

Short communication

Relationship between water departure and capacity loss of α and β -PbO₂ using an all solid-state system: Estimation of proton diffusion coefficient

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

Laboratoire d'Energétique et Electrochimie du Solide, Université Ferhat ABBAS, Sétif 19000, Algeria

Available online 15 December 2005

Abstract

The proton diffusion coefficient for both fresh and heat-treated (140 and 230 °C, respectively) α and β -PbO₂ electrodes was estimated at room temperature using Galvanostatic Intermittent Titration Technique (GITT). PbO₂ samples were prepared by electroformation of cured plates. HSbO₃·xH₂O with a conductivity of $3.29 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$, was used as solid protonic conductor (SPC) electrolyte. It was found that when structural water is removed, the capacity of both α and β -PbO₂ electrodes decreases and the ohmic drop increases. The departure of structural water affects considerably the value of proton diffusion coefficient.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Lead oxide; Positive active material; Solid electrolyte; Protonic conductor; Diffusion coefficient

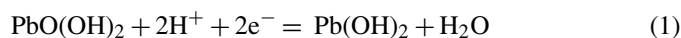
1. Introduction

The lead-acid battery derives its power from the electrochemical energy released during the conversion of PbO₂ to PbSO₄ on the positive plate and Pb to PbSO₄ on the negative plate. The capacity of the positive plate depends mainly on the ratio between the two forms of lead dioxide. In general, electrochemically prepared lead dioxides are non-stoichiometric and exhibit high electrochemical activity, whereas chemical forms are nearly stoichiometric and are reputed to be inactive. The origin of the electrochemical activity is essentially linked to the presence of hydrogen species in the phase composition of PbO₂. It is thought to exist in the form of hydroxyl groups coupled with the reduction of Pb⁴⁺ to Pb²⁺ or as interstitial protons with quasi-free electrons [1,2].

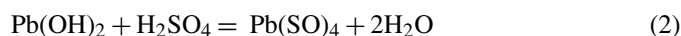
Pavlov [3] showed that lead dioxide active mass is a gel-crystal system with proton and electron conductivity. Using XPS technique, the author [4] found that more than 30% of the surface layer of PbO₂ is hydrated. In our previous work [5], the DTA analysis of both α and β -PbO₂ showed two distinct exothermic peaks, associated with the existence of two types of water: the first one, which disappears at 140 °C is adsorbed on the surface of PbO₂ particles. The second one is localized in the gel zones of PbO₂ and may be removed at 230 °C.

This water plays an important role in the mechanism of PbO₂ reduction and the gel zones have a great influence on the capacity of PAM, its drive-off by heating affects considerably the electrochemical and electrical properties of PAM [5–8].

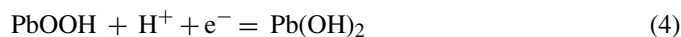
According to Pavlov et al. [9], during discharge of the positive active material, the reduction of PbO(OH)₂, present in the gel zones, to PbSO₄ proceeds in two stages: the first is an electrochemical one and occurs in the bulk of the agglomerates and particles. It can be expressed by the Eq. (1):



The second is a chemical reaction between Pb(OH)₂ and H₂SO₄, which leads to the formation of PbSO₄ according to Eq. (2):



In a paper of ours [10], we studied the mechanism of the reduction of α and β -PbO₂ electrodes using an all solid-state system to avoid any interference of PbSO₄. The kinetic tests and the coulometric data presented in that study showed that the process of PbO₂ reduction includes two electrochemical stages (one electron is consumed during each stage) taking place in the gel zones according to a proton–electron mechanism or a double-injection process. It can be expressed by the Eqs. (3) and (4), respectively:



* Corresponding author.

E-mail address: Zerroual@yahoo.fr (L. Zerroual).

In the present study, we investigate the relationship between the structural water departure and the capacity loss of PbO_2 using a solid proton conductor as electrolyte. The proton diffusion coefficient D was estimated for both α and β - PbO_2 electrodes.

2. Experimental

2.1. Preparation of PbO_2 active material

α and β - PbO_2 samples were prepared by electroformation of cured battery plates, respectively, in alkaline and acidic solutions. After washing in running water for several hours to remove excess of NaOH in α - PbO_2 and H_2SO_4 in β - PbO_2 plates, respectively, the plates were dried overnight at 110°C .

