

Influence of pH of the H₂SO₄ solution on the phase composition of the PbO₂ active mass and of the PbO₂ anodic layer formed during cycling of lead electrodes

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Abstract

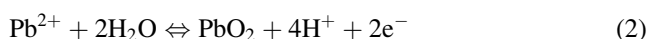
During charge and discharge of lead-acid batteries the concentration of the H₂SO₄ solution in the pores of the active material and in the interface grid/active mass varies widely. In this investigation, the influence of pH of the H₂SO₄ solution on the phase composition of the positive active mass (PAM) and of the interface PAM/grid is studied. The influence of pH on the phase composition of the interface is determined indirectly by cycling Pb electrodes between 0.70 and 1.60 V (versus Hg/Hg₂SO₄) in H₂SO₄ solutions of various concentrations and determining the phase composition and the structure of the anodic layer formed. The influence of pH on the phase composition of the PAM is investigated by immersing fully charged PAM samples into H₂SO₄ solutions of various concentrations and determining the phase composition of the PAM and the size of the α-PbO₂, β-PbO₂ and PbSO₄ crystals. It has been found that the outer sub-layer of the anodic layer participates in the cycling processes and its phase composition depends on the pH of the solution and on the potential scan rate. The reduction rate of PbO₂ in this sub-layer depends on the solution pH. If the reduction of PbO₂ proceeds in solutions with pH between –1.0 and –0.50, the rate of the processes is high. When it proceeds at pH > –0.50 the reduction rate is lower. This behaviour of the PbO₂/PbSO₄ electrode influences the power performance of the lead-acid battery when the positive plates are the power limiting component. The rate of oxidation of PbSO₄ to PbO₂ is determined by the pH of the solution because the solubility of PbSO₄ depends on pH. In concentrated solutions the solubility of PbSO₄ is low, the charge process is slow and some unoxidised PbSO₄ may remain in the charged plate. In diluted H₂SO₄ solutions, the solubility of PbSO₄ is high and PbSO₄ crystals are oxidised fully during charge. It has been found that the phase composition of the PAM depends on the pH of the solution since the hydrated part of the PbO₂ particles interacts with the ions in the solution as a result of which the crystal zones/hydrated zones and hydrated zones/solution equilibria are changed. The content of α- and β-PbO₂ crystal zones in the PAM depends on the pH of the solution. In the pH region between –0.75 and 0, SO₄²⁻ ions which have penetrated into the hydrated gel zones react with Pb²⁺ ions from the nonstoichiometric part of the PAM (PbO_{2-δ}) forming PbSO₄ molecules, which leave the hydrated zones and enter the solution forming PbSO₄ crystals there. When the PAM is immersed in solutions with pH between 0 and –1.0, the content of the crystal phases of α- and β-PbO₂ decreases. In this pH region the average size of the β-PbO₂ crystals decreases while that of α-PbO₂ remains constant or increases slightly. The results of this investigation evidence that the PAM is a dynamic system, which interacts with the ions in the solution, and hence the phase composition of the PAM depends on the concentration of the H₂SO₄ solution.

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1. Introduction

The reactions that proceed on the PbO₂/PbSO₄ electrode can be represented by the following equations:



The oxidation of PbSO₄ to PbO₂ and the reduction of PbO₂ to PbSO₄ proceed through a dissolution–precipitation

mechanism. The anodic current on oxidation of PbSO₄ is presented by the following equation [1]

$$i = nFSk(C_{\text{Pb}^{2+}}^x C_{\text{H}^+}^y) \quad (3)$$

where *S* is the reaction area of PbO₂ (positive active mass (PAM)). It changes during the time of the reaction. *k* is a rate constant which depends on the potential and on temperature, *n* is the number of electrons involved in the electrochemical reaction. *C*_{Pb²⁺} and *C*_{H⁺} are the concentrations of Pb²⁺ and H⁺ ions, respectively, *x* and *y* are the reaction orders of Pb²⁺ and H⁺ ions in the anodic reaction.

It is evident from Eq. (3) that the rate of the anodic reaction, and hence the structure of the crystals formed,

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depend on the pH of the solution and on the concentration of Pb^{2+} ions. The concentration of Pb^{2+} ions is determined by the solubility of PbSO_4 (Eq. (1)). It has been established that the solubility of PbSO_4 depends on the concentration of the H_2SO_4 solution [2,3]. It features a maximum at 1.0 M concentration and decreases both above and below this concentration. In a 5.0 M H_2SO_4 solution the solubility of PbSO_4 is six times smaller than in a 1.0 M solution. This dependence of the solubility of PbSO_4 on $C_{\text{H}_2\text{SO}_4}$ exerts a strong influence both on the charge and discharge processes in the lead-acid battery. The above influence affects the structure of the PAM and the morphology of the PbO_2 and PbSO_4 particles.

The influence of the H_2SO_4 concentration on the processes of PbSO_4 oxidation to PbO_2 was studied by Takehara and Kanamura for the case of PbO_2 electrodeposited on Au substrate for concentrations ranging between 0.1 and 5.0 M H_2SO_4 [4–6]. The highest rate of PbSO_4 oxidation to PbO_2 was found in 0.50 M H_2SO_4 solution, and the transformation of the PbSO_4 layer into PbO_2 one was illustrated by SEM micrographs. Czerwinski et al. [7] investigated, via cyclic linear voltammetry, the electrochemical properties of a lead electrode immersed in H_2SO_4 solutions with concentrations ranging between 0.05 and 5.0 M. The anodic and cathodic peaks appearing in the voltammograms due to the reduction of PbO_2 and the oxidation of PbSO_4 were studied and, based on the results obtained, the authors determined the changes in anodic layer properties.

The aim of the present investigation is to study the influence of the concentration of H_2SO_4 (i.e. pH of the solution and the concentration of Pb^{2+} ions in it) on the phase composition of the anodic layer formed during cycling of a $\text{PbO}_2/\text{PbSO}_4$ electrode in solutions of various pH, as well as on the phase composition of the lead dioxide active mass (PAM) in lead-acid batteries. The results of this study will provide indirect information about the processes taking place in the positive plates during charge and discharge of the lead-acid battery. Our investigations were carried out in H_2SO_4 solutions with concentrations between 0.05 and 5.0 M, i.e. the H_2SO_4 concentration range in which lead-acid batteries operate.

2. Experimental methods

2.1. Determination of the influence of pH of the H_2SO_4 solution on the electrochemical properties of the $\text{PbO}_2/\text{PbSO}_4$ electrode

A classical three-electrode glass cell was used. Smooth Pb (99.999%) electrodes were immersed in sulphuric acid solutions of various pH. The reference electrode was a Hg/ Hg_2SO_4 one filled with the same electrolyte as the one in the cell. A platinum plate was used as counter electrode. The working electrode was subjected to cyclic linear voltammetric sweeps between 1.6 and 0.7 V at a scan rate of 100 mV/s for 1 and 16 h. Fig. 1 shows schematically the changes in the

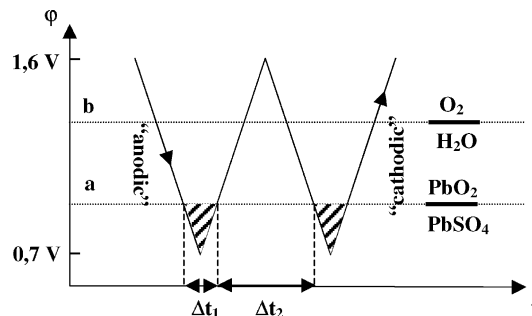


Fig. 1. Polarization conditions of anodic layer preparation.

potential of the $\text{PbO}_2/\text{PbSO}_4$ electrode with time as well as the values of the equilibrium potentials of the $\text{PbO}_2/\text{PbSO}_4$ and $\text{O}_2/\text{H}_2\text{O}$ electrodes.

