

Short communication

Investigation of pseudocapacitive properties of RuO₂ film electrodes prepared by polymeric precursor method

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Abstract

RuO₂ electrodes were prepared by polymeric precursor method. Initially the composition variables were investigated using a factorial design and in a second step the calcination temperature was studied between 250 and 600 °C. Cyclic voltammograms in acid medium show no changes in the profile for different preparation temperature. On the other hand, a high decrease of the current density occurs as the calcination temperature is increased. Consequently, the specific capacitance of the electrodes also decreases. Specific capacitances of 70 F g⁻¹ were obtained for films prepared at 250 °C.

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1. Introduction

As well as the conventional capacitors, in the electrochemical capacitors the stored charge is a function of the voltage. However, they present different fundamental characteristics: electrochemical capacitors present high power at low energy density [1]. Therefore, the electrochemical capacitors can improve the performance of batteries and of the conventional capacitors, considering the power density and energy density, respectively, when combined to these devices. In the search for “clean technologies”, several studies on electrochemical capacitors have been performed, mainly in hybrid systems, together with batteries, for its use in different applications [2–4]. Moreover, the electrochemical capacitors have high pulse-power capability and could be used as sources in power pulsed lasers and as an alternative to the conventional capacitors [5,6].

The electrochemical capacitors can be divided in two categories, according to their mechanism of energy storage. The first one involves the charge storage in the electrochemical double layer of the electrode/electrolyte interface. The second mechanism is observed mainly in materials that involve the absorption

or insertion of electro-active species into the solid phase accompanied by charge transfer processes. As this process occurs in the bulk of the electrode, the capacitance values for these systems are much larger than for those systems whose charge is stored only on the surface. The capacitance, in this case, is expressed in terms of capacitance by mass, usually given by F g⁻¹. The term “redox pseudocapacitance” was introduced by Conway et al. [5,7] to describe this charge storage mechanism. Several transition metal oxides, such as RuO₂ [8–12], IrO₂ [13,14], NiO_x [15,16], MnO₂ [17–20], Co₃O₄ [21], nitrites [22,23] and conductor polymers such as polyaniline [24–26], polypyrrol [26] and polythiophene [27,28] present this behavior.

Ruthenium oxide is well known due to its electrocatalytic activity for O₂ and Cl₂ evolution reactions [29,30]. Moreover, RuO₂ has also been investigated for its use in energy storage devices. RuO₂ is stable under a wide potential range in which redox reversible reactions occur, besides the high capacitance values, great cyclability and high conductivity [10,11,31,32]. Since the pseudocapacitance of RuO₂ results from surface reactions and the specific capacitance is proportional to the specific surface area of the electrode, it is obvious that an effective increase of surface area can lead to a specific capacitance increase. However, other factors, such as the crystalline structure, can also modify the capacitive characteristic. Although the anhydrous ruthenium oxide (RuO₂) presents high values of

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specific capacitance, it is in its hydrous and amorphous form ($\text{RuO}_x(\text{OH})_y$) that this oxide exhibits the highest capacitance values that have been described [11]. According to Horvart-Radošević et al. [33], this occurs because the amorphous and hydrous oxide have more availability of the OH^- sites on the surface of the oxide. On the other hand, Zheng and Jow [8] attributed the increase of the specific capacitance to a contribution of the bulk of RuO_2 . According to the authors [8], the bulk of RuO_xOH_y can be permeable to the electrolyte ions.

Considering the high specific capacitance values obtained with electrodes prepared by sol–gel, in this work we prepared RuO_2 electrodes using a variation of the sol–gel method, the polymeric precursor method [34]. This method is based on the polyester formation starting from metal citrates following of thermal degradation of organic part. Usually, citric acid (CA) and ethylene glycol (EG) are used to prepare the polyester. The advantage of this method is simplicity and low cost, compared to the conventional sol–gel routes. The properties of the oxide formed are dependent on the composition variables (CA:EG:metal salt molar ratios), as well as the heat treatment conditions. Both the understanding and the control of these factors are very important in order to modulate the characteristics of the desired material. In this work the polymeric precursor method was used for the first time to prepare RuO_2 electrochemical capacitors. The first part of this paper shows the composition variables study using the factorial design methodology [35], and subsequently, the heat treatment temperature effect was investigated.

