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Electrochemical behaviour of a lead electrode in phosphoric acid

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Abstract A lead electrode was studied in 6 and 12 *M* H_3PO_4. Oxidation of a freshly polished electrode occurred in the −0.5 to −0.3 V vs. SCE range, and led to $PbHPO_4$ growth on the electrode surface. The dissolution of this layer by electrochemical reduction occurred between −0.5 and −0.7 V. The influence of temperature (20 °C and 65 °C) was investigated and showed that the anodic and the cathodic peaks were increasing, and more markedly for the 12 *M* H_3PO_4. The ratio $Q_{cathodic}/Q_{anodic}$ (Q = electrical charge flowing through the electrode) was equal or close to the unity at 20 °C and decreased as the temperature was increased. The influence of Cl^-, Br^- and I^- ions was also evaluated. The addition of Cl^- and Br^- predominantly led to $Pb_5(PO_4)_3Cl$ and $Pb_5(PO_4)_3Br$, respectively, while I^- led to a mixture of PbI_2 and $PbHPO_4$.

Key words Lead · Phosphoric acid · Halide ions · Cyclic voltammetry

Introduction

As far as we are aware, no study on the electrochemical behaviour of lead in concentrated phosphoric acid solutions has been published previously. Because the use of lead acid batteries is quite universal nowadays, Pb and Pb/PbO_2 electrodes have been widely studied in H_2SO_4, but in H_3PO_4 only addition effects have been studied.

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Bullock [1] demonstrated that 0–0.2% of H_3PO_4 added to the electrolyte were sufficient to modify the morphology of the PbO_2 corrosion film, and proved the intermediate formation of $Pb_3(PO_4)_2$, which prevented the formation of $PbSO_4$ during the oxidation of Pb to PbO_2 [2]. Hefny et al. [3] studied lead behaviour in phosphate solutions for a pH range from 2 to 10, using impedance measurements, and found that $PbHPO_4$ and $Pb_3(PO_4)_2$ were present in an adherent layer. Carr and Hampson [4] concluded that the formation of $PbHPO_4$ occured during the PbO_2 reduction process. A study performed by Laitinen and Watkins [5] demonstrated the inhibiting effect of phosphate ions on PbO_2 growth, and the presence of Pb(IV) in solution. Garche et al. [6] using various techniques such as cyclic voltammetry, potential step, impedance and electron microscopy, observed that the crystal size of $PbSO_4$ considerably decreased as phosphoric acid was added, and they showed its positive influence. Venugopalan [7], studying the performance of lead electrodes in sulfuric acid electrolyte containing antimony, noticed significant improvement when phosphoric acid was added. Stenberg et al. [8] confirmed this observation by coulometric and voltammetric measurements. More recently, Meissner [9] has extensively discussed the positive effects of H_3PO_4 addition in sulfuric lead batteries, outlining sulfation prevention and extension of the cycle life.

The aim of this paper is to study lead electrode behaviour in concentrated phosphoric acid solutions (6 and 12 *M*), in order first to better understand the $PbHPO_4$ formation and reduction, and second to study lead corrosion when some halides are present. The influence of temperature is also evaluated.

Experiment

Voltammetric studies were performed with a PGP 201 potentiostat (Radiometer, Denmark) and monitored by a PS1 IBM (USA) computer with ELCOM 201 software (Radiometer, Denmark). The electrical charges Q flowing through the lead electrode were cal-

culated using the ELCOM software. Four identical measurements were done for each experiment and the mean value was calculated.

Cyclic voltammetry was performed at 500 mV min^{-1}, in unstirred solutions, starting from potentials which were more negative than the rest potential of the lead electrode.

The working electrode was a 0.5 cm diameter, 99.99% purity, lead rod (0.196 cm^2 area), embedded in Pyrex glass and available from Aldrich (USA). The oxide and carbonate layers were eliminated by polishing the electrode with 15 μm CSi paper followed by 6 μm diamond paste. The electrode was then quickly washed with distilled water, dried with a soft filter paper and used immediately. The reference electrode was a KCl saturated calomel (+0.2415 V vs. SCE at 25 °C) immersed in a saturated Na_2SO_4 bridge, and a large graphite rod was used as an auxiliary electrode. All measurements are reported vs. the SCE.

The electrochemical cell was temperature controlled using a thermostat (Julabo, Germany). Oxygen was removed by nitrogen bubbling.

H_3PO_4, KCl, KBr and KI were of analytical grade (Prolabo, France) and the solutions were made with distilled water.

The scanning electron microscopy observations were made on lead plate samples, prepared in the same manner as the rod, using a S800 model (Hitachi, Japan) in the Centre of Electronic Microscopy Applied to Biology and Geology (CMEABG, University Lyon I). The X-ray diffraction analysis was performed with a D 500 diffractometer (Siemens, Germany) in the Henri Longchambon centre of the University Lyon I.

Results and discussion

Rest potential in H_3PO_4

The rest potential of a freshly cleaned lead electrode immersed in the solution was found to be close to −0.520 V for 6 *M* H_3PO_4 and to −0.540 V in 12 *M* H_3PO_4, regardless of the temperature. The standard deviation was never more than 10 mV. These values are more cathodic than the standard potential of the Pb^{2+}/Pb couple (−0.368 V) owing to the instantaneous chemical formation of superficial $PbHPO_4$ not shown by X-ray diffraction.

Lead behaviour in pure H_3PO_4; effects of concentration and temperature

The voltammogram obtained during the forward scan starting from −1.3 and performed up to +1.9 V with a freshly polished electrode in 6 *M* H_3PO_4 at 20 °C exhibited a sharp oxidation peak in the −0.5 to −0.3 V potential range. Solvent oxidation occurred significantly for potentials larger than +1.9 V. During the reverse scan the reduction of the formed compounds occurred in the −0.5 to −0.7 V range and hydrogen evolution became noticeable at −1.2 V.

