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Influence of various metallic oxides on the kinetic of the oxygen evolution reaction on platinum electrodes

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Abstract

Pt, $_{50}$Pt-$_{50}$RuO$_2$ and $_{50}$Pt-$_{50}$IrO$_2$ electrodes were prepared on titanium (Ti) substrate by thermal decomposition techniques. The micrographs of $_{50}$Pt-$_{50}$RuO$_2$ and $_{50}$Pt-$_{50}$IrO$_2$ have revealed that their surfaces are rough with cracked structures in contrast to platinum which exhibits smooth, compact and homogeneous surface. The richer the electrode surface in platinum, thinner is the crack size and also more compact is the electrode surface. The electrodes have also been characterized electrochemically by cyclic voltammetry in acidic (HClO$_4$) and alkaline (KOH) electrolytes. These characterizations showed that the surface of the $_{50}$Pt-$_{50}$RuO$_2$ and $_{50}$Pt-$_{50}$IrO$_2$ electrodes were composed of platinum and metal dioxide active sites. The Tafel slope obtained on Pt, $_{50}$Pt-$_{50}$RuO$_2$ and $_{50}$Pt-$_{50}$IrO$_2$ for the oxygen evolution reaction (OER) were respectively 120, 90 and 44 mV dec^{-1} in acid electrolyte. In the alkaline electrolyte, they were 119, 87 and 42 mV dec^{-1} on Pt, $_{50}$Pt-$_{50}$RuO$_2$ and $_{50}$Pt-$_{50}$IrO$_2$ electrodes, respectively, indicating that for the prepared electrodes, Tafel slopes are the same in acidic and in alkaline media. Moreover, in acidic and in alkaline media, the kinetic of the oxygen evolution reaction was faster on $_{50}$Pt-$_{50}$RuO$_2$ and $_{50}$Pt-$_{50}$IrO$_2$ than Pt owing to a synergetic effect of Pt and the oxides. That additional effect of the surface component $_{50}$Pt-$_{50}$RuO$_2$ and $_{50}$Pt-$_{50}$IrO$_2$ electrodes let them possess higher electrocatalytic activity towards OER than Pt in the two media. Though the kinetic of the oxygen evolution reaction is practically the same in acidic and alkaline media for all the electrodes, OER occurred at lower overpotential in alkaline electrolyte than in acidic electrolyte on the prepared electrodes.

Introduction

Oxygen evolution reaction (OER) has been extensively studied in electrochemistry because of its importance in many fields such as fuel cells, wastewater treatment, chlorine evolution, corrosion, water electrolysis [1-7]. OER reaction kinetics and mechanism aspects drew a great attention and still continue to be investigated. Because of the use of electrochemistry to solve environment pollution problems [8-10], a particular interest was directed towards the search of better electrocatalysts that could lead to a decrease of the OER overpotential. In the above mentioned field, platinum played an important role because of its good electronic and corrosion resistance properties. Although platinum is known to be one of the best electrocatalyst in acidic electrolytes, its high cost requires its replacement with new materials. Used for the oxidation of organics such as methanol and ethanol, platinum undergoes electrode fouling consequently reducing its electrooxidation activities. Since it is known that OER depends mainly on chemical and structural properties of electrode materials surface, our interest was focused on platinum and transition metal oxide modified platinum electrodes. Indeed, since the discovery of Dimensionnally stable anodes (DSAs) by Beer around 1970, a lot of research efforts were made on such kind of electrodes in relation to a variety of processes has been carried out including OER. It has been shown that among the DSAs, iridium dioxide and ruthenium dioxide exhibit good OER performance. In prior investigation in our team, it has been shown that combining 50 % molar ratio of Pt and metallic oxides led to higher activity for organic oxidations [11]. The aim of the present study was to investigate the electrocatalytic activity and the kinetics of the OER on the same kind of electrode *i.e.* platinum modified with various transition metal oxides.

Experimental

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), $RuCl_3,\times H_2O$ (Fluka) and $H_2IrCl_6,6H_2O$ (Fluka). All the precursors were dissolved in pure isopropanol (Fluka) used as solvent. 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 $1.6 \times 1.6 \times 0.5$ 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 in air to allow the solvent evaporation. Then after, it is put in a furnace at 400 °C for 15 min in air to allow the decomposition of the precursor. Theses steps were repeated until the desired mass 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.

The voltammetric measurements were performed under either 1 mV s^{-1} or 100 mV s^{-1} 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 were reported against SHE according to the following relation: E / V $vs.$ SHE = E / V $vs.$ SCE + 0.25. To decrease the contribution of ohmic losses, the reference electrode was mounted in a luggin capillary and placed close to the working electrode by a distance of 1 mm. In fact, ohmic drop is known to increase the value of the Tafel slope and careful attention was to be paid on it during experiment. In order to reduce totally the residual ohmic drop, the polarization curve should be corrected according to method described elsewhere [12-15]. A brief description of the correction is given as followed.