2.2. Preparation of solid protonic conductor electrolyte

$\text{HSbO}_3 \cdot x\text{H}_2\text{O}$ was prepared according to the method described by Fournier [11]. The sample presents a conductivity of $3.29 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ determined at room temperature and 80% humidity.

2.3. Discharge capacity measurements

Galvanostatic discharges were carried out in a three-electrode cell; the counter electrode and the reference electrode using the SPC/Pt , H_2 , $\text{H}_2\text{O}_{\text{vap}}$ system have already been presented in previous work [10]. Discharge tests were carried out at a constant current of 0.3 mA. All experiments were conducted at room temperature.

2.4. Estimation of proton diffusion coefficient

The proton diffusion coefficient for both fresh and heat-treated (140 and 230°C , respectively) α and β - PbO_2 electrodes was estimated at room temperature using Galvanostatic Intermittent Titration Technique (GITT).

Discharge tests were conducted at a constant current of 2 mA and the curves $E=f(t)$ was recorded. Intermittent galvanostatic discharges were carried out in the same conditions by applying a current of 2 mA during 3 min in each sequence, then the current was switched off and the cell was left to relax. The curves $E_{i=0}=f(x)$ were recorded.

3. Results and discussions

3.1. Discharge capacities

The discharge curves of α and β - PbO_2 samples are represented, respectively, in Figs. 1 and 2. In Table 1 we report the values of the capacities. We can see that fresh β - PbO_2 exhibits relatively high capacity compared to α - PbO_2 .

When the samples are heated, respectively, at 140 and 230°C the capacities of both α and β - PbO_2 decrease. We record a capacity loss of 33 and 8%, respectively, for α and β -samples heated at 140°C . This shows that water adsorbed on the surface of PbO_2 particles has a great influence on the electrochemical activity of

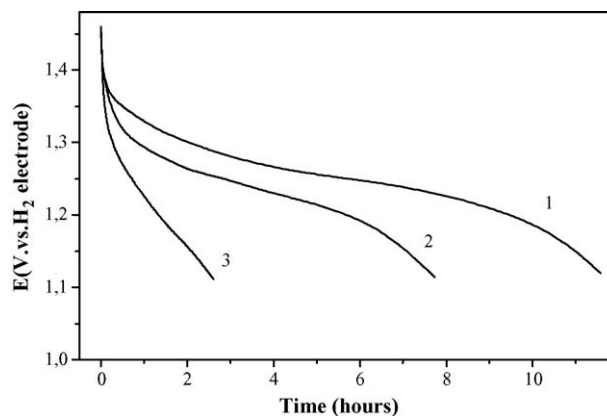


Fig. 1. Galvanostatic discharge curves of α - PbO_2 samples under a current of 0.3 mA: (1) fresh, (2) heated at 140°C , and (3) heated at 230°C .

α - PbO_2 . The departure of structural water affects considerably the capacities of both α and β - PbO_2 . It has more effect on the α form than the β one.

The drive-off of water present as hydroxyl groups in the gel zones of PbO_2 leads to an accumulation of the protons at the surface of the particles, the electrode is polarised and the potential decreases. This explains the increase of the ohmic drop.

3.2. Estimation of proton diffusion coefficient

In Figs. 3 and 4, respectively, we represent the curves of α and β - PbO_2 samples discharged at a constant current of 2 mA. We remark that the departure of structural water provokes a decrease in the potential as well as an increase of the ohmic drop. The α form seems to be more affected than the β one.

Figs. 5 and 6, represent the variation of the potential with \sqrt{t} , respectively, for α and β - PbO_2 samples discharged at a constant current of 2 mA. We notice a linear variation of the potential with \sqrt{t} , and a change in the slope values of the curves recorded for samples heated at 140 and 230°C .

