

## PbO<sub>2</sub> Synthesis by Complexation and Electrooxidation of Pb<sup>2+</sup> in Poly[4-(pyrrol-1-yl methyl) benzoic acid] Film

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**Abstract:** Actually, lead dioxide (PbO<sub>2</sub>) is used as electrodes (cathode) in electrochemical power generators in particular in car batteries. The synthesis of lead dioxide is essentially obtained by chemical or electrochemical oxidation of lead salts processes. A very ambitious objective of this study is based on preparing lead dioxide by a newly developed method carried out in our laboratory. This consists in a first step to deposit a conductive polymer film poly[4-(pyrrol-1-yl methyl) benzoic acid] having complexing properties performed by electrochemical oxidation in acetonitrile medium of the monomer 4-(pyrrol-1-yl methyl) benzoic acid on the surface of a substrate such as carbon felt having a very high specific surface. In a second step, we proceed to the incorporation of lead dioxide by complexing the metal cations of lead in the polymer film performed by immersion of the modified electrode in a solution of lead nitrate to complex the Pb<sup>2+</sup> cation with the carboxylic group COOH present in the polymer structure followed by electrooxidation in a solution free of lead to precipitate lead dioxide into the polymer in the form of metal microparticles. This material is used as the cathode material in batteries.

**Keywords:** Conductive polymer, Modified electrodes, Lead dioxide, Batteries

### Introduction

The structure of the electrode/electrolyte interface, where the electrochemical reaction takes place, is of great importance in the orientation of the reaction that occurs at the surface of the electrode. The work published in recent years on the modification of the surface of an electrode shows the interest granted by the researchers in the development of efficient electrode / electrolyte interface structures allowing a good orientation of the electrochemical reaction that occurs at the electrode and control techniques of physicochemical properties. Modification of the electrode surface with polymer films containing metal particles is an effective technique for developing modified electrodes having specific electrocatalytic, electronic and magnetic properties.

In this paper, we describe a novel method and easiest way to synthesis lead dioxide by complexation Pb<sup>2+</sup> ions in a poly[4-(pyrrol-1-yl methyl) benzoic acid] film and electrooxydation of the complex formed (polymer-lead) to the formation and precipitation of lead dioxide in the polymer film. We may expect from this procedure a better dispersion of the metal in the polymer film and the formation of particles of smaller sizes [1-8].

### Experimental

After the deposition of poly[4-(pyrrol-1-yl methyl) benzoic acid] on a platinum electrode obtained by controlled potential electrochemical oxidation of the monomer in acetonitrile solution 10<sup>-1</sup> M LiClO<sub>4</sub> as electrolyte, the modified electrode is either oxidized in aqueous 10<sup>-1</sup> M in NaNO<sub>3</sub> and containing 5x10<sup>-3</sup> M in Pb(NO<sub>3</sub>)<sub>2</sub>, or it is immersed in an aqueous solution in a metal salt of Pb(NO<sub>3</sub>)<sub>2</sub> 10<sup>-2</sup> M for a few minutes to complex ions lead by the polymer film due to the protons of H<sup>+</sup> that are present in the carboxyl group of polypyrrole. The electrode is then washed with distilled water several times to remove excess metal cations associated with the non-polymer, and then immersed in aqueous solution of 10<sup>-1</sup> M in NaNO<sub>3</sub> to oxidize the lead ions in complexed lead dioxide. This process can be repeated several times. Both deposition techniques of lead dioxide on the surface of the modified electrode are shown in Figure 1.