The overpotential η / V observed in the experiment can be given by

$$\eta \text{ / V} = a + b \ln j + jR \tag{1}$$

where a / V is the Tafel constant, b / V dec^{-1} is the Tafel slope, j / A cm^{-2} is the current density and R / Ω cm^{-2} is the total area-specific uncompensated resistance of the system, which is assumed to be constant. The derivative of equation (1) with respect to current density gives equation (2) from which b and R can be easily obtained by plotting dη / dj as a function of 1/j

$$\frac{\mathrm{d}\eta}{\mathrm{d}j} = \frac{b}{j} + R \tag{2}$$

The estimation of R allows correcting the experimental overpotential by substracting the ohmic drop jR according to equation (3)

$$\eta_{\text{corr}} = \eta - jR \tag{3}$$

where η_{corr} stands for the corrected overpotential

During the calculations, the derivatives dη/dj was replaced by their finite elements $\Delta\eta/\Delta j$ estimated from each pair of consecutive experimental points.

The apparent exposed area of the working electrode was 1 cm^2.

For the electrochemical investigations HClO$_4$ (Fluka), KOH (Fluka) were used as received for the preparation of the solutions employed in that work with distilled water. All the experiments were made at ambient temperature of 25 °C.

Results and discussion

Physical characterization of the prepared electrodes

In Figure 1, the micrographs of the prepared electrodes were presented. It appears that the surface was 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 were observed like those of DSA's [16,17]. Such finding indicated that the electrode surface of the $_{50}$Pt-$_{50}$RuO$_2$ electrode is composed by platinum and ruthenium dioxide. 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 electrode surface is highly rough with more cracks. The size of the cracks are thinner as 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.
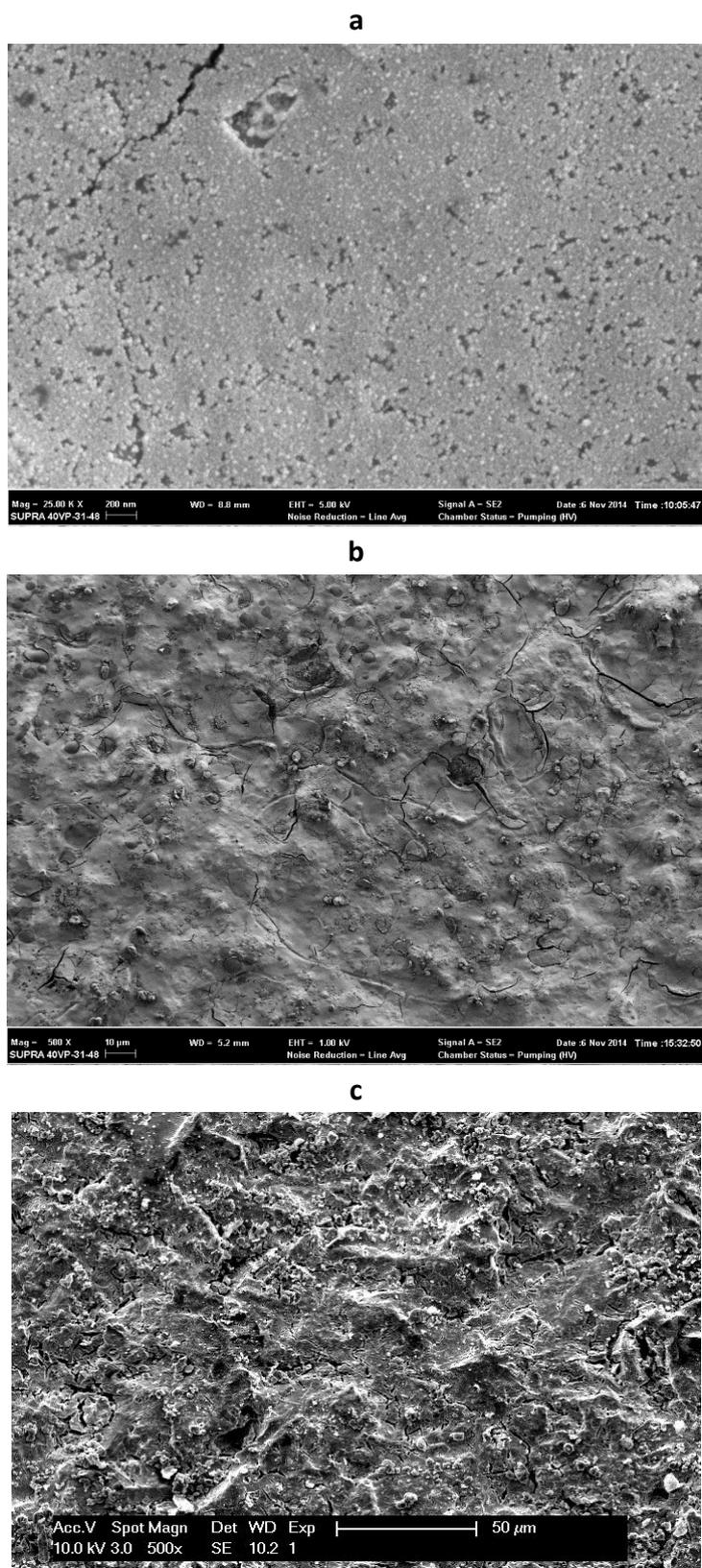
a

b

c

Figure 1: *Scanning electron micrographs of Pt(**a**), $_{50}Pt\text{-}_{50}RuO_2$(**b**) and $_{50}Pt\text{-}_{50}IrO_2$(**c**)*

