



Carbon – Science and Technology

ISSN 0974 – 0546

<http://www.applied-science-innovations.com>

ARTICLE

Received : 05/11/2009, Accepted : 15/12/2009

Electrochemical characterization of ruthenium oxide on carbon paste electrodes in acid system.

O. Martinez-Alvarez, M. Miranda-Hernandez

Dpto. Materiales Solares, Centro de Investigación en Energía, Universidad Nacional Autónoma de México, Apartado Postal 34, Temixco, Mor. 62580, México.

A comparative study of the electrochemical behavior of ruthenium in the electrolytic system 10^{-2} M RuCl_3 / 1 M HClO_4 at $\text{pH}=1$ was carried out using carbon paste electrodes prepared with carbon black (nanostructured). Measurements of absorbance in the region of visible spectrum showed that the electroactive species is an oxy aquocomplex $[\text{RuO}(\text{H}_2\text{O})_4]^{2+}$. Studies of cyclic voltammetry of reversed potentials (E_r) allowed for the description of the oxidation processes involved. The oxidation process explained the electrochemical formation of a ruthenium oxide (RuO_4) which appeared with a defined potential value. This permitted its electrochemical growth on the paste electrodes. Capacitive behavior of this oxide in the system 1 M HClO_4 was also characterized and its specific capacitance (F/g) was evaluated applying a current pulse. The obtained specific capacitance is of 120 Fg^{-1} .

1. Introduction : Due to its electrocatalytic properties, metallic ruthenium and some of its compounds are used as materials for electrodes in development and design of generation and energy storage devices (fuel cells and electrochemical capacitors) [1-3]. Recently, electrode materials with small quantities of metallic particles or particles of oxides of this metal have been prepared, supported by different matrices (such as carbon). They are an interesting alternative that benefits different electrocatalytic processes [4-6], where even in small quantities, ruthenium shows its electrocatalytic capacity, a characteristic associated with successive interfacial processes of charge transference, where the metal participates directly. This fact deserves special attention, since it is known that ruthenium is a very active metal, presenting eight oxidation states and with each of them stable aqueous electrolyte and organic compounds have been reported [5-9]. Specifically, the use of ruthenium in electrocatalytic processes or for charge storage require great stability of the electrode material associated with the real identity of the ruthenium electroactive species incorporated into the matrix. Although studies of chemical characterization of these species have been reported, little is known about ruthenium electrochemical activity. Due to the great interest on ruthenium supported on carbon materials and considering the limited electrochemical studies reported, this work presents an electrochemical study of ruthenium on carbon paste electrodes (CPE) prepared with different materials of nanostructured carbon black, using an electrolytic bath of 10^{-2} M RuCl_3 /1M HClO_4 at $\text{pH}=1$. It

is important to mention that several characterizations and evaluation studies on carbon electrodes (paste or vitreous carbon), with or without electrochemically grown metallic particles, for use in electrocatalytic processes, electrochemical storage of hydrogen or as electrochemical capacitors have been reported in our work group [10-13]. Besides its low cost and easy preparation, CPEs present great versatility of application because they are malleable and it is possible to adapt them to any physical current collector configuration; a fact that allows us to propose them as the electrode material for this study.

2. Experimental : Electrochemical measurements were carried out with a GAMRY / PC14 / 300 Potentiostat / Galvanostat / 2RA750 equipment, in a conventional three electrode cell. A graphite bar was the counter electrode, and a saturated calomel electrode was used as reference electrode (+0.215 V vs. NHE). These electrodes were kept in separate compartments, and a carbon paste electrode was the working electrode. The paste was prepared with silicon oil (Aldrich) and nanostructured carbon (Columbian Chemicals, Co.). The sample corresponded to two types of carbon (nCB₁, nCB₂): 16, 8 nm mean particle size, 246, 545 m²/g BET-surface areas. Carbon paste electrodes were prepared with a relation in weight of carbon material and silicon oil of 32:68% (nCB₁): and 47:53% (nCB₂). The paste (0.15g was always used for all electrodes) was supported in a 0.2-mm thickness Teflon ring (0.62 cm²) with stainless steel as the back contact. The electrolytic

system was 10^{-2} M $\text{RuCl}_3/1\text{M HClO}_4$ to $\text{pH}=1$. All solutions were prepared with deionized water (ultra-pure Milli-Q), previously bubbled with N_2 for 30 min. Cyclic voltammetry was used to describe the potential range of work. The initial rest potential ($E_{i=0}$) was increased in a positive direction up to various potentials limits (E_λ), where the sweep direction was reversed. Ruthenium oxide was formed on the carbon paste electrodes in 10^{-2} M $\text{RuCl}_3/1\text{M HClO}_4$ at $\text{pH}=1$, by 25 cycles of potential sweeping at a rate of 20 mV/s, in a potential range from 0.55 to 1.3 V vs. SCE. The capacitance behavior was evaluated in 1M HClO_4 , using cyclic voltammetry and current constant pulses.

