

Role of hydration water in the reduction process of PbO_2 in lead/acid cells

R. Fitas, L. Zerroual *, N. Chelali, B. Djellouli

Laboratoire d'Energétique et d'Electrochimie du Solide, Université de Setif, Setif, 19 000 Algeria

Abstract

The influence of 'hydrogen loss' on the electrochemical properties of both $\alpha\text{-PbO}_2$ and $\beta\text{-PbO}_2$ was studied using galvanostatic discharge and cyclic voltammetry. The thermal decomposition of electroformed PbO_2 shows two types of hydration water: the first type, which disappears at low temperature, is adsorbed on the surfaces of the PbO_2 particles, and the second one is localized within the PbO_2 crystal structure. The reduction process of PbO_2 in lead/acid cells is mainly determined by diffusion processes within the oxide. The hydrogen diffusion coefficient \tilde{D}_H in lead dioxide has been determined at 25 °C; the values obtained are between 0.42 and $1.67 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. The removing of 'structurally bonded' water, by heating the samples at 230 °C, affects considerably the electrochemical properties of PbO_2 and leads to a decrease in \tilde{D}_H .

Keywords: Lead/acid batteries; Hydration water; Lead dioxide

1. Introduction

The lead/acid battery derives its power from the electrochemical energy released during the conversion of $\alpha\text{-PbO}_2$ and $\beta\text{-PbO}_2$ to PbSO_4 on the positive plate, and Pb to PbSO_4 on the negative plate.

The major factor contributing to the decline in capacity of the positive plate during charge/discharge cycling was considered to be a progressive decrease in the degree of electrical contact between the PbO_2 particles in the plate and between these particles and the grid. The change in conductivity is mainly due to the combined effects of grid corrosion and a gradual softening of the plate mass and shedding of the PbO_2 particles.

In 1973, Caulder and co-workers [1,2] proposed a so-called 'hydrogen loss' model for positive plate failure. Their results indicated that the decreased activity was associated with the loss of hydrogen species from the PbO_2 , accompanied by an increase in its degree of structural order.

This model stimulated a revival of interest in the solid-state chemistry of PbO_2 and considerable research effort has been mobilized in attempts to observe differences in the crystal structure [3–7], hydrogen content [5,7–10], and order/disorder [4,7,11] of PbO_2 prepared by electrochemical and non-electrochemical routes. These and other studies suggested mechanisms for the inclusion of hydrogen either into

the crystal structure of PbO_2 itself [5,9,12] or on the surfaces of PbO_2 particles [7,9,13].

According to the literature, the question of the possible influence of hydrogen and preparation conditions on the electrochemical activity of PbO_2 are still open since many of the studies have provided ambiguous or conflicting data. To cite some of these studies: it is well known that the capacity of $\alpha\text{-PbO}_2$ is lower than that of $\beta\text{-PbO}_2$ [14–16], however, more recently, Rüetschi [17] showed that $\alpha\text{-PbO}_2$ has a higher inherent capacity than $\beta\text{-PbO}_2$. Furthermore, recent studies [18] suggested that heat-treatment of PbO_2 results in a decline in capacity of the positive plate material. On the other hand, Hill and Madsen [7] concluded that the decrease in battery capacity with cycling service is not a function of the loss of hydrogen species from the crystal structure of electrochemical active PbO_2 .

The present work aims to study the role of hydrogen, present in lattice as H_2O and/or OH groups, in the reduction process of PbO_2 in H_2SO_4 solution, using electrochemical techniques such as cyclic voltammetry and galvanostatic discharge. Differential thermal analysis (DTA) is also used.

2. Experimental

Three categories of plate were tested in this study: (i) fresh $\alpha\text{-}$ and $\beta\text{-PbO}_2$ plates; (ii) $\alpha\text{-}$ and $\beta\text{-PbO}_2$ plates heated at 140 °C for 8 h, and (iii) $\alpha\text{-}$ and $\beta\text{-PbO}_2$ plates heated at

* Corresponding author.