2. Experimental

2.1. Preparation of the RuO_2 electrodes

Metallic titanium plates with purity of 99.7% (TiBrazil) with $A = 1.0 \text{ cm}^2$ were used as substrate to prepare the electrodes. The substrates were treated by sandblasting, followed by a chemical treatment in hot 10% (w/w) oxalic acid solution for 10 min. Finally, the electrodes were washed with Milli-Q water and dried at 150°C . The RuO_2 solution was prepared using the precursor polymeric method by the addition of the RuCl_3 to ethylene glycol (EG) under stirring at 70°C . After that, citric acid (CA) was slowly added. Both stirring and temperature were maintained until the complete dissolution of the complex. To study the effect of the composition of the solutions a factorial design (Table 1) was used. The variables investigated were the Ru:CA:EG molar ratios. The best composition obtained in this study was used in the investigation of the calcination temperature. The precursor solution was painted over the substrate and heat treated at 110°C during 10 min to promote the polymerization, at 250°C during 10 min to improve the adhesion of the oxide, and then at different

Table 1
Preparation variables to RuO_2 electrodes

Factors	Level (–)	Level (+)
C-CA/EG (M/M)	1:4	1:10
M-CA/Ru (M/M)	3:1	10:1

Table 2
Factorial design 2^2 matrix and specific capacitances response

Runs	Samples	C	M	CM	C (F g^{-1})
1	1:3:12	–	–	+	23.5 ± 1.5
2	1:3:30	+	–	–	18.5 ± 2.5
3	1:10:40	–	+	–	16.5 ± 2.5
4	1:10:100	+	+	+	13.5 ± 2.5

temperatures between 250 and 600°C during 10 min. This deposition and calcination procedure was repeated 10 times for the compositional study and five for the temperature investigation.

2.2. Factorial design

In the initial step of this work the CA:EG and CA:Ru variables were investigated using a 2^2 factorial design. The calculation of the response of a factorial design is performed using matrix calculations combining all variables at their different values [35]. In a factorial design, n^k experiments must be accomplished, where n is the number of variables (factors) and k is the number of different values (levels) of each variable. The experiments are usually performed in two levels. Therefore, to accomplish a factorial design with two variables, studied at two levels, only four measurements are necessary. The variables and their respective (+) high and (–) low levels are presented in Table 1. The matrix of the experiments is shown in Table 2. Each sample was prepared in duplicate in order to estimate the standard error associated to individual response determination.

2.3. Electrochemical characterization

Cyclic voltammetry measurements were performed using a PARC EG&G mode 263 potentiostat/galvanostat. Measurements were carried out in a three-electrode cell. A Pt plate and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. The Ti/ RuO_2 electrodes were used as working electrodes. The measurements were performed at 25°C in $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$.

2.4. Physical characterization

The surface morphology was analyzed by scanning electron microscopy (SEM-Zeiss model 940A). The structures of powders were analyzed by X-ray diffraction with a diffractometer (Siemens model D5000), using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$).

3. Results and discussion

3.1. Compositional preparation variables study of the RuO_2 electrodes

The electrodes prepared were characterized by cyclic voltammetry measurements in acid medium at $v = 20 \text{ mV s}^{-1}$ (Fig. 1). The capacitive voltammetric profile observed is characteristic of the RuO_2 electrodes. According to the literature, the pseudocapacitance is derived mainly from the Ru(II)/Ru(III) and

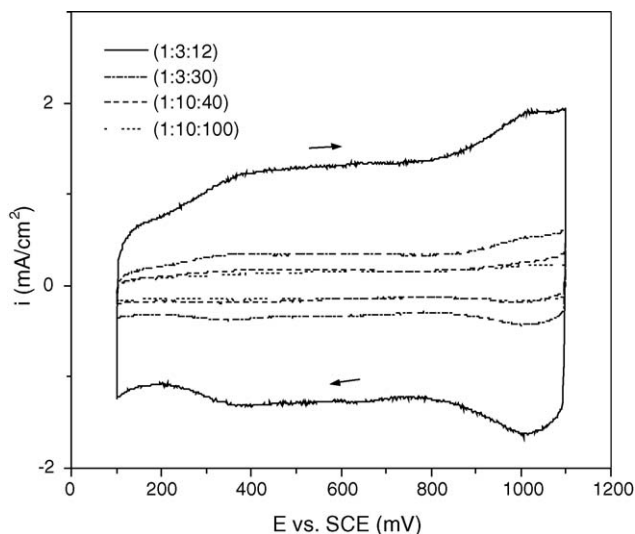


Fig. 1. Cyclic voltammograms of the RuO₂ electrodes in 1.0 mol L⁻¹ H₂SO₄ solution, $v = 20 \text{ mV s}^{-1}$ and $T_{\text{calcination}} = 400 \text{ }^\circ\text{C}$.