The electrochemical behaviour of lead was studied using the multicycles technique and 10 successive cycles were done in the −0.7 to −0.3 V potential range starting from −0.7 V. For each cycle the values of the anodic and cathodic charges (Q_a and Q_c) flowing through the electrode during the forward and reverse scans were evaluated and the ratio Q_c/Q_a was calculated.

Figure 1 contains the typical voltammograms obtained during the first cycle in 6 and 12 *M* H_3PO_4 at 20 °C and 65 °C. The shape of the anodic peak indicates a superficial reaction and, as confirmed by X-ray analysis, this was due to $PbHPO_4$ formation according to an EC mechanism, which could be written as follows:

$$Pb \rightleftharpoons Pb^{2+} + 2e^-$$

$$Pb^{2+} + HPO_4^{2-} \rightleftharpoons PbHPO_4$$

On the voltammograms performed at 65 °C we notice a small anodic peak appearing during the reverse scan from −0.3 to −0.47 V, probably due to the oxidation of free Pb. This free Pb may appear because the potential reaches the values where $PbHPO_4$ begins to be dissolved, baring the metal, which reacts a second time. This phenomenon seems favoured by an increase of the temperature.

Figure 2 contains the mean values of Q_a which were obtained during the 10 successive cycles performed in 6 and 12 *M* H_3PO_4 at 20 °C and 65 °C, and the values of the ratio Q_c/Q_a for both concentrations are summarised in Table 1. Accoring to the mean values of Q_a observed in 6 and 12 M H_3PO_4 (data of Fig. 2), and assuming that a uniform layer of lead is involved in the $PbHPO_4$ formation, it is possible to evaluate the thickness of this

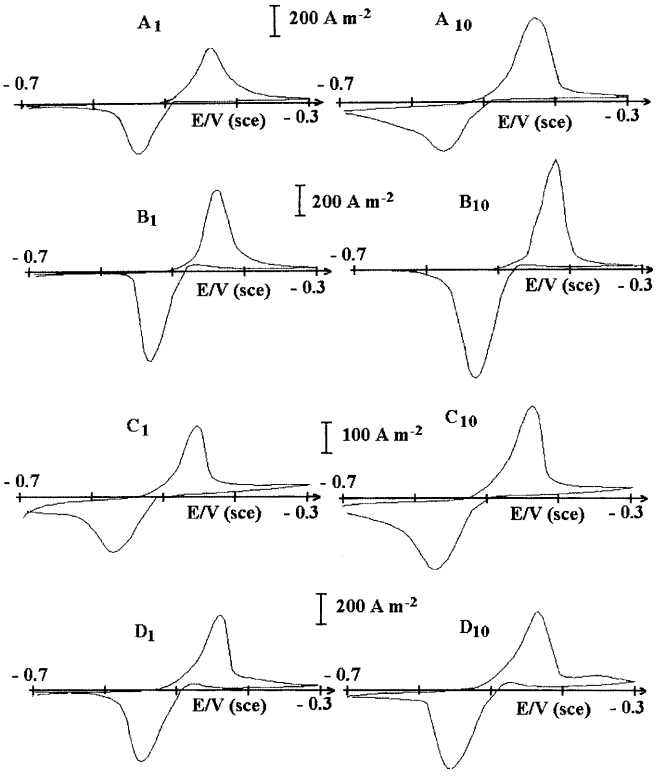


Fig. 1 First and tenth typical multicycle voltammograms of a lead electrode in H_3PO_4. Influences of acid concentration and temperature. Starting potential −0.7 V; scan rate 10 mV s^{-1}; electrode area 0.196 cm^2. A_1 and A_{10} 6 *M* H_3PO_4, $\theta = 20$ °C; B_1 and B_{10} 6 *M* H_3PO_4, $\theta = 65$ °C; C_1 and C_{10} 12 *M* H_3PO_4, $\theta = 20$ °C; D_1 and D_{10} 12 *M* H_3PO_4, $\theta = 65$ °C

layer. Values ranging from 0.2 to 0.5 μm were found. The thickness of the $PbHPO_4$ layer was not quantified because of its heterogeneous morphology (see Fig. 3).

Effects of acid concentration

From the experiments performed at room temperature, it appeared that the lead oxidation was significantly greater in 6 *M* than in 12 *M* H_3PO_4. For the first cycle the ratio Q_c/Q_a was very close to 1.

During the successive cycles the anodic charges increased to reach a constant value. The process was quicker in the 12 *M* than in the 6 *M* acid, but anodic charges rose in a similar proportion for both concentrations. The cathodic charges also increased and the ratio Q_c/Q_a remained constant in 12 *M* H_3PO_4, but decreased slightly for the 6 *M* acid.

Effects of temperature

The increase of the acid temperature to 65 °C caused an increase in the oxidation rate and at this temperature the anodic charge became larger in 12 *M* than in 6 *M* H_3PO_4.

The ratio Q_c/Q_a for the first cycle was lowered by increasing the temperature, slightly in the 6 *M* acid and more significantly in the 12 *M* acid. The ratio continued to decrease during successive cycles.

