

Influence of the coupling of IrO₂ and PtO_x on the charging / discharging process at the electrode / electrolytic solution interface

Kambiré Olló¹, Pohan Lemeyonouin Aliou Guillaume², Kouakou Yao Urbain¹, Kimou Kouakou Jocelin³, Koffi Konan Sylvestre³, Kouadio Kouakou Etienne³, and Ouattara Lassiné³

¹UFR Sciences et Technologies, Université de Man, BP 21 Man, Côte d'Ivoire

²UFR Sciences Biologiques, Université Peleforo Gon Coulibaly de Korhogo, BP 1328 Korhogo, Côte d'Ivoire

³Laboratoire de Chimie Physique, UFR SSMT, Université Félix Houphouët-Boigny de Cocody, Abidjan, 22 BP 582 Abidjan 22, Côte d'Ivoire

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ABSTRACT: This work aimed to determine the voltammetric charges at the electrode / electrolytic solution interface of the IrO₂, PtO_x and IrO₂-PtO_x electrodes. The scanning electron microscope characterization (SEM) showed the presence of the IrO₂ and PtO_x coating deposited on titanium supports. Also, this characterization revealed that the surface of the prepared electrodes is porous and rough. The cyclic voltammetry measurements allowed to show that the voltammetric charge is high at low scan rates. This result is due to the accessibility of the internal and external surfaces of prepared electrodes by electrolytic solution. In contrast, for the high scan rates, only the external (geometric) surface is in touch with the electrolyte. The voltammetric charge decreases when the pH of electrolyte increases. Regardless of the electrolytic solution the voltammetric charges increases in the order: PtO_x < IrO₂ < PtO_x-IrO₂. In the absence of free protons (KClO₄ and KOH medium), the electrolyte diffuses inside the pores of the deposit regardless of its composition. Thus, all our electrodes have a large number of internal active sites. This study revealed that the processes which take place at the electrode / electrolyte interface are complex. These processes depend on several factors including the composition of the deposit, the proton concentration, etc. The linear correlations between the total voltammetric charge (q^*_{tot}) and the total capacitance (C_{tot}) show that they can be used to represent the extension of the electrochemically active surface.

KEYWORDS: Voltammetric charge, capacitance, porosity, electrode, active sites.

1 INTRODUCTION

The electrodes with high electrocatalytic performances have brought significant improvements in wastewater treatment [1-3]. Among of these, iridium dioxide (IrO₂), a Dimensionally Stable Anode (DSA[®]), has attracted researchers' attention in the past decade [4-7]. This electrode is a well-known as having high chemical and physical stability. Commonly, IrO₂ electrode can be easily prepared by the thermal decomposition method [8-10]. Due to its high stability in the solution and low oxygen/chlorine evolution potential, IrO₂ electrode has been many applications [2, 11 and 12]. These properties make it to be a promising candidate in electrochemical supercapacitors research [13-15].

For understanding the electrocatalytic behaviour of IrO₂ electrode, the study of electrochemical surface properties is of fundamental importance. Cyclic voltammetry technique, is usually used for this investigation. This technical allow to determine the voltammetric charge (q^*) who reveal the reaction process to the electrode / electrolyte interfacial [16-18]. From literature, q^* can be influenced by scan rate of electrolyte on the electrodes and also by the temperature of the medium [19-22]. Indeed, some authors indicated that the influence of the scan rate to the voltammetric charge is due to the slow diffusion of protons within the coating of the electrode [17]. Besides, the increase in the voltammetric charge gradually as the temperature

increases has been explained by the increase of the amount of the active sites of the electrode. Also, by the increase of amount of the protons that were involved in the solid state surface redox process on the electrode surface [22].

When the DSA electrodes (IrO₂ and RuO₂) were used for wastewater treatment for example, authors coupled them to the platinum to perform a high degradation yield of the pollutants and have high timelife of the electrodes [12, 23-24]. But the investigation to a better understanding the charging/discharging mechanism of these coupled electrodes does not exist by our knowledge.

Thus, the development of new electrodes, the determination of the surface structure as well as the study of their electrochemical behavior through a simple voltammetric method motivated this work. Indeed, voltammetry is known as a technique providing surface information in the electrode / electrolyte interfacial processes. In this work, the electrodes of IrO₂, PtO_x and IrO₂-PtO_x (50 % molar ratio) will be prepared and characterized using voltammetric measurements.

2 MATERIAL AND METHODS

The electrodes used for this work were prepared from metal precursors. These precursors were prepared from H₂PtCl₆.6H₂O (Fluka) and H₂IrCl₆.6H₂O (Fluka). The precursors were diluted in isopropanol (Fluka). Then the electrodes were prepared by following the following procedure: (i) application of the precursor solution with a brush on the treated surface of the titanium support of dimension (1.6 cm x1, 6 cm x 0.5 cm), (ii) baking at 80 ° C for 10 minutes to evaporate the solvents, (iii) thermolysis in an oven at 400 ° C for 15 minutes, (iv) removal from the oven and cooling. The succession of operations going from (i) to (iv) constitutes the deposition protocol for one layer. In general, several layers have been applied in order to obtain the desired thickness. More than three sequential layers are always deposited to ensure good coverage of the substrate. The final step is calcination at 400 ° C for 1 hour in the oven. The electrodes prepared by this technique are the electrodes of IrO₂, PtO_x and IrO₂-PtO_x (50% by mole of each element). For each electrode, approximately 5 g / cm² is deposited.

The XPS analysis was carried out with a Kratos Axis-Ultra Spectrometer using a monochromatic Al K α X-Ray source, operated at 15 kV, and a pass energy of 20 eV.

The electrochemical measurements were carried out with an Autolab ECHOCHEMIE Potentiostat (PGSTAT 20) connected by interface to a computer. These measurements were carried out with an electrochemical cell with 3 electrodes. The working electrodes (WE) used are the prepared electrodes. The counter electrode (CE) was a platinum wire and the reference electrode (RE) was a saturated calomel electrode (SCE). To overcome the potential ohmic drop, the reference electrode was mounted in a luggin capillary and placed close to the working electrode by a distance of 1 mm. The apparent exposed area of the working electrode was 1 cm².

