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## Electrochemical behaviour of lead in hydrochloric acid solution in the presence of inorganic ions

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### Abstract

The electrochemical behaviour of lead electrode in hydrochloride solution containing various oxo-anions at different concentrations was studied by using of cyclic voltammetry (CV) method. Results obtained show that the addition of these inorganic compounds decreases the anodic and cathodic currents peaks according to the following order:  $\text{H}_2\text{PO}_4^- > \text{HPO}_4^{2-} > \text{SO}_4^{2-}$ . It's revealed also that the cathodic current density related to the reduction of  $\text{Pb}^{2+}$  ions dissolved in solution decreases with the oxo-anions concentration. When the addition of sulphates ions concentration reaches  $0.34 \text{ mol L}^{-1}$ , the formation of  $\text{PbSO}_4$  is highly favoured. Therefore, the interstices between the crystals of  $\text{PbSO}_4$  encourage the dissolution of lead and the formation of insoluble  $\text{PbCl}_2$  layer on the lead surface involving the passivation phenomenon.

**Keywords:** Corrosion; Lead; Oxo-anions; Hydrochloride acid; Cyclic voltammetry.

### 1. Introduction

Lead is considered as one of the vital metals owing to its wide industrial applicability. The most important application of lead is its widespread usage in acid storage batteries [1]. It's known that lead is corroded in diluted hydrochloric acid solution. Chloride ions are the most aggressive agent of lead, numerous works focused on the electrochemical behaviour of this metal in various aggressive solutions [2-7]. It's observed the passivation phenomenon due to the formation of  $\text{PbCl}_2$  layer on the electrode surface occurs at any chloride concentration. Except, in  $\text{NaCl}$  solution where  $\text{pH} > 6.5$  where the layer formed is  $\text{Pb}(\text{OH})\text{Cl}$  [8].

Different compounds were used as inhibitors to reduce the corrosion effect of the aggressive solutions; we cite the organic compounds containing heteroatoms [9-17]. They act by adsorption on the metal surface through heteroatoms such as sulphur, phosphorus, oxygen and nitrogen, or by double or triple bonds and aromatic rings. On the other hand, several authors tested the effect

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of the addition of inorganic anions ( $\text{SO}_4^{2-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{CrO}_7^{2-}$ ,  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ ...) in aggressive solutions. The results obtained revealed that some of these ions inhibit the corrosion phenomenon while others accelerate it [18-20].

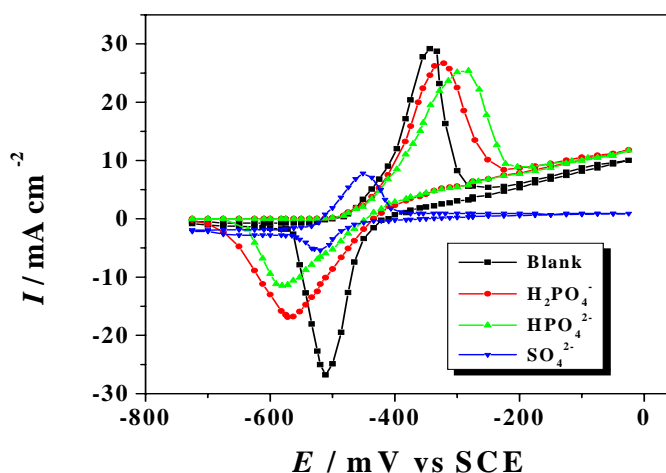
The aim of this work is to study the effect of the addition of the oxo-anions such as  $\text{SO}_4^{2-}$ ,  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$  on the corrosion and passivation behaviour of lead electrode in diluted hydrochloride acid solution.