Δt_1 and Δt_2 give the time periods during which PbSO_4 and PbO_2 are thermodynamically stable. Their values are $\Delta t_1 = 500 \text{ mV}/v_{\text{sw}}$ and $\Delta t_2 = 1300 \text{ mV}/v_{\text{sw}}$, where v_{sw} is the potential scan rate. $\Delta t_2 = 2.6\Delta t_1$, i.e. only part of the PbO_2 formed is reduced to PbSO_4 and the latter is oxidised to PbO_2 during the next anodic sweep, Δt_2 .

The dependence of the reduction rate of PbO_2 in the anodic layer on the pH of the solution was determined through cathodic voltammetric sweeps in the potential region from 1.60 to -1.50 V versus Hg/ Hg_2SO_4 electrode at a scan rate of 1 mV/s. From the area of the cathodic peak of PbO_2 reduction, we determined the thickness of the PbO_2 layer and its dependence on the pH of the solution.

2.2. X-ray diffraction method for determining the phase composition and the size of the crystals in the anodic layer and in the PAM

The phase composition of the anodic layer was determined by X-ray diffraction (XRD) analysis. The following diffraction lines were selected for characterization of the crystalline phases in the anodic layer and in the PAM: $d = 0.350 \text{ nm}$ for $\beta\text{-PbO}_2$, $d = 0.300 \text{ nm}$ for PbSO_4 and $d = 0.311 \text{ nm}$ for $\alpha\text{-PbO}_2$. Tetragonal-PbO has a characteristic line with $d = 0.312 \text{ nm}$, i.e. this line is common for $\alpha\text{-PbO}_2$ and tetragonal-PbO. The average size of the crystals of the above phases was estimated from the half-widths of the above diffraction lines.

The changes in phase composition across the thickness of the anodic layer, formed after 16 h of cycling between 1.6 and 0.7 V at a scan rate 100 mV/s, were investigated through XRD analyses by removing sub-layers from the electrode surface. The phase composition of the anodic layer was presented as a function of the pH of the solution for three sub-layers: the outer sub-layer contacting the electrolyte, the middle sub-layer and the inner sub-layer contacting the electrode metal surface.

The structure of the anodic layer and the crystal morphology of the particles were observed by scanning electron microscopy.

Table 1
Solutions used for the experiments

pH	−1.0	−0.75	−0.62	−0.50	−0.25	0	0.50	1.0
Concentration (M)	5.00	2.81	2.06	1.56	0.86	0.5	0.18	0.05
s.g. of H ₂ SO ₄	1.285	1.17	1.125	1.095	1.050	1.030	1.010	1.0

2.3. Determination of the influence of the pH of the H₂SO₄ solution on the phase composition of the PbO₂ active mass (PAM)

Charged battery positive plates were subjected to 10 charge–discharge cycles and then charged up to a charge factor $F_{ch} = 150\%$. The positive active material was extracted from the grid, washed, dried and ground into powder. Equal amounts of this active material were put in a series of H₂SO₄ solutions of various pH but of equal volume. After 2-h stay in the solution, the PAM samples were filtered and X-rayed. Diffractograms of dry PAM and of PAM that had stayed in H₂SO₄ solutions of various pH were recorded. On grounds of the results obtained, the dependences of the content of α -PbO₂, β -PbO₂ and PbSO₄, and of the average crystal size of these phases, on pH of the solution were determined.

2.4. Concentrations of the H₂SO₄ solutions in which the measurements were carried out

The investigation was performed using H₂SO₄ solutions with pH ranging from −1.0 to +1.0. The pH values, and the concentrations of the H₂SO₄ solutions used, are summarised in Table 1. They belong to the battery electrolyte range between the fully charged and the fully discharged states.

3. Experimental results and discussion

3.1. Dependence of the electrochemical properties and the phase composition of the anodic layer on pH of the H₂SO₄ solution

3.1.1. Electrochemical properties of the anodic layer formed during cycling of the electrode in H₂SO₄ solutions with various pH

Fig. 2 shows voltammograms for lead electrodes cycled in four different solutions at a scan rate of 100 mV/s for 16 h. Two peaks are observed in the voltammograms. The anodic peak A is due to formation of lead dioxide, and the cathodic peak C₁ is to the reduction of this phase.

At pH −1.0, peak C₁ is well pronounced. The reduction reaction is fast and only small amounts of lead dioxide are accumulated in the anodic layer on cycling. At higher pH values, the reduction of lead dioxide occurs at more negative potentials. Hence, larger amounts of lead dioxide are accumulated in the anodic layer on cycling.

The amount of each phase formed in the anodic layer was estimated by reducing these phases at a low scan rate. For this purpose voltammetric sweeps at 1 mV/s down to −1.5 V were carried out after the electrodes were cycled for 16 h at 100 mV/s between 1.6 and 0.7 V. The cathodic parts of six voltammograms for solutions with pH between −1.0 and 0 are shown in Fig. 3. These illustrate the reduction of PbO₂ in the potential range between 1.3 and 0.5 V, and of PbO and PbSO₄ in the potential range between −0.7 and −1.5 V. Peak C₁ is an indication for the reduction of PbO₂ to PbSO₄, peak C₂ for the reduction of PbO to Pb, and peak C₃ for the reduction of PbSO₄ to Pb.

The data in Fig. 3 indicate that pH of the solution has a strong influence on the profile (width) of the C₁ peak determined by the reduction rate of PbO₂ to PbSO₄. We assume that the peak width (W_p) is the potential region

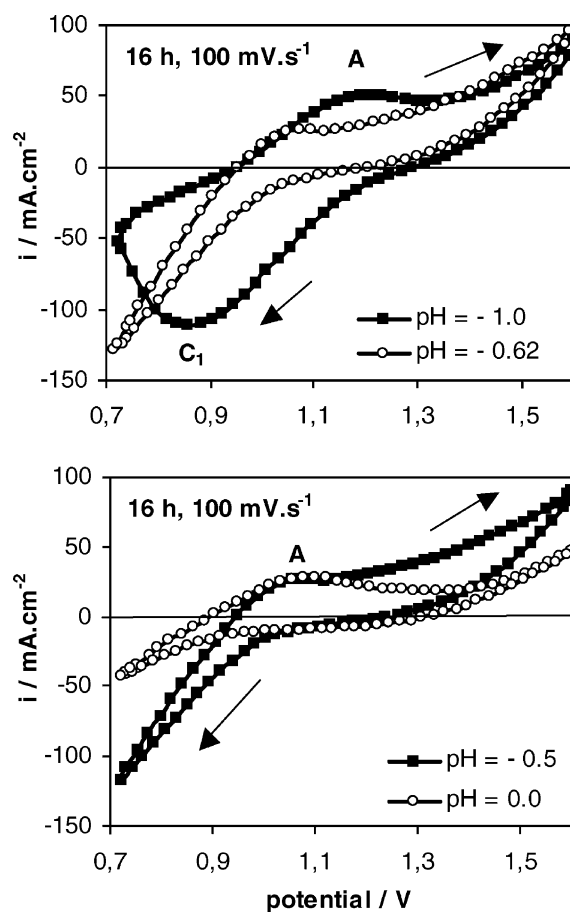


Fig. 2. Voltammograms for electrodes cycled at a scan rate of 100 mV/s for 16 h in H₂SO₄ solutions with various pH.