Ru(III)/Ru(IV) transitions, and possibly Ru(IV)/Ru(VI) transition [12,36], whose potential values (versus SCE) are:

Ru(II) → Ru(III) between 0.0 and 0.2 V

Ru(III) → Ru(IV) between 0.2 and 0.8 V

Ru(IV) → Ru(VI) between 0.8 and 1.2 V

The electrodes obtained starting from 1:3:12 resin, i.e. CA/EG = 1:4 and CA/Ru = 3:1 ratios, present the highest current density values associated to redox process. The charge density was about four times higher than the charge of 1:3:30 electrodes (CA/EG = 10:1; CA/Ru = 3:1). Table 3 shows the specific capacitance values calculated starting from cyclic voltammograms of the RuO₂ samples. In Table 2, it is observed that the specific capacitance increases as the CA and Ru concentrations increase in the precursor resin. However, the maximum value obtained (23.5 F g⁻¹) is considered low compared to literature values [8–10]. These low values occur due to the high temperature of the heat treatment of these samples (400 °C), which could lead to the formation of the crystalline and anhydrous ruthenium oxide with low surface area.

The specific capacitance values were used as response factor in the resolution of the 2² factorial design to quantify the effect of the variables, as shown in Table 3. The letter **I** corresponds to an estimate mean of every experiment. The main effects are represented by **C** (CA/EG) and **M** (CA/Ru). **C** × **M**

Table 3
Estimate of the preparation variables effects for the 2² factorial design

	Estimative (F g ⁻¹)
<i>I</i> (average)	18.0 ± 1.2
Main effects	
C (CA/EG)	-4.0 ± 2.3
M (CA/Ru)	-6.0 ± 2.3
Two-factors Interaction	
C × M	1.0 ± 2.3

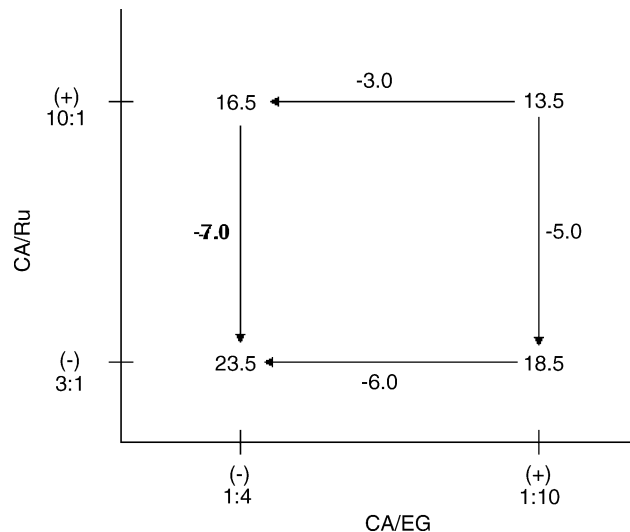


Fig. 2. Diagram of the variable effects.

corresponds to interaction effects of two variables. It is opportune to emphasize that the values shown in Table 3 are not the response values (property, in this case, specific capacitance), but the effect, positive or negative, produced on the material property when the variable is changed from the low level to the high level. The CA/Ru molar ratio is the most important effect which was -6.0 F g⁻¹ (±2.3 F g⁻¹). The negative sign indicates that the specific capacitance decreases when the amount of the metal in the resin decreases, i.e. the CA/Ru ratio was changed from 3:1 to 10:1. The CA/EG ratio effect in the capacitance is 4.0 (±2.3). Finally, the interaction of two variables is less significant than the experimental error indicating that this effect can be neglected.

