



Electrodeposited Co-W alloys and their prospects as effective anode for methanol oxidation in acidic media



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ABSTRACT

Electrodeposited Co-W alloys having different composition and structure were tested as anodes for methanol electrooxidation. The structure of electrodeposited Co-W alloys having various tungsten content is either nano-crystalline (3 and 18 at.% of W) or “amorphous-like” (30 at.% of W). The electrodeposition was performed on the stainless steel substrate from citrate-borate bath at 60 °C and a cathodic current density 10 mA·cm⁻². Alloys having different compositions were obtained by varying pH from 5 to 8. A well-defined crystalline structure was indicated for Co-W having 3 at.% and 18 at.% of W: these deposits have a hexagonal close packed (hcp) structure typical for electrodeposited pure Co. The high content of W in the alloy (~30 at.%) leads to the formation of nano-crystalline structure (“amorphous-like”). The electrocatalytic activity of prepared Co-W alloys was examined by means of cyclic voltammetry in the mixture of 1 M CH₃OH and 0.1 M H₂SO₄. The electrooxidation of methanol depends on the content of W in the alloy. It was found that the crystalline Co-3 W and Co-18 W alloys are inactive for methanol oxidation, and the electrochemical alloys dissolution occurs in the tested media. Whereas, the high content of W (~30 at.%) in the Co-W coating prevents the continuous Co-W alloy dissolution and it might be used as anode for the methanol oxidation in the acidic media. The annealing of Co-W deposits was performed at 600 °C for 1 h in the air and formation of Co₃O₄ and CoWO₄ compounds with simultaneous decrease of tungsten content in the alloys were detected. The annealed Co-W coatings show lower activity toward methanol electrooxidation compared to as-deposited Co-30 at.% W.

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1. Introduction

Fuel cells based on methanol oxidation reaction (MOR) could replace combustion engines for a variety of applications due to their easy transportation, handling, storage, low operating temperatures and higher energy density compared to the hydrogen [1–3]. Methanol oxidation has been extensively investigated since the early 1970's and a multistep oxidation mechanism was determined involving O–H bond scission in methanol followed by sequential dehydrogenation to CH₂O, then to CO or CO₂ [4]. The resulted products of oxidation (CO₂, HCHO, HCOOH and HCOOCH₃) depend on methanol concentration, temperature, electrode roughness and time of electrolysis. Platinum is the most common catalyst for methanol oxidation, but it is very sensitive to the reaction intermediates such as CO as it poisoning losses catalyst activity [5]. It was found that in the acidic media platinum exhibits the higher catalytic activity for the oxidation of methanol and it is more

resistant toward poisoning by CO, so usually perchloric and sulfuric acids are commonly used as the supporting electrolytes for studies of methanol electrooxidation [6]. The interest in investigation of methanol oxidation on platinum electrodes in alkaline media is lower due to its progressive carbonation by CO₂ [7]. Accordingly, the acidic electrolytes are generally preferred for practical application. Nevertheless, the price of pure platinum is relatively high and the search of more active and less expensive catalysts with great stability for the methanol oxidation reaction has resulted in the development of new binary and ternary catalysts based on modifications of Pt with some other metal [4,8]. Therefore, a number of other materials have been investigated for their suitability as methanol oxidation catalysts, including TiO₂ [9] and Cu(111) [10]. Meanwhile, as the small price of electrodes for methanol fuel cells has been still a key factor, only a few studies have been made to investigate electrodeposited alloys as anode materials for possible application in methanol oxidation reaction. Relatively cheap electrodeposition technique offers the possibility to prepare alloy coatings with easy control of their composition, thickness and homogeneity of the surface. In [11] the electro-catalytic activity of electrodeposited Pt-Ni alloy layers on an inert substrate (Au) electrode for methanol oxidation

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reaction was investigated. It was shown that the onset of electrooxidation shifted to less anodic potential values (approximately by 160 mV vs Hg/Hg₂SO₄ electrode), while also the current density values obtained for Pt-Ni alloy surfaces were higher for 15 times than those of pure Pt. In [12] it was demonstrated that the anodic current peak, a measure of oxidation reaction rate of methanol, is considerably higher using the electrochemically prepared Fe-W alloy in comparison with pure Fe. In addition, the electrodeposited Co-W alloy was presented as a promising anodic catalyst for direct methanol fuel cells [13]. Partially amorphous structure Co-W alloys with W content < 10 wt.% in the composition exhibited good corrosion resistance and catalytic activity in highly corrosive media such as H₂SO₄ and KOH. It is well known that W alloys with iron group metals, especially Co-W, have drawn much more attention because of their unusual mechanical, tribological, magnetic and anti-corrosion properties toward acidic and alkaline media and ability to improve catalytic properties of alkaline water electrolysis [14,15]. Heat treatment of the electrodeposited Co-W alloys enhances their corrosion resistance and it is attributed to the formation of stoichiometric compounds, surface oxides and the precipitation of stable phases in the microcracks [16]. Moreover, they are considered as environmentally safe alloys and can be easily prepared by simple and effective electrodeposition technique.

Considering the great performance of W alloys for methanol oxidation, the aim of this study was the electrochemical preparation and characterization of optimal composition of Co-W alloys electrodeposited from ammonia-free bath and possibilities to apply these alloys for methanol electrooxidation reaction in the acidic solution.

