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Research Paper

Anodic Oxidation of Chlorides on Platinum Modified by Metallic Oxides

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Abstract: *In this work, Pt, $_{50}$Pt-$_{50}$IrO$_2$ and $_{50}$Pt-$_{50}$RuO$_2$ electrodes have been prepared at 400°C on titanium plates used as substrates. They have been characterized voltametrically in HClO$_4$, ferri/ferrocyanide, NaCl and HClO$_4$+ NaCl. These investigations showed that the surface of $_{50}$Pt-$_{50}$RuO$_2$ and $_{50}$Pt-$_{50}$IrO$_2$ electrodes were composed by both platinum and metal dioxide active sites but the surface of $_{50}$Pt-$_{50}$RuO$_2$ is enriched in platinum and $_{50}$Pt-$_{50}$IrO$_2$ is enriched in iridium dioxide. The electrochemical investigation with ferri/ferrocyanide redox couple showed that Pt and $_{50}$Pt-$_{50}$RuO$_2$ electrodes have almost the same electric conductivity. $_{50}$Pt-$_{50}$IrO$_2$ has an electric conductivity lower but close to that of the platinum. The onset of the chlorine evolution reaction (CER) potential respects Nernst's law. Through CER investigation, it has been shown that Pt and $_{50}$Pt-$_{50}$RuO$_2$ possess the same electrocatalytic property slightly higher than that of $_{50}$Pt-$_{50}$IrO$_2$. The Tafel slope obtained on Pt, $_{50}$Pt-$_{50}$RuO$_2$ and $_{50}$Pt-$_{50}$IrO$_2$ for the CER were respectively 31, 31 and 40 mV/dec in chlorides containing perchloric acid electrolyte indicating that CER mechanism led to the same rate determining step on Pt and $_{50}$Pt-$_{50}$RuO$_2$ electrodes but different to that of $_{50}$Pt-$_{50}$IrO$_2$.*

Keywords: Platinum, Ruthenium Dioxide, Iridium Dioxide, Tafel Slope, Electrocatalytic Activity, Chlorine Evolution Reaction.

1. Introduction

Recent development in anode technology have stimulated great interest in the behavior of platinum group under anodic conditions [1-9].That interest in platinum is due to its good electronic properties, to its inertness characteristic and to its corrosion resistant properties [4-9]. But, platinum remains very expensive and undergoes surface change such as passivation phenomena, chloride adsorption when used in various media such as strong chloride media [10, 11]. Used also in the oxidation of various organics such as methanol, ethanol in presence or in absence of chloride, its surface undergoes fouling decreasing its performance and influences its electrochemical behavior towards various species during wastewater treatment for instance [10-12].Generally, to improve the electrochemical performance of the platinum electrode by hampering the electrode's surface fouling, it is associated to other metals or metal oxides [1, 2]. Interested in using electrochemical techniques for the treatment of urban wastewater, lagoon wastewater and hospital wastewater which are complexes media containing chloride species, platinum electrodes combined with metal oxide such as RuO_2 or IrO_2 will be used due to the fact that RuO_2 or IrO_2 are low cost (compared to platinum) and are electronic-conductor metal. From our previous works, it has been shown that combining about 50% molar ratio of Pt and metallic oxides led to electrodes with higher activity for organic oxidation [2] due to the synergistic effect of both platinum and oxides. Moreover, it has been shown that during the oxidation of organics species in presence of chloride, reactive species resulting from chloride oxidation are involved in the oxidation process [1, 12, 13]. Thus, it important to investigate the electrochemical behavior of combined electrodes towards such species in order to investigated the oxidation of chloride and also to determine the mechanisms of CER at this kind of electrodes. Since it has also been shown that thermal decomposition was effective to prepare high conductivity, high physical stability, electrocatalytics anodes for industrial use, that technique has been chosen for the electrodes preparation [14].

In the present work, pure platinum anode and platinum modified by RuO_2 or IrO_2 at 50% molar ratio have been developed by thermal decomposition technique followed by their electrochemical characterization in acid media and their study in acid free or containing chloride ions.

2. Experiments

The electrodes used in the following work were all prepared in our laboratory with appropriate metallic precursors. The coating precursors were prepared from $H_2PtCl_6,6H_2O$(Fluka), $RuCl_3,xH_2O$(Fluka) and $H_2IrCl_6,6H_2O$ (Fluka). All the precursors were dissolved separately in 10 mL of pure isopropanol (Fluka) used as solvent. The concentration of the precursors were 0,044 mol/L, 0,02 mol/L and 0,096 mol/L for $H_2PtCl_6,6H_2O$, $H_2IrCl_6,6H_2O$ and $RuCl_3,xH_2O$ respectively. The commercial products were used as received without any further treatment.

The titanium substrates on which the electrode films were deposited have the following dimension 1.6 cm x 1.6 cm x 0.5 cm. The surface of each substrate was sandblasted to ensure good adhesion of the deposit on it. After, sandblasting, all the substrates were washed vigourously in water and then in isopropanol to clean their surface from residual sands. The substrates were then dried in an oven at 80°C and weighed. After that, the precursor was applied by a painting procedure on the titanium (Ti) substrate then put in an oven for 15 min at 80 °C to allow the solvent evaporation. Then after, it is put in a furnace at 400 °C for 15 min to allow the decomposition of the precursor. Theses steps were repeated until the desired weight of the coating is reached. A final decomposition of 1 h was done at 400 °C. The electrodes prepared by this technique are platinum (Pt), platinum-iridium dioxide ($_{50}$Pt-$_{50}$IrO$_2$) and platinum-ruthenium dioxide ($_{50}$Pt-$_{50}$RuO$_2$) electrodes. For the combined electrodes, a mixture of 50% molar ratio of the corresponding precursor was used. The deposit loading was about 5 g/m^2 on each Titanium substrate.

The physical characterization of the electrodes were performed using a scanning electronic microscopy (SEM, ZEISS, SUPRA 40VP) device belonging to Petroci in Abidjan in Côte d'Ivoire.

The voltammetric measurements were performed on the prepared electrodes in a three-electrode electrochemical cell using an Autolab PGStat 20 (Ecochemie). The counter electrode (CE) was a platinum wire and the reference electrode (RE) was a saturated calomel electrode (SCE). All the potential are referred to a saturated hydrogen electrode (SHE). 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 cm^2.

Products such as HClO$_4$ (Fluka), NaCl (Fluka), K$_3$Fe(CN)$_6$(Fluka) and K$_4$Fe(CN)$_6$ (Fluka) were used as received. All the solutions used in the current work have been prepared with distilled water. All the electrochemical experiments were made at ambient temperature of 25 °C.

