Pseudocapacitive behavior of $\text{Ti/RhO}_x + \text{Co}_3\text{O}_4$ electrodes in acidic medium: application to supercapacitor development

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Abstract

Mixtures of $\text{RhO}_x + \text{Co}_3\text{O}_4$ have been electrochemically studied by cyclic voltammetry in acid solution as a function of composition. The electrodes were prepared by thermal decomposition at 400°C of mixtures of nitrate precursors. Their electrochemical behavior shows substantial dependence on the electrode's composition. The Co site controls the electrochemical behavior of the system in the 5–10 mol.% Rh composition range. A significant increase in the electrodes' active area is observed for compositions corresponding to more than 10 mol.% RhO_x in admixture with Co_3O_4 . Above 10 mol.% Rh, the voltammetric curves become more similar to that for RhO_x and then RhO_x becomes able to stabilize the Co_3O_4 in the mixture. Electrodes of this kind have been found to perform as good materials in electrochemical capacitor applications, exhibiting specific capacitances of $500\text{--}800\text{ F g}^{-1}$ over to 20–60 mol.% RhO_x composition range. The large specific capacitance exhibited by this system arises from a combination of the double-layer capacitance and the pseudocapacitance associated with Rh surface redox-type reactions.

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1. Introduction

Electrochemical capacitors (EC) or supercapacitors are being developed as an alternative to pulse batteries, and they have been considered as a promising high power energy source for digital communication devices and electric vehicles. The EC technology has been reviewed for a number of electrode materials, including carbon, conducting polymers and transition metal oxides [1–4]. Thus, the EC electrode materials should have a large surface area for charge accumulation, and an appropriate pore structure for electrolyte wetting and rapid ionic motion.

Amorphous $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ has been found to possess significant energy storage capabilities due to its ability to act as a “proton condenser”, and it represents the best material for application in electrochemical capacitors [5]. RuO_2 systems prepared by the sol–gel process possess very high specific capacitance (720 F g^{-1}) [5], which is associated with surface redox reactions including the participation of proton

exchange between the surface groups and the electrolytic solution.

Noble metal oxides such as IrO_2 and RhO_x also appear as alternatives for applications as electrode materials in electrochemical capacitors. These oxides show characteristics similar to those as observed for the RuO_2 . They are conducting materials with high surface area when prepared as films deposited on a metallic substrate [6]. These oxides possess high double-layer capacitance, and the reversible redox surface processes can enhance the energy density of a device.

However, up to the present, not many researches are found applied to the study of these materials as a basis in the construction of electrochemical capacitors [3,7,8]. This is related to the fact that these oxides, as expensive as RuO_2 are costly for commercial use. A considerable reduction in the cost of the electrode material is needed to make such supercapacitor technology commercially viable. Alternative strategies have been pursued in this regard. The dispersion of a noble transition oxide in other less expensive oxide matrices has been examined with this objective [9,10]. In this context, $\text{Ti/RhO}_x + \text{Co}_3\text{O}_4$ mixed electrodes were prepared as candidates for a supercapacitor device. The effect adding of Co_3O_4 to the electrochemical performance of RhO_x -based electrode in $0.5\text{ mol dm}^{-3}\text{ H}_2\text{SO}_4$

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was analyzed as a function of composition of the electrode. The potential range of the redox processes, the degree of their reversibility, and the specific capacitance values were established by means of cyclic voltammetry (CV). In addition, the structure and morphology of the $\text{Ti/RhO}_x + \text{Co}_3\text{O}_4$ electrodes were also systematically examined.

2. Experimental

2.1. Electrode preparation

Oxide layers of nominal composition $\text{Ti/RhO}_x(1-y) + \text{Co}_3\text{O}_4(y)$ ($0 \leq y \leq 1$) were deposited on a Ti support by thermal decomposition at 400°C of ca. 0.1 mol dm^{-3} from solutions of $\text{Rh}(\text{NO}_3)_3$, and $\text{Co}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ in a HNO_3 , 6.0 mol dm^{-3} . The Rh precursor solution was prepared by precipitating $\text{Rh}(\text{OH})_3$ from a $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ solution by addition of NaOH . The $\text{Rh}(\text{OH})_3$ obtained was filtered off, washed several times with Milli-Q quality water and dissolved in 6.0 mol dm^{-3} HNO_3 , thus resulting in the rhodium nitrate precursor solution. This procedure is the same employed by De Campos et al. in their preparation of the $\text{Rh}(\text{NO}_3)_3$ precursor solution [11].