2. Materials and methods

Co-W deposits were electrodeposited onto stainless steel (type 304) substrates from citrate-borate electrolyte at different pH under galvanostatic mode at 10 mA·cm⁻². The plating bath consisted of (mol·L⁻¹): CoSO₄·7H₂O–0.2, Na₂WO₄·2H₂O–0.2, C₆H₈O₇–0.04, H₃BO₃–0.65, Na₃C₆H₅O₇–0.25. The pH of solutions was adjusted to 5.0, 6.7 and 8 ± 0.1 by concentrated H₂SO₄ and NaOH solutions. The electrolyte temperature was maintained at 60 ± 2 °C by means of a water bath. The thickness of the deposits was calculated from gravimetric and elemental analysis data and in all cases was ~ 10 μm.

Electrodeposition was performed in a standard three-electrode cell. A platinum mesh was used as a counter electrode, and saturated Ag/AgCl acted as a reference electrode. All electrode potentials in this paper are presented with respect to the saturated Ag/AgCl electrode. Before the electrodeposition, the stainless steel substrates were washed with detergent and rinsed in the ultrasonic bath with water and then with acetone to remove any contaminants from the surface. In order to improve the adhesion of alloys to the substrates, a nickel seed layer was electrodeposited from an electrolyte containing 1 M NiCl₂ and 2.2 M HCl, at a cathodic current density of 10 mA·cm⁻² for 1 min. Co-W alloy coatings were annealed in air atmosphere in a tube furnace at 600 °C under for 1 h.

The morphology and chemical composition of the coatings was examined by scanning electron microscope (SEM) using Hitachi TM3000 equipment complemented with an energy dispersive X-ray spectroscopy (EDS) analyzer for elemental analysis. The structure of the alloys was studied by X-ray diffraction method using Rigaku MiniFlex II diffractometer with Cu Kα radiation in the 2θ range from 30 to 100°.

Cyclic voltammetry measurements were performed using programmable potentiostat/galvanostat (Autolab N302). Experiments were performed in the potential range from –0.2 to 2.0 V in 0.1 M H₂SO₄ + 1 M CH₃OH solution at room temperature at the scan rate 10 mV s⁻¹. A platinum rode was used as a counter electrode and Ag/AgCl was used as a reference electrode. All potentials were measured and presented also against saturated Ag/AgCl electrode.

3. Results and discussions

3.1. Composition, surface morphology and structure of electrodeposited Co-W alloys

In this study the Co-W alloys coatings were electrodeposited from citrate electrolyte. The composition of Co-W alloys from this electrolyte could be varied in a wide range by changing the pH only, because the electrochemical reactions in the given complex system are dependent on a number of Co(II) and W(VI) complexes with citrates and their distribution strongly depends on pH [14,17–20]. Thus, tungsten content is low (< 8 at.%) in Co-W alloys electrodeposited at pH 5, increases from 13 to up to 30 at.% with increasing current density at pH 6.7; whereas at pH 8, the amount of tungsten in the Co-W coatings varies only from 30 to 36 at.%. Thereby, in order to reveal the influence of Co-W alloys composition on their effective use as anode in methanol electrooxidation reaction, there were three marginal cases investigated having different tungsten content (see Table 1), namely Co-3 at.% W (case 1, pH 5), Co-18 at.% W (case 2, pH 6.7), and Co-30 at.% W (case 3, pH 8). The coatings were obtained at the same current density of 10 mA·cm⁻² and 60 °C.

Anodic oxidation of methanol is heterogeneous reaction; therefore it is very important to investigate the microstructure and morphology of the surface of anode material. SEM images of as-deposited Co-W coatings are shown in Fig. 1. Obviously, even a small amount of W in the coating considerably changes the surface morphology. A needle-like structure with extended acicular crystallites that is typical for electrodeposited pure cobalt coating (Fig. 1a) is eliminated after an introduction of tungsten into the alloy. Co-W deposit having ~ 3 at.% of tungsten consists of densely packed polyhedral crystallites with pronounced grain boundaries (Fig. 1b). An increase in W percentage up to 18 at.% does not considerably affect the shape of the crystallites, but results in an increase in their size (Fig. 1c). When tungsten content reaches ~ 30 at.%, the morphology of the Co-W alloy changes considerably, the structure becomes more compact and a spherical cluster surface consists from large number of smaller size nodular-shape grains (Fig. 1d).

The changes of alloy composition and morphology are directly reflected in the structural changes. XRD patterns of investigated alloys are presented in Fig. 2. Noticeably, that even the small tungsten amount (“case 1”) incorporated into Co lattice significantly changes the texture of hcp Co lattice: the hexagonal close-packed {100}-textured film, which is characteristic for electrodeposited Co, transforms into {110} textured film while texture {100} weakens sufficiently. This small amount of tungsten causes a strong disorientation of blocs, and maximum angle in the electrodeposited films can reach tens of degrees, that facilitates the growth of defects and multi-domain more readily, therefore, decreasing the texture [21].