3. Results and Discussion

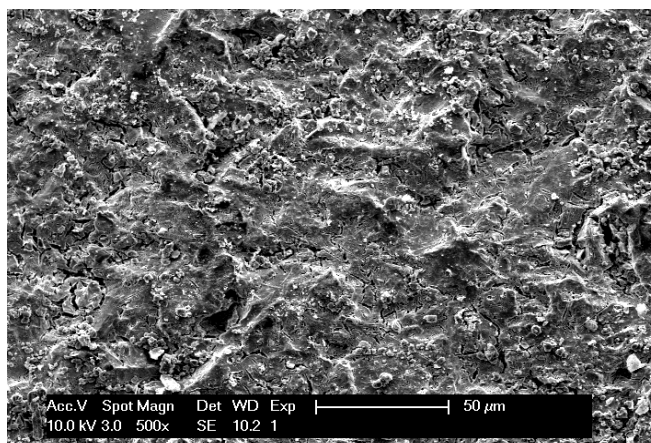## 3.1. Physical Characterization of the Prepared Electrodes
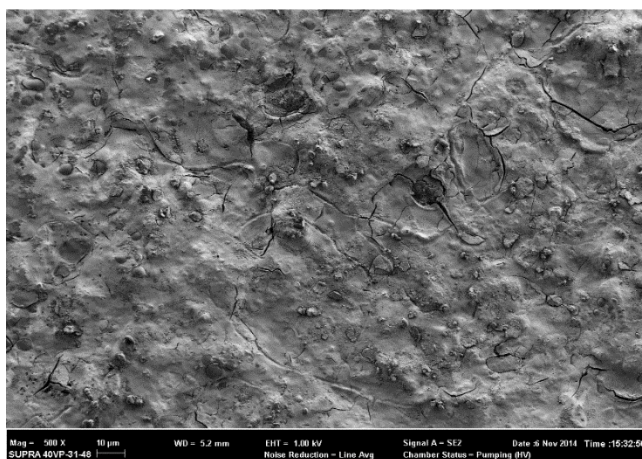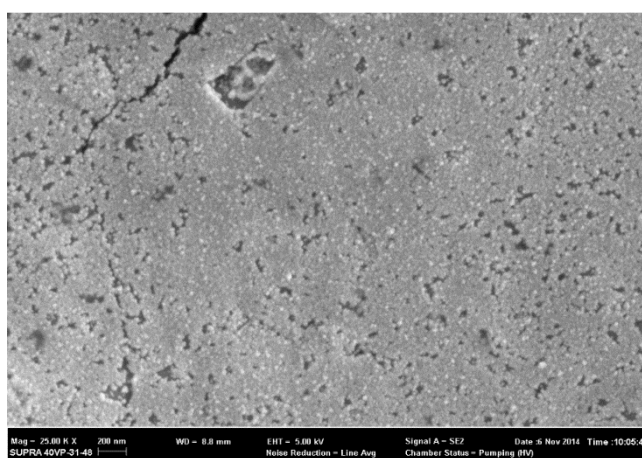
Figure 1: Scanning electron micrographs of Pt(a), $_{50}$Pt-$_{50}$RuO$_2$(a) and $_{50}$Pt-$_{50}$IrO$_2$(c)

Figure 1 presents the micrographs of the as prepared electrodes by thermal decomposition of appropriate metallic precursors. The titanium substrate seems to have its surface totally covered by the deposit. The surface of the platinum electrode seems to be smooth, compact and almost homogeneous (figure 1a). The surface of $_{50}$Pt-$_{50}$RuO$_2$ (figure 1b) is rough and seems to be compact as that of platinum but cracks are observed like those of DSA's. Such finding indicated that the electrode surface of the $_{50}$Pt-$_{50}$RuO$_2$ electrode is composed by platinum and ruthenium dioxide but rich in platinum. In figure 1c, the prepared $_{50}$Pt-$_{50}$IrO$_2$ electrode is shown and its surface presents almost the same characteristic as $_{50}$Pt-$_{50}$RuO$_2$ but in this case, the surface of the electrodeis highly rough with more cracks. That lets think that the surface of the electrode is rich in iridium dioxide. The size of the cracks are thinner as that generally observed at such magnification for pure DSAs possibly due to the presence of platinum which contributes to render the combined electrode surface to have compact structures.

3.2. Electrochemical Characterization of the Electrodes

In Fig. 2a, the voltammogram of the platinum electrode recorded in 1 M HClO$_4$ was presented. Thisvoltammogram was similar to that was generally obtained with the platinum electrodes in acid electrolyte [1, 2, 15].The Oxygen evolution reaction started at potential around 1.51V/SHE. That electrode led to the appearance of well-defined peaks related to the adsorption and desorption of hydrogen in the potential domain of 0 V to0.4 V/SHE. The double layer region with an almost zero current was observed followed by a current increase related to the formation of the platinum oxide. A sharp peak that is characteristic of the reduction of platinum oxide appeared at the potential of 0.72 V/SHE in the reverse potential scan. Fig. 2b presented the voltammograms of all investigated electrodes in HClO$_4$ 1 M. As a general response, the modified electrode led to voltammograms resembling to that of pure platinum electrode. That result indicated that the surface of the modified electrodes is partly composed of platinum clusters. The voltammetric charges of the combined electrode are higher than that of platinum. That is possibly due to the presence of metal oxides on the electrode surface. The $_{50}$Pt-$_{50}$RuO$_2$electrode presents a feature that is close to that of platinum than $_{50}$Pt-$_{50}$IrO$_2$. That result indicated that RuO$_2$ has more electronic and structure affinity with platinum than IrO$_2$ towards platinum. The oxygen evolution reaction started at potential around 1.41V/SHE and 1.43V/SHE on$_{50}$Pt-$_{50}$IrO$_2$ and $_{50}$Pt-$_{50}$RuO$_2$ respectively.
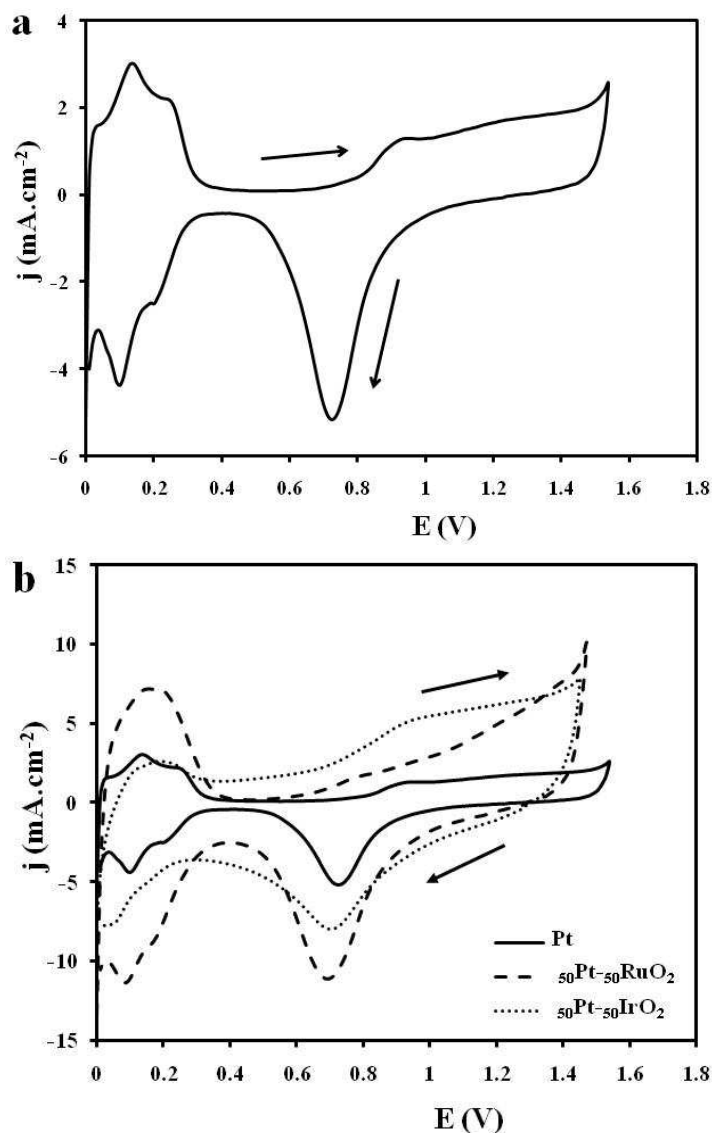
Fig. 2: Cyclic voltammetry of the electrodes in $HClO_4$ 1 M: (a): Pt; (b): Pt,$_{50}$Pt-$_{50}$RuO$_2$and$_{50}$Pt-$_{50}$IrO$_2$;CE: platinum wire, RE: SHE, T=25°C, v=100mV/s