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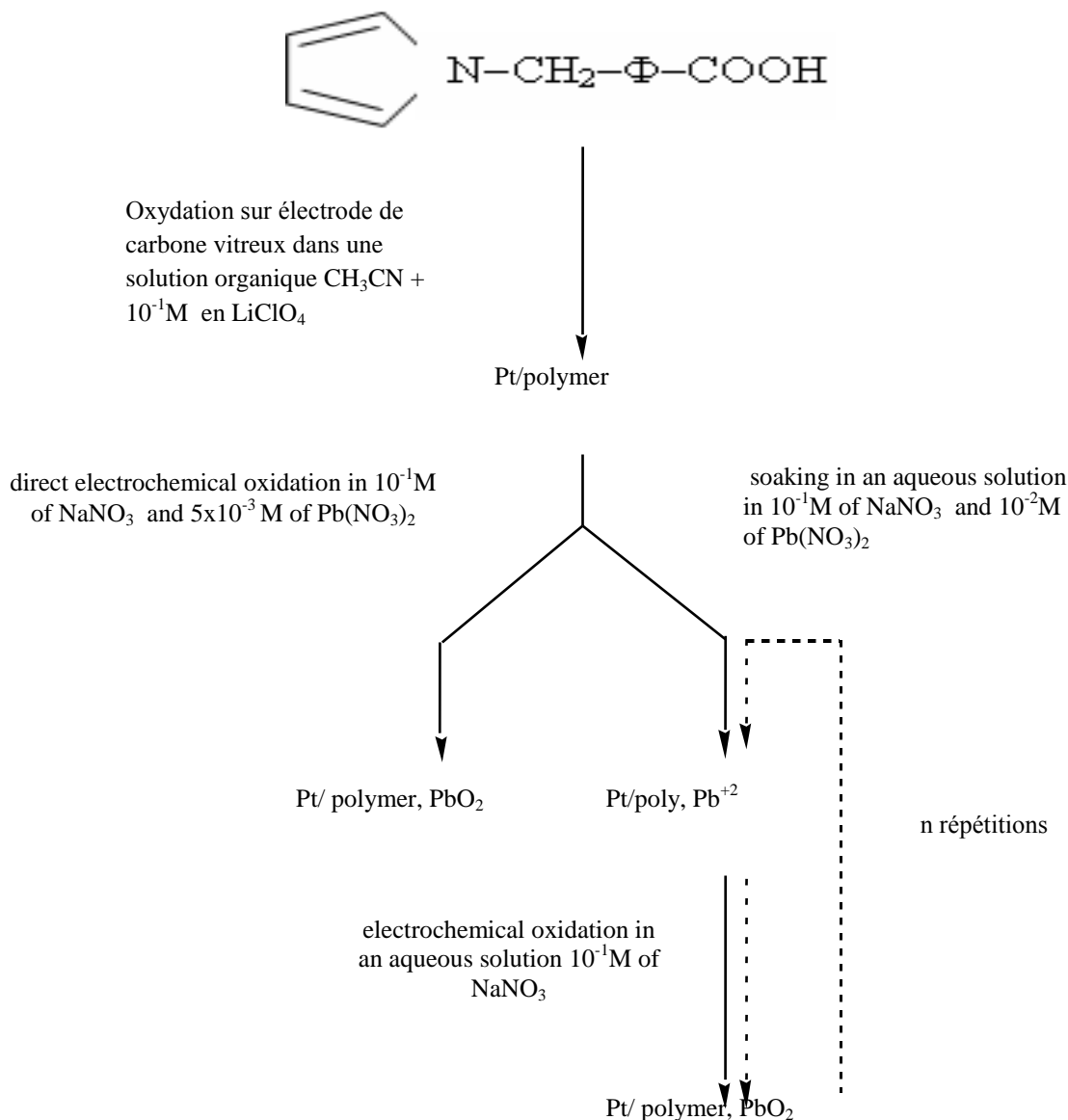


Figure 1. Techniques of preparing a platinum electrode modified with  $\text{PbO}_2$  particles

### Electropolymerization of 4-(pyrrol-1-yl methyl) benzoic acid

The electrochemical behavior of the monomer was studied by cyclic voltammetry on platinum electrode ( $\Phi = 3 \text{ mm}$ ) in an acetonitrile medium ( $\text{CH}_3\text{CN}$ ),  $10^{-1} \text{ M}$  of lithium perchlorate ( $\text{LiClO}_4$ ) and  $4 \times 10^{-3} \text{ M}$  of 4-(pyrrol-1-yl methyl) benzoic acid. The presence of an irreversible oxidation peak around 1,2 V/ECS corresponding to the oxidation of monomer (polymerization) and consequently to the formation of poly [4-(pyrrol-1-yl methyl) benzoic acid] deposited on the surface of the electrode (figure 2 a). The record shows a subsequent increase in current waves of oxidation and reduction peaks observed around 0,6-0,8 V, indicating that the polymer is starting to be deposited on the surface of the electrode. The current intensity of the peaks is seen to stabilize after several cycles (figure 2 b).