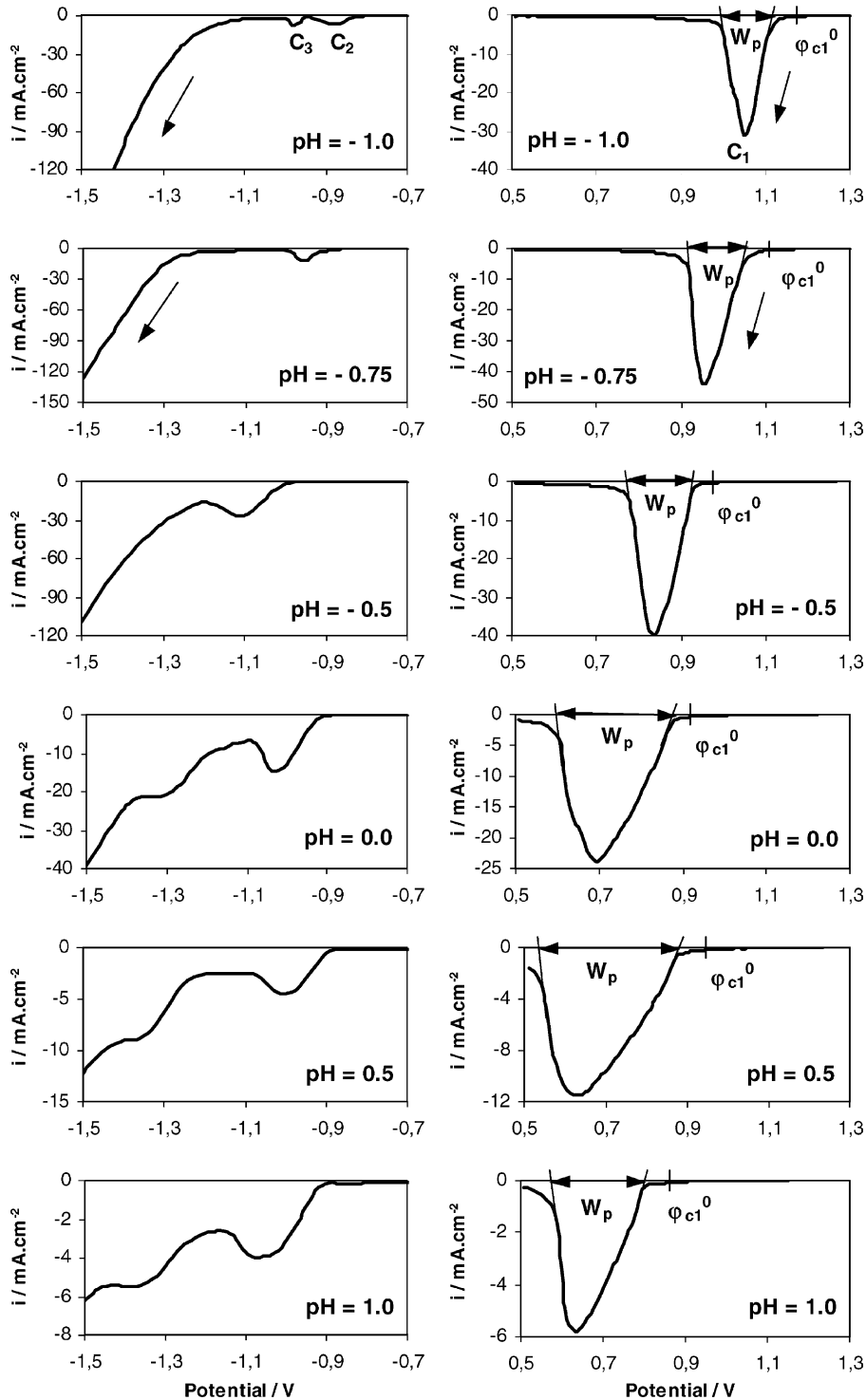


Fig. 3. Cathodic sweep voltammograms at scan rate 1 mV/s after 16 h of electrode cycling between 1.6 and 0.7 V at 100 mV/s in H_2SO_4 solutions of various pH.

enclosed between the cross points of the linear approaches of the two peak fronts with the potential axis (Fig. 3).

Two pH regions can be distinguished depending on the peak width.

(a) In the first one between pH -1.0 and -0.50 , the width of peak C_1 increases slightly from 60 to 73 mV on

increasing pH (Table 2). For electrodes polarised in solutions with pH -0.75 and -0.50 , peak C_1 is very high, i.e. the rate of the reduction of PbO_2 to PbSO_4 is high and PbO_2 is reduced within a narrow potential range during the cathodic sweep.

(b) In the second region, between pH 0 and 1.0, the peak width increases with pH increase from 140 mV for pH

Table 2
Width (W_p) of the PbO_2 reduction peak C_1 (in mV) as a function of pH of the solution in which the reduction proceeds

I region		II region	
pH	W_p (mV)	pH	W_p (mV)
-1.0	60	0	140
0.75	67	0.50	173
-0.50	73	1.0	120

0, through a maximum of 170 mV at pH 0.50, and then decreases to 120 mV for the electrode discharged in a solution with pH 1.0 (Fig. 3 and Table 2). A wide reduction peak is observed in the voltammograms. The peak current is relatively low which indicates that the reduction of PbO_2 is strongly impeded. A more thorough analysis of the voltammograms shows that in the second region the cathodic peak comprises two partially overlapping peaks. This is most clearly visible for the reduction of PbO_2 in a solution with pH 0.50.

The dependence of the potential $\varphi_{C_1}^0$, at which the reduction of PbO_2 starts, on pH of the solution was also analysed. Fig. 4 presents the potentials at which the current becomes negative (i.e. the beginning of PbO_2 reduction to $PbSO_4$) as a function of solution pH. A linear dependence was established:

$$\varphi_{C_1}^0 = A - 0.196 \text{ pH}$$

The fact that the dependence $\varphi_{C_1}^0$ versus pH is linear indicates that this potential is related to the reduction of one of the PbO_2 phases.

