

Lead dioxides as cathodic materials for lithium polymer cells

N. Chelali* and J. Guitton

Laboratoire d'Ionique et d'Electrochimie du Solide (LIESG), associé au CNRS (URA D1213), ENS d'Electrochimie et d'Electrometallurgie de Grenoble, INPG-ENSEEG, B.P. 75, 38402 Saint-Martin-D'Hères Cedex (France)

(Received July 20, 1992; in revised form January 28, 1993; accepted February 4, 1993)

Abstract

The cathodic behaviour of both varieties α - and β -PbO₂ in the presence of lithium ion was studied. The chemical lithiation was obtained by reaction with n-butyllithium. The chromatographic analysis of the chemical products revealed both octane and butane. The presence of butane as coproduct could be due to the hydrogen substitution reaction with n-butyllithium. The electrochemical behaviour was studied with deposited PbO₂ cathodes on stainless steel with a LiClO₄/polyethylene oxide electrolyte. By using slow scan voltammetry, the cathodic reduction process results in the peak reduction at potential 2.4 V versus Li/Li⁺ for α -PbO₂ and 2.74 V versus Li/Li⁺ for β -PbO₂. The present work suggests that cathodic reduction is lithium intercalation in surface-layered PbO₂ molecules.

Introduction

Many metal dioxide cathodes for lithium nonaqueous cells have been investigated and proposed [1–5]. Among them, α - and β -varieties of lead dioxide are potentially suitable materials because of their high densities [6]. However, the electrochemical activities of many lead oxides in LiClO₄/P(OE)₈ electrolyte are not known. No report in the literature is given on the cathodic discharge voltammetry of cells based on electrochemically-prepared PbO₂. Only the discharge characteristics at low rate current densities with organic electrolyte of cathodes based on chemically-prepared PbO₂ have been examined [4–9]. A detailed understanding of the insertion conditions is important to achieve improvements in the theory of the PbO₂ electrode. For this reason, we investigated the cathodic behaviour of electrochemically-prepared α - and β -lead dioxides in lithium cells.

The aim of these series of experiments is to gain precise information on the cathodic behaviour of both phases of lead dioxide in lithium/polymer electrolyte cells. The study was carried out by using slow scan voltammetry (20 mV/h) and low rate galvanostatic discharge. Chemical reduction was achieved by using n-butyllithium.

Experimental

Materials

Lead dioxides used were synthesized according to following procedure. α -PbO₂ was prepared by alkaline electroformation according to ref. 10. β -PbO₂ was electro-

*Present address: Institut de Chimie Industrielle, Université de Sétif, 19000, Algeria.

chemically prepared by anodic oxidation from a nitric acid solution (12%) saturated with lead nitrate at 30 mA/cm^2 following the procedure described in ref. 11. Their crystalline structures were confirmed by X-ray diffraction using a Philips diffractometer type PW1700 with Cu $K\alpha$ radiation filtered with Ni.

Cell construction

The experimental cell consisted of a metal lithium (Lithco) anode disc (diameter: 20 mm and thickness: 0.5 mm) separated from the cathodic disc (diameter: 16 mm) by a film of $\text{LiClO}_4/\text{P}(\text{OE})_8$.

The composite cathode phase consisted of 52% (volume) of active materials, 8% of acetylene black and 40% of $\text{LiClO}_4/\text{P}(\text{OE})_8$ dissolved in acetonitrile. The cathodes were prepared by depositing the mixture on a stainless-steel disc (diameter: 16 mm) substrate. The cathode thus prepared was dried in air for 30 min.

The solid polymer electrolyte consisted of a 300 to 500 μm thick film of lithium perchlorate/poly(ethylene oxide) complex ($\text{LiClO}_4/\text{P}(\text{OE})_8$). The film was based on a high molecular mass poly(ethylene oxide) (Janseen) (mol. wt. = 5×10^6) and lithium perchlorate (Fluka) dissolved in acetonitrile (Prolabo) previously distilled, dried and kept on a molecular sieve. The amounts of $\text{P}(\text{OE})_8$ and LiClO_4 were calculated in such a way that the ratio O/Li was equal to 8. The $\text{LiClO}_4/\text{P}(\text{OE})_8$ electrolyte was prepared, dried and kept in an anhydrous argon atmosphere. In both electrolytes the content of water was fixed by the atmosphere within the glove box that is less than 1 ppm. For the low rate discharge and voltammetry, the different parts were placed in button cell casings (Toshiba Company). Assembly and crimping were carried out in the glove box. The temperature was maintained at 80°C .