Brushing on both sides of $10 \text{ mm} \times 10 \text{ mm} \times 0.15 \text{ mm}$ Ti support, which was pre-treated by sandblasting and etched in boiling 10% oxalic acid, the mixtures of appropriate volumes of precursors were spread at the desired mole ratio. After each application, the solvent was evaporated at about 90°C and the dried layer fired for 5 min, under a 51 min^{-1} O_2 stream, in a preheated oven. The procedure was repeated until the desired catalyst loading was achieved ($2.43\text{--}2.88 \text{ mg cm}^{-2}$). The total deposited mass on the Ti support was calculated based on the sum of the specific density of the RhO_2 (7.195 g cm^{-3}) and Co_3O_4 (6.07 g cm^{-3}) [12] considering the desired mole ratio and a nominal coating thickness value constant ($2 \mu\text{m}$). The electrodes were then annealed for 1 h at 400°C . The mounting of the electrodes in a Teflon holder has been described elsewhere [13].

2.2. Electrochemical measurement

The surface features of the mixed oxides were characterized in situ by cyclic voltammetry at 20 mV s^{-1} in the potential range of $0.4\text{--}1.4 \text{ V RHE}^{-1}$ in 0.5 mol dm^{-3} H_2SO_4 solutions. The electrodes were submitted to continuous cyclization of the potential by 100 cycles to evaluate their chemical stability and to reach a stationary surface condition. The double-layer changing region was determined by changing the positive and negative potential limits. The differential capacity (C_d) of the oxide–solution interface was obtained from CV measurements from 2 to 150 mV s^{-1} . The C_d -values were obtained from the slope of the j (mA cm^{-2}) versus v (mV s^{-1}) graphics (when j is the current-density at the potential $E = 0.6 \text{ V}$ or 1.4 V RHE^{-1} and v the voltage sweep-rate (dV/dt) s^{-1}).

The specific capacitance, C_s , was obtained by dividing the differential capacity values by the Rh mass content (m_{Rh}) of the oxide layer (g cm^{-2}). The Rh mass was calculated from its mol.% present in the total mass deposited on titanium. This was done with the objective of evaluating the effect of the reduction of the amount in the precious component on the total charge capacity.

2.3. Potential, solution and equipment

Electrochemical measurements were performed using a four-compartment cell with two counter electrodes (platinized platinum wires) facing the working electrode from opposite sides, and a Luggin capillary approaching the electrode from below in order to minimize uncompensated Ohmic drop. Electrode potentials were measured and reported against that of an hydrogen electrode (RHE) in the same supporting electrolyte. The electrochemical experiments were carried out with an ECO CHEMIE Autolab Potentiostat–galvanostat (PGSTAT30) interfaced to a computer. All experiments were carried out in 0.5 mol dm^{-3} H_2SO_4 (Merck) solutions volumetrically prepared using Milli-Q quality distilled water. The air in these solutions was expelled and stirring achieved by bubbling nitrogen. All the experiments were carried out at room temperature, ca. 298 K .

The coating morphology was examined by scanning electron microscopy (SEM). The compositions of samples were analyzed by the energy-dispersive X-ray (EDX) measurements. Both analyses used a Zeiss Model DSM 960 electron microscope coupled to a microanalyzer, Link Analytical Model QX 2000. Quantitative analysis of the coating was performed by EDX. The atomic percentages of the elements were obtained by corrections for matrix interference, atomic number, absorbance and fluorescence (ZAF correction). Metallic cobalt (99.998% pure) was used for equipment calibration. Iridium and cobalt reference standards (Micro-Analysis Consultants, Cambridge shire) were used for internal calibration. The experimental errors, based on the ZAF correction algorithm, were always below 1% (wt.%).

