VILNIUS UNIVERSITY

INSTITUTE OF CHEMISTRY

OF CENTER FOR PHYSICAL SCIENCES AND
TECHNOLOGY

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INFLUENCE OF COBALT OXIDE NANOSTRUCTURING ON ELECTROCHEMICAL PSEUDO-CAPACITANCE

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INTRODUCTION

Development of highly efficient electrochemical energy capacitors and accumulators have recently become an important subject of electrochemical science and technology, first and foremost owing to an increased demand in portable and telecommunication devices, as well as electrical and hybrid engines. Electrochemical capacitors are widely used in electric devices in military, aviation, space, medicine industries, as well as in production of household appliances.

Electrochemical capacitors are electric energy sources intended for rapid energy accumulation and release. They are distinguished for a greater power, a longer self-discharge time and a greater number of work cycles as compared to those of traditional electrochemical batteries. Electrochemical capacitors are divided into electrochemical double-layer capacitors and redox super-capacitors in accordance with the way they accumulate energy.

Effective super-capacitors are mainly produced of ruthenium oxide, which has a highest specific capacitance among most of metal oxides. However, the devices based on this oxide have an essential drawback – high cost, which limits wider commercialisation. High price of ruthenium oxide limits it's application mainly to those fields, where a strong electric current pulse is needed, such as robot technology or expensive hybrid automobile engines. Therefore, it is important to find cheaper metal oxides with efficient electric capacitance performance, which could substitute or partly replace ruthenium dioxide. In this respect, manganese and nickel oxides are among the most widely studied ones, but they did not show sufficiently good electrochemical capacitance characteristics.

In recent years, cobalt oxide attracted considerable attention as a promising alternative in production of electrochemical super-capacitors. Cobalt oxide is significantly cheaper when compared to ruthenium oxide, moreover, it is relatively non-toxic, and preliminary studies have showed rather high electrical efficiency of its electrochemical reduction oxidation cycles. Therefore, cobalt oxide appears to have considerable promise for production of highly effective capacitors. In our work, we

proposed rather simple and cost effective methods, which allow markedly increasing the pseudo-capacitance of cobalt oxides on parent substrates.

Major goal of the work was:

To investigate the electrochemical nanogravimetric behaviour of cobalt oxide in an alkaline medium and to form cobalt hydro/oxide structures of superior electrochemical capacitance by means of electrochemical nanostructuring as well as forming compositions with cobalt sulphide and ruthenium/ruthenium oxide.

The objectives of the work:

1. To choose optimal conditions of electrochemical cobalt deposition in order to obtain nanostructured Co precursor with a great actual surface area.

2. To evaluate the influence of cobalt nanostructuring on the Co hydro/oxide electrochemical pseudo-capacitance.

3. To determine the pseudo-capacitance characteristics of $Co(OH)_2$-CoS and Co-Ru composition and to study their capacitive behaviour depending on substrate nanostructuring.

Statements to be defended:

1. Electrochemical Co nanostructuring (nano-fiber structure) markedly increases both the actual surface area of the electrode and its electrochemical capacitance.

2. The capacitance of Co hydro/oxides formed on the electrochemically deposited nanostructured Co substrate is approximately fivefold higher than those formed on mechanically treated metallurgic cobalt substrate.

3. Formation of cobalt sulphide and hydroxide composition and subsequent heat treatment significantly increases electrochemical pseudo-capacitance of the system.

4. Co-Ru composition formed on the nanostructured Co substrate exhibits specifically high pseudo-capacitance, which is determined by electrochemical interaction of Ru(III) with nanostructured Co substrate.

Scientific novelty:

- Experimental conditions were identified, at which nano-fiber cobalt structures are formed by means of electrochemical metal deposition in an alkaline medium.

- The cobalt surface nano-structuring increases the actual surface area of the precursor for hydro/oxide formation in an anodic potentiodynamic mode and thereby increases the electrochemical capacity of the oxide.

- The cobalt hydro/oxide layers formed by the anodic polarization method show distinctive reduction-oxidation peaks, which are due to multi-step charge transfer reactions: Co - Co(II) - Co(III) - Co(IV). The first step of charge transfer is accompanied by an exponential growth in the electrode mass, whereas the other stages actually do not have significant influence on the electrode mass.

- The obtained results show that the applied Co substrate nanostructuring increases the capacity of the anodic-mode formed cobalt oxides approximately fivefold.

- It has been established that the pseudo-capacity of the sulphide composition formed on the nano-fiber Co substrate (18% CoS) is threefold as great as that of the system without sulphides.

- A new method to form cobalt hydro/oxide with superior pseudo-capacitance performance has been proposed. The method is based on formation of the composition with sulphide $Co(OH)_2$ – CoS and its annealing at a high temperature.

- Co-Ru composition formed on the nano-fiber Co substrate exhibited a particularly high pseudo-capacitance (~ 1200 F g^{-1}).

Practical value

The possibilities to markedly increase the pseudo-capacitor characteristics of cobalt hydro/oxide structures, which are important in design of cheap and effective electrochemical capacitors, were revealed.

EXPERIMENTAL

Cobalt coatings with a nano-fibre structure were deposited from the electrolyte for Zn-Co alloy electroplating as described in patent [1] with only difference that zinc ions were excluded from the plating bath. The electrolyte was prepared using analytical class purity reagents $CoSO_4 \times 7H_2O$ (20 g l^{-1}), NaOH (100 g l^{-1}), ligand (40 g l^{-1}) and triply distilled water.

