Mechanism of formation of anodic excursion peaks on lead electrode in sulfuric acid

Bo Zhang [a,b], Juhua Zhong [b,*], Bo Zhang [b], Zhenmin Cheng [a]

[a] *State Key Laboratory of Chemical Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, PR China*
[b] *Department of Physics, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, PR China*
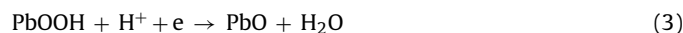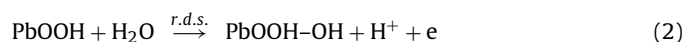
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ABSTRACT

Potential step and linear sweep voltammetry are proposed in combination for the anodic excursion peaks (AEPs) measurement of lead in sulfuric acid during cathodic scanning in the positive potential range. The overall procedure of measurement is composed of three steps. The first one is to polarize the lead electrode with negative potential, which is necessary for passivated $PbSO_4(O)$ formation. Then, the polarization potential is stepped to positive to make sure that pure Pb could be oxidized to produce PbO_n intermediate. Finally, a low-rate cathodic linear sweep voltammetry measurement is conducted in a small potential range. Four AEPs have been observed without reduction of PbO_2 to $PbSO_4$, which is in confliction with the conventional understanding that AEPs would appear accompanying with a large reduction peak for PbO_2 discharge. A new mechanism is therefore proposed that AEPs corresponds to the oxidation of PbO_n intermediate in the cathodic scanning, so AEPs can be used to indicate the difficulty for the oxidation of Pb to PbO_2, and could be applied to characterize the corrosion resistance of lead alloy grid in the positive plate of a lead-acid battery.

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1. Introduction

When pure lead electrode immersed in sulfuric acid solution is subjected to anodic polarization in the positive potential range, the surface of lead electrode will be corroded to form Pb/tet-$PbO/PbSO_4/PbO_2$ multilayer compounds. Such an electrochemical corrosion process observed in the lead current collector of positive plate has commonly caused the failure of lead-acid batteries in many applications. Although extensive studies on the corrosion films on lead electrodes in sulfuric acid solution have been reported, the mechanism of some phenomena emerged during the process of the formation of multilayer film are still not clarified. The authors of this paper believe that the degree of corrosion of lead electrodes might be detected or reflected by "anodic excursion peaks" (AEPs), which appears in the main reduction process [1–8].

It has been suggested by Sunderland in the early 1970s that the AEPs was attributed to the oxidation of water to oxygen and protons by PbOOH species during the reduction of PbO_2 [1]:

$$PbO_2 + H^+ \rightarrow PbOOH \tag{1}$$

$$PbOOH + H_2O \xrightarrow{r.d.s.} PbOOH\text{-}OH + H^+ + e \tag{2}$$

$$PbOOH + H^+ + e \rightarrow PbO + H_2O \tag{3}$$

This opinion was supported by Fletcher and Mattews [2], who carried out photoelectric experiments and found no photocurrent during the anodic reaction. Many others proposed that the occurrence of AEPs was due to the oxidation of metallic lead in the inner layer [3–6], since the reduction of PbO_2 to $PbSO_4$ would result in an increase in molar volume, which makes the sulfate layer broken, and causes the inner metallic lead exposed to the sulfuric acid solution, and inevitably leaves the oxidation of the inner lead which produces the anodic current during the cathodic scanning process. However, recently, Darowicki and Andrearczyk [7] investigated the changes of the impendence spectra and AFM images as a function of potential, and concluded that no breaking was observed when AEPs appeared.

In the investigation of AEPs, the commonly used method is cyclic voltammetry (CV) [1–6], or linear sweep voltammetry (LSV) [9]. Sharpe [10,11] investigated the process of reduction of α-PbO_2 and β-PbO_2 to $PbSO_4$ successfully and several AEPs were obtained by using potential step method and low-rate cathodic linear sweep voltammetry (LSV) in combine. However, they did not investigate the influence of negative polarization, and unfortunately, the several AEPs were considered as one anodic peak, which ignored the discovery of the exact mechanism of AEPs.

