

Influence of Ag as alloy additive on the oxygen evolution reaction on Pb/PbO₂ electrode

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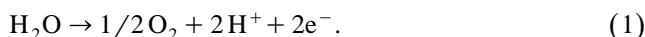
Abstract

When a Pb/PbO₂ electrode is polarised in the PbO₂ potential region ($\varphi \geq 1.0$ V vs. Hg/Hg₂SO₄ reference electrode), oxygen is evolved in parallel to PbO₂ formation. The rate of oxygen evolution depends on potential, temperature and alloying additives. In this investigation, the influence of Ag as alloying additive on the oxygen evolution reaction is studied using linear sweep voltammetry. Based on Tafel and Arrhenius plots, the influence of Ag on the oxygen overvoltage and on the activation energy of the process is determined. It was found that Ag from the metal surface is oxidized and Ag ions are incorporated into the PbO₂ layer where they decrease both the activation energy and the oxygen overvoltage of the process. Ag also changes the α/β -PbO₂ ratio and the structure of the PbO₂ layer. © 2000 Elsevier Science S.A. All rights reserved.

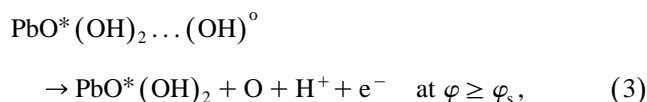
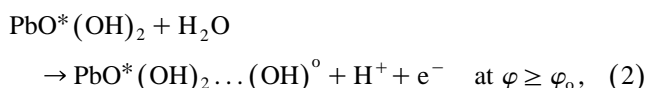
Keywords: Ag; Pb–Ag; Alloy; Pb/PbO₂; Oxygen overvoltage; Oxygen evolution

1. Introduction

On polarisation of a Pb/PbO₂ electrode in H₂SO₄ solution at potentials more positive than 1.0 V (vs. Hg/Hg₂SO₄ electrode), oxygen is evolved as a result of the reaction:



This reaction proceeds on the positive plates of lead-acid batteries at the end of charge and during overcharge. The rate of O₂ evolution depends on the potential, the temperature and the nature and concentration of alloying additives used. In a recent paper of ours, we have investigated the processes taking place during oxygen evolution on the lead dioxide electrode and have proposed a mechanism of the elementary reactions involved in this process [1a,1b]. According to this mechanism, the oxygen evolution reaction takes place in a certain number of active centres located in the gel zones (PbO*(OH)₂) of the PbO₂ layer. The elementary reactions involved in this process are:



Here, PbO*(OH)₂ denotes an active centre and PbO*(OH)₂... (OH)^o a blocked active centre in the gel zones of the lead dioxide layer. Reaction (2) proceeds at potentials more positive than its initial potential φ_0 , and reaction (3) at potentials above φ_s . The values of the initial potentials φ_0 and φ_s depend on the temperature, on the structure of the PbO₂ layer and on the alloying additives.

Silver is often used as an alloying additive for preparation of grids for lead-acid batteries. Pb–Ag alloys have an increased corrosion resistance [2,3] and better mechanical properties [4]. Batteries with Pb–Ag grids have good deep cycling behaviour [4]. It has been found that additions of silver accelerate oxygen evolution on the battery grids [5] and decrease the oxygen overvoltage [6,7]. Ag changes the structure of PbO₂ [6] and increases the value of the ratio α/β -PbO₂ in the corrosion layer [7].

The aim of this investigation is to determine the influence of Ag concentration in the Pb–Ag alloy on the oxygen evolution reaction that proceeds on the Pb/PbO₂ electrode.

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2. Experimental

Pb–Ag alloys have an eutectic point at 2.5 wt.% Ag [8]. Ag has a limited solid state solubility in lead; the α -crystals contain between 0.05 wt.% Ag at 25°C and 0.15 wt.% Ag at 70°C. We have used four under-eutectic Pb–Ag alloys (in addition to pure lead) in this investigation: with 0.05 and 0.10 wt.% Ag, denoted as “low-Ag alloys”, which correspond to the solid solution phase (α -Pb), and with 0.28 and 0.56 wt.% Ag, denoted as “high-Ag alloys”, which contain α -Pb and Pb–Ag eutectic.

