Formation of composite Co–Ru oxides/hydroxides for supercapacitors on a nano-structured Co substrate

Svetlana Lichušina*,

Vitalija Jasulaitienė,

Algirdas Selskis,

Konstantinas Leinartas

*Center for Physical Sciences
and Technology,
Saulėtekio St. 3,
LT-10257 Vilnius, Lithuania*

A new method of the formation of composite Co–Ru oxides/hydroxides material without a binder for supercapacitors has been proposed. The layers of mixed Co–Ru oxides/hydroxides were formed by the chemical reaction of $RuCl_3$, dissolved in isopropyl alcohol, with a surface of electrochemically deposited nano-structured Co. The surface and bulk composition of synthesized Co–Ru oxides/hydroxides layers were studied by the X-ray photoelectron spectroscopy method. It was determined that the composite Co–Ru layer consisted of mixed oxyruthenium and cobalt hydroxide species of various oxidation states. The layer is characterized by a relatively uniform Co/Ru ratio throughout the bulk. An examination of the surface of formed layers by scanning electron microscopy showed its developed porous morphology. The electrochemical behaviour, the influence of Co substrate on the properties of Co–Ru oxide/hydroxides electrode and stability of the formed layer in 40 g l^{-1} NaOH solutions were evaluated by the cyclic voltammetry method. The specific capacitance values of ~1230 F g^{-1} for the composite Co–Ru oxides/hydroxides electrode on the nano-structured Co substrate were determined. Multiple CV cycling of electrodes confirmed good stability of the synthesized Co–Ru oxides/hydroxides layer without a binder.

Keywords: ruthenium oxide, cobalt oxide, pseudo-capacitance

INTRODUCTION

Electrochemical supercapacitors are energy storage devices that possess higher energy density than conventional dielectric capacitors and higher power density than batteries [1]. Electrochemical capacitors can be categorized into two groups: double-layer capacitors and redox- or pseudo-capacitors. The former electrode materials mainly include high surface area activated carbon and their capacitance is generated from the electric double layer due to charge separation at the electrode and electrolyte interface [2, 3]. Energy storage in pseudo-capacitors arises from the Faradic reactions occurring in the electrode material. Such supercapacitors usually consist of transition metal oxides, conducting polymers or composites containing these materials [4]. Ruthenium oxide RuO_2 is one of the most promising eligible

electrode materials for supercapacitor applications due to its high specific capacitance, higher energy compared to that of high surface area carbon materials, and better electrochemical stability compared to that of conducting polymers. For instance, the specific capacitance for hydrous RuO_2 ranges from 600 to 1170 F g^{-1} depending on the preparation procedure, measurement conditions, used substrate, etc., as compared to that of carbon-based (12–208 F g^{-1}) or conductive polymers, e. g. *p*-doped poly(pyrrole), poly(3-methylthiophene) (25 F g^{-1}) [5–20]. However, despite the remarkable performance of this material, pure RuO_2 is too expensive for large-scale commercialization. A partial substitution of RuO_2 by oxides of less noble metals and development of new RuO_2-based composites appears to be a promising alternative strategy [21, 22].

It has been reported [19] that only a very thin layer of RuO_2 participates in the charge-storage process and the bulk material under this layer remains inactive and causes low

* Corresponding author. E-mail: svetlana.lichusina@ftmc.lt

gravimetric capacitance. Several different approaches have been investigated to maximize the active surface area of RuO_2: deposition of RuO_2 on high surface area materials such as carbon nanotubes [23], formation of binary oxide electrodes since it was found that the surface area could be increased for mixed metal oxides by dispersion of RuO_2 in other less expensive oxide matrices [24], and preparation of electrodes at the lowest possible temperatures [25].