Fig. 3 gives also the reduction peaks of PbO to Pb (peak C_2) and of $PbSO_4$ to Pb (peak C_3). In the most negative potential region of the voltammetric sweep, a reaction of H_2 evolution due to H_2O decomposition proceeds as well. These processes depend strongly on the pH of the solution. It can be expected that the structure of PbO and of $PbSO_4$ will also influence the profile and the location of peaks C_2 and C_3 on

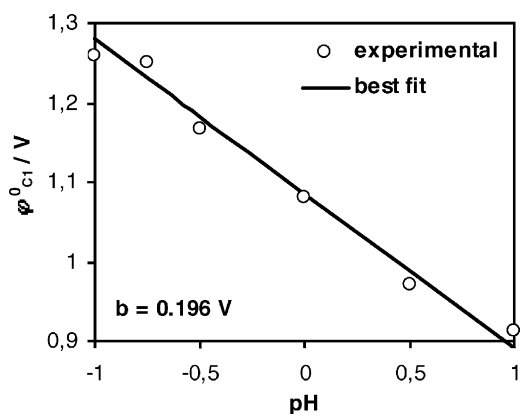


Fig. 4. Dependence of the potential, at which the electrochemical reaction of reduction of PbO_2 begins, on the pH of the H_2SO_4 solution.

the potential scale. The structures of PbO and $PbSO_4$ in their turn depend on the crystallisation processes of these phases during PbO_2 reduction. Tetragonal- PbO is formed at the metal/anodic layer interface both during cycling and probably during some periods of the reduction of PbO_2 [8]. Judging only by the shape of the voltammograms for PbO and $PbSO_4$ reduction to Pb , and by the position of their reduction peaks, it is rather difficult to draw unambiguous conclusions about the elementary processes involved in the reduction of these phases.

3.1.2. Anodic layer thickness as a function of solution pH

The thickness of the anodic layer was determined by two methods:

- By coulometric determination of the thickness of the PbO_2 layer. This was achieved through cathodic linear voltammetric sweeps at 1 mV/s in solutions with various pH during which the PbO_2 layer, formed on cycling between 0.7 and 1.6 V, was reduced to $PbSO_4$. From the area of peak C_1 , we calculated the quantity of electricity, and from it the thickness of the PbO_2 layer formed. It was assumed that the PbO_2 phase was a film with a density of 9.3 g/cm^3 . The PbO_2 layer thickness calculated as a function of solution pH is shown in Fig. 5 for electrodes cycled 1 and 16 h. The anodic layer is thicker than the PbO_2 layer because it comprises tetragonal- PbO and PbO_n ($1 < n < 2$) phases which are formed by the oxidation of Pb in H_2SO_4 solution [8].
- From XRD data, i.e. judging by the absorption of X-ray radiation by the anodic layer. The changes in intensity of the characteristic diffraction line for Pb ($d = 0.286 \text{ nm}$) were determined. The estimation of the anodic layer thickness in this case is relative. The thickness of the layer cannot be determined in micrometers without plotting a standard curve. The thicker the anodic layer, the lower the intensity of the Pb diffraction line. Fig. 6 shows in arbitrary units the change in thickness of the anodic layer formed for 1 h of cycling in solutions with

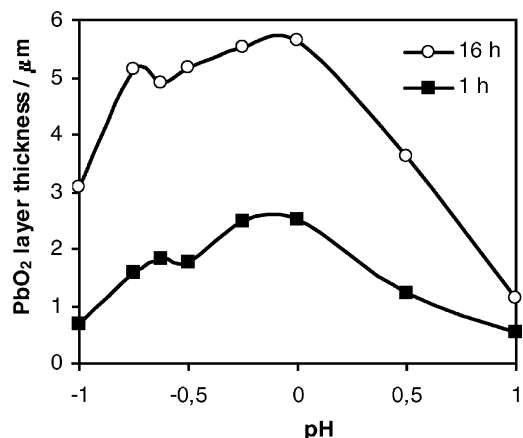


Fig. 5. PbO_2 layer thickness (coulometric data) as a function of pH.

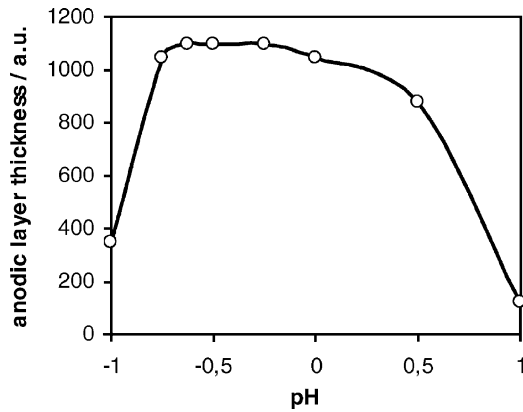


Fig. 6. Anodic layer thickness (XRD data) as a function of pH.

various pH. The anodic layer formed after 16 h of cycling is rather thick and no Pb diffraction lines can be seen in the diffractograms.

The curves illustrating the dependence of the thickness of the anodic layer (Fig. 6) and of the PbO_2 layer (Fig. 5) on pH of the solution have similar profiles. The thickest anodic layer is formed in the pH region between -0.75 and 0.50 (Fig. 6). According to the coulometric data the thickest PbO_2 layer is formed in the pH region between -0.75 and 0 .

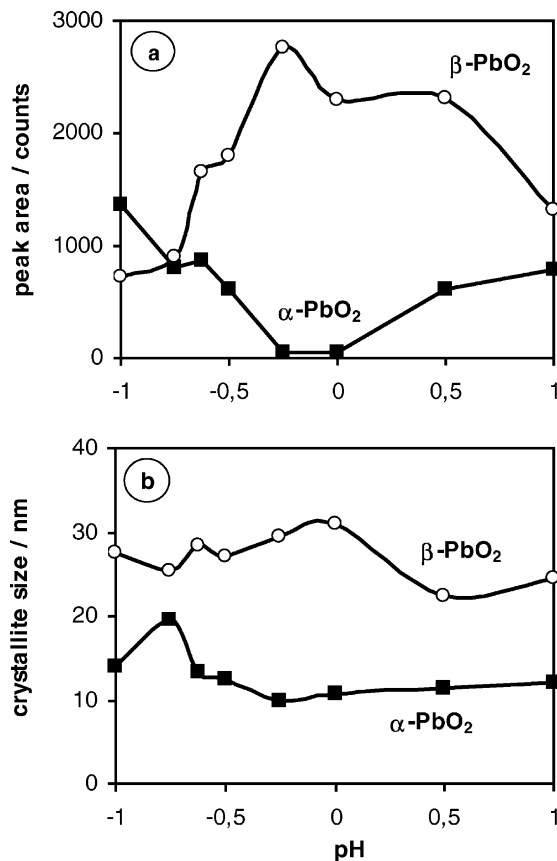


Fig. 7. (a) Amount of β - and α - PbO_2 crystals in the anodic layer; (b) average size of β - and α - PbO_2 crystals in the anodic layer.

3.1.3. Phase composition of the anodic layer as a function of solution pH

Fig. 7a presents the peak areas of the characteristic lines for α - and β - PbO_2 as a function of pH of the solution. Fig. 7b shows the size of α - and β - PbO_2 crystals versus solution pH. The figure illustrates the phase composition of the outer and part of the middle sub-layers which are involved in the cycling processes. No tetragonal- PbO is formed in these sub-layers.