Chemical lithiation

Lead dioxide previously dried from 48 h at 140°C under vacuum, was mixed with an excess of 1.6 M n-butyllithium solution in hexane (Fluka). The mixture was then put in a sealed container and stirred for 15 days. All operations were done in a dry glove box where the moisture content was less than 2 ppm. Chromatography was used for chemical analysis.

Electrochemical support

Our studies were carried out on a multichannel microprocessor controlled potentiostat/galvanostat that allows to sweep the potential step by step (20 mV/h) while recording the dynamics of the intercalation during each potential level. It has been designed for studying small cells (capacity in the 100 μAh –100 mAh range) and low kinetics, corresponding to intercalation processes, i.e., with equilibration times 0.1 to 1000 h. In order to examine the structural change of lead dioxide cathode, X-ray diffraction analysis were carried out on chemically- and electrochemically-reduced dioxide.

Results and discussion

Slow scan voltammetry

The open-circuit voltage (OCV) of the $\text{PbO}_2|\text{LiClO}_4/\text{P}(\text{OE})_8|\text{Li}$ cells exceeded 3 V. We have used very slow scan voltamperometry techniques (20 mV/h) to determine the electrode behaviour during discharge. The cells were discharged to 1.5 V. Reduction voltammetry curves of the α - and β - PbO_2 in $\text{LiClO}_4/\text{P}(\text{OE})_8$ electrolytes are shown

in Figs. 1(a) and 2(a), respectively. One current peak is observed when the potential is swept to the reduction range (3–2 V versus Li/Li⁺). However, the current peak value for β -PbO₂ is higher than that of α -PbO₂. The peak characteristics are summarized in Table 1.

The dependence of the equilibrium voltage on the degree of insertion $V=f(x)$ curves corresponding to α -PbO₂ and β -PbO₂ are reported in Figs. 1(b) and 2(b), respectively. We observed that degrees of discharge of α -PbO₂ and β -PbO₂ are not the same. In order to examine the cell performance, other cells with different capacities were discharged by the same techniques. The results are reported in Table 2. From the results, a complicated behaviour is to be expected. The two varieties are different by their OCV and their reduction peak potential. The α -PbO₂ exhibits a reduction peak at 2.64 V versus Li/Li⁺. The reduction peak of β -PbO₂ is found at 2.7 V versus Li/Li⁺.

The degree of discharge is constant for α -PbO₂ when the capacity of the cell changes. For β -PbO₂, the degree of reduction decreases when the capacity increases.

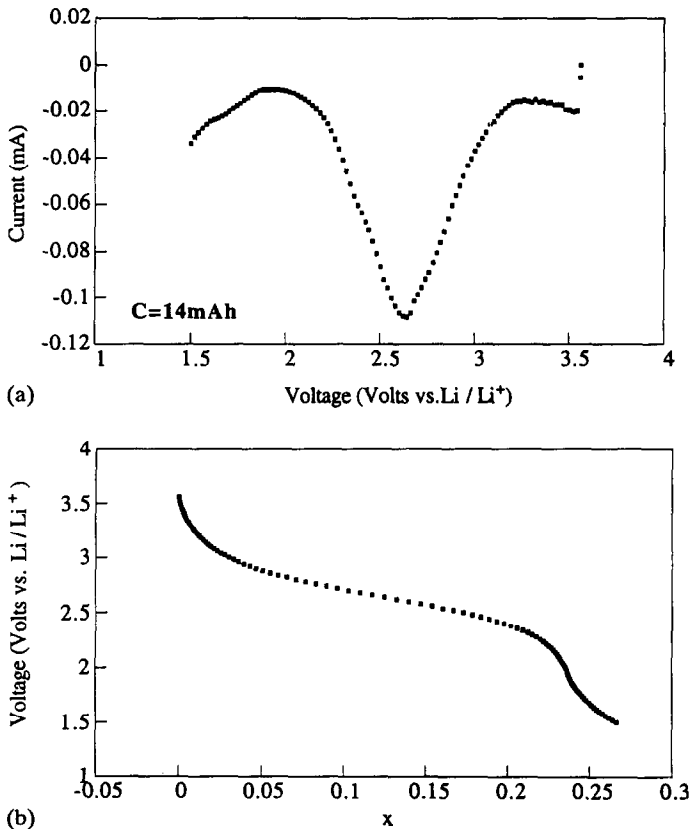


Fig. 1. (a) Voltamperogram of first lithium reduction of α -PbO₂ at -20 mV/h with LiClO₄/P(OE)₈ electrolyte operated at 80 °C; x value is obtained by capacity value reported in the Fig. which is calculated from the theoretical active mass of cathode material. (b) Voltage-composition curve obtained from integration of the voltamperogram with normalization at 1.5 V; corresponding capacity is indicated in the Fig.