This study was performed at room temperature of 25 ° C.

3 RESULTS AND DISCUSSION

3.1 PHYSICAL CHARACTERIZATION OF THE PREPARED ELECTRODES

The characterization of the morphology of the sandblasted titanium support is presented in Figure 1a. This figure shows that the surface of the titanium is rough. This makes it possible to promote good adhesion of the catalytic deposit and better ohmic contact between the deposit and the titanium support [1].

The Scanning electron micrographs (SEM) of the surface of the prepared electrodes (IrO₂, PtO_x and IrO₂-PtO_x) are presented in photos 1b, 1c and 1d of Figure 1. Compared to the photo of figure 1.a, it appears that the different deposits completely cover the titanium substrate. The photo of the iridium oxide electrode shows several cracks and a few pores in accordance with the literature [25]. The cracks observed on the surface of iridium oxide occur during cooling of the deposit due to the mechanical stresses produced by the difference in the coefficients of thermal expansion of the substrate and the deposit. The platinum oxide electrode has a smooth, compact and almost homogeneous surface [12]. The coupled IrO₂-PtO_x electrode has a rough and compact surface due to the presence of platinum oxide on its surface. There are also small cracks that show the presence of iridium oxide on the surface of this electrode.

The figure 2 shows the XPSs of the prepared electrodes. On the XPS spectrum of pure platinum, we note the presence of three intense peaks at 70, 312 and 335 eV, which characterize the presence of platinum on titanium. Two very close peaks are observed at 218 and 224 eV. These two peaks would characterize the presence of platinum oxide. On the spectrum of the electrode (50 mol% of each element) in addition to the peaks observed at 70, 312 and 335 eV, characteristic of the presence

of platinum, we have peaks at 61, 296 and 494 eV. These three new peaks are also present on the spectrum of the pure iridium oxide electrode. They would be characteristic of the presence of iridium oxide. These results show the presence of deposits produced on the prepared electrodes.

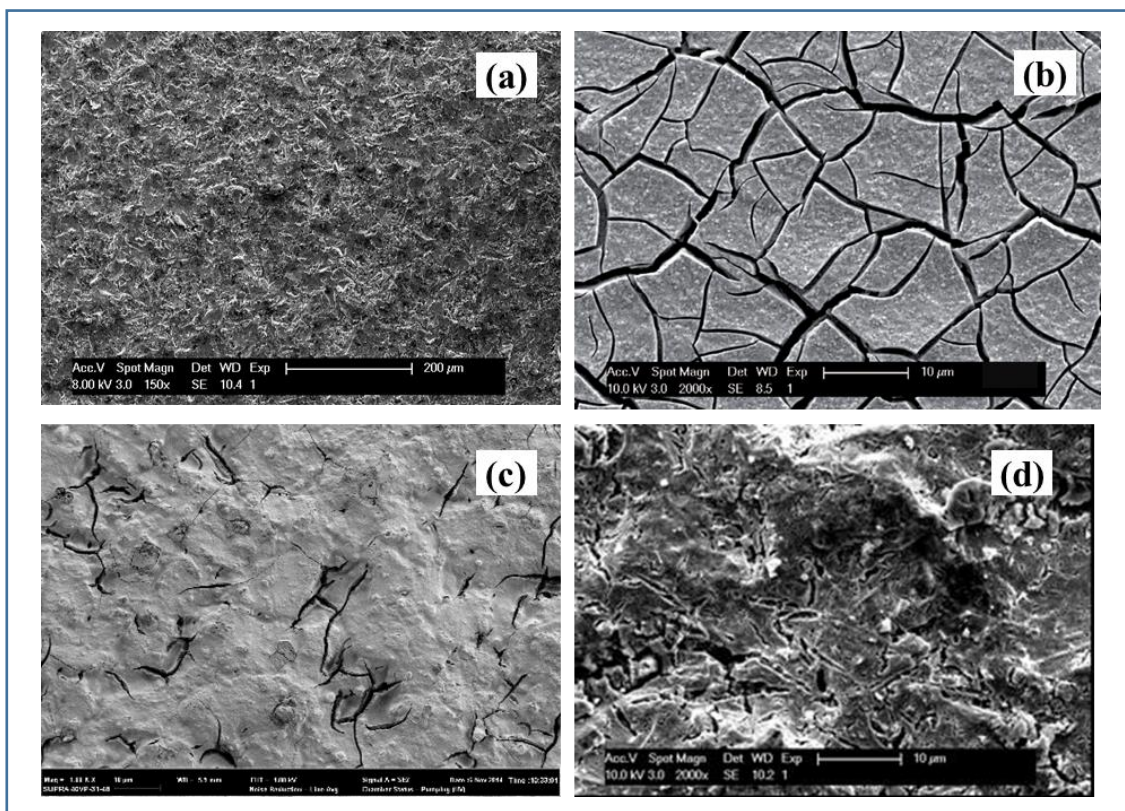


Fig. 1. Scanning electron micrographs of sandblasted titanium surface (a), IrO_2 , PtO_x (c) and $\text{IrO}_2\text{-PtO}_x$ (d)