The microstructural investigation was carried out by X-ray diffraction analysis (XRD) of the Ti-supported film. These analyses were performed on a D5005 SIEMENS diffractometer using $\text{Cu K}\alpha$ radiation (30 kV , 30 mA).

3. Results and discussion

3.1. Morphology, microstructure and composition characterization

Fig. 1 shows typical SE micrographs for freshly prepared $\text{Ti/RhO}_x(1-y) + \text{Co}_3\text{O}_4(y)$ electrodes as a function of the composition. The film morphology is influenced by the nominal composition of oxide layer.

Fig. 1. SEM micrographs of $\text{Ti/RhO}_x(1-y) + \text{Co}_3\text{O}_4(y)$ electrodes as a function of layer oxide composition. (A) $y = 1.0$; (B) $y = 0.8$; (C) $y = 0.5$; (D) $y = 0$. Magnification, $500\times$.

The Ti/RhO_x electrode shows a non-crystalline layer, with cracks distributed randomly on the electrodes surface like these thermally prepared RuO_2 . The introduction of the second component, Co_3O_4 , promoted a more continuous appearance of the “cracked-mud” morphology (Fig. 1) until a 50 mol.% Co_3O_4 composition was attained. This morphological aspect is characteristic of the thermally-prepared oxide layers [14] resulting in electrodes with high surface area. The layers are homogeneous and rough with a non-crystalline appearance, when their thermal decomposition was incomplete. The overall picture suggests that the $\text{RhO}_x + \text{Co}_3\text{O}_4$ mixture leads to a significant increase in the specific surface area of the oxide coating. Above 60 mol.% Co_3O_4 contents, the morphology takes on a more compact aspect similar to that frequently described for the $\text{Ti/Co}_3\text{O}_4$ electrodes obtained under the same experimental conditions

[15,16]. This result suggests that the morphological aspect of the oxide layer is controlled by cobalt for electrodes rich in this component.

Fig. 2 shows the relationship between the nominal content and the experimental atomic percentages obtained from the EDX analyses. The values thus obtained do not lead to the surface composition of the film; they are representative of nominal composition within a depth of approximately $1.0\text{ }\mu\text{m}$ of oxide layer.

The results showed that the real composition of the oxide layer is quite close to the nominal value. Electrodes with intermediate composition values showed the Co content to be slightly higher than the nominal value thus suggesting an enrichment of this component in the oxide layer.

The XRD pattern recorded for the $\text{Ti/RhO}_x(1-y) + \text{Co}_3\text{O}_4(y)$ system is shown in Fig. 3 as a function of the

Fig. 2. Comparison between nominal and real composition Ti/RhO_x (1 - *y*) + Co₃O₄ (*y*) (0 ≤ *y* ≤ 1) oxide layer from energy dispersive X-ray analyses.

composition. It is possible to observe only the peaks related to the titanium substrate for the Ti/RhO_x samples. The absence of X-ray diffraction peaks related to the Rh-oxide structure indicates that the Ti/RhO_x sample is amorphous. Similar results were obtained by De Campos et al. [11] using [Rh(H₂O)₆](NO₃)₃ as precursor, fired at 430 °C for a duration of <4 h. Roginskaya et al. [15] only obtained lines due to α-Rh₂O₃, and the rutile phase after having employed temperatures above 500 °C. These results are consistent with the decomposition of the precursors being possibly incomplete at the annealing temperature employed.

The Ti/Co₃O₄ X-ray spectrum shows wide and low intensity peaks related to the spinel structure. This behavior is consistent with the incomplete decomposition expected for the Co precursor at the temperature employed during the calcination stage [17].

Only the peaks related to the Co₃O₄ spinel phase are observed in the XRD pattern of the Ti/RhO_x + Co₃O₄

Fig. 3. X-ray diffraction patterns of Ti/RhO_x (1 - *y*) + Co₃O₄ (*y*) (0 ≤ *y* ≤ 1) electrodes as a function of layer oxide composition. (A) *y* = 1.0; (B) *y* = 0.8; (C) *y* = 0. Position of the peaks expected for the (●) Ti and (○) Co₃O₄.