In the present work, some new attempts will be made to investigate this phenomenon by combining potential step method and

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* Corresponding author. Tel.: +86 21 6425 1493; fax: +86 21 6425 2018.
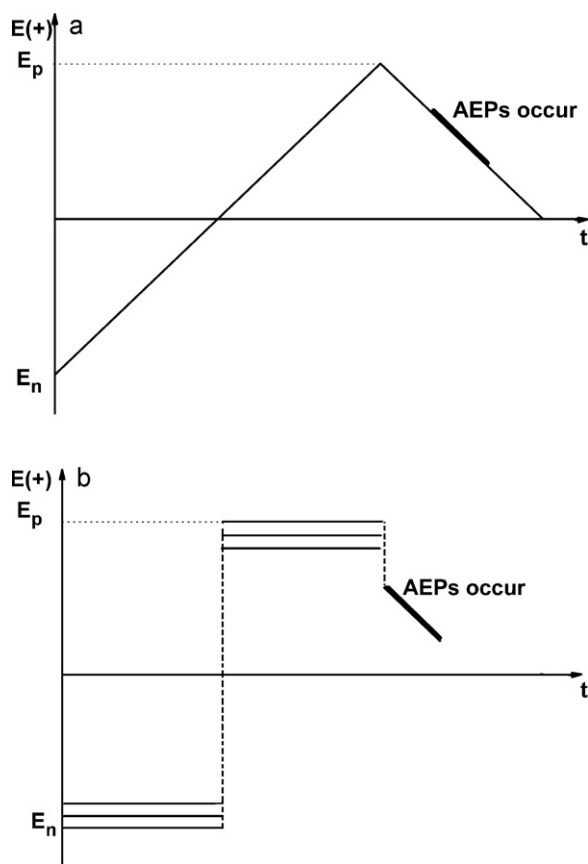*E-mail addresses:* jhzhong@ecust.edu.cn, phyzjh@126.com (J. Zhong).

Fig. 1. Potential waveforms of the chronovoltamperometrical experiments applied on the working electrode: (a) general cyclic-voltammetry (CV); (b) potential step combined with linear sweep voltammetry (LSV).

LSV to obtain the exact condition of the occurrence of AEPs, and then to propose a more exact mechanism.

2. Experimental and methods

2.1. Electrodes and experimental cell

The electrochemical investigation on lead was performed in a three electrode system in 4 M sulfuric acid solution using an electrochemical working station (CHI 650C). The reference electrode was a Hg/Hg$_2$SO$_4$/4 M H$_2$SO$_4$ electrode. All potentials in this work are presented vs. this reference electrode. A platinum foil was employed as the counter electrode. The working electrode was a pure lead rod (>99.994%) which has an apparent exposed area of about 0.6 cm^2, grinded successively with three grades of abrasive paper, rinsed with anhydrous ethanol (AR), and then washed with doubly distilled water. All experiments were conducted at ambient temperature (∼25 °C).

3. Methods

In order to confirm the condition of the occurrence of AEPs, linear sweep voltammetric measurements combined with potential step polarization were conducted. The comparison of the potential waveform of this method with that of general cyclic voltammetry (CV) method is given in Fig. 1. It is shown that the effects of negative and positive potential on formation of AEPs could be effectively studied by the combined technique. The lead electrode was firstly designed to be prepolarized under a specified negative potential, and stepped to a specified positive potential. After prepolarization,
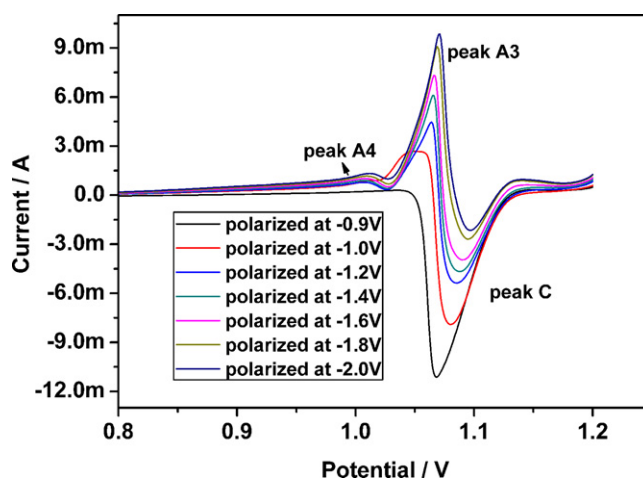

Fig. 2. Voltammograms obtained at 1.2–0.8 V for samples prepolarized at different negative polarization potentials (−0.9 V, −1.0 V, −1.2 V, −1.4 V, −1.6 V and −2.0 V) for 100 s and at the same positive polarization potential of 2 V for 10 s.

a low-rate cathodic linear sweep voltammetric (LSV) measurement was conducted in a potential range from 1.2 V to 0.8 V with the scanning rate being kept at 5 mV/s. The prepolarization of the working electrode was conducted in three ways: (1) changing the negative polarization potential while keeping the positive polarization potential constant, (2) changing the positive polarization potential while keeping the negative polarization potential constant, (3) keeping the negative and positive polarization potentials both constant and varying the positive polarization time.