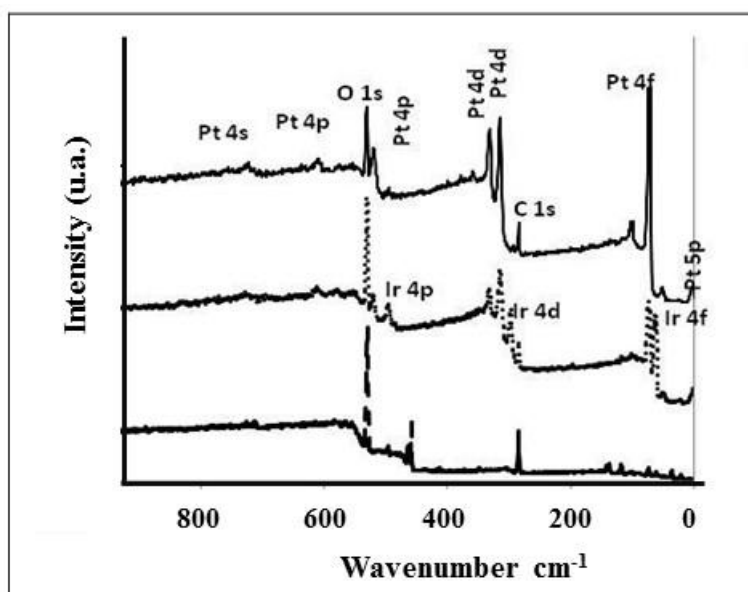


Fig. 2. XPS spectra of PtO_y , IrO_2 and $\text{IrO}_2\text{-PtO}_y$

3.2 ELECTROCHEMICAL CHARACTERIZATION OF THE ELECTRODES

shows the cyclic voltammograms of the prepared electrodes recorded in perchloric acid medium 0.1 M in the potential domain of -0.25 to 1.05 V / SCE. The PtO_x electrode has several regions. From -0.25 to 0 V / SCE, there are various peaks related to hydrogen adsorption and desorption [11, 26]. Then from 0 to 0.34 V / SCE, no peak is observed. From 0.34 V / SCE, an increase in the current in the forward potential scan is observed on the voltammogram [11, 26]. On the cyclic voltammogram recorded with the IrO₂ electrode, a voltammetric charge greater than that of platinum is observed. This result shows the presence of several active sites on the iridium dioxide electrode. The existence of these active sites is due to the presence on the electrode surface of cracks and a few pores.

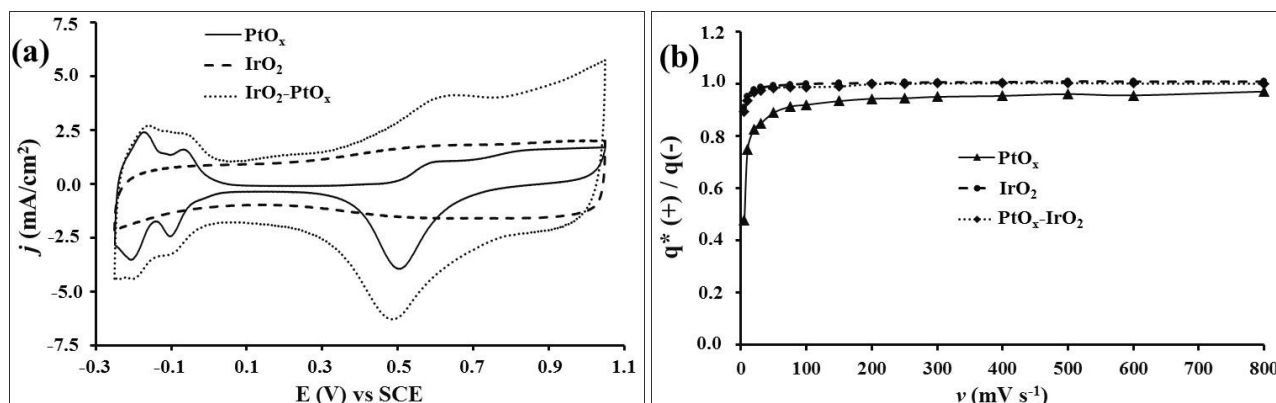


Fig. 3. (a) Cyclic voltammogram recorded on the electrodes in 0.1 M HClO₄ at 10 mV/s; (b) The ratio of voltammetric charges $|q^*(+)/q^*(-)|$ according to the scan rate

With the IrO₂-PtO_x electrode, a voltammetric charge greater than that of PtO_x and IrO₂ is observed. We also note that the curve is somewhat similar to that of platinum. This voltammogram shows that its surface is composed of platinum oxide and iridium dioxide. The addition of iridium oxide to platinum resulted in an electrode with a high voltammetric charge and therefore high active sites than that of platinum oxide. The voltammogram examen of the IrO₂ electrode (Figure 3a) revealed a quasi-symmetrical appearance in the potential domain explored. Nevertheless, below 0.4 V, there would be an increase in the cathodic current in absolute value in an acidic medium. To better appreciate these observations, the ratio of the voltammetric charges $q^*(+)/q^*(-)$ was calculated from the measurements carried out in 0.1 M HClO₄ medium for the electrodes prepared and presented in Figure 3b. With the IrO₂ electrode, it can be seen that at low potential scan rates, the cathodic charge is greater than the anodic charge. This result shows that at low potential scan rates, probably irreversible (slow) processes occurring at the electrode were not fully recovered during the anodic scan. However, the cathodic charge is nearly equal to the anode load for all high scan rates [24]. The curve $q^*(+)/q^*(-) = f(v)$ of the IrO₂-PtO_x electrode is identical to that of IrO₂. With the PtO_x electrode, the $q^*(+)/q^*(-)$ ratio is less than 1 regardless of the potential scan rate. This indicates that with this electrode probably irreversible (slow) processes occurring at the electrode and were not fully recovered during the anodic scan.