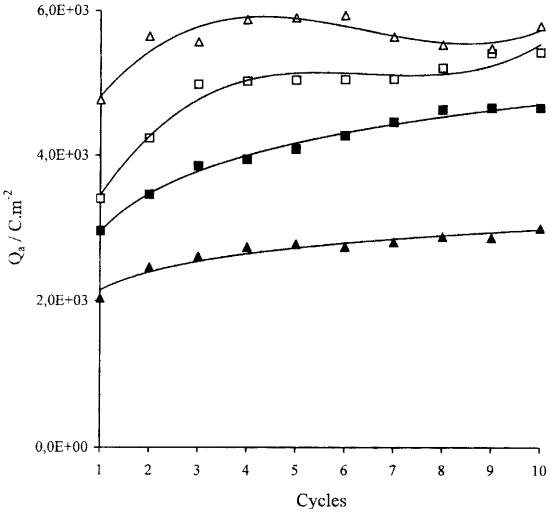


Fig. 2 Variations of the electric charge flowing through the electrode for the oxidation process Q_a during successive cycles. Effect of acid concentration and temperature. ■ 6 *M* H_3PO_4 $\theta = 20$ °C; ▲ 12 *M* H_3PO_4, $\theta = 20$ °C; □ 6 *M* H_3PO_4, $\theta = 65$ °C; △ 12 *M* H_3PO_4, $\theta = 65$ °C

The increase of Q_a during the successive cycles could be explained by an increase of the effective electrode area, caused by the deposition of small particles of lead during the cathodic scans.

Sample examination by scanning electron microscopy

The most representative photographs are shown in Fig. 3. Observations were made on lead samples after one and ten oxidation-reduction cycles performed in 6 *M* and 12 *M* H_3PO_4 at 20 °C (final potential −0.7 V). These samples were then compared with a freshly polished lead sample (Fig. 3a).

After one cycle, no changes could be observed in 12 *M* H_3PO_4, but in the 6 *M* H_3PO_4 small $PbHPO_4$ crystallites remained after the reduction scan. After 10 cycles, the lead surface appeared rougher and aggregates of $PbHPO_4$ crystals remained. The number of these aggregates appeared significantly larger in 6 *M* acid (Fig. 3b) than 12 *M* acid (Fig. 3c). These observations are consistent with the previous hypothesis concerning the electrode area growth and also the experimental values of the Q_c/Q_a ratio.

The SEM photographs of samples prepared by a single scan from −0.7 up to −0.3 V at 20 °C in 6 *M* acid showed that the surface was covered by well-shaped $PbHPO_4$ crystals (Fig. 4a). In 12 *M* acid there were fewer crystals, which were also not so well formed.

The increase of temperature caused an increase in both the number of crystals and their thickness.

Influence of halide ions

Chloride, bromide and iodide ions were introduced as potassium salts. Halide effects were studied from 0.015 to 0.073 *M* halide in 6 and 12 *M* H_3PO_4. Temperature effects were also investigated.

The nature of the anodic compounds was determined by X-ray analysis, and their shapes were examined by SEM (Fig. 4b–d).

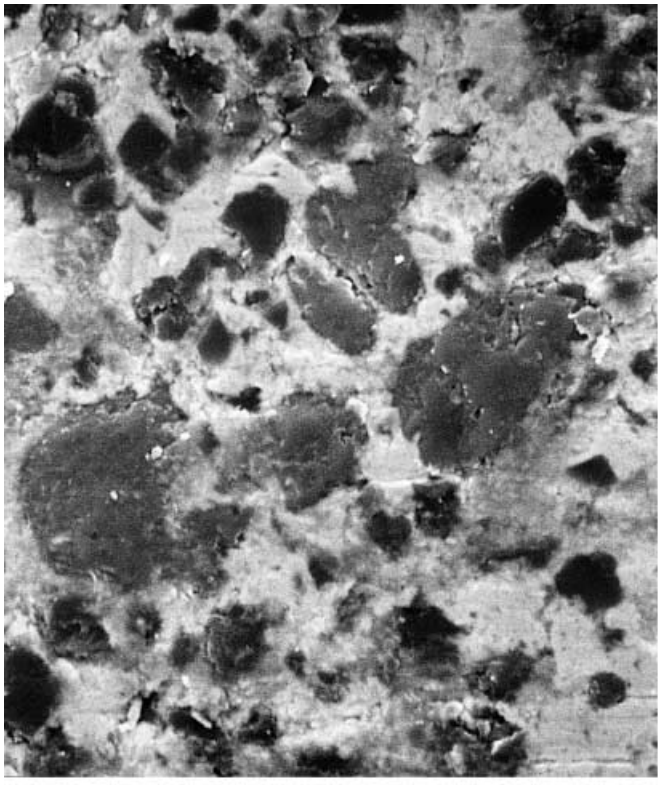
Halide effects on the rest potential, the voltammogram shapes and the variations of Q_a and Q_a/Q_c were studied.

Influence of chloride ions

The rest potential was unchanged by the addition of chloride ions. The shapes of the voltammograms were little changed by the addition of chloride ions, except for 0.073 *M* chloride added in 6 *M* acid at 65 °C (Fig. 5). In

Table 1 Influence of the acid concentration and temperature on the values of Q_a, Q_c and on the ratio Q_c/Q_a, obtained during the first and tenth cycles performed between −0.7 to −0.3 V

	Q_{a1} (C m^{-2})	Q_{a10} (C m^{-2})	Q_{c1} (C m^{-2})	Q_{c10} (C m^{-2})	Q_{c1}/Q_{a1}	Q_{c10}/Q_{a10}
6 *M*, 20 °C	2956	4643	3015	4318	1.02	0.93
6 *M*, 65 °C	3404	5412	3370	4925	0.99	0.91
12 *M*, 20 °C	2034	2991	2095	2961	1.03	0.99
12 *M*, 65 °C	4829	5892	4056	4419	0.84	0.75