Electrochemical characterization of the electrodes in perchloric acid medium

Cyclic voltammetric measurements were performed on a platinum electrode in perchloric acid 1 M under a scan rate of 100 mV s^{-1} and the results were depicted in Figure 2a. The figure showed the usual feature generally observed with polycrystalline platinum in acidic media [18]. Well defined adsorption and desorption peaks located in the potential domain between 0 and 0.4 V

were shown. The double layer region characterized by an almost zero current in the forward potential scan followed by oxide formation domain (0.74 V-1.51 V) and an oxide reduction peak at 0.72 V (backward potential scan) were also presented. A rapid increase in the current related to OER started at 1.51 V.

In Figures 2b and 2c, the voltammograms resulted from the investigation made on the platinum modified electrodes were presented. For such investigation, $_{50}Pt-_{50}IrO_2$ and $_{50}Pt-_{50}RuO_2$ have been used. As a general response, the modified electrodes led to voltammograms resembling to that obtained with 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 electrodes are higher than that of platinum. That is due to the presence of metal oxides on the electrode surface. The voltammogram of the $_{50}Pt-_{50}RuO_2$ electrode presents a feature that bears more resemblance to that of platinum than the voltammogram of $_{50}Pt-_{50}IrO_2$ compared to that of platinum. That result indicated that RuO_2 has more electronic and structure affinity with platinum than IrO_2 towards platinum. It can also be deduced from those results that $_{50}Pt-_{50}RuO_2$ surface is composed of much platinum clusters due to its migration from the inside of the coating to its surface during the thermal decomposition of the precursor. But in case of $_{50}Pt-_{50}IrO_2$, a hindering effect of IrO_2 on platinum migration occurs that results in lower spread of platinum on such composite electrode surface. Although this observation is made, presence of metal oxide and platinum on the electrode surface showed synergetic effect i.e. increasing in active sites than platinum used alone. In the high potential domain, using oxygen evolution as a probe reaction to investigate the electrocatalytic activity of the prepared electrodes, it appeared that the onset of the potential at the increase in current are 1.43 V; 1.41 V and 1.51 V on $_{50}Pt-_{50}RuO_2$, $_{50}Pt-_{50}IrO_2$ and Pt respectively. From these results, it appears that $_{50}Pt-_{50}IrO_2$ and $_{50}Pt-_{50}RuO_2$ are more electrocatalytic for OER than pure platinum owing to their low overpotential for OER than pure platinum electrode. For the prepared composite electrodes $_{50}Pt-_{50}IrO_2$ appeared to be more catalytic for OER than $_{50}Pt-_{50}RuO_2$. Such result is in accordance with the above obtained result and is explained by the fact that the surface of $_{50}Pt-_{50}RuO_2$ is mostly composed by platinum than on $_{50}Pt-_{50}IrO_2$ electrode. Indeed, mixing metallic oxides such as transition metal oxide led to an increase in the electrocatalytic behavior of platinum and/or the prepared electrode towards oxygen evolution reaction.

Plotting log *j* versus the potential *E*, straight lines were obtained in the Tafel region as shown in Figure 3. The obtained Tafel slopes are presented in Table 1.

It is worth noting that Tafel slopes are an indicator of electrocatalytic activity. In fact, the lower the Tafel slope the faster the kinetics of the reaction and the more active the electrocatalyst is. From Table 1, it could be noticed that pure platinum exhibits a Tafel slope of 120 mV dec^{-1} which is higher than those obtained on the composite electrodes. The Tafel slope of $_{50}Pt-_{50}RuO_2$ is higher than that of $_{50}Pt-_{50}IrO_2$. The exchange current densities have been determined (Table 1) and the obtained values indicated that the system O_2/H_2O is kinetically slow on all the investigated electrodes. Meanwhile, from these findings, regarding the Tafel slopes, it appears that OER is more rapid on $_{50}Pt-_{50}IrO_2$ than on $_{50}Pt-_{50}RuO_2$ and sluggish on pure platinum electrode. These results are in accordance with the above obtained results where the onset of the potential of OER was concerned. In fact, as the surface of the electrode is dominated by platinum clusters in the following order $_{50}Pt-_{50}IrO_2 < _{50}Pt-_{50}RuO_2 < Pt$ as shown by voltammetric investigation in acidic medium, an increase in the Tafel slope is observed.