Fig. 4. Open-circuit potential, *E*_{oc}, as a function of RhO_x content (nominal) measured in 0.5 mol dm⁻³ H₂SO₄: (●) as-prepared electrodes and (○) after electrochemical study.

mixture (including the Ti peak from the metallic Ti substrate) regardless of the composition. The results indicate that the oxide coatings consist of a mixture of crystalline and hydrous amorphous phases containing predominately Rh and Co oxy-hydroxide species. It was demonstrated that the amorphous form of the hydrous ruthenium oxide has a much higher specific capacitance than that of the RuO₂ in its crystalline form [18].

3.2. Electrochemical characterization

3.2.1. Open-circuit potential measurements

Fig. 4 shows the open-circuit potential, *E*_{oc}, as a function of the composition of the oxide layer before and after the electrochemical studies (after storing the electrodes for 2 months in water). The measurements were performed 15 min after the immersion of the electrodes in the electrolytic solution.

The freshly prepared Ti/Co₃O₄ electrodes show an *E*_{oc} value very different from the theoretical expected value for the Co(II)/Co(III) couple (*E*[°] = 1.018 V RHE⁻¹) [19]. A comparison amongst the standard potential values of the possible solid-state transitions [19] suggests that the electrode possesses Co surface sites in a reduced state, so that the surface electrochemistry is probably controlled by the Co/CoO couple.

The substitution of only 5 mol.%, from one component by the other, causes a strongly significant change in the *E*_{oc}, leading to a value more characteristic of the Co(II)/Co(III) couple. The presence of the 5–10 mol.% Rh in the oxide layer is sufficient to promote the oxidation of Co surface sites. The Co(II)/Co(III) redox transition is probably responsible for the electrochemical response of the system. After the introduction of 20 mol.% Rh, the open-circuit potential reaches a value close to 0.90 V RHE⁻¹, regardless of the composition of oxide layer, thus suggesting that it is the surface electrochemistry that is mainly controlled by Rh sites. This *E*_{ca}-value does not, however, allow us to determine which redox pair controls the behavior of the

Fig. 5. Cyclic voltammograms of (Ti) Co_3O_4 and (Ti) RhO_2 electrodes obtained at different potential limits as a function of oxide layer composition in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 20 mV s^{-1} : (---) 2 and (—) 100 cycles of potential scan. Interval of: (A) and (B) 0.4 and 1.4 V and (C) and (D) 0.3 and 1.5 V RHE^{-1} . (A) and (C) Co_3O_4 ; (B) and (D) RhO_x . (Inset in (A) shows the voltammetric behavior between 0 and 1.4 V RHE^{-1} for 10 cycles of potential scan.)

electrochemical surface of the oxide layer. A comparison of the standard potentials, of the possible solid-state transitions involved [19], suggests that this potential can be reflecting the contributions of several redox couples involving different oxidation states of rhodium.

The dominance of the electrochemical behavior by cobalt oxide for 0–10 mol.% Rh, and by rhodium oxide for electrodes containing 20–80 mol.% Rh is qualitatively consistent with the SEM results which show that the oxide layer morphology changes in a similar way with the electrode composition.

3.2.2. Voltammetric behavior

Some representative cyclic voltammograms, recorded after 2 and 100 cycles, are shown in Figs. 5 and 6 for two different potential windows.

As can be seen from the voltammogram inset in Fig. 5A, the Co_3O_4 voltammetric profile is completely determined by an anodic current on the initial cycles of the potential between 0.4 and 1.4 V RHE^{-1} . This result is in agreement with the E_{oc} measurement and indicates that all Co surface sites must be oxidized in order to restore the voltammetric behavior characteristic of this system [16,20] in acid medium. After 100 cycles, the voltammetric behavior is similar to that described by Da Silva et al. [16] for the Co_3O_4 electrode prepared at 470°C , with a pair of peaks at approximately 1.0 V RHE^{-1} attributed to the Co(II)/Co(III) solid-state redox transition. This result shows that the Co_3O_4 structure is formed only after some cycling of the potential.