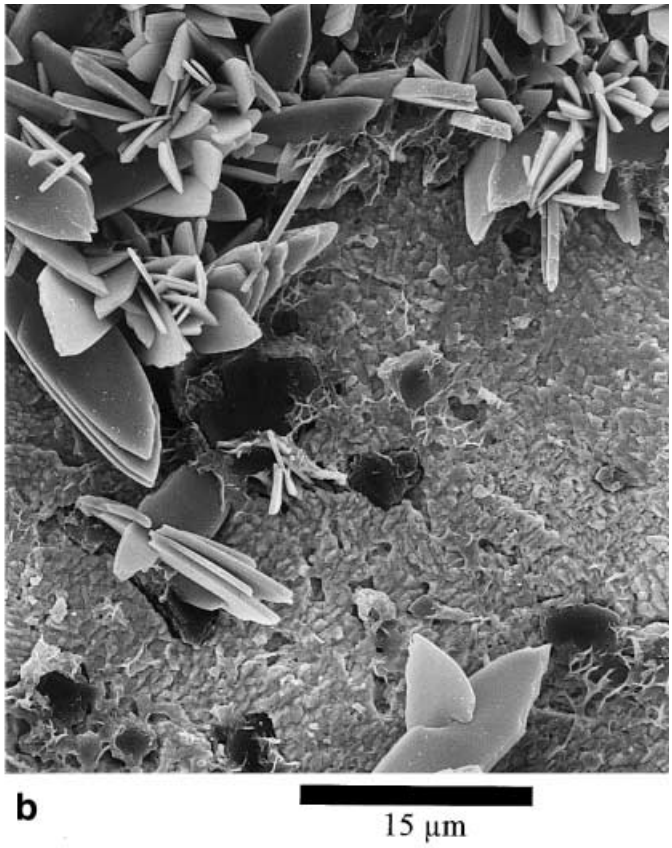
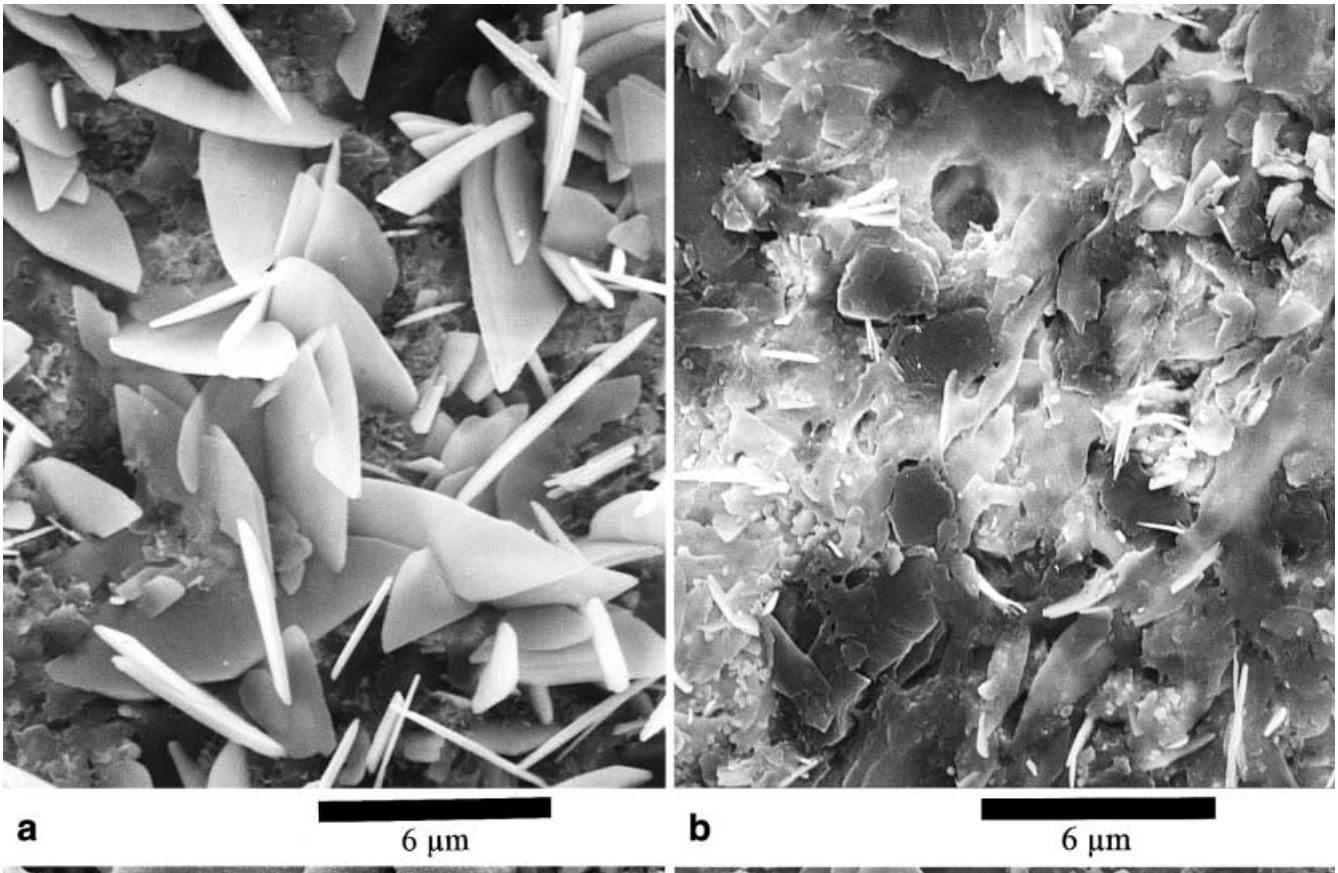


Fig. 3a–c SEM photographs of lead electrode: **a** after polishing and rinsing; **b** after ten successive oxidation-reduction cycles in 6 *M* H_3PO_4 at 20 °C; **c** after ten successive oxidation-reduction cycles in 12 *M* H_3PO_4 at 20 °C. Experiments were started at −0.7 V and stopped after the last reduction scan at −0.7 V

