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Research Paper

Influence of Chlorides on the Electrochemical Oxidation of Formic Acid on Thermally Prepared Platinum Electrodes

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Abstract: *Rough and compact platinum electrode was prepared thermally at 400°C on a titanium substrate. The analysis of its surface has revealed that platinum existed at various oxidizing state. In chlorides containing perchloric acid electrolyte, a quasi-reversible peak related to the chlorine/chloride redox process appeared on the voltammogram. The adsorption of chlorides on the platinum surface rather than hydroxyl radicals (or water) rendered the platinum oxide formation/reduction process more irreversible. In presence of formic acid, the oxidation peaks observed in free chlorides containing electrolyte have disappeared as chlorides were added to the acid solution showing the deactivation of the platinum active sites by the chemisorbed chlorides. That hampered direct oxidation of formic acid onto the electrode surface at low potential. But at high potential and in the presence of the chlorides, formic acid oxidation occurs indirectly via chlorine or hypochlorite species resulting from the oxidation of chlorides.*

Keywords: Platinum, chloride, formic acid, cyclic voltammetry, adsorption

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1. Introduction:

Actually, the situation of the pollution of our environment especially our lagoons is alarming notably the water pollution[1]. That pollution is caused by agricultural activities by the use of pesticides and also caused by the wastewater coming from industries which unfortunately are not treated. Since water is important for human life it becomes imperious to develop techniques that could be used to treat the wastewaters. Among the large variety of pollutants that exist in the wastewaters, the organic waste notably the non biodegradable organics are those which caused the serious problems. Biological treatment is found to be inefficient for such pollutants. Advanced oxidation processes producing high oxidation potential hydroxyl radicals are often investigated for the pretreatment or the treatment of the wastewaters but high sludge could be produced in some cases. Electrocatalysis seems to be an increasingly popular way for the wastewater treatment and environmental friendly[2-5]. For such a treatment, the electrode material plays an important role. Since platinum is one of the most used electrode material among the noble metals due to its high electrical conductivity and its chemical inertness[6] it is chosen as a good candidate for our investigations. Besides its properties, platinum has efficiently been used in several electrochemical investigations such as electronics, oxygen and chlorine evolution reactions, fuel cell applications, organics oxidation[7-13] even if, it sometimes suffers from deactivation by adsorbed carbon monoxides[14;15]. It has been pointed out in literature that the quality of the Pt films and also its reactivity depends mainly on the substrate temperature, deposition rate and chemical composition of the starting material i. e. depends on the preparation technique of the electrode materials. Thermal preparation was found to be suitable to prepare a good quality of platinum electrode with variable thickness of the platinum coating [6].

The physico-chemical analysis of the real wastewaters that were withdrawn from our lagoons revealed that they have a complex composition with a high amount of chlorides. As a preliminary investigation, a model compound such as formic acid representing a model synthetic wastewater will be treated in chlorides free or containing electrolyte. Thus in the present work, platinum will be prepared by the thermal techniques and then characterized physically and electrochemically. Its behavior in chlorides containing electrolyte will be investigated and the chlorides influence on the formic acid oxidation on the platinum electrode will be carried out by cyclic voltammetry.

2. Materials and Methods:

The electrode used in the following work was prepared in our laboratory with an appropriate metallic precursor. The coating precursor was prepared from $H_2PtCl_6,6H_2O$ (Fluka). The precursor was dissolved in pure isopropanol (Fluka) used as solvent. The commercial product was used as received without any further treatment.

The titanium substrate on which the electrode film was 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 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 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 weight of the coating was reached. A final decomposition of 1 h was done at 400 °C. The loading of the deposit was about 5 g/cm^2 on the titanium substrate.

The morphology of the electrode was analyzed by means of a Scanning Electron Microscopy device (SEM, JEOL 6300F). The crystalline structure was examined by X-Ray diffraction (XRD) using a Siemens equipment with a Cu cathode. The XPS analysis was 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. Pt and O spectra were deconvoluted using the CasaXPS computer program.