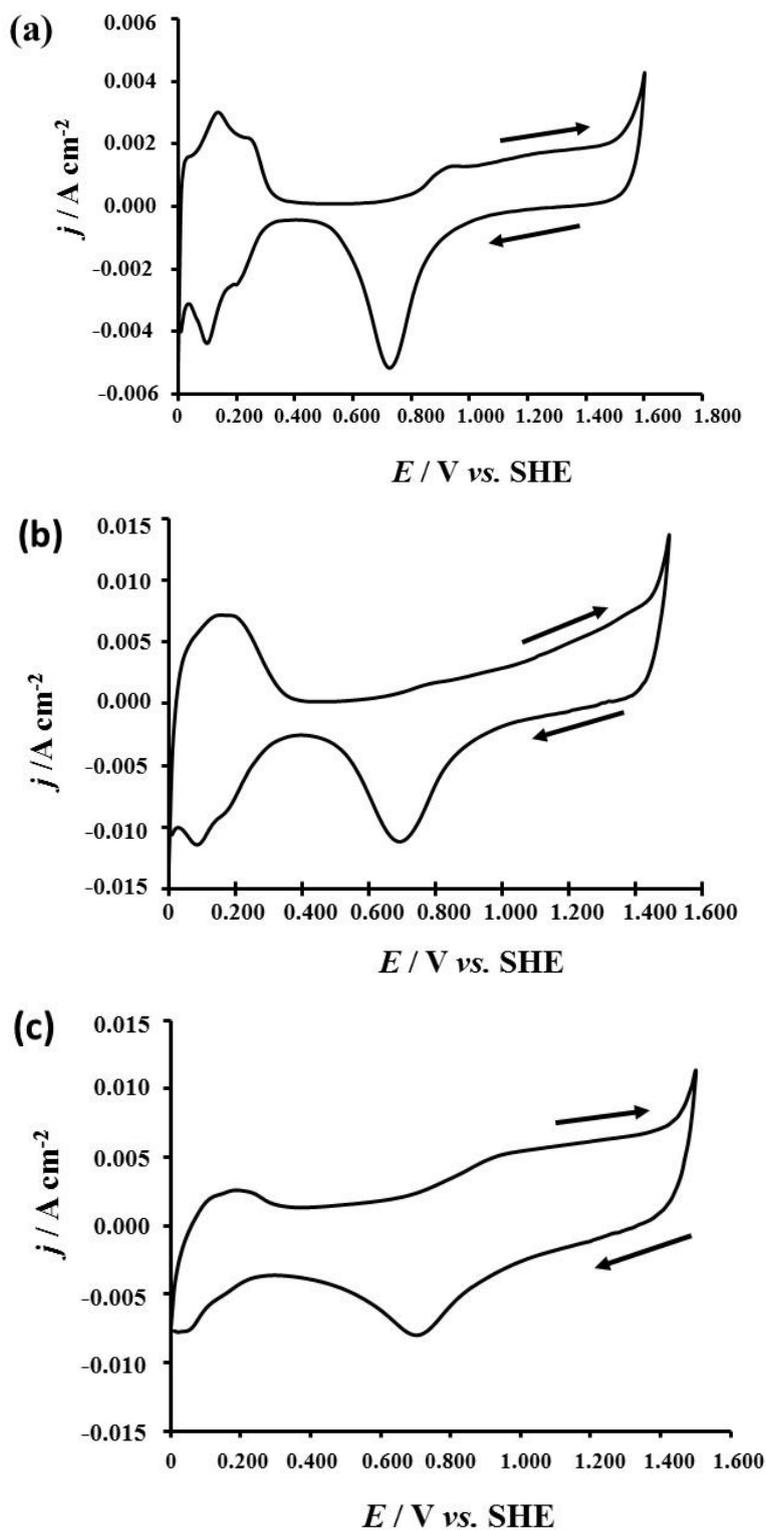**Figure 2:** *Cyclic voltammograms of Pt (**a**), $_{50}Pt$-$_{50}RuO_2$ (**b**) and $_{50}Pt$-$_{50}IrO_2$ (**c**) in 1 M $HClO_4$ at 100 mV s^{-1}, CE: platinum, T = 25°C*

Table 1: *Tafel slopes and exchange current densities of various electrodes in 1 M $HClO_4$; v =1 mV s^{-1}; CE : platinum; T = 25 °C*