A better visualization of the preparation variables effect on specific capacitance of the RuO₂ electrodes is shown in the geometric representation presented in Fig. 2. The rise of ruthenium precursor concentration leads to an increase of the electrodes specific capacitance, and this effect is more pronounced for more concentrated resin, with CA/EG = 1:4 (-7 versus -5). The increase of the CA amount in the polyester preparation also leads to an increase of the capacitance, and this effect is two times higher for the precursor resin with high metal content (CA/Ru = 3:1). The response obtained by factorial design 2² is in agreement with a previous paper [37], where the effect of the preparation variables on Nb₂O₅ thin films is investigated. In a general way, the increase in the electrochemical properties of the transition metal oxides prepared with this method is related to the increase of the polymerization degree of the precursor resulting in a long-chain polymer. Then, the mass transport during the calcination could be slower and the grain does not grow, leading to a high surface area sample.

3.2. Calcination temperature effect on RuO₂ properties

Due to the important influence of the calcination temperature on oxide electrochemistry properties observed to other systems, we decided to further study this variable.

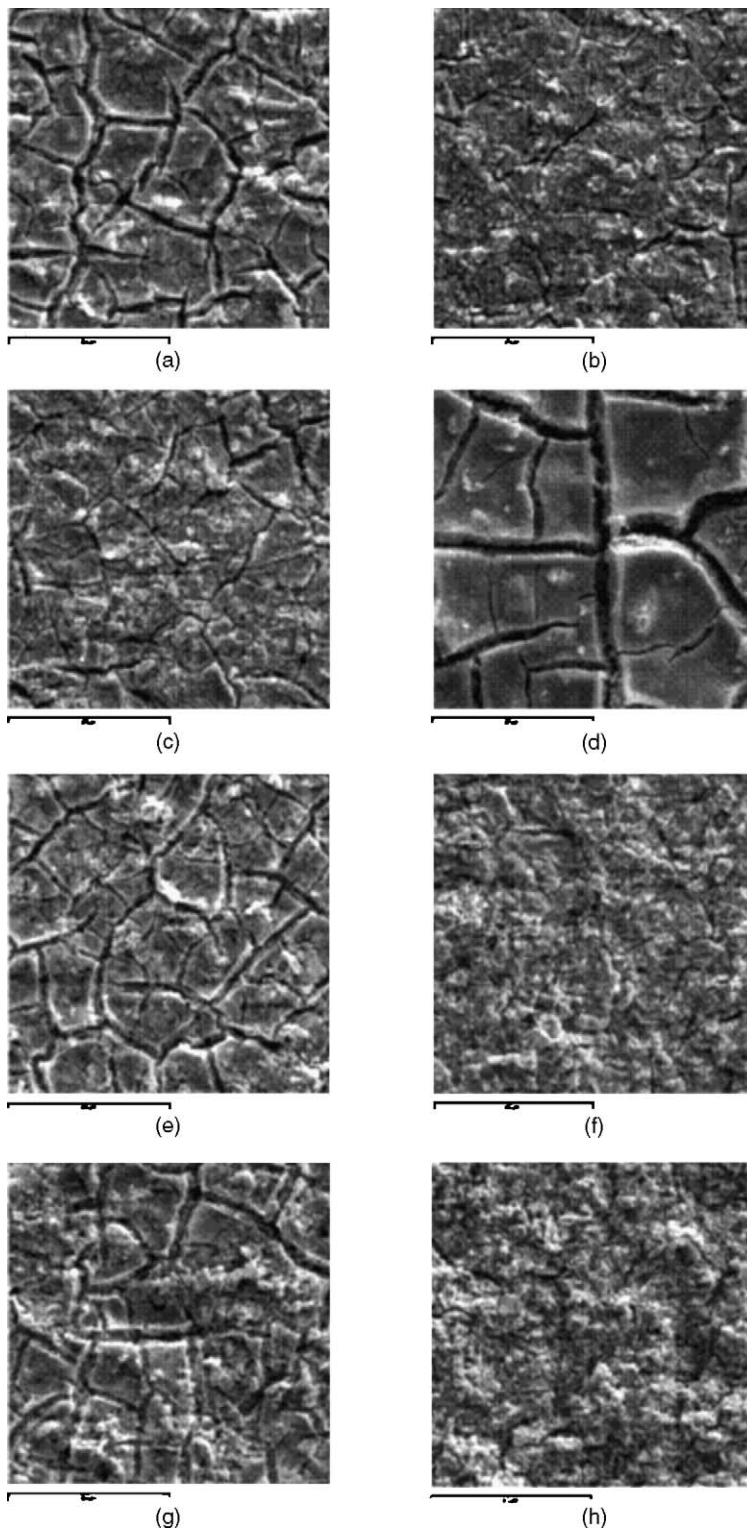


Fig. 3. Scanning electron micrographs of RuO₂ heat treated at: (a) 250 °C, (b) 300 °C, (c) 350 °C, (d) 400 °C, (e) 450 °C, (f) 500 °C, (g) 550 °C and (h) 600 °C. Magnification 1000 \times .

The morphologic analysis of the samples treated at different temperatures is shown in Fig. 3. Cracks are observed in the surface of the samples, and they become narrower as the temperature is increased, developing an apparently compact granular structure. These morphologic variations could be associated to

the decrease of the specific capacitance of the electrodes, as will be shown later.

Cyclic voltammograms of RuO₂ electrodes prepared at different temperatures are shown in Fig. 4. The voltammetric behavior is the same for all the samples. A decrease of current

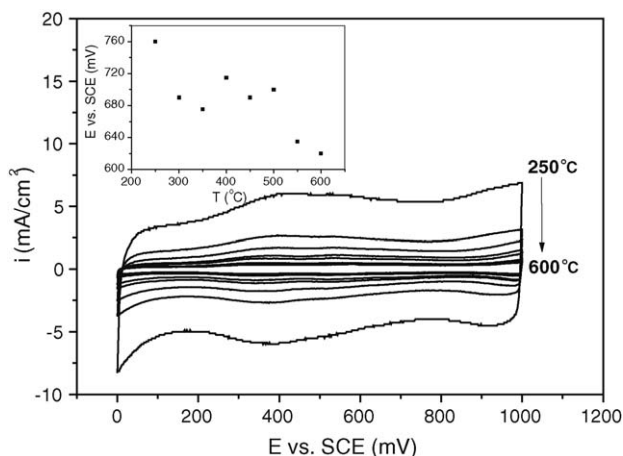


Fig. 4. Cyclic voltammograms of the RuO₂ electrodes prepared at different temperatures, 1.0 mol L⁻¹ H₂SO₄ solution and $v = 20 \text{ mV s}^{-1}$. The insert shows the open circuit potential as a function of the temperature preparation.

density of the redox process occurs as the calcination temperature is increased. This behavior was expected, since amorphous and hydrous electrodes prepared at low temperatures by sol-gel methods [8,9,11] presented the highest specific capacitance values that decrease drastically with the increase of the temperature. In the insert in Fig. 4, the variation of the open circuit potential (E_{ca}) as a function of the preparation temperature is shown. It is observed that E_{ca} decreases as the temperature increases. Literature data shown that RuO₂ monocrystals present E_{ca} around 0.65 V (versus HRE) in acid medium, while, polycrystalline electrodes obtained at 400 °C present E_{ca} of 0.94 V (versus HRE) [38]. According to Lodi et al. [39], this difference is related to the variation in the properties of the oxide surface. RuO₂ monocrystals are obtained at temperature and pressure conditions that lead to the formation of a material with perfect crystalline structure and free from impurities. On the other hand, polycrystalline electrodes are obtained at temperatures around 400 °C and present polycrystalline structure with high defect density and/or impurity. For Ardizzone and Trasatti [29,38] changes in the E_{ca} value are associated to the presence of OH sites at the surface.

Since the specific capacitance is related to the voltammetric charge, which is a function of the active sites density, it is possible to establish a relationship between the capacitance and the temperature of heat treatment of the electrodes. The profile of the specific capacitance of the electrodes as a function of the calcination temperature is presented in Fig. 5. It is observed that the capacitance decreases with the increase of the temperature. Although it is not presented here, the charge of these electrodes exhibits a linear dependence with $v^{-1/2}$, characterizing a semi-infinite diffusion process.