4. Results

4.1. Investigation of polarization potential on AEPs

4.1.1. Dependence of AEPs on negative polarization potential

In the first way, prepolarization of the lead electrode samples was first conducted at 2 V for 10 s to transform the surface into oxidation state. After the samples had been held at different negative potentials for 100 s, it was stepped to 2 V for 10 s for positive polarization. After prepolarization, a low-rate cathodic linear sweep voltammetric (LSV) measurement was followed immediately from 1.2 V to 0.8 V, automatically controlled by the CHI software. Since PbO could be reduced to Pb from −0.75 V to −0.94 V, while PbSO$_4$ could be reduced to Pb under the potentials lower than −0.95 V [12,13]. So, in order to demonstrate the effects of the reduction of PbO and PbSO$_4$ on AEPs, negative polarization potentials were respectively set at −0.9 V, −1.0 V, −1.2 V, −1.4 V, −1.6 V, −1.8 V and −2.0 V, corresponding to different samples. Fig. 2 shows the voltammograms of the different samples prepolarized under the diverse negative potentials. The result showed that as the negative potential was decreased, the current of AEPs increased, but the current of peak C corresponding to the reduction of PbO$_2$ to PbSO$_4$ decreased, which means that as the negative polarization potential was decreased, the quantity of PbO$_2$ formed during successive positive polarization became small and the anodic reactions corresponding to AEPs' formation became intensive. It was also observed that AEPs appeared only when the negative polarization potential was lower than −0.9 V. That is to say, AEPs occurs only when PbSO$_4$ is reduced, and the reduction of PbO has no effect on the occurrence of AEPs. In our previous study [14], we proposed two types of PbSO$_4$, denoted as PbSO$_4$(O) and PbSO$_4$(R), which are suggested to be formed according to:

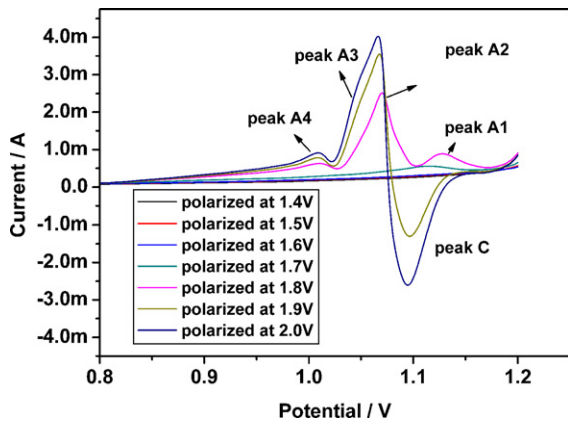$$Pb + HSO_4^- \rightarrow PbSO_4(O) + H^+ + 2e \qquad (4)$$
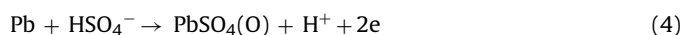
Fig. 3. Voltammograms obtained at 1.2–0.8 V for samples prepolarized at −2 V for 100 s and at different potentials (1.4 V, 1.5 V, 1.6 V, 1.7 V, 1.8 V, 1.9 V and 2.0 V) for 10 s.

It was observed that only when the positive polarization potential is higher than 1.6 V, AEPs could be formed. When the positive polarization potential was 1.7 V or 1.8 V, AEPs was observed but there was no cathodic peak for PbO_2 to $PbSO_4$, which means the reduction of PbO_2 may have no effect on AEPs. When the positive polarization potential was higher than 1.8 V, the currents of AEPs and peak C both increased as the positive polarization potential was increased. From these results, it is conceived that positive polarization would have no effect on AEPs' formation unless the polarization potential is higher than 1.6 V, which means AEPs' formation depends on whether Pb(II) could be oxidized into high-valent lead compounds or not.

$$PbO_2 + 3H^+ + HSO_4^- + 2e \rightarrow PbSO_4(R) + 2H_2O \qquad (5)$$

From Eqs. (4) to (5), two forms of $PbSO_4$ are generated with much different properties. The $PbSO_4(O)$ from the oxidation of Pb has a compact structure and low reaction activity, and $PbSO_4(R)$ from the reduction of PbO_2 has a loose structure and high reaction activity. It was also found that $PbSO_4(O)$ can be formed under positive polarization only when the electrode was prepolarized under the potentials lower than −1 V. Similarly, the formation of AEPs and $PbSO_4(O)$ need consistent negative polarizing condition, which means that the formation of AEPs may be related to the $PbSO_4(O)$.