3. Results and Discussion : It has been reported that aqueous solutions of ruthenium salts present certain instability due to the chemical activity of the metal, which shows different oxidation states. Electrolytic baths of ruthenium require a period of time to stabilize the compound in the more stable oxidation state, under the established experimental conditions. A method commonly used and reported to identify the species of ruthenium is to measure the absorbance in the UV-Visible spectrum; several species have been identified and reported by this method [14-16]. In order to establish the electroactive species present in the electrolytic system 10^{-2} M $\text{RuCl}_3/1\text{M HClO}_4$ at $\text{pH}=1$, absorbance measures were performed in the visible region of the spectrum immediately after preparing the electrolytic bath and during a certain period of time, until no more changes in the measurement were observed. Figure 1 shows the absorption spectra in the electrolytic system 10^{-2} M $\text{RuCl}_3/1\text{M HClO}_4$ at $\text{pH}=1$, obtained during the first two days, as well as the absorbance spectrum of water and that of the supported electrolyte, 1M HClO_4 (both marked in the figure), for comparison. The spectrum obtained starting the third day is also showed (Figure 1b).

The response between the first two days was different, as can be observed in figure 1 (Figure 1a). Starting the third day and on, until the last day, the response became stable and presented two maximums: I (310 nm) and II (490 nm). This indicated that the dissolution had become stabilized and therefore the more stable chemical species had been formed (Figure 1b). Several spectrophotometric studies of ruthenium compounds, with similar spectra to that, showed in the figure 1b have been reported in literature. This response corresponds to $[\text{RuO}(\text{H}_2\text{O})_4]^{2+}$. Reactions 1 and 2 have been proposed using ruthenium salt [14-18]. The presence of species Ru(IV) in perchloric acid has been acknowledged in other studies carried out by several authors [16,19,20]; therefore, $[\text{RuO}(\text{H}_2\text{O})_4]^{2+}$ was considered the electroactive species in the system 1M HClO_4 .

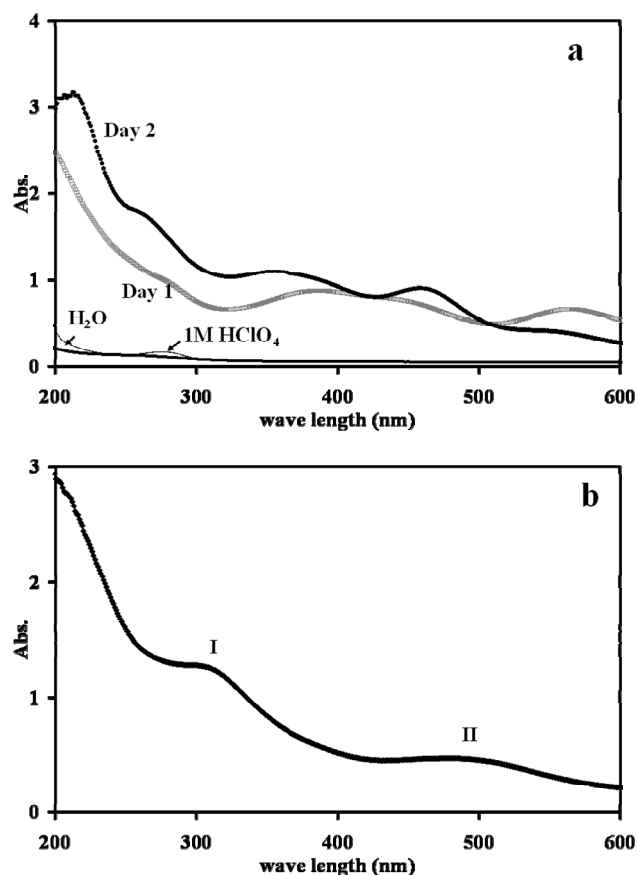
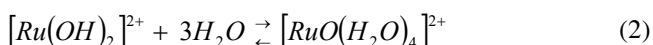
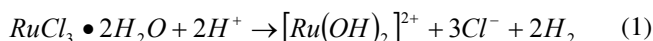


Figure 1. Absorption spectra of the system 10^{-2} M $\text{RuCl}_3/1\text{M HClO}_4$ at $\text{pH}=1$, obtained during thirteen days and comparison absorbance spectra of water and the support electrolyte 1M HClO_4 , on the first and second days (a), and final response (b).