Although the voltammetry was conducted over 100 cycles over the investigated potential interval, the anodic current is always much higher than the cathodic current. This behavior suggests that a much greater number of cycles is necessary

Fig. 6. Cyclic voltammograms of $\text{Ti/RhO}_x (1-y) + \text{Co}_3\text{O}_4 (y)$ ($0 \leq y \leq 1$) electrodes obtained at different potential limits as a function of oxide layer composition in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 20 mV s^{-1} . Interval of: (A), (B) and (C) 0.4 and 1.4 V and (D), (E) and (F) 0.3 and 1.5 V RHE^{-1} . (A) and (D) $y = 0.7$; (B) and (E) $y = 0.5$; (C) and (F) $y = 0.2$; (---) 2 and (—) 100 cycles of potential scan.

in order to establish a condition of reversibility between the oxidized and reduced sites required for proper manifestation of pseudocapacitance.

It is also possible to observe the existence of a non-compensated cathodic process at approximately 0.4 V RHE^{-1} , after the cathodic switching of potential. The presence of this cathodic current is probably related to the partial reduction of the Co surface sites when the fresh electrode is submitted to cathodic scan. Under these condition, it is possible to observe a continuous decrease in the voltammetric charge, with cycling at the $\text{Ti/Co}_3\text{O}_4$ electrodes (see Fig. 5C), an effect probably related to gradual dissolution of the oxide layer. Similar behavior has been described in the literature and attributed to the cathodic dissolution of the CoO formed during the cathodic potential sweep in the acid medium [14,20]. This dissolution process has limited the use of Co_3O_4 electrodes to alkaline media for which the electrochemical behavior has been intensively studied.

The partial substitution of Co_3O_4 by RhO_x promotes some changes in the voltammetric behavior of the $\text{Co}_3\text{O}_4 + \text{RhO}_x$ mixtures (Fig. 6). For electrodes having a Rh content in the 0–10 mol.% range, the voltammetric behavior is similar to that observed for the $\text{Ti/Co}_3\text{O}_4$ coating. No characteristic surface redox transitions involving Rh sites are then observed. The voltammetric current decreased continually when electrodes with 5–10 mol.% Rh content were submitted to continuous cycling of the potential between 0.4 and 1.4 V RHE^{-1} at 20 mV s^{-1} . This result indicates that the Co sites control the electrochemical behavior of the system in the 5–10 mol.% Rh composition range.

A significant increase in the current is observed for mixtures containing more than 10 mol.% Rh and then the voltammetric profiles become more similar to those for the

Ti/RhO_x electrode. The voltammetric response is typical of a non-ideal condenser [3,21]. It is possible to observe a broad hump, covering the 0.8–1.5 V RHE⁻¹ interval, associated with surface redox, followed by the onset of the oxygen evolution reaction (OER). The broadness of the peaks associated with the surface redox can be explained in terms of a large heterogeneity in the surface sites thus becoming difficult to distinguish the nature of redox transition for RhO_x-based electrodes.

This behavior is very similar to that mentioned in the literature concerning RhO_x electrodes prepared from Rh-chloride as precursor [11,22,23]. De Campos et al. [11] attributed the absence of well-defined peaks in the voltammetric profile due to the presence of residual chloride in the oxide layer, substituting some oxy and hydroxyl groups, in the cross-linked polymeric hydrous Rh-oxy-hydroxide structure that are generally formed in the film when the precursor used in the preparation of the oxide layer does not contain chlorides. Similar voltammetric behavior, to that observed for the RhO_x electrode prepared from a Rh-chloride precursor, suggests that the preparation methodology of the precursor solution, adopted by us, did not allow elimination of all residual Cl derived from the precursor.

The similarity between the anodic and cathodic current values for electrodes containing more than 10 mol.% Rh, and the absence of a non-compensated cathodic process after cathodic switching of potential, observed in the Co-rich mixture, suggest that the RhO_x is able to stabilize the Co₃O₄ in the oxide layer. The absence of a continuous decrease in the voltammetric charge with n , between 0.4 and 1.4 V RHE⁻¹, observed with the electrodes having Rh content above 10 mol.%, confirmed this result (Fig. 6).