The voltammetric measurements were performed on the prepared electrode in a three-electrode electrochemical cell using an Autolab PGStat 20 (Ecochemie). The counter electrode was a platinum wire and the reference electrode was a saturated calomel electrode (SCE). All the potential were reported against SCE. To overcome the potential ohmic drop, the reference electrode was mounted in a luggin capillary and placed close to the working electrode by a distance of 1 mm. The 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), HCOOH (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.

3. Results and Discussion:

The SEM image of the platinum film was shown in figure 1. The film presented a rough surface and an almost compact structure.

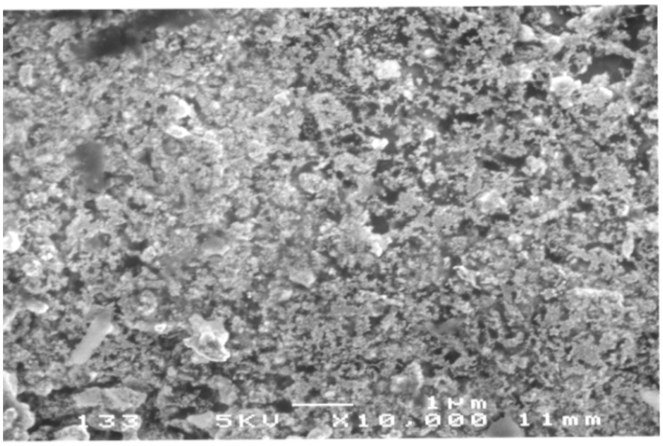

Figure 1: SEM image of the thermally prepared platinum electrode, T=400°C in presence of air

Figure 2 presented the wide range XP spectrum for the as-grown platinum electrode. This spectrum indicated that the surface of the electrode was almost free of impurities regardless of the presence of the carbon C1s. The spectrum data obtained are consigned in table 1. From that table, it appeared that the surface of the deposit was mainly composed by platinum, oxygen and carbon. The signal of the titanium used as substrate in that work was absent in the total survey of figure 2 indicating that that substrate was totally covered by the deposit. At the investigated temperature, 400°C, it could be suggested that no titanium oxide was formed at the titanium and the deposit interface. The presence of C1s on the surface of the electrode could be due to the organic contaminants from the sample preparation. From that result, platinum could be present at the titanium surface in different oxidized states. Thus detail information about Pt4f and O1s was determined by carrying out the quantitative deconvolution of the Pt4f and O1s spectra presented in figure 3 and 4 respectively. The spectra resulted from the deconvolution of Pt4f and O1s spectra were inserted in figures 3 and 4 respectively. The detail data resulting from the deconvolution were given in table 2.

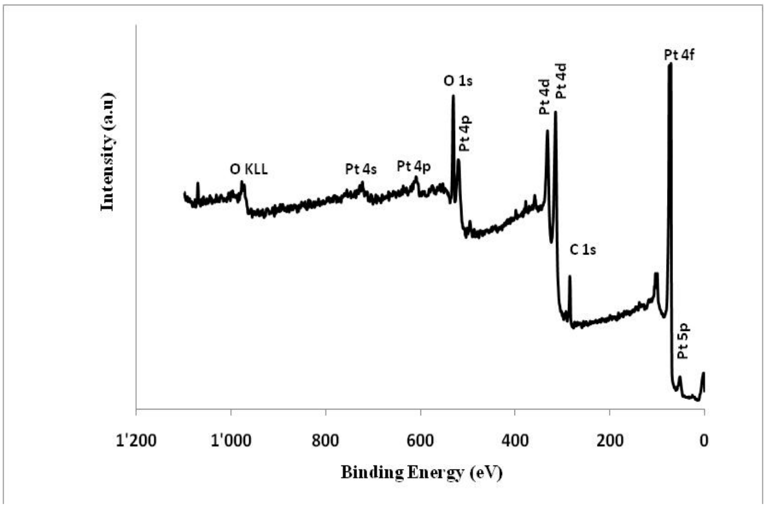

Figure 2: XPS survey of the thermally prepared platinum electrode

Table 1: XPS analysis of the as-grown platinum surface

	B.E (Ev)	**Atomic conc. (%)**	**Mass conc. (%)**
O 1s	531,6	36,67	10,3
Ti	464,3	0	0
Pt 4f	71,1	23,69	81,15
C 1s	284,7	39,53	8,34