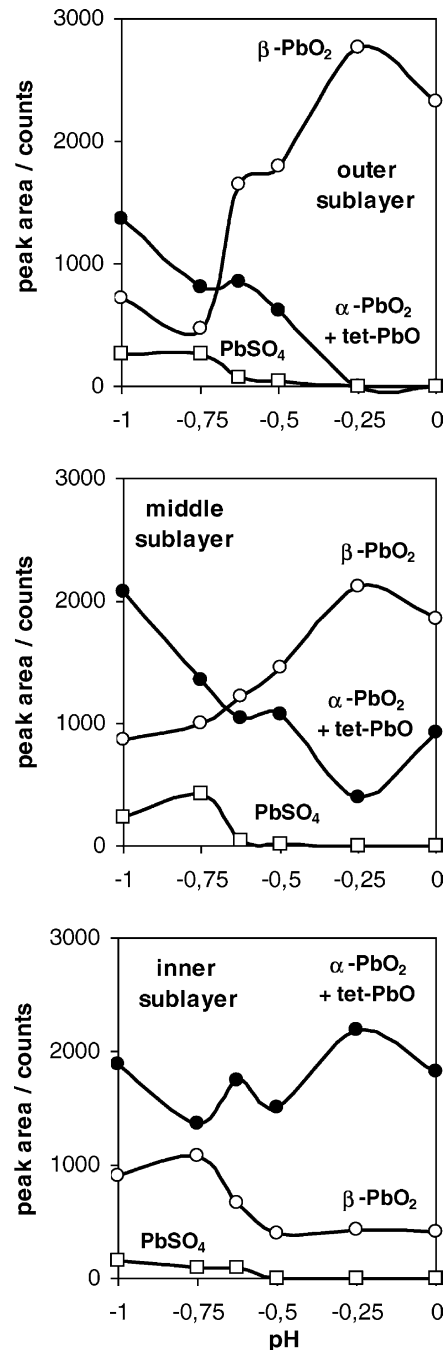


Fig. 8. Phase composition of the three sub-layers of the anodic layer formed during 16 h of cycling of a Pb electrode between 0.70 and 1.60 V at 100 mV/s as a function of pH of the H_2SO_4 solution.

The maximum amount of β -PbO₂ and the minimum amount of α -PbO₂ are formed in the pH region between -0.50 and 0.50 . The crystals of α -PbO₂ are about 10 nm in size in the pH region between -0.25 and 1.0 . In the pH region between -1.0 and -0.50 the size of the α -PbO₂ crystals features a maximum at pH -0.75 . In the pH region between -1.0 and 0 , the crystals of β -PbO₂ are sized between 25 and 30 nm. Their size decreases slightly when the anodic layer is formed in solutions with pH values above 0 . The largest size of β -PbO₂ crystals (32 nm) is observed in anodic layers formed on cycling in a H₂SO₄ solution with pH 0 .

3.1.4. Changes in phase composition in the depth of the anodic layer

During cycling of the Pb/PbO₂/PbSO₄ electrode only the outer part of the anodic layer is involved in the reactions of PbO₂ reduction to PbSO₄ and PbSO₄ oxidation to PbO₂. Hence, the phase composition of the outer sub-layer will differ from those of the middle and inner sub-layers, which are determined by the reactions of lead oxidation. In order to distinguish between these sub-layers, we will call the sub-layer, which is involved in the cycling processes, “secondary” (or Planté) layer, and the one whose phase composition is determined by the processes of Pb oxidation, “primary” (or corrosion) layer.

Fig. 8 presents the dependence of the phase composition of the inner, middle and outer sub-layers on pH of the solution in the range between -1.0 and 0 .

The phase composition of the outer sub-layer, formed in the pH region between -1.0 and -0.75 , comprises α - and β -PbO₂, and PbSO₄, the amount of α -PbO₂ being greater than that of β -PbO₂. Though the voltammetric sweep was interrupted (before taking out the electrode from the electrolyte) at

1.60 V (i.e. quite deep into the PbO₂ potential region), some PbSO₄ crystals remained unoxidised. This outer sub-layer contains more α -PbO₂ than β -PbO₂. Such a phase composition of the anodic layer is rather “strange”. When formed in solutions with pH > -0.25 , the phase composition of the secondary sub-layer becomes “normal”. β -PbO₂ is the dominating phase while PbSO₄ almost disappears. The amount of α -PbO₂ decreases and it also disappears when the solution is with pH > -0.25 . This behaviour of the phase composition of the secondary sub-layer in the strong acidic region should be attributed to the low solubility of PbSO₄ in these solutions.

The SEM micrographs in Fig. 9 show the microstructure of the anodic layer formed during cycling in a solution with pH -0.75 . As is evident from the micrographs, PbO₂ is formed within the crystal matrix of the PbSO₄ covering its surface. This is due to the low solubility of the PbSO₄ crystals in a strongly acidic electrolyte.

Eq. (3) shows that the rate of PbSO₄ oxidation to PbO₂ depends on $C_{\text{Pb}^{2+}}$ in the H₂SO₄ solution. The latter is determined by the solubility of PbSO₄. The rate of the electrochemical oxidation of Pb²⁺ to Pb⁴⁺ ions determines the concentration of Pb⁴⁺ ions in the solution. Since these ions are unstable in H₂O, they are hydrated to Pb(OH)₄, the latter being dehydrated partially to PbO(OH)₂ or completely to PbO₂ [9,10]. These processes are related to the formation of particles, agglomerates and aggregates of PbO₂ [11]. Thus, the structure of the secondary sub-layer depends on the pH of the H₂SO₄ solution. Since at pH -0.75 the solubility of PbSO₄ is low, the electrochemical reaction will proceed at the highest rate in the contact zones of the PbSO₄ crystal with the PbO₂ surface. The diffusion path of Pb²⁺ ions there is the shortest and their flux is the biggest [10]. The PbO₂ phase formed grows on the surface of the PbSO₄ crystals, which is observed in Fig. 9.