230 °C for 8 h. The preparation method of the samples, the chemical and thermal procedures are reported in Ref. [18].

The electrochemical measurements were carried out in a three-electrode cell. The working electrode is at 1 cm distance from a platinum rectangular-shaped counter electrode having an apparent surface area of 5 cm². A Hg/Hg₂SO₄/5 M H₂SO₄ reference electrode was used. All the experiments were carried out at 25 °C. Galvanostatic discharges were performed with current densities of 30 and 40 mA cm⁻² for α - and β -PbO₂, respectively, and the potential–time curves were recorded.

The voltammograms were recorded after cycling the electrodes in the 1.2–0.6 V potential range versus Hg/Hg₂SO₄ at different sweep rates (5–100 mV s⁻¹) and potential–current curves were recorded.

3. Results and discussions

3.1. DTA analysis

The DTA runs were carried out in air at a heating rate of 5 °C min⁻¹. The thermograms of α - and β -PbO₂ are given in Fig. 1(a) and (b). Both α -PbO₂ and β -PbO₂ give a first endothermic peak in the 50–120 °C range corresponding to the departure of physisorbed water. By increasing the temperature, the β -PbO₂ sample showed a shoulder at 150 °C and a shaped peak at 230 °C. In the same temperature range, α -PbO₂ showed two distinct exothermic peaks. These exothermic peaks were associated with the existence of two types of water: the first one, which disappears at low temperature, is adsorbed on the surface of the PbO₂ particles. The second one may be localized in the crystal structure of PbO₂ itself and may be removed after heating at 230 °C.

The results are in agreement with earlier results found by Gavarrí et al. [19]. Using neutron quasi-elastic scattering, they confirmed the existence of two types of proton motion: a rotation-like local, and a translational motion.

3.2. Galvanostatic discharge

Galvanostatic discharge curves are shown in Figs. 2 and 3, referring to the first discharge after filling the cell.

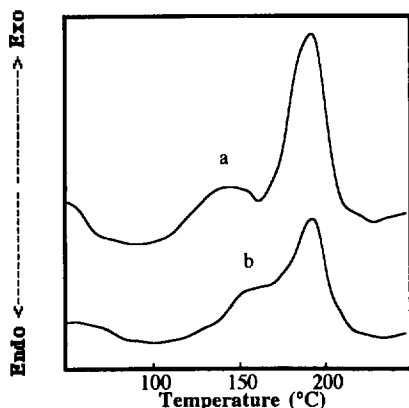


Fig. 1. DTA curves of (a) fresh α -PbO₂ and (b) fresh β -PbO₂.

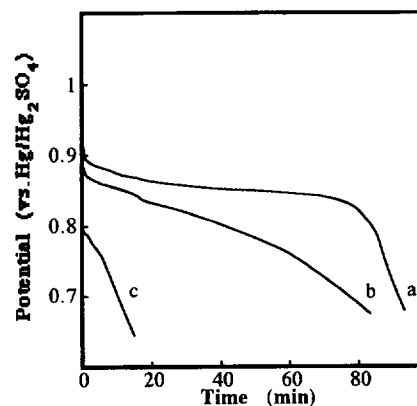


Fig. 2. Potential–time curves for the galvanostatic discharge of: (a) fresh α -PbO₂; (b) α -PbO₂ heated at 140 °C, and (c) α -PbO₂ heated at 230 °C in 5 M H₂SO₄ at a current density of 30 mA cm⁻².

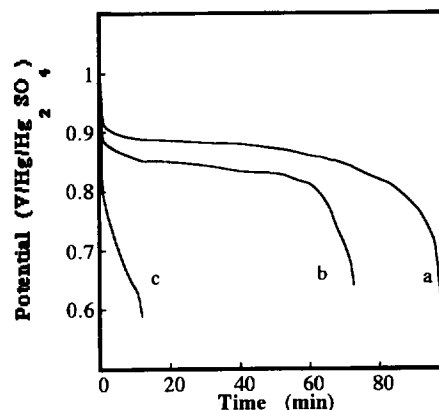


Fig. 3. Potential–time curves for the galvanostatic discharge of: (a) fresh β -PbO₂; (b) β -PbO₂ heated at 140 °C, and (c) β -PbO₂ heated at 230 °C in 5 M H₂SO₄ at a current density of 40 mA cm⁻².

Both α - and β -PbO₂ showed a potential plateau at 0.9 V due to the conversion of PbO₂ to PbSO₄.

After removing structural water by heating the samples at 230 °C, this plateau disappeared completely (see Figs. 2(a) and 3(a)) and an important decrease in potential is observed. This evidences the existence of this plateau at 0.9 V being associated with the presence of hydrogen within the PbO₂ lattice. These hydrogen-combined species play an important role in the reduction mechanism of PbO₂. Their drive-off by heating affects the capacity of PbO₂ considerably.

Adsorbed water on the surface particles has no influence on the kinetic behaviour of β -PbO₂ electrode (Fig. 2(b)). On the other hand, in the case of α -PbO₂ electrode (Fig. 3(b)), this entity changes the behaviour of the electrode. This results in a gradual decrease in potential, and the plateau characteristic of PbO₂ conversion to PbSO₄ tends to disappear progressively.

3.3. Cyclic voltammetry

Voltammograms for α - and β -PbO₂ in 5 M H₂SO₄ at different sweep rates (5–100 mV s⁻¹) are shown in Figs. 4 and 5. In both cases, the shape of the voltammograms changes considerably with the sweep rate. In addition, the

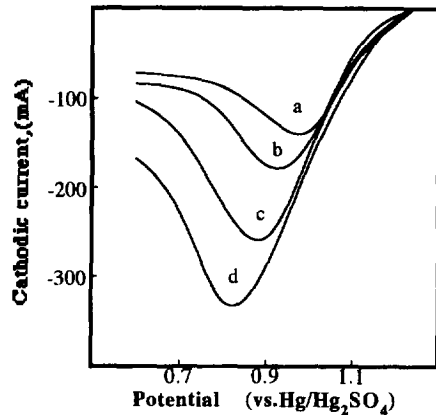


Fig. 4. Cyclic voltammograms of α -PbO₂ in 5 M H₂SO₄ at different sweep rates: (a) 5 mV s⁻¹; (b) 25 mV s⁻¹; (c) 50 mV s⁻¹, and (d) 100 mV s⁻¹.

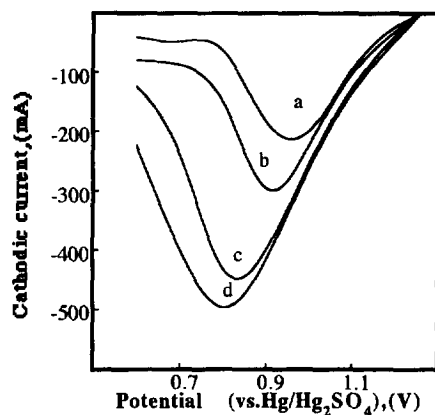


Fig. 5. Cyclic voltammograms of β -PbO₂ in 5 M H₂SO₄ at different sweep rates: (a) 5 mV s⁻¹; (b) 25 mV s⁻¹; (c) 50 mV s⁻¹, and (d) 100 mV s⁻¹.

cathodic potential peak E_{pc} shifts negatively with increasing sweep rate, ν ; the current at the peak on the voltammogram, I_p , increases with $\nu^{1/2}$, but is not proportional to it.

This behaviour is characteristic of quasi-reversible systems. In such a case and for a solution diffusion controlled process

$$I_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} \nu^{1/2} C_0^* K(\Lambda, \alpha) \quad (1)$$

where n is the number of electrons, A the electrode surface area, C_0^* the bulk concentration of H⁺ ions, D the diffusion coefficient and $K(\Lambda, \alpha)$ a constant introduced by Matsuda and Ayabe [20]. This constant depends mainly on the value of the cathodic charge-transfer coefficient, α , and the dimensionless parameter, Λ . From Eq. (1) it is possible to estimate the diffusion coefficient, D .