Though the values of specific capacitance of pure cobalt oxide (40 F g^{-1} [26], 290 F g^{-1} [27]) are considerably lower than those of RuO_2, Co_3O_4 is also considered as a favourable electrode material for supercapacitors. At the same time high electrochemical stability, environmental friendliness and sufficiently lower costs of Co_3O_4 in comparison with those of RuO_2 make it a potential candidate for use as a component of binary oxide electrodes. As shown by Krstajić and Trasatti, less than 10% of RuO_2 in the Co_3O_4 matrix was sufficient to attain the same pseudo-capacitance as pure RuO_2 [28]. Another positive impact of Co_3O_4 can also be noted: an incorporation of Co in some metal oxides can markedly improve the electrochemical properties of mixture [21].

Electrochemically deposited Ru–Co mixed oxides on single-walled carbon nanotubes exhibited specific capacitance similar to that of RuO_2 (~620 F g^{-1}) at low potential scan rates. However, at higher scan rates the mixed metal oxide electrode showed superior performance (~570 F g^{-1}) when compared to that of the pure RuO_2 electrode (~475 F g^{-1}). This increase in capacitance at high scan rates was attributed to the role of Co in providing enhanced electronic conduction [22].

Polymeric materials, i. e. binders (e. g. polyvinylidene-fluoride PVDF, polytetrafluoroethylene PTFE), are usually used to immobilize the electrode active material. A very important factor for the efficiency of a supercapacitor is electrode material conductivity. However, an excessive amount of a binder essentially increases the electrode resistance and, consequently, decreases the specific power of a supercapacitor [29]. The search and optimization of binder content in the system is quite a task. The most favourable solution of this problem would be the formation of the electrode composition that is firmly adhered to the substrate without any binder.

The aim of the study was to propose a novel method for the synthesis of oxyruthenium species on a nano-structured Co substrate, which have a good adhesion to the substrate without a binder, and to study the composition, electrochemical properties and stability of the composite Co–Ru oxides coatings formed in an alkaline solution.

EXPERIMENTAL

Cobalt coatings 3 μm thick were electrochemically deposited in the electrolyte containing $CoSO_4 \times 7H_2O$ (40 g L^{-1}), NaOH (100 g L^{-1}) and N-(Hydroxyethyl)-ethylendiamin (60 g l^{-1}) [30]. The copper plates of 1 cm² in area were used as substrates. Before the deposition copper substrates were pre-treated with a suspension of MgO powder, rinsed in 20% H_2SO_4 and finally in deionized water. The nano-fibre structure Co coatings were deposited in the galvanostatic mode at i_k = 40 mA/cm² by using a potentiostat PI-50-1 from Belarus as a power source. The duration of Co deposition was 20 min.

Analytical grade ruthenium trichloride salt ($RuCl_3$) and isopropyl alcohol (2-propanol – $(CH_3)_2CHOH$), both from Sigma-Aldrich, were used for the preparation of an oxidizing $RuCl_3$ solution. The deionized water (conductivity <0.5 μS/cm) was used to remove the excess of chlorides from the electrode surface. The mass of the formed active material on the Co substrate was controlled by a MXA 5/1 microbalance from Radwag, Poland, with a weighing accuracy of 1×10^{-6} g.

The elemental composition of the formed layers was analyzed by X-ray photoelectron spectroscopy (XPS). The binding energy spectra of Ru, Co, C and O were recorded by a spectrometer ESCALAB MK II from VG Scientific, UK, using the X-ray radiation of AlK_a anode (energy 1486 eV, constant pass energy of 20 eV). The pressure in the UNV spectrometer chamber was maintained at 1.33×10^{-7} Pa. For the determination of elements distribution at varying layer depths, the surface of the sample was etched by an ionized argon (Ar^+) beam at a vacuum of 5×10^{-4} Pa. An accelerating voltage of 2 kV and an Ar^+ ions beam current of 50 μA cm^{-2} corresponded to the surface etching rate of ca. 7 nm min^{-1}. The spectra for every element were recorded 3–5 times, averaged and compared with the standards [32].