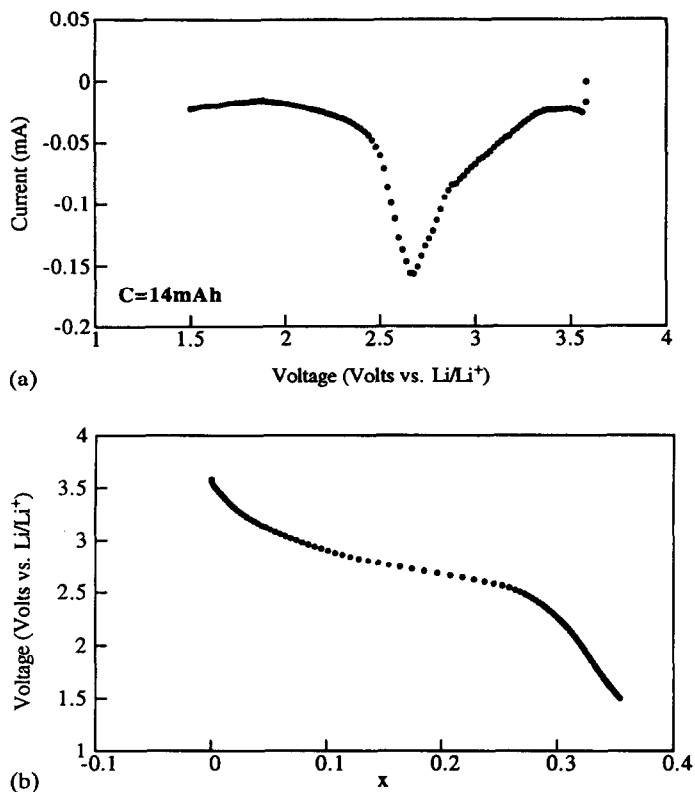


Fig. 2. (a) Voltamperogram of first lithium reduction of β - PbO_2 at -20 mV/h with $\text{LiClO}_4/\text{P}(\text{OE})_8$ electrolyte operated at 80°C ; x value is obtained by capacity value reported in the Fig. which is calculated from the theoretical active mass of cathode material. (b) Voltage-composition curve obtained from integration of the voltamperogram with normalization at 1.5 V; corresponding capacity is indicated in the Fig.

TABLE 1

Comparative electrochemical characteristics for both α - and β - PbO_2

| | OCV (V) | Nominal voltage (V) | Capacity (mAh) | $E(\text{peak})$ (V) | $I(\text{peak})$ (mA) | Reduction (%) |
|---------------------------|------------|---------------------------|-------------------|-------------------------|--------------------------|------------------|
| α - PbO_2 | 3.600 | 1.5 | 14 | 2.64 | 0.108 | 25 |
| β - PbO_2 | 3.682 | 1.5 | 14 | 2.70 | 0.160 | 38 |

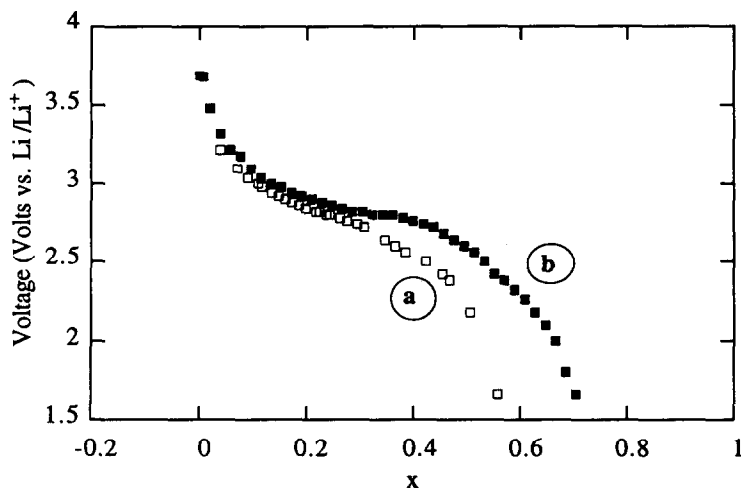
Low-rate galvanostatic discharge

The low-rate discharge tests were carried out at 0.05 mA/cm² in the cell. The results are shown in Fig. 3. Both types of PbO_2 showed a single plateau. Their cathodic capacity is not very different. To a 1.5 V end voltage, β - PbO_2 showed 68% and α - PbO_2 58% of utilization.