The “case 2” is preferentially {101} textured film, whereas the texture of {100} characteristic for electrodeposited cobalt was disappeared. The XRD patterns of this Co-W coating demonstrates a strong peak at 2θ = 46.5° which is attributed to Co₃W. A small shift of 2θ position in comparison with indicated in PDF card no 65–3520 occurs probably due to formation of Co solid solution in the Co₃W phase [17]. Nanocrystalline (“amorphous-like”) structure of Co-W alloy was observed, when the tungsten content in the coatings deposited at 60 °C is > 25–27 at.%. In this “case 3” only one broad peak in the proximity of 2θ = 43.5° is seen. It is difficult to determine to which phase this peak is attributed because

Table 1
Influence of the electrolyte pH on Co-W alloy composition and cathodic current efficiency.

pH of the plating bath	W content, at.%	Current efficiency, %
5.0	3.0	75.5
6.7	18.0	70.1
8.0	30.0	25.5

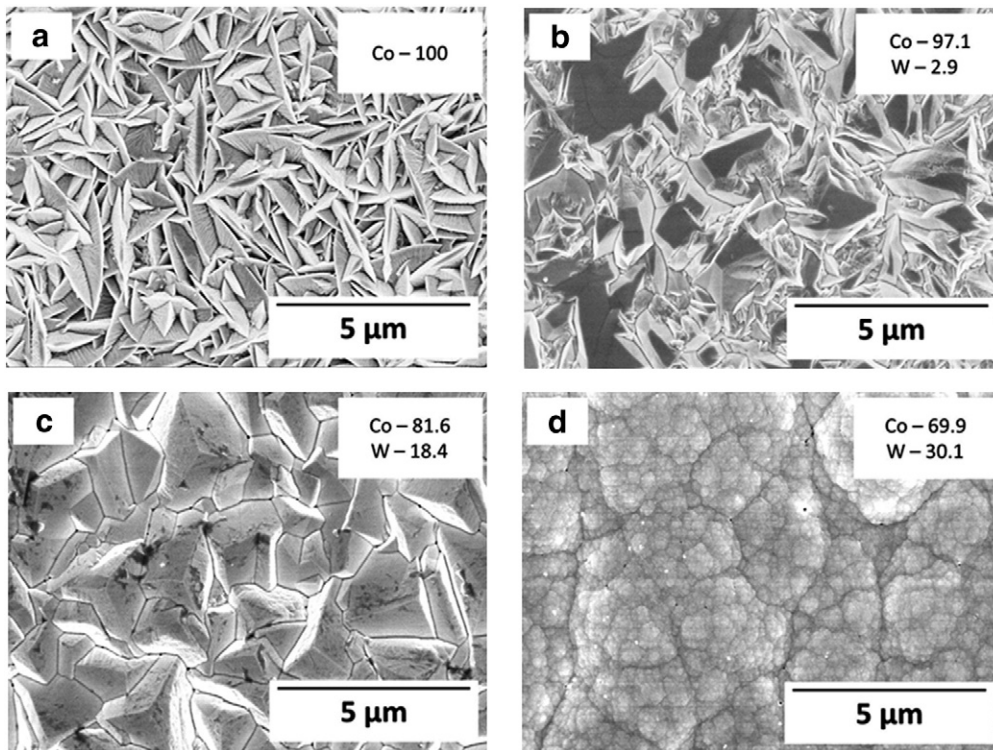


Fig. 1. SEM micrographs of pure Co and Co-W alloys deposited at different pH: (a) 6.7; (b) 5.0; (c) 6.7; (d) 8.0. Compositions of alloys are given in at.%.

the characteristic peaks for Co(W) and Co_3W phase is overlapped. Such peak broadening could be attributed to the reduction of crystallite size of the alloy with an increase of the percentage of W in the deposit.

The abovementioned changes of composition, morphology and structure are the targets of interplay during co-deposition process: the co-deposition of cobalt and tungsten as well as the hydrogen evolution as side reaction undergoes via intermediate adsorption stages and they are interdependent, that lead to increase of W content with increase of pH, lowering of hydrogen overvoltage, and decrease of grain size as follows. Firstly, the increase of the W fraction in the alloy with pH correlates well with the rapid raise in the concentration of some W(VI)-citrate complexes in the solution such as $(\text{WO}_4)(\text{HCitr})\text{H}^{4-}$ at $\text{pH} > 5$. Secondly, the alkalization occurring in the near-electrode zone due to

intense hydrogen evolution during electrolysis, especially at higher pH of solution leads to the increase of tungsten content in the coating, which could be linked to the rise in concentration of electrochemically active W(VI)-citrate complexes with pH. Finally, the formation of adsorbed (heterogeneous) layers on the surface containing intermediates of Co(II) and W(VI) with simultaneous hydrogen evolution facilitate the start the crystallization of Co-W on new spots that causes decrease of the grain size.

Thus, this complex interplay yields the decreasing of both cathodic current efficiency (Table 1) and the grain size with increase in tungsten content with resulted “amorphous-like” structure. Therefore, the alloys obtained at pH 8 contains the highest amount of tungsten (≥ 30 at.%), and due to the intensive hydrogen evolution consist of finest grains

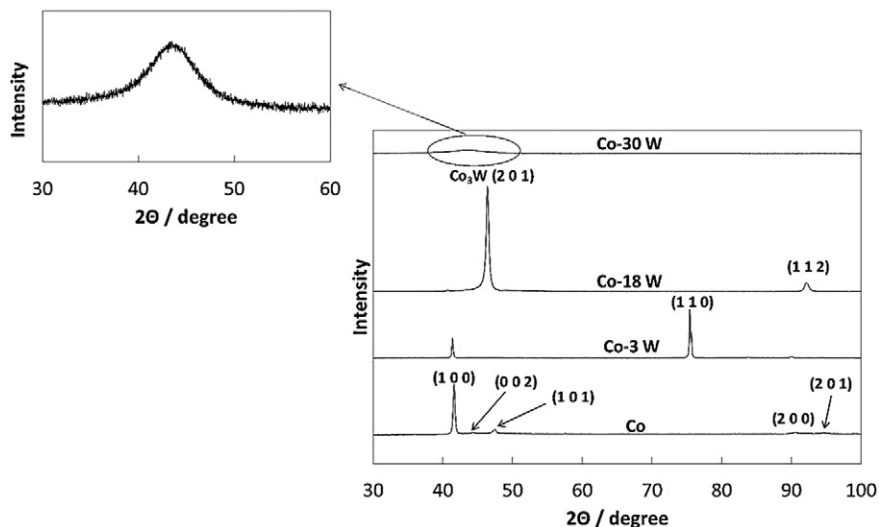


Fig. 2. XRD patterns of as-deposited pure Co and Co-W coatings. Compositions of alloys are given in at.%.

that are smaller than 5 nm and have the low current efficiency (25.5%) in comparison with obtained at pH 5 (75.5%), where they have coarse-grained structure with ~5 – nm.