The surface morphology and elemental composition of Co–Ru composites were also examined by a scanning electron microscope (SEM) EVO 50 EP from Carl Zeiss SMT AG, Germany, equipped with energy dispersive and wave dispersion X-ray spectrometers INCA from Oxford Instruments, UK.

Electrochemical Cyclic Voltammetry (CV) studies were performed to estimate the capacitance of the synthesized material in a 40 g L^{-1} NaOH electrolyte. Prior to measurements the test solution was deoxygenated by high purity Ar (99.999%). CV measurements were performed in a three-electrode cell by using a P/G Parstat 2273 from Princeton Applied Research, USA. The Co substrates coated by a layer of synthesized composite Co–Ru oxides/hydroxides were mounted in a special holder and used as working electrodes. The area of the working electrode exposed to the electrolyte was 0.5 cm². A platinum foil of ~4 cm² as a counter electrode and an Ag/AgCl system (in a saturated KCl solution) as the reference were employed. All potentials in the electrochemical measurements are referred to the Ag/AgCl scale. The temperature of solutions was 20 ± 1 C. All chemicals from Sigma-Aldrich used in the electrochemical studies were of analytical grade.

RESULTS AND DISCUSSION

Thin layers of mixed Co–Ru oxides were chemically synthesized on the surface of electrochemically deposited nano-

structured Co coatings. The structure and morphology characteristics of the Co coatings were detailed in our previous study [30].

The standard reduction potential of Ru/Ru^{2+} (E^0 = 0.455 V, Ru^{3+}/Ru^{2+} = 0.248 V vs SHE) is higher than that of the Co/Co^{2+} pair (E^0 = −0.277 V vs SHE), so it is highly probable that Co can be oxidized by RuCl$_3$ according to the following galvanic replacement reaction:

$$3Co + 2RuCl_3 + 6H_2O \rightarrow 3Co(OH)_2 + 2Ru + 6HCl. \quad (1)$$

The following procedure of composite Cu–Ru oxides/hydroxides formation was used: a quantity of ~5 μL of the oxidizing solution (RuCl$_3$ salt dissolved in isopropyl alcohol to prevent premature hydrolysis) was uniformly dropped over the top of a freshly deposited nano-structured Co electrode; the electrode was dried at 60 °C for 1 h and after that it was aged in air at ambient temperature for 3 days. It is known that RuO$_2$ × 2H$_2$O can be obtained by oxidation of Ru(OH)$_3$ in the air [31]. The water, required for hydrolysis of RuCl$_3$ and reaction (1), originates from ambient air. The aged sample was soaked for 2 h in deionized stirred water to remove the excess of Cl$^-$ ions. The yield of the material formed on the surface of nano-structured Co electrodes was controlled through dissolving different amounts of RuCl$_3$ in isopropyl alcohol. The mass of synthesized material was evaluated by weighing the electrode just before and after completion of the Co–Ru oxides formation procedure.