►

Fig. 4a–d SEM photographs of the species formed at the lead electrode during one oxidizing scan started at −0.7 V and stopped at −0.3 V in 6 *M* H_3PO_4 at 65 °C. Effects of halide ions: **a** pure acid; **b** with 0.015 *M* Cl^- added; **c** with 0.015 *M* Br^- added; **d** with 0.015 *M* I^- added


a
6 μm
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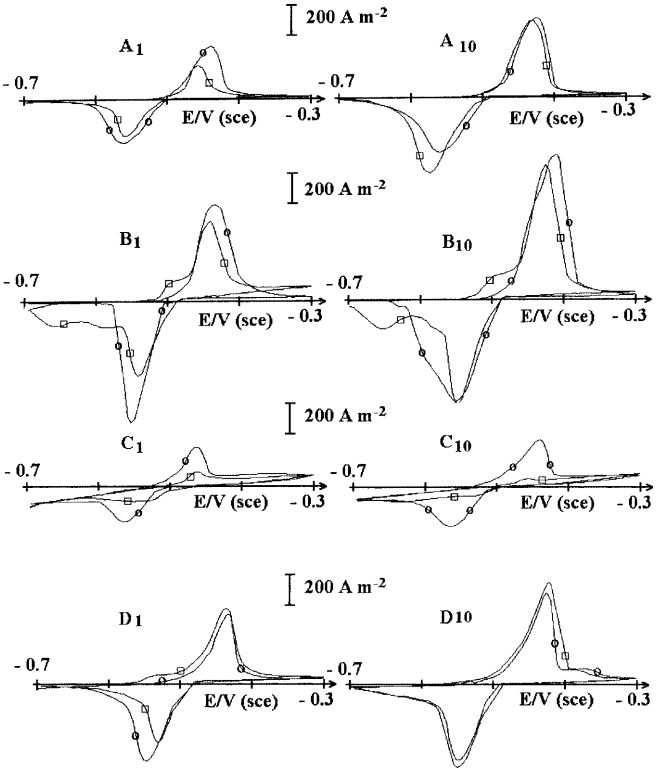

Fig. 5 First and tenth typical multicycle voltammograms of a lead electrode in H_3PO_4 in the presence of chloride ions. Influences of temperature, chloride ions and acid concentrations. Starting potential −0.7 V scan rate 10 mV s^{-1}; electrode area 0.196 cm^2. ○ $[Cl^-]$ = 0.015 *M*; □ $[Cl^-]$ = 0.073 *M*. A_1 and A_{10} 6 *M* H_3PO_4, $\theta = 20$ °C; B_1 and B_{10} 6 *M* H_3PO_4, $\theta = 65$ °C; C_1 and C_{10} 12 *M* H_3PO_4, $\theta = 20$ °C; D_1 and D_{10} 12 *M* H_3PO_4, $\theta = 65$ °C

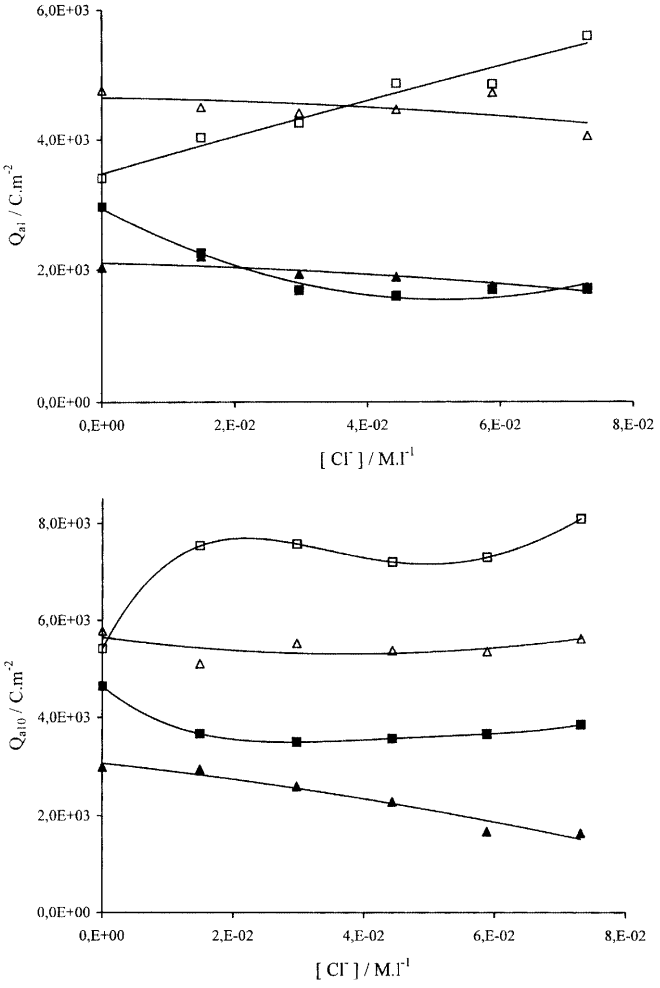

Fig. 6 Effect of chloride concentration on the electric charge flowing through the electrode during the oxidation process for the first (Q_{a1}) and the tenth (Q_{a10}) cycles performed at various acid concentrations and temperatures. ■ 6 *M* H_3PO_4, $\theta = 20$ °C; ▲ 12 *M* H_3PO_4, $\theta = 20$ °C; □ 6 *M* H_3PO_4, $\theta = 65$ °C; △ 12 *M* H_3PO_4, $\theta = 65$ °C

this case a wave appeared before the anodic peak, and the reduction process went on until −0.7 V (Fig. 5, voltammograms B_1 and B_{10}).