3.3 VOLTAMMETRIC CHARGE OF THE ELECTRODES

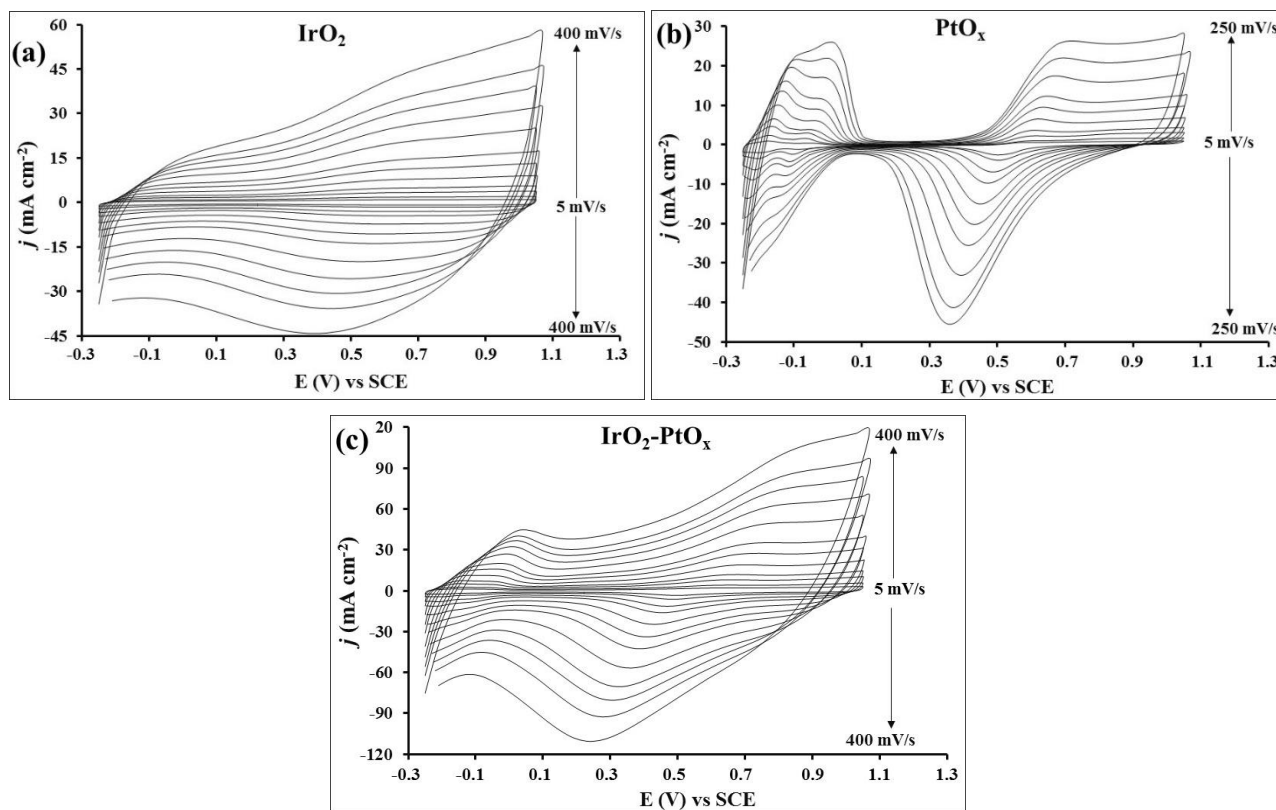


Fig. 4. Voltammograms carried out at different potential scan rates in 0.1 M HClO₄ on the prepared electrodes

The electrodes were scanned at several potential scan rates from -0.25 to 1.05 V / SCE. shows the results obtained. The general shape is always the same, regardless of the potential scan rate. However, for potential scan rates below 30 mV / s and above 150 mV / s, the appearance of the voltammograms changes significantly. This change is due to the relatively slow phenomena occurring at the electrode surface at low potential scan rates and the uncompensated ohmic drop in solution at high potential scan rates.

The electrochemical activity of the electrodes can be characterized by the voltammetric charge q^* of the voltammograms between the hydrogen evolution and the oxygen evolution. This charge is obtained by integrating the voltammograms surfaces. This integration between -0.25 and 1.05 V / SCE led to the determination of the total charge q presented as a function of the potential scan rate in figure 5. This figure shows that the voltammetric charge decreases rapidly at low potential scan rate and stabilizes at high potential scan rate regardless of the medium with the three electrodes. The voltammetric charge generally increases with the molar concentration of H⁺. Figure 5d shows the voltammetric charge of IrO₂-PtO_x electrode as a function of pH at several potential scan rates. This figure shows that the voltammetric charge decreases as the pH increases.