4.1.2. Dependence of AEPs on the positive polarization potential

In order to investigate the influence of positive polarization on AEPs' formation, the second way of prepolarization of the lead electrode samples were first held at −2 V for 100 s, and then stepped to 1.4 V, 1.5 V, 1.6 V, 1.7 V, 1.8 V, 1.9 V and 2.0 V subsequently each for 10 s. Then the samples were measured through the low-rate cathodic linear sweep voltammetry (LSV) from 1.2 V to 0.8 V, and the results are shown in Fig. 3.

4.1.3. Development of AEPs with positive polarization time

Considering that the degree of oxidation of $PbSO_4$ to PbO_2 was controlled by positive polarization time, the lead electrodes were designed to be polarized under a constant positive potential for different times. In this regard, for the third way of prepolarization, the samples were first polarized at −2 V for 60 s, and were then stepped to 2 V for 1 s to 250 s, corresponding to different samples. Parts of the results of the LSV measurement are given in Fig. 4. In Fig. 4(a), it was observed that four AEPs (A1, A2, A3 and A4) were generated when the positive polarization time was 2 s. However, when the positive polarization time was extended to 4 s, peak A1 disappeared and peak C appeared, which means that PbO_2 could be formed in this polarization situation. It was also shown that the currents of peaks A3, A4 and C increased as the positive polarization time was prolonged. Specifically, peak A2 increased to its highest value when the positive polarization time was 12 s and disappeared at 20 s. In Fig. 4(b), peak A3 reached its maximum at 40 s and disappeared when the positive polarization time was longer than 80 s,
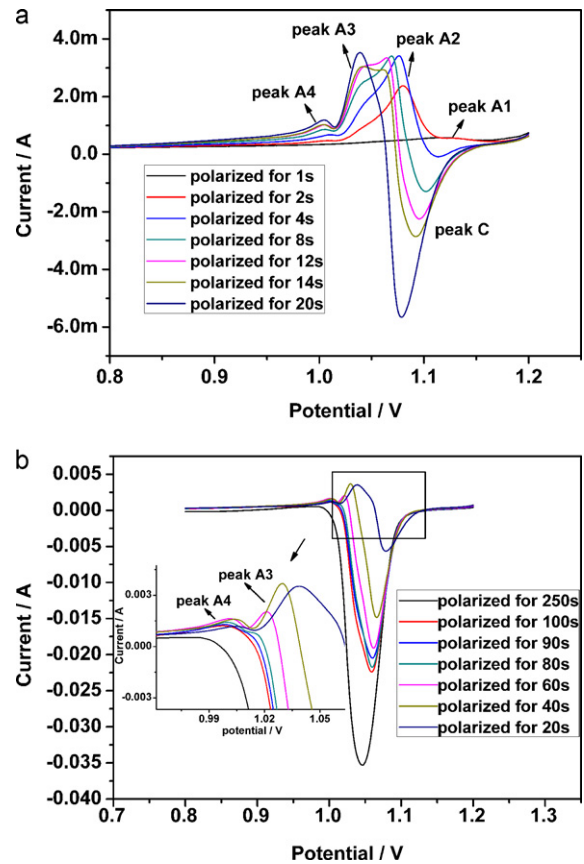

Fig. 4. (a) Voltammograms obtained at 1.2–0.8 V for samples prepolarized at −2 V for 60 s and at 2 V for 1 s, 2 s, 4 s, 8 s, 12 s, 14 s and 20 s. (b) Voltammograms obtained at 1.2–0.8 V for samples prepolarized at −2 V for 60 s and at 2 V for 20 s, 40 s, 60 s, 80 s, 90 s, 100 s and 250 s.
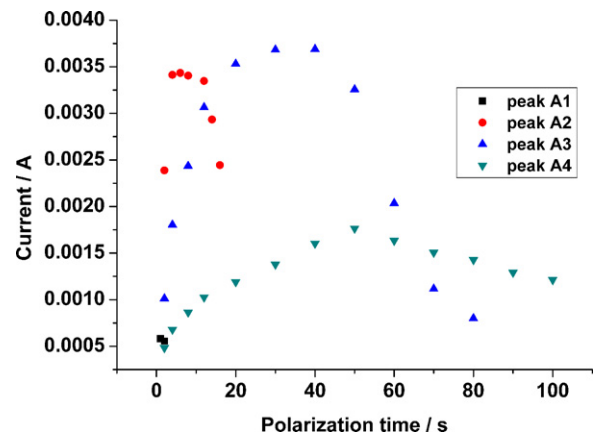

