuose borohidrido ir metanolio kuro elementuose. Šie katalizatoriai buvo gaminami iš įvairių metalų (platiną, kobaltą, molibdeną, volframą, rutenį ir manganą), juos dengiant ant grafeno paviršiaus, formuojant metalų lydinius. Disertacinio darbo metu buvo formuojami PtW/GR, PtMo/GR, PtCoM/GR (M = Mn, Ru, Mo) katalizatoriai taikant mikrobangų sintezės metodą. Ištirtos ir optimizuotos pastarųjų katalizatorių gavimo sąlygos, o jų aktyvumas buvo įvertintas NaBH₄ ir CH₃OH oksidacijos reakcijoms.

Nustatyta, kad PtW/GR ir PtMo/GR katalizatoriai, kuriuose nusodinto Pt įkrova yra nuo 25 iki 69 μg cm⁻², pasižymi ženkliai didesniu elektrokataliziniu aktyvumu NaBH₄ ir CH₃OH oksidacijos reakcijoms nei Pt/GR katalizatorius. Susintetinti PtW/GR katalizatoriai, kuriuose Pt:W molinis santykis yra 1,6:1, 2,3:1 ir 7,1:1, ir PtMo/GR katalizatoriai, kuriuose Pt:Mo molinis santykis yra 43:1, 7:1 ir 3:1, pasižymi didesniu elektrokataliziniu aktyvumu natrio

borohidrido oksidacijos reakcijai, lyginant su W/GR ir Mo/GR katalizatoriais. Išmatuotos natrio borohidrido oksidacijos srovės tankio vertės yra 1,2-1,5 karto didesnės ant PtW/GR katalizatorių lyginant su Pt/GR katalizatoriumi ir žymiai didesnės, t.y. apie 81,2-101,1 karto už natrio borohidrido oksidacijos srovės tankio vertes ant W/GR katalizatoriaus. PtMo/GR katalizatorių atveju, išmatuotos natrio borohidrido oksidacijos srovės tankio vertės yra 22,7-31,9 kartų didesnės nei jos yra ant Mo/GR katalizatoriaus. Didžiausiu masės aktyvumu natrio borohidrido oksidacijos reakcijai pasižymėjo PtW/GR ir PtMo/GR katalizatoriai kuriuose Pt:W ir Pt:Mo molinis santykis yra atitinkamai 1,6:1 ir 3:1.

Didžiausiu elektrokataliziniu aktyvumu metanolio oksidacijai pasižymėjo PtW/GR katalizatorius, kuriame Pt:W molinis santykis yra lygus 1,6:1. Išmatuotos metanolio oksidacijos srovės tankio vertės ant PtW(1,6:1)/GR, PtW(2,3:1)/GR ir PtW(7,1:1)/GR katalizatorių yra atitinkamai apie 2,1, 1,6 ir 1,4 kartus didesnės negu jos yra ant Pt/GR katalizatoriaus ir žymiai didesnės, t.y. apie 7,8, 6,0 ir 5,2 kartus, už metanolio oksidacijos srovės tankio vertes ant W/GR katalizatoriaus.

Nustatyta, kad didžiausiu elektrokataliziniu aktyvumu metanolio oksidacijos reakcijai pasižymėjo PtCoMn/GR katalizatorius, kuriame Pt:Co:Mn molinis santykis yra lygus 1:3:1 lyginant su PtCoRu(1:2:2)/GR, PtCoMo(7:2:1) ir Pt/GR katalizatoriais. Susintetinti PtW/GR, PtMo/GR, PtCoMn/GR, PtCoRu/GR ir PtCoMo/GR katalizatoriai yra perspektyvios medžiagos ir gali būti naudojamos žemos temperatūros kuro elementuose.

LIST OF PUBLICATIONS

In Clarivate Analytics Web of Science

1. T. Kilmonis, L. Tamašauskaitė-Tamašiūnaitė, A. Balčiūnaitė, J. Vaičiūnienė, M. Skapas, E. Norkus. “*Microwave-assisted synthesis of platinum-tungsten/graphene catalysts*”. *Chemija* 27 (2016) 143-149.
2. T. Kilmonis, A. Nacys, D. Šimkūnaitė, L. Tamašauskaitė-Tamašiūnaitė, A. Balčiūnaitė, E. Norkus. “*Investigation of methanol electro-oxidation on graphene supported platinum-tungsten catalyst*”. *Chemija* 30(3) (2019) 146-153.
3. T. Kilmonis, A. Nacys, A. Balčiūnaitė, V. Kepenienė, J. Jablonskienė, J. Vaičiūnienė, M. Skapas, L. Tamašauskaitė-Tamašiūnaitė, E. Norkus. “*One-pot microwave-assisted synthesis of graphene supported PtCoM (M = Mn, Ru, Mo) catalysts for low temperature fuel cells*”. *J. Electrochem. Soc.* (2019) (submitted).

In Other Referred International Journals

1. T. Kilmonis, L. Tamašauskaitė-Tamašiūnaitė, A. Balčiūnaitė, J. Vaičiūnienė, E. Norkus. “*Investigation of the graphene supported platinum-tungsten catalysts prepared by microwave synthesis as electrocatalysts for borohydride oxidation*”. *ECS Transactions* 68(3) (2015) 45-53.

Publications in International Conferences

1. T. Kilmonis, L. Tamašauskaitė-Tamašiūnaitė, A. Balčiūnaitė, J. Vaičiūnienė, E. Norkus. “*Investigation of the graphene supported platinum-tungsten catalysts prepared by microwave synthesis as electrocatalysts for borohydride oxidation*”. *ECS Conference on Electrochemical Energy Conversion & Storage with SOFC-XIV: Glasgow, Scotland* (2015) C-0632.

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6. L. Tamašauskaitė-Tamašiūnaitė, V. Kepėnienė, A. Nacys, T. Kilmonis, D. Žurauskaitė, V. Pakštas, E. Norkus. “*Non-noble metal alloys prepared by microwave synthesis for oxygen reduction*”. 19th International Conference: Materials, Methods & Technologies: Elenite, Bulgaria (2017) 6.
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9. L. Tamašauskaitė-Tamašiūnaitė, T. Kilmonis, A. Balčiūnaitė, J. Jablonskienė, J. Vaičiūnienė, E. Norkus. “*Microwave-assisted synthesis of graphene supported PtCoM (M = Mn, Ru, Mo) catalysts for low temperature fuel cells*”. In: *Proceedings of 256th ACS National Meeting & Exposition*: 19-23 August, Boston, MA, USA (2018), ID 2951423, ENFL-528 (oral presentation).

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2017-09-30 till now	Junior Research Associate, Department of Catalysis, Center for Physical Sciences and Technology
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Participation in scientific projects

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