Cobalt hydroxide layer was formed electrochemically on the cobalt substrate in 1 M NaOH by applying 10 cycles within the polarization interval E = -1.0 V to 0. 6 V at v = 20 mV s^{-1}.

Cobalt sulphide and cobalt hydroxide composite was formed on the cobalt substrate by applying 10 voltammetric cycles at 20 mV s^{-1} within the potential interval E = -0.3 V to 0.4 V in the solution 10 g l^{-1} Na_2S + 5 g l^{-1} NaOH.

Composition of Co-Ru oxide on the substrate of Co was formed by a chemical process dropping $RuCl_3 \cdot xH_2O$ which was dissolved in a mixture of isopropyl alcohol and Nafion (4:1).

A Parstat 2273 potentiostat from Princeton Applied Research Instruments (USA) was used to carry out cyclic voltammetry measurements. A three-electrode cell with platinum foil as a counter electrode and a saturated silver/silver chloride as reference electrode were used. The electrolyte was 1 M NaOH, which was deoxygenated by Ar gas prior to measurements.

Electrochemical quartz crystal microbalance (EQCM) measurements were performed using the above potentiostat in conjunction with a microgravimetric unit PAR 922 from Princeton Applied Research Instruments (USA). Quartz discs with a fundamental frequency f_0 of 5 MHz were employed. The proportion coefficient of the oscillator between the frequency and the mass change was $K = 18$ ng Hz^{-1} cm^{-2}. A sub-layer of iron was sputtered onto quartz discs by a magnetron sputtering technique using the equipment from Leybold Vacuum (Germany).

The surface micro-topography was studied by scanning electron microscopy, SEM (EVO 50 EP from Carl Zeiss SMT AG, Germany) with energy dispersive and wave dispersion x-ray spectrometers EDS (Oxford, UK). The sample surface was analysed by x-ray photoelectron spectroscopy (XPS).

RESULTS AND DISCUSSION

The Co electrochemical deposition characteristics were studied in-situ by depositing the coating under EQCM control. One side of the quartz oscillator was coated by iron using a magnetron sputtering technique. Fig. 1 provides data on mass and potential change during galvanostatic deposition of cobalt.

The rectilinear mass growth from the very beginning till ca. 1.5 h indicates a constant deposition rate, while during longer electrolysis time the rate tends slightly to decrease. The current efficiency derived from mass change rate according to the Faraday's low was approximately 50 %.
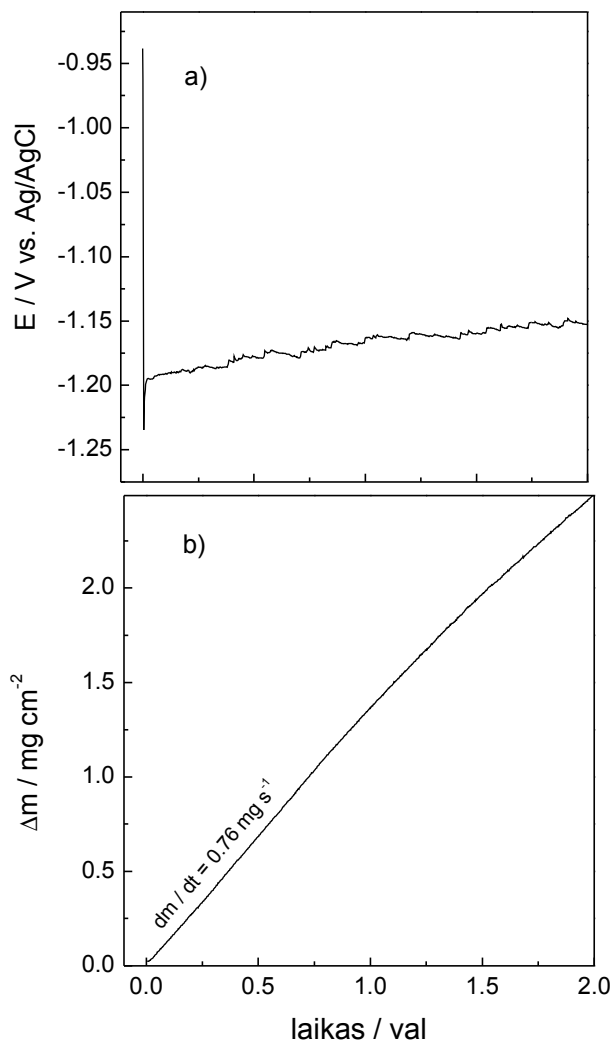
Fig. 1. *Potential and mass change during galvanostatic deposition of cobalt at $i_c = 2$ mA cm^{-2} determined by EQCM.*