3.1. Study of the oxidation processes :

Figure 2 shows the voltammetry response obtained on the electrodes (a) nCB_1 and (b) nCB_2 , at a scan rate of 20 mV/s in the system 10^{-2} M $\text{RuCl}_3/1\text{M HClO}_4$ at $\text{pH}=1$, when different reversed potentials values (E_λ) were applied. The scan started in a positive direction with respect to the system potential at rest ($E_{i=0}$). When considering the interval $0.9 \leq E_\lambda \leq 1.1\text{V}$ (in both figures), a formation of an oxidation process O' ($E = 0.95\text{V}$) was observed, and when the sweep direction was reversed, a reduction process R' ($E = 0.83\text{V}$) appeared. Then, it is worth mentioning that when the sweep was performed (in any of the two studied directions), one of the two processes O' or R' appeared at very similar potential values (these responses are not presented). Nevertheless, independently of the initial sweep direction, either O' or R' were present, a reason to say that the electrolytic bath contains the pair redox: Ruthenium (IV)/(III) as the initial chemical species of the system 10^{-2} M $\text{RuCl}_3/1\text{M HClO}_4$ at $\text{pH}=1$.

On the other hand, figure 3 shows the comparison between voltammetry responses of electrodes nCB_1 and nCB_2 , corresponding to intervals $0.95 \leq E_\lambda \leq 1.1\text{V}$ (a) and $1.2 \leq E_\lambda \leq 1.3\text{V}$ (b).

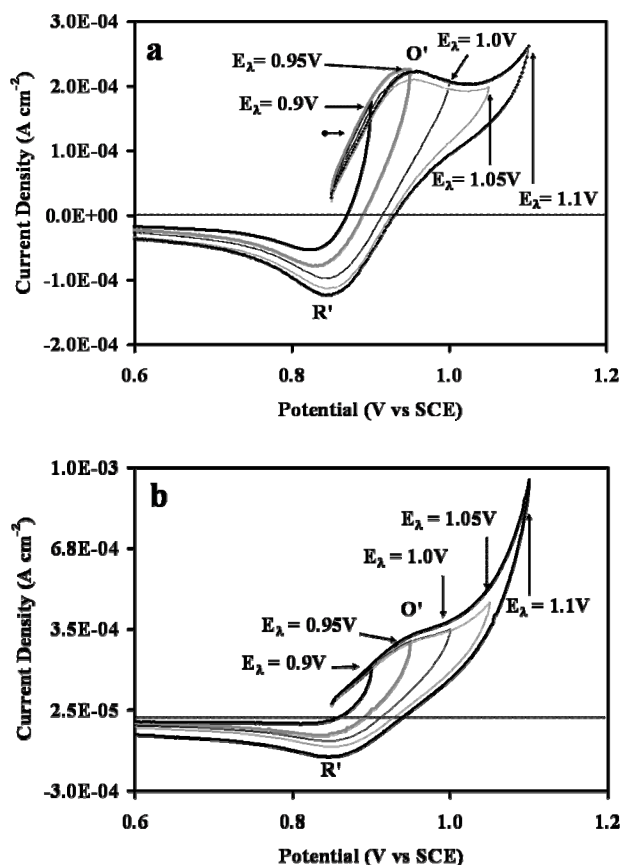


Figure 2. Voltammetry response obtained on electrode nCB₁ in the system 10⁻²M RuCl₃/1M HClO₄ at pH=1, at scan rate of 20 mV/s, with increases of 50 mV. The potential sweeping started in a positive direction with respect to the potential of null current, and ended at different E_λ.