Electrodes	Tafel slope / mV dec^{-1}	Exchange current density j_0 10^4 / A cm^{-2}
Pt	120	0.728
$_{50}Pt$-$_{50}RuO_2$	90	4.375
$_{50}Pt$-$_{50}IrO_2$	44	1.069
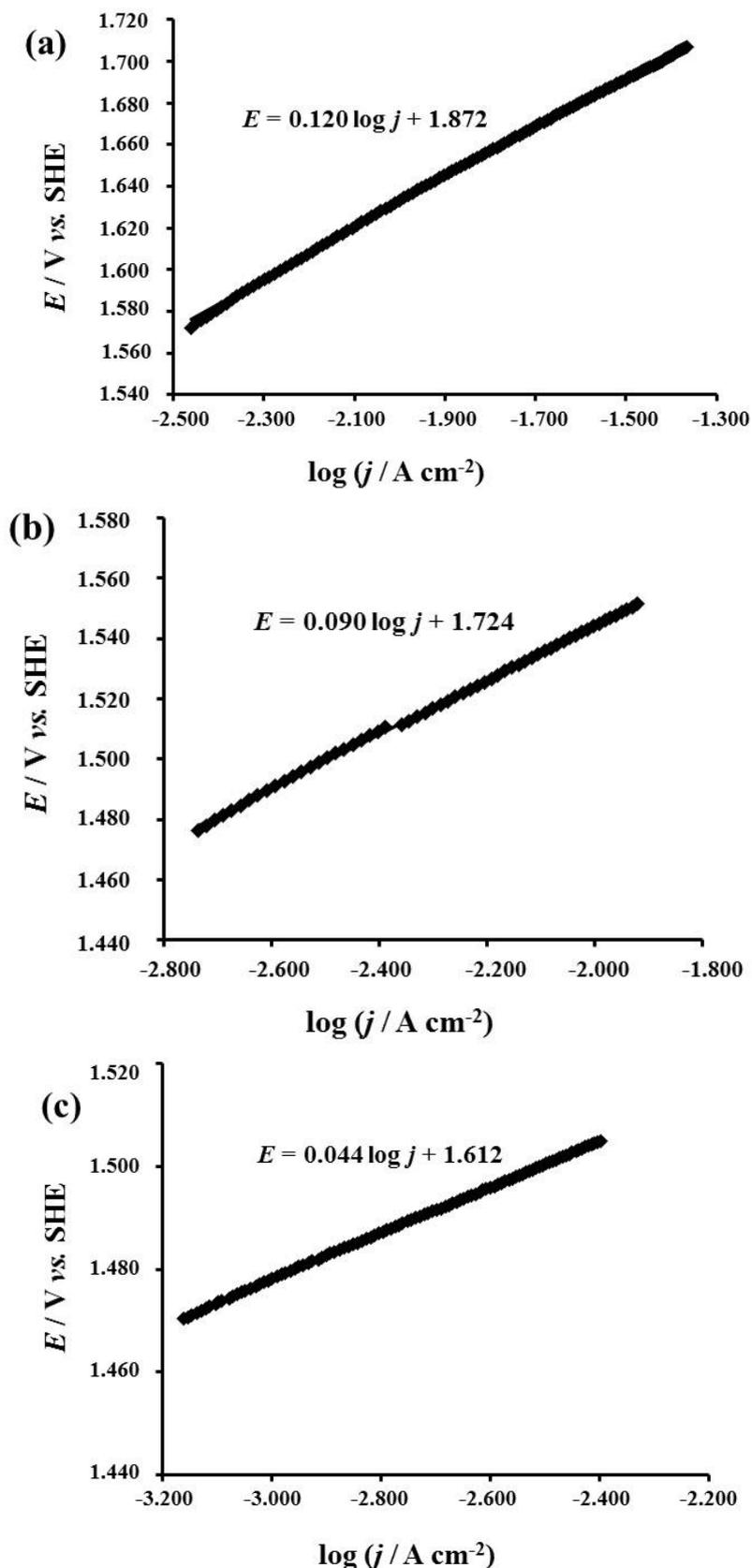
Figure 3 : *Tafel line of Pt (**a**), $_{50}Pt$-$_{50}RuO_2$ (**b**) and $_{50}Pt$-$_{50}IrO_2$ (**c**) in perchloric acid 1 M ;*
v =1 mV s^{-1}; CE : platinum; T = 25°C

Although the Tafel slopes delineate the rapidity of the kinetics occurring on the electrode surface, it is also related to the rate determining step in the OER mechanism. The electrodes

presented thus different rate determining steps. From the literature, a globally accepted OER mechanism is described as followed in acidic media [14, 19].

$$S + H_2O \rightarrow S\text{-}OH + H^+ + e^- \tag{4}$$

$$S\text{-}OH \rightarrow SO + H^+ + e^- \tag{5}$$

$$2SO \rightarrow 2S + O_2 \tag{6}$$

where S stands for electrode active sites; OH and O represent adsorbed intermediates.

If the step (4) is the rate determining step, current density associated with reaction (4) can be given as:

$$j_1 = kF[H_2O]\Gamma\left(1-\theta_1-\theta_2\right)exp\left[\frac{\alpha F}{RT}\eta\right] \tag{7}$$

j - current density, k - constant of the kinetic of the reaction, Γ - total active sites, θ_1 and θ_2 : rate of adsorbed OH and O respectively, α - charge transfer coefficient, η - overpotential

Taking into account a second electron transfer taking place in step (5), the total faradic current density can be obtained through the following equation:

$$j = 2j_1 = 2kF[H_2O]\Gamma\left(1-\theta_1-\theta_2\right)exp\left[\frac{\alpha F}{RT}\eta\right] \tag{8}$$

Considering K as

$$K = 2kF[H_2O]\Gamma(1-\theta_1-\theta_2) \tag{9}$$

(8) becomes

$$exp\left[\frac{\alpha F}{RT}\eta\right] = \frac{j}{K}. \tag{10}$$

Then

$$\eta = \frac{RT\ln 10}{\alpha F}\log j - \frac{RT\ln 10}{\alpha F}\log K \tag{11}$$

The expression of the Tafel slope is obtained by doing

$$b_a = \left(\frac{\partial \eta}{\partial \log|j|}\right)_{P,T,C_R} = \frac{RT\ln 10}{\alpha F} \tag{12}$$

In the experimental condition b_a= 120 mV dec^{-1}.

When each of the steps (5) and (6) is considered as a rate determining step, the corresponding Tafel slope would be 40 mV dec^{-1} and 15 mV dec^{-1} respectively.