SEM images in Fig. 2 (a, b) show the surface morphology on a sub-micrometer scale of Co deposits formed on a low carbon steel plate (a) and magnetron sputtered Fe (b) which was used for EQCM measurements. The structure consists of randomly distributed nano-fibres, which thickness is in the order of tens of nanometres and the length is in the order of hundreds of nanometres.
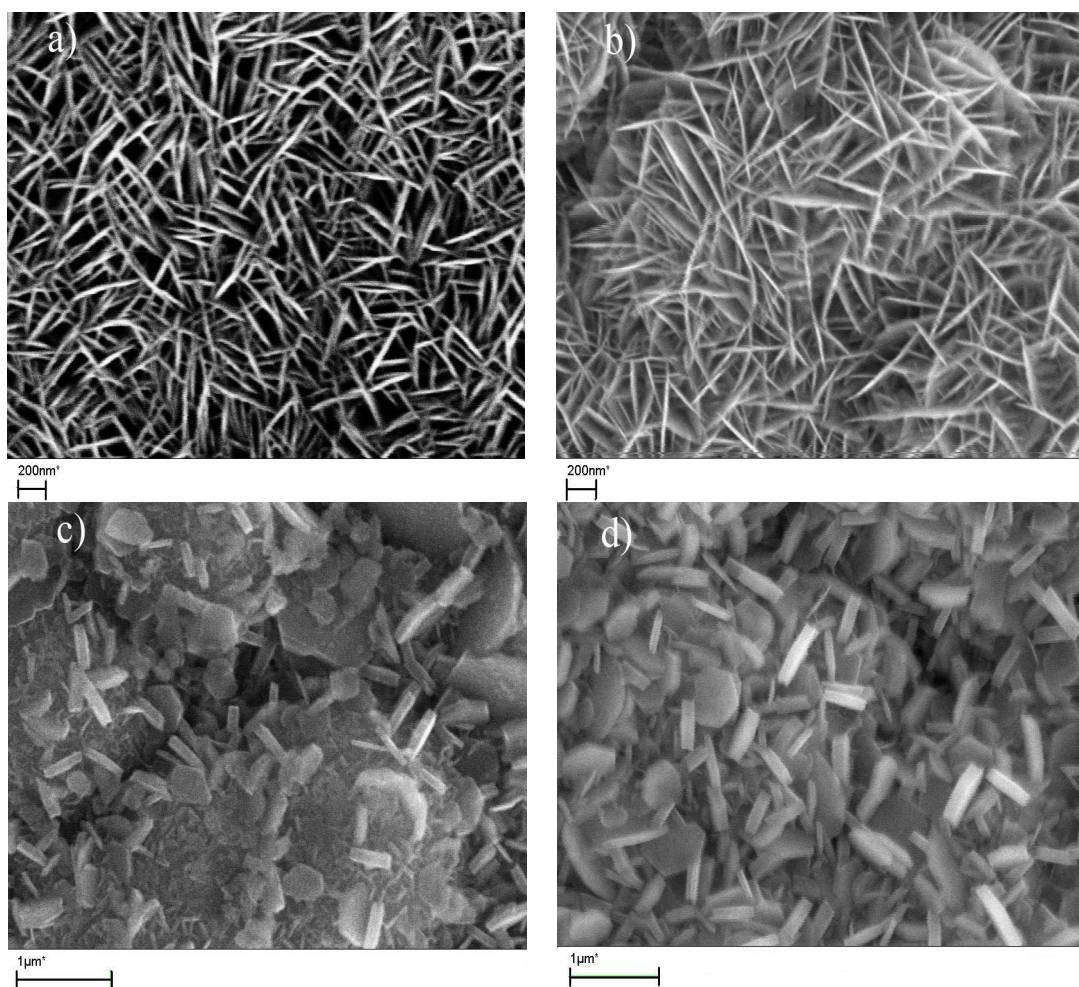
Fig. 2 *SEM images of nano-fibre structure as deposited cobalt on steel* (**a**) *and on sputtered iron* (b) *and after the cycling in 1 M NaOH* (**c**) *and* (**d**).

During the prolonged oxidation-reduction cycles, the fibre-like structure is transformed into thicker highly packed cobalt hydroxide hexagonal platelets (c) and (d). Cyclic voltammetry (Fig. 3) indicate highly irreversible behaviour of the electrode during the initial cycling.
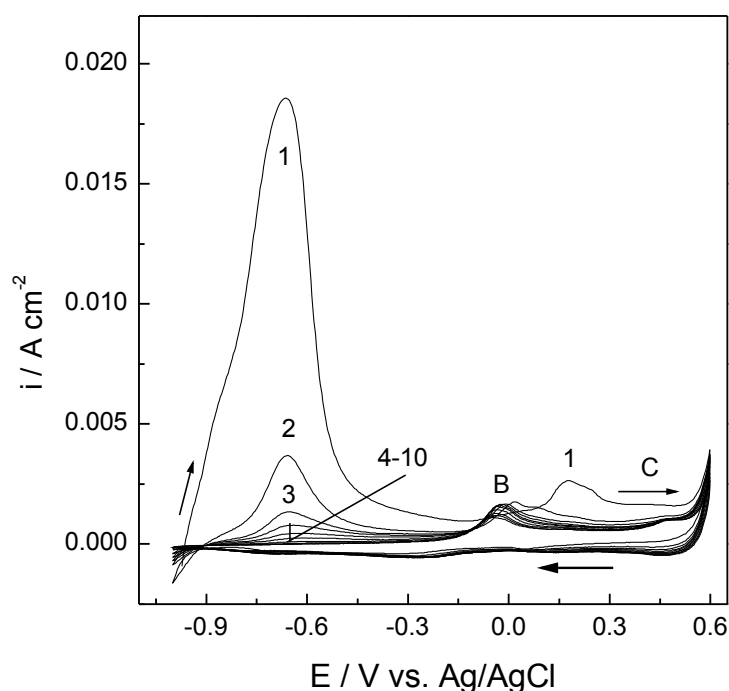
Fig. 3 *Cyclic voltammetry curves for electrochemically deposited cobalt on the steel substrate in 1M NaOH at a potential scan rate of 20 mV s^{-1}, 10 cycles.*