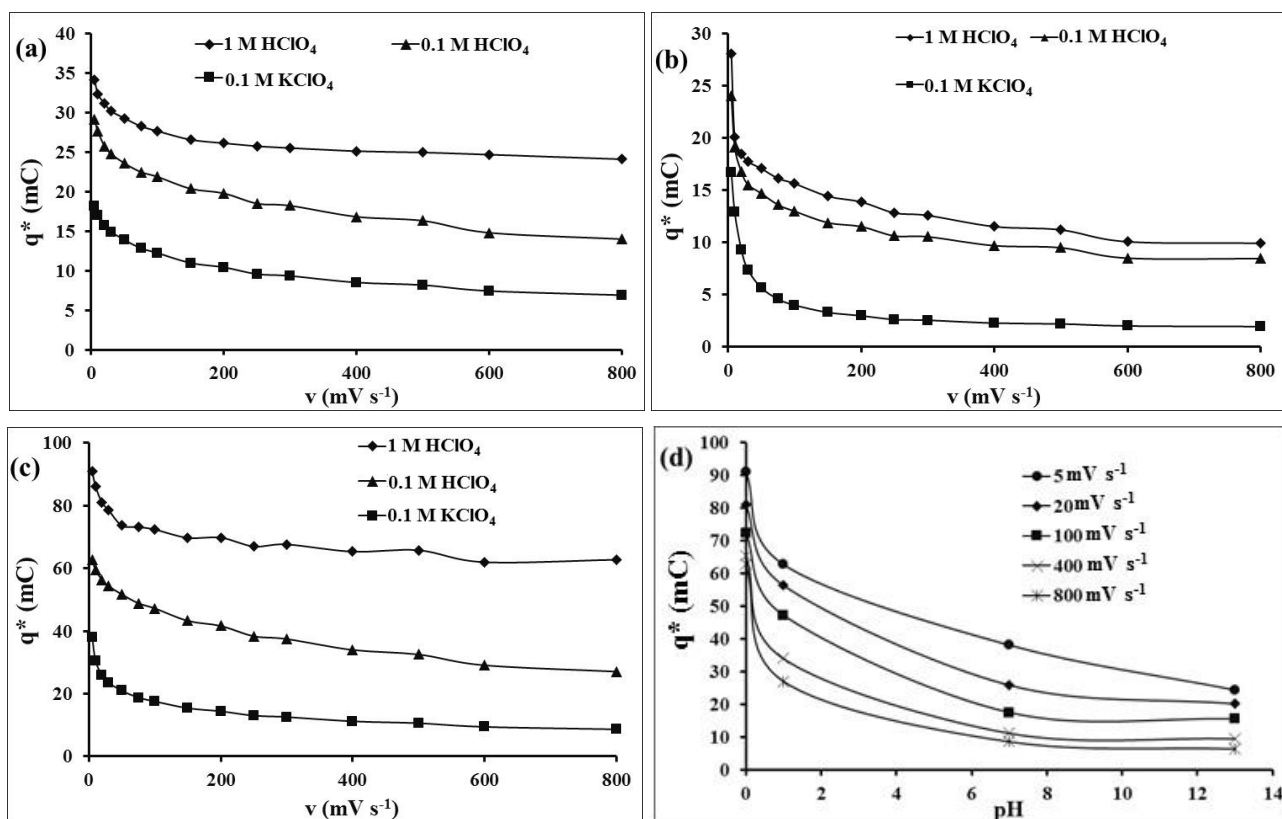


Fig. 5. (a-c) Influence of the supporting electrolyte on the voltammetric charge on the prepared electrodes (a: IrO₂; b: PtO_x; c: IrO₂-PtO_x); (d) Influence of the pH on the voltammetric charge at different potential scan rates

For all the electrodes, we notice a decrease in voltammetric charge as the scan rate increases. From 100 mV/s, this charge seems stable. The IrO₂-PtO_x electrode shows higher values of the voltammetric charge (q) than that observed for IrO₂ and PtO_x (Figure 6). This suggests an increase in the electroactive surface area promoted by the coupling of platinum oxide and iridium dioxide. On the other hand, with the PtO_x anode, the values of the voltammetric charge (q^*) are the lowest for a given potential scan rate.

At low potential scan rates, electrolyte penetrates through the pores of the deposit. The internal and external surfaces therefore become accessible. At high potential scan rates, only the external (geometric) surface is concerned.

To explain the behavior of the electrode in different media, we will use the approach proposed by Trasatti et al. [27, 28]. This approach is based on accessibility to electrode active sites. As the potential scan rate increases, the observed decrease in voltammetric charge is explained by the exclusion of the inner part of the electrode. This exclusion is due to the slow diffusion of protons at through the porous structure of the electrode, the voltammetric charge is therefore attributed to the surface redox couples according to faradic reactions [19, 29].

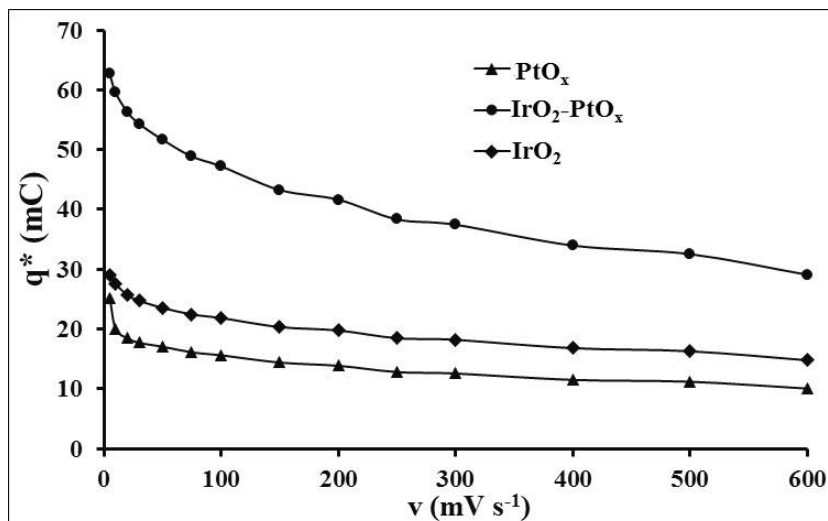


Fig. 6. Evolution of the voltammetric charge as a function of the potential scan rate of the electrodes prepared in 0.1 M HClO₄ medium

The values of voltammetric charges at extreme scan rate ($v = 0$ and $v = \text{infinity}$) are useful for understanding the mechanism of charge storage. Thus, the external charge of the electrode will be determined based on the model of Trasatti et al. [27, 28], equation 1 will allow the determination of the electrode external charge.

$$q^*(v) = q^*_{\text{ext}} + k_1 v^{-1/2} \quad (1)$$

With k_1 : constant; v : potential scan rate; $q^*(v)$: measured voltammetric charge; $q^*_{\text{ext}}(v)$: external voltammetric charge (surface).

According to equation 1, $q^*(v) = f(v^{-1/2})$ is an affine line. For an infinite scan rate corresponding to the extreme (largest) value of the potential scan rate, $q^*(v) = q^*_{\text{ext}}$ is the ordinate at the origin. To obtain the internal load, Trasatti and collaborators proposed another relationship.

$$\frac{1}{q^*(v)} = \frac{1}{q^*_{\text{tot}}} + k_2 v^{1/2} \quad (2)$$

With k_2 : constant; v : potential scan rate; $q^*(v)$: measured voltammetric charge; $q^*_{\text{tot}}(v)$: total voltammetric charge (surface + internal).

According to equation 2, $\frac{1}{q^*(v)} = f(v^{1/2})$ is a line representative of an affine function. For a scan rate corresponding to the zero potential scan rate (lower extreme) $\frac{1}{q^*(v)} = \frac{1}{q^*_{\text{tot}}}$ is the ordinate at the origin. Only the points which result from the high potential scan rates (50 mV / s to 250 mV / s) are used for the determination of the external charge [30]. On the other hand, the points corresponding to the low scan rate (from 5 mV / s to 30 mV / s) are used for the determination of the total charge [30].

From the measurements carried out, Figures 7a and 7b made it possible to determine the external and total charges of the IrO₂-PtO_x anode in 0.1 M HClO₄ medium. Thus, the external and total charges of the three electrodes were determined in different mediums. The results obtained are recorded in These values also made it possible to determine the internal charges and the porosity of the electrodes ($\varphi = q^*_{\text{int}} / q^*_{\text{tot}}$).