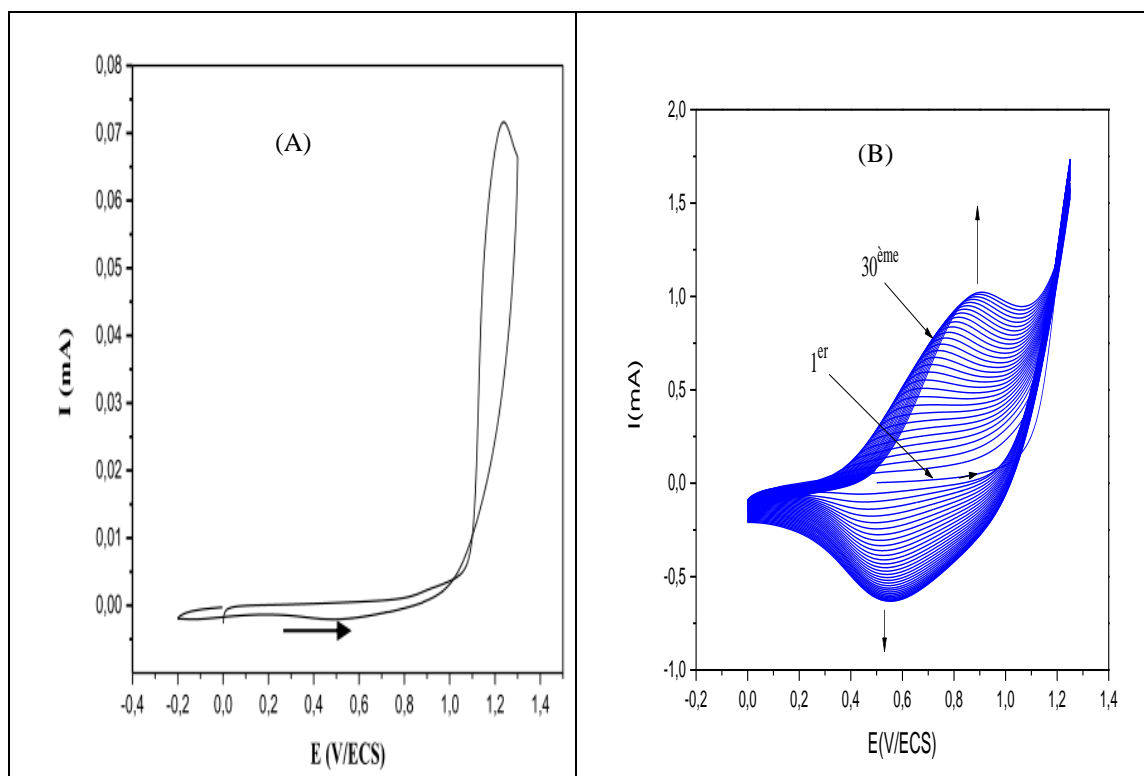


Figure 2: Electropolymerization of monomer on a platinum electrode in  $\text{CH}_3\text{CN}$  in 0.1 M  $\text{LiClO}_4$  and  $4 \times 10^{-3}$  M of monomer at the speed of  $v = 100$  mV/s.

### Study of the electrochemical behavior of lead (II) on platinum electrode

The electrochemical behavior of lead (II) was studied on a platinum electrode of  $0.07 \text{ cm}^2$  ( $\phi = 3 \text{ mm}$ ) of area by digital cyclic voltammetry in an aqueous solution containing  $10^{-2}$  M of  $\text{Pb}(\text{NO}_3)_2$  and  $10^{-1}$  M of  $\text{NaNO}_3$  (figure 3). The obtained curve is characterized by the presence of oxidation peak in the vicinity of 1,4 V/SCE corresponding, to the oxidation of lead II ions in lead IV. In the return sweep is also observed one peak in the vicinity of 0,9 V/SCE corresponding to the reduction of oxidized specie (figure 3 a).

Successive scans show an increase in the intensities of the reduction and oxidation peaks. The increase in peaks is due to the change in the state of surface of the electrode during sweeps (figure 3 b)

### Effect of concentration

In order to see the influence of the concentration of the solution on the electrochemical behavior of lead, different concentrations were prepared and studied by cyclic voltammetry. The curves obtained (figure 4) show an increase in the intensity of the peak of oxidation and reduction with the increase of the concentrations. A slight displacement of the peak potential has been observed due to the surface of the electrode. These results confirm that the peaks obtained correspond well to those of lead reduction and oxidation.