A glass three-electrode electrochemical cell was used comprising a smooth flat working Pb–Ag electrode of 4 cm², a Pt counter electrode and a Hg/Hg₂SO₄ reference electrode (all potentials in this work are referred vs. the latter). All investigations were performed in 0.5 M H₂SO₄ solution. The potential was controlled by a scanning potentiostat and the temperature by a thermostat. The PbO₂ layer was prepared by linear sweep voltammetry (LSV) between 1.10 and 1.40 V at a scan rate of 100 mV/s for 3 h, employing two methods denoted by “stairs” and “levels” and described in Refs. [1a,1b]. By the “stairs” method, the electrode system was formed at constant temperature of 70°C. Then the LSV curves were recorded at a scan rate of 1 mV/s (stationary polarization curves) at temperatures 70, 60, 50, 40, 30 and 20°C. By the “levels” method, the Pb/PbO₂ electrode was prepared at each of the above temperatures and then the LSV curves were recorded at 1 mV/s at the same temperatures. A new electrode was prepared for each temperature level.

3. Results and discussion

Fig. 1 presents polarization curves for Pb–Ag electrodes. The data are obtained by LSV at 1 mV/s (stationary process) and at 100 mV/s (non-stationary process) at 20° and 30°C (low temperature) and 60° and 70°C (high temperature) employing the “stairs” (Fig. 1a,b) and the “levels” (Fig. 1c,d) methods of oxygen electrode measurements.

The current values for 0.05% and 0.1% Ag alloy electrodes are very close to that for the pure Pb electrode at the same potential. The voltammograms for the Pb–0.28% Ag and Pb–0.56% Ag electrodes have higher current values than that for the pure Pb electrode. The influence of Ag increases at higher temperatures.

A hysteresis between the anodic and cathodic sweeps of the voltammograms for Pb–Ag electrodes appears at a sweep rate of 1 mV/s and increases with increasing the Ag content in the alloy (Fig. 2). The voltammograms for the Pb–0.28% Ag and Pb–0.56% Ag electrodes feature a shoulder caused by the occurrence of an additional electrochemical process. These electrodes belong to the eutectic alloys and the eutectic Ag phase seems to perform its influence separately. The shoulder is due to the presence of Ag ions in the anodic layer. Ag from the Pb–Ag alloy is

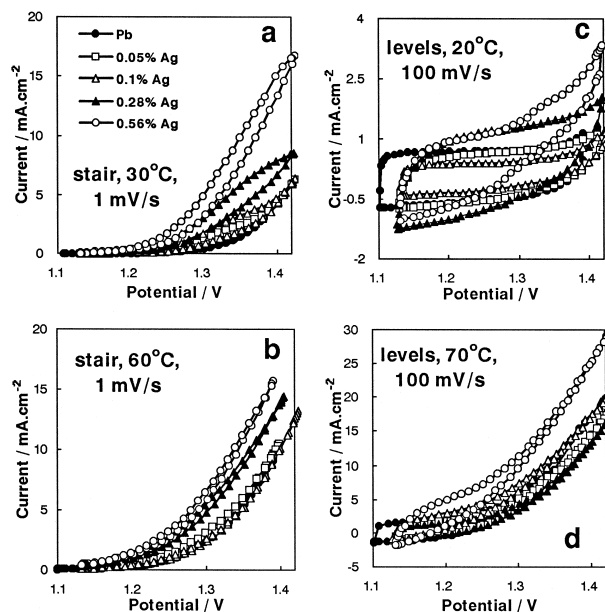


Fig. 1. Linear voltammetric sweeps between 1.10 and 1.40 V for Pb and Pb–Ag alloys: (a, b) sweep rate 1 mV/s; (c, d) sweep rate 100 mV/s (legend in a).

oxidized at these high potentials (Ag⁺ above 0.12 V and Ag²⁺ above 1.30 V) [9] and leaves the alloy surface penetrating into the PbO₂ layer. Ag²⁺ ions are known as strong oxidizers, which may attack H₂O and Pb²⁺ [10]. Thus, Ag ions may change the nature of the oxygen evolution active centres decreasing the oxygen overvoltage.

Fig. 3 presents the Tafel curves plotted using the data from the anodic branch of the voltammograms (1 mV/s) in Fig. 1.

The curves for pure Pb and for the low-Ag alloys feature a non-linear part (passive potential zone) and a Tafel linear part (active potential zone) [1a,1b]. For the high-Ag alloys, the shape of the curves is more complicated because of the presence of an anodic shoulder (Fig. 1a). Ag causes the curves to shift towards lower potentials. The influence of Ag increases with increase in the Ag content. The low-Ag alloys have a weaker effect on the overvoltage especially at elevated temperatures, whereas high-Ag ones have a stronger effect on the oxygen evolution reaction.