Fig. 5. Peak currents of four anodic excursion peaks as a function of positive polarization time.

and peak A4 nearly disappeared at 250 s. The peak currents of the four AEPs varying with the polarization time are given in Fig. 5. It shows that as the polarization time was increased, the four peaks reaching their maximum were in the order of A1, A2, A3 and A4, and so sequence was for their disappearance. It can be concluded that the formation of AEPs needs positive polarization, but polarization with a long time would weaken AEPs, and also the four different peaks may be relative with the degree of the oxidation of Pb(II) to Pb(IV).

5. Discussion

Based on our experimental results and the results in the literature [5,7,9], the occurrence of AEPs depends on both the negative and positive polarizations. At least three possible reasons are proposed for the reason why two polarizations are needed for the formation of the four AEPs. The first one is that during the cathodic scanning, PbO_2 is reduced and makes its structure expanded owing to the increase in molar volume, so the inner metallic lead formed during negative polarization will be exposed in sulfuric acid solution, which would be oxidized to PbO_n ($1 < n < 2$) during the cathodic scanning and four AEPs are observed. However, this explanation can not account for why AEPs did not appear when PbO was reduced to Pb in the negative polarization (see Fig. 2). Neither can it explain why AEPs was observed without the reduction of PbO_2 to $PbSO_4$ (see Fig. 3 or Fig. 4(a)).

The second explanation is that the occurrence of AEPs is due to the oxidation of water by PbOOH, resulting in the increase of the value of "n" in the PbO_n compounds, as shown in Eq. (2). So the effect of negative polarization is to reduce the value of "n" in the oxide layer, which will benefit AEPs' formation, while the effect of positive polarization is to form PbO_2 and to be reduced to PbOOH. However, this hypothesis does not justify why four AEPs occurred without the reduction of PbO_2 and why the reduction of PbO to Pb (the value of "n" also decreased) has no effect on AEPs' formation. Also, both the two hypotheses can not explain why the peak currents of AEPs showed a trend from rising to falling with the increase of the positive polarization time.

In explaining the corrosion of Pb electrode in H_2SO_4, Ruetschi [15] suggested that the Pb/PbO-α-$PbO_2/PbSO_4$ multilayer, where PbO-α-PbO_2 equivalents to PbO_n, was formed on the surface of lead electrode when polarized at $0.5\sim1.0$ V in 4.2 M H_2SO_4 for 24 h. While $Pb/PbO_n/PbSO_4$ was transformed to Pb/α-PbO_2/β-PbO_2 when polarized at the potential above 1.2 V for 24 h, where α-PbO_2 is formed on the outer layer of PbO_n [16], and the oxidation of $PbSO_4$ to β-PbO_2 occurs on the surface of α-PbO_2 [17]. Therefore, if Pb electrode was polarized at 2 V in a short time, the corrosion layer could be composed of a complicated $Pb/PbO_n/\alpha$-PbO_2/β-$PbO_2/PbSO_4$ multilayer structure, since the corrosion of Pb in H_2SO_4 solution is a diffusion-control process, which is mainly controlled by the transfer of ions through the outer $PbSO_4$ layer. On the basis of the experimental conclusion that AEPs' formation needs passivated $PbSO_4(O)$ layer and positive polarization with a short time, AEPs is suggested to be related to the multilayer structure in the corrosion layer.

So, for the third explanation, we assume that when lead electrode is polarized at 2 V in a short time, the passivated $PbSO_4(O)$ layer inhibits the oxidation of Pb(II) to Pb(IV), resulting in the incomplete oxidation product PbO_n, which will be oxidized to α-PbO_2 to form AEPs during the cathodic scanning. The proposed reaction mold occurred on the surface of lead electrode under various polarization conditions is given in Fig. 6. According to Pavlov's research in series [16,18–20], in the Pb/tet-$PbO/PbSO_4$ structure, tet-PbO is incompletely oxidized via solid-phase reaction to non-stoiometric PbO_n at high positive potential, which is determined by the transportation of OH^- species through the passivated $PbSO_4$ layer. This takes place via the electrochemical reaction