According to these results and regarding the Tafel slopes of Table 1, one can consider that the rate determining step occurring on the platinum electrode is related to the hydroxyl radical adsorption on the active sites of that electrode (step 4) since the Tafel slope is 120 mV dec^{-1}. Such a result has been found by many other authors on platinum in acidic media [20,21]. With $_{50}$Pt-$_{50}$IrO$_2$, a Tafel slope of 44 mV dec^{-1} was found. That result indicated that the rate determining step is given by equation (5) of the proposed mechanism. With $_{50}$Pt-$_{50}$RuO$_2$, the obtained Tafel slope is 90 mV dec^{-1} which is almost close to 120 mV dec^{-1}. Rate determining step is similar to that

obtained with pure platinum but the kinetic of the OER is higher on that electrode than platinum owing to either a mixed kinetic control proceeding via unstable adsorption species such as S-OH* (Equations 13 and 14) [14,19] or the synergetic effect of the two surface components (Pt and RuO_2).

$$S + H_2O \rightarrow S\text{-}OH^* + H^+ + e^- \qquad (13)$$

$$S\text{-}OH^* \rightarrow S\text{-}OH \qquad (14)$$

Electrochemical characterization of the prepared electrodes in alkaline electrolyte

In the 0.5 M potassium hydroxide electrolyte, voltammograms have been recorded on platinum electrode. The obtained result is depicted in Figure 4a. The trend of the curve is different to that of platinum in acidic medium. The voltammogram presents a rectangular shape in the potential window explored.

Figures 4b and 4c show the voltammograms recorded on $_{50}Pt\text{-}_{50}IrO_2$ and $_{50}Pt\text{-}_{50}RuO_2$ electrodes. All the voltammograms showed almost the same feature. In the low potential domain, one observed superimposed voltammograms of platinum and $_{50}Pt\text{-}_{50}RuO_2$ indicating that the surface of $_{50}Pt\text{-}_{50}RuO_2$ electrodes is rich in platinum clusters. The onset of the oxygen evolution reaction potential decreased highly as platinum is associated with transition metal oxides (IrO_2 and RuO_2). The obtained potential values are 0.67 V, 0.67 V and 0.78 V for $_{50}Pt\text{-}_{50}IrO_2$, $_{50}Pt\text{-}_{50}RuO_2$ and Pt respectively. It appears that adding transition metal oxide such as ruthenium dioxide and iridium dioxide to platinum leads to electrodes with a higher electrocatalytic activity towards oxygen evolution reaction than pure platinum electrodes. That finding is in accordance with the results that are obtained in acidic medium indicating that the enhancement of the electrocatalytic activity of the composite electrodes could be due to a synergetic effect of the two elements that exist on the electrode surface.

Stability in the voltammograms was observed in that medium. That is the sign that no other oxide growth of the electrodes surface happened. In both media, platinum modified with IrO_2 or RuO_2 possesses the best electrocatalytic activity for OER than pure platinum.

The Tafel slopes of the electrodes used in this study have been determined in alkaline medium. The ohmic drop correction has been carried out like in acidic medium. Figure 5 shows the measured Tafel line of the electrodes. The obtained Tafel slopes are consigned in Table 2.
It appears that the slope decreases in the following order Pt>Pt-RuO_2>Pt-IrO_2 indicating that the rate determining steps are not the same on all the electrodes. Regarding the Tafel slopes, $_{50}Pt\text{-}_{50}IrO_2$ seemed to behave as the best electrocatalyst for oxygen evolution reaction. In contrast, Pt presents the lowest electrocatalytic activity towards oxygen evolution reaction. Coupling platinum and iridium or ruthenium oxides helps to increase oxygen evolution kinetics. The exchange current densities have been determined (Table 2) and the obtained values indicated that the system O_2/OH^- is kinetically low on all the investigated electrodes. It worth indicating that the same Tafel slope was obtained on the prepared electrodes independently of the nature of the electrolyte.

Table 2. *Tafel slopes of the prepared electrodes in KOH 0.5 M; v =1 mV s^{-1}; CE : platinum ; RE : SHE ; T = 25°C*