The switching potential investigation showed that the best potential interval for surface characterization by CV is from 0.3 up to 1.55 V (an increase of the cathodic current is observed below of 0.3 V). However, the voltammetric current decreases continually when electrodes with 0–30 mol.% Rh content are submitted to continuous potential cycling between 0.3 and 1.55 V RHE⁻¹, suggesting that the 40–100 mol.% Rh composition is the most promising composition (see Fig. 6D–F) for practical development.

3.3. Charge capacitance evaluated by cyclic voltammetry (CV)

Fig. 7A shows a typical set of curves obtained at various sweep-rates (ν) for the Ti/RhO_x (0.5) + Co₃O₄ (0.5) electrode, representing the system behavior. The voltammetric curves were recorded over a potential interval of 1.3 V for all analyzed electrodes. Values for the differential capacitance (C_d) of the solid–solution interface were estimated from these CV experiments by measuring the slope of the voltammetric current-density versus sweep-rate plot at $E = 0.6$ and 1.4 V RHE⁻¹. The corresponding dependence on the charging current is also showed in Fig. 7B and C for two distinct potentials chosen from the voltammetric behavior. Capacitance values obtained from cyclic voltammetry as a function of sweep-rate have been extensively employed [3,24,25]. Usually the accessible C_d is dependent on ν and is often potential dependent for fundamental reasons connected with the structure of the double layer [26] and the surface site active redox process [21]. In this way, two different values of potentials were chosen within electrochemical stability range with the purpose of representing the system behavior in capacitive and pseudocapacitive current conditions.

No linear behavior was observed for the charging current as a function of the sweep rate for the 100 and 95 mol.% Co regardless of the potential range of the CVs. This behavior is related to a loss of mass due to the cathodic dissolution of this component in acidic medium. The 90–0 mol.% Co electrodes j (mA cm⁻²) versus ν plot, obtained at the $E = 0.6$ V RHE⁻¹, show a linear behavior. The slope of this straight line supplies the value of a differential capacity, C_d , directly related to the real surface area of the electrode, which is influenced by the film morphology (pores, intergranular contacts, cracks, etc.).

The C_d value shows a dependence on the oxide composition, increasing proportionally to the fraction of rhodium. The highest C_d values were obtained at intermediate compositions with a maximum at 50–60 mol.% RhO_x content, suggesting that the oxide mixtures having intermediate compositions have the highest specific surface area. This result is consistent with the SEM analysis, which revealed a “cracked-mud” morphology over this composition range.

Fig. 7. (A) Voltammetric behavior of Ti/RhO_x (0.5) + Co₃O₄ (0.5) electrode as a function of the scan rate, ν , in 0.5 mol dm⁻³ H₂SO₄ at 20 mV s⁻¹. (B) Graph of j (mA cm⁻²) vs. ν measured at $E = 0.6$ V RHE⁻¹, (C) at $E = 1.4$ V RHE⁻¹.

While the graph of j (mA cm^{-2}) versus v obtained for $E = 1.4 \text{ V RHE}^{-1}$ shows only one linear region to the 10–40 mol.% Rh electrodes compositions, above 40 mol.% Rh it is possible to distinguish two linear regions being one with a somewhat lower slope at a scan rate $>20 \text{ mV s}^{-1}$ (Fig. 7C).

According to the CV studies and SEM analyses, the change in the slope as a function of scan rate is observed for samples that possess the highest active surface area (50–100 mol.% Rh). This behavior is related to the fact that the differential capacity, C_{d1} , obtained at $E = 1.4 \text{ V RHE}^{-1}$ has a pseudocapacitive nature due to the contributions of the solid-state surface redox transitions, which are proportional to the specific surface area [27]. The solid-state redox transition process, in the conductive oxide occurs with the participation of proton-exchange between the oxide–OH surface groups and the electrolytic solution [28]. For rough and porous electrodes, it is assumed that protons can penetrate the solid structure through intergranular areas, so that the sites located in the bulk of the oxide can also be reached to participate in the redox reaction [28]. At a lower sweep-rate, protons have enough time to diffuse to the inner and less accessible active surface regions thus providing access to a much higher number of active sites. When greater scan rates are employed, the inner surface related to the oxide microstructure is not able to take part in the double-layer charging because of some difficulty supply of the protons [29]. In this way, the electrochemical response can be attributed only to the utilization of active sites on the surface of the oxide.