$$PbO + (2n-2)OH^- \xrightarrow{V_1} PbO_n + (n-1)H_2O + (2n-2)e^- \qquad (6)$$
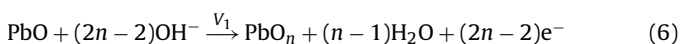
whose rate depends on the porosity of $PbSO_4$ layer and the electric field strength in $PbSO_4$ layer, which in return depends on the composition of multilayer structure. In order to analysis the electric field strength in $PbSO_4$ layer, let us for simplicity assume that the potential drops linearly across the oxide layer. The potential in the inner pure lead is marked by φ_e, and drops to φ_0 at the oxide/$PbSO_4(O)$
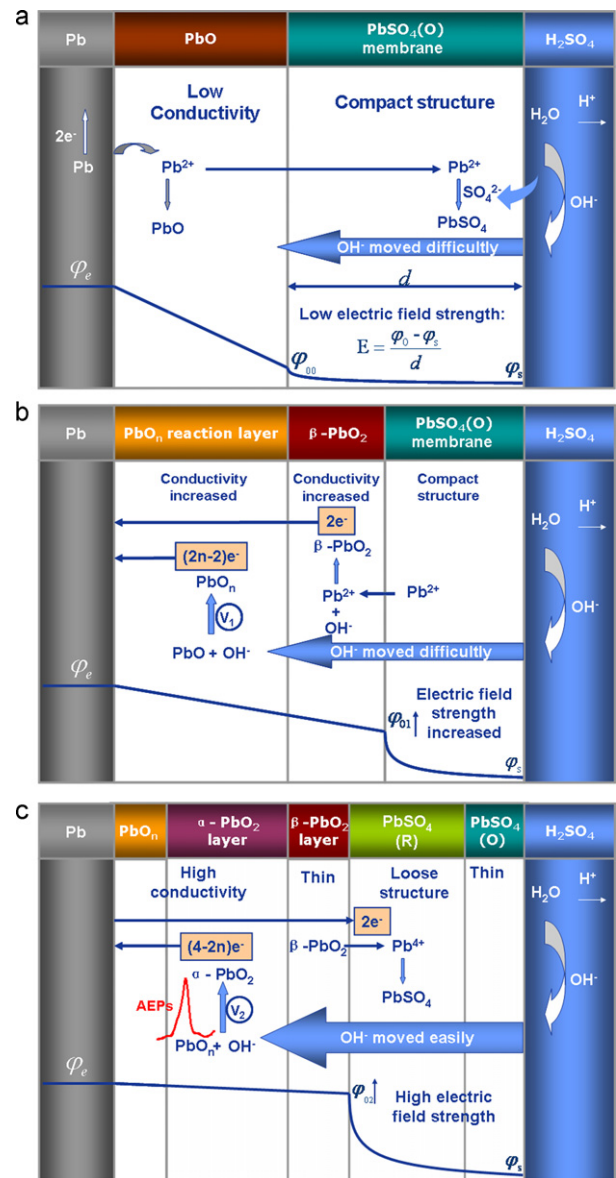

Fig. 6. The proposed scheme of the elementary reactions on the multilayer surface of the working electrode: on different conditions: (a) when the positive polarization potential was stepped to 2 V; (b) when polarized at 2 V for 20 s; (c) when the LSV measurements conducted from 1.2 V to 0.8 V.

interface, whose value depends on the oxide layer thickness and electric conductivity. Since $PbSO_4$ is dielectric, the potential drops sharply across $PbSO_4(O)$ layer to φ_s at the $PbSO_4(O)$/solution interface, which does not change with φ_0. The electric field strength in $PbSO_4$ layer could be represented by:

$$E = \frac{\varphi_0 - \varphi_s}{d} \qquad (7)$$

which determines the electro-migration rate of OH^- through $PbSO_4(O)$ layer, where d is the thickness of $PbSO_4(O)$ layer. When pure lead is polarized at 2 V, the Pb/tet-$PbO/PbSO_4(O)$ multilayer structure is formed immediately, and the low electric conductivity of PbO [16] causes that the oxide/$PbSO_4(O)$ interface potential φ_0 has a low value of φ_{00}, so the electric field strength E is low according to Eq. (7), which would result in the slow electro-migration rate of OH^- through $PbSO_4(O)$ layer. Also the ion-transfer resistance of $PbSO_4(O)$ is nearly six times than that of $PbSO_4(R)$ [14], which means that the compact $PbSO_4(O)$ layer is a barrier for OH^- transportation. Therefore, as the positive polarization time is extended,

Table 1
Development of AEPs corresponding to oxidation of PbOn to PbO2 vs. positive polarization time. ("↑" stands for increase of peak; "↓" stands for decrease of peak; "O" stands for disappearance of peak.).