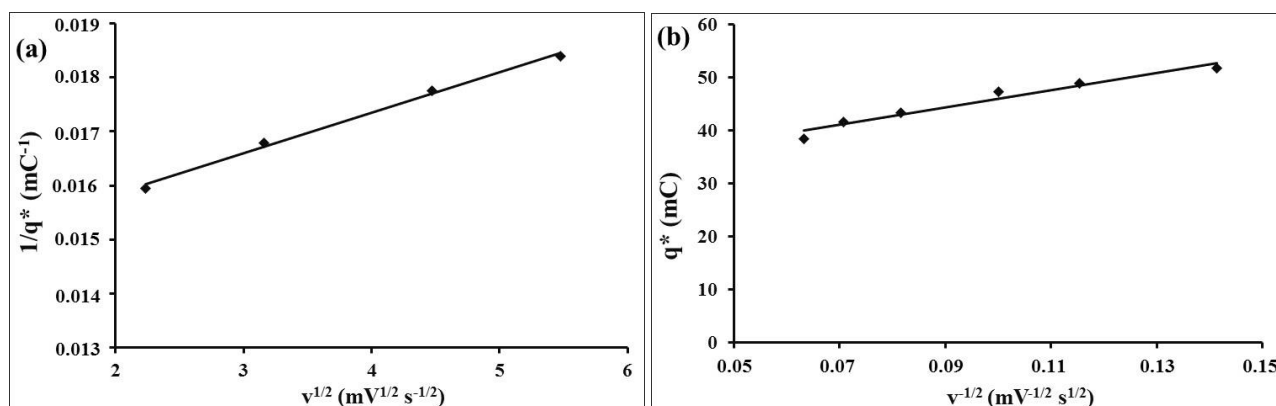


Fig. 7. Extrapolation curves for the determination of the total charge (a) and the external charge (b) in 0.1 M HClO₄, WE: IrO₂-PtO_x

The analysis of shows that the charge ratio q_{int}^* / q_{tot}^* is different from zero for all the electrodes and in all the solutions studied. This shows that the surface of the deposit is porous and rough. With the PtO_x electrode, ϕ shows the highest values. For high values of ϕ , the internal charge and therefore the internal surface of the pores which contributes to the total charge is important. In other words, at high ϕ , the number of internal active sites of the electrode which participate in the total charge is high because although the size of the pores decreases, the electrolyte manages to diffuse through these pores and consequently allows reactions between the ionic species of the electrolyte with the internal surface of the deposit. With IrO₂ and IrO₂-PtO_x, we have almost identical values of ϕ for a given electrolyte.

In the KClO₄ and KOH medium, the porosity value remains high for all the electrodes. From these observations, it is possible to think that the surface redox processes, the proton concentration, the composition of the deposit, influence the capacitive phenomena. In fact, in the absence of free protons, the solution diffuses inside the pores of the deposit regardless of its composition and suggests that all the electrodes have a large number of internal active sites. Whereas the behavior of the electrode changes when the medium is strongly acidic. In these media, surface reactions influence capacitive phenomena.

Tableau 1. Extrapolated values of charges for electrodes prepared in different media

	Electrodes	IrO ₂	PtO _x -IrO ₂	PtO _x
1 M HClO ₄	q_{tot}^* (mC)	37.04	102.04	46.30
	q_{ext}^* (mC)	22.86	63.40	7.77
	q_{int}^* (mC)	14.18	38.64	38.53
	ϕ	0.38	0.38	0.83
0.1 M HClO ₄	q_{tot}^* (mC)	33.00	69.93	31.95
	q_{ext}^* (mC)	15.15	29.55	10.04
	q_{int}^* (mC)	17.85	40.38	21.91
	ϕ	0.54	0.58	0.69
0.1 M KClO ₄	q_{tot}^* (mC)	21.19	61.73	19.50
	q_{ext}^* (mC)	6.50	7.07	0.30
	q_{int}^* (mC)	14.69	54.66	19.20
	ϕ	0.69	0.88	0.98

3.4 CAPACITANCE

From the curves $i = f(E)$ the capacitances were determined by normalizing the current by the potential scan rate and by the geometric surface. shows the results obtained. By normalizing the current by the potential scan rate and the geometric surface of the electrode, the capacitive effect is highlighted. This makes it possible to better compare the voltammograms at the different potential scan rates. The normalized curves show that the capacitance is not constant throughout the potential domain explored. It depends on the potential and is influenced by surface processes or reactions, namely surface redox reactions and reactions between surface and species in solution.