In Fig. 8A and B it is possible to compare the behavior of q_a , C_d and C_{d1} values as a function of the composition of the electrode (where q_a is the anodic voltammetric charge between 0.4 and 1.4 V RHE $^{-1}$, C_d the differential capacity in the 0.6 V, and C_{d1} the differential capacity at 1.4 V RHE $^{-1}$ measured at lower scan rate).

Fig. 8. (A) Voltammetric anodic charge, q_a , measured between 0.4 and 1.4 V RHE $^{-1}$: (●) before and (○) after 100 cycles of potential scan. (B) (*) C_d and (●) C_{d1} values measured at 0.6 V and 1.4 V RHE $^{-1}$, respectively, and (○) specific capacitance, C_s , as a function of the composition of the electrode.

The comparison of q_a versus mol.% Rh (Fig. 8A) with the C_{d1} versus mol.% Rh (Fig. 8B) curves reveals a striking similarity between these plots. It is well known that q_a is proportional to the number density of active surface sites, so it can be taken as a relative measure of the electrochemically active surface area [30]. The similarity of behavior between q_a and C_{d1} suggests that C_{d1} can also be used as an adequate parameter for describing the active surface area of the oxide coatings. These parameters remain low up to about 10 mol.% Rh, then they increase steeply up to a maximum at 60 mol.% Rh, and finally, decrease towards Rh-rich compositions. Since Co₃O₄ does not contribute to the surface redox charge significantly, the maximum at 60 mol.% Rh is indicative of high active surface area effect due to the greater degree of dispersion of the electroactive component after introduction of the Co₃O₄. The introduction of higher amounts than 60 mol.% Rh probably promotes a saturation of the concentration of this species in the surface of the electrode, favouring the formation of particles of greater size.

The absence of similarity between q_a and C_d versus mol.% Rh curves is consistent with the fact that the C_d value only provides a measure of the real surface related to the morphology of the electrode, while the C_{d1} value can be considered as a relative measure of the electrochemically active surface area of the electrode. Thus, only C_{d1} is proportional to the number of active sites displayed to the electrolytic solution.

In Fig. 8B it is possible to compare the C_d and C_{d1} behavior as a function of the oxide-layer composition. For the Co-rich electrodes, C_d and C_{d1} have similar values, indicating that under these conditions the real surface area due to the morphology of the oxide layer, is the dominant parameter determining the capacitance value, and that the Co surface redox transition contributes little to the pseudocapacitance of the system. Above 20 mol.% Rh, the values of C_{d1} increase significantly showing that the contribution of the solid-state redox transition, involving Rh active sites, is the predominant factor in producing an increase of the charge capacity in the system.

Then, the specific capacitance, C_s , can be obtained by dividing the C_{d1} value by the Rh mass content (m_{Rh}) of the oxide layer (g cm^{-2}). Although the specific capacitance of mixed oxides should be reported on the basis of the total weight of the oxide, in the present paper the C -value is measured as a function of the noble-metal oxide (Rh) content. This is done with the purpose of evaluating the effect of the amount of reduction of the precious-metal component on the total charge capacity in the system.

The effect of the substitution of RhO_x by Co₃O₄ in the C_s -values is shown in Fig. 8B. The value of 81 F g^{-1} , obtained for 100 mol.% Rh electrode shows how higher charge storage capacity of this system arises when compared to that of the Co₃O₄ electrode. Thus, this value is at least twice that obtained for the RuO₂· x H₂O electrode prepared at the same calcination temperature [5]. This behavior can be related to

the presence of amorphous Rh-oxy-hydroxide species which facilitate proton transport in pathways consisting of the most internal regions of the oxide layer, thus increasing the number of Rh active sites in contact with the electrolytic solution. Since the amount of energy stored is proportional to the amount of active sites present in the electrode surface, this three-dimensional bulk storage mechanism can lead to much higher values of volume energy-density of the electrode structure.