A large initial peak followed by much smaller one (around E_{peak} = 0.2 V) is observed during the first cycle. When the cycling progresses, the behaviour turns gradually from irreversible to reversible one and the second peak shifts to potentials ca. 0.0 V. The transition and the peak is attributed to irreversible $Co(OH)_2$ deposition followed by electrochemical formation of CoOOH, which will be discussed in more detail below. Fig. 4 demonstrates a prolonged cycling experiment (selected are the curves for the cycles 11, 330 and 1000). Several distinctive peaks are observed on the curves (A, B and C). The figure compares cathodic and anodic branches: one can be seen that the cathodic branch is mirrored by an anodic one or *vice versa*. The current responses around E_{peak} = 0.4 V ÷ 0.5 V increase during the cycling as is evident from the curves for the 11th cycle with those of higher numbers. The data also indicate a high cycle life of the oxide structure, which is important from the point of view of practical application.
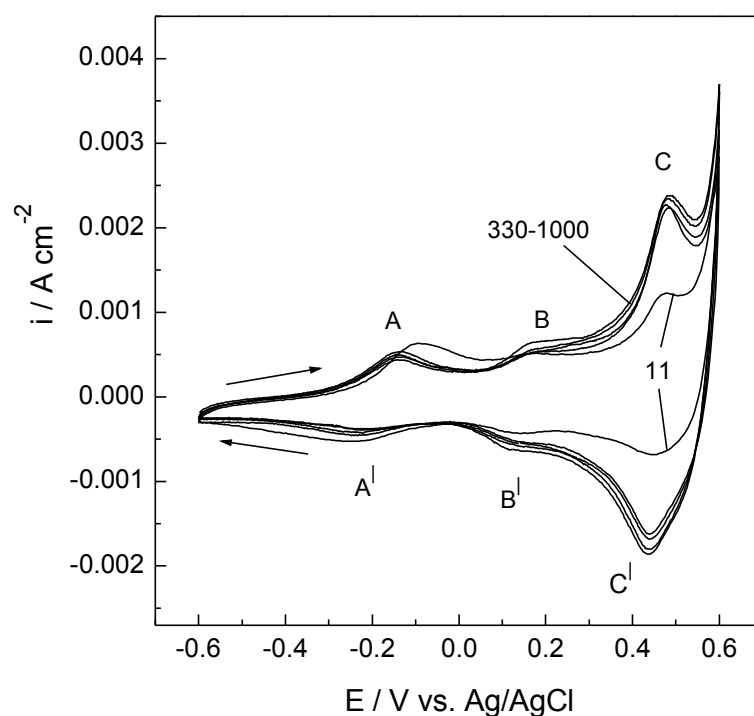
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Fig. 4 *Subsequent cycling of the electrode up to 1000 cycles following the measurements shown in Fig. 3*

The curves for the cycles 330 and 1000 differ negligibly what indicates a good stability performance of the system. The EQCM measurements reveal the electrode mass effects associated with electrochemical reactions (Fig. 5).

The irreversible anodic current peak observed during the first polarization cycle yields an exponential mass growth with a further transition to a quasi-passive behaviour within a wide potential range (ca. -0.3 V ÷ 0.6 V). When reversing the potential scan, the electrode holds the passivity over a wide potential range. The mass gain is observed again at the negative end of the voltmassogram. With the number of cycles, the increase in mass is getting suppressed and approaches some limit ($\Delta m_l \approx 70$ µg cm^{-2}). Thus, two regions could be distinguished: the negative one ($E = -1.0$ V ÷ 0.0 V) where mass gain could occur and the positive one ($E = 0.0$ V ÷ 0.6 V) where no remarkable mass effects are observed.
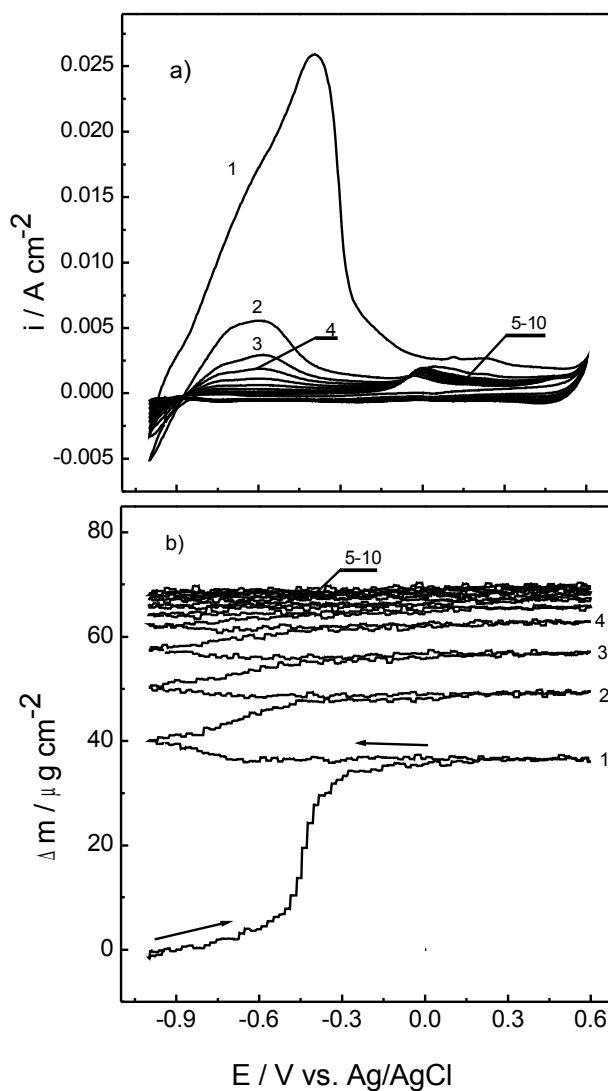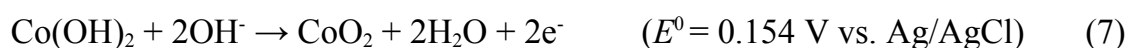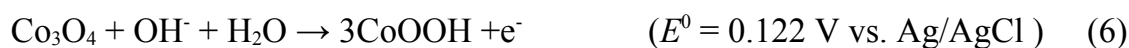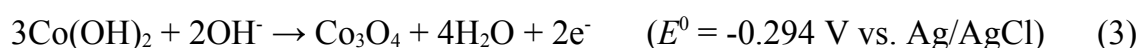
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Fig. 5 *EQCM and cyclic voltammetry data in 1 M NaOH for electrochemically deposited cobalt. Potential scan rate – 20 mV s⁻¹*