In figure 3a, processes O' and R', corresponding to electrodes nCB₁ and nCB₂, practically appearing at the same potential (E = 0.95 and 0.83V respectively) can be observed. In figure 3b, a sudden increase of current in the limit of potential can be observed. This response was characteristic of each electrode, being nCB₂ the one that showed the greater magnitude of current. It is important to mention that the process O'₁ (E = 1.25V) appeared only in electrode nCB₁; nevertheless, when the sweep direction was reversed the reduction process R'₁ occurred (in both electrodes). Even though in nCB₂ a well defined process of good oxidation did not happen, the fact that R'₁ appeared indicates the possibility of some reduced species of ruthenium present.

Considering the values of potential where oxide O'₁ appeared (nCB₁) in our study and comparing them with reactions reported in literature, it is possible to say that O'₁ can be associated to RuO₄, which forms from the electroactive species, as reactions (3) and (4) show [1,14, 21-25]:

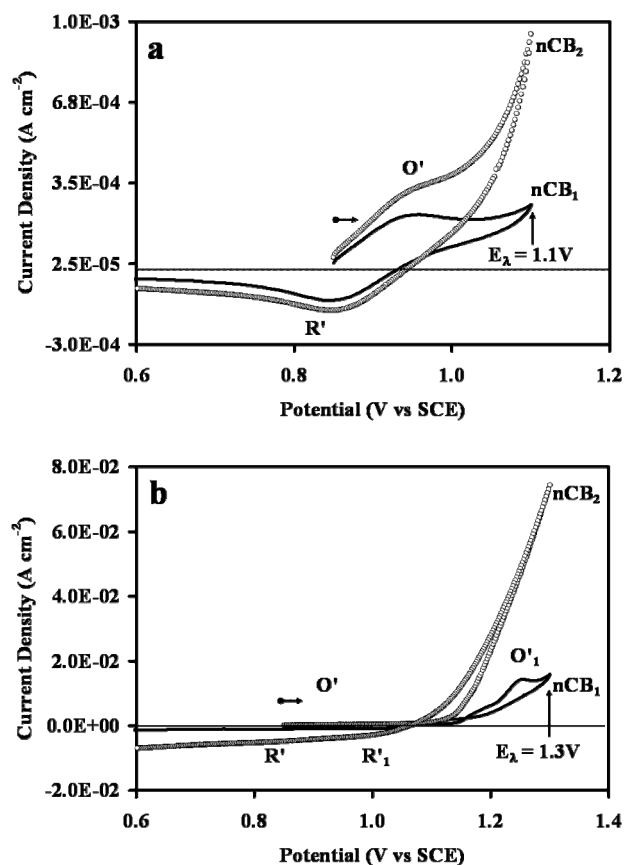


Figure 3. Comparison of the voltammetry response corresponding to electrodes nCB₁ and nCB₂ obtained in the system 10⁻²M RuCl₃/1M HClO₄ at pH=1, at scan rate of 20 mV/s, in different intervals of potential.

It is important to mention that Kötz [22, 26] and Lam [27] associate the formation of RuO₄ with a process of evolution of O₂ on the electrode material prior or parallel to the oxidation reaction of the electrolyte; a fact that is reflected in the voltammetry response shown in figure 3, where at the limit of potential (1.3 V) there is a sudden increase of current associated to the evolution of O₂ in such a way that in these electrodes the formation of RuO₄ is possible. The electrochemical formation of ruthenium oxide was carried out by voltammetry, applying a potential sweeping during 25 successive cycles in the range 0.55 to 1.3 V vs. SCE, at 20 mV/s, in the system 10⁻²M RuCl₃/1M HClO₄ at pH=1. Figure 4 shows the responses obtained when the previously described conditions were applied.

It is important to notice in figure 4 that the current response increases with the number of cycles in both electrodes. It has been reported that oxide formation of ruthenium by cyclic voltammetry, where metallic ruthenium is used as electrode material, shows a progressive increase in its response with cycling, which indicates a greater amount of oxide generated in the electrode [5]. In figure 4a (electrode nCB₁), the R'₁ (E = 0.95V) process previously described, which represents the reduction of ruthenium oxide formed in the surface of the electrode keeps manifesting, whereas in figure 4b (electrode nCB₂) this process (R'₁) disappears with cycling. Generally, the response is very different from that

shown in electrode nCB₁. In electrode (nCB₂), for instance, a strong contribution of the oxidation process in the electrolytic media is happening very close to the limit 1.3 V, as shown in figure 4, where the current density suddenly increases.