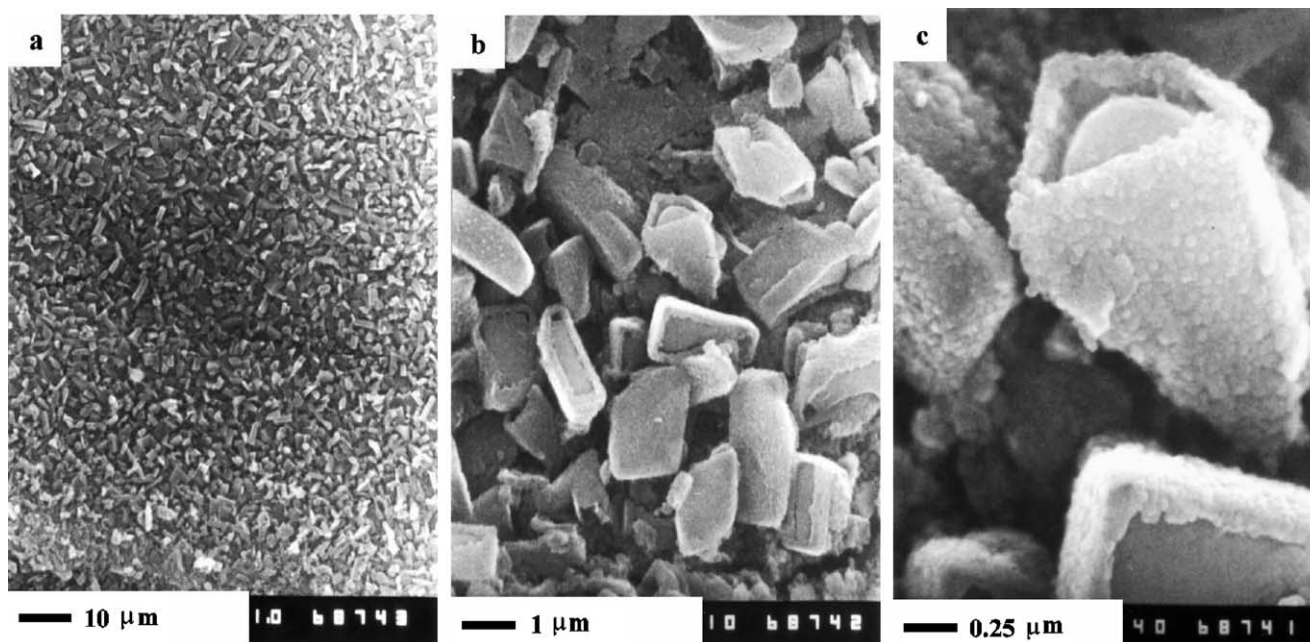


Fig. 9. SEM micrographs of the secondary structure of the anodic layer formed during cycling of a Pb electrode in a solution with pH -0.75 .

Fig. 8 shows that in the middle sub-layer of the anodic layer the amount of α -PbO₂ increases with pH increase throughout the whole pH range of the investigation, while the amount of β -PbO₂ decreases substantially compared to that in the secondary sub-layer. In the inner sub-layer α -PbO₂ and tetragonal-PbO are the dominating phases. β -PbO₂ is formed in small quantities, and PbSO₄ as traces only, in solutions with pH ranging between -1.0 and -0.50 . These experimental results support the mechanism, according to which Pb is oxidized by oxygen diffusing through the anodic layer: $\text{Pb} \rightarrow \text{tetragonal-PbO} \rightarrow \text{PbO}_n \rightarrow \alpha\text{-PbO}_2$ ($1 < n < 2$) [12–14], and β -PbO₂ is formed by the oxidation of PbSO₄ [15].

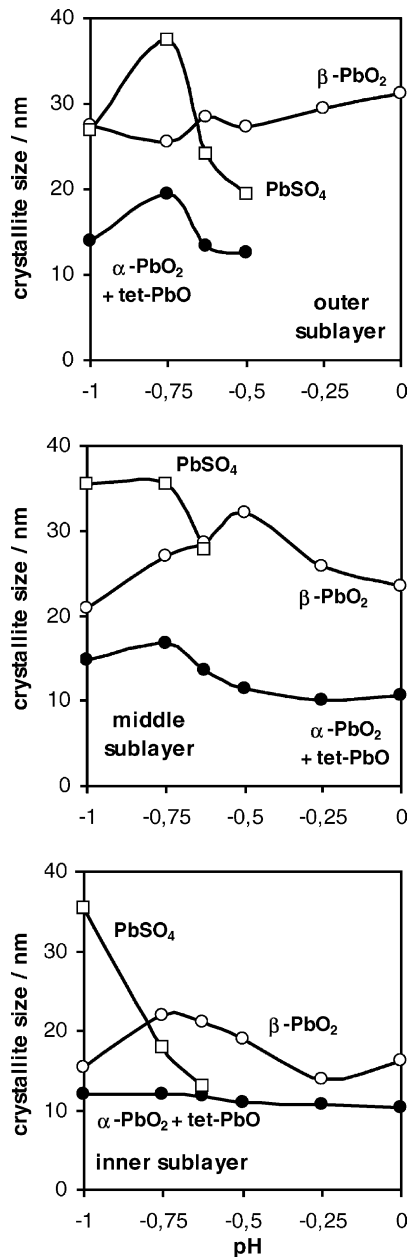


Fig. 10. Average crystal sizes of α -PbO₂, β -PbO₂ and PbSO₄ vs. solution pH for the inner, middle and outer sub-layers of the anodic layer.

Table 3

Crystallite size of the phases in the three sub-layers formed during 16 h of electrode cycling between 1.6 and 0.7 V at 100 mV/s

	Outer sub-layer (nm)	Middle sub-layer (nm)	Inner sub-layer (nm)
β -PbO ₂	25–32	20–32	15–23
α -PbO ₂ /tetragonal-PbO	12–20	10–16	12–13
PbSO ₄	20–38	35–25	35–18

Fig. 10 presents the pH dependencies of the crystallite size (calculated from XRD data) for all four phases formed during cycling of lead electrode in solutions of various pH. Table 3 gives the crystallite size data for the phases in the three sub-layers. The general trend observed is: the closer to the metal surface, the smaller the size of the crystallites. α -PbO₂ or tetragonal-PbO have the smallest crystallites and PbSO₄ the largest ones which decrease in size in the inner layer with pH increase.

3.1.5. Shedding of particles from the anodic layer

It has been established that part of the anodic layer sheds on cycling of the electrodes for 16 h. The deposit that had fallen to the bottom of the cell was collected, dried and weighed. Fig. 11 presents the amount of shed anodic layer versus pH of the solution. Shedding was estimated in percent of the maximum shed amount (at pH -0.25).

The biggest quantity of shed anodic layer is observed for electrodes cycled in the pH region between -0.50 and 0 . Fig. 12 presents photographs of the micro and macrostructures of a secondary anodic layer formed on cycling in a solution with pH -0.25 for 1 and 16 h. It can be seen that the secondary layer is built mainly of prismatic particles in the case of 1 h of cycling, and of round shaped particles in the case of 16 h cycling. Obviously, serious changes occur in the morphology of PbO₂ particles during cycling. Secondly, the PbO₂ particles in the outer layer are well separated as building elements of the anodic layer and not all of them are tightly connected to the primary anodic layer. When the electrode potential is higher than 1.45 V, oxygen is evolved

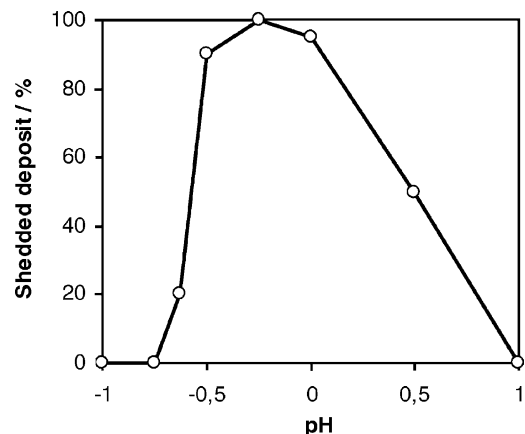


Fig. 11. Anodic layer shedding as a function of pH.