Fig. 6 shows the effect of the temperature in the process of crystallization of RuO₂ powder. The peaks marked with (*) correspond to the pattern of tetragonal structure RuO₂ (JCPDS No. 21.1172). However, a great amount of metallic ruthenium was observed. A possible explanation for this fact can be related to the preparation method. The electrodes calcination process was accomplished in air. As this process begins on the sample

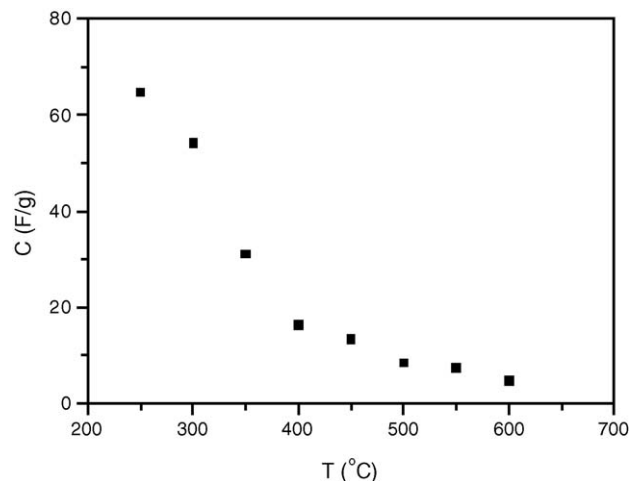


Fig. 5. Specific capacitance as a function of the temperature.

surface, owing to the oxygen availability, the oxygen partial pressure inside the sample could be insufficient to oxidize the organic portion to CO₂. Then, the CO that is formed could react with Ru ions reducing them to the metallic state. It is also observed that, to powder samples, the higher the heat treatment temperatures, the smaller the oxide surface area is. This decrease of the surface area occurs as a function of the increase of the crystallite size with the increase of the temperature of heat treatment. The grain size increases, and consequently, the active area exposed decreases, then the specific capacitance of the electrode decreases.

The largest values of specific capacitance presented were obtained by Zheng and co-workers [8,9] and Long et al. [11], 720 and 900 F g⁻¹, respectively. These oxides were prepared in powder form at low temperatures and the electrodes were manufactured with the use of the binders. In the study of the temperature effect accomplished by Zheng et al. [9], an abrupt decrease was observed in the capacitance value when the oxide was treated at 200 °C. Besides, some researchers proposed that although the amorphous oxide possesses high capacity of charge

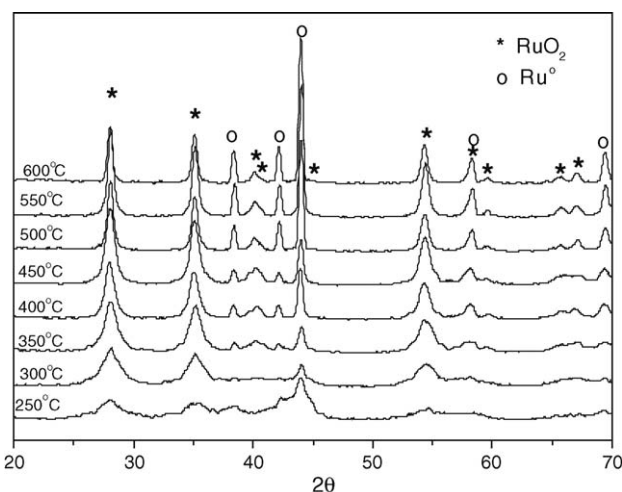


Fig. 6. XRD patterns of the powder RuO₂ prepared at different temperatures for 1 h.

storage, the efficiency decreases quickly with the cycling of the electrode. It is important to point out that the comparison of the results shown in the literature with the results herein presented cannot be done since we worked with films and generally the literature data refer to compacted particle samples, which leads to large surface area. We prepared electrodes at temperatures lower than the 250 °C, nevertheless the deposits show low adherence and impurities from the partial calcination of the organic portion.

4. Conclusions

The use of the factorial design leads to a quick optimization of the oxide synthesis conditions. The influence of the precursor resin composition on the RuO₂ electrodes capacitive property is evident. CA/Ru molar ratio was the variable that showed higher effect and the best results were obtained with electrodes carried out with resin content Ru:CA:EG in ratio 1:3:12.

The temperature of heat treatment is an important effect on the RuO₂ capacitance. The higher the temperature of heat treatment, the lower the specific capacitance is. The maximum specific capacitance value was of 74 F g⁻¹ for the sample treated at 250 °C.

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