Electrodes	Tafel slope, mV dec^{-1}	Exchange current density j_0 10^4 / A cm^{-2}
Pt	119	0.186
$_{50}Pt\text{-}_{50}RuO_2$	87	0.140
$_{50}Pt\text{-}_{50}IrO_2$	42	10.83
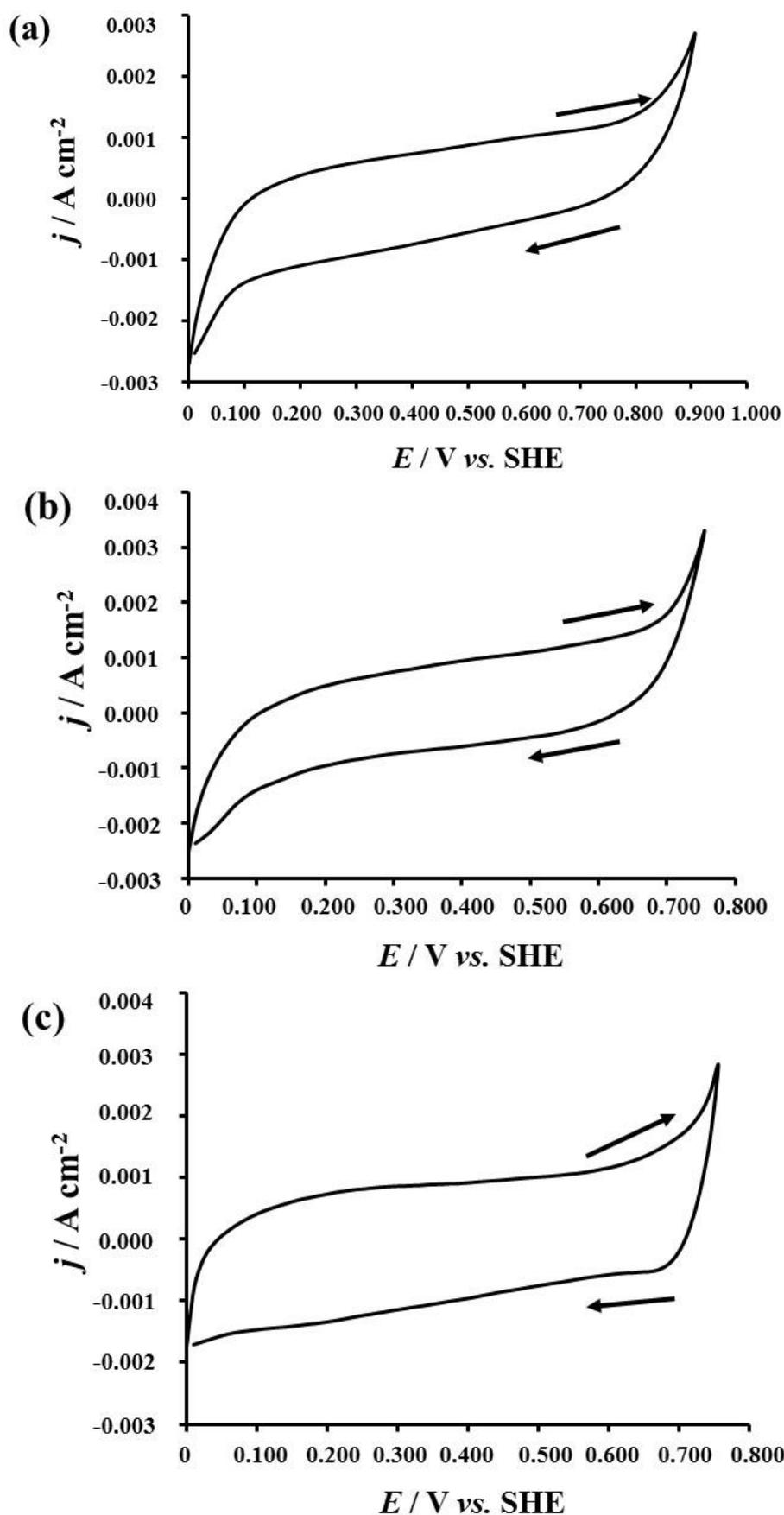
Figure 4. *Cyclic voltammograms of Pt (**a**), $_{50}$Pt-$_{50}$RuO$_2$ (**b**) and $_{50}$Pt-50IrO$_2$ (**c**) in KOH 0.5 M at 100 mV s^{-1}, CE : platinum, T= 25°C*
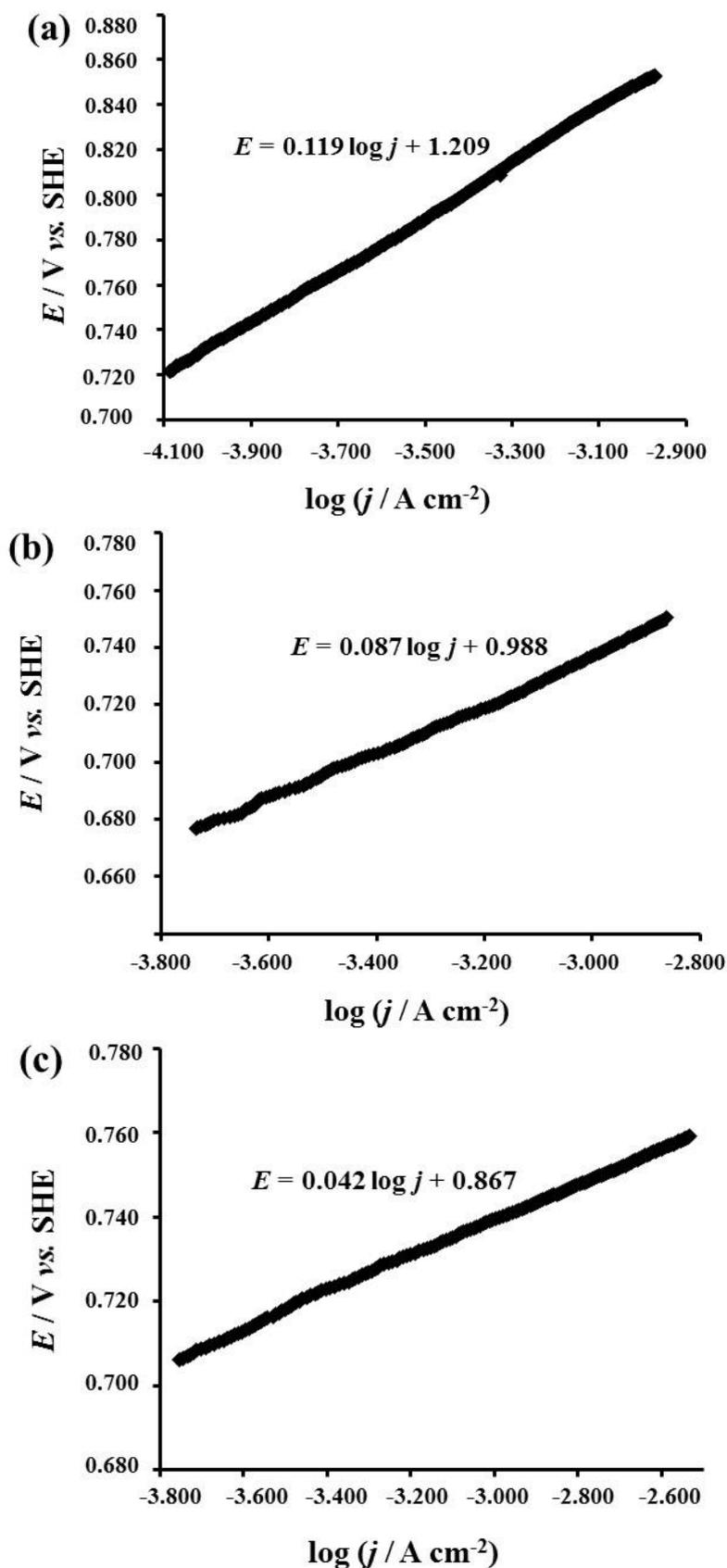
Figure 5. Tafel line of Pt (**a**), $_{50}$Pt-$_{50}$RuO$_2$ (**b**) and $_{50}$Pt-$_{50}$IrO$_2$ (**c**) in KOH 0.5 M; v = 1 mV s^{-1}; CE : platinum, T = 25°C