The following criteria have been selected to characterize the influence of Ag on the oxygen evolution reaction: (i) the Tafel slope b of the linear part of the polarization curves; (ii) the potential φ at which the current is 1 mA ($\log i = -3$), selected as a measure of the oxygen overvoltage; (iii) the potential φ_s above which the second electrochemical reaction of oxygen evolution begins, and (iv) the activation energy of the process. The estimation of the Tafel slopes and of the activation energy for the high-Ag alloys is complicated due to the presence of a new anodic process, which is responsible for the appearance of

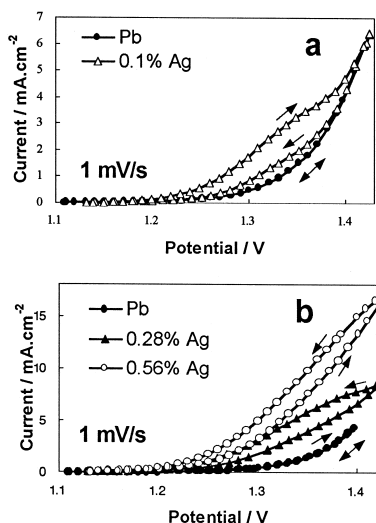


Fig. 2. Hysteresis between the anodic and cathodic sweeps of the voltammograms: (a) low-Ag alloy, (b) high-Ag alloys.

the shoulder in the voltammograms (Fig. 1). To determine the slopes of the Tafel curves for these alloy electrodes, we have used the linear part of the plots, which is closest to the passive potential zone.

The dependence of the Tafel slope b on temperature for oxygen electrodes polarized by both methods is presented in Fig. 4.

The coefficient b depends on the mechanism of the oxygen evolution reaction. For the pure Pb/PbO₂ electrode, b depends but slightly on temperature and has a value of about 115 mV/dec. Ag causes the value of b to change and influences its dependence on temperature. For the “levels” series below 50°C, Ag increases the value of b up to 160 mV/dec, whereas for the “stairs” series, b decreases down to 80 mV/dec. Above 50°C, b has higher values for the high-Ag electrodes than for pure lead in both series of measurements. For the low-Ag electrodes, b

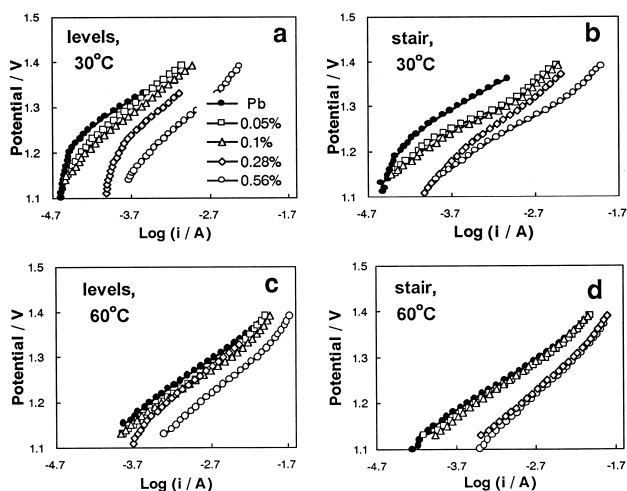


Fig. 3. Tafel plots of the voltammetric data at 1 mV/s from Fig. 1: (a, b) at 30°C, (c, d) at 60°C; legend in Fig. 1a.

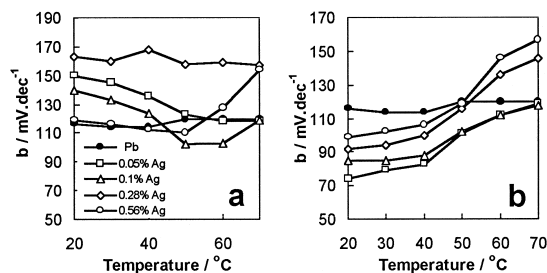


Fig. 4. Tafel slopes calculated from Fig. 3 as a function of temperature: (a) “levels” series, (b) “stair” series.

is equal to or lower than the b value for the oxygen electrode at pure Pb/PbO₂ electrode. Obviously, the Ag ions from the PbO₂ layer are involved into the mechanism of the oxygen evolution reaction even when present in the Pb–Ag alloy in very small amounts. These results indicate that Ag in the eutectic phase has a different influence on the oxygen evolution reaction compared to the case when Ag is contained in the α -Pb solid solution.

Fig. 5 presents the dependence of the thermal coefficient $d\varphi_s/dT$ of the initial potential φ_s of reaction (3) as a function of Ag content in the alloy.

Even at the lowest amounts of Ag, the thermal coefficient decreases more than twice. With further increase in Ag content, $d\varphi_s/dT$ decreases slightly. This indicates that either Ag increases the number of active centres available for the oxygen evolution or it decreases the activation energy needed for reaction (3) to proceed. This is an electrocatalytic effect of silver on reaction (3).

Arrhenius plots were built in order to determine the activation energy of the oxygen evolution reaction. The calculated values for E_a are presented in Fig. 6 as a function of the potential. Ag decreases significantly the activation energy of oxygen evolution. This effect is stronger with higher Ag contents.

The function E_a/φ features a maximum, which is clearly expressed for the “levels” series of tests. The potential corresponding to the maximum does not depend on the Ag content. Such a dependence has already been observed for oxygen evolution at a pure Pb electrode [1a,1b]. It was assumed that before the maximum, the reaction proceeds in active centres with different activation

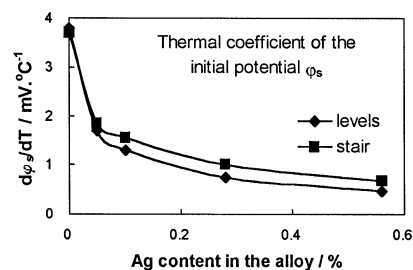


Fig. 5. Dependence of the thermal coefficient of the initial potential φ_s of the second oxygen evolution reaction (3) on Ag content.

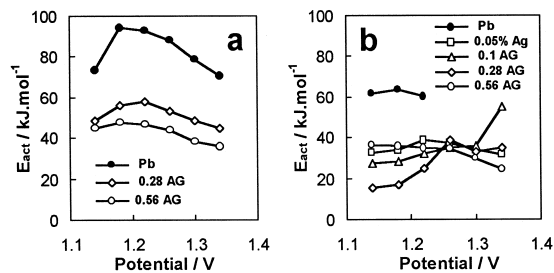


Fig. 6. Dependence of the activation energy on the potential: (a) ‘‘levels’’, high temperatures, (b) ‘‘stair’’, low temperatures.

energies. With increase in electrode potential, the number of active centres with higher activation energy, which are involved in the reaction, increases. The maximum indicates that all active centres N_0 in the gel zones are involved in the oxygen evolution reaction. After the maximum, the activation energy decreases with potential increase. This is due to the decrease of the potential barrier which an electron has to overcome when an oxygen atom is formed. The general kinetic equation connected with the activation energy is:

$$I = kN_0 \exp(-E_a/RT); \quad \varphi > \varphi_{\max} \quad (5)$$

Using this equation and based on the data in Fig. 5, it can be concluded that Ag decreases the activation energy of oxygen evolution (E_a) and probably increases the number of active centres (N_0) in the gel zones of the PbO_2 layer.

The influence of Ag alloying additives on oxygen evolution can be related to changes in the structure of the PbO_2 layer. We compared X-ray diffractograms of lead dioxide layers obtained during electrode preparation. The intensities of the characteristic diffraction lines with $d = 0.311$ nm for α - PbO_2 and tet- PbO , and $d = 0.350$ nm for β - PbO_2 , were used as a criterion to judge about the influence of the structure on the oxygen evolution. Ag increases the amount of α - PbO_2 formed. It has also been found that the additives change the ratio hydrated (gel)/crystal zones in PbO_2 , increasing the amount of the

hydrated part. On grounds of the available data, however, we could not find any direct correlation between the α/β - PbO_2 ratio and the oxygen evolution overvoltage. This is in agreement with the assumption that the oxygen evolution reaction proceeds in the hydrated (gel) zones of the lead dioxide particles.

4. Conclusions

1. Alloying additives of Ag decrease the overvoltage of the oxygen evolution reaction on a Pb/PbO_2 electrode. This effect increases significantly with rising the Ag content.
2. Alloying additives of Ag decrease the activation energy of oxygen evolution.
3. Silver changes the nature and increases the number of active centres in the gel zone of the PbO_2 layer.
4. Ag increases slightly the amount of α - PbO_2 in the corrosion layer. The oxygen overvoltage does not depend on the α/β - PbO_2 ratio.

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