The D versus $K(\Lambda, \alpha)$ curve is given in Figs. 6 and 7 for α - and β -PbO₂, respectively.

One may notice that the diffusion coefficient, D , decreases with increasing $K(\Lambda, \alpha)$. Removing of adsorbed water on surface particles affects the kinetic properties of the electrode and a discrepancy in D is observed. This discrepancy is important when considering the α -PbO₂ electrodes. This indicates that the first type of water plays an essential role in the reduction mechanism of α -PbO₂, whereas, in the case of β -

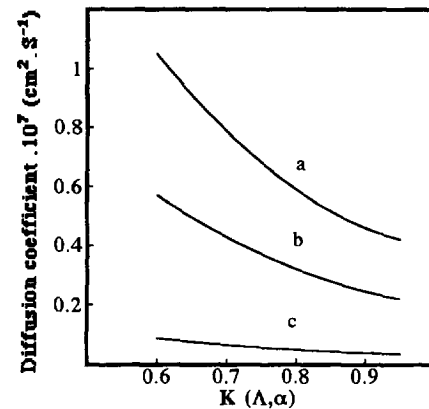


Fig. 6. Diffusion coefficient \tilde{D}_H vs. $K(\Lambda, \alpha)$ obtained for: (a) fresh α -PbO₂; (b) α -PbO₂ heated at 140 °C, and (c) α -PbO₂ heated at 230 °C.

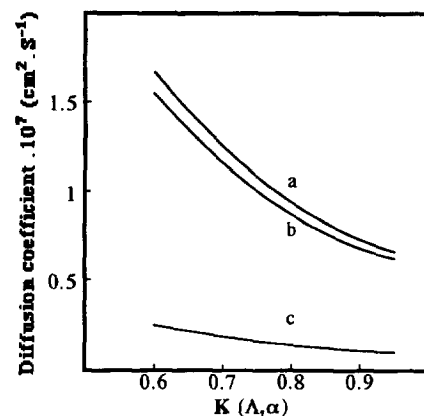


Fig. 7. Diffusion coefficient \tilde{D}_H vs. $K(\Lambda, \alpha)$ obtained for: (a) fresh β -PbO₂; (b) β -PbO₂ heated at 140 °C, and (c) β -PbO₂ heated at 230 °C.

PbO₂, it has almost no influence and a slight decrease in D is obtained.

In the light of these results one may suppose that this type of water is differently localized within the PbO₂ lattice and that it depends on the crystallographic structure of PbO₂.

This explains the difference in the shape of the DTA curves recorded of α - and β -PbO₂ illustrated in Fig. 1.

After driving off structural water, the diffusion coefficient is almost independent of the charge-transfer rate. This may be explained by a loss in electrochemical activity of PbO₂, due to the departure of hydrogen by heating the samples at 230 °C. Gavarrí et al. [19] attributed to these protons a translation motion with $D_t = 3 \times 10^{-6}$ cm² s⁻¹.

The values of D estimated on the basis of Eq. (1) are of the same magnitude of those found by Münzberg and Pohl [21] for the chemical diffusion coefficient of hydrogen in PbO₂ obtained from the electrochemical method at different pH's and concentrations of Pb²⁺

$$\tilde{D}_H = (0.4 - 4.9) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$$

One may conclude that the kinetics of PbO₂ reduction is determined mainly by a diffusion process within the oxide.

4. Conclusions

The stoichiometry of lead dioxide is changed by insertion or dissolution of hydrogen during the charge/discharge

process. The hydration water, present on the surface particles and localized in the PbO_2 particle, plays an important role in the process.

The kinetics of this process is determined mainly by diffusion of hydrogen within the oxide. The difference in the values of \bar{D}_H , calculated for fresh and heat-treated α - and β -samples, may be explained by the way and form these hydrogen species are bonded in PbO_2 .

Nuclear magnetic resonance and/or nuclear quasi-elastic scattering will be of great help to understand this difference in behaviour of the lead dioxide polymorphs.

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