The electrochemical characterization of the electrodes with ferri/ferrocyanide redox couple has also been carried out. The obtained results are presented in Fig.3. All the voltammograms present an oxidation and reduction peaks of the redox system. Detailed analysis led to a difference between the peaks potentialsto be higher than 60mV (Table 1) at 25°C indicating that the redox process is not totally reversible. The observed high values between peak potential for all the investigated electrodes could also result from the involvement of the thin film titanium oxide interlayer formed between titanium and the deposits (Pt, $_{50}$Pt-$_{50}$IrO$_2$, $_{50}$Pt-$_{50}$RuO$_2$) in the overall surface process. The voltammograms of $_{50}$Pt-$_{50}$RuO$_2$ electrode present the same height of the peak current compared to Pt. But that of $_{50}$Pt-$_{50}$IrO$_2$ electrode is slightly low. That indicates that the platinum modified ruthenium dioxide electrodes seem to have the same conductivity as the platinum electrodes. That conductivity is slightly low for the $_{50}$Pt-$_{50}$IrO$_2$ electrode possibly because the electrode surface which is involved in the redox process is dominated by IrO$_2$.
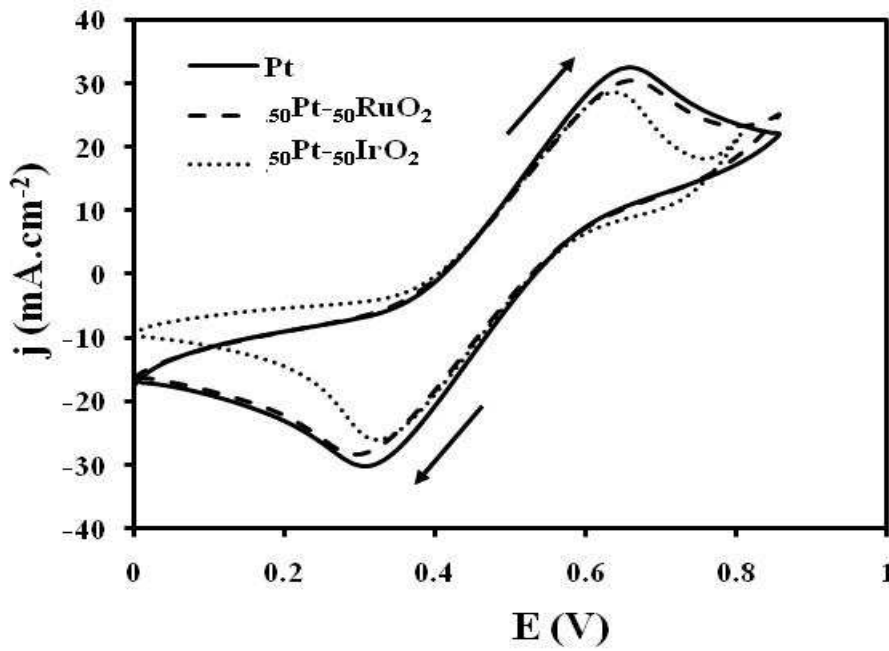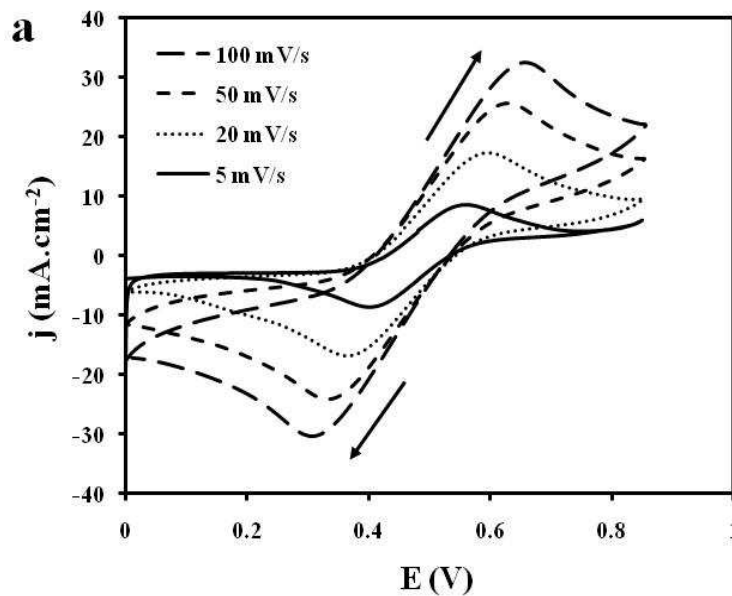
Fig. 3: Cyclic voltammetry of the ferri/ferrocyanideredox couple on all the prepared electrodes, v=100 mV/s, C=100mM, CE: platinum wire, RE: SHE, T=25°C

Table 1: ΔEp (difference between the peaks potentials) of theferri/ferrocyanide redox couple on theprepared electrodes, v=100 mV/s, C=100 mM, CE: platinum wire, RE: SHE, T=25°C

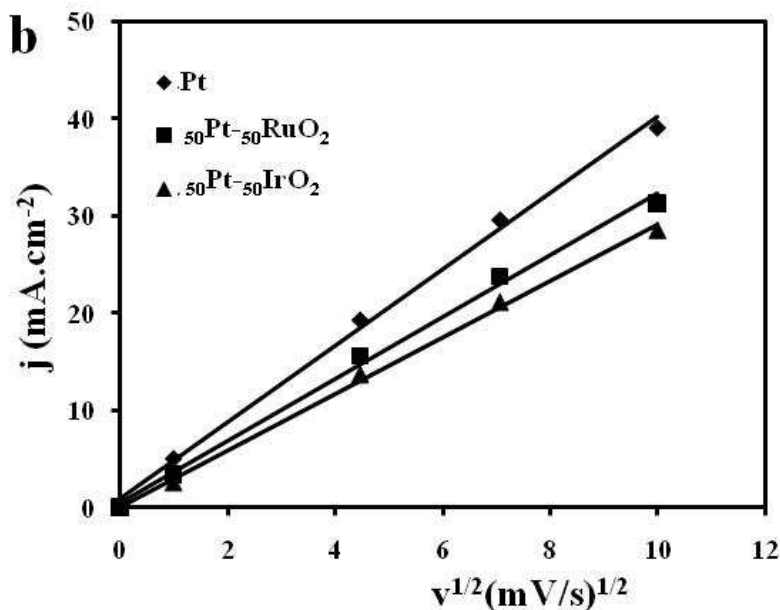| Electrodes	ΔEp(V)
Pt	0,352
$_{50}Pt-_{50}RuO_2$	0,362
$_{50}Pt-_{50}IrO_2$	0,312

Fig. 4: (a) Cyclic voltammetry investigation ferri/ferrocyanide redox couple on Pt at different scans rates; **(b)**Evolution of current peak against the square root of the scan rate for the all electrodes; C=100 mM, CE: platinum wire, RE: SHE, T=25°C

The evolution of the peak current against the potential scan rate was examined for the platinum electrode in ferri/ferrocyanide redox couple. The obtained results were illustrated in Fig. 4a. The oxidation and reduction current peaks increase when the potential scan rate increases. The oxidation current peaks have been plotted against the square root of the potential scan rate for all electrodes. The results are presented in Fig. 4b. A linear evolution is observed for all the electrodes indicating that the process is diffusion controlled. The slightly low conductivity of the $_{50}$Pt-$_{50}$IrO$_2$ electrode led to a straight line with a low slope compared to the others.

Before studying chlorine evolution in acid media, preliminary investigations have been carried out in neutral solution containing chlorides. On Pt electrode the obtained results are presented in Fig. 5a. In this voltammogram, no peak was observed in the domain 0 to 1 V/SHE. Current intensity is practically zero in this domain. In this electrolyte (NaCl) the peaks related to the adsorption and desorption of hydrogen observed in perchloric acid media are absent. A fast increase of the current intensity is observed after 1.32V/SHE. This rapid increase of the current intensity corresponds to chlorine evolvement. A reduction peak appeared at the potential around 1.20 V/SHE in the backward potential scan.

Fig. 5b presented the results of the cyclic voltammetry measurement realized on the platinum electrode in chlorides and in chlorides containing perchloric acid electrolyte. In chlorides containing perchloric acid electrolyte, an increase of the voltammetric charge is observed. Moreover anodic and cathodic peaks appeared after 1.2 V/SHE on Pt electrode in that medium. The anodic peak was followed by a rapid increase in the current intensity. The observed anodic and cathodic peak could result from the oxidation of chlorides into chlorine and from the reduction of the chlorine into chlorides respectively. The chlorine evolvement was observed by the rapid increase in the current intensity. Fig. 5b showed that in acid medium the current of CER is very high than the current of CER in neutral solution. This result shows that protons H$^+$ allows the kinetics of CER to be rapid. The acidification of the solution favors the CER to occur. Such a result can explain that local acidification in the vicinity of the electrode surface can help the CER to occur rapidly even in neutral electrolytes.
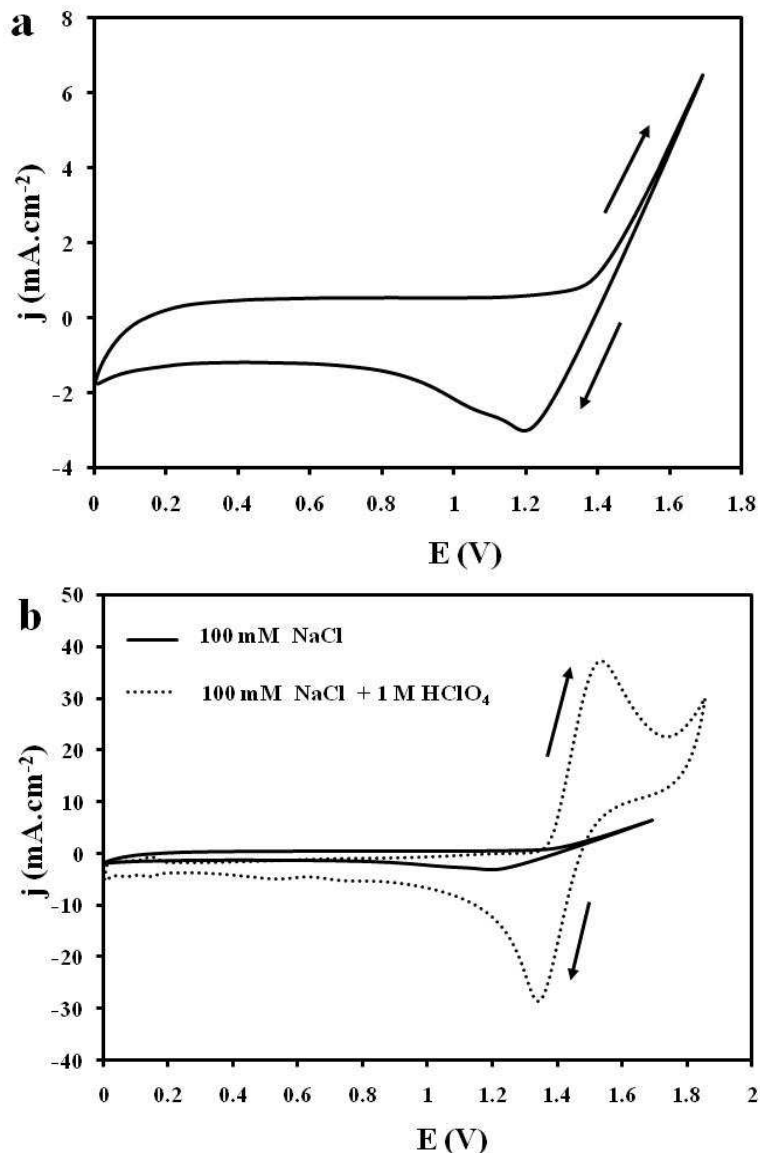
Fig. 5: Cyclic voltammetry of the Pt electrode: **(a)** in NaCl100 mM, **(b)**in NaCl 100 mM containing 1 M $HClO_4$; v=100mV/s, CE: platinum wire, RE: SHE, T=25°C

Fig. 6 presents the results of the cyclic voltammetry measurements realized on all the electrodes in chlorides containing perchloric acid electrolyte. These results showed that the voltammogramsof Pt and $_{50}Pt$-$_{50}RuO_2$ electrodes are practically the same. $_{50}Pt$-$_{50}IrO_2$ also presents chloridesoxidation and reduction peaks but peak current intensities in absolute value are lower than those of platinum. In Fig.6, one observed that when platinum is associated to iridium dioxide, the onset of the potential of the rapid increase of the current is low than that of pure platinum. But in case of platinum associated to ruthenium dioxide, the rapid current increase starts at almost the same potential. That finding corroborates the above obtained results and indicates that electronic and structural affinity may exist between platinum and ruthenium dioxide. Taking into account the results withdrawn from the cyclic voltammetric characterization of the electrodes in electrolytes free of chloride, these obtained results could be due to the fact that the richer is the electrode's surface in platinum, the higher is the onset of the potential of the rapid increase of the current. Finally, CER seems to be rapid on $_{50}Pt$-$_{50}IrO_2$ and sluggish on both Pt and $_{50}Pt$-$_{50}RuO_2$.
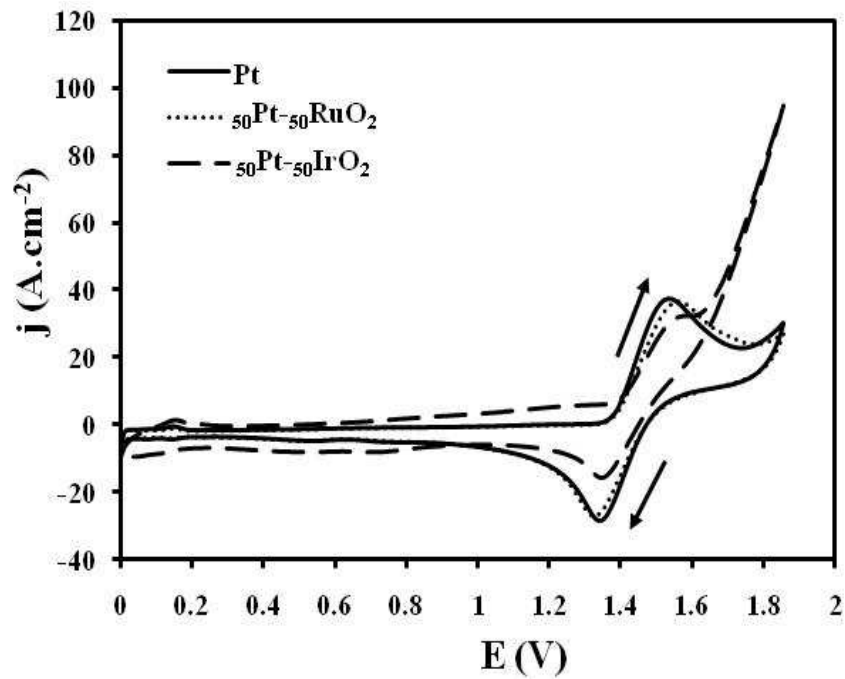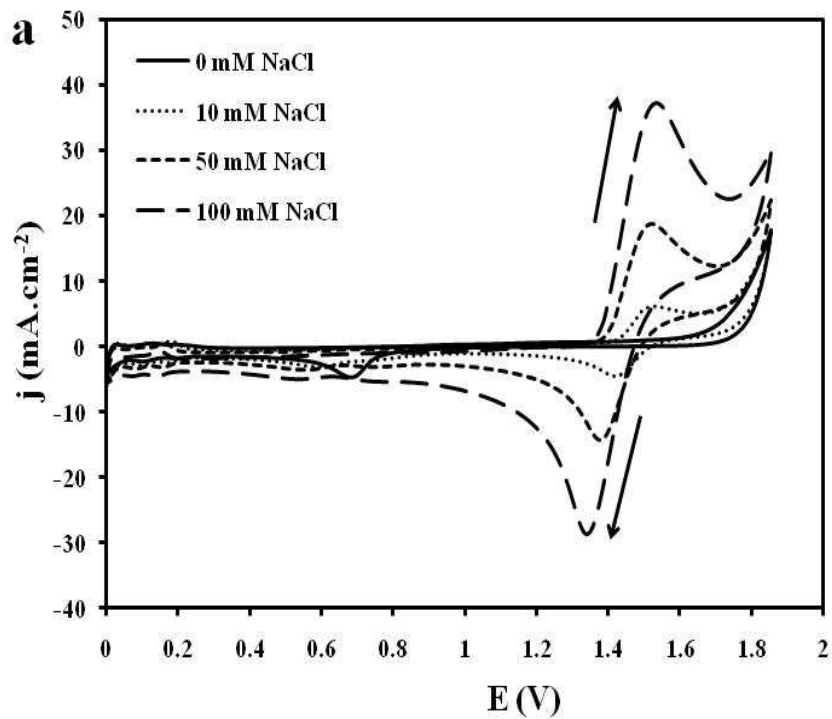
Fig. 6: Cyclic voltammetry of the electrodes in chlorides (100 mM) containing 1 M
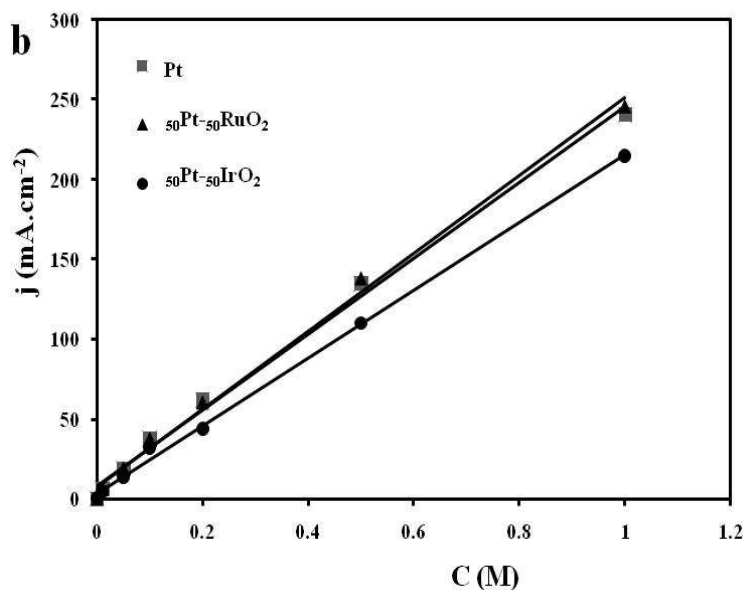HClO$_4$;CE:platinum wire, RE: SHE, T=25°C, v=100mV/s

Fig. 7: (a) Cyclic voltammetry of the platinum electrode inchlorides containing 1 M HClO$_4$; **(b)** Evolution of the anodic peaks current intensity against the NaCl concentration for the all electrodes; v=100 mV/s, CE: platinum wire, RE: SHE, T=25°C.

As the concentration of chlorides increased, the current intensity increased too (Fig.7a). Plotting the anodic peaks current intensity against the concentrations of the chlorides, straight lines were obtained (Fig. 7b) indicating that the appearance of those peaks was directly related to chlorides.
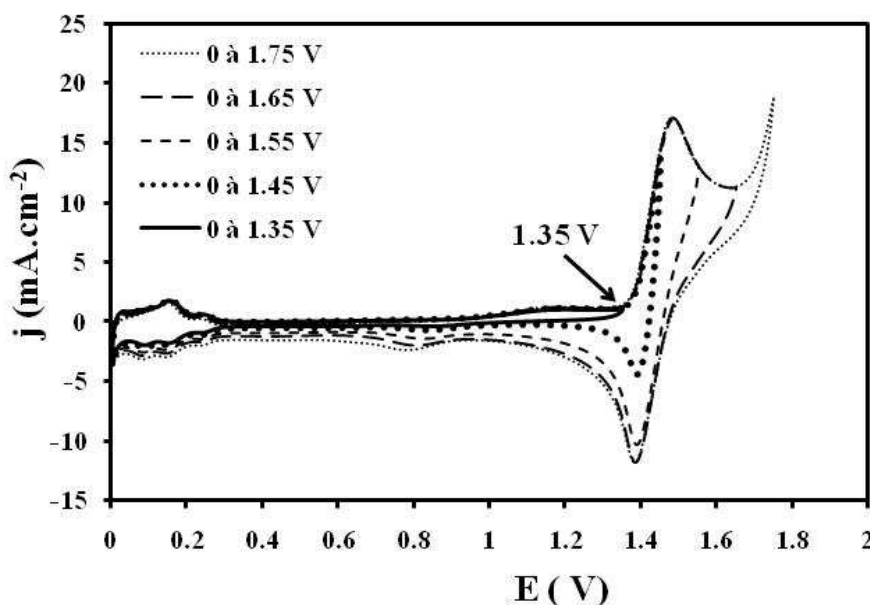

Fig. 8: Cyclic voltammetry curves taken at 100 mV/s on Pt in chlorides (100 mM) containing 1M HClO$_4$, between 0 V/SHE and positive potentials varying from 1.35 to 1.75 V/SHE; CE: platinum wire, RE: SHE, T=25°C

With the aim to verify the relationship between both peaks associated to the redox couple Cl$_2$/Cl$^-$ in the solution, the positive potentials were varying from 1.35 to 1.75 V/SHE.The results for platinum electrode are shown in Fig.8. The intensity of the reductioncurrent peak of the chlorine into chlorides decrease withthe decrease in the positivepotentials. These results show that both reactions are bound. It confirms that the formed chlorine is partially reduced to chloride in the reverse potential scan.

These results were attested by the fact that for a positive potential limit fixed at 1.35 V/SHE, no peaks other than those related to platinum are present. The same observation wasmade on $_{50}Pt$-$_{50}IrO_2$ and on $_{50}Pt$-$_{50}RuO_2$ in chlorides containing $HClO_4$ (not shown).

3.2. Influence of the Chloride Concentration on its Oxidation on the Electrodes

In Fig.9, various concentrations of NaClin $HClO_4$ 1 M electrolyte were investigated at 0.5 mV/s on the Pt electrodes. These results show that for the low concentrations of chlorideions, gas evolve in the same domain as the oxygen evolution reaction domain. But, increasing the concentration of NaCl, a decrease of the onset of the potential related to gas release is observed.For the high concentrations of chlorides, high decease of gas evolvement potentials related to chlorine evolution is observed. These results let think that for low concentration of chlorides, oxygen evolution reaction is favored, while for the high concentration of chlorides, chlorine evolution reaction is favored. Fig.9 also shows that the starting potential of chlorine evolvement in acid solution varies with the chloride ionsconcentration. The onset of the potential related to chloride oxidation process on all the investigated electrodes in $HClO_4$ 1 M containing NaCl were plotted against the logarithm of chlorides concentration. The results are presented in Fig.10. The obtained curves are straight lines. The characteristics of the curves are presented in the Table 2. The slopes of obtained straight lines are independent of the electrode.
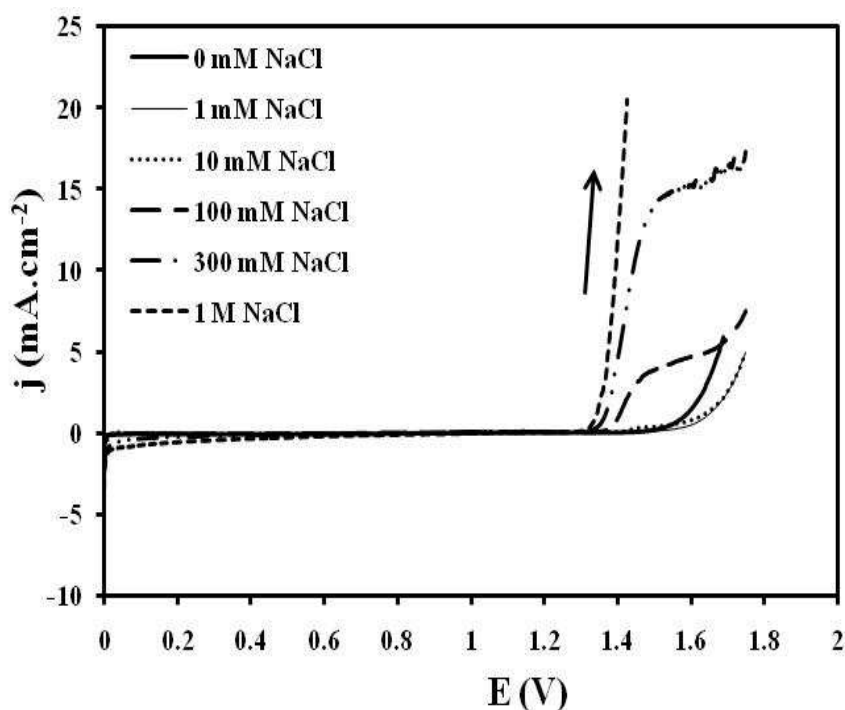

Fig. 9: Linear voltammetry of platinum electrode in $HClO_4$ 1M with various concentrations of NaCl; v = 0. 5 mV/s, CE: platinumwire, ER:SHE, T = 25°C
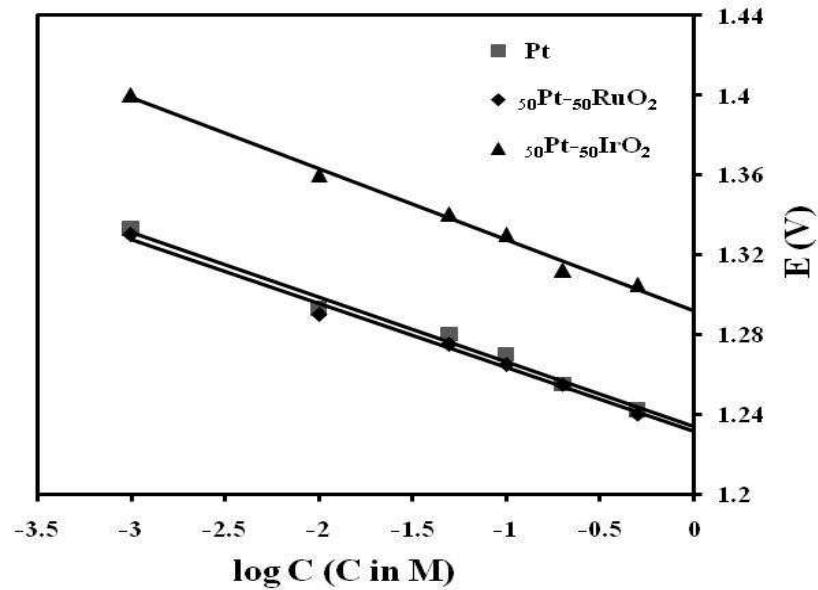
Fig. 10: The onset of the potential at CER on electrodes in HClO$_4$ 1M contain Cl$^-$against the logarithm of chlorides concentrations; v =0. 5 mV/s; CE: platinum wire, ER: SHE, T = 25°C

Table 2: Equations of the onset of the potential at CER in HClO$_4$ 1M contain Cl$^-$against the logarithm of chlorides concentration; v =0.5 mV/s; CE: platinum wire, ER: SHE, T = 25°C

Electrodes	Equation of straight line E = log (C)
Pt	E= - 0.032 log (C) + 1.236
$_{50}$Pt-$_{50}$RuO$_2$	E= - 0.032 log (C) + 1.229
$_{50}$Pt-$_{50}$IrO$_2$	E= - 0.035 log (C) + 1.292

Considering the global equation of the chloride oxidation:

$$2\ Cl^- \longrightarrow Cl_2\ +\ 2\ e^- \tag{1}$$

The relation of Nernst can be given as followed:

$$E = E^O + \frac{RT}{nF}\ln\frac{a_{Cl_2}}{a_{Cl^-}} \tag{2}$$

Where E^0: standard potential of the redox couple; a_{Cl_2} and a_{Cl^-} are activity respectively of Cl$_2$ and Cl$^-$; n:number of electrons; F: faraday constant; T: temperature in Kelvin

At room temperature (25°C or 298, 15 K):

$$\frac{RT}{F}\ln 10 = 0.059\ V/ENH \tag{3}$$

Then, (2) becomes:

$$E = E^O + \frac{0.059}{n}\log\frac{a_{Cl_2}}{a_{Cl^-}} \tag{4}$$

During this reaction, 2 electrons are exchanged, so (4) becomes:

$$E = E^O + 0.03\log\frac{a_{Cl_2}}{a_{Cl^-}} \tag{5}$$

$$E = \left(E^O + 0.03 \log a_{Cl_2} - 0.03 \log \gamma_{Cl^-}\right) - 0.03 \log C \tag{6}$$

Where γ_{Cl^-} : activity coefficient of Cl^-

Considering $E^{0\prime}$ as $E^{0\prime} = E^O + 0.03 \log a_{Cl_2} - 0.03 \log \gamma_{Cl^-}$ $\tag{7}$

(6) becomes: $E = E^{0\prime} - 0.03 \log(C)$ $\tag{8}$

$E^{O\prime}$ is the apparent standard redox potential

The value of 0.03 is close to slope of E= f (log (C)) straight lines determined experimentally with all the electrodes. These results show that the onset of the potential of the chloride oxidation reaction respects Nernst's Law. It is worth indicating that on Pt and on $_{50}$Pt-$_{50}$RuO$_2$ electrodes, chlorine production starts at the same potential around 1.24 V/SHE but it starts at 1.30V/SHE on $_{50}$Pt-$_{50}$IrO$_2$. Pt and $_{50}$Pt-$_{50}$RuO$_2$ electrodes seem to be more electrocatalytic than $_{50}$Pt-$_{50}$IrO$_2$ electrode towards chloride oxidation.

After long term use of the electrodes in various chloride containing electrolyte, cyclic voltammetry measurements have been performed on them. The obtained results with $_{50}$Pt-$_{50}$RuO$_2$ electrodes are depicted in figure 11. All the other electrodes led to the same observation (not shown). Using the electrodes in chlorides containing electrolyte, the surface of the electrode undergoes modification. The change was observed through the decrease of the voltammetric charge in perchloric acid before and after the use of the electrodes in chlorides solution indicating the departure of part of the deposit from the electrodes surface. Meanwhile, the voltammograms of the electrodes still resemble to those found on as prepared electrode presented in figure 2.
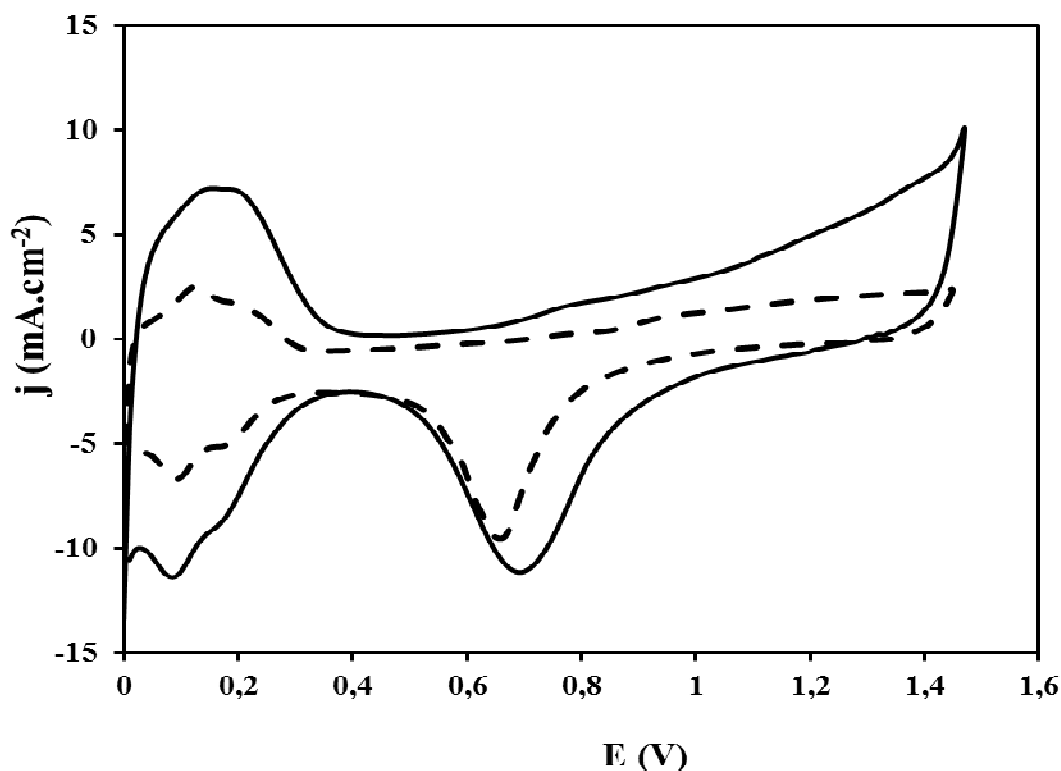

Figure 11: Cyclic voltammograms of Pt-RuO$_2$ in perchloric acid 1M before (solid line) and after (dashed line) its intensive use in chloride containing electrolyte

3.3. Kinetics and Mechanisms of the Chlorine Evolution Reaction

At the electrodes, the contribution of the ohmic drop to the measured potential leads to distortion of the anodic polarization curve resulting in a deviation of the Tafel plotfrom linearity. Thus, in order to determine a Tafel slope, we have performed anohmic drop correction taking into account the total uncompensated resistance R of the studied system. R includes not only the resistance of the electrolyte (which can increase in presence of gas bubbles) but also that of the electrode and the contacts in the outer circuit. In order to reduce totally the residual ohmic drop, correction of the obtained polarization curve has been made according to method described elsewhere [16-19].
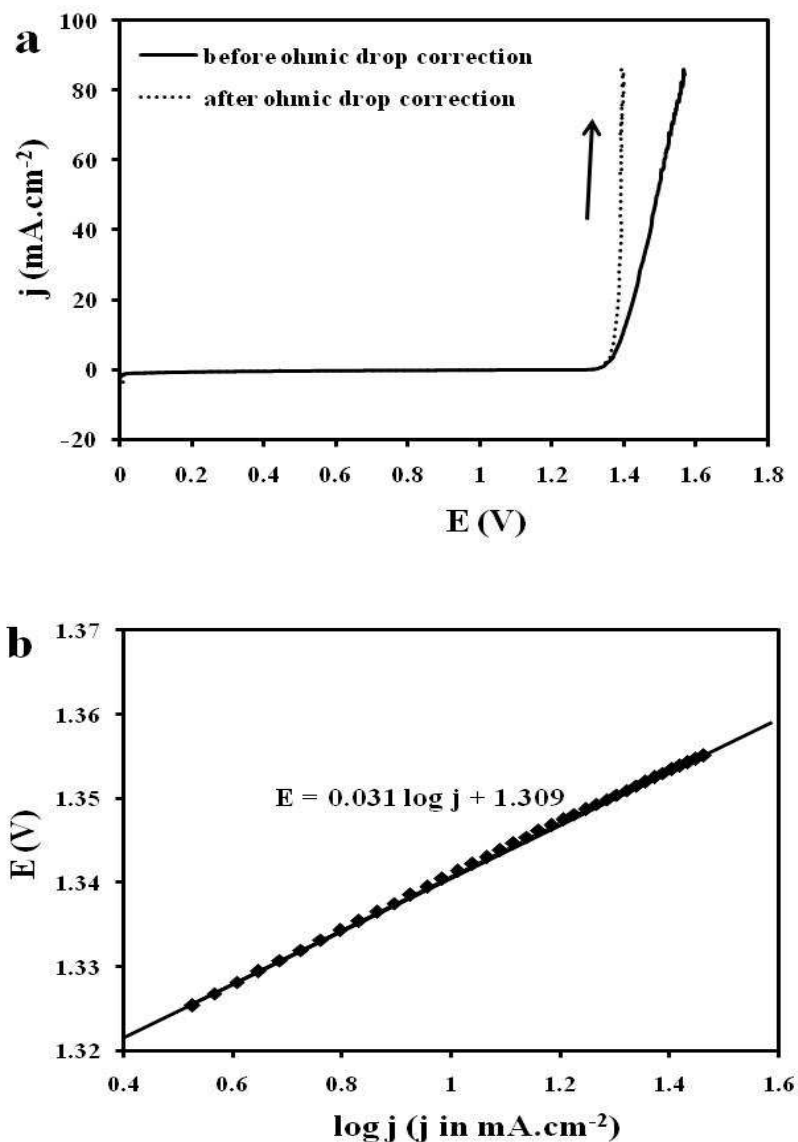

Fig. 12: (a) Current–potential curves before and after ohmic drop correction recorded in chlorides 1 M containing perchloric acid electrolyte 1M,on platinumelectrode at 0.5 mV/s, **(b)** Curve E=f(logj) realized after ohmic drop correction; CE: platinum, RE: SHE, T = 25°C
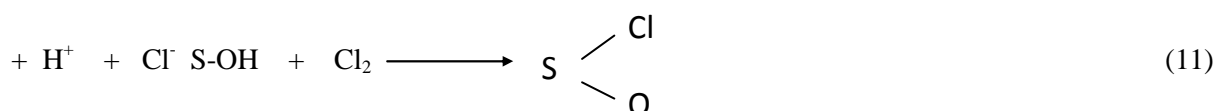
Fig. 12a shows a typical steady polarization curve for the chlorine evolution reaction on Pt electrode in chlorides 1 M containing perchloric acid electrolyte 1 M before and after ohmic drop correction. In

Fig. 12b, the corresponding Tafel plot obtained after ohmic drop correction is given. From that figure, a Tafel slope 31 mV/dechas been determined on platinum electrode for CER. The same correction was also performed on the polarization curve recorded on $_{50}Pt$-$_{50}IrO_2$ and on $_{50}Pt$-$_{50}RuO_2$ electrodes (not shown). The obtained Tafel slopes are consigned in Table 3. These results show that the kinetics of CER on Pt and $_{50}Pt$-$_{50}RuO_2$ electrodes are more rapid than $_{50}Pt$-$_{50}IrO_2$ in chlorides containing acid electrolyte due to the fact that the corresponding Tafel slopes are 31mV/dec, 31mV/dec and 40mV/decrespectively. Investigation carried out with pure IrO_2 led to a Tafel slope that is close to 40mV/dec in the same experimental condition confirming that $_{50}Pt$-$_{50}IrO_2$ electrode surface is dominated by IrO_2

Table 3: Tafel slopes of the prepared electrodes in chlorides 1 M containing perchloric acidelectrolyte 1M; v = 0.5 mV/s; CE: platinum; RE: SHE; T = 25°C

Electrodes	Tafelslope (mV/dec)
Pt	31
$_{50}Pt$-$_{50}RuO_2$	31
$_{50}Pt$-$_{50}IrO_2$	40

In literature, several mechanisms of CER in acid media were proposed [20-24]. But the usually suggested mechanism is the one taking into account the catalytic effect of the metallic sites of the electrode [21]. Augustynski and all [25] were the first ones to highlight the oxidation of the metallic sites before chlorides oxidation thanks to methods of analysis of surface.

$$S\text{-OH} \longrightarrow S\text{-O} + H^+ + e^- \tag{9}$$

$$S\text{-O} + Cl^- + e^- \longrightarrow S \begin{smallmatrix} \diagup Cl \\ \diagdown O \end{smallmatrix} \tag{10}$$

$$+ H^+ + Cl^- \ S\text{-OH} + Cl_2 \longrightarrow S \begin{smallmatrix} \diagup Cl \\ \diagdown O \end{smallmatrix} \tag{11}$$

Where S stands for electrode active sites.

This mechanism predicts the following Tafel slopes: 120 mV/decif step 9 is the rate determining step (rds),40 mV/dec for step 10 and 30 mV/dec for step 11.

The measured Tafel slopes indicate that step 11 is the rds for the chlorine evolution on platinum and on$_{50}Pt$-$_{50}RuO_2$ regarding the results obtained in the current work. With $_{50}Pt$-$_{50}IrO_2$, a Tafel slope of 40 mV/dec was found. This result indicated that the rate determining step is 10 of the proposed mechanism.

4. Conclusion

Three electrodes consisted in platinum and platinum modified with metallic oxides have been developed in this work. Their electrochemical characterization in various media showed that combining platinum with metallic oxides, the electrodes behave as the richer component of their surface. Thus, in chlorides free or containing perchloric acid electrolyte, Pt and $_{50}Pt$-$_{50}RuO_2$electrodes presented practically the same voltammograms and also the same Tafel slope regarding CER. They possess the same electrocatalytic properties towards chloride oxidation and the same rate determining step in the mechanism of CER (31 mV/dec). The voltammogram of$_{50}Pt$-$_{50}IrO_2$ electrode presents a feature that resembles to that of Pt but with a high voltammetric charge typical of IrO_2. With $_{50}Pt$-

$_{50}IrO_2$, the obtained Tafel slope is 40 mV/dec.Thus kinetically, CER is more rapid on Pt and $_{50}Pt$-$_{50}RuO_2$ electrodes than $_{50}Pt$-$_{50}IrO_2$ in chlorides containing acid electrolyte.

Acknowledgements

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