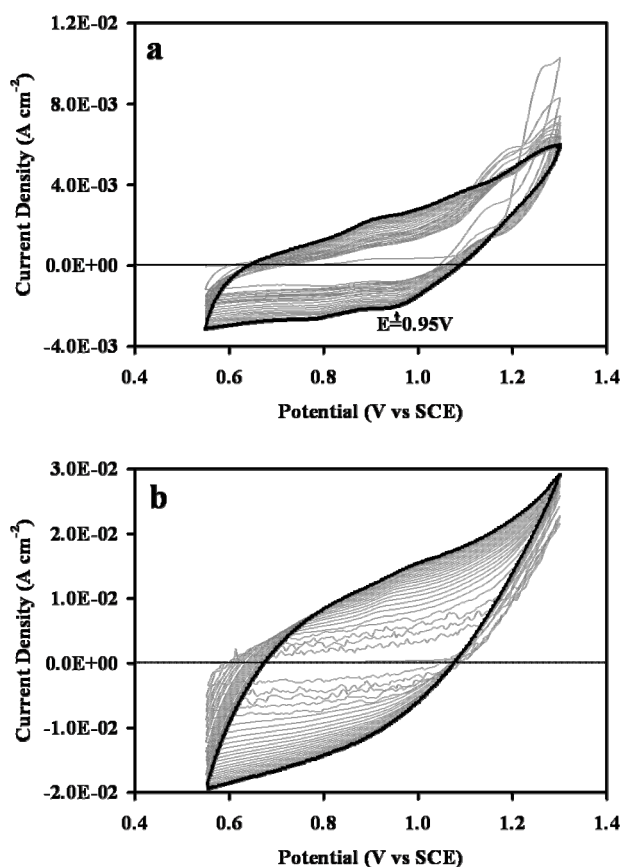


Figure 4. Voltammetry response corresponding to ruthenium oxide growth in electrodes nCB₁ (a) and nCB₂ (b), when applying 25 successive cycles at scan rate of 20 mV/s in the system 10⁻²M RuCl₃/1M HClO₄ at pH=1, at the potential range 0.55 to 1.3 V, and emphasizing the last cycle (black line).

Comparing both responses in figure 4 it can be seen that the current magnitude presents the following tendency: nCB₁<nCB₂; the amount of charge associated to the amount of oxide mass is expected to follow the same tendency.

On the other hand, the amount of ruthenium oxide formed on the electrodes was estimated using Faraday Law; that is, by evaluating the area under the curve of the voltammetry response corresponding to the formation of this oxide (25 successive cycles), to obtain charge (Q). In this way the mass in the CPE's obtained from nanostructured carbon, associated with ruthenium was (nCB₁mox) = 0.297 mg and for the other electrode (nCB₂mox) = 1.23 mg.

3.2 Characterization of capacitive behavior of ruthenium oxides :

Characterization of capacitive behavior of ruthenium oxides/CPE was carried out by voltammetry technique, at a

scan rate of 20 mV/s in the potential range -0.3 to 0.8V vs. SCE in 1M HClO₄. Figure 5 shows the comparison of voltammetry response corresponding to 25 successive cycles of sweeping, for each one of the electrodes nCB₁ (a) and nCB₂ (b), without (i) and with ruthenium oxide previously grown in the range of 0.55 to 1.3 V (ii). Figure 5c shows the comparison of responses obtained in the last cycle (cycle 25) corresponding to electrodes nCB₁ (ii) and nCB₂ (iii) with ruthenium oxide, and without ruthenium oxide (i).