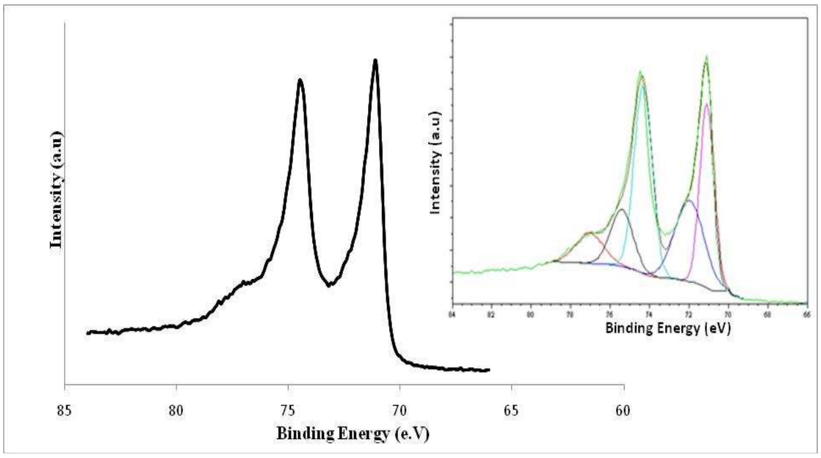

Figure 3: Pt4f spectrum withdrawn from the total survey of figure 2 and located between 65eV and 80 eV. Result of the Pt4f spectrum deconvolution (inset)

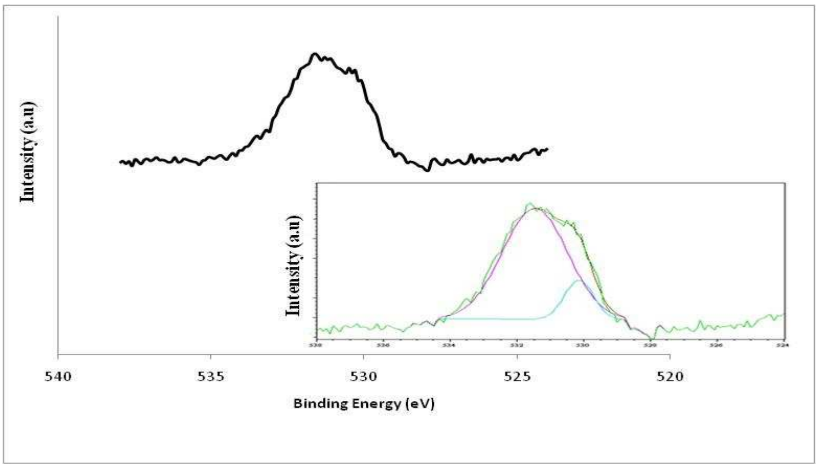

Figure 4: O 1s spectrum withdrawn from the total survey of figure 2 and located between 520eV and 535 eV. Result of the O 1s spectrum deconvolution (inset)

Table 2: Summary of the deconvolution results of the Pt4f and O1s spectra for the prepared electrodes

Element	**O1s**		**Pt4f**	
	Energy (eV)	Concentration percentage	Energy (eV)	Concentration percentage
Pt	530,15	13,76	71,1	24,77
			71,97	22,72
	531,46	86,24	74,32	32,23
			75,4	12,28
			77,03	08,00

Table 2 indicated two contributions for O1s and five contributions for Pt4f. This result indicated that Pt existed in the deposit in different oxidized states[16]. The spectrum of Pt4f was splitted in five peaks with the binding energies of 71,1eV, 71,97eV, (74,32-75,4) eV and 77,03eV corresponding according to the literature to Pt(0), $Pt(OH)_2$, PtO and PtO_2 respectively.