## 2. Experimental

Electrochemical measurements were recorded with a potentiostat type Amel 550 using a linear sweep generator type Amel 567 at a scan rate of 20 mV/min. Cyclic voltammetry scan range was from -750 to 0 mV/SCE then return to -750 mV/SCE. Before recording each cyclic voltammetry curve, the lead electrode was polarised at -1000 mV/SCE for 10 min. We used for all electrochemical tests a conventional three electrodes electrolysis cylindrical Pyrex glass cell. Saturated calomel electrode (SCE) and platinum electrode are used as reference and Auxiliary electrodes, respectively. The working electrode is in form of disc from lead (99.99%) sheet of the surface  $0.5 \text{ cm}^2$ . Prior each experiment, the surface of the working electrode was polished with different emery paper up 1000 grade, washed thoroughly with acetone and rinsed with bi-distilled water. The experiments were carried out in  $0.3 \text{ mol L}^{-1}$  HCl at  $25^\circ \text{C}$ . The test solution was prepared by dilution of analytical grade 37% HCl with double distilled water. The solution test is also de-aerated for with pure nitrogen. Gas bubbling is maintained prior and through the experiments.

## 3. Results and discussion

Cyclic voltammograms for the lead in  $0.3 \text{ mol L}^{-1}$  HCl with and without addition of different oxo-anions at  $0.1 \text{ mol L}^{-1}$  are shown in Fig. 1. The corresponding electrochemical parameters are given in the Table 1.



**Fig. 1.** Cyclic voltammograms for the lead electrode in  $0.3 \text{ mol L}^{-1}$  HCl at different oxo-anions at  $0.1 \text{ mol L}^{-1}$ .

From the results obtained, we noted that the addition of the anions studied at  $0.1 \text{ mol L}^{-1}$  in diluted HCl decreases the anodic and cathodic currents peaks according to the following order:



This order can be interpreted with the aid of the repulsion theory of the pair's electrons of the valence layers [21]. In fact, the molecular geometry of these anions is tetrahedral shape. The central atom «S» of  $\text{SO}_4^{2-}$  anions is more electronegative than the atom «P» of both  $\text{HPO}_4^{2-}$  and

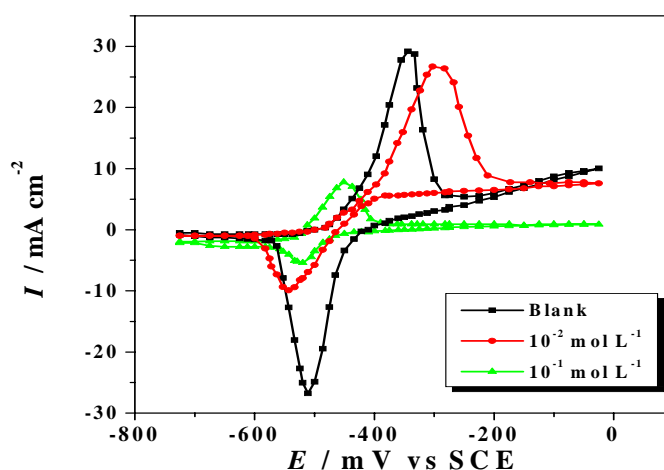
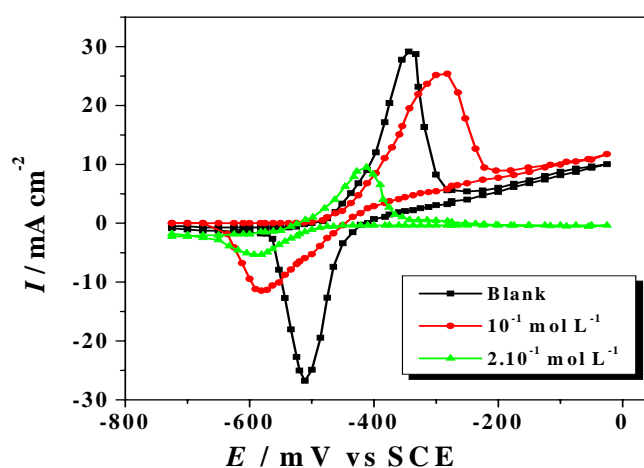
$\text{H}_2\text{PO}_4^-$  anions, moreover the electronic density in  $\text{SO}_4^{2-}$  anion is higher which facilitate the transfer of the electrons toward metal producing the coordination link, therefore, a strong adsorption occurs. The existence of two double bonds in  $\text{SO}_4^{2-}$  makes it more voluminous than other anions. On the other hand, the electrostatic repulsion due to the negative charges is more important around  $\text{HPO}_4^{2-}$  than  $\text{H}_2\text{PO}_4^-$ , consequently, it's observed an increasing of the molecular area of  $\text{HPO}_4^{2-}$  on the surface of lead in comparison with  $\text{H}_2\text{PO}_4^-$ .