Figs. 7 and 8, illustrate the variation of the potential $E_{i=0}$ with x (the quantity of hydrogen injected in PbO_2), respectively, for α and β - PbO_2 samples discharged at a constant current of 2 mA. The different values of D were calculated from the following

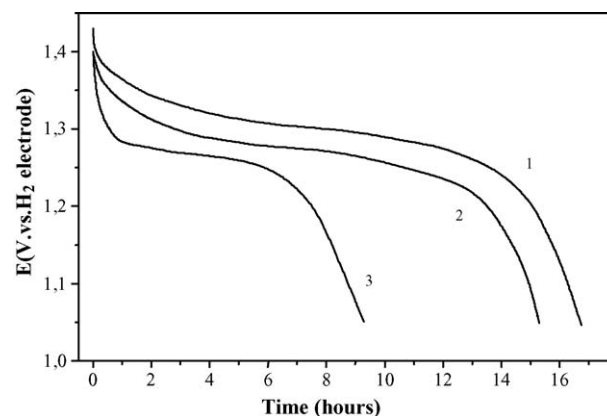


Fig. 2. Galvanostatic discharge curves of β - PbO_2 samples under a current of 0.3 mA: (1) fresh, (2) heated at 140°C , and (3) heated at 230°C .

Table 1
Discharge capacities of α and β -PbO₂ samples

Samples	α -PbO ₂	α heated at 140 °C	α heated at 230 °C	β -PbO ₂	β heated at 140 °C	β heated at 230 °C
Capacity (mAh g ⁻¹)	35.22	23.67	07.65	48.81	45.03	26.52
Capacity loss (%)	–	32.79	78.27	–	07.74	45.66

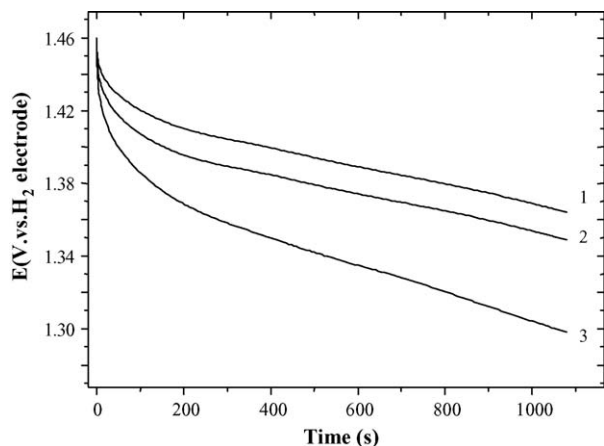


Fig. 3. Galvanostatic discharge curves of α -PbO₂ samples under a current of 2 mA: (1) fresh, (2) heated at 140 °C, and (3) heated at 230 °C.

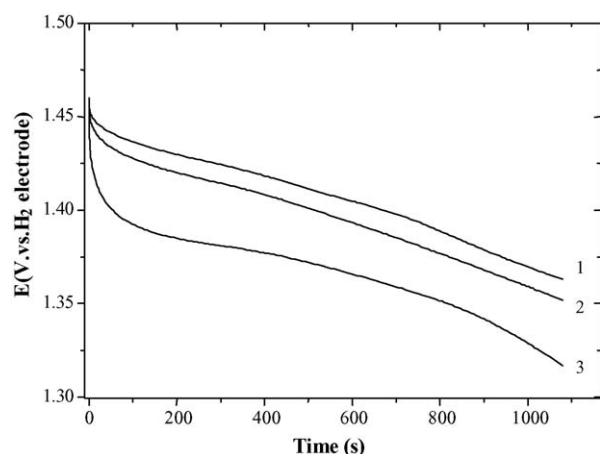


Fig. 4. Galvanostatic discharge curves of β -PbO₂ samples under a current of 2 mA: (1) Fresh, (2) heated at 140 °C, and (3) heated at 230 °C.

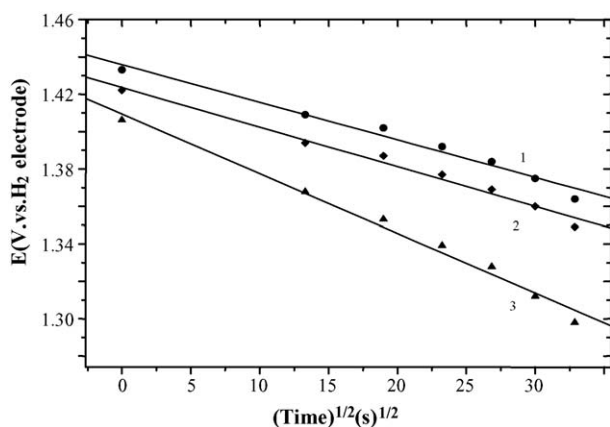


Fig. 5. α -PbO₂ potential electrodes vs. \sqrt{t} : (1) fresh, (2) heated at 140 °C, and (3) heated at 230 °C.