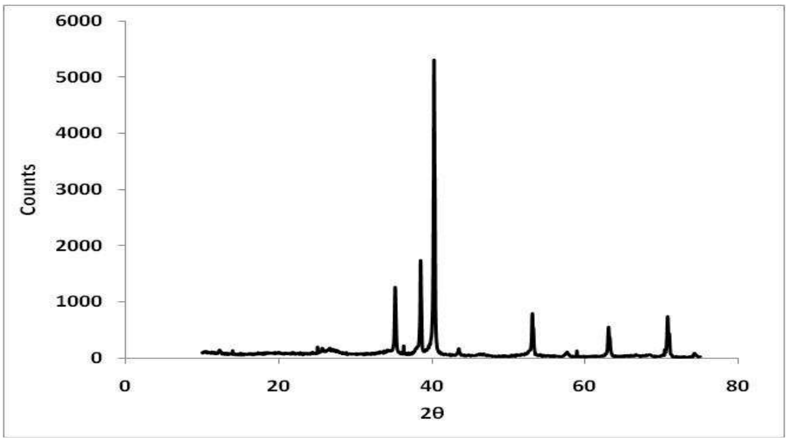

Figure 5: XRD of the thermally prepared platinum electrode

X-Ray diffraction pattern of the platinum deposit was presented in figure 5. XRD was known to be a bulk method which could give information on the bulk structure of the deposit and its support. The spectrum was analyzed and the peaks located at 2θ= 40,04 and 53,24° could be assigned to Ti[17]. The peaks corresponding to polycrystalline Pt were present at 2θ=40 and 68°. The peaks located at 35,24 and 63,20 corresponded to PtO_2. Those results indicated that the deposit was a mixture of Pt with zero-valence and its oxidized form confirming the results of XPS results.

The electrochemical characterization of the electrodes with the ferri-ferrocyanide system was carried out. The results obtained on the platinum electrode were presented in figures 6 and 7. Detail analysis of the obtained voltammograms was made and it led to the determination of the gap between the peak potentials, the ratio of the absolute value of the anodic to cathodic peak current intensity, and the apparent equilibrium potential for equimolar redox couple. Those results were consigned in table 3.

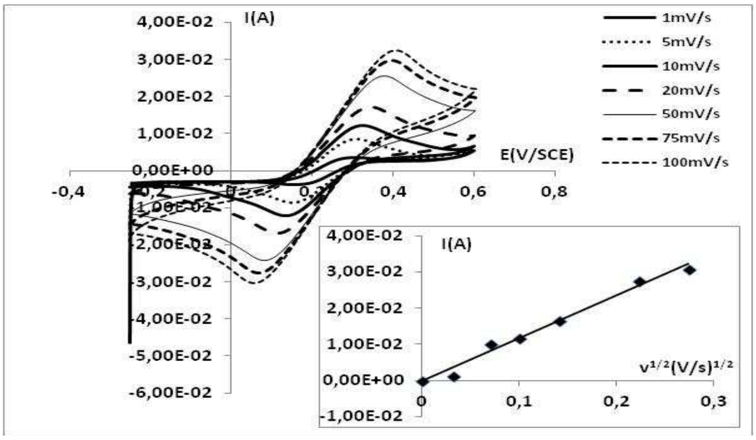

Figure 6: Cyclic voltammograms for the reaction of the ferri/ferrocyanide redox couple on a platinum electrode. Influence of the potential scan rates. C=100mM (equimolar concentration of both species), T=25°C, CE: Pt wire, RE: SCE (inset: plot of the peak current intensity versus the square root of the potential scan rate)

The voltammograms showed the oxidation and reduction peaks of the redox system (figures 6; 7). The potential of the peak increased with the potential scan rates and also with the concentration of the redox couple species. The evolution of the peak current intensity against the square root of the potential scan rate and the concentration were examined. The obtained results were inserted in figure 6 and in figure 7 respectively. A linear evolution has been observed in both cases. It indicated that the process was controlled by diffusion at the platinum electrode surface.

Table 3: Kinetic parameters resulted from the ferri/ferrocyanide redox couple investigation on the platinum electrode

Scan rate (V/s)	**|Ipa/Ipc|**	**E°'(V/SCE)**	**ΔEp**
0,100	**1,07**	**0,2350**	**0,343**
0,075	**1,08**	**0,2305**	**0,327**
0,050	**1,06**	**0,2315**	**0,291**
0,020	**1,02**	**0,2305**	**0,225**
0,010	**1,04**	**0,2320**	**0,188**
0,005	**1,01**	**0,2315**	**0,149**
0,001	**1,13**	**0,2270**	**0,066**

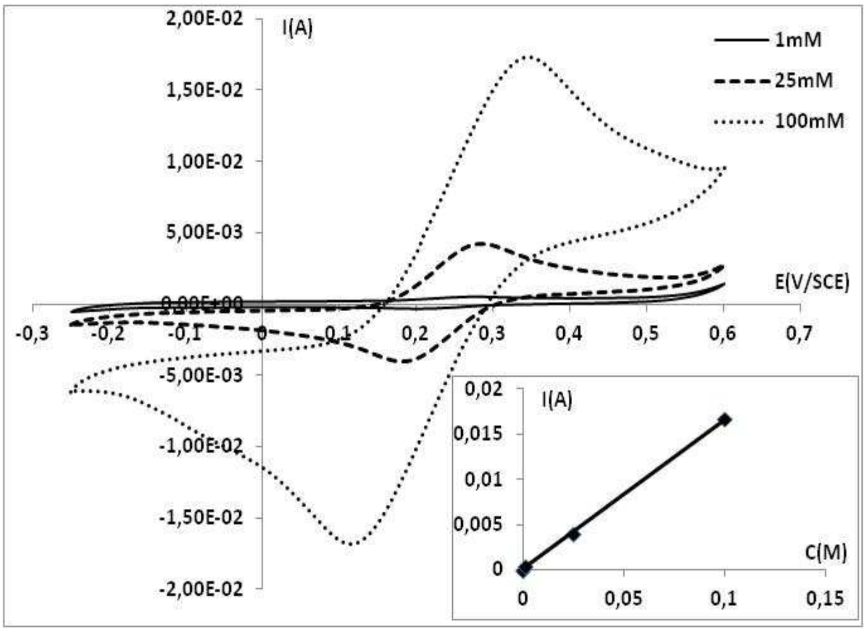

Figure 7: Cyclic voltammograms for the reaction of the ferri/ferrocyanide redox couple on a platinum electrode. Influence of the concentration of the redox species. v= 20mV/s, T=25°C, CE: Pt wire, RE: SCE (inset: plot of the peak current intensity versus the equimolar concentration of both the redox species)

From table 3, one observed that the gap of the peak potential is high than 60 mV. The ratio of the peak current density was almost 1 and the apparent (or formal) standard redox potential was equal to (0,233±0,002) V/SCE. The slope of the straight lines of the figures inserted in figure 6 and 7 led to the determination of the diffusion coefficient of the redox couple species. That diffusion coefficient was about $1,247.10^{-5}$ cm^2/s for the potassium ferrocyanide and about $1,463.10^{-5}$ cm^2/s for the potassium ferricyanide. The diffusion coefficients determined in that work were in the same order of magnitude as those found in literature to be around $0,763.10^{-5}$ cm^2/s[18]. The slight change in the values of the diffusion coefficients of our investigations compared to those of the literature could result from the use of the geometric surface area instead of the electrode real surface area for its determination. The anodic and the cathodic charge transfer coefficient calculated were 0,407 and 0,436 respectively. The electrode showed a quasi-reversible behavior towards the redox couple used and that result was in accordance with that found in literatures[19]. Those results indicated that the techniques used to prepare the electrode (thermal preparation) led to an electrode that presented similar behavior towards the ferri/ferrocyanide redox couple as the electrodes which were prepared by other techniques.

Figure 8 presented the results of the cyclic voltammetry measurements realized on the platinum electrode in chlorides containing perchloric acid electrolyte. The concentration of the chlorides was varied from 0 to 1M. In the absence of chlorides, the voltammogram recorded on the platinum electrode was similar to that was generally obtained with the platinum electrodes in the acidic electrolyte. The oxygen evolution reaction started at potential around 1,43V/SCE. In presence of chlorides, anodic and cathodic peaks appeared after 1V/SCE and 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. As the concentration of chloride was increased, the current intensity increased too (figures 8; 9). Plotting the peak current intensity against the concentration of the chlorides, a straight line was obtained (inset of figure 9) indicating that the appearance of those peaks was directly related to the chlorides.

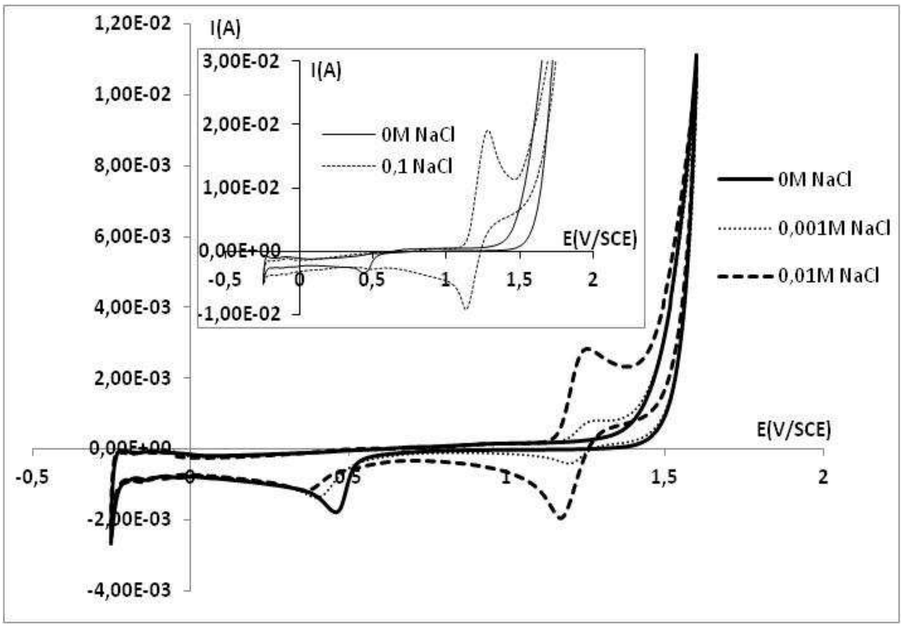

Figure 8: Influence of chlorides on the electrode response of platinum electrode, v=20 mV/s; T=25°C; WE: Pt; RE: SCE; CE: Pt wire

The platinum oxide reduction peaks observed at around 0,48V/SCE in absence of chlorides decreases in absolute value and its potential shifted in the negative direction as the concentration of the chlorides was increased. That peak disappeared as the concentration of the chlorides attained 100mM (inset of figure 8). In fact, that result could indicate that chlorides influence the kinetic of the platinum oxide formation/reduction process. That oxide formation/reduction process became more irreversible in presence of chlorides possibly due to their adsorption at the platinum surface rather than hydroxyl radicals (or water). As the concentration of the chlorides was increased, the surface of the platinum tended to be totally covered by the chlorides which have inhibited or have retarded considerably the oxide formation/reduction process[20-22]. That was due to the specific adsorption of chlorides on the platinum surface competitively with oxygen[21]. This competitive specific adsorption has retarded or has restrained the formation of the oxide film and that finding was in accordance with that presented in literature for a bright and polished platinum electrode[20;23;24].

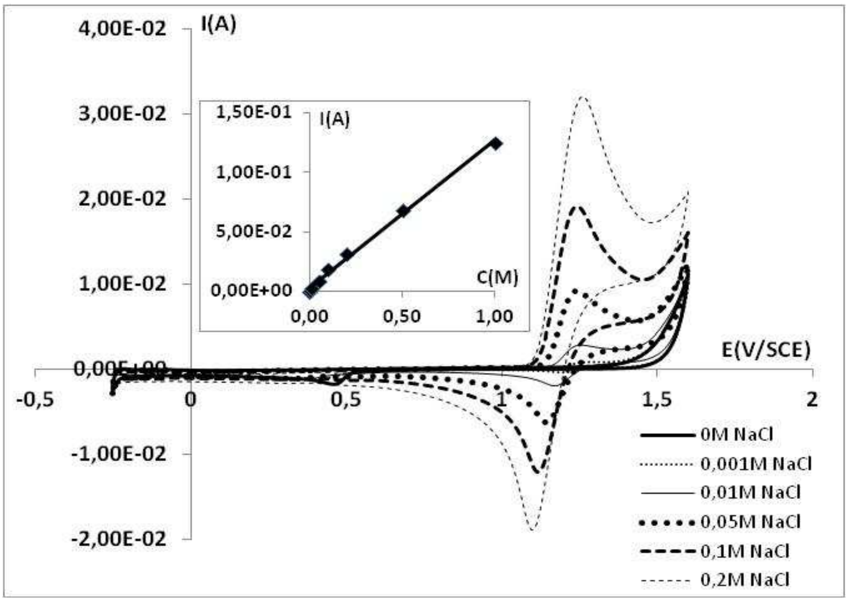

Figure 9: Evolution of the current peak against the concentration of chlorides, v=20 mV/s; T=25°C; WE: Pt; RE: SCE; CE: Pt wire

From the thermodynamics point of view, chloride solutions should favor oxygen evolution rather than chlorine evolution because the equilibrium potential of oxygen evolution (0,97V/SCE) is lower than that of chlorine (1,1V/SCE). But due to the local acidification near the electrode layer and probably due to other kinetic conditions, chlorine evolution reaction was predominant. That could also be favored by the morphology of the deposit film especially due to the roughness surface of the prepared platinum electrode.

Cyclic voltammogram presented in figure 10 was made on the platinum electrode in perchloric acid electrolyte in absence and in presence of formic acid. The obtained voltammograms were in good agreement with those previously reported in literature. In presence of formic acid, three anodic peaks located near 0,287V, 0,696V and 1,267V in the right direction and two overlapping peaks located at 0,478V and at around 0,278V in the left direction appeared. Since it is well-known that the electrooxidation of HCOOH at a platinum electrode surface yields CO_2 (and H) as the final product and CO as the predominant stable intermediate, it is apparent that all the noticeable current concerning HCOOH decomposition can be attributed to the oxidation of HCOOH and/or CO to CO_2. The hydrogen adsorption/desorption charges were significantly suppressed, indicating that the surface active sites have been almost totally blocked. The first anodic peak was due to the oxidation of HCOOH to CO_2 on surface sites that remained unblocked by CO. For the second anodic peak, the oxidation of surface CO is obviously involved. After the formation of the surface oxides, the electrode became quite inactive. At even higher potentials, some catalytically active surface oxides were formed, accounting for the third anodic peak. On the left direction, the surface remained inactive until partial reduction of the irreversibly formed surface oxides. The anodic peaks observed in the left direction demonstrated the real catalytic activity of the Pt surface, since neither CO nor oxide exists noticeably on the surface.

In presence of chlorides in the perchloric acid electrolyte, cyclic voltammogram that was recorded during the oxidation of HCOOH on the platinum electrode was presented in figure 11. The concentration of the formic acid varied from 0 to 1M. Keeping the concentration of the organic compound constant, the concentration of the chlorides was varied from 0,01M to 0,05M (inset of figure 11).

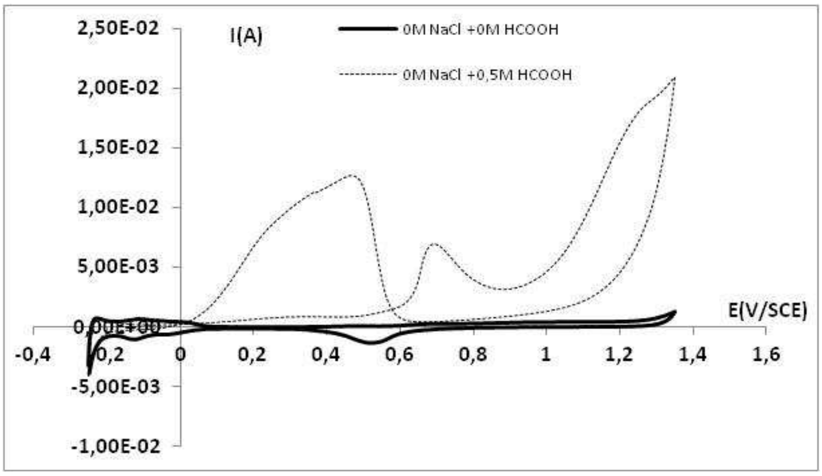

Figure 10: Oxidation of formic acid in absence of chlorides, v=20 mV/s; T=25°C; WE: Pt; RE: SCE; CE: Pt wire

From figure 11, one observed that in presence of formic acid in the chlorides containing electrolyte, no formic acid oxidation peak was observed as it has been seen in figure 10 but the current after 1,28V increased in intensity as the concentration of HCOOH was increased. That result indicated that the species resulted from the electrochemical oxidation of the chlorides are involved in the oxidation of HCOOH at the platinum electrode surface.

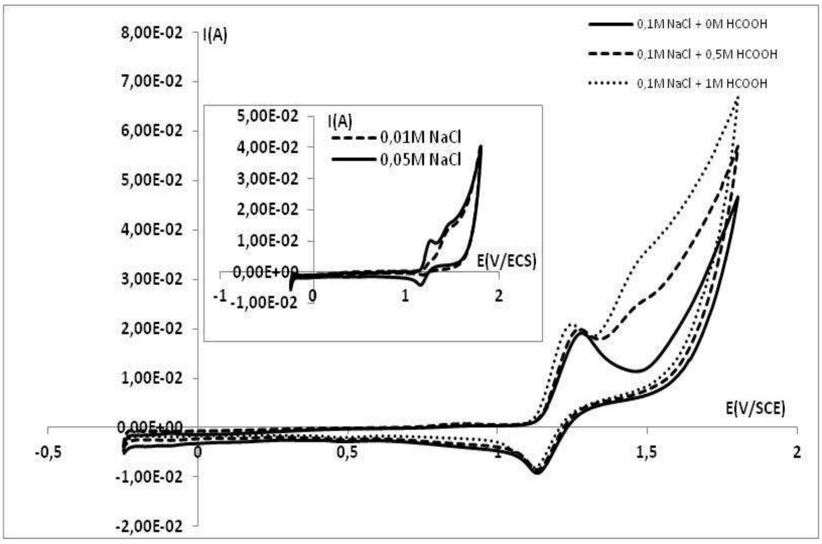

Figure 11: Oxidation of formic acid on platinum electrode in presence of chlorides, v=20 mV/s; T=25°C; WE: Pt; RE: SCE; CE: Pt wire

Increasing the concentration of the formic acid and keeping that of the chlorides constant, the peaks related to the chlorides oxidation and reduction processes did not change in intensity. But keeping the concentration of the organic compound constant and changing that of the chlorides, the peaks related to the chlorides redox processes have increased in intensity and the current intensity recorded after the oxidation peak of chlorides remained almost unchanged (inset of figure 11). Those results confirmed the fact that the quasi-reversible peaks were directly related to the electrochemical oxidation of chlorides. Thus the oxidation of formic acid in chlorides containing electrolyte was an indirect process occurring in the vicinity of the electrode surface and/or in the bulk of the solution. The absence of the anodic oxidation peaks of the formic acid as that observed in figure 10 could be due to the platinum active sites deactivation by the chlorides which were hardly and specifically adsorbed on the electrode surface inhibiting the adsorption of HCOOH and consequently hampering its oxidation to occur directly on the electrode surface at low potential[10,25,26].

The specifically adsorbed chlorides on the platinum electrode have modified the oxidation mechanism of the formic acid. In absence of chlorides, the oxidation of formic acid was catalyzed either by the naked platinum surface, or adsorbed hydroxyl radicals or the oxide formed at the platinum surface. But, in presence of chlorides, the oxidation of the formic acid took place at high potential indirectly by the intermediate of the oxidation product of chlorides possibly chlorine in the form of hypochlorite.

4. Conclusion:

The thermally prepared platinum electrode at 400°C has presented a rough and an almost compact surface. The analysis of the electrode surface has revealed that platinum existed in several oxidized state. That electrode presented a quasi reversible behavior towards the ferri/ferrocyanide redox couple. In chlorides containing acid electrolyte, a couple of peaks related to the chloride oxidation/reduction process appeared on the voltammograms. In the solution containing chlorides, the platinum oxide formation/reduction process was made more irreversible due to the adsorption of chlorides on the electrode surface. In the absence of chlorides, the oxidation of the formic acid led to the presence of several oxidation peaks but in presence of chlorides those peaks disappeared. That result has shown that chlorides have considerably influenced the mechanism of the oxidation of the organic compound. At the high potential values, the formic acid was oxidized with the involvement of the species resulted from the chlorides oxidation such as chlorine in the form of hypochlorite. Thus, the oxidation of formic acid occurred mainly in an indirect process in the vicinity of the electrode surface and/or in the bulk of the solution.

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