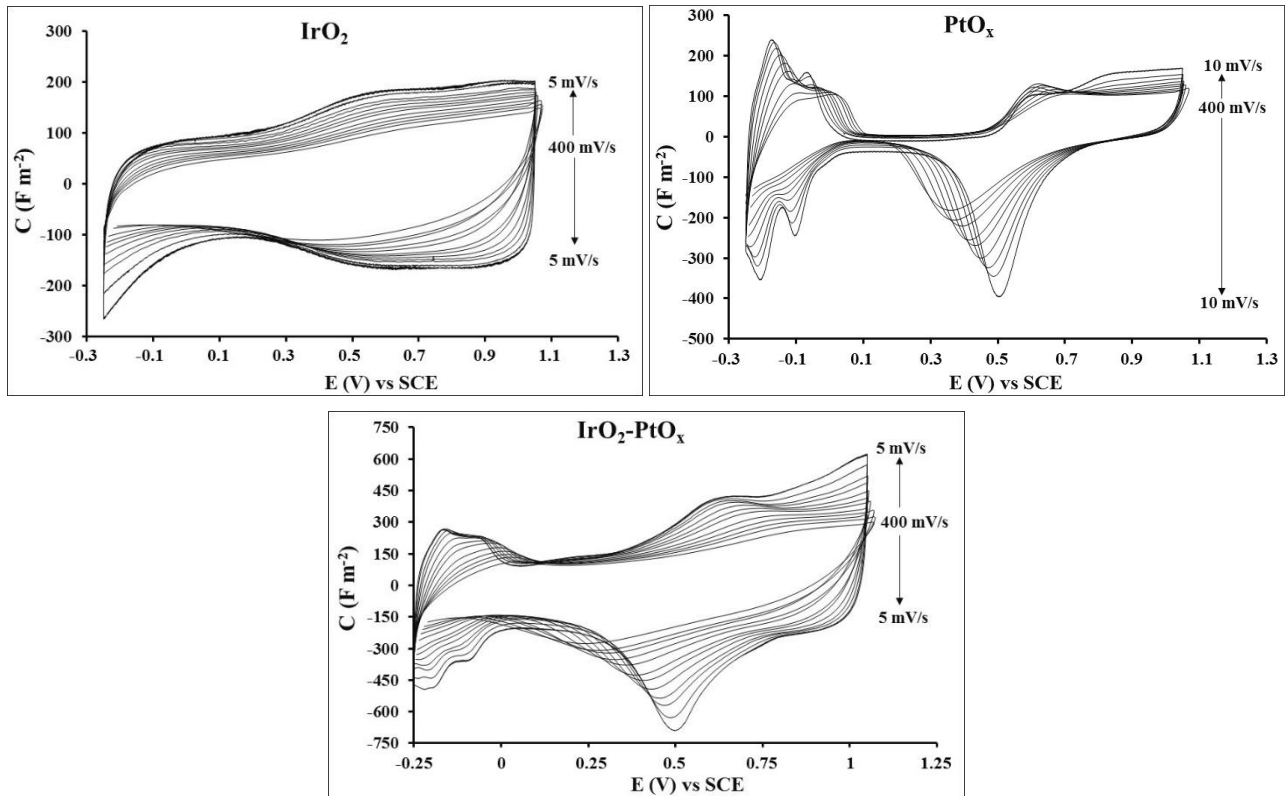


Fig. 8. Capacitance curves as a function of potential in 0.1 M HClO₄ medium

To eliminate surface redox phenomena, an approach using capacitance (current normalized to the potential scan rate) will be used [31]. This consists in choosing on the curve $i = f(E)$ potentials in the domain where no faradic reaction occurs.

Thus, it is possible, by reasoning as did Trasatti et al [32]., to deduce that the curvature of the graph would be linked to the non-participation of part of the total surface of the electrode to surface processes, that which is found in the pores, when the potential scan rate becomes high. For high potential scan rate, access of the electrolyte to these internal pore surfaces is difficult.

By defining capacitance by the relation of Trasatti et al [32].:

$$C_d = \left(\frac{dj_c}{dv} \right)_E \quad (3)$$

It appears that for low values of the potential scan rate:

$$j_c = C_{dv} \quad (4)$$

and for high values of the potential scan rate:

$$j_c = j_{c,o} + C_{dv} \quad (5)$$

Where $j_{c,o}$ is the value extrapolated to $v = 0$ of the capacitive current which would make it possible to determine the value of the capacitance at this scan rate.

The total capacitive current (i_{ctot}) is the sum of the capacitive currents flowing on the surface and inside (pores) of the electrode;

$$j_{ctot} = j_{c,int} + j_{c,ext} \quad (6)$$

Where $j_{c, \text{int}}$ and $j_{c, \text{ext}}$ are the voltammetric current densities referring to internal and external surface regions of the oxide, respectively. Consequently, by applying to eq. 7 the definition represented by eq. 3, the following interfacial capacitances can be obtained [31]:

$$C_{\text{tot}} = C_{\text{int}} + C_{\text{ext}} \quad (7)$$

Where, C_{tot} and C_{int} are the total, internal, and external differential capacitances, respectively.

Inspired by the electrochemical porosity concept proposed in the literature [28, 31, 33] defined the morphology factor (ϕ) as an intensive parameter to describe the contribution of the inner surface regions of the oxide layer to the voltammetric response:

$$\phi = \frac{C_{\text{int}}}{C_{\text{tot}}} \quad (8)$$

From our hypothesis, this factor would not be influenced by surface redox processes due to the judicious choice of potential. The exploration of capacitive currents in this area led to the curves in

The values of the capacitances were determined at $E = 0.15 \text{ V} / \text{SCE}$ in different support electrolytes because the value of the porosity factor is practically constant around this potential. This potential lies in the double layer domain. The results obtained are presented in

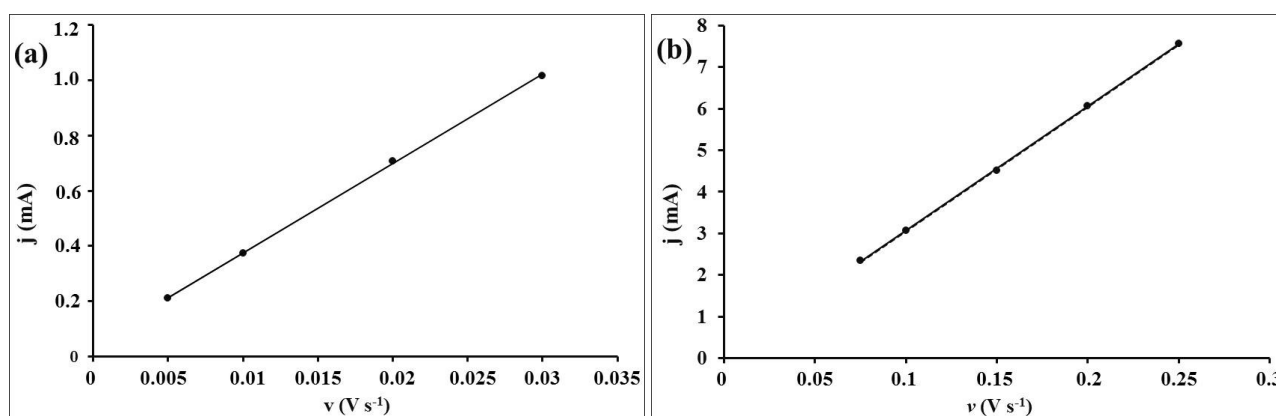


Fig. 9. Curve $i = f(v)$ for $E = 0.4 \text{ V} / \text{SCE}$; (a): at low scan rates; (b): at high scan rates on IrO₂-PtO_x in 0.1 M HClO₄