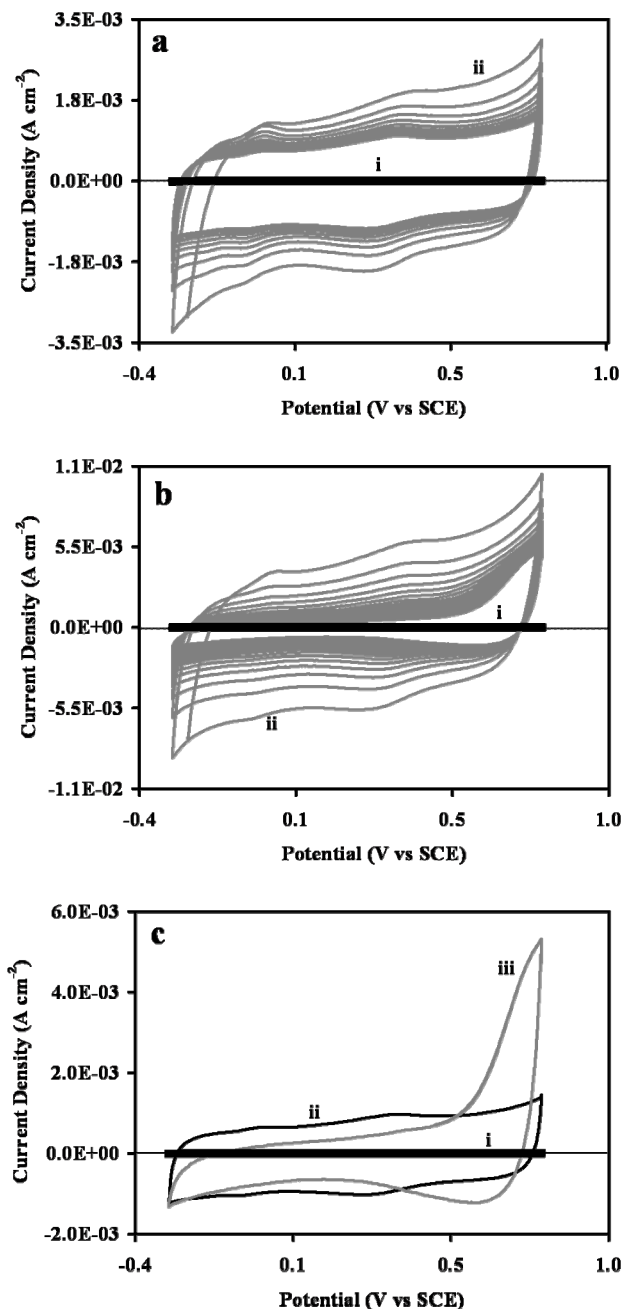
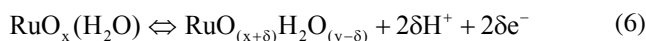
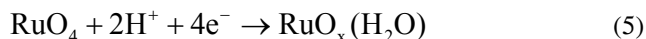


Figure 5. Comparison of voltammetry response corresponding to 25 successive cycles obtained in electrodes nCB₁ (a) and nCB₂ (b), without (i) and with ruthenium oxide previously grown, in the range 0.55 to 1.3 V vs. SCE (ii). The response obtained in the last cycle (cycle 25) in both electrodes is also shown (c).

Figure 5a, and b show that the electrodes with ruthenium oxide (ii) have a current density greater than the electrodes without oxide (i). Generally, both electrodes present a lower current in the first cycles of sweeping and later they become stabilized at a certain cycle for each electrode. On the other hand, it can be observed in figure 5c that for electrode nCB₁ (ii) the response of capacitive behavior is present during the 25 successive cycles, while electrode nCB₂ (iii) shows a very different response, that is, it loses the typical form of a charge cumulative process. This result is quite interesting since it has been reported that this accumulation is directly proportional to the BET area; i.e., the greater the area, the greater the charge storage. In this case, it does not happen in that way and this electrode is discarded for charge storage.

With respect to the pseudocapacitive behavior of electrode nCB₁, two current shoulders can be seen between 0.3 and 0.35 V, a characteristic which has been reported widely as the associated response with the charge/discharge mechanism of ruthenium oxides and the interaction with the H⁺ of electrolytic media [1, 7, 28-31] which is represented by the following reactions:



Reaction (5) shows the interfacial transformation of Ru(VIII) to Ru(IV) which is necessary to induce the charge/discharge process. Later, in reaction (6) the charge/discharge route appears as the well-known proton/electron mechanism, where the electrolyte diffusion of H⁺ is indispensable. In order to show if a diffusive process is present in the voltammetry response, a study at different scan rates, from 20 to 300 mV/s was carried out. Figure 6 shows the corresponding results to electrode nCB₁, where an increase of density in current can be observed as the scan rate increases. Also, the response form does not change, which indicates that the charge/discharge process through the proton/electron mechanism (pseudocapacitive) manifests in this material. Relation I_p vs. $v^{1/2}$ is linear, which indicates a diffusion process in which H⁺ is involved.