During the successive cycles, Q_a and Q_c increased, as in pure acid. The variations of Q_a measured during the first and the tenth cycles are shown in Fig. 6. The values of Q_a decreased slowly as the chloride concentration increased except at 65 °C in 6 *M* H_3PO_4, in which case the addition of chloride ions caused an important increase of Q_a. The ratios Q_c/Q_a were not significantly changed by the addition of chloride ions and always remained close to the values obtained in the pure acids.

Examination by SEM of the sample prepared with 0.015 *M* chloride in 6 *M* H_3PO_4 (Fig. 4b) showed the presence of badly shaped crystals, smaller than those obtained under the same conditions with pure acid (Fig. 4a). A careful examination of the surface of the electrodes by X-ray diffraction revealed the presence of $Pb_5(PO_4)_3Cl$ and $PbHPO_4$.

Influence of bromide ions

The rest potential became progressively more cathodic when the bromide ion concentration increased. This decrease was more significant at 65 °C than at 20 °C. For 0.073 *M* bromide ions added, the values were respectively −0.540 and −0.580 V in 6 *M* acid at 20 °C and 65 °C, and −0.630 and −0.650 V in 12 *M* H_3PO_4.

In 6 *M* acid at 20 °C the addition of bromide ions caused a shift of the anodic peak to more anodic potentials, and the appearance of a small prewave (Fig. 7, A_1). During the successive cycles the cathodic peak became sharper than in pure acid. The major changes could be observed at 65 °C for the upper bromide concentration (Fig. 7, B_1). The prewave observed during the first anodic scan at 20 °C became larger and the peak itself decreased in such a significant way that it became identical to the prewave. During the forward scan the anodic peak shifted to a more cathodic value (−0.65 V) and was preceded by a reduction wave located in the potential range of the previous cathodic peak. During the further cycles the differences between pure acid and the bromide-added acid became less significant, except for the highest bromide concentration.

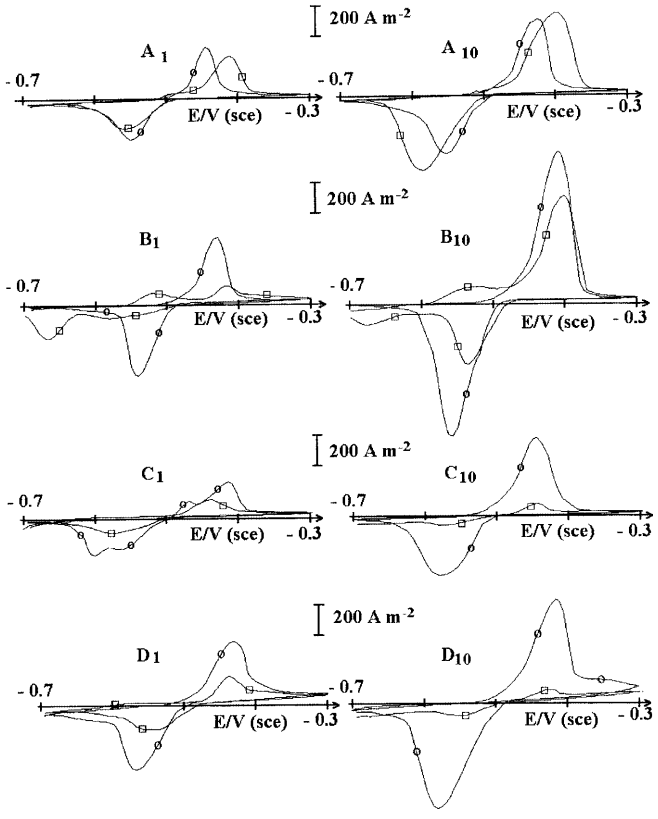

Fig. 7 First and tenth typical multicycle voltammograms of a lead electrode in H_3PO_4 in the presence of bromide ions. Influences of temperature, bromide ions and acid concentrations. Starting potential −0.7 V scan rate 10 mV s^{-1}; electrode area 0.196 cm^2. ○ $[Br^-] = 0.015$ *M*; □ $[Br^-] = 0.073$ *M*. A_1 and A_{10} 6 *M* H_3PO_4, $\theta = 20$ °C; B_1 and B_{10} 6 *M* H_3PO_4, $\theta = 65$ °C; C_1 and C_{10} 12 *M* H_3PO_4, $\theta = 20$ °C; D_1 and D_{10} 12 *M* H_3PO_4, $\theta = 65$ °C