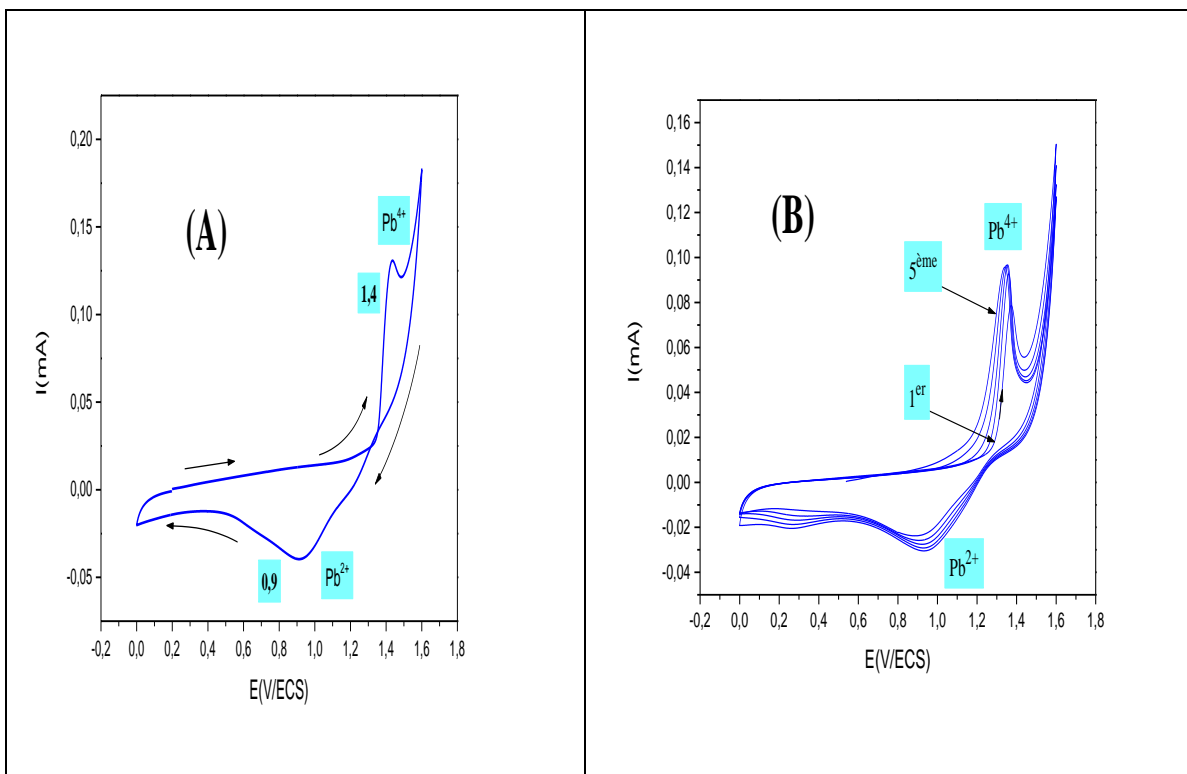


Figure 3: Cyclic voltammery curve of Pb (II) in an aqueous solution  $10^{-1}$  M  $\text{NaNO}_3$  and  $5 \times 10^{-3}$  M  $\text{Pb}(\text{NO}_3)_2$  at the scan speed of 100 mV/s, at pH =5.

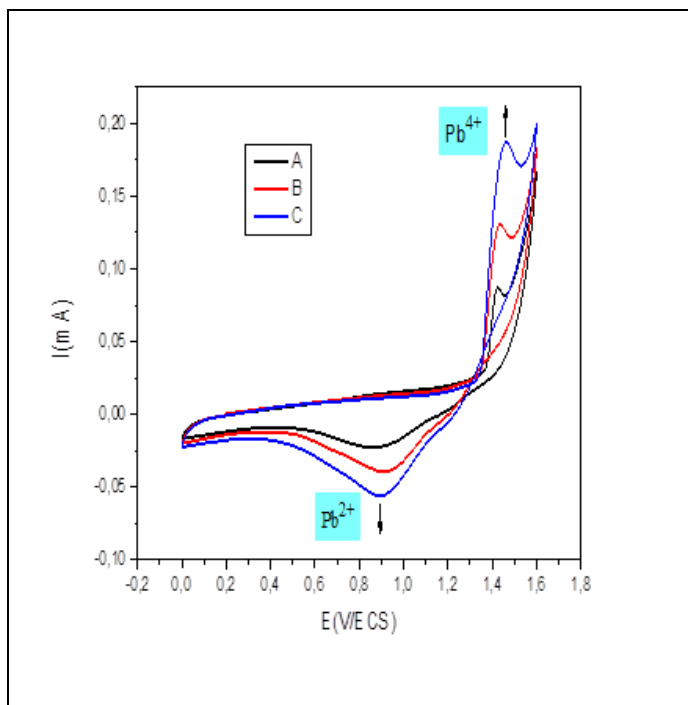


Figure 4 : Voltammograms of lead nitrate at different concentrations, plotted in aqueous solution 0,1 M of  $\text{NaNO}_3$  at  $v=100$  mV/s and PH=5 (A)  $2 \cdot 10^{-3}$  M; (B)  $5 \cdot 10^{-3}$  M ; (C)  $10^{-2}$  M

### pH effect

In order to see the influence of the pH of the medium on the electrochemical behavior of lead, we have prepared three solutions, at pH = 2, pH = 5 and pH = 7 by adding a few drops of sodium hydroxide (NaOH) or 1M of nitric acid ( $\text{HNO}_3$ ). Then studied by cyclic voltammetry. The curves obtained are grouped together in figure 5.

It can be seen from the curves obtained that the current density of the oxidation and reduction peaks at pH = 2 and 5 are the most intense. The latter decrease by increasing the pH of the medium and become insignificant from 5. In fact, the solution becomes cloudy indicating the beginning of the formation of a white precipitate of lead hydroxide observed especially at pH 7. According to results obtained it can be concluded that the best pH of the medium for lead is the strongly acidic medium. We also note from the curves obtained a displacement of the potential of the peak, which shows that the activated electro lead species are not the same.

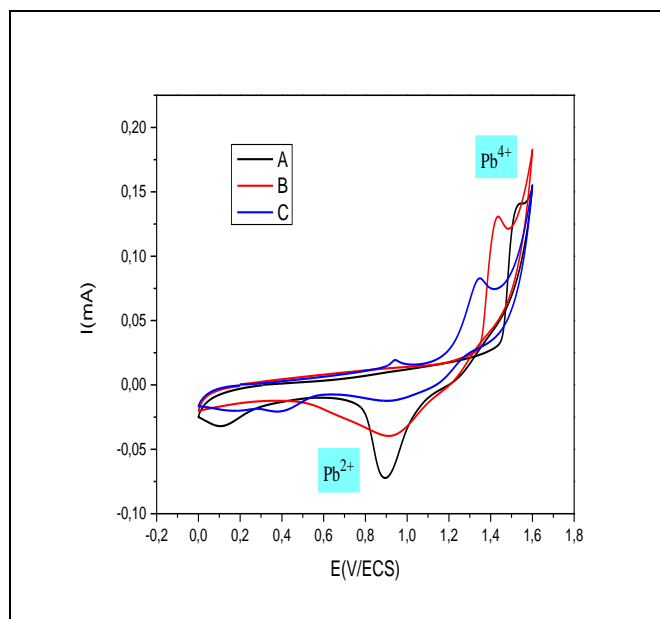


Figure 5 : Voltammograms of lead nitrate at different pH, plotted in aqueous solution 0,1 M of  $\text{NaNO}_3$  at  $v=100$  mV/s (A) :  $pH = 2$ , (B) :  $pH = 5$ , (C) =7.

### Insertion of lead dioxide in the polymer film

After depositing a benzoic pyrrole film on the platinum electrode, the latter was studied in a solution of 0.1M acetonitrile in  $\text{LiClO}_4$ , and after polymer overoxidation, we studied the electrochemical behavior. cations of lead by cyclic voltammetry in a 0,1 M aqueous solution in  $\text{NaNO}_3$  after soaking for 30 minutes of the electrode modified by the polymer film in a solution of  $\text{Pb}(\text{NO}_3)_2$ . The curve obtained is shown in figure 6. It is characterized by the presence of an intense oxidation peak in the vicinity of 1,5V / ECS corresponding to the oxidation of  $\text{Pb}^{2+}$  to  $\text{Pb}^{4+}$ . In the return scan, a peak near 1,1 V / ECS is also observed, due to the reduction of  $\text{Pb}^{4+}$  to  $\text{Pb}^{2+}$  (figure 6 a).

Successive scans (figure 6 b) show that the  $\text{Pb}^{2+}$  cations remain in the polymer film after several cycles. A slight shift of the peak potential to the most positive values has been observed. This result clearly shows the insertion of the lead dioxide in the polymer film by complexation of the lead cations by the carboxylic group present in the polymer backbone followed by its electrooxidation to precipitate the lead dioxide in the form of microparticles.

### Characterization of the composite material by impedance spectroscopy

In Figure 6 are shown the impedance diagrams of the different electrodes. The impedance diagrams are composed of an arc of circles at high frequencies corresponding to a charge transfer process and of a straight line at low frequencies corresponding to a diffusion regime (Figure 7 (A), curves b, c, d, e), except the case prior to deposition the electrode diagram presents a line all across the spectrum characteristic of a diffusion process (Figure 7 (A), diagram a). After an increase in the range of frequencies between 0 and  $7 \text{ k}\Omega\text{cm}^2$ , we observe that the platinum electrode has the best electrical properties, Figure 7 (B), diagram a). The impedance diagram of the electrode after deposition of lead oxide has an arc and then a very steep right slope corresponding to a blocking system. Although the electrical properties of the material decreases after deposition of the polymer film (Figure 7 (B), diagram c) and the complexation of lead (Figure 7 (B), diagram d), the latter becomes more important after oxidation of lead in the film polymer (Figure 7 (B), diagram e).

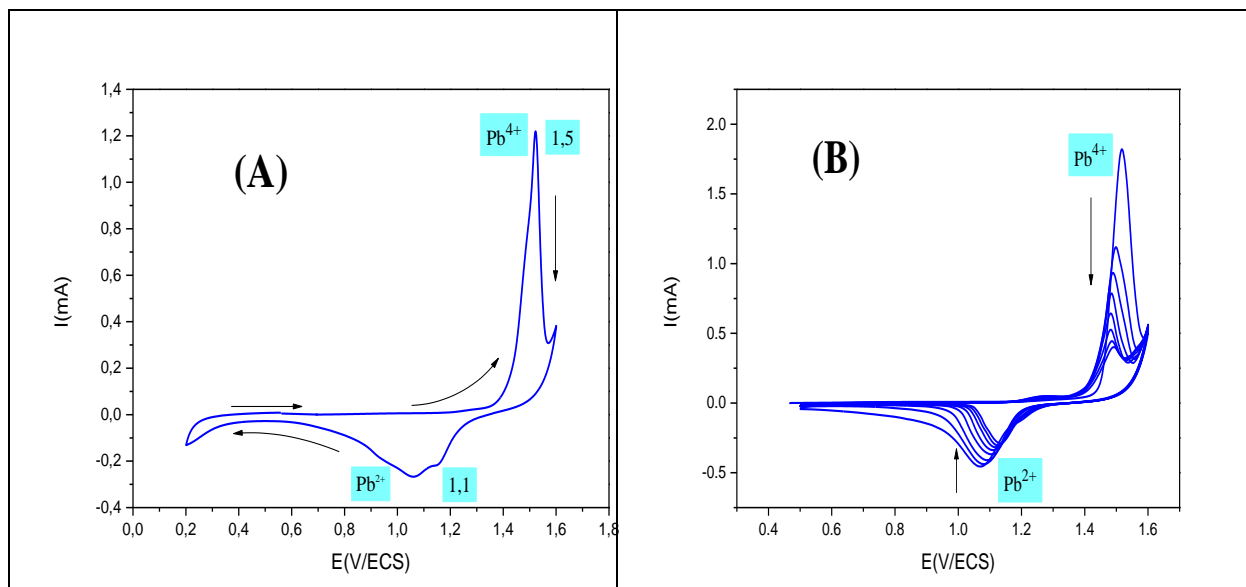
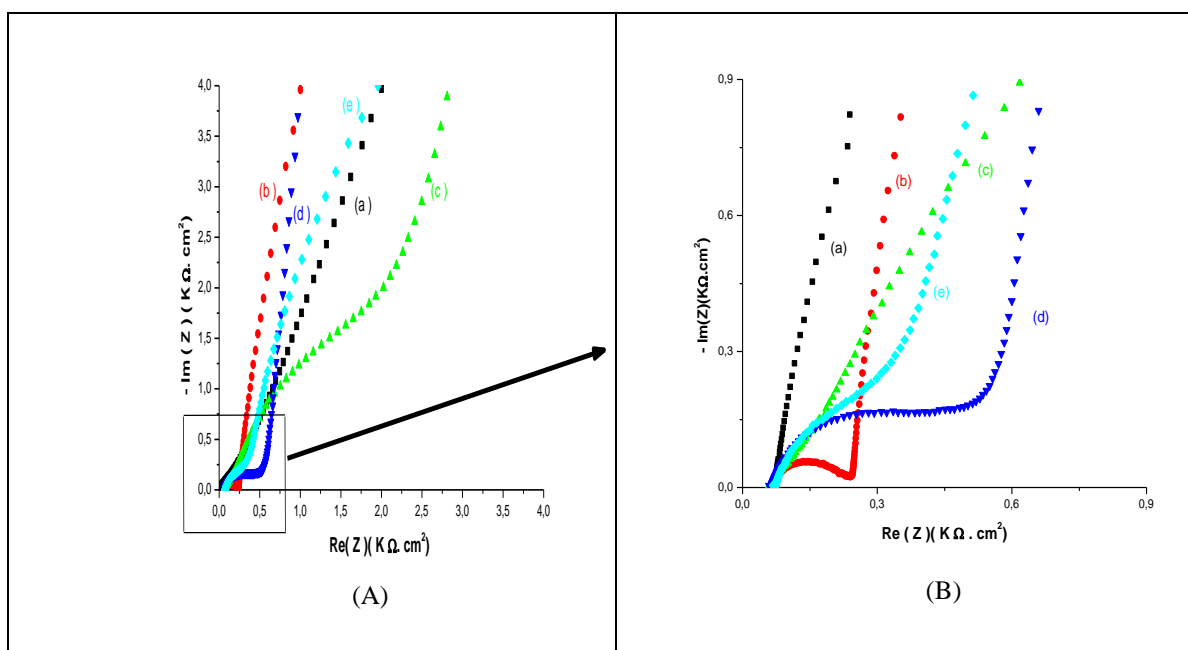