3.2. Electrochemical activity of as-deposited Co-W alloys for methanol electrooxidation reaction and their corrosion behavior in acidic medium

In this study, the electro-oxidation of methanol was performed in a mixed solution containing 0.1 M H₂SO₄ and 1 M CH₃OH at room temperature. Typical cyclic voltammetric (CV) curves for different compositions of Co-W catalysts are shown in Fig. 3 (a) and (b). As it can be clearly seen from Fig. 3a, for the cast Co and Co-W alloys having small percentage of W (<18 at.%) the high anodic current densities are observed and they are attributed to the active dissolution of Co-W alloys. The curves were almost linear and no significant peaks of methanol electro-oxidation were observed, which indicates that these Co-W alloys do not possess the electro-catalytic activity toward methanol electro-oxidation reaction.

As it was reported earlier [22], the corrosion resistance of electrodeposited Co-W alloys having <25 at.% of W is very poor. In this case the corrosion rate of the coatings in acidic media is really high and values of anodic current density reach up to 350 mA·cm⁻². According to the literature, due to the oxygen evolution an increase in current density also should be obtained at potentials >1.03 V (vs Ag/AgCl). However, in our case the current density grows mostly because of active Co-W alloys dissolution in acidic media. The corrosion process occurs through the entire alloy layer up to the substrate, and complete coating dissolution is occurred.

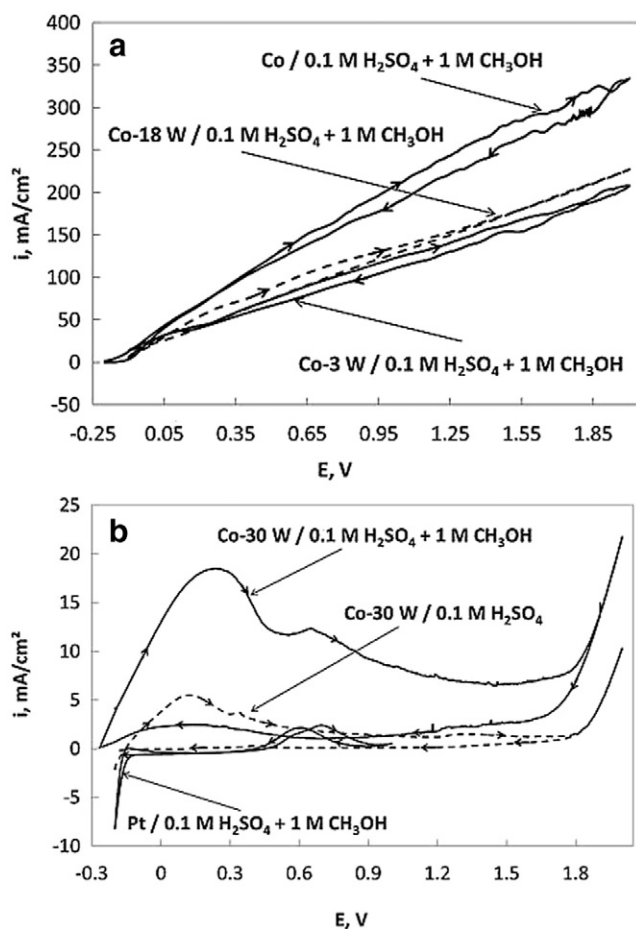


Fig. 3. Cyclic voltammograms recorded on the various as-deposited Co-W alloy catalysts; the composition is given in at.%. Arrows show a potential scan direction.

When the W content in the deposit is about 30 at.%, only the top surface layer is affected by corrosion process. Thus, after anodization of this alloy in 1 M CH₃OH and 0.1 M H₂SO₄ solution the coating is retained, but Co content in the alloys decreased from 70 to 67 at.%, accordingly W content increased from 30 to 33 at.%, which can be linked with Co faster dissolution. After removing the top layer by gentle polishing, the same W initial content was detected, namely ~30 at.% as it was before the experiment. A baseline CV curve of Co-30 W alloy was also collected in 0.1 M H₂SO₄ (without methanol), and the current (~5 mA·cm⁻²) can be attributed to the corrosion reaction (Fig. 3b), and it is sufficiently smaller than that for Co-W alloys having less content of W.