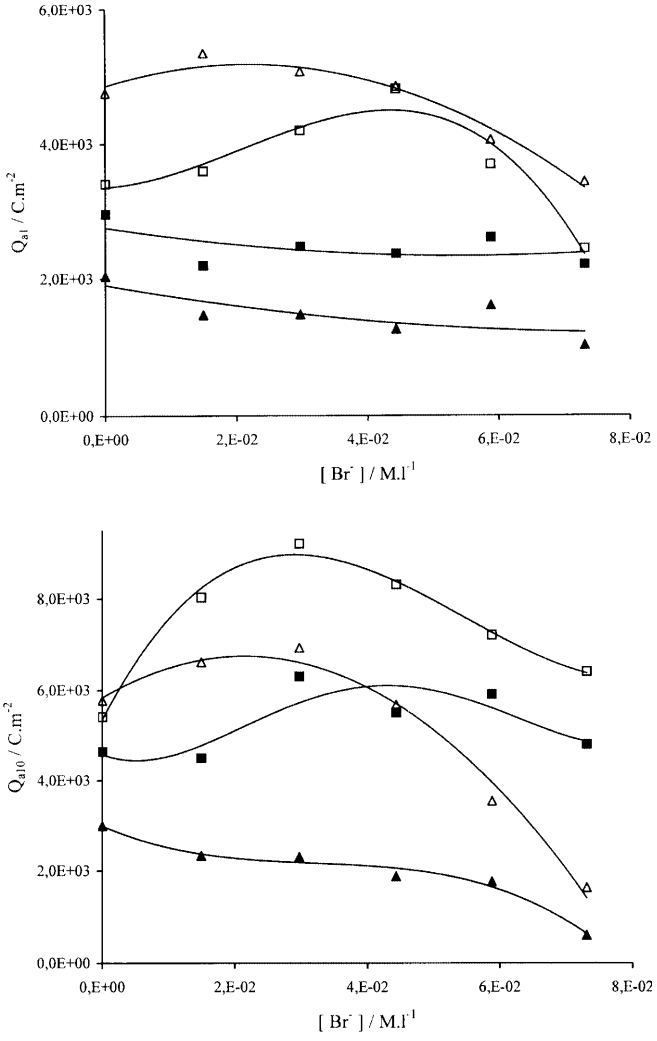

Fig. 8 Effect of bromide concentration on the electric charge flowing through the electrode during the oxidation process for the first (Q_{a1}) and tenth (Q_{a10}) cycles performed at various acid concentrations and temperatures. ■ 6 *M* H_3PO_4, $\theta = 20$ °C; ▲ 12 *M* H_3PO_4, $\theta = 20$ °C; □ 6 *M* H_3PO_4, $\theta = 65$ °C; △ 12 *M* H_3PO_4, $\theta = 65$ °C

In 12 *M* acid at 20 °C the first addition of bromide ions led to two coalescent anodic and cathodic peaks during the first scan (Fig. 7, C_1). For upper concentrations only, one anodic and one cathodic peaks were observed. The shape of the voltammograms obtained during the further cycles became progressively similar to those in pure acid. At 65 °C the anodic peaks were shaped as in pure acid but the cathodic peaks dragged more than in pure acid.

The variations of Q_a obtained during the first and the tenth cycles are shown in Fig. 8. The addition of bromide at 20 °C caused a small decrease of Q_a during the first cycle in 6 *M* and for all cycles in 12 *M* acid. The bromide effects were more important for experiments performed at 65 °C and especially in 6 *M* acid, where the Q_a values of the tenth cycle showed a maximum much higher than the value obtained in pure acid.

In 6 *M* at 20 °C the ratio Q_c/Q_a was quite constant during the ten cycles and close to 0.95 for all bromide ion concentrations. For experiments performed at 65 °C the ratio Q_c/Q_a decreased progressively when bromide ions were added. The ratio calculated for the first cycle varied from 0.99 in pure acid to 0.85 with 0.073 *M* bromide ions; for the tenth cycle the influence was more significant and the ratio decreased from 0.91 to 0.65.

In 12 *M* acid at 20 °C, for bromide ions concentration lower or equal to 0.030 *M*, the ratio Q_c/Q_a was constant during the ten cycles and a little smaller than in pure acid (respectively 0.95 and 0.90 for 0.015 and 0.030 *M* bromide). When the bromide ion concentration increased, the first cycle ratio Q_c/Q_a decreased drastically to 0.55, but during the successive cycles it regularly increased up to 0.78, and the values obtained were identical for all bromide concentrations. In 12 *M* acid at 65 °C the ratio Q_c/Q_a calculated for the first cycle was lowered by the addition of bromide (0.80 to 0.60); it increased regularly during the successive cycles, and finally the values reached were higher than in pure acid (1 to 0.90).

Examination by SEM of a sample prepared with 0.015 *M* bromide added to 6 *M* H_3PO_4 showed the

presence of two kind of crystals; large platelets, similar to those obtained in pure acid, and cubic crystallites of approximately 0.6 μm edge (Fig. 4c). X-ray diffraction patterns revealed the presence of $Pb_5(PO_4)_3Br$ and $PbHPO_4$.

Influence of iodide ions

The complete study was only carried out in 6 *M* acid at 20 °C. In the other cases the addition of iodide was stopped at 0.030 *M* because the oxidation and reduction peaks were too badly shaped and too small for the upper concentrations.

The addition of iodide ions caused few changes in the rest potential, excepted at 65 °C in 6 *M* acid, where it became more cathodic (−0.590 V for 0.030 *M* iodide).

The addition of iodide ions caused significant changes in the shape of the voltammograms (Fig. 9). In 6 *M* acid at 20 °C the anodic peak dragged up to −0.3 V and the peak potential shifted towards more anodic values (−0.4 V). The reduction process occurred at a more cathodic potential (−0.6 V). In 6 *M* acid at 65 °C the changes were most noticeable, principally for the first cycle where an important oxidation peak was observed during the reverse scan (Fig. 9, B_1). When the iodide concentration was 0.03 *M*, this peak was more intense than the peak observed during the forward scan, and it disappeared during the further cycles. The reason is certainly the same as in the case of 6 *M* and 12 *M* H_3PO_4 at 65 °C. However, in this case the PbI_2 and $PbHPO_4$ were formed simultaneously and the weak adherence of the former could explain the large Pb oxidation peak observed during the first reverse scan. During the successive cycles, the reduction peaks dragged more and more.