The XPS method was used to study the chemical composition and oxidation states of the Co and Ru compounds formed on the surface of the Co substrate. Typical core-level spectra of Co 2p$_{3/2}$ and Ru 3d are shown in Fig. 1. Experimental binding energy spectra of Co 2p$_{3/2}$ electrons at the surface top and at a depth of 20 nm are presented in Figs. 1a, b (black lines). The deconvolution of Co 2p$_{3/2}$ spectra into constituents (green lines) suggests that at both depths Co exists both in non-oxidized (binding energy peak centered at 778.3 eV) and oxidized states (binding energy peaks of 782.2, 781.3 and 780.1 eV, which corresponded to CoOOH, Co(OH)$_2$ and Co$_3$O$_4$, respectively [32]). It can be noted that at the coating surface lower quantities of non-oxidized Co were determined. The experimental binding energy spectra of Ru 3d electrons are presented in Figs. 1c, d (black lines). The deconvolution of surface spectra into constituents (green lines) made it possible to distinguish the binding energy peaks of 281.6, 285.8, 284.6 and 286.9 eV (Fig. 1c). The constituent with binding energy peaks at 281.6 and 285.8 eV was attributed to RuO$_2$ and the photoelectron intensities at 284.6 and 286.9 eV were assigned to RuO$_3$. For the XPS spectra, obtained at 3.5 nm and deeper, its major intensity was measured at 279.8 eV (Fig. 1d). The analysis of spectra gives grounds to the conclusion that it might be assigned to a non-oxidized Ru state [32, 32]. It is obvious that metal (non-oxidized) Ru, which is produced in reaction (1), is confined in the vicinity of the Co substrate. It should also be mentioned that on the surface of composite Co–Ru coatings only oxidized Ru was detected (Fig. 1c). So, according to the XPS analysis of the formed layer, the surface oxyruthenium species exist in mixed oxidation states. It should be noted that the peaks of binding energies for different oxidation states of Ru are very close and a strict identification of the composition is rather complicated. The data of XPS analysis were used for the quantitative evaluation of the ratio of two main components, i. e. Co and Ru,
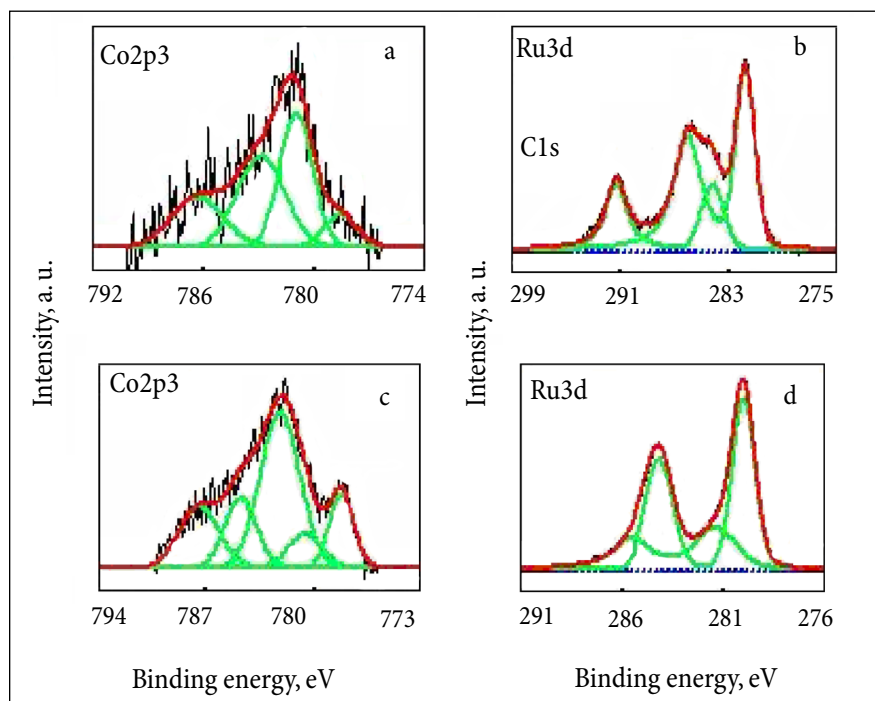

Fig. 1. Binding energy spectra of Co 2p$_{3/2}$ and Ru 3d electrons of the composite Co–Ru oxides/hydroxides layer: surface (a, c) and in 20 nm depth (b, d). Coloured online

through the layer thickness (Table). As can be seen, the layer bulk, i. e. depths more than 7–10 nm, is characterized by a sufficiently constant Co/Ru ratio. It is probably that a uniform distribution of components positively affects the capacitive properties, stability and performance of the layer.