Polarization time / s	PbO ⟹ PbO$_{1.37}$ ⟹ PbO$_2$ (Peak A1)	PbO$_{1.44}$ ⟹ PbO$_2$ (Peak A2)	PbO$_{1.55}$ ⟹ PbO$_2$ (Peak A3)	PbO$_{1.57}$ ⟹ PbO$_2$ (Peak A4)
0~1	↑	O	O	O
2~8	O	↑	O	↑
8~20	O	↓	↑	↑
20~40	O	O	↑	↑
40~50	O	O	↓	↑
50~80	O	O	↓	↑
80~250	O	O	O	↓
More than 250	O	O	O	O

tet-PbO is incompletely oxidized to nonstoiometric PbO$_n$ (see Eq. (6)), and part of PbSO$_4$(O) is further oxidized to β-PbO$_2$ on the surface of PbO$_n$ layer [16]. So the multilayer structure is transformed from Pb/tet-PbO/PbSO$_4$(O) to Pb/PbO$_n$/β-PbO$_2$/PbSO$_4$(O) as the polarization time is increased. Then, during the cathodic scanning from 1.2 V to 0.8 V, β-PbO$_2$ is reduced to PbSO$_4$(R) which has a loose structure, benefiting the transfer of OH$^-$. Also, tet-PbO has been transformed to PbO$_n$ with a higher electric conductivity [16], which increases the potential at the oxide/PbSO$_4$(O) interface from φ_{00} to φ_{01}, whose value is unknown, but is obviously more positive than φ_{00}. While in the pretreatment process, part of PbSO$_4$(O) was oxidized to β-PbO$_2$ but then was reduced to PbSO$_4$(R), the thickness of PbSO$_4$ layer d can be regarded as invariant in redox process. Therefore by evaluating the expression (7), the electric field strength E is increased by φ_{01}, which benefits the electromigration of OH$^-$ species, which means that the oxidation of PbO or PbO$_n$ would become easier than that proceeded during the positive polarization. Also, since the α-PbO$_2$ could be formed in this potential range [9], the oxidation of PbO$_n$ to α-PbO$_2$ goes on:

$$PbO_n + (4 - 2n)OH^- \xrightarrow{V_2} \alpha\text{-}PbO_2 + (2 - n)H_2O + (4 - 2n)e^- \quad (8)$$
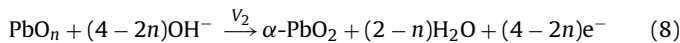
corresponding to the AEPs.

When lead electrode was prepolarized at -0.9 V, even though PbO is reduced to Pb, the surface of electrode is still PbSO$_4$(R) layer with loose structure before the positive polarization [14]. So the transfer of OH$^-$ through the PbSO$_4$(R) layer is easy during positive polarization, which causes tet-PbO to be oxidized thoroughly to α-PbO$_2$. Therefore, no AEPs occurs during the cathodic scanning shown in Fig. 2. When the negative polarization potential was -1.0 V or lower, PbSO$_4$(O) was formed on the outer layer during the subsequent positive polarization, which inhibits the oxidation of tet-PbO to α-PbO$_2$ and results in the formation of a large quantity of PbO$_n$. Also, the lower the negative polarization potential is, the more the quantity of PbSO$_4$(O) is formed, so the inhibition of PbSO$_4$(O) on the oxidations of tet-PbO to α-PbO$_2$ and PbSO$_4$ to β-PbO$_2$ is greater. Therefore, during the cathodic scanning, AEPs for the oxidation of PbO$_n$ to α-PbO$_2$ becomes higher but peak C corresponding to the reduction of β-PbO$_2$ to PbSO$_4$ becomes lower as the negative polarization potential is decreased, as shown in Fig. 2. When the electrodes were prepolarized at -2 V for 100 s in the second way of prepolarization, the quantities of pure Pb on the surface of different samples were the same, which means the inhibition of PbSO$_4$(O) on the oxidation of tet-PbO to α-PbO$_2$ would be same. After the polarization potential was stepped to different positive one, only when the positive polarization potential is higher than the equilibrium potential of Pb(II)/Pb(IV), the oxidation of Pb(II) to high-valent lead compounds could proceed. Since the oxidation of tet-PbO to PbO$_n$ precedes the oxidation of PbSO$_4$ to PbO$_2$ as the positive polarization potential is increased [21], when the positive polarization potential was increased to 1.7 V, the oxidation of tet-PbO to PbO$_n$ began but the oxidation of PbSO$_4$(O) to β-PbO$_2$ did not take place. Therefore, during the cathodic scanning, AEPs appeared without the cathodic peak C. As the positive polarization potential was unceasingly increased, the quantities of PbO$_n$ and PbO$_2$ increased, so during the cathodic scanning the currents of AEPs and cathodic peak C both increased, as shown in Fig. 3, but which can not be explained by Sharpe's hypothesis [11]. So far, it can be concluded that the use of negative polarization is to form the passivated PbSO$_4$(O) layer to prevent the oxidation of PbO$_n$ to α-PbO$_2$, while the positive polarization makes the tet-PbO oxidized to PbO$_n$ and increases the electric field strength in the PbSO$_4$ layer, which would be beneficial to the oxidation of PbO$_n$ during the cathodic scanning. In this regard, it is not difficult to understand why the two polarizations are needed for the occurrence of AEPs.