Figure 6 : Cyclic voltammetry of lead on a platinum electrode modified with a polymer film in a 0.1 M aqueous solution in NaNO<sub>3</sub> after dipping in Pb(NO<sub>3</sub>)<sub>2</sub>. at  $v=100$  mV/s. (A) : first cycle, (B) : repetitive scanning



**Figure 7:** (A) - Impedance diagrams of an aqueous 0.1 M NaNO<sub>3</sub> in the frequency range between 100 kHz and 10 MHz on an electrode (a) platinum electrode, (b) electrode covered with a layer of lead in an applied potential to 1,5 V/SCE, (c) polymer film alone, (d) platinum electrode modified with a film of poly [4-(pyrrol-1-yl methyl) benzoic acid] and then soaked in a solution of 10<sup>-2</sup> M of Pb(NO<sub>3</sub>)<sub>2</sub> for 30 minutes, (e) platinum electrode modified with a polymer film and then dipped in a solution of 10<sup>-2</sup> M of Pb(NO<sub>3</sub>)<sub>2</sub> for 30 minutes and oxidized at the potential of 1,5 V/SCE in the absence of Pb(NO<sub>3</sub>)<sub>2</sub>. (B) After expansion of the frequency domain.

## Conclusion

I have presented a new method of preparing lead dioxide PbO<sub>2</sub> by complexation of lead ions in polymer films by the carboxylic group (COOH) of the polymer and thereafter by carrying an electrooxidation to precipitate the particles of PbO<sub>2</sub> into the polymer films. The electrochemical study showed the deposition of a polymer film on the surface of the platinum electrode and the insertion of lead dioxide particles.

The impedance diagram of the electrode after deposition of metallic lead has an arc and then a very steep right slope corresponding to a blocking system. The electrical properties of the material become more important after incorporation of lead dioxide in the film of polymer. We obtained a new material composite for applications in electrochemical generators as a cathode in batteries and in electrocatalysis.

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