Ta b l e . **Elemental composition of composite Co–Ru oxides/hydroxides layer determined by XPS**

Element at. %	Etching depth, nm						
	0	**3.5**	**7**	**14**	**21**	**28**	**42**
Co	2.1	20.5	18.2	17.3	16.5	16.5	16.2
Ru	36.4	27.1	31.8	36.9	38.9	40.0	40.9
Co/Ru	1/17	1/1.3	1/1.8	1/2.1	1/2.4	1/2.4	1/2.5

The XPS analysis confirmed that the "layer formation" reaction (1) took place on the Co substrate and a thin layer consisting of a mixture of metallic Co and Ru and their oxides was formed.

The morphology of the formed composite Co–Ru oxides/hydroxides films was examined by the SEM method. Typical SEM images of the nano-structured Co substrate and the surface of the Co–Ru oxides/hydroxides coating formed are shown in Fig. 2. As can be seen, the formed coating is porous: a substantial amount of cracks and holes can be seen in the Co–Ru film (Fig. 2b). It should be noted that a similar structure is characteristic both of electrodeposited films of metal oxides [34, 35] and those prepared by thermal decomposition [36]. Such a porous, cracked surface was proposed to be favourable for the penetration of the electrolyte [35]. The surface composition, determined by the SEM energy dispersive X-ray method, showed that it consisted of 62.1 at.% of oxygen, 16.4 at.% of Co, 19.1 at.% of Ru and 2.4 at.% of Cl. It can be mentioned that the Co/Ru ratio is close to the values measured by the XPS method. The SEM energy dispersive X-ray analysis has shown that chloride was not completely removed from the coating.

CV measurements were performed to characterize the electrochemical behaviour of the composite Co–Ru oxides/hydroxides layer formed. Typical CV diagrams of this electrode (nano-structured Co/Co–Ru oxides layer) measured in a 40 g L^{-1} NaOH solution at 20 mV s^{-1} are shown in Fig. 3 (Curve 2). As can be seen, this CV exhibits very broad peaks in both the anodic and cathodic scans at a potential of ~0.12 V. According to [4, 31] these redox peaks certainly corresponded to the Ru(IV)/Ru(III) couple. It is also important to emphasize the mirror-like shape of the CV curve, which indicates an almost perfect electrochemical capacitive behaviour of the thin-film electrode studied. As mentioned above, Co oxides also exhibit pseudo-capacitive properties [26, 27]. To evaluate their influ-
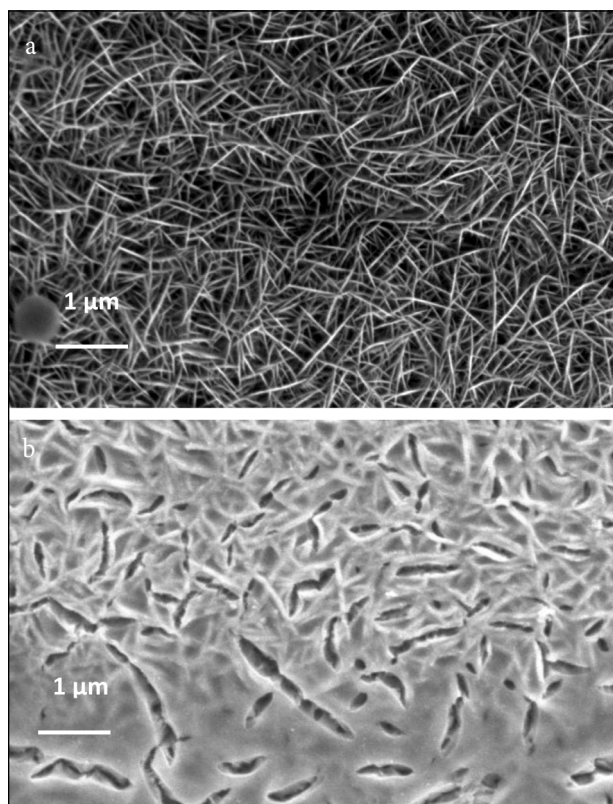