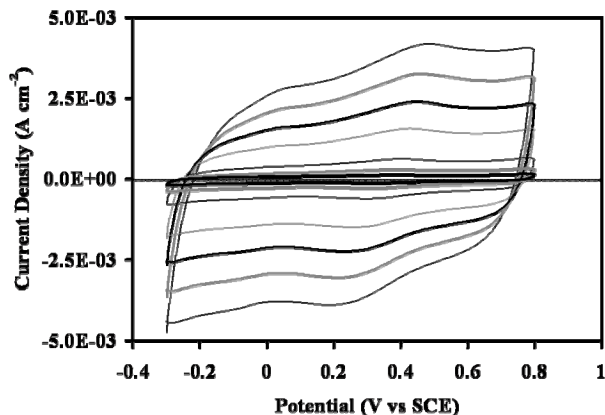


Figure 6. Voltammetry response corresponding to electrode nCB₁ at different scan rates with ruthenium oxide.

3.3 Evaluation of charge/discharge in CPE with ruthenium oxide :

The charge/discharge process in the system 1M HClO₄ was evaluated applying a double current pulse during 100s by 50 consecutive cycles in the electrode nCB₁ with ruthenium oxide grown electrochemically. The current magnitude was selected considering the voltammetry response in figure 5, which was $I = \pm 5 \times 10^{-4}$ A. Figure 7a shows the response potential vs. time obtained during the current pulse applied to nCB₁. Figure 7b shows the specific capacitance based on the number of cycles obtained in the system 1M HClO₄, evaluated from the chronopotentiometry data.

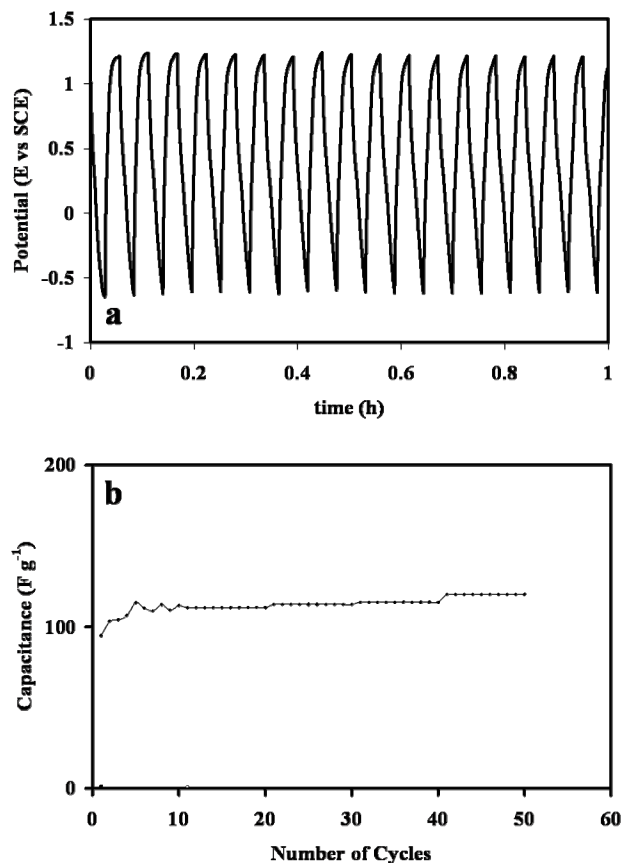


Figure 7. Response potential vs. time (a) corresponding to the first cycles after applying a double current pulse $\pm 5 \times 10^{-4}$ A to electrode nCB₁. Specific capacitance, based on the number of cycles, evaluated from the chronopotentiometry data is also shown (b).

4. Conclusion : The study of the system: 10⁻²M RuCl₃/1M HClO₄ at pH=1 by UV-Visible allowed to describe the oxy aquocomplex $[\text{RuO}(\text{H}_2\text{O})_4]^{2+}$ as the electroactive species in the system. Considering this electroactive specie, the oxidization process described the formation of one oxide RuO₄, which forms from RuO₂•H₂O, through the proposed mechanism. This oxide was grown on carbon paste electrodes, and its capacitive behavior and amount of charge stored were evaluated in the 1M HClO₄ system. The results obtained here are quite interesting because the hypothesis that to a greater BET

area, greater charge storage was not fulfilled in our case; the material with smaller BET area behaved better and the other one lost all its capacitive behavior. On the other hand, the obtained capacitance value is similar to the one reported in literature. This fact allows proposing the acid system as an alternative for the growth and formation of ruthenium oxide.

Acknowledgments :

This work was financially supported by DGAPA-UNAM (No. IN110506-3), Proyecto Universitario de Nanotecnología-UNAM (PUNTA) and CONACYT. O. Martínez-Alvarez, acknowledge CONACyT for scholarship.