In Fig. 8B, it is also possible to compare the C_s and C_{dl} behavior as a function of the oxide layer composition. As the electrochemical behavior of the system is evidently controlled by Co sites in the 5–10 mol.% Rh composition interval, the high value of C_{dl}/m_{Rh} ratio is related to the fact of the contribution of the Co active sites not being considered for the calculated one of the capacitance value.

While the C_{dl} value increases up to 60 mol.% Rh content, the C_s -values are approximately constant in the 30–60 mol.% Rh composition range. This behavior suggests that, as also observed in the RuO_2 and IrO_2 systems, the active surface area of the electrode increases proportionally with the Rh mass content (m_{Rh}) of the oxide layer [31,32].

It is interesting to observe that C_s and C_{dl} values only change in a similar way for the 60–100 mol.% Rh range content. Thus, in the interval of the composition, both parameters decrease with the Rh content in the oxide layer, indicating that a real decrease surface area is the main factor responsible for the reduction of the charge capacity in the system. In fact, assuming that the electrode surface is saturated with Rh species over this composition range, the reduction of the C_s and C_{dl} observed with Rh-rich compositions can be related to a change of the surface micro-structures, due to the growth of surface particles with the increasing of the Rh concentration.

C_s values, on the order of $500\text{--}800\text{ F g}^{-1}$, are obtained for the 20–60 mol.% Rh electrodes, and are compatible with those measured for hydrated RuO_2 prepared by the sol-gel process (720 F g^{-1} were measured for the powder formed at 150°C) [5]. The large specific capacitance exhibited by this system arises from a combination of the double-layer capacitance (due to high surface area) and the pseudocapacitance associated with the surface redox-type reactions.

The value of 799 F g^{-1} obtained for the 20 mol.% Rh electrode suggests that this composition shows the best characteristics for the application on supercapacitors devices. However, the voltammetric current decrease, observed for electrodes in the 0–30 mol.% Rh composition range (when they were submitted to continuous cycling of the potential between 0.3 and 1.55 V RHE^{-1}) suggests that this range actually does not provide an electrochemically stable material. As the choice of the best composition for this application must contain a relation between cost-benefit (lower amount of the noble metal and higher charge-storage capacity), the electrodes with 40–50% mol RhO_x represent the best composition for practical applications.

4. Conclusions

The electrochemical behavior of (Ti) $RhO_x + Co_3O_4$ electrodes is very dependent on the composition of the oxide layer. Co sites control the electrochemical behavior of the system in the 5–10 mol.% Rh composition range. However, no characteristic surface-redox transitions involving Rh sites are observed in the voltammograms. The continuous decrease in the voltammetric charge with cycle number n , observed for the 5–10 mol.% Rh electrodes is related to the electrochemical instability of the oxide layer, due to the cathodic dissolution of CoO formed during the cathodic potential sweep.

A significant increase in the current is observed for mixtures containing more than 10 mol.% Rh, then the voltammetric profiles become more similar to these for Ti/ RhO_x electrodes, indicating that the Rh sites control the electrochemistry of the system. The absence of a continuous decrease in the voltammetric charge with n , between 0.4 and 1.4 V RHE^{-1} observed with electrodes having Rh contents above 10 mol.%, suggests that RhO_x is able to stabilize the Co_3O_4 in the oxide layer.

The higher C_d values, measured for $E = 0.6\text{ V RHE}^{-1}$, were obtained at intermediate compositions, giving a maximum at 50 mol.% RhO_x , thus confirming that oxide mixtures having intermediate composition present the highest specific surface areas.

Co-rich electrodes show similar C_d and C_{dl} values, suggesting that for these conditions, the real surface area determined by the morphology of the oxide layer is the dominant parameter determining the specific capacitance value. The high C_{dl} -values observed with the >20 mol.% Rh electrodes indicate that the contribution of the solid-state redox transition, involving Rh active sites, is the predominant factor leading to the increase of the charge capacity in the system.

The electrodes described above have been found to perform in superior electrochemical capacitor applications, exhibiting specific capacitance values of $500\text{--}800\text{ F g}^{-1}$ over the 20–60 mol.% RhO_x composition range. The large specific capacitances exhibited by these systems arise from a combination of the double-layer capacitance, with the pseudocapacitance associated with surface Rh redox-type reactions.

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