Fig. 2. SEM images of the nano-structured Co substrate (a) and the composite Co–Ru oxides/hydroxides layer formed on the nano-structured Co substrate (b)

ence on the performance of the composite Co–Ru oxides/hydroxides layer CVs of the uncoated nano-structured Co substrate were measured (Fig. 3, Curve 1). A quantitative comparison of both CVs suggests that the contribution of
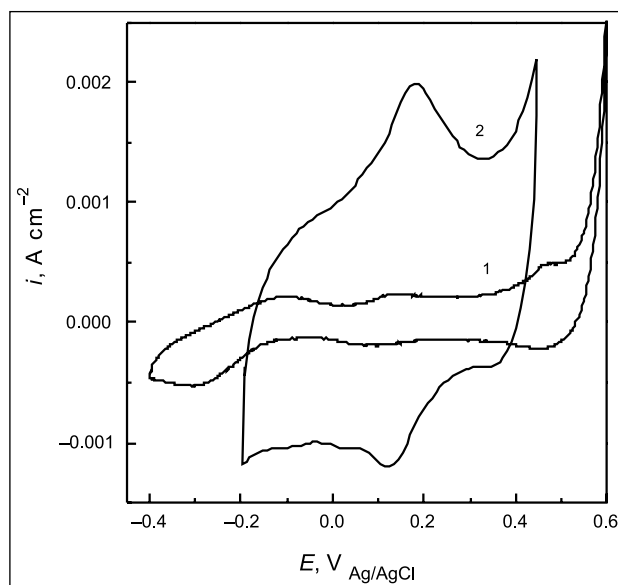

Fig. 3. Cyclic voltammograms of the nano-structured Co electrode (1) and that of composite Co–Ru oxides/hydroxides formed on the nano-structured Co substrate (2) in 40 g L^{-1} NaOH, $v = 20$ mV s^{-1}

the specific capacitance of Co substrate to the total capacitance of the studied thin film is negligible. On the other hand, the comparison of the measured CV (Fig. 3, Curve 2) with that of hydrous ruthenium oxide prepared by the sol–gel method [5, 6] revealed that the electrochemical properties of these two oxides films were quite close. The above results imply that it is ruthenium oxide that mainly governs the electrochemical behaviour of the composite Co–Ru film synthesized by the proposed method.

The measured CV dependences were used to evaluate the capacitance of the studied materials. As known, the specific capacitance of electrode (C) at the cycle number N can be calculated according to the equation

$$C = q_a/m\Delta V, \qquad (2)$$

where q_a, m and ΔV denote the anodic charge of the Nth anodic scan, the mass of active material and the potential window, respectively. So, for the studied Co–Ru oxides layer at the 10th anodic scan number the values were the following: $q_a = 0.04$ A s cm⁻², m $= 0.00005$ g cm⁻², $\Delta V = 0.65$ V and calculated C $= 1230$ F g⁻¹.