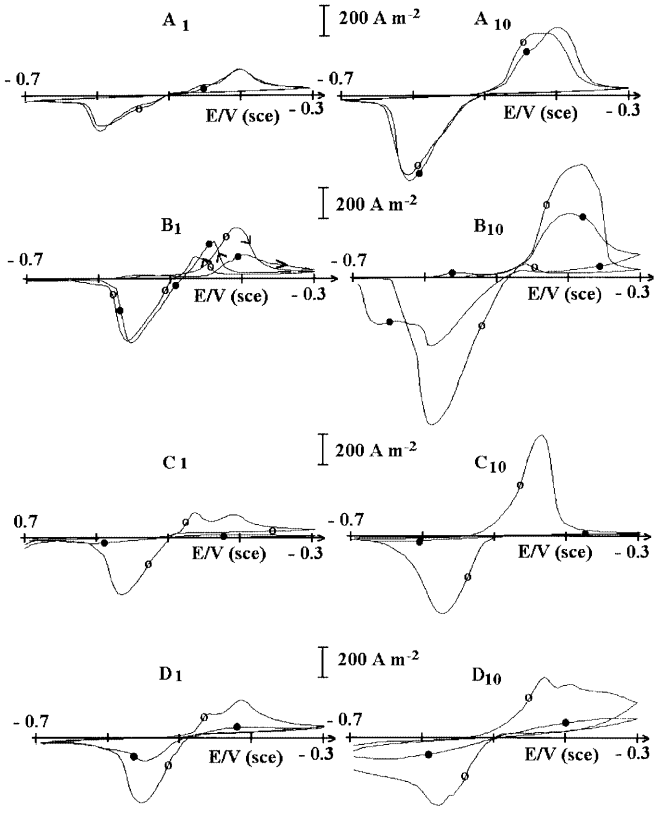

Fig. 9 First and tenth typical multicycle voltammograms of a lead electrode in H_3PO_4 in the presence of iodide ions. Influences of temperature, iodide ions and acid concentrations. Starting potential −0.7 V; scan rate 10 mV s^{-1}; electrode area 0.196 cm^2. ○ $[I^-] = 0.015$ *M*; ● $[I^-] = 0.03$ *M*. A_1 and A_{10} 6 *M* H_3PO_4, $\theta = 20$ °C; B_1 and B_{10} 6 *M* H_3PO_4, $\theta = 65$ °C; C_1 and C_{10} 12 *M* H_3PO_4, $\theta = 20$ °C; D_1 and D_{10} 12 *M* H_3PO_4, $\theta = 65$ °C

In 12 *M* acid at 20 °C for 0.015 *M* iodide ions, the first oxidation curve appeared as two badly separated peaks (Fig. 9, C_1), and the further cycles led to the same shape as in pure acid. The reduction peaks were almost identical to those in pure acid. For 0.030 *M* iodide ions in the solution, the oxidation and reduction processes were quite undetectable. In 12 *M* at 65 °C for 0.015 *M* iodide the shape of the first voltammograms were similar to those performed at 20 °C, but the heights of the two oxidation peaks were inverted, and they remained during all ten cycles, with variable heights. For 0.030 *M* iodide the oxidation and reduction peaks were badly shaped. In all cases, oxidation and reductions were not achieved at the chosen potentials.

In 6 *M* acid at 20 °C and 65 °C the values of Q_a and Q_c obtained during the first cycle decreased slightly when iodide was added. During the successive cycles, Q_a and Q_c increased and became higher than in pure acid.

In 12 *M* acid, when the iodide ion concentration increased the values of Q_a and Q_c decreased a little for experiments performed at 20 °C and strongly at 65 °C. In both cases they grew with the number of cycles. This increase was especially significant (approximately double) when the iodide concentration was 0.015 *M* and the temperature 65 °C.

In 6 *M* acid at 20 °C the ratio Q_c/Q_a calculated for the first cycle decreased slightly (0.96 to 0.89) when the iodide concentration increased up to 0.073 *M* and it remained quite constant during the successive cycles. At 65 °C the ratio Q_c/Q_a calculated for the first cycle was strongly lowered by the iodide addition (0.75) but increased progressively (up to 0.95) during the further cycles. The increase of iodide concentration caused no significant changes in the values of Q_c/Q_a.

In 12 *M* acid at 20 °C the ratio Q_c/Q_a for the first cycle decreased from 0.98 to 0.85 when the iodide concentration increased from 0.015 to 0.030 *M*. During the successive cycles it increased regularly up to 1 and 0.95. At 65 °C the addition of iodide was less influential on the ratio Q_c/Q_a, and in both cases it varied from 0.90 for the first cycle to 1 until the fifth cycle.

The yellow colour of the formed compound suggested the presence of PbI_2, which was confirmed by X-ray analysis. On the SEM photographs, PbI_2 appeared as numerous small platelets of 0.6 μm mean diameter and some larger ones could be observed (Fig. 4d). The adherence of the lead iodide to the lead electrode was very

low and the major part was removed during rinsing of the sample for SEM examinations.

Conclusions

From our study, one may conclude that in H_3PO_4 solutions, without any additive, the increases of the electrical charge Q_a flowing through the electrode during the oxidising process, and the changes of reduction efficiency expressed by ratio Q_c/Q_a, are essentially due to changes in the surface morphology. During the oxidation scan, lead dissolves and a part gives solid $PbHPO_4$ at the electrode surface and another smaller part diffuses towards the bulk solution. The subsequent reduction scan restores the metal as small crystallites, the morphology of which depends on the origin: Pb^{2+} or $PbHPO_4$. The compactness of the new electrode surface is less than that of the initial rod, and the electrode area is increased. In addition, it was observed that $PbHPO_4$ obtained during the oxidation scan is not completely transformed into Pb during the reverse scan, as outlined by SEM photographs.

Addition of chloride, bromide and iodide induces noticeable perturbations on the shape of the curves. $Pb_5(PO_4)_3Cl$ and $Pb_5(PO_4)_3Br$ have been identified, but $PbHPO_4$ is still present. In the case of iodide, the PbI_2 formation predominates and no mixed compound may be evidenced. The principal effect of halides is to make the salt layer brittle, leading to some losses of material falling down in the cell. This effect is larger with iodide ions.

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