TABLE 2

Variation of utilization percentage with capacity of cells

| Capacity (mAh) | α -PbO ₂ utilization (%) | β -PbO ₂ utilization (%) |
|----------------|--|---|
| 3 | 25 | 80 |
| 6 | 23 | 60 |
| 10 | | 50 |
| 12 | | 46 |
| 14 | 25 | 38 |

Fig. 3. Discharge curves of Li/PbO₂ cells at a rate of 0.05 mA/cm²: (a) α -PbO₂, and (b) β -PbO₂.

The results of the present investigation indicate that the behaviour of these dioxides is correlated with their structures. Essentially, both structures consist of lead ions at the centre of half the available octahedra formed by close-packed layers of oxygen atoms. In the β -form, the lead ions are packed to give straight chains of octahedra while in the α -form there are zigzag chains in same plane as the β -chains, but perpendicular to them. In the real structures the effect of the ion sizes has been to distort these idealized structures.

Cell reaction

In order to examine the structural changes of lead dioxide cathode after discharge to 1.5 V end voltage, X-ray analysis were carried out. Fig. 4(e) and 5(e) show a set of X-ray diffraction patterns of the resulting products at 20% depth-of-discharge for α -PbO₂ and 50% for β -PbO₂. The X-ray patterns of these discharge products of α - and β -PbO₂ cathode are unchanged. The relative intensity of the set of peaks decreased. The possible modifications that occur during the electrochemical reduction of lead dioxide were not observed.

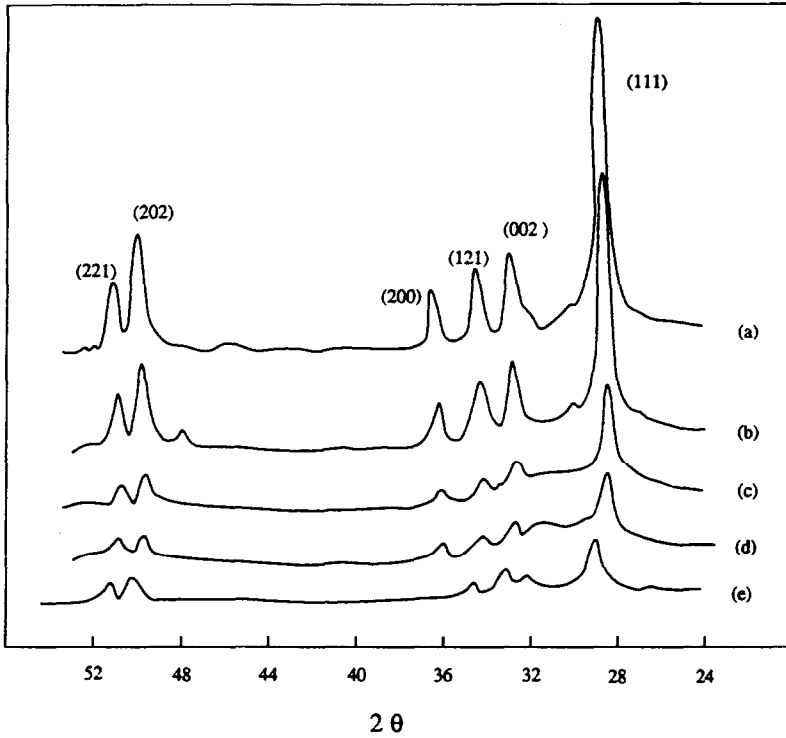


Fig. 4. X-ray diffraction profiles of α - PbO_2 : (a) pure variety; (b, c and d) chemical reduction with 0.5, 1 and 1.5 Li, respectively, and (e) reduction product at 20% depth-of-discharge.