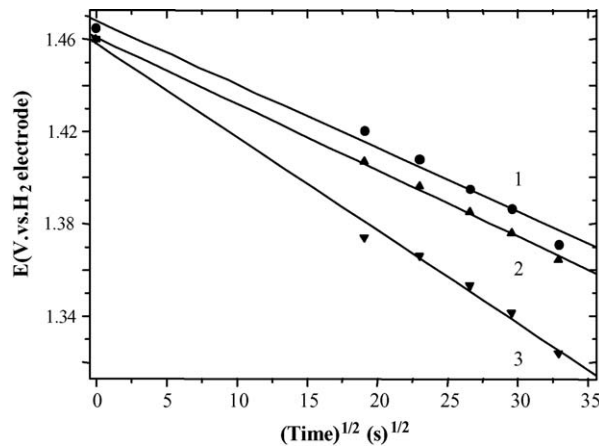


Fig. 6. β -PbO₂ potential electrodes vs. \sqrt{t} : (1) fresh, (2) heated at 140 °C, and (3) heated at 230 °C.

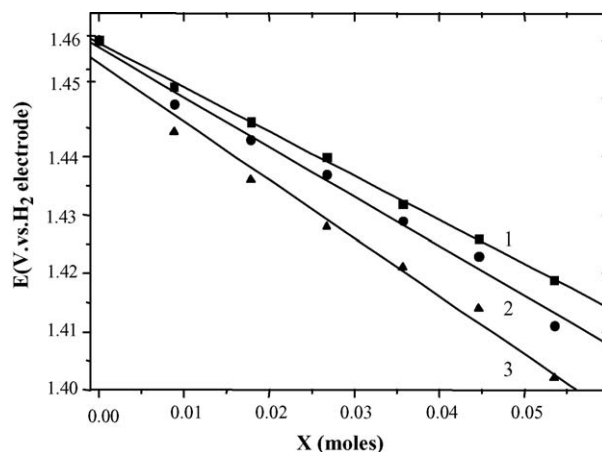


Fig. 7. α -PbO₂ potential electrodes vs. x : (1) fresh, (2) heated at 140 °C, and (3) heated at 230 °C.

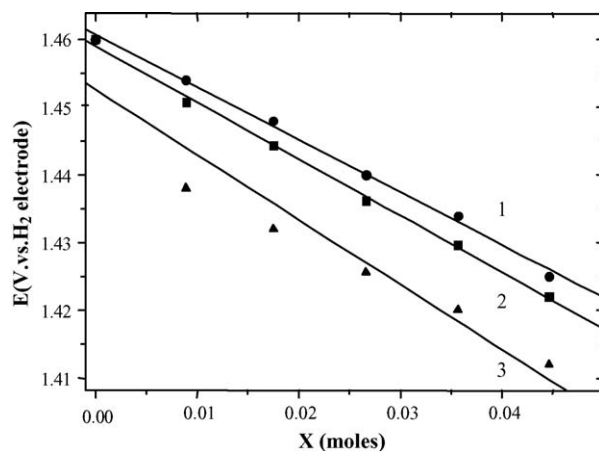


Fig. 8. β -PbO₂ potential electrodes vs. x : (1) fresh, (2) heated at 140 °C, and (3) heated at 230 °C.

Table 2
Calculated proton diffusion coefficient of α and β -PbO₂ samples

Samples	α -PbO ₂	α heated at 140 °C	α heated at 230 °C	β -PbO ₂	β heated at 140 °C	β heated at 230 °C
D ($\times 10^7$ cm ² s ⁻¹)	1.50	1.18	0.67	2.20	1.73	1.18

Eq. (5):

$$S\sqrt{D} = \frac{2IV_M}{F\sqrt{\pi}} \frac{\frac{\partial E_{i=0}}{\partial x}}{\frac{\partial E}{\partial \sqrt{t}}} \quad (5)$$

where S : geometric area of the working electrode; D : proton diffusion coefficient; I : current intensity; V_M : molar volume of PbO₂; F : Faraday's constant; $\partial E_{i=0}/\partial x$: slope of the curve $E=f(x)$; $\partial E/\partial \sqrt{t}$: slope of the curve $E=f(\sqrt{t})$; x : the quantity of hydrogen injected in PbO₂.