Thus, Co-W alloy containing 30 at.% of W demonstrates high activity and good stability as a catalyst for methanol oxidation reaction in the acidic media. For comparison the electrooxidation in the same solution on Pt is also shown. Generally, the methanol oxidation on Pt electrode occurs at the potential of 0.15 V and the rate increases considerably at the potentials above 0.4 V, where the hydroxyl groups on a Pt surface are formed. Finally, it was found that methanol oxidation current reached the maximum current density in the potential range of 0.67–0.7 V. The decrease in the oxidation current beyond this potential range is attributed to further oxidation of Pt surface leading to passivation and loss of activity toward methanol oxidation reaction [23]. On the reverse scan, the methanol oxidation peak appeared at an electrode potential of 0.55–0.6 V and the anodically formed oxide film reduces to metallic platinum [23,24]. In this study, the onset of oxide formation was observed at 0.69 V and the oxide reduction peak appeared at 0.6 V. In case of Co-30 W alloy the oxidation reaction occurs at about 0.67 V and this potential and the shape of CV curve is similar to the typical Pt electrode CV shape, whereas no peak at this potential was noticed in the voltammogram for Co-30 W deposit in the absence of methanol. The enhancement in catalytic activity by Co-W catalyst may be attributed to the increase in its real surface area, synergic effect by the interaction between Co and W, which prevents the active Co dissolution during the methanol oxidation reaction.

3.3. Electrochemical performance of oxidized Co-W alloys for methanol oxidation reaction

It was shown [13] that thermal treatment increases the catalytic activity of Co-W alloy for methanol oxidation in both acidic and alkaline media because the thermal treatment of the W alloy coatings improves their crystalline structure and new phases are formed. There are two stable bulk phases of cobalt oxide: the (fcc) type rock salt structure of CoO and the cubic spinel structure of Co₃O₄; they exhibit interesting electronic and magnetic properties and can be used as catalysts in some reactions [25]. In order to prepare oxidized Co-W alloys they were heated for 1 h at 600 °C in air atmosphere. This temperature has been chosen as the optimal for further experiments, because at lower temperature (400 °C) amorphous structure of Co-30 W alloys remains stable and no corresponding peaks for Co oxides were noticed. After heat treatment at higher temperature (700 °C) the coatings were poorly adhered to the stainless steel substrate and many cracks on the surface were observed. The surface morphology after thermal treatment of Co-W catalysts and pure Co at 600 °C is presented in Fig. 4.

As it is seen, the crystalline Co-W coatings having <18 at.% of tungsten in their composition after heat treatment demonstrates similar surface morphology with the presence of open pores and blurry grain boundaries. However, EDS analysis showed that they consist only of elemental Co and O (Fig. 5 a). In contrary, Co-W alloy having 30 at.% of W after annealing contained only ~1 at.% of tungsten (Fig. 5) and this significant decreasing of W content dramatically changes the morphology of the deposit compared to that of as-deposited one. As-deposited Co-30 W coating contains spherical and smooth bright nodules on its surface, and after annealing it demonstrates polyhedral crystallites of the irregular size. In both cases, Co-30 W electrodeposits even after annealing are cracks-free, in comparison with results of work [26].

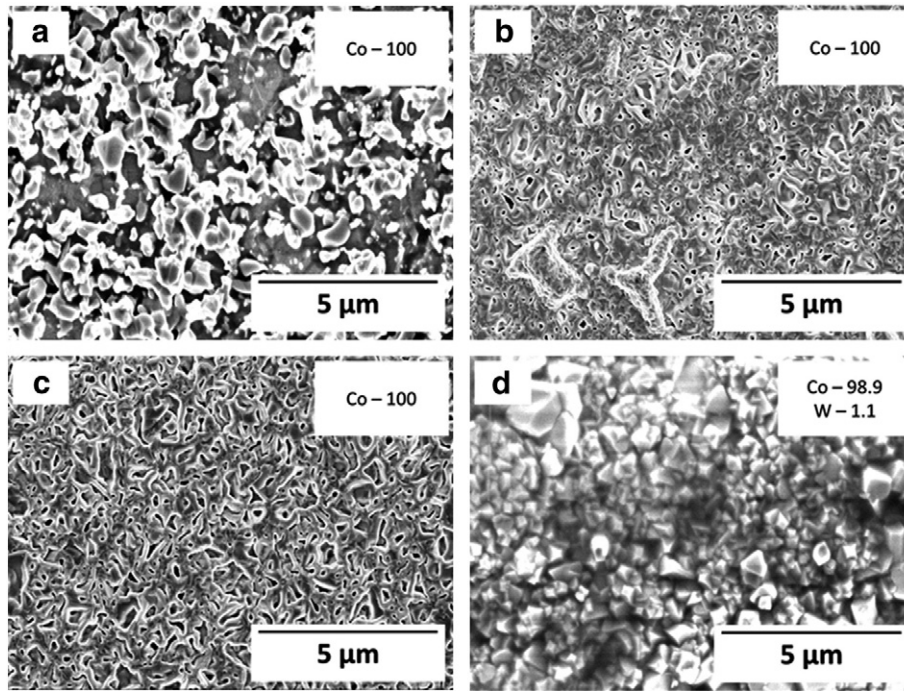


Fig. 4. SEM micrographs of pure Co (a) and Co-W alloys deposited at different pH: 5(b); 6.7 (c); 8(d) after heat treatment at 400 °C for 1 h.

XRD analysis (Fig. 6) confirmed the crystalline structure of all investigated coatings after heating at 600 °C in the open air. The results are similar to previous studies, where it was shown that the Co-W alloys having high content of W in their composition (24.5 at.%) demonstrates a clear polycrystalline structure after heating for 4 h in vacuum from 400 °C to 800 °C [17]. Meanwhile Co-W deposits containing higher tungsten percentage in their composition recrystallized from

amorphous-like to polycrystalline Co_3W structure at 600 °C. XRD patterns of as-deposited Co-3 at.% W alloy after annealing indicated that they consist of pure hcp Co and phases of oxidation products (Co_3O_4 and CoWO_4) (Fig. 6). The detected peak positions of CoWO_4 phase are in accordance with [27]. For Co-W alloy coating having higher amount of W a pure hcp Co phase after heat treatment in X-ray spectrum disappears. Interestingly in the case of annealed Co-18 at.% W alloy a strong peak at $2\theta = 46.5^\circ$ corresponding to Co_3W phase was observed like in the same as-deposited coating. Although EDS analysis showed extremely low W content in the alloy after heat treatment at 600 °C in the air a small amount of Co_3W phase also was observed in XRD patterns of annealed Co-30 at.% W sample. This could be attributed to the higher penetration depth of X-ray beam ($\sim 4 \mu\text{m}$) in course of XRD analysis compared to the EDS technique ($\sim 1 \mu\text{m}$). As the X-rays penetrate deeper during XRD test, therefore the characterization of the deeper inner layer of the thin film can be performed. It was proven by the EDS analysis

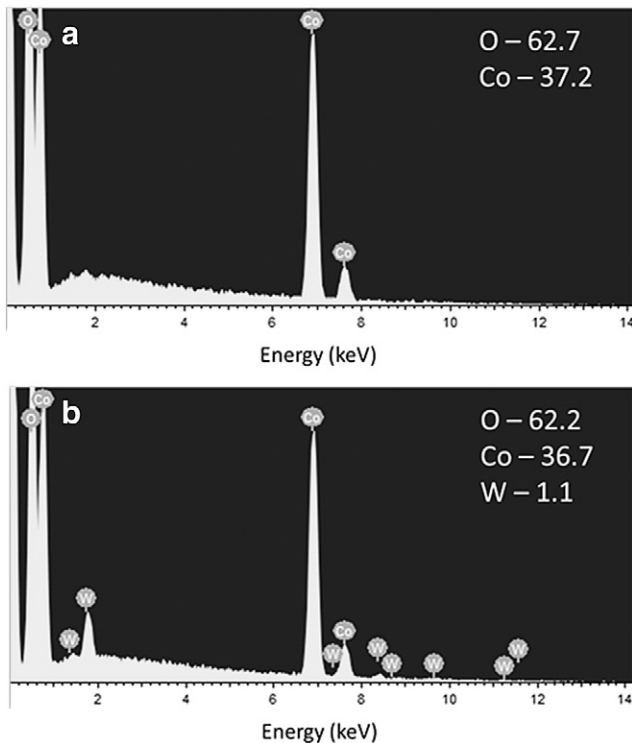


Fig. 5. EDS spectra of (a) Co-18.4 W and (b) Co-30.1 W alloys coating after heat treatment at 600 °C for 1 h. Composition is given in at.%.

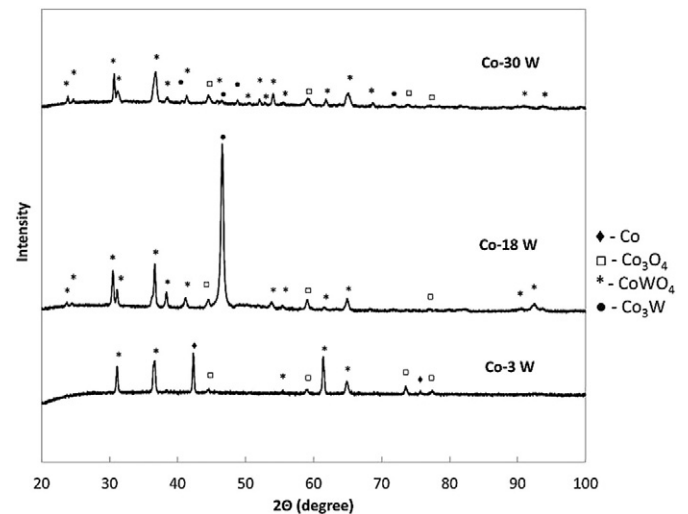


Fig. 6. XRD patterns of Co-W alloys after heating for 1 h at 600 °C in the open air. The composition (in at.%) is given for as-deposited alloys.

performed after gentle polishing of the annealed sample having <2 at.% of W, that inner layer has higher W content of ~19 at.%. This could be the reason of the formation of Co_3W phase in XRD results. Furthermore, the patterns of heat treated Co-30 at.% W alloy coating indicated the formation of Co_3O_4 and CoWO_4 phases as well.

In all investigated cases after heat treatment of Co-W alloys at 600 °C using XRD technique there were no peaks attributed to tungsten oxide phases. That is in contradictory with known fact that pure tungsten starts to oxidize in vacuum by residual oxygen at about 400 °C and above 900 °C the sublimation of WO_3 takes place. This could be attributed to different W structure in pure W metal and in the alloy, which could cause the tungsten sublimation in Co-W alloy at lower temperature (600 °C) in open air. The above-mentioned EDS data show that nanocrystalline alloys sublimate gradually from top to bottom of the coating.

Electrocatalytic properties of the heat-treated and oxidized Co-W alloy electrodes toward methanol oxidation were investigated under the same conditions as for as-deposited alloys, and corresponding cyclic voltammograms are shown in Fig. 7. The cyclic voltammograms for Co-30 W alloys were recorded in the potential range from –0.2 up to 1.0 V in order to prevent the dissolution of cobalt from the surface of the electrode at more positive potentials. A baseline CV curve of annealed Co-W alloy was also recorded in 0.1 M H_2SO_4 solution (without methanol). In this case, Co-W deposit shows an oxidation peak at 0.11 V which corresponds to the Co dissolution from the alloy. This behavior is similar to the noticed for as-deposited Co-W coating. As it was expected, Co-W deposits initially contained <18 at.% of W, after heating became totally inactive for methanol oxidation reaction (Fig. 7 (a)). Whereas the annealed Co-W alloy with having initially 30 at.% of W demonstrates a small methanol oxidation peak at 0.7 V in sulfuric acid and methanol mixture (Fig. 7 b). In this case the peak current density of the methanol

oxidation on the heat treated Co-W electrode is $0.135 \text{ mA} \cdot \text{cm}^{-2}$, which is sufficiently lower than indicated for as-deposited Co-30 W alloy coating ($12.3 \text{ mA} \cdot \text{cm}^{-2}$) or pure Pt electrode ($2.4 \text{ mA} \cdot \text{cm}^{-2}$). The decrease in catalytic activity might be attributed to the reduction of tungsten content in the alloy and the inhomogeneity of surface morphology. In addition, the significant increase in cathodic current density during the reverse scan was not observed as for as-deposited alloys probably due to irreversible oxidation of methanol.

4. Conclusions

Electrodeposited Co-W alloys having various tungsten content and structure ranged from nanocrystalline (3 and 18 at.% of W) and “amorphous-like” (30 at.% of W) had been electrodeposited from citrate-based solutions and tested as anodes for methanol electrooxidation in the mixture of 1 M CH_3OH and 0.1 M H_2SO_4 . As-deposited Co-3 at.% and Co-18 at.% coatings were totally inactive for methanol oxidation, and the electrochemical alloys dissolution occurs in the tested media. Only Co-30 at.% W alloy is an active electrocatalyst for methanol oxidation. It is more effective electrode for methanol electrooxidation than pure Pt because of higher anodic peak current density ($12.3 \text{ mA} \cdot \text{cm}^{-2}$) attributed to the electrooxidation of methanol. After heating for 1 h at 600 °C in air atmosphere the structure of Co-W coatings transformed from “amorphous-like” (nanocrystalline) to crystalline one and new phases are occurred (Co_3O_4 , CoWO_4) simultaneously with decrease of tungsten content in the alloy due to the volatilization of tungsten oxides. It was found that heating resulted the lower Co-W alloy activity toward methanol electrooxidation compared to both “as-deposited” Co-30 at.% W and pure Pt electrodes.

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References

- J.R.C. Salgado, E. Antolini, E.R. Gonzalez, Carbon supported Pt-Co alloys as methanol-resistant oxygen-reduction electrocatalysts for direct methanol fuel cells, *Appl. Catal., B* 57 (2005) 283–290.
- E. Antolini, J.R.C. Salgado, E.R. Gonzalez, The methanol oxidation reaction on platinum alloys with the first row transition metals: the case of Pt-Co and -Ni alloy electrocatalysts for DMFCs: a short review, *Appl. Catal., B* 63 (2006) 137–149.
- E.R. Gonzalez, A. Mota-Lima, Catalysts for methanol oxidation, in: R. Corti, E.R. Gonzalez (Eds.), *Direct Alcohol Fuel Cells – Materials, Performance, Durability and Applications* Springer Science + Business Media Dordrecht 2014, pp. 33–62.
- T. Iwasita, Electrochemical oxidation of methanol, *Electrochim. Acta* 47 (2002) 3663–3674.
- Z. Jusys, T.J. Schmidt, L. Dubau, K. Lasch, L. Jörissen, J. Garche, R.J. Behm, Activity of PtRuMeOx (Me = W, Mo or V) catalysts towards methanol oxidation and their characterization, *J. Power Sources* 105 (2002) 297–304.
- M. Metikos-Hukovic, R. Babic, Y. Piljac, Kinetics and electrocatalysis of methanol oxidation on electrodeposited Pt and Pt₇₀Ru₃₀ catalysts, *J. New Mater. Electrochem. Syst.* 7 (2004) 179–190.
- A.V. Tripković, K.D. Popović, J.D. Lović, V.M. Jovanović, A. Kowal, Methanol oxidation at platinum electrodes in alkaline solution: comparison between supported catalysts and model systems, *J. Electroanal. Chem.* 572 (2004) 119–128.
- T. Iwasita, H. Hoster, A. John-Anacker, W.F. Lin, W. Vielstich, Methanol oxidation on PtRu electrodes. Influence of surface structure and Pt–Ru atom distribution, *Langmuir* 16 (2000) 522–529.
- A. Serov, C. Kwak, Review of non-platinum anode catalysts for DMFC and PEMFC application, *Appl. Catal., B* 90 (2009) 313–320.
- Z.J. Zuo, L. Wang, P.D. Han, W. Huang, Insights into the reaction mechanisms of methanol decomposition, methanol oxidation and steam reforming of methanol on Cu(111): a density functional theory study, *Int. J. Hydrog. Energy* 39 (4) (2014) 1664–1679.
- J. Mathiyarasu, A.M. Remona, A. Mani, K.L.N. Phani, V. Yegnamaran, Exploration of electrodeposited platinum alloy catalysts for methanol electro-oxidation in 0.5 M H_2SO_4 : Pt-Ni system, *J. Solid State Electrochem.* 8 (2004) 968–975.
- C.N. Tharamani, P. Beera, V. Jayaram, N.S. Begum, S.M. Mayanna, Studies on electro-deposition of Fe–W alloys for fuel cell applications, *Appl. Surf. Sci.* 253 (2006) 2031–2037.
- T. Shobba, S.M. Mayanna, C.A.C. Sequeira, Preparation and characterization of Co–W alloys as anode materials for methanol fuel cells, *J. Power Sources* 108 (2002) 261–264.