According to Zyryanov and Gusev [22] and Powder Diffraction File Alphabetical Index, PbO$_n$ can exist as PbO$_{1.37}$, PbO$_{1.44}$, PbO$_{1.55}$, and PbO$_{1.57}$. So, we hypothesize that during the cathodic scanning, the PbO$_n$ species (PbO$_{1.37}$, PbO$_{1.44}$, PbO$_{1.55}$, and PbO$_{1.57}$) are oxidized to α-PbO$_2$, forming the four AEPs. In the third way of prepolarization, as the positive polarization time was increased, the degree of oxidation of PbO to PbO$_n$ increased, which means that the value of "n" in the PbO$_n$ increased. According to the sequence of the four peaks reaching their maximum and the sequence of their disappearance with the increase of the positive polarization time, we propose that the peaks A1, A2, A3 and A4 respectively correspond to the oxidation of PbO$_{1.37}$, PbO$_{1.44}$, PbO$_{1.55}$, and PbO$_{1.57}$ to α-PbO$_2$. The oxidation of the four compounds varying with the positive polarization time is given in Table 1. When the polarization time was 1 s, PbO$_n$ existed as PbO$_{1.37}$; when polarization time was 2 s, PbO$_n$ existed as PbO$_{1.37}$, PbO$_{1.44}$, PbO$_{1.55}$, and PbO$_{1.57}$. As the polarization time was increased, the ratio of PbO$_n$ with high value of "n" in the PbO$_n$ layer increased, so the peak for the oxidation of PbO$_{1.57}$ was the last to reach its maximum. It can be concluded that the

peak potential of the oxidation of PbO_n decreases with the increase of the value of "n", which means that the transition enthalpy of oxidation of PbO_n to PbO_2 decreases with the increase of the value of "n", which is consistent with the results obtained by thermal transformation of PbO_2 to PbO_n [23]. When the polarization time was increased to 250 s, nearly all the PbO was oxidized to α-PbO_2, resulting in the disappearance of all AEPs during the cathodic scanning. Obviously, AEPs reflected the degree of the oxidation of Pb(II) to high-valent lead compounds, which could be applied in characterizing the corrosion resistance of lead current collector, which means that the lead current collector with high AEPs would have high corrosion resistance, or else, have lower AEPs or no AEPs.

6. Conclusion

In this paper we have studied the conditions of the occurrence of AEPs in detail combining potential step with linear sweep voltammetry (LSV). Through a series of experiments, it is essential to put forward some meaningful conclusions in below:

When the lead electrode was polarized at -2 V for 100 s, and stepped to 2 V for 2 s, four AEPs occurred without the cathodic peak for the reduction of PbO_2, which can not be explained reasonably by all existing mechanisms for AEPs formation.

The experimental data showed that AEPs' formation is closely relative with $PbSO_4(O)$ and the process of the oxidation of Pb(II) to high-valent lead compounds. Therefore, it is proposed for the first time that AEPs corresponds to the oxidation of intermediate compounds PbO_n, the formation of which is dependent on the inhibition of the compact $PbSO_4(O)$ layer on the oxidation of PbO to PbO_2. Meanwhile, the four AEPs correspond to the oxidation of PbO_n compounds with different values of "n".

AEPs formation is the result of the incomplete oxidation of lead electrode, so the electrode with high AEPs means that it has a high corrosion resistance, which could be applied to characterize the corrosion resistance of lead alloy current collector.

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