Oxygen evolution reaction is known to be a complex reaction. It depends normally on many factors such as electrode materials, experimental condition, and electrode preparation conditions.

The following oxygen evolution reaction mechanism that has received much agreement among researchers in alkaline electrolytes is proposed as followed [22-24].

$$S + OH^- \rightarrow SOH + e^- \tag{15}$$

$$SOH + OH^- \rightarrow SO^- + H_2O \tag{16}$$

$$SO^- \rightarrow SO + e^- \tag{17}$$

$$2SO \rightarrow 2S + O_2 \tag{18}$$
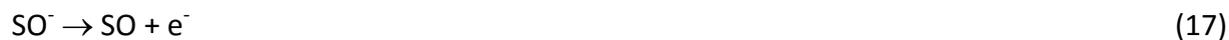
S represents the electrode active sites; OH, O^- and O represent the adsorbed intermediates.

Assuming step (15) of that mechanism as the rate determining step, the Tafel slope determined theoretically was about 120 mV dec^{-1}. In the case that the rate determining step is supposed to be step (16), the Tafel slope would be 60 mV dec^{-1}. Tafel slopes are 40 mV dec^{-1} and 15 mV dec^{-1} in alkaline electrolyte if steps (17) and (18) were considered as rate determining steps respectively. Considering the platinum electrode with a Tafel slope of 119 mV dec^{-1}, the rate determining step in the oxygen evolution process on this electrode is step (15). With $_{50}Pt$-$_{50}IrO_2$ the Tafel slope is about 42 mV dec^{-1} which is close to 40 mV dec^{-1}. Thus, on this electrode, step (17) could be the rate determining step in the oxygen evolution reaction. For the $_{50}Pt$-$_{50}RuO_2$ electrode, the Tafel slope is 87 mV dec^{-1}. As has been observed in acidic medium, that value is almost close to 120 mV dec^{-1} indicating that platinum effect seems to dominate the totally surface effect. Step (15) could be the rate determining step in the OER process.

Conclusion

The micrographs of $_{50}Pt$-$_{50}RuO_2$ and $_{50}Pt$-$_{50}IrO_2$ have revealed that their surfaces are rough with cracked structures. That of platinum was smooth, compact and homogeneous. The richer the electrode surface in platinum, thinner is the crack size and also more compact is the electrode surface.

Cyclic voltammetry investigations have revealed the presence of both IrO_2 or RuO_2 and Pt on the thermally prepared $_{50}Pt$-$_{50}RuO_2$ and $_{50}Pt$-$_{50}IrO_2$ electrode surface. The addition of metallic dioxide to platinum leads to electrodes with higher electrocatalytic activity than platinum towards oxygen evolution used as probe reaction. That electrocatalytic enhancement is due to a synergetic effect of the surface component. All the prepared electrodes showed different rate determining steps. Tafel slopes are found to be almost the same in acid and in alkaline electrolytes indicating the same rate determining steps for each electrode.

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