To elucidate the influence of substrate morphology for the capacitive properties of the mixed Co–Ru oxides/hydroxides layer, the last one was formed on the bulk Co substrate ("bulk Co/Co–Ru oxides/hydroxides layer" electrode). The measured CV of the Co–Ru oxides/hydroxides layer on the bulk Co substrate (Curve 1) and on the nano-structured one (Curve 2) are shown in Fig. 4. As can be seen, rather low currents are characteristic of the "bulk-based" electrode. The value of the specific capacitance C of this type of Co–Ru electrode, calculated according to Eq. (2),
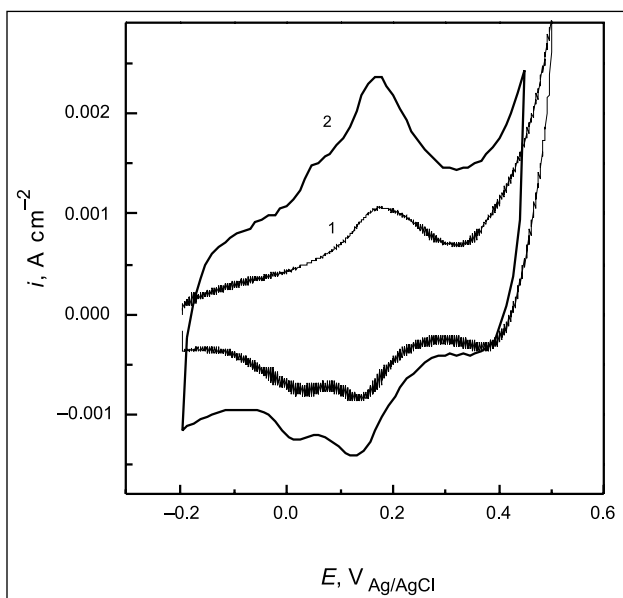
was ~490 F g⁻¹, i. e. the ordinary electrochemical nano-structuring of Co substrate made it possible to attain ~2.5 times higher pseudo-capacitance.

To evaluate the stability of composite Co–Ru oxides layers, the method of multiple electrode potential cycling in the same NaOH solution was applied. The results of 100 cycles test of the studied electrode are shown in Fig. 5. The numbers on the CV indicate the cycle number. The first cycle CV of the uncoated nano-structured Co substrate is also presented in Fig. 5. As clearly seen, an increase in the number of cycles led to a monotonous decline in voltammetric currents and after the 100th cycle only 40% of the initial pseudo-capacitance value remained. The decrease in electrode pseudo-capacitance was attributed to a gradual leaching of Ru from the Co–Ru oxides/hydroxides layer due to highly probable formation of RuO_4^{2-} in a NaOH solution in the range of potentials applied [31]. It can be noted that an orange tint, which is specific of ruthenates (VI), was visible with the naked eye at the surface of the Co–Ru electrode after its prolonged exposure to the solution.
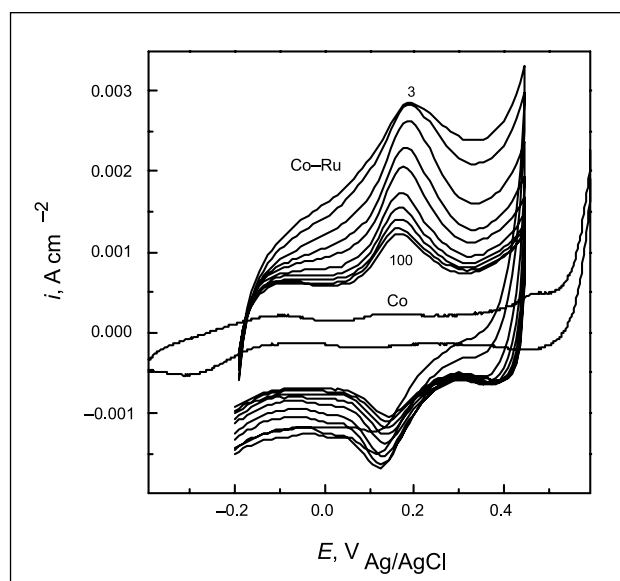

Fig. 5. Cyclic voltammograms of composite Co–Ru oxides/hydroxides formed on the nano-structured Co substrate. The numbers on the curves indicate the cycle number. The CV (the first cycle) of the uncoated nano-structured Co substrate is denoted as "Co"

Despite the decrease in electrode pseudo-capacitance after multiple CV tests, the Co–Ru oxides/hydroxides layers formed were substantially more stable than those of as-deposited hydrous ruthenium oxide – RuO_2 xH_2O [35–37]. For example, for RuO_2 xH_2O electrodes, which were formed by electrophoretic deposition without a binder, the pseudo-capacitance declined so rapidly that only 4% of the initial value was maintained after 50 CV cycles [38]. A poor electrochemical stability of pure RuO_2 xH_2O was explained in

Fig. 4. Cyclic voltammograms of composite Co–Ru oxides/hydroxides formed on the bulk Co substrate (1) and on nano-structured Co substrate (2), 40 g L⁻¹ NaOH, $v = 20$ mV s⁻¹

terms of an irreversible reduction of a portion of the oxide at potentials more negative than −0.1 V. An irreversible oxidation of Ru (IV) at potentials more positive than ~0.4 V [31] also supports the loss of the active material.