References :

- [1] B. E. Conway, *Electrochemical Supercapacitors*, Kluwer Academic Publishers/Plenum Press, New York, 1999.
- [2] B. E. Conway, *J. Electrochem. Soc.*, 1991, 138, 1539-1548.
- [3] S. Sarangapani, B. V. Tilak, C. P. Chen, *J. Electrochem. Soc.*, 1996, 143, 3791-3799.
- [4] R. Kotz, M. Carlen, *Electrochim. Acta*, 2000, 45, 2483-2498.
- [5] W. Sugimoto, K. Yokoshima, Y. Murakami, Y. Takasu, *Electrochim. Acta*, 2006, 52, 1742-1748.
- [6] C. C. Wang, C. C. Hu, *Mater. Chem. Phys.*, 2004, 83, 289-297.
- [7] C. C. Hu, W. C. Chen and K. H. Chang, *J. Electrochem. Soc.*, 2004, 151, A281-A290.
- [8] T. Liu, W. G. Pell, B. E. Conway, *Electrochim. Acta*, 1997, 42, 3541-3552.
- [9] V. Pan Panic', T. Vidakovic', S. Gojkovic', A. Dekanski, S. Milonjic', B. Nikolic. *Electrochim. Acta*, 2003, 48, 3805-3813.
- [10] O. Martínez-Alvarez, M. Miranda-Hernández, *Carbon Sci. Tech.*, 2008, 1, 30-38.
- [11] M. Miranda-Hernández, M. E. Rincón, I. González. *Carbon*, 2005, 43, 1961-1967
- [12] M. Miranda-Hernández, Marina E. Rincón. *J. Solid State Electrochem.*, 2005, 9, 646– 652
- [13] M. Miranda-Hernández and I. González. *J. Electrochem. Soc.*, 2004, 151, C220-C228.
- [14] E. A. Seddon, K. R. Seddon , *The chemistry of ruthenium*, Elsevier Science Publishers B. V. Amsterdam, The Netherlands, 1984.
- [15] F. P. Gortsema and J. W. Cobble, *J. Am. Chem. Soc.*, 1961, 83, 4317-4321.
- [16] R. M. Wallace and R. C. Propst, *J. Am. Chem. Soc.*, 1969, 91, 3779-3785.
- [17] A. Crown, A. Wieckowski, *Phys. Chem. Chem. Phys.*, 2001, 3, 3290-3296.
- [18] W. Chrzanowski, H. Kim and A. Wieckowsk, *Catal. Lett.*, 1998, 50, 69-75.
- [19] D. K. Atwood and T. de Vries, *J. Am. Chem. Soc.*, 1962, 84, 2659-2661.
- [20] L. W. Niedrach and A. D. Tevebaugh, *J. Am. Chem. Soc.*, 1951, 73, 2835-2837.
- [21] J. J. Jow, H. J. Lee, H. R. Chen, M. S. Wu, T. Y. Wei, *Electrochim. Acta*, 2007, 52, 2625-2633.
- [22] R. Kötz, S. Stucki, D. Scherson, D. M. Kolb, *J. Electroanal. Chem.*, 1984, 172, 211-219
- [23] M. Pourbaix, "Atlas of Electrochemical Equilibria: In Aqueous Solutions", Pergamon, London, 1966, p. 343.
- [24] A. J. Bard, R. Parson, *Standard Potentials in Aqueous Solution*, ISBN 824772911, 1985
- [25] Lj.M. Gajić-Krstajić, t. Lj. Trišović, N. V. Krstajić, *Corros. Sci.*, 2004, 46, 65-74.
- [26] R. Kötz, H. J. Lewerenz, S. Stucki, *J. Electrochem. Soc.*, 1983, 130, 825-829.
- [27] K.W. Lam, K.E. Jonson, D.D. Lee, *J. Electrochem. Soc.*, 1978, 74, 1069-1076.
- [28] J. P. Zheng, *Electrochem. Solid-State Lett.*, 1999, 2, 359-361.
- [29] J. Wen, Z. Zhou, *Materials Chemistry and Physics*, 2006, 98, 442-446.
- [30] C. C. Hu, M. J. Liu, K. H. Chang, *J. Power Sourc.*, 2007, 163, 1126-1131.
- [31] C. C. Hu, W. C. Chen, *Electrochim. Acta*, 2004, 49, 3469-3477.