Chemical lithiation with *n*-butyllithium

It is well known that lead dioxide contains hydroxyl ions [12]. The origin of the electrochemical activity has been linked variously with the hydrogen contents of the material [13]. Nuclear magnetic resonance as well as neutron inelastic studies [14] show that protons are not incorporated in the structure as pure loosely-bound water in pockets. Furthermore, a neutron diffraction study [15] has shown that there is no evidence for Pb or O vacancies. In addition, such defects are not necessary for explaining the well-known electrical conductivity of PbO_2 . As a consequence, it is generally admitted that the chemical formula is [14, 15]:



or,



The composition may be described using the formula:



and,



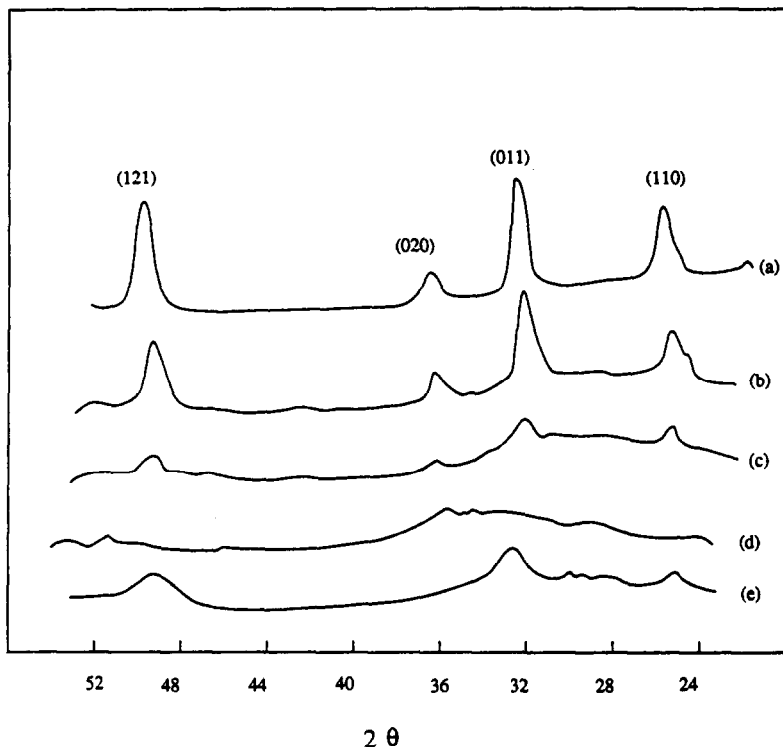
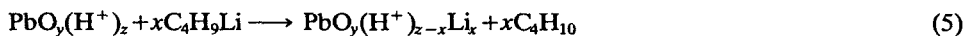


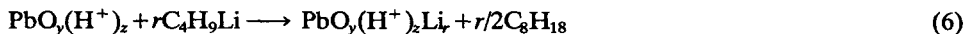
Fig. 5. X-ray diffraction profiles taken after reduction of β - PbO_2 : (a) pure variety; (b, c and d) chemical reduction with 0.5, 1 and 1.5 Li, respectively, and (e) reduction product at 50% depth-of-discharge.

It has been shown that the contact between the PbO_2 crystallites and the n-butyllithium is realized through an hydrated layer on the surface which confers an acidic character to this compound. These atoms could partially be exchanged in an acid-base reaction with n-butyllithium. Thus, the butyllithium reaction with hydrogen PbO_2 can follow two different paths:

(i) acid-base reaction: proton transfer



(ii) redox reaction: electron transfer



Depending on whether the reaction is acid-base or redox, either butane or octane are obtained.

The chromatographic analysis of the reaction products with α - and β - PbO_2 revealed the presence of both butane and octane (Fig. 6). This indicates that both reactions occur simultaneously.

In order to examine the structural change three samples of dioxides were chemically reduced using 0.5, 1 and 1.5 M n-butyllithium at room temperature. The reductions were interrupted after 15 days. The dioxides were then washed in hexane, dried and studied by X-ray diffraction analysis.