The first region could be attributed to formation of a cobalt oxide and hydroxide according to the reactions [2, 3]:

$$Co + 2OH^- \rightarrow Co(OH)_2 + 2e^- \tag{1}$$

$$Co + 2OH^- \rightarrow CoO + H_2O + 2e^- \tag{2}$$

Standard potentials of these reactions at pH 14 are $E^0 = -0.918$ V vs. Ag/AgCl for (1) and $E^0 = -0.892$ V vs. Ag/AgCl for (2). The first reaction under our conditions is more likely as our measurement relates to highly alkaline medium.

The current peaks A, B and C, as denoted in Fig. 3, indicate three electrochemical transformations of the hydro/oxide. Several reactions could be relevant according to their standard potentials [2, 3]:

$$3Co(OH)_2 + 2OH^- \rightarrow Co_3O_4 + 4H_2O + 2e^- \quad (E^0 = -0.294 \text{ V vs. Ag/AgCl}) \quad (3)$$

$$CoO + OH^- \rightarrow CoOOH + e^- \quad (E^0 = -0.274 \text{ V vs. Ag/AgCl}) \quad (4)$$

$$Co(OH)_2 + OH^- \rightarrow CoOOH + H_2O + e^- \quad (E^0 = -0.156 \text{ V vs. Ag/AgCl}) \quad (5)$$

$$Co_3O_4 + OH^- + H_2O \rightarrow 3CoOOH + e^- \quad (E^0 = 0.122 \text{ V vs. Ag/AgCl}) \quad (6)$$

$$Co(OH)_2 + 2OH^- \rightarrow CoO_2 + 2H_2O + 2e^- \quad (E^0 = 0.154 \text{ V vs. Ag/AgCl}) \quad (7)$$

$$CoOOH + OH^- \rightarrow CoO_2 + H_2O + e^- \quad (E^0 = 0.462 \text{ V vs. Ag/AgCl}) \quad (8)$$

According to the EQCM data (Fig. 5), the electrochemical transformations indicated by the voltammetric peaks in Fig. 4 are not associated with remarkable mass effects. Thus, the EQCM data allow elucidating the electrochemical mechanism. The reactions (5), (7) and (8) which correspond to the peaks A, B and C are most likely as these reactions does not predict significant mass change of the electrode (except of that due to proton release, which is relatively small).

Some comment is necessary concerning the second current peak, which starts around $E = 0.1$ V in Fig. 3. This peak is observed only for the first polarization cycle, while it disappears in subsequent cycles (2-10). Instead, a new peak appears at more negative potentials, $E_{peak} \sim 0.0$ V. The voltmassogram on Fig. 6 indicates that the peak under consideration is accompanied by a mass increase ca. 2-3 µg cm^{-2}. This implies the reaction (6), i.e. the transition $Co_3O_4 \rightarrow 3CoOOH$, whose standard potential is $E^0 = 0.122$ V vs. Ag/AgCl, and the electrode mass is increased due to attachment of twoadditional

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oxygen atoms and one proton. During the backwards scanning, the CoOOH is converted rather to $Co(OH)_2$ than to Co_3O_4. So that the reaction (6) is getting suppressed during the subsequent cycles and the conversion $Co(OH)_2 \rightarrow CoOOH$ becomes prevailing ($E^0 = -0.156$ V vs. Ag/AgCl) with almost no change in mass (5) what is in agreement with the experimental observations. Thus, the measurements identify three main electrochemical processes: the hydroxide formation by the reaction $Co \rightarrow Co(II)$ and the subsequent oxidation stages $Co(II) \rightarrow Co(III) \rightarrow Co(IV)$ within the oxide, which determines pseudocapacitance of the system.
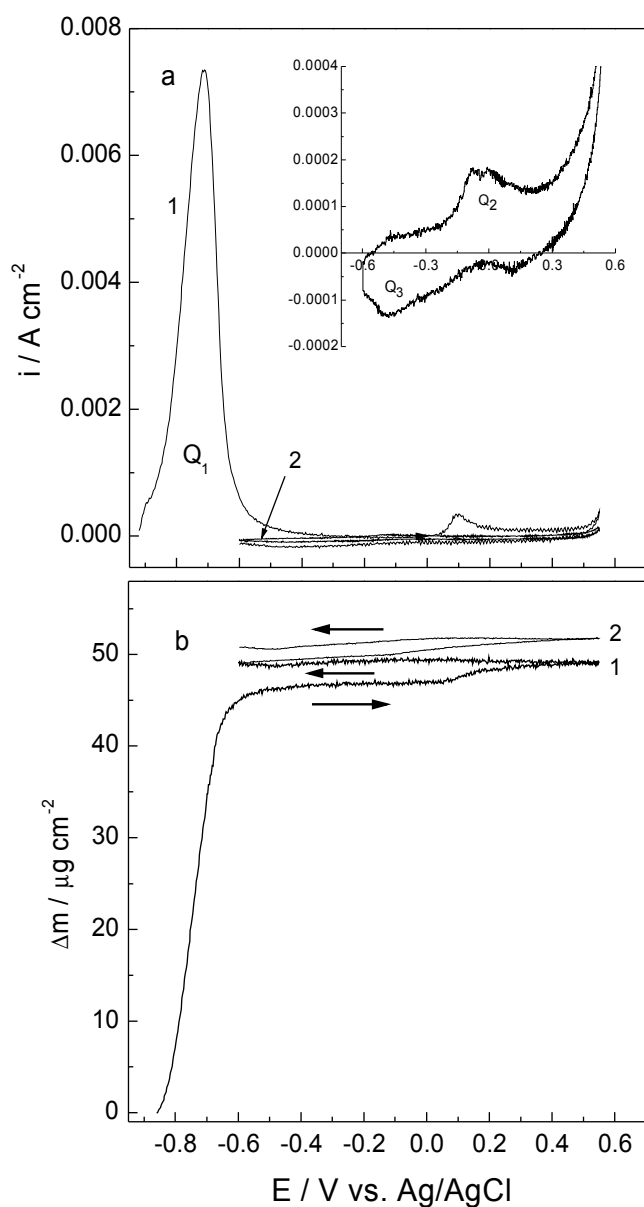

