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INVESTIGATION OF THE ELECTROCHEMICAL BEHAVIOUR OF THERMALLY PREPARED Pt-IrO_2 ELECTRODES

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ABSTRACT. Different IrO_2 electrodes in which the molar percentage of platinum (Pt) varies from 0 %mol Pt to 100 %mol Pt were prepared on titanium (Ti) substrate by thermal decomposition techniques. The electrodes were characterized physically (SEM, XPS) and electrochemically and then applied to methanol oxidation. The SEM micrographs indicated that the electrodes present different morphologies depending on the amount of platinum in the deposit and the cracks observed on the 0 %mol Pt electrode diminish in size tending to a compact and rough surface for 70 %mol Pt electrode. XPS results indicate good quality of the coating layer deposited on the titanium substrate. The voltammetric investigations in the supporting electrolyte indicate that the electrodes with low amount of platinum (less than 10 %mol Pt) behave as pure IrO_2. But in the case of electrodes containing more than 40 %mol Pt, the voltammograms are like that of platinum. Electrocatalytic activity towards methanol oxidation was observed with the electrodes containing high amount of platinum. Its oxidation begins at a potential of about 210 mV lower on such electrodes than the pure platinum electrode (100 %mol Pt). But for electrode containing low quantity of Pt, the surface of the coating is essentially composed of IrO_2 and methanol oxidation occurs in the domain of water decomposition solely. The increase of the electrocatalytic behaviour of the electrodes containing high amount of Pt towards methanol oxidation is due to the bifunctional behaviour of the electrodes.

KEY WORDS: Iridium dioxide, Platinum, Methanol oxidation, Electrocatalytic activity

INTRODUCTION

Since the dimensionally stable anodes (DSA) was developed into chlor-alkali industry, the electrochemical behaviour of the transition metal oxide with the metallic conductivity supported by valve metals such as titanium has paid much attention [1-4]. Among the dimensionally stable anodes, iridium oxide anodes present excellent electrocatalytic properties and good stability in strong acid solution for chlorine evolution and oxygen evolution [5-8]. They can generate hydroxyl radicals and active chlorine species to destroy refractory organic waste into carbon dioxide [9-12]. But, the oxidation of organic compounds occurs in the domain of water decomposition, i.e. at higher overpotential leading to high energy consumption [13, 14]. A decrease of the overpotential of organic matter oxidation should be done to lower the energy consumption by developing new electrocatalyst that can perform it [15]. In fact, the electrocatalytic oxidation of small organic molecules especially methanol and its reaction intermediates has been widely investigated and continues to be considered as model molecules but also in connection with technological and environmental problems [16]. Thus many studies have been carried out on electrochemical treatment of organic compound and several anode materials have been tested. For example, platinum was the best catalyst which was used in electrochemistry for small organic oxidation etc. But, deactivation of such a catalyst in the oxidation of the organic matter occurs. To enhance the platinum activity, several additives consisting of metals like Sn, Ru, Os etc were used leading to bifunctional active materials. Although electrocatalyst based on Pt [17] and Pt-Ru [18] alloys exhibit good activities, high costs of materials are often much prohibited. Thus a desire to develop new combined active

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*Corresponding author. E-mail: ouatlassine@yahoo.fr anodes for water treatment with a high stability has kept our attention. Due to the good properties of several anode materials consisted of a mixture of IrO_2 and Pt will be developed in order to find the best electrocatalyst for small organic (methanol) oxidation. The electrodes will be characterized physically and electrochemically and then applied for small organics oxidation.

EXPERIMENTAL

Platinum modified iridium oxides electrodes were prepared by the thermal decomposition method on titanium substrates. The precursor solution is made by the dissolution of $H_2IrCl_6.6H_2O$ (Fluka) and $H_2PtCl_6.6H_2O$ (Fluka) in pure isopropanol (Fluka). Prior to the deposition and to ensure maximum adhesion of the coating, the substrate (titanium) was sandblasted. Electrodes of different xPt-(1-x)IrO_2 percentage molar of each element were prepared where x represents the percentage molar of platinum in the precursor. For the prepared electrodes x corresponds to: 0 %, 10 %, 40 %, 70 %, and 100 %.

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 450 °C for 15 min to allow the decomposition of the precursor. These steps were repeated until the desired mass of the coating is reached. A final decomposition of 1 h was done at 450 °C.

The SEM micrograph of the electrodes was taken by Scanning Electron Microscopy (SEM, JEOL 6300F). The XPS analyses were carried out with a Kratos Axis-Ultra Spectrometer using a monochromatic Al Kα X-Ray source, operated at 15 kV and a pass energy of 20 eV.

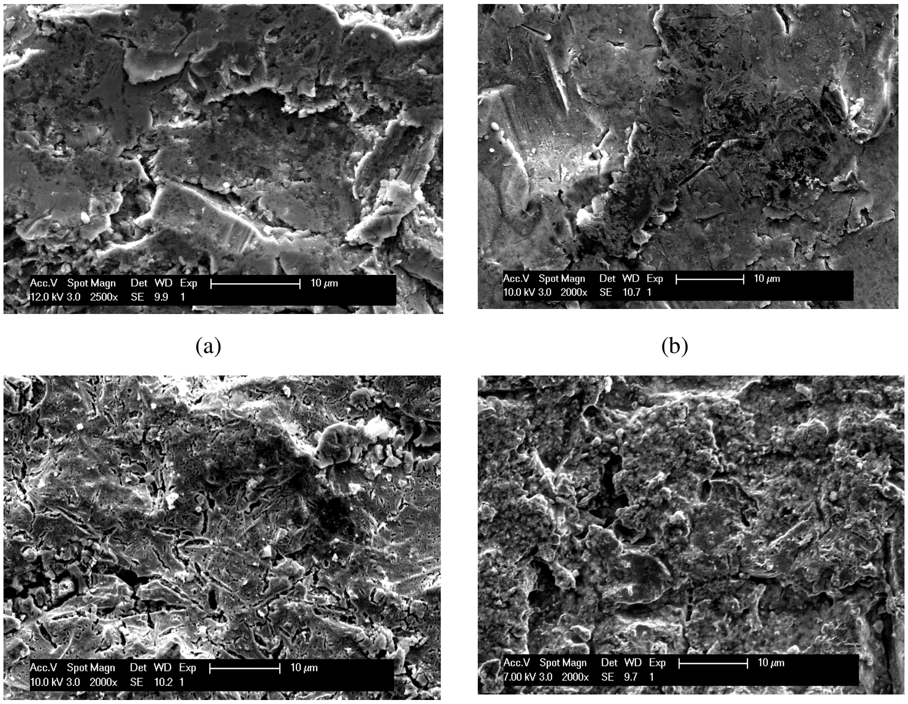
The electrochemical measurements were performed in a three-electrode electrochemical cell using an Autolab PGStat 20 (Echochemie). The counter electrode was a platinum wire and the reference electrode was a saturated calomel electrode (SCE (0.249 V/SHE)). All the potential are referenced against the standard hydrogen electrode (SHE). The apparent exposed area of the working electrode was 0.78 cm^2. The experiments were made at 25 °C. The supporting electrolyte used was 1 M perchloric acid ($HClO_4$). The potential was scanned from 0 V/SHE to 1.5 V/SHE. The scan rates are 5 mV/s, 20 mV/s and 100 mV/s. The potentials were scanned at first in the anodic direction and then in the cathodic direction.

All the solutions were made with distilled water with analytical grade reagents.

RESULTS AND DISCUSSION

Physical characterization of the electrodes

Figure 1a-d show the SEM images of the electrodes surface. One observes that the morphology of the deposit changes as the platinum molar percentage increases. In pure IrO_2, i.e. 0 %mol Pt electrode (Figure 1a), the SEM micrograph presents superimposed layers of IrO_2, cracks and some pores. The consistent of the deposit do not allow the observation of the substrate. In Figure 1b, SEM image was taken on the 10 %mol Pt electrode. The surface of that deposit seems to be more continuous and the crack size diminishes due to the presence of platinum inside the IrO_2 lattice which modifies its internal structure. In Figure 1c, the deposit containing 40 %mol Pt presents small cracks size and different small pits. One observes in that Figure some small disperse platinum crystal on the deposit. Finally in Figure 1d, the deposit containing 70 %mol Pt presents porous and very rough surface.



(a) (b)

(c) (d)

Figure 1. SEM images of the electrodes containing: (a) 0 %mol Pt (pure IrO_2), (b) 10 %mol Pt, (c) 40 %mol Pt, and (d) 70 %mol Pt.

The XPS measurements were taken on the electrodes and the results were presented in Figure 2. The spectra of the electrodes containing 10 to 70 %mol Pt presents the same feature. They are similar to that of 0 %mol Pt (pure IrO_2) with obviously the absence of Pt signal in the spectrum. This result shows the good quality of the coating layer deposited on the titanium substrate. According to the position of Ir and Pt signals in the XPS spectra of the 10 %mol Pt to 70 %mol Pt electrodes, the deposit is composed with IrO_2 and Pt [19, 20]. The XPS spectra recorded in the Pt 4f region of the samples Pt-IrO_2 show two peaks at 71.2 eV and 74.6 eV suggesting that the platinum particles are in the metallic form (inset of Figure 2) [21]. On all the spectra, Ti signal is absent indicating that the substrate is totally covered by the deposit. The Pt signal intensity increases when the molar percentage of platinum increases in the deposit while the intensity of Ir signal decreases. That could be explained by the fact that as the platinum amount increases in the deposit; enrichment of the coating surface with platinum occurs.

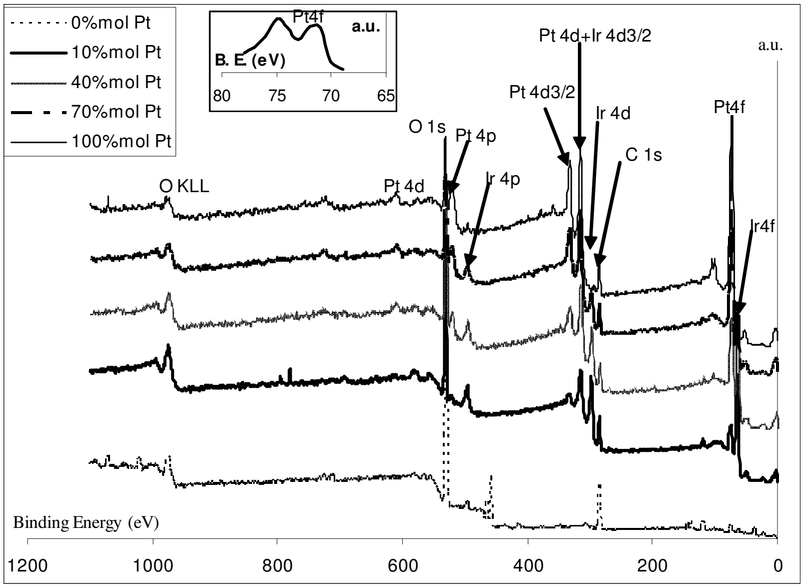


Figure 2. XPS spectra of all the electrodes prepared (the inset shows the Pt 4f region).

Electrochemical behaviour of the electrodes in the supporting electrolyte

Figure 3 presents the cyclic voltammetry measurements realized on the different electrodes in the supporting electrolyte consisted of 1 M $HClO_4$. This Figure presents the stable voltammograms taken after hydration under several potential scans in 1 M $HClO_4$. The voltammogram of the 0 %mol Pt electrode is the typical curve usually observed for IrO_2. A reversible broad peak characteristic of the redox transition of Ir(III)/Ir(IV) is observed at around 0.9 V on the voltammogram. A similar feature with a slight increase in the voltammetric charge is obtained with the 10 %mol Pt electrode. In this case, the reversible peak is well defined. And in the domain of low potential, hydrogen evolution occurs. For 40 %mol Pt and 70 %mol Pt, the voltammograms change considerably when compared to the first two voltammograms. The general feature resembles to that of pure platinum electrode (inset Figure 3). One observes the adsorption and desorption peaks of hydrogen followed by hydrogen evolution at low potential. A very small double layer region between 0.35 V and 0.4 V is observed followed by an increase in the current density characteristic of the formation of platinum oxide layer. The reversible peaks of the redox transition of Ir(III)/Ir(IV) are present again. In the negative going sweeping potential, platinum oxide reduction peak is also observed.

In fact, this result indicates that for small amount of platinum in the deposit, the Pt seems to be inside the IrO_2 matrix. The electrode surface in that case is essentially composed of IrO_2. When the platinum molar percentage reaches 40 %mol or 70 %mol, Pt exists on the coating surface and that could explain why the shape of the voltammogram resembles to that of Pt [22, 23].

Electrochemical oxidation of methanol on the electrodes

In order to study the electrocatalytic properties of the prepared electrodes, they have been used for methanol oxidation.

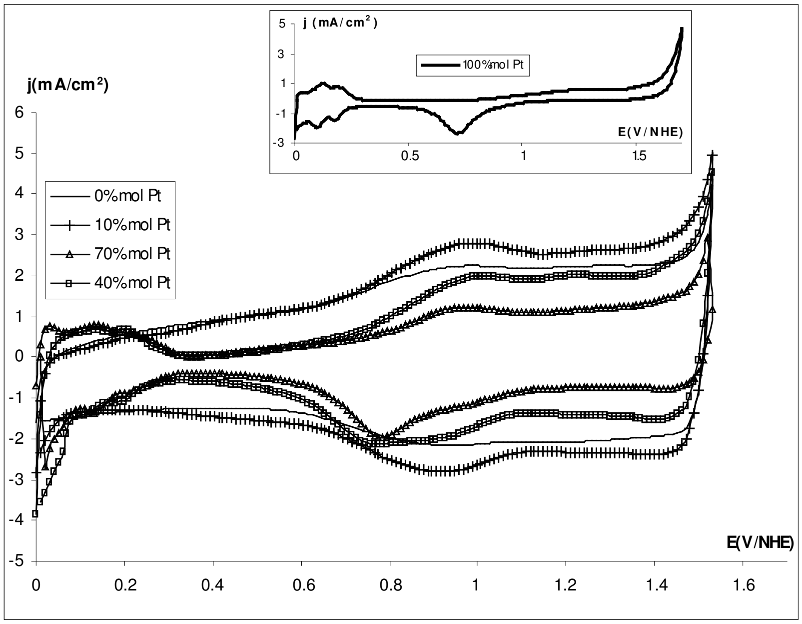


Figure 3. Cyclic voltammetry measurement realized in 1 M $HClO_4$, T = 25 °C, v = 100 mV/s (the inset corresponds to pure platinum (100 %mol Pt) voltammogram).

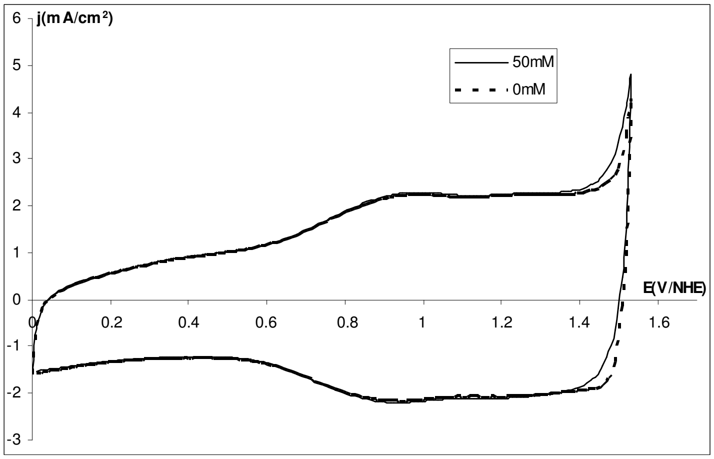


Figure 4. Cyclic voltammetry on 0 %mol Pt electrode (pure IrO_2) in 1 M $HClO_4$ and methanol with different concentration, v = 100 mV/s, T = 25 °C.

Figure 4 presents the voltammogram realized on 0 %mol Pt electrode (pure IrO_2) in absence and in presence of methanol. One observes that, in the domain of water stability (0 - 1.35 V), no modification of the voltammograms is observed in the presence of methanol. But at higher anodic potential, a decrease of the overpotential of oxygen evolution is observed in the presence of methanol. This result is in accordance with the literature [11]. The same result is obtained with the 10 %mol Pt electrode (Figure 5).

Figure 6 shows the results obtained on the 40 %mol Pt electrode in presence of methanol. One observes that the current density starts to increase after 0.49 V followed by a methanol oxidation peak at 0.9 V. The height of the peak increases as the methanol concentration increases. The peak is followed by an increase in the current density. A decrease of the overpotential of oxygen evolution occurs at higher anodic potential. The shift of the oxygen evolution overpotential in the negative direction became important as the concentration of methanol increases. In the backward of the voltammogram, a decrease of the current density in absolute value is observed at about 0.65 V. In the low potential domain, a considerable change in the voltammograms is not observed although methanol concentration increases. The voltammograms of Figure 7 present the same general feature as those in Figure 6. In Figure 7 and in the inset of Figure 7, the current density is higher than that of Figure 6 and in the backward of the voltammograms, a very well defined oxidation peak is observed at about 0.65 V. The investigation made at 5 mV/s and presented in Figure 8 indicates the catalytic oxidation of methanol on the 40 %mol Pt electrode. This effect becomes more important as the platinum amount increases to reach 70 %mol Pt in the deposit.

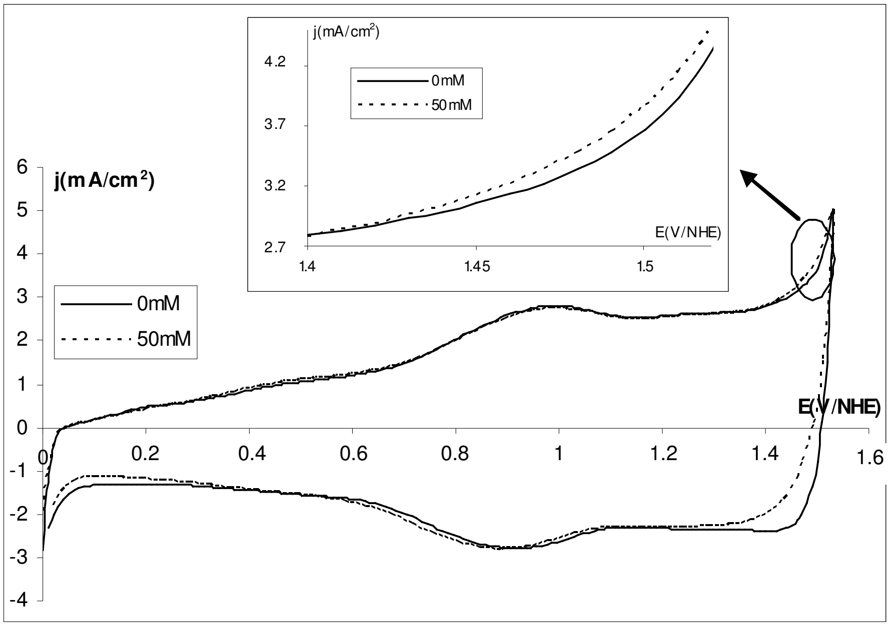


Figure 5. Cyclic voltammetry on 10 %mol Pt electrode in 1 M $HClO_4$ and methanol with different concentration, v = 100 mV/s, T = 25 °C (the inset is a magnification of a portion of total voltammogram).

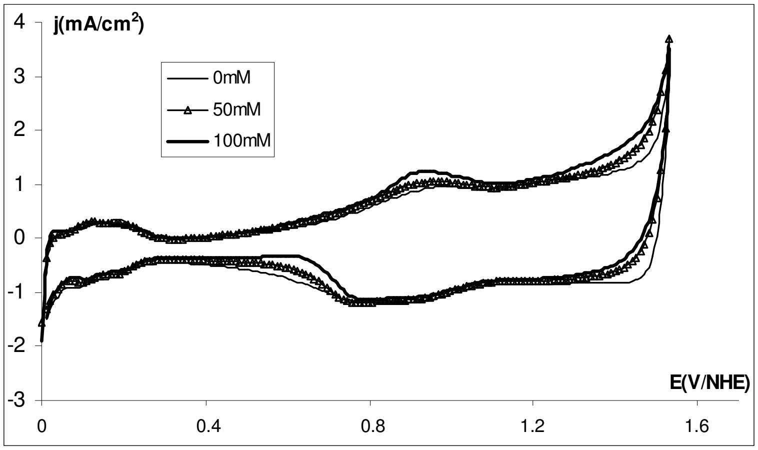


Figure 6. Cyclic voltammetry on 40 %mol Pt electrode in 1M $HClO_4$ and methanol with different concentration, v = 100 mV/s, T = 25 °C.

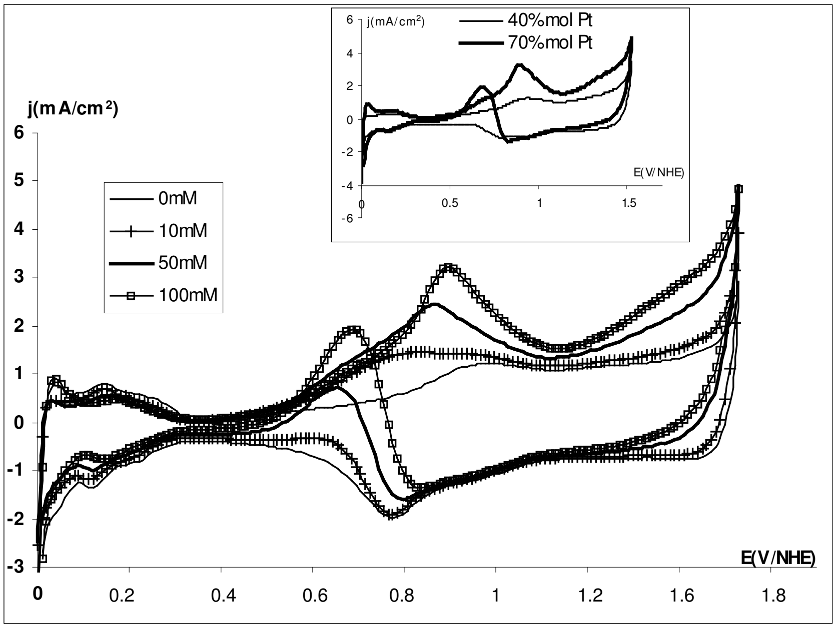


Figure 7. Cyclic voltammetry on 70 %mol Pt electrode in 1 M $HClO_4$ and methanol with different concentration, v = 100 mV/s, T = 25 °C (the inset shows the results of the oxidation of 100 mM of methanol on 40 %mol Pt and 70 %mol Pt electrodes).

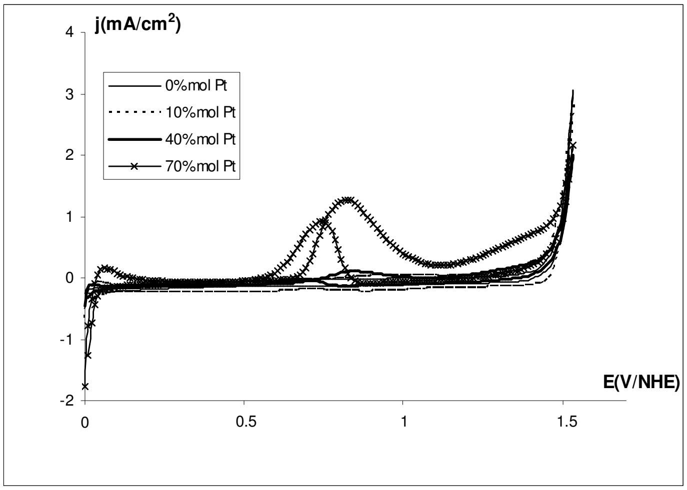


Figure 8. Cyclic voltammetry on the prepared electrodes in 1 M $HClO_4$ and 100 mM methanol, v = 5 mV/s, T = 25 °C.

Figure 9 shows the measurement taken on the thermally prepared pure platinum electrode (100 %mol Pt). It shows that the methanol oxidation current density starts to increase at about 0.70 V followed by an anodic peak at 0.9 V. That is a characteristic of the anodic oxidation of methanol. After this peak the current decline, as the surface was poisoned by the formation of carbon monoxide [24]. An oxidation peak characteristic of methanol re-oxidation is also observed in the backward of the voltammogram with a peak potential equal to 0.68 V. A disappearance of the adsorption and desorption peaks is observed on that electrode in the domain of low potential.

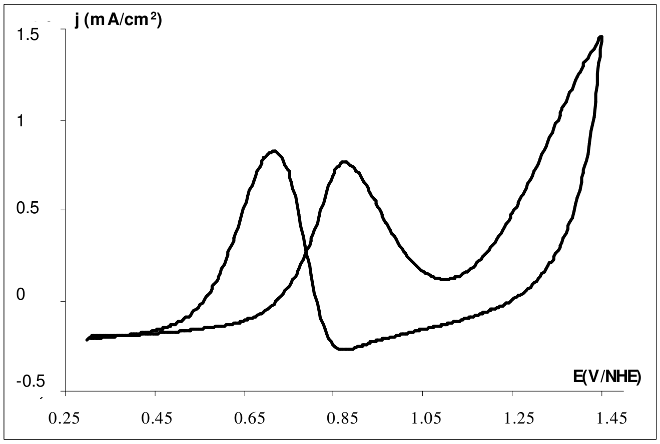


Figure 9. Cyclic voltammetry on 100 %mol Pt electrode in 1M $HClO_4$ and 100 mM methanol, v = 20 mV/s, T = 25 °C.

In fact, the electrodes surface composition influences the electrochemical behaviour of the electrodes. Thus, no oxidation of methanol occurs on 0 %mol Pt electrode in the domain of water stability since no modification is observed on the voltammograms in absence and in the presence of methanol. That indicates the non-electrocatalytic behaviour of this electrode towards methanol oxidation in that domain. But the decrease of the overpotential of oxygen evolution on the same electrode in the domain of the higher potentials indicates that intermediates resulting from water decomposition are involved in methanol oxidation process. This result is in accordance with the result of Comninellis *et al.* [11, 25-26] where they suggested that the decomposition of water leads to hydroxyl radicals which react with IrO_2 leading to IrO_3. And this active layer reacts with methanol for its oxidation. For 10 %mol Pt electrode, methanol oxidation process is principally realized by IrO_2 according to the described oxidation process since for this amount of platinum in the deposit, it has been indicated that platinum does not exist at the surface of the coating layer. The 10 %mol Pt electrode behaves like pure IrO_2 (0 %mol Pt electrode). For electrodes containing 40 %mol Pt and 70 %mol Pt, a combined methanol oxidation process occurs. And the methanol oxidation begins at potential of about 210 mV lower than the pure platinum. Thus, these electrodes present a catalytic behaviour towards methanol oxidation due to the presence of platinum on the electrode surface. The best electrode is the 70 %mol Pt electrode for methanol oxidation. The decrease of the overpotential of methanol oxidation could be due to a bifunctional behaviour of the deposit. Indeed, the existence of platinum at the deposit surface lowers in a catalytic way the oxidation of methanol potential. Such electrodes present electrocatalytic behaviour for methanol oxidation. In fact, we suggest that during the methanol oxidation process, dissociative adsorption of methanol occurs on the platinum active sites. During this process, carbon monoxides (CO) are strongly chemisorbed on platinum active sites. They are responsible for its deactivation by blocking the platinum active sites as has been observed in the case of pure platinum (i.e. disappearance of hydrogen adsorption and desorption peak, Figure 9). In the same oxidation process, the discharge of water occurs and leads to the formation of IrO_3. Then reaction between the active oxygen of IrO_3 and CO takes place to produce CO_2 which is rapidly evolved from the electrode surface. That liberates the electrode active sites allowing continuous methanol oxidation to occur. This mechanism can explain the increase of the kinetic of methanol oxidation on those electrodes diminishing the methanol oxidation potential to be 210 mV lower than the pure platinum.

CONCLUSIONS

The morphology of the electrodes depends on the amount of platinum in the deposit. As the platinum molar percentage increases in the deposit, the cracks observed on the 0 %mol Pt electrode diminishes in size tending to a compact and rough surface for 70 %mol Pt electrode. It has been indicated that as the molar percentage of Pt increases in the deposit, surface enrichment with platinum occurs. XPS results indicate also that thick deposits were prepared due to the absence of Ti signal in the spectra.

The voltammetric investigations in the supporting electrolyte indicate that the electrodes with low amount of platinum (less than 10 %mol Pt) shows voltammograms with the same shape as pure IrO_2. But in the case of electrodes with high amount of platinum (more than 40 %mol Pt), the voltammograms are like that of platinum. These results indicate the absence of platinum on the surface for electrodes containing low amount of platinum and surface enrichment with platinum for the deposit containing more than 40 %mol Pt. The electrodes containing high amount of Pt present high catalytic activity for methanol oxidation. That oxidation begins at potential of about 210 mV lower on such electrodes (>40 %mol Pt) than the pure platinum electrode. But for electrodes containing low quantity of Pt, the surface of the coating is essentially composed of IrO_2 and methanol oxidation occurs in the domain of water decomposition solely. The increase of the electrocatalytic behaviour of the electrodes containing high amount of Pt towards methanol oxidation was explained by their bifunctional behaviour. In fact, during the methanol oxidation process, carbon monoxides (CO) which were strongly chemisorbed on platinum active sites react with the active oxygen of the higher oxide IrO_3 to produce CO_2 which is rapidly evolved from the electrode surface that liberates the electrode active sites allowing continuous methanol oxidation to occur. This result could be important for fuel cell application and for the wastewater treatment.

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