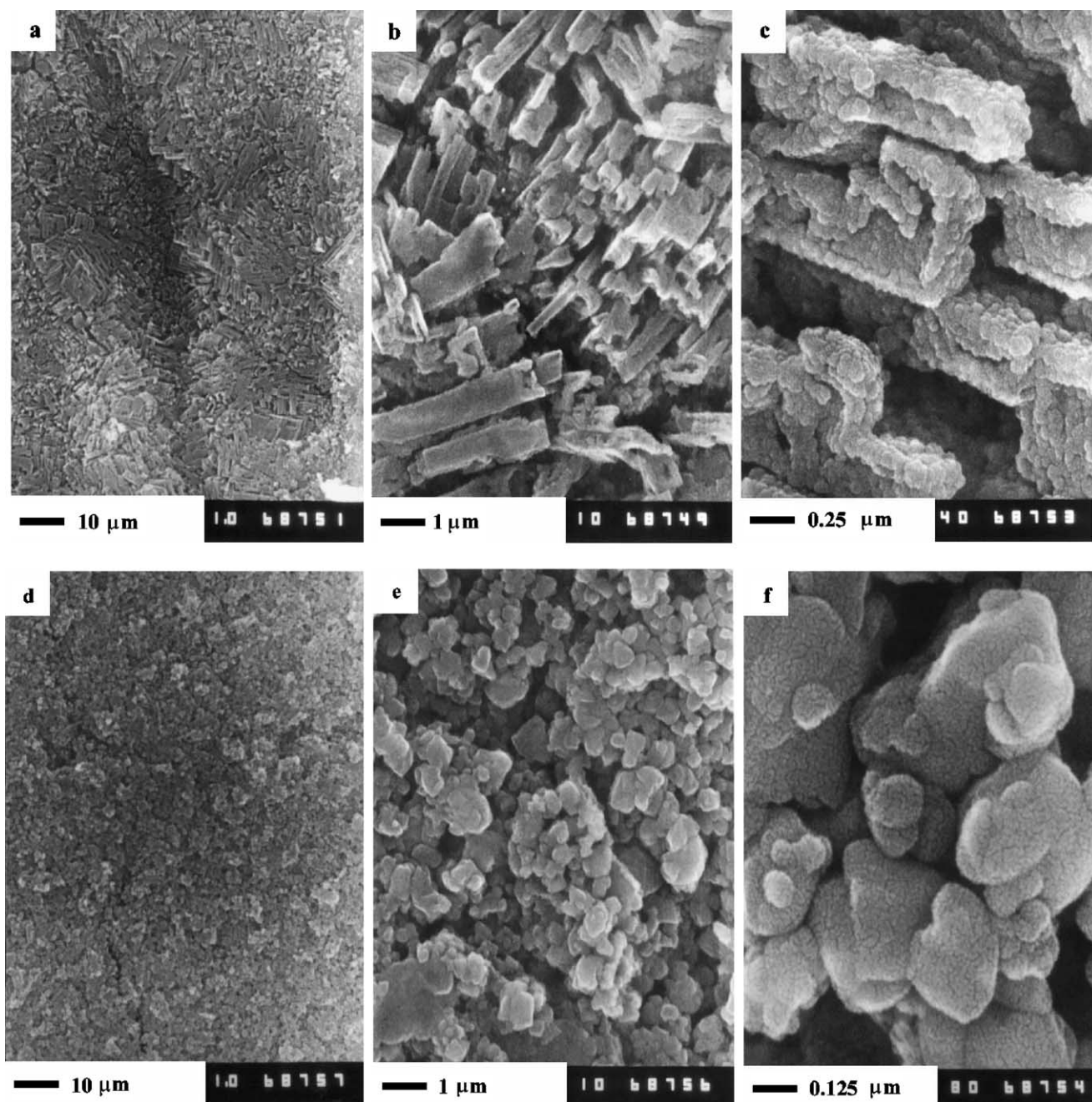


Fig. 12. Macro and microstructures of the secondary anodic layer formed during cycling of a lead electrode in H_2SO_4 solution with pH -0.25 for 1 h (Fig. 12a-c) and for 16 h (Fig. 12d-f). Part of the PbO_2 aggregates shed off the anodic layer.

in the anodic layer and its gas bubbles can detach some of the loosely connected PbO_2 particles from the secondary layer, which will then be shed.

3.2. Influence of pH of the solution on the crystal structure and phase composition of the PbO_2 active mass of the lead-acid battery

As established earlier, PbO_2 particles comprise crystal and hydrated (gel) amorphous zones [16]. The crystal zones contain a certain number of crystallites of α - or β - PbO_2 . The

crystal zones are in dynamic equilibrium with the hydrated ones. The latter in turn are in equilibrium with the ions in the solution. How strong is the influence of the concentration of the H_2SO_4 solution on the above equilibria, and hence on the phase composition of the PAM? In order to answer this question, we immersed equal portions of PAM from charged positive plates of a lead-acid battery into H_2SO_4 solutions of various pH and after 2 h of stay in the solution, the phase composition of the wet PAM was determined.

Fig. 13 shows the peak areas of the characteristic diffraction lines for β - PbO_2 , α - PbO_2 and PbSO_4 as a function of pH

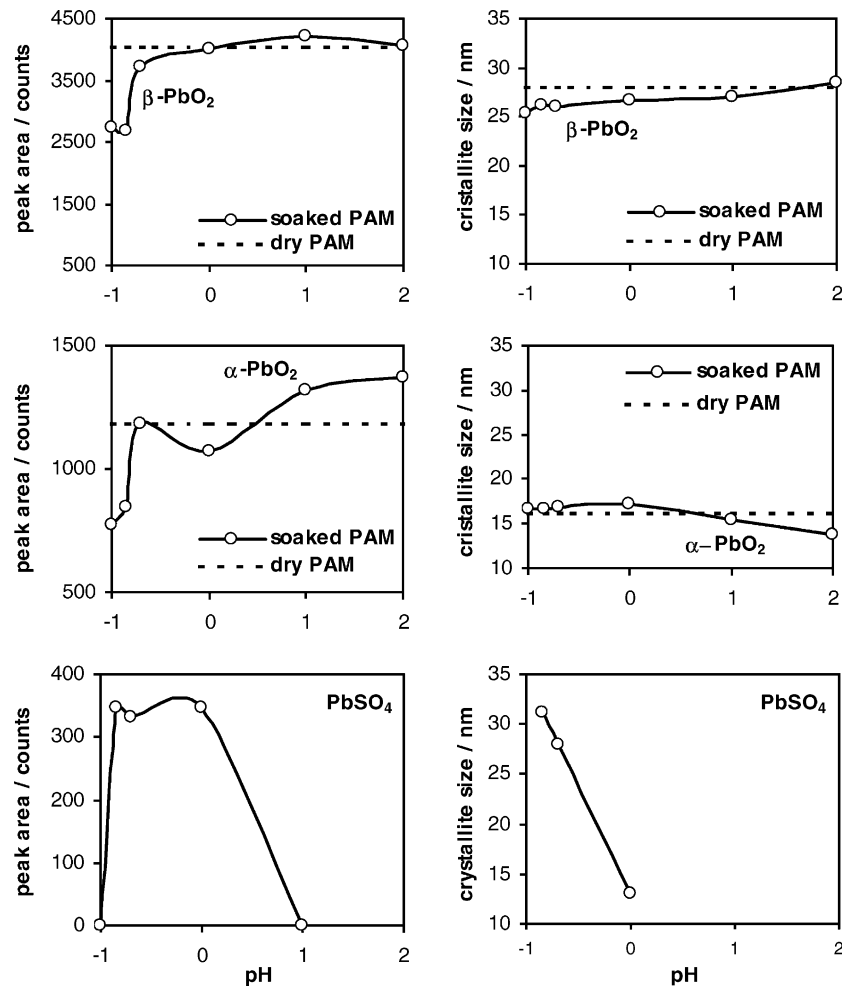


Fig. 13. XRD peak areas and average crystal size of α -PbO₂, β -PbO₂ and PbSO₄ in the PAM as a function of solution pH after 2-h stay in H₂SO₄ solution.

of the H₂SO₄ solution. The charged PAM contains no tetragonal-PbO as it is immediately oxidized at the potentials of positive plate cycling. The crystal sizes of the three phases are also presented in the figure. The peak intensities and the crystal sizes for the dry PAM samples before being immersed in the solutions of various pH are shown by dashed lines.