Considerable prolongation of stable performance of the formed Co–Ru oxides/hydroxides electrodes may be achieved by heat treatment at >200 °C: this procedure is commonly applied for these types of objects. More than 90% of initial pseudo-capacitance was retained after 200 cycles for the RuO_2 xH_2O electrodes, heat-treated at 250 °C [38].

CONCLUSIONS

A new Co–Ru oxides/hydroxides material without a binder for supercapacitors was synthesized on the electrochemically deposited nano-structured Co substrate by the chemical reaction with $RuCl_3$, dissolved in isopropyl alcohol. Three-day ageing of freshly formed specimens was applied for ultimate arrangement of the layers. The XPS analysis showed that the Co–Ru layers consisted of mixed oxyruthenium and cobalt hydroxide species of various oxidation states. The layers are also characterized by a relatively uniform Co/Ru ratio throughout the bulk. The SEM analysis gave the evidence of developed porous morphology of the coatings. The electrochemical behaviour, influence of the Co substrate on the properties of the Co–Ru oxides/hydroxides electrode and the stability of the formed layer in 40 g l^{-1} NaOH solutions were studied by the CV method. The specific capacitance values of ~1230 F g^{-1} for the composite Co–Ru oxides/hydroxides electrode on the nano-structured Co substrate were determined. Multiple CV cycling of the electrodes confirmed a good stability of the synthesized Co–Ru oxides/hydroxides layer without a binder.

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Svetlana Lichušina, Vitalija Jasulaitienė, Algirdas Selskis, Konstantinas Leinartas

Co-Ru OKSIDŲ / HIDROKSIDŲ MIŠINIO SUPERKONDENSATORIAMS FORMAVIMAS ANT NANOSTRUKTŪRIZUOTO Co PAGRINDO

S a n t r a u k a

Pasiūlytas naujasis Co-Ru oksidų / hidroksidų mišinio, naudojamo superkondensatoriuose, formavimo be rišiklio metodas. Co-Ru oksidų / hidroksidų sluoksniai buvo formuojami cheminės reakcijos tarp $RuCl_3$, ištirpinto izopropilo alkoholyje, ir elektrochemiškai nusodinto nanostruktūruoto Co paviršaus. Co-Ru oksidų / hidroksidų sluoksnio sudėtis paviršiuje ir sluoksnio gylyje buvo tiriama rentgeno fotoelektronų spektroskopijos metodu. Nustatyta, kad Co-Ru sluoksnis sudarytas iš oksirutenio ir įvairaus Co oksidacijos laipsnio hidroksido mišinio. Nustatyta, kad Co / Ru santykis per visą sluoksnio gylį išlieka gana vienodas. Tyrimas skenuojančiu elektroniniu mikroskopu parodė, kad suformuotų sluoksnių paviršius charakterizuojamas porėta morfologija. Ciklinės voltamperometrijos metodu įvertinti Co-Ru oksidų / hidroksidų elektrodo elektrocheminė elgsena, Co substrato įtaka ir suformuoto sluoksnio stabilumas 1 M NaOH tirpale. Nustatyta, kad Co-Ru oksidų / hidroksidų sluoksnio, suformuoto ant nanostruktūruoto Co pagrindo, specifinė talpa yra ~1230 F g^{-1}. Daugkartinė ciklinė poliarizacija Co-Ru oksidų / hidroksidų be rišiklio elektrodo patvirtino jo gerą stabilumą.