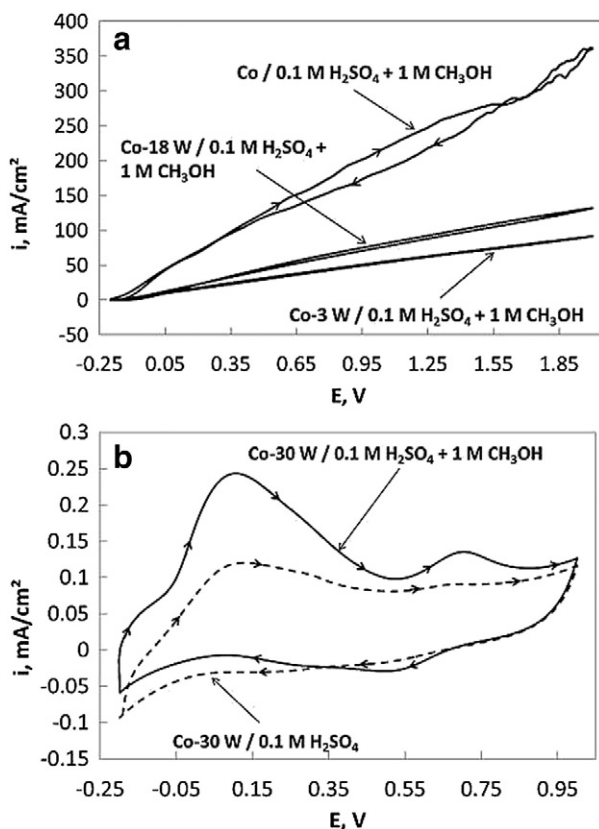


Fig. 7. Cyclic voltammograms recorded on the annealed Co-W catalyst in the mixture of 0.1 M H_2SO_4 and 0.1 M methanol at room temperature. Composition (in at.%) is provided for as-deposited alloys (prior heating at 600 °C). Arrows show a potential scan direction.

- [14] N. Tsyntaru, H. Cesiulis, M. Donten, J. Sort, E. Pellicer, E.J. Podlaha-Murphy, Modern trends in tungsten alloys electrodeposition with iron group metals, *Surf. Eng. Appl. Electrochem.* 48 (2012) 13–44.
- [15] C. Fan, D.L. Piron, A. Sleb, P. Paradis, Study of electrodeposited nickel-molybdenum, nickel-tungsten, cobalt-molybdenum, and cobalt-tungsten as hydrogen electrodes in alkaline water electrolysis, *J. Electrochem. Soc.* 141 (1994) 382–387.
- [16] P. Bera, H. Seenivasan, K.S. Rajam, V.K.W. Grips, XRD, FESEM and XPS studies on heat treated Co–W electrodeposits, *Mater. Lett.* 76 (2012) 103–105.
- [17] N. Tsyntaru, H. Cesiulis, A. Budreika, X. Ye, R. Juskenas, J.P. Celis, The effect of electrodeposition conditions and post-annealing on nanostructure of Co–W coatings, *Surf. Coat. Technol.* 206 (2012) 4262–4269.
- [18] F. Su, C. Liu, P. Huang, Effect of complexing agents and pH on microstructure and tribological properties of Co–W coatings produced by double pulse electrodeposition, *Appl. Surf. Sci.* 258 (2012) 6550–6557.
- [19] N. Tsyntaru, G. Kaziukaitis, C. Yang, H. Cesiulis, H.G.G. Philipsen, M. Leis, J.-P. Celis, Co–W nanocrystalline electrodeposits as barrier for interconnects, *J. Solid State Electrochem.* 18 (2014) 3057–3064.
- [20] N. Tsyntaru, H. Cesiulis, E. Pellicer, J.-P. Celis, J. Sort, Structural, magnetic, and mechanical properties of electrodeposited cobalt-tungsten alloys: intrinsic and extrinsic interdependencies, *Electrochim. Acta* 104 (2013) 94–103.
- [21] L.S. Palatnik, M. Ya, V.M. Fuks, Kosevich, *Mekhanizm Obrazovaniya i Substruktura Kondesirovannykh Plenok*, Izdatel'stvo Nauka, Moscow, 1972 (in Russian).
- [22] H. Cesiulis, A. Budreika, Hydrogen evolution and corrosion of W and Mo alloys with Co and Ni, *Physicochem. Mech. Mater.* 8 (2010) 808–814.
- [23] G. Hou, J. Parrondo, V. Ramani, J. Prakash, Kinetic and mechanistic investigation of methanol oxidation on a smooth polycrystalline Pt surface, *J. Electrochem. Soc.* 161 (2014) F252–F258.
- [24] M. Metikos-Hukovic, R. Babic, Y. Piljac, Kinetics and electrocatalysis of methanol oxidation on electrodeposited Pt and Pt70Ru30 catalysts, *J. New Mater. Electrochem. Syst.* 7 (2004) 179–190.
- [25] M.M. Natile, A. Glisenti, Study of surface reactivity of cobalt oxides: interaction with methanol, *Chem. Mater.* 14 (2002) 3090–3099.
- [26] P. Bera, H. Seenivasan, K.S. Rajam, V.K.W. Grips, XRD, FESEM and XPS studies on heat treated Co–W electrodeposits, *Mater. Lett.* 76 (2012) 103–105.
- [27] X. Chun Song, E. Yang, R. Ma, H. Fang Chen, Y. Zhao, Sodium dodecyl sulfate-assisted synthesis of CoWO₄ nanorods, *J. Nanopart. Res.* 10 (2008) 709–713.