**Table 1**

Electrochemical parameters derived from CV curves for the lead electrode in  $0.3 \text{ mol L}^{-1}$  HCl with different oxo-anions at  $0.1 \text{ mol L}^{-1}$ .

Inhibitor	$I_{pa} / \text{mA cm}^{-2}$	$I_{pc} / \text{mA cm}^{-2}$	$E_{pa} / \text{mV vs SCE}$	$E_{pc} / \text{mV vs SCE}$
Blank	29.1	26.7	-343	-511
$\text{H}_2\text{PO}_4^-$	28.4	16.3	-321	-565
$\text{HPO}_4^{2-}$	25.6	11.5	-282	-580
$\text{SO}_4^{2-}$	7.8	5.3	-451	-519

Figs. 2 and 3 illustrate the cyclic voltammetry curves of lead in aggressive solution in the presence of different concentrations  $\text{SO}_4^{2-}$  and  $\text{HPO}_4^{2-}$  anions, respectively. The electrochemical parameters related to these figures are gathered in Table 2.

**Fig. 2.** Cyclic voltammograms for the lead electrode in  $0.3 \text{ mol L}^{-1}$  HCl at different concentrations of  $\text{SO}_4^{2-}$ .**Fig. 3.** Cyclic voltammograms for the Pb electrode in  $0.3 \text{ mol L}^{-1}$  HCl at different concentrations of  $\text{HPO}_4^{2-}$ .

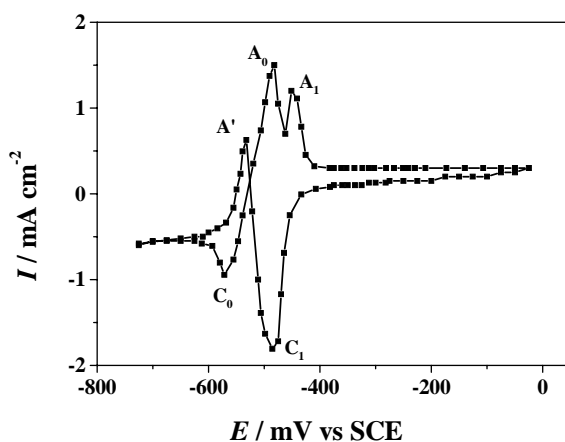
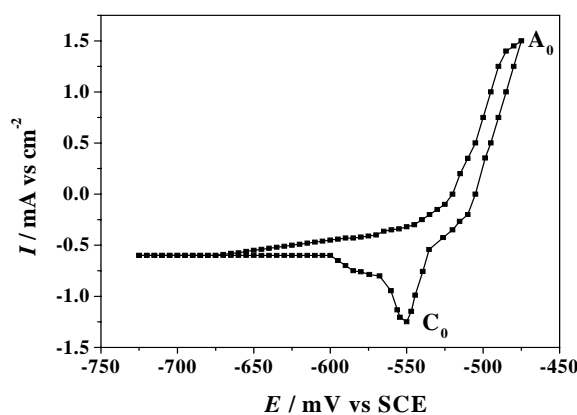
**Table 2**Electrochemical parameters related to lead in 0.3 mol L<sup>-1</sup> HCl with and without SO<sub>4</sub><sup>2-</sup> and HPO<sub>4</sub><sup>2-</sup>.

Inhibitor	C (mol L <sup>-1</sup> )	I <sub>pa</sub> / mA cm <sup>-2</sup>	I <sub>pc</sub> / mA cm <sup>-2</sup>	E <sub>pa</sub> / mV vs SCE	E <sub>pc</sub> / mV vs SCE
Blank	0.3	29.1	26.7	-343	-511
HPO <sub>4</sub> <sup>2-</sup>	0.1	25.6	11.5	-282	-580
	0.2	9.5	3.1	-412	-580
SO <sub>4</sub> <sup>2-</sup>	0.01	26.9	9.7	-302	-543
	0.1	7.8	5.3	-451	-519

The addition of sulphates ions at concentrations lower than 0.34 mol L<sup>-1</sup> dose not modify the cyclic voltammetry curves of the lead electrode in 0.3 mol L<sup>-1</sup> HCl solution with apparition of anodic and cathodic peaks. We indicate that the cathodic current intensity related to the reduction of Pb<sup>2+</sup> ions dissolved in solution decreases while the sulphate content increases (Table 2). This is due to the fact that the addition of the sulphates ions favours the precipitation of Pb<sup>2+</sup> ions dissolved in solution.