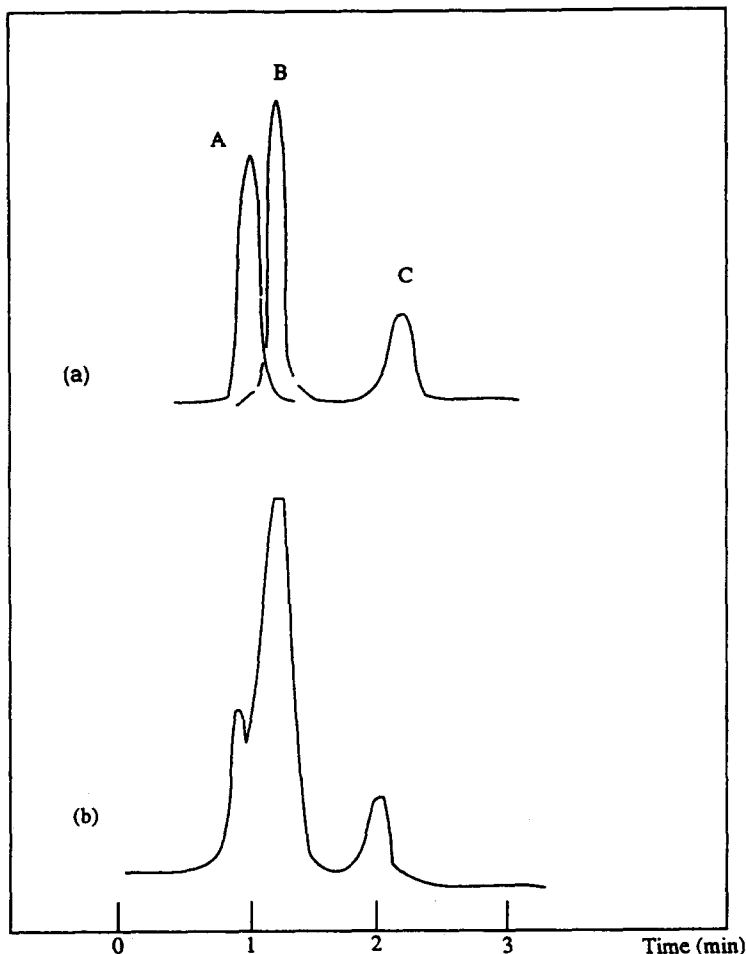


Fig. 6. Chromatographic spectra at room temperature: (a) blank test curve A: 0.5 cm^3 of butane, curve B: $1 \mu\text{l}$ of hexane and curve C: $1 \mu\text{l}$ of octane; (b) solution of PbO_2 in n-butyllithium after 15 days.

$\alpha\text{-PbO}_2$ case

Figure 4 shows the X-ray diagrams of the pure $\alpha\text{-PbO}_2$ and its reduction product. During the course of the reduction no new compound is formed. Unreduced and reduced dioxides belong to the same phase. X-ray diagram of the samples, reduced with 1 and 1.5 Li, show that the intensity of the peaks decreases.

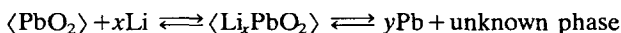
$\beta\text{-PbO}_2$ case

The $\beta\text{-PbO}_2$ studied has a different X-ray diagram (Fig. 5). During its reduction the intensity of peaks decreased continuously with increasing lithium concentration. The reduction product was obtained when 1.5 Li leads to an amorphous product phase.

After that, the samples were heated in vacuum for 24 h at 270°C . X-ray diagrams were plotted. The data indicated the presence of lead. No intermediate stage was observed on the chemical reduction process of these two dioxides.

Products resulting from both electrochemical and chemical reduction of PbO_2 varieties have the same crystallographic structure as the initial phase. During the course of the reduction no new compound is formed. Unreduced and reduced dioxides are the only existing phases. X-ray diagrams show that during reduction the relative intensity of the peak decreased. The chemical reduction of these two dioxides used in homogeneous phases leads to a dioxide with a crystal lattice less ordered than that of the basic dioxide. We must admit in this case a subsequent slow evolution to polyphased systems of type III as usually discussed with insertion material [16].

The reaction will be:



Conclusions

This work shows the complexity of the cathodic reduction mechanism of both α - and β - PbO_2 . A peak reduction for both α - and β - PbO_2 using a very slow scan voltammetry was reported. During chemical lithiation with n-butyllithium, we found that PbO_2 could exchange both protons and electrons. In electrochemical cells, the cathodic reduction process results in the peak reduction at potential 2.4 V versus Li/Li^+ for α - PbO_2 and 2.74 V versus Li/Li^+ for β - PbO_2 . PbO_2 cathodic reduction seems to be a lithium intercalation in surface-layered PbO_2 molecules since the reaction with n-butyllithium gives octane as a reaction coproduct.

Further investigations are in progress to confirm our hypothesis.

References

- 1 F. