OXYGEN AND CHLORINE EVOLUTION ON RUTHENIUM DIOXIDE MODIFIED BY PLATINUM IN ACID SOLUTIONS

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ABSTRACT

RuO_2 and $_{50}RuO_2$-$_{50}Pt$ electrodes have been prepared thermally at 400°C on titanium substrate. The electrochemical measurements made in $HClO_4$, ferri/ferrocyanide and $HClO_4$ containing NaCl have shown that the surface of $_{50}Pt$-$_{50}RuO_2$ was composed by ruthenium dioxide and platinum active sites. The electrochemical investigation with ferri/ferrocyanide redox couple showed that RuO_2 and $_{50}RuO_2$-$_{50}Pt$ electrodes have almost the same electric conductivity. The Tafel slopes obtained on RuO_2 and $_{50}RuO_2$-$_{50}Pt$ for the chlorine evolution reaction (CER) were respectively 40 and 31 mV/dec in acid electrolyte indicating that the kinetic of CER was rapid on $_{50}RuO_2$-$_{50}Pt$ than RuO_2 owing to a synergetic effect of RuO_2 and Pt. That additional effect of the surface component in $_{50}RuO_2$-$_{50}Pt$ electrode let them possess high electrocatalytic activity towards CER than RuO_2 in chlorides containing perchloric acid electrolyte. The gap between the onset of the CER and the onset of the OER on $_{50}RuO_2$-$_{50}Pt$ is higher than that of pure ruthenium oxide. Combining Pt and RuO_2 allows a clear separation between O_2 and Cl_2 evolvement on $_{50}RuO_2$-$_{50}Pt$ electrode.

Keywords : *ruthenium dioxide, platinum, Tafel slope, voltammetry, electrocatalytic activity, chlorine evolution reaction, oxygen evolution reaction.*

RÉSUMÉ

Dégagement d'oxygène et de chlore sur le dioxyde de ruthenium modifie par le platine en milieu acide

Les électrodes RuO_2 et $_{50}RuO_2$-$_{50}Pt$ ont été préparées à 400 °C sur des plaques de titanes utilisés comme support. Les mesures voltammétriques effectuées dans différents milieux ($HClO_4$, $KClO_4$, ferri-ferrocyanure de potassium, $HClO_4$ + NaCl) ont montré la présence des grains de platine et de dioxyde de ruthénium sur la surface de l'électrode de $_{50}RuO_2$-$_{50}Pt$.

Les études menées dans le ferri-ferrocyanure de potassium ont montré que les électrodes de RuO_2 et $_{50}RuO_2$-$_{50}Pt$ ont pratiquement la même conductivité électrique. La mesure des pentes de Tafel a donné 40 et 31 mV/déc pour le dégagement de dichlore respectivement sur les électrodes RuO_2 et $_{50}RuO_2$-$_{50}Pt$. Ces valeurs de pente de Tafel montrent que la cinétique de dégagement de dichlore est plus rapide sur l'électrode $_{50}RuO_2$-$_{50}Pt$ que sur l'électrode RuO_2 due aux effets synergiques de Pt et RuO_2. Le mélange Pt et RuO_2 permet d'avoir une électrode d'activité électro-catalytique élevée pour le dégagement de dichlore par rapport à celle du dioxyde de ruthénium pure en milieu acide perchlorique contenant des ions chlorures. La différence de potentiel entre le début de dégagement de dichlore et de dioxygène sur l'électrode $_{50}RuO_2$-$_{50}Pt$ est plus élevée par rapport à celle obtenue avec l'électrode RuO_2. La combinaison de Pt et RuO_2 permet de réaliser une nette séparation entre le potentiel de dégagement de dichlore et celui du dégagement de dioxygène sur l'électrode $_{50}RuO_2$-$_{50}Pt$.

Mots-clés : *dioxyde de ruthénium, platine, pente de Tafel, voltammetrie, activité électro-catalytique, réaction de dégagement de dichlore, réaction de dégagement de dichlore.*

I - INTRODUCTION

Dimensionally stable anodes (DSA) have been well succeeded for recent years due to their versatile electrocatalytic properties and stability [1]. These electrodes have shown significant activity for all common gas evolution reactions (O_2, Cl_2). Up to now, the most widely industrial application of these electrodes is for Cl_2 production [1]. In this field, the electrode material plays an important role in both Cl_2 yield and purity, since the chlorine evolution reaction (CER), is affected by the presence of O_2 from the oxygen evolution reaction (OER) [2, 3]. To achieve high Cl_2 current efficiency, then it is necessary to have a high gap between the onset of the CER and the onset of the OER. Then the nature of the anodic electrode is very important for the CER. It has been shown in literature that RuO_2 and IrO_2 electrodes have good electrocatalytic activity for CER and OER in acid medium [2, 4]. Besides RuO_2 being somewhat more active for the OER, compared to IrO_2, it has the additional advantage of being much cheaper than the later while showing adequate stability under acid conditions [5]. However, the onset of the OER is close to that of the CER on RuO_2 electrode. Then it is necessary to couple RuO_2 with the platinum because platinum possesses a high onset potential of the OER and it can contribute to separate the onset potential of the OER to that of CER. Platinum has also been found as good candidate for that purpose because of its good electronic properties, its inertness characteristic and its corrosion resistant properties [6-9]. In prior investigation in our team, it has been shown that combining 50% molar ratio of RuO_2 and Pt by thermal decomposition led to electrodes with higher activity for organic oxidation [6].

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The aim of the present study is to investigate the electrocatalytic activity and the kinetics of the CER and the OER on the RuO_2 electrode modified with platinum.

II - EXPERIMENTAL

The electrode used in the following work was prepared in our laboratory with an appropriate metallic precursor. The coating precursors were prepared from $RuCl_3,xH_2O$ (Fluka) and $H_2PtCl_6,6H_2O$ (Fluka). The precursors were dissolved in pure isopropanol (Fluka) used as solvent. The commercial products were used as received without any further treatment. The titanium substrate on which the electrodes film were deposited has the following dimension 1.6 cm x 1.6 cm x 0.5 cm. The surface of the titanium substrate was sandblasted to ensure a good adhesion of the deposit on it. After sandblasting, the substrate was washed vigourously in water and then in isopropanol to clean its surface from residual sands. The substrate was then dried in an oven at 80°C and weighted. After that, the precursors were applied by a painting procedure on the titanium (Ti) substrate then put in an oven for 15 min at 80 °C to allow the evaporation of the solvent. 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 coating weight was reached. A final decomposition of 1 h was done at 400 °C. The loading of the deposit was about 5 g/m^2 on the titanium substrate.

The voltammetric measurements were performed on the prepared electrode 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 geometric surface area of the working electrode in contact with the electrolyte was 1 cm^2. For the electrochemical investigations $HClO_4$ (Fluka), NaCl (Fluka), $K_3Fe(CN)_6$ (Fluka), $K_4Fe(CN)_6$ (Fluka) and KOH (Fluka) were used as received for the preparation of the solutions employed in that work with distilled water. All the electrochemical experiments were made at ambient temperature of 25 °C.

III - RESULTS AND DISCUSSION

III-1. Electrochemical characterization of the prepared electrodes

The electrodes have been characterized in KOH 1 M solution containing equimolar concentrations of ferri/ferrocyanide. The results of these investigations that have been carried out with RuO_2 electrode are presented in *Figure 1a*. The voltammetric measurements realized on $_{50}RuO_2$ -$_{50}$Pt led to

curves (not shown) giving the same feature as those shown in *Figure 1a.* The anodic and cathodic peaks generally observed for such a couple were present in *Figure 1a.*
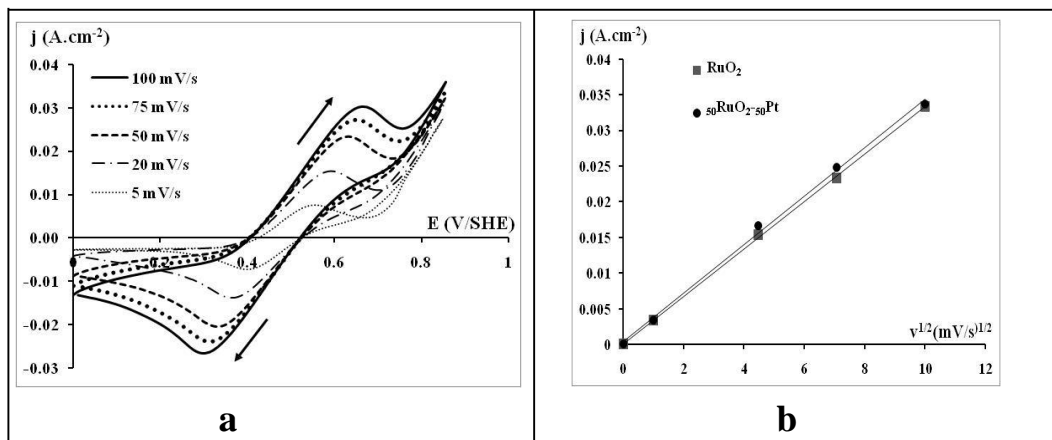

Figure 1 : *(a) Cyclic voltammetry investigation ferri/ferrocyanide redox couple on RuO₂ at different potential scans rates; (b) Evolution of anodic peaks current density against the square root of the scan rate for the all electrodes; C =100 mM, CE : platinum wire, RE : SHE, T =25°C*

The oxidation and reduction current peaks increase when the potential scan rate increases. The anodic peaks current densities plotted against the square root of the potential scan rate for all electrodes are presented in *Figure 1b*. A linear evolution is observed for all the electrodes indicating that the process is diffusion controlled [7, 10]. The anodic peak potential increases with potential scan rates and the difference between anodic and cathodic peaks potential led to values higher than 60 mV *(Table 1)* at 25°C indicating that the redox process is not totally reversible at those electrodes surface.

Table 1 : *The gap between the peak potentials of the electrodes in 100 mM ferri/ferrocyanide electrolyte at 50, 75 and 100 mV/s, supporting electrolyte : KOH 1 M, CE : platinum wire, RE : SHE, T =25°C*

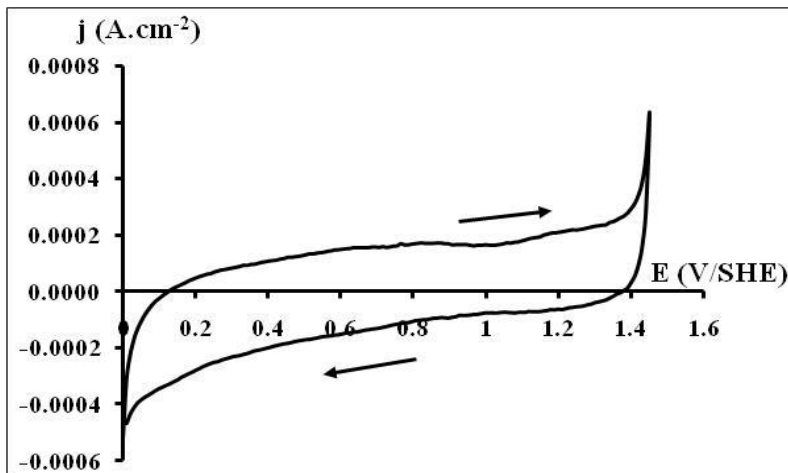| Electrodes	RuO_2	$_{50}RuO_2$-$_{50}Pt$
100 mV/s	0.365	0.362
75 mV/s	0.332	0.335
50 mV/s	0.296	0.310

Figure 2 : *Cyclic voltammetry of the RuO$_2$ electrode in HClO$_4$ 1M at v =100 mV/s, CE : platinum wire, RE : SHE, T =25°C*

Figure 2 presented the result of the cyclic voltammetry measurement realized on RuO$_2$ electrode in perchloric acid electrolyte. This voltamogram has a rectangular shape with waves of low current density at 0.85 V and 1.16 V. According to literature [12-14], the presence of these waves could be due respectively to the redox transitions of Ru (III) / Ru (IV) and Ru (IV) / Ru (VI) scanning at the surface of the electrode. A rapid increase in the current related to OER started at 1.39 V.
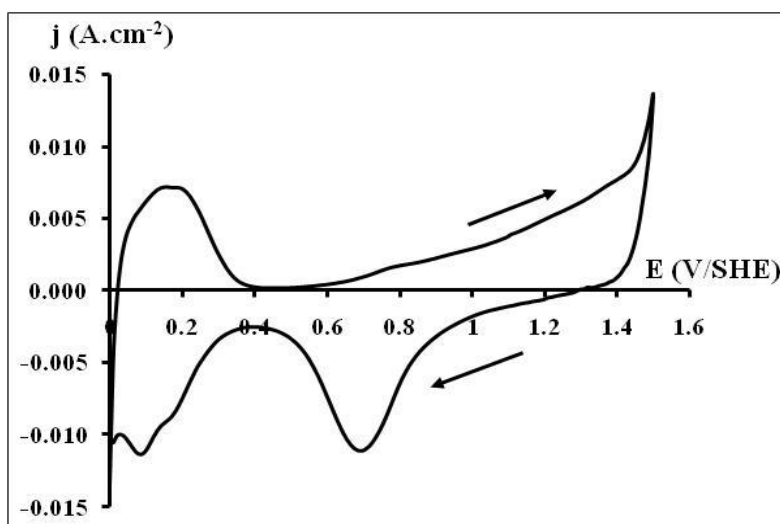
Figure 3 : *Cyclic voltammetry of the $_{50}$RuO$_2$-$_{50}$Pt electrode in HClO$_4$ 1M at v =100 mV/s, CE : platinum wire, RE : SHE, T =25°C*

In *Figure 3,* the voltamogram resulted from a voltammetric measurement on the $_{50}RuO_2$-$_{50}Pt$ electrode in $HClO_4$ 1 M at v =100 mV/s was presented. That electrode led to the appearance of peaks related to the adsorption and desorption of hydrogen in the potential domain of 0 V to 0.4 V/SHE. A sharp peak that is characteristic of the reduction of platinum oxide appeared around 0.7 V in the reverse potential scan. These results indicated that the surface of the modified electrode is partly composed of platinum clusters [6, 7]. The voltammetric charge of the combined electrode is higher than that of RuO_2. $_{50}RuO_2$-$_{50}Pt$ electrode possesses more active sites than RuO_2 because ruthenium dioxide possesses important active sites added to those of platinum. The presence of weak waves observed on RuO_2 electrode around 0.76 V and 1.3V corresponds respectively to the transitions redox Ru (III) / Ru (IV) and Ru (IV) / Ru (VI) that take place at the surface of the electrode. These results indicate the presence of ruthenium clusters on $_{50}RuO_2$-$_{50}Pt$ electrode. The oxygen evolution reaction started at potential around 1.43 V. *Figure 4* presented the results of the linear voltammetry measurement realized on RuO_2 electrode in chlorides containing perchloric acid electrolyte. A fast increase of the current density is observed after 1.3 V. This rapid increase of the current density corresponds to the chlorine evolvement because in the absence of chlorides the rapid increase of the current density is observed after 1.39 V. On this electrode, the CER started potential is low than OER started potential. These results showed that CER is fast than OER on RuO_2 electrode.
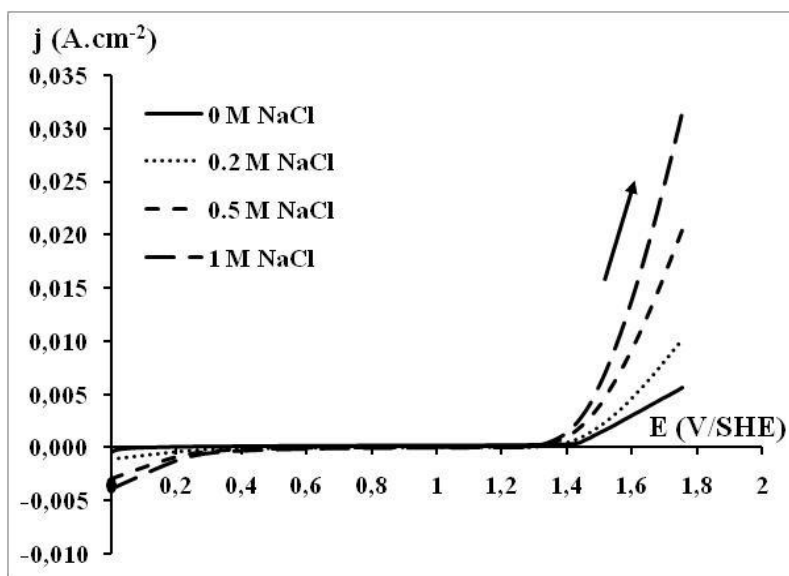

Figure 4 : *Cyclic voltammetry of the RuO_2 electrode in $HClO_4$ 1 M containing various concentrations of NaCl; v =100 mV/s, CE : platinum wire, RE : SHE, T =25°C*

Figure 4 showed that on RuO_2 the onset of the oxygen evolution reaction potential and chlorine evolution reaction potential are close and it's difficult to distinguish the current density of O_2 and Cl_2 evolvement. As the concentration of chlorides increased, the current density increased too *(Figure 4)*. Plotting the current density (E=1.6 V) against the concentrations of the chlorides, straight lines were obtained *(Figure 5)* indicating that the appearance of those current density was directly related to chlorides.
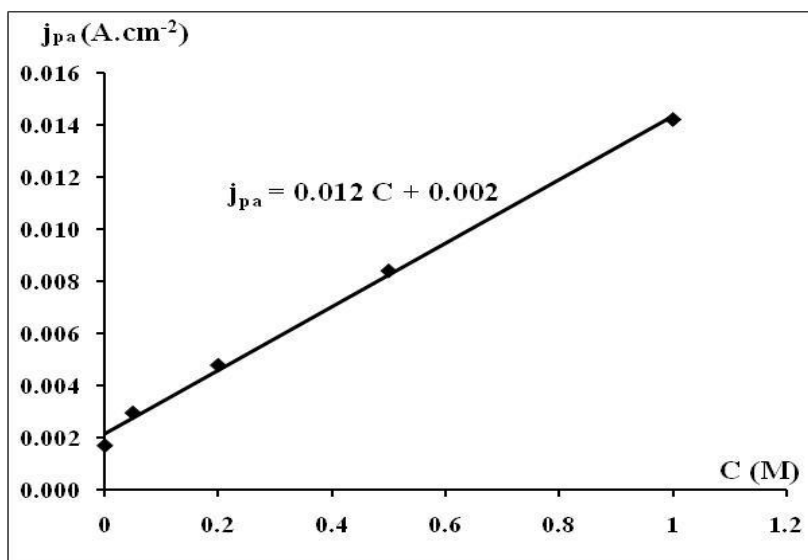
Figure 5 : *Evolution of the anodic peaks current density against the NaCl concentration for RuO₂ electrode; v =100 mV/s, CE : platinum wire, RE : SHE, T =25°C*

In $HClO_4$ 1 M containing various concentrations of NaCl, voltamograms have been recorded on $_{50}RuO_2$-$_{50}Pt$ electrode. The obtained results are presented in *Figure 6.* Anodic peaks appeared after 1.4 V. The anodic peak was followed by a rapid increase of the current density. The observed anodic peak could result from the oxidation of chlorides into chlorine. The chlorine evolvement was observed by the rapid increase of the current density. This figure showed that in acid medium containing chlorides the current of CER is very high than the current of OER in $HClO_4$ solution. As the concentration of chlorides increased, the current intensity increased too *(Figure 6)*. Plotting the anodic peaks current intensity against the concentration of the chlorides, straight lines were obtained *(Figure 7)* indicating that the appearance of those peaks was directly related to chlorides. These results confirmed the oxidation of chlorides into chlorine.
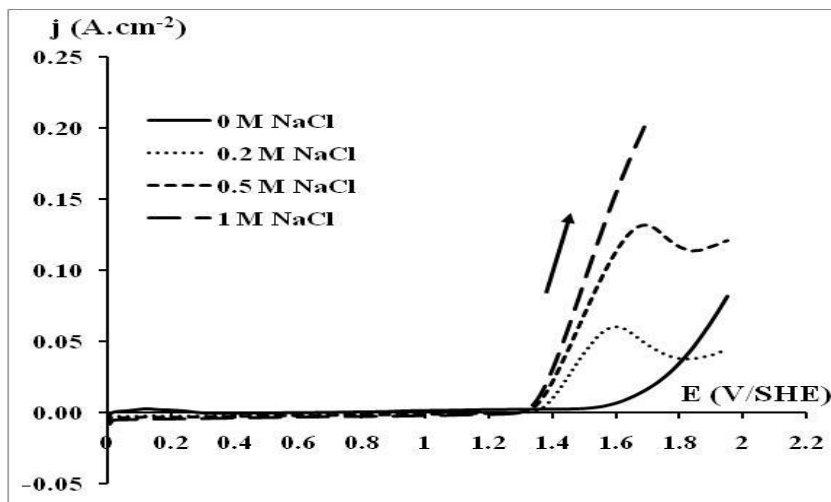
Figure 6 : *Cyclic voltammetry of the $_{50}RuO_2$-$_{50}Pt$ electrode in $HClO_4$ 1 M*
containing various concentrations of NaCl at v =100 mV/s,
CE : platinum wire, RE: SHE, T=25°C

In $HClO_4$ containing chlorides and in $HClO_4$ free of chlorides the obtained curves indicate that for low concentration of chlorides, both OER and CER occurs in the same potential domain indicating simultaneous evolvement of both gases. For high concentrations of chlorides, a net separation is observed. CER occurs early than OER.
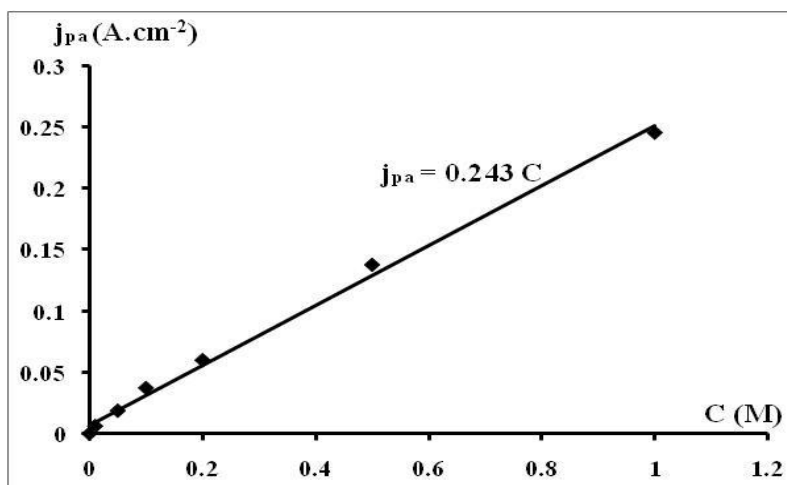
Figure 7 : *Evolution of the anodic peaks current density against the NaCl*
concentration for $_{50}RuO_2$-$_{50}Pt$ electrode at v =100 mV/s,
CE : platinum wire, RE : SHE, T =25°C

Table 2 : *The gap between the onset of the CER in HClO$_4$ 1 M containing NaCl 1 M and the onset of the OER in HClO$_4$ 1 M, v=100mV/s, CE: platinum wire, RE: SHE, T=25°C*

Electrodes	RuO$_2$	$_{50}$RuO$_2$-$_{50}$Pt
ΔE(V)	0,09	0,19

The gap between the onset of the CER in HClO$_4$ 1 M containing NaCl 1 M and the onset of the OER in HClO$_4$ 1 M have been determined on all the electrodes. The obtained results are presented in ***Table 2***. The *Table II* showed that the gap between the onset of the CER and the onset of the OER on $_{50}$RuO$_2$-$_{50}$Pt is higher than that of pure ruthenium. From such results, it appears clearly the net separation of O$_2$ and Cl$_2$ evolvement on $_{50}$RuO$_2$-$_{50}$Pt electrode

III-2. Tafel lines

In ***Figure 8***, corrected and uncorrected polarization curve from ohmic drop on RuO$_2$ electrode in HClO$_4$ 1 M were presented. The same correction was also performed on the polarization curve recorded on $_{50}$RuO$_2$-$_{50}$Pt in acid medium and on all the electrodes in HClO$_4$ 1 M containing NaCl 1 M (not shown). The ohmic drop correction reduces totally the residual ohmic drop.
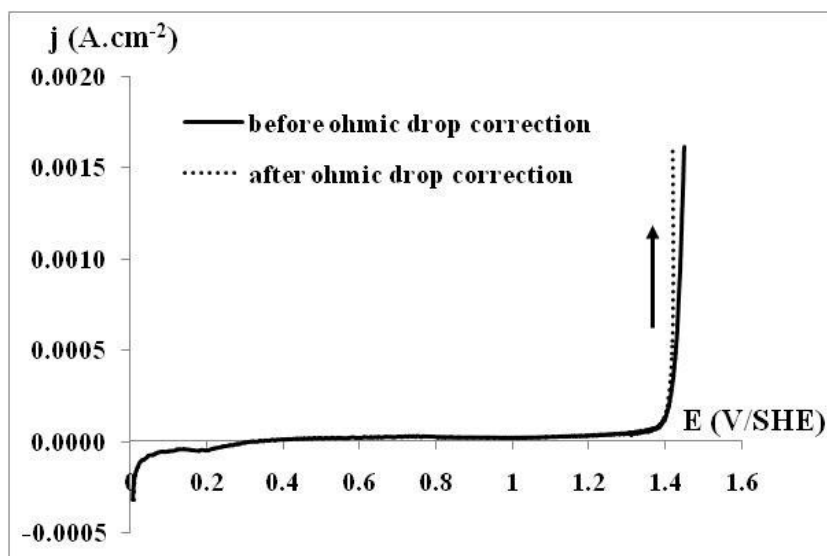

Figure 8 : *Current Density–potential curves before and after ohmic drop correction recorded in HClO$_4$ 1 M on* RuO$_2$ *electrode at 1 mV/s, CE : platinum wire, RE : SHE, T = 25°C*

The correction of the obtained polarization curve has been made according to the method described elsewhere [15-18]. In *Figure 9,* $E = f(\log j)$ are presented. The obtained Tafel slopes are presented in *Table 3*
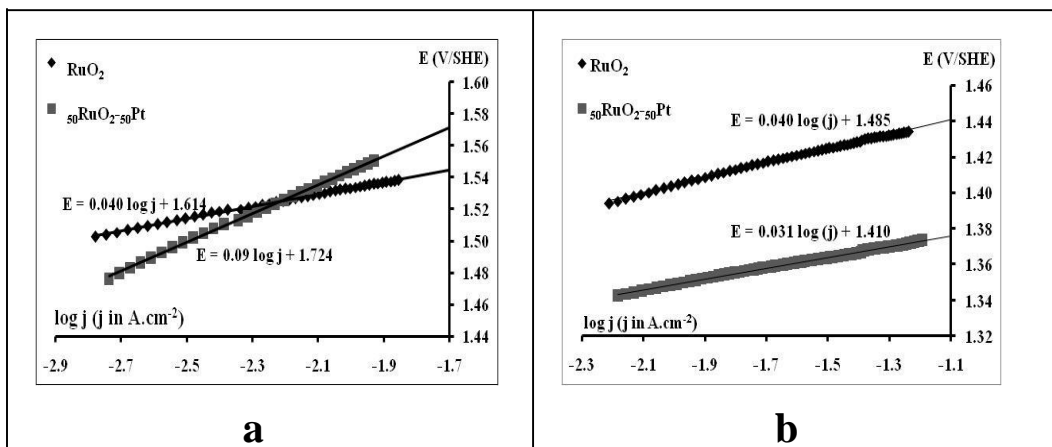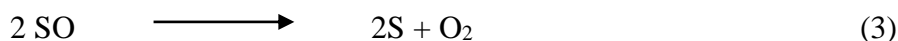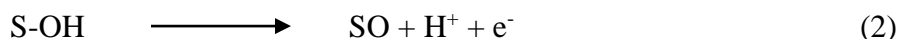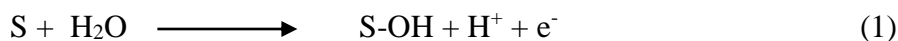

Figure 9 : *Tafel line of RuO₂ and ₅₀RuO₂-₅₀Pt: (a) in HClO₄ 1 M; (b) in HClO₄ 1 M containing NaCl 1M; v =1 mV/s; CE: platinum wire; ER: SHE, T = 25°C*

Table 3 : *Tafel slopes in the domain of OER and CER on RuO₂ and ₅₀RuO₂-₅₀Pt.*

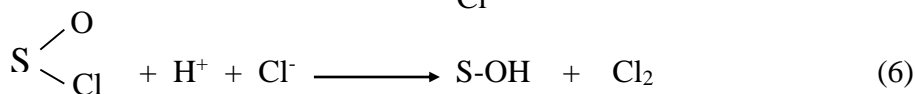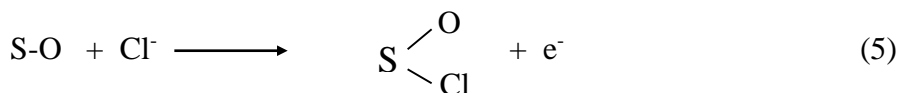| Electrodes	OER	CER
RuO₂	40	40
₅₀RuO₂-₅₀Pt	90	31

According to the Tafel slopes, next general electrode mechanism earlier proposed for the OER from acid medium, is stated as followed [17, 19, 20]:

$$S + H_2O \longrightarrow S\text{-}OH + H^+ + e^- \tag{1}$$

$$S\text{-}OH \longrightarrow SO + H^+ + e^- \tag{2}$$

$$2\,SO \longrightarrow 2S + O_2 \tag{3}$$

Where S stands for active sites and OH, O are adsorption intermediates.

This mechanism predicts the following Tafel slopes: 120 mV/dec if step (1) is the rate determining step (rds), 40 mV/dec for step (2) and 15 mV/ dec for step (3).The 40 mV/dec, obtained from RuO_2 electrodes, suggests that the step known as electrochemical oxide path (2) is the rate determining step (rds). 90 mV/dec is obtained for $_{50}RuO_2$-$_{50}Pt$. This Tafel slope is close to 120 mV/dec. In this case, step (1) could be considered as the rate determining step (rds). It has been shown from the voltammetric investigations that the surface of the electrode undergoes modification leading to a higher oxide. And in literature several authors found that metallic sites undergo oxidation before chlorides oxidation thanks to surface analysis methods [21-23]. Considering the obtained experimental data, the mechanism proposed for the CER from acid medium can be given as followed :

$$S\text{-OH} \longrightarrow S\text{-O} + H^+ + e^- \qquad (4)$$

$$S\text{-O} + Cl^- \longrightarrow S\overset{\displaystyle O}{\underset{\displaystyle Cl}{<}} + e^- \qquad (5)$$

$$S\overset{\displaystyle O}{\underset{\displaystyle Cl}{<}} + H^+ + Cl^- \longrightarrow S\text{-OH} + Cl_2 \qquad (6)$$

Where S stands for active sites.

This mechanism predicts the following Tafel slopes: 120 mV/dec if step (4) is the rate determining step (rds), 40 mV/dec for step (5) and 30 mV/ dec for step (6). The 40 mV/dec slope, obtained from RuO_2 electrode, suggests that the CER the path (5) is the rate determining step (rds). $_{50}RuO_2$-$_{50}Pt$ electrode show 31 mV/dec, which suggests the step (6) is the rate determining step (rds).

IV - CONCLUSION

The voltammetric investigations have revealed the presence of both RuO_2 and Pt on the thermally prepared $_{50}RuO_2$-$_{50}Pt$. $_{50}RuO_2$-$_{50}Pt$ electrodes are more electrocatalytic (1.24 V/SHE) than RuO_2 (1.30 V/SHE) for the CER. The Tafel slope obtained on RuO_2 and $_{50}RuO_2$-$_{50}Pt$ for the chlorine evolution reaction (CER) were respectively 40 and 31 mV/dec in acid electrolyte. Then coupling RuO_2 with Pt leads to electrode having more electrocatalytic and more kinetic properties than RuO_2 electrode for CER. The gap between the onset of the CER and the onset of the OER on $_{50}RuO_2$-$_{50}Pt$ is high than that of pure ruthenium.

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