In the pH region between -1.0 and 0 , the quantities of the α - and β -PbO₂ phases decrease compared to those in the dry PAM. At higher pH values, the amount of β -PbO₂ crystals is a bit higher than in the dry PAM, and the content of α -PbO₂ crystals is higher by 14%. In the pH region from 0 to -1.0 , where the amounts of the α - and β -PbO₂ phases decrease, PbSO₄ crystals are formed. The peak for PbSO₄, however, is lower than the relative decrease of the peak areas for α - and β -PbO₂, which indicates that only part of the α - and β -PbO₂ crystals are involved in the formation of PbSO₄. Another part of these phases is hydrated and thus become amorphous at pH < 0 . The average size of β -PbO₂ crystallites decreases slightly in highly acidic solutions (pH < 1.0), while that of α -PbO₂ crystallites remains constant at pH < 0.50 . The phenomena that proceed in PAM on changing the solution pH

support the idea that the PAM is a dynamic system whose particles are in equilibrium with the ions in the solution [9,16].

Two hypotheses can be assumed for the formation of PbSO₄ crystals:

- Self-discharge processes take place in the PAM as a result of which oxygen is evolved. These processes are probably not so fast, as for the 2-h stay of PAM in the H₂SO₄ solution substantial quantities of PbSO₄ crystals are formed which are readily registered by XRD.
- PbO₂ has a nonstoichiometric composition, PbO_{2- δ} , i.e. it contains a certain quantity of Pb²⁺ ions. They will be present in both hydrated and crystalline zones of the particles. On the other hand, it has been shown that SO₄²⁻ and HSO₄⁻ ions penetrate into the hydrated zones and a certain equilibrium is established between their content in the gel zones and in the solution [17]. They can react with Pb²⁺ ions and PbSO₄ molecules formed in the hydrated zones. When PbSO₄ molecules dissolve in the solution they form a crystalline phase.

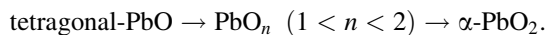
The results obtained from the present investigation of the dependence of the phase composition of the PAM on the pH

of the solution indicate that the PAM is in dynamic interaction with the solution and each change in pH of the solution brings about changes in both the phase composition of PAM particles and the size of α - and β -PbO₂ crystallites.

4. Conclusions

1. The concentration of the H₂SO₄ solution influences the phase composition and the structure of the anodic layer formed during cycling of Pb electrodes in solutions with various pH in the following ways:

- (a) It has been established that the rate of reduction of PbO₂ in the outer sub-layer depends on the pH of the H₂SO₄ solution. If the pH is within the range between -1.0 and -0.50 , the reduction rate is high. In this pH range the battery will have high power (if limited by the positive plates). If the discharge proceeds in solutions with pH value between -0.50 and 0 , the rate of reduction of PbO₂ to PbSO₄ is limited to a lower value and the battery will have a lower power output.
- (b) The rate of oxidation of PbSO₄ to PbO₂ depends on the pH of the H₂SO₄ solution. This dependence is determined by the dependence of the solubility of PbSO₄ on the concentration of H₂SO₄ solutions. In solutions with pH lower than -0.50 (strongly concentrated solutions), the solubility of PbSO₄ is low and the oxidation process PbSO₄ \rightarrow PbO₂ is slowed down. In the present investigation the time period during which the charge proceeds is short, part of the PbSO₄ in the outer sub-layer remains unoxidized. When the oxidation of PbSO₄ to PbO₂ proceeds in solutions with pH above -0.50 , the solubility of PbSO₄ is high and the whole amount of PbSO₄ is oxidized to PbO₂. After discharge of the battery, the H₂SO₄ concentration is low and thus at the beginning of the next charge cycle, the charge efficiency will be high. During charge, the concentration of H₂SO₄ increases and the solubility of PbSO₄ is reduced which causes the charge efficiency to decrease. For a limited charge time some unoxidized PbSO₄ remains in the charged PAM.
- (c) The phase composition of the anodic layer varies with the distance from the metal surface. The closer to the metal surface, the higher the content of α -PbO₂ and tetragonal-PbO in this layer, and the lower the content of β -PbO₂. The influence of pH on the quantity of α -PbO₂ and tetragonal-PbO is weaker in the internal layers close to the metal. Besides, the closer to the metal surface, the smaller the average size of the crystals (which approach the nanoscale). These experimental findings support the proposed mechanism according to which lead is oxidized by intercalation of oxygen into the anodic layer and the following solid-state reactions proceed: Pb \rightarrow



β -PbO₂ is formed as a result of PbSO₄ oxidation.

2. The concentration of H₂SO₄ exerts a strong influence on the phase composition and the structure of the PAM as follows:
 - (a) When the PAM is immersed in solutions with pH between -1.0 and 0 , the quantity of the crystal zones of α - and β -PbO₂ decreases. This decrease is due to the shift of the crystal zones/hydrated zones equilibrium towards the hydrated zones. In this process, the average size of β -PbO₂ crystals decreases, while that of α -PbO₂ remains unchanged.
 - (b) The ions in the solution exert an influence on both equilibria: hydrated zones/solution and crystal zones/hydrated zones in the PbO₂ particles and agglomerates. A certain amount of SO₄²⁻ ions from the solution penetrate into the gel zones and react with Pb²⁺ ions from the nonstoichiometric part of the PAM (PbO_{2- δ}). PbSO₄ molecules are formed. They can leave the hydrated zones of PbO₂ particles and form PbSO₄ crystals in the porous PAM. Such a process takes place in the pH region between -0.75 and 0 . In highly dilute solutions the concentration of H₂SO₄ is not sufficient for these processes to proceed, while at pH -1.0 the concentration of H₂SO₄ is so high that large amounts of PbSO₄ are formed probably in the hydrated layer without forming a crystal lattice. When pH increases from -0.75 to 0 the size of the PbSO₄ crystals decreases from 30 to 10 nm.

The results of the present investigation indicate that both the corrosion layer/PAM interface and the PAM are dynamic systems, which are in interaction with the ions of the solution and their phase composition and structure depend strongly on the concentration of H₂SO₄ and on the polarization conditions.

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