The values of D , the proton diffusion coefficient are summarized in Table 2.

From these results we can see that the D values calculated for β -PbO₂ are much higher than that of the α form. In addition, the departure of structural water seems to affect greatly the D values for both varieties. This may be explained by the fact that when water is removed, the gel zones are reorganized giving a crystal like particles with poor protonic conductivity. The resistance between particles increases and the proton diffusion coefficient decreases.

4. Conclusion

The mechanism of PbO₂ reduction takes place in the gel zones. It is a proton–electron mechanism. During discharge of the positive battery plate, the reduction of PbO₂ to PbSO₄ proceeds in three stages: the two first stages are electrochemical and occur in the bulk of the particles. They can be expressed by Eqs. (3) and (4). Whereas the third one is a chemical reaction of Pb(OH)₂ with H₂SO₄. The quantity of protons injected in PbO₂ is proportional to the quantity of Pb⁴⁺ ions present in the gel zones as PbO(OH)₂. The potential is fixed by the equilibrium between Pb⁴⁺ and Pb²⁺ ions. Taking in account these considerations, one can express the mechanism of PbO₂ reduction as a double injection process of electron and proton according to the Eq. (6):

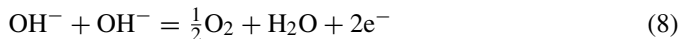


where $\langle \rangle$ and $\langle \text{H} \rangle$ denote the free and hydrogen occupied sites. The potential of the electrode can be written as:

$$E = E^0 + \frac{RT}{F} \ln \frac{[\langle \rangle]}{[\langle \text{H} \rangle]} \quad (7)$$

$[\langle \rangle]$ and $[\langle \text{H} \rangle]$ express, respectively, the concentrations of free and hydrogen occupied sites.

The departure of water affects not only the capacity of PAM but also its electrical properties. When heated lead dioxide lattice is reordered under oxygen evolution and combined water. This reaction is associated with a reduction of Pb⁴⁺ to Pb²⁺ according to Eqs. (8) and (9):



As a result, the resistance between the particles of PbO₂ increases giving an increase of the ohmic drop. This phenomenon can be considered as one of the causes of PAM degradation since the charge transfer occurs at the grid/PAM interface, i.e. the corrosion layer. Monahov et al. [12] in their study on grid corrosion layer made SEM and TEM observations and noticed the presence of gel like (hydrated) structures. Furthermore, the electrode is polarised and its potential decreases considerably leading to a capacity loss and a decrease in the values of D (proton diffusion coefficient). The difference in the D values recorded between the two polymorphs may be related to the way this proton species are arranged within the PbO₂ lattice.

Nuclear magnetic (NMR) as well as inelastic and quasi-elastic neutron scattering (NQES) studies will give certainly more details on the configuration of the proton and its relationship with the electrochemical activity of PbO₂.

References

- [1] R.J. Hill, I.C. Madsen, J. Electrochem. Soc. 131 (7) (1984) 1486.
- [2] J.P. Pohl, H. Rickert, J. Power Sources 6 (1976) 59.
- [3] D. Pavlov, J. Electrochem. Soc. 139 (11) (1992) 3075.
- [4] D. Pavlov, J. Electrochem. Soc. 136 (11) (1989) 3189.
- [5] R. Fitas, L. Zerroual, N. Chelali, B. Djellouli, J. Power Sources 64 (1997) 57.
- [6] D. Pavlov, J. Power Sources 40 (1992) 169.
- [7] R. Fitas, L. Zerroual, N. Chelali, B. Djellouli, J. Power Sources 58 (1996) 225.
- [8] R. Fitas, L. Zerroual, N. Chelali, B. Djellouli, J. Power Sources 85 (2000) 56.
- [9] D. Pavlov, I. Balkanov, P. Rachev, J. Electrochem. Soc. 134 (1987) 2390.
- [10] R. Fitas, N. Chelali, L. Zerroual, B. Djellouli, Solid State Ionics 127 (2000) 49.
- [11] T. Fournier, Thèse docteur ingénieur, Grenoble (1986).
- [12] B. Monahov, D. Pavlov, J. Appl. Electrochem. 23 (1993) 1244.