Tableau 2. Capacitance values for electrodes prepared in different media at $E = 0.15 \text{ V}$

	Electrodes	IrO ₂	PtO _x -IrO ₂	PtO _x
1 M HClO ₄	C _{tot} (mF)	19.2	34.0	22.0
	C _{ext} (mF)	15.9	27.9	13.6
	C _{int} (mF)	3.3	6.1	8.4
	$\phi = C_{\text{int}}/C_{\text{tot}}$	0.17	0.18	0.38
0.1 M HClO ₄	C _{tot} (mF)	16.0	22.0	14.1
	C _{ext} (mF)	3.0	17.6	7.8
	C _{int} (mF)	1.3	4.4	6.3
	$\phi = C_{\text{int}}/C_{\text{tot}}$	0.19	0.20	0.45
0.1 M KClO ₄	C _{tot} (mF)	5.2	15.3	4.1
	C _{ext} (mF)	3.8	9.8	1.5
	C _{int} (mF)	1.4	5.5	2.6
	$\phi = C_{\text{int}}/C_{\text{tot}}$	0.27	0.36	0.63

This study was carried out at a potential of 0.15 V / SCE because at this value, whatever the medium and whatever the composition of the deposit, we are in the double layer domain, a domain exempt from the processes surface redox where the electrode / electrolyte interface appears as a pure capacitor.

It can be seen that in the different media, the internal capacitance is lower than the external capacitance for each electrode. It is also noted that the values of the porosity or morphological factor ϕ are different from zero. The analysis in generally shows that the porosity factor ϕ increases with decreasing proton concentration. It is almost constant with the composition of the deposit for each medium. This result corroborates the results previously discussed with the total charge (q) of the electrode. The evolution of ϕ in shows that the interfacial processes are complex. Using 0.15 V / SCE, the measurements show that surface redox processes also occur. Nevertheless, at this value, it is possible to approximate the true morphology of the electrode which shows that the prepared deposits tend to form a compact surface of the prepared electrodes.

It emerges from this study that the processes which take place at the electrode / electrolyte interface are complex and depend on several factors including the composition of the deposit, the proton concentration, etc. The determination of ϕ with the capacitive charges (q) shows that this approach does not allow to have a clear idea of the morphology of the electrode because it is greatly influenced by surface redox phenomena and resistive phenomena. While the determination of ϕ from the capacitances, choosing the appropriate potential gives a good idea of the texture of the deposit. However, in the double-layer domain where the 0.15 V / SCE potential has been chosen, even low-intensity surface redox processes occur.

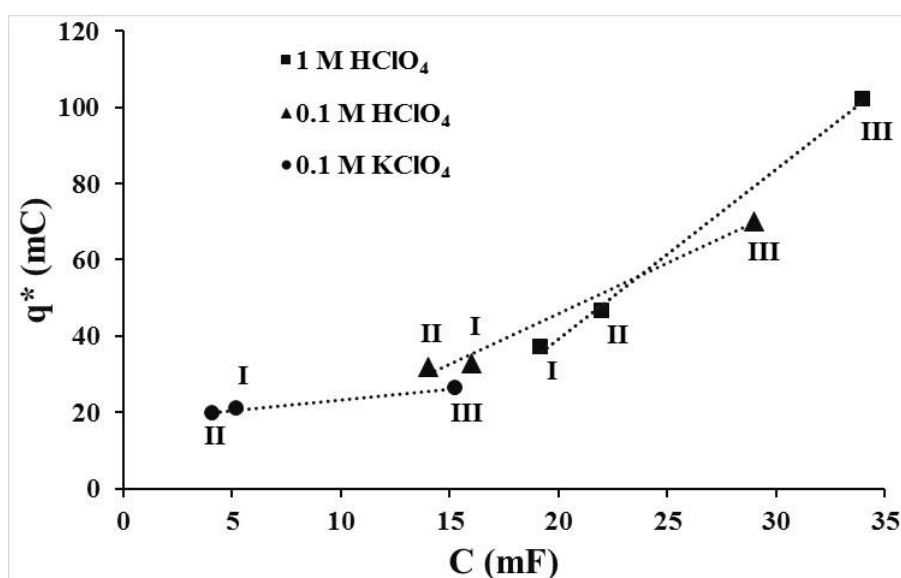


Fig. 10. Linear correlation between the extensive (C_{tot} and q^*_{tot}) surface parameters obtained for IrO₂ (I), PtO_x (II) and IrO₂-PtO_x (III) electrodes

shows the linear correlations between the ranges (C_{tot} and q^*_{tot}) in 1 M HClO₄, 0.1 M HClO₄ and 0.1 M KClO₄ medium. According to these results, there is a good correlation between the different methodologies proposed by Trasatti et al [17]. and by Da Silva et al [31]. Overall, the data presented in suggests that C_{tot} and q^*_{tot} can be used to represent the extension of the electrochemically active surface.

4 CONCLUSION

The physical and electrochemical characterizations carried out showed the presence of deposits on the surface of the electrodes. The surface of the prepared electrodes is porous and rough.

The study showed that the voltammetric charge is high at low scan rates than at high scan rates. It decreases rapidly at low potential scan rates and stabilizes at high potential scan rates regardless of the medium with the three electrodes. At low potential scan rates, electrolyte penetrates through the pores of the deposit. The internal and external surfaces therefore become accessible. At high potential scanning speeds, only the external (geometric) surface is concerned. The voltammetric

load generally decreases as the pH increases. Note that the increasing order of the voltammetric charges of our electrodes prepared regardless of the electrolytic solution is: PtO_x < IrO₂ < IrO₂-PtO_x

In the absence of free protons, the solution diffuses inside the pores of the deposit regardless of its composition and suggests that all the electrodes have a large number of internal active sites. It emerges from this study that the processes which take place at the electrode / electrolyte interface are complex and depend on several factors including the composition of the deposit, the proton concentration, etc. The linear correlations between C_{tot} and q_{tot} show that they can be used to represent the extension of the electrochemically active surface.

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