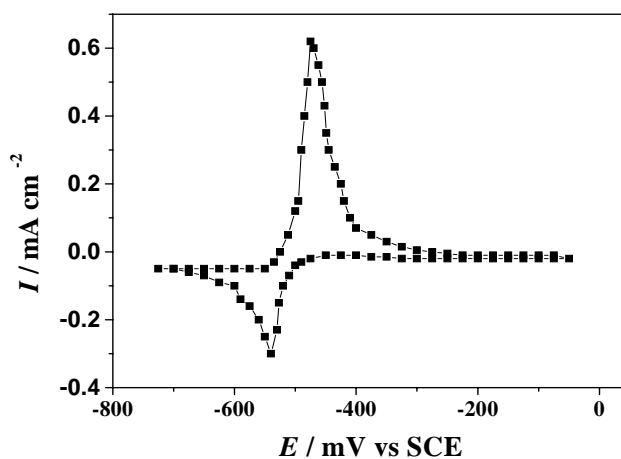
The absence of positive hysteresis loop neither in HCl solution nor in the presence of oxo-anions indicates that Pb doesn't suffer from localized attack in these test solutions.

When the sulphates ions concentration attains 0.34 mol L<sup>-1</sup>, we observed two anodic peaks A<sub>0</sub> and A<sub>1</sub> at the values potentials - 495 and - 457 mV/SCE, respectively and two other cathodic peaks C<sub>0</sub> and C<sub>1</sub> at -551 and -490 mV/SCE, respectively (Fig. 4).

**Fig. 4.** Cyclic voltammety curves of lead electrode in 0.3 mol L<sup>-1</sup> HCl + 0.34 mol L<sup>-1</sup> SO<sub>4</sub><sup>2-</sup>.**Fig. 5.** Cyclic voltammety curves of lead electrode in 0.3 mol L<sup>-1</sup> HCl + 0.34 mol L<sup>-1</sup> SO<sub>4</sub><sup>2-</sup>.

We tested to identify by cyclic voltammetry the homologous signals by isolating the first signal; that means that applying the potential just in the range started from -750 to -500 mV/SCE. Fig. 5 shows the apparition of both peak  $A_0$  corresponding to the oxidization region and peak  $C_0$  which corresponds to the reduction domain whereas the peak  $C_1$  situated in this same domain of potential doesn't appear.

We remark that the peak  $C_0$  corresponds to the reduction of the product formed in the peak  $A_0$  and  $C_1$  is related to the product formed in the peak  $A_1$ . The peak  $A_0$  is due to the reactivity of the sulphates ions and to the formation of insoluble  $PbSO_4$  on the electrode surface. Such compound is also observed on the same Pb electrode in  $0.34 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  (Fig. 6).



**Fig. 6.** Cyclic voltammetry curves of lead electrode in  $0.34 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ .

Sternberg and Mateescu [22] showed that the  $PbSO_4$  layer formed on the electrode lead surface is porous. The interstices between the crystals of  $PbSO_4$  favour the dissolution of lead and the formation of insoluble  $PbCl_2$  again at the peak  $A_1$  peak. We note also the apparition of a peak  $A'$  in oxidization region formed during the reduction of  $PbCl_2$ , this result is mainly due to the rearrangement of the lead surface polished [23].

#### 4. Conclusions

From the overall experimental results the following conclusions can be deduced: a) The presence of the oxo-anions studied act follows the order:



b) When the concentration of the oxo-anions ( $\text{SO}_4^{2-}$ ) increase in the solution, the reduction of  $\text{Pb}^{2+}$  and the formation of  $\text{PbSO}_4$  become more important which facilitate the passivation phenomenon by the formation of  $\text{PbCl}_2$  layer on the lead surface. c) The lead becomes more passivable as function of oxo-anions concentration.

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