Fig. 6 *EQCM and cyclic voltammetry data in 1 M NaOH for electrochemically deposited cobalt. Potential scan rate – 2 mV s^{-1}.*

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Sulphide incorporation into the hydroxide structure leads to appearance of a distinctive current peak at $E = 0.1$ V $\div$ 0.15 V (Fig. 7).
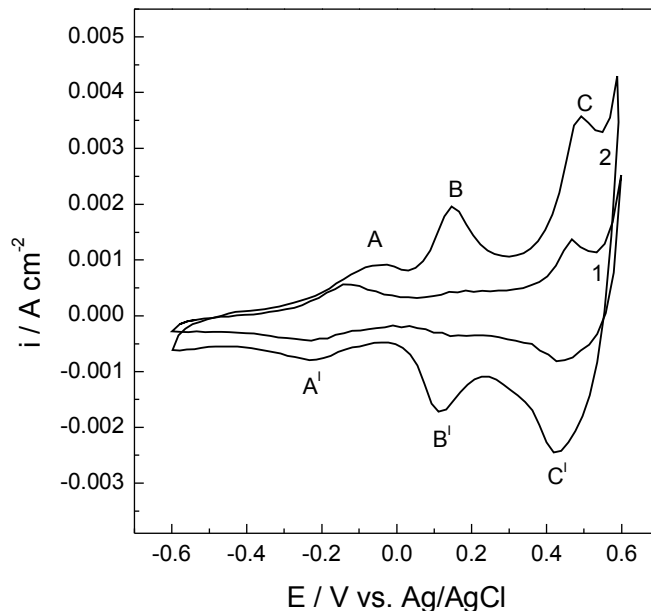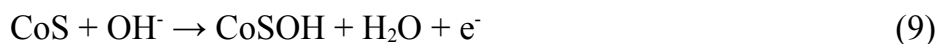

Fig. 7 *Cyclic voltammetry curves for electrochemically deposited cobalt on the steel substrate (1) and for cobalt sulphide and cobalt hydroxide composite (2) in 1M NaOH at a potential scan rate of 20 mV s^{-1}*

The peak location corresponds to that reported recently in the literature on electrochemical redox behaviour of single cobalt sulphide [4, 5]. The mechanism of electrochemical oxidation of cobalt sulphide in alkaline medium remains to be debatable. The authors assumed electrochemical reactions in analogy to those for Co(OH)$_2$ or CoO$_2$, as the potential of electrochemical oxidation of cobalt sulphide is similar to that of the cobalt oxide and oxygen as an element belongs to the same family as sulphur [4, 5]:

$$CoS + OH^- \rightarrow CoSOH + H_2O + e^- \qquad (9)$$

$$CoSOH + OH^- \rightarrow CoSO + H_2O + e^- \qquad (10)$$

It is a common knowledge that the electrochemical capacitance (C), which is due to redox reactions, may be estimated from cyclic voltammetric curves by calculating the charge passed during discharging (the anodic polarization, Q) divided by the potential range in which the curves were recorded (ΔE). It has been found for the sulphide-free hydroxide for 100th cycle capacitance value to be as high as $C \approx 0.03$ F cm^{-2}. It is an important result that the capacitance of the nano-structured sample was up to 5 times higher when compared to that of a mechanically abraded cobalt surface (with emery paper, grade 2500). This difference is caused by much higher actual surface area of the fibre-modified surface. Another important result is that the sulphide-containing sample exhibited an enhanced capacity up to three times ($C \approx 0.09$ F cm^{-2}) when compared to the sulphide free counterpart.

SEM image in Fig. 8 show the flake like microtopography of the sulphide containing deposit.
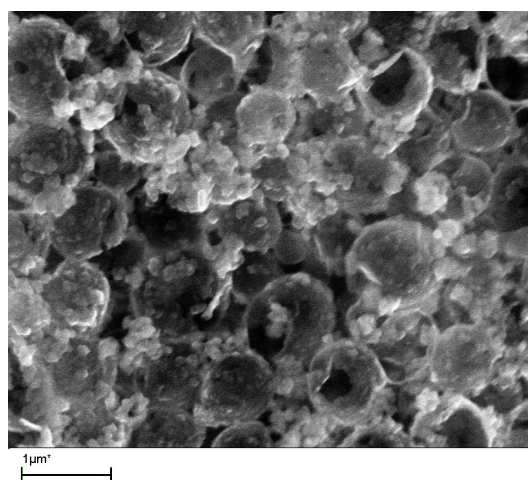

Fig. 8 *SEM image of cobalt sulphide and cobalt hydroxide composite.*

Specific capacitance value is usually expressed as per one gram of electro active material. This is well reasoned when studying electro active materials formed on foreign substrates which are frequently assumed to be electrochemically inert ones, for instance, $Co(OH)_2$ on stainless steel [6] or CoS_x on nickel [4, 5, 7]. In our case, however, the "per gram" approach has some specific features and has not to be straightforward adopted.

The cobalt hydroxide is formed *in situ* on the parent metal, which is electrochemically active and any anodic polarization event leads to hydroxide formation until it reaches a limiting mass (EQCM measurements, Fig. 5). While only some part (most probably outer area) of the product is redox active, the conventional "per gram" calculation would involve both the active and the "ballast" parts reducing the calculated capacitance performance. It is also important that the EQCM measurements determine mainly the oxygen mass attached to the substrate (as O^{2-} or OH^-) not taking into account the metal mass (Co^{2+}), thus, to calculate the product exact mass, its exact chemical composition has to be known.

According to Fig. 5, the entire increase in the electrode mass after 10 cycles is $\Delta m \approx 70$ µg cm^{-2} that is due mainly to O^{2-} attachment (the contribution by proton is relatively small). Assuming $Co(OH)_2$ as a product, one can calculate the mass of hydroxide $\Delta m \approx 117$ µg cm^{-2}. Taking into account the charge passed during the polarization cycle and the width of the polarization interval, we obtained capacity value $C = 256$ F per one gram of totally developed $Co(OH)_2$, i.e. not entirely electro active one. Thus, a question arises which part of the entire structure participated in the capacitive process?

When comparing the electricity quantity of the hydroxide layer formation (Q_1, Fig. 6) with that responsible for the capacitance (Q_2 or Q_3, insertion in the Figure), one can be seen that the quantities differ about one order of magnitude. So, the value $Q_1 = 0.565$ A s^{-1} was calculated for the two-electron transition Co $\rightarrow$ Co(II) leading to hydroxide formation, and $Q_2 \sim Q_3 \sim 0.055$ A s^{-1} was found for the equally two-electron transition process Co(II) $\rightarrow$ Co(III) $\rightarrow$ Co(IV), which determines the capacitance. Such difference implies that only some 10% of the entire hydroxide structure took part in the capacitive process. Thus, the capacitance value calculated per one electro active gram of hydroxide will be close to the limit 2421 F g^{-1}, which predicts the Faraday's law for $Co(OH)_2$ under our experimental conditions. This implies reliability of the active part estimation of entire $Co(OH)_2$ mass taken from EQCM data.

The voltammetric measurements (Fig. 7) have shown that sulphide-containing sample exhibited enhanced electrochemical capacity performance, which was up to three

times higher when compared to the sulphide free counterpart. Such effect could be explained in terms of sulphide-assisted development of actual surface area of hydroxide. The authors of [7] studied chemically prepared cobalt sulphide in alkaline medium and pointed out that cobalt sulphide exhibited poor electrochemical capacitance during the first polarization cycles. With prolonged polarization, however, the capacitance increased up to impressive value 910 F g^{-1}. The reason of superior capacitance performance is attributed to electrochemical sulphide transformation to hydroxide in some outer area, which has distinctively highly developed surface. The electrochemical reconstruction of the hydroxide should be responsible for good energy storage rather than the sulphide itself. In our experiments, the sulphide-hydroxide structure was deposited electrochemically, thus, it is quite possible that the mentioned sulphide - hydroxide transformation took place already in the preparation stage.

In the work the influence of Co nanostructurization on the pseudocapacity of Co-Ru composition has been studied. The calculated specific capacity of Co-Ru composition on the nanostuctured Co substrate is ~1200 F g^{-1}.Meanwhile, the specific capacity of Co-Ru composition on metallurgical Co was no more than 490 F g^{-1}. Thus, it can be stated that Co substrate nanostructurization increases its capacity nearly threefold. The data obtained suggest, that Co-Ru electrodes possess pronounced capacitor properties due to the chemical interaction of $RuCl_3 \cdot xH_2O$ with nanostructured Co.

CONCLUSIONS

1. The experimental conditions of electrochemical cobalt deposition were determined, under which Co nano-fibre structure with great actual surface area is formed. The optimal formation conditions are as follows: electrolyte – $CoSO_4 \cdot 7H_2O$ – 20 g l^{-1}, NaOH (100 g l^{-1}), ligand – 40 ml l^{-1}, current density – 40 mA cm^{-2}, room temperature.

2. The cobalt hydro/oxide structure exhibiting a high electrochemical pseudo-capacitance has been formed on Co nano-fibre precursor using a linear anodic polarization mode. Nanogravimetric measurements have shown that the oxide was formed mainly during the first polarization cycle as indicated a characteristic growth of the electrode mass. The electrode mass remained nearly constant while the potential was returned in the negative direction.

3. It has been determined by the cyclic voltammetry method, that cobalt hydro/oxide in the alkaline medium shows distinctive oxidation-reduction peaks and corresponding pseudo-capacitor behaviour. The oxide layer showed high charging-discharging stability, it withstands a few thousand polarization cycles. Electrochemical charge transfer reactions Co(II) - Co(III) - Co(IV) are not associated with any significant mass effects.

4. The influence of Co substrate structural features on the pseudo-capacity of cobalt hydro/oxides has been studied. For this purpose, studies with the fibre nanostructure, magnetron sputtering coating and mechanically treated cobalt surfaces were performed. It has been established that the capacity of oxides formed on the nano-fibre structure is fivefold higher as compared to that of the oxides formed on the mechanically treated surfaces.

5. A new method of cobalt oxide formation, which provides superior capacitance characteristics, has been proposed. The method is based on the formation of $Co(OH)_2$-CoS composition and its annealing at a high temperature. Cobalt sulphide incorporation into cobalt hydroxide matrix increases the capacity about threefold. Specific capacitance of the compositions annealed at 310˚C

was found as high as 1080 F g^{-1}, whereas that of not thermally treated composition was 730 F g^{-1}.

6. The Co-Ru composition formed on the nanostructured fibre Co substrate has shown a specifically high capacitance (1200 F g^{-1}). It has been determined that the superior capacitance performance of this system is determined by the interaction of Ru (III) with the nanostructured Co substrate.

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Santrauka

Energijos kaupiklių kūrimas pastaraisiais metais tapo svarbia medžiagų mokslo aktualija. Elektrocheminiai kondensatoriai pasižymi didesne galia, ilgesniu savaiminio išsikrovimo laiku ir didesniu darbo ciklų skaičiumi, negu tradicinės elektrocheminės baterijos. Didžiausia savitąja talpa pasižymi rutenio oksidai, tačiau šių oksidų praktinį taikymą riboja didelė kaina ir todėl aktyviai ieškoma pigesnių pakaitalų. Pastaraisiais metais aktyviai tiriamas kobalto oksidas. Jis yra žymiai pigesnis už rutenio oksidą, preliminarūs tyrimai rodo jo perspektyvumą aukšto našumo kondensatorių gamybai. Platesniems taikymams svarbu yra surasti ekonomiškai efektyvius ir palyginti paprastus metodus, leidžiančius padidinti kobalto oksidų pseudotalpas. Palyginus su cheminiais metodais, elektrocheminis metodas turi pranašumų: jis yra palyginti paprastas, pigus, be to galima lengvai kontroliuoti oksidų paviršiaus cheminę sudėtį ir struktūrą.

Taigi, galima teigti, kad padidintos talpos kobalto oksido gavimas, panaudojant pagrindo (Co) elektrocheminį nanostruktūrinimą, yra aktuali problema.

Mūsų darbe nustatytos kobalto elektrocheminio nusodinimo sąlygos, kurioms esant yra formuojama pluoštinė Co nanostruktūra, pasižyminti dideliu paviršiaus plotu. Ištirta pseudotalpa kobalto hidro/oksidų, suformuotų ant skirtingų substratų: nanostruktūrinės kobalto dangos, magnetroninės - plazminės dangos ir metalurginio Co. Pseudotalpinė kobalto hidro/oksidų elgsena buvo ištirta ciklinės voltamperometrijos metodu kartu su elektrocheminėmis kvarco kristalo svarstyklėmis (EKKM). Anodinės poliarizacijos būdu ant įvairių substratų buvo suformuoti kobalto hidro/oksido sluoksniai. Oksidiniai sluoksniai parodė grįžtamą redukcijos-reoksidacijos ir atitinkamą pseudotalpinę elgseną. Nanogravimetriniai matavimai parodė charakteringą elektrodo masės augimą per pirmąjį anodinį potencialo skleidimą ir praktiškai nekintančią masę per grįžtamąjį potencialo skleidimą. Per kelis tūkstančius anodinių ciklų buvo parodyta, kad oksidinis sluoksnis išliko stabilus. Nustatyta, kad hidro/oksidų, suformuotų ant nanostruktūrinės Co dangos, talpa maždaug 5 kartus didesnė nei suformuotų ant metalurginio Co. EKKM duomenys parodė, kad elektrocheminės Co(II) $\leftrightarrow$ Co(III) $\leftrightarrow$ Co(IV) reakcijos nėra susijusios su žymiais elektrodo masės pokyčiais. Pasiūlytas naujas kobalto oksido, pasižyminčio labai geromis pseudotalpinėmis charakteristikomis,

formavimo būdas, kurio esmę sudaro sulfidinės $Co(OH)_2$ – CoS kompozicijos formavimas ir kaitinimas. Kobalto sulfido įterpimas į kobalto hidroksidą padidina talpą apie 3 kartus. Iškaitintos prie 310^0 C kompozicijos savitoji talpa sudarė 1080 F g^{-1}, tuo tarpu nekaitintos 730 F g^{-1}. Ypatingai didele talpa (1200 F g^{-1}) pasižymėjo Co-Ru kompozicija, suformuota ant nanostruktūrinio Co substrato. Nustatyta, kad šios sistemos talpines savybes lemia Ru (III) sąveika su nanostruktūriniu Co.

Apibendrinant gautus rezultatus, galima teigti, kad elektrocheminis nanostrūkturinio Co substrato formavimas gali būti pasiūlytas kaip palyginti paprastas ir ekonomiškai efektyvus metodas, leidžiantis ženkliai padidinti kobalto oksidų pseudotalpas.

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INFLUENCE OF COBALT OXIDE NANOSTRUCTURING ON ELECTROCHEMICAL PSEUDO-CAPACITANCE

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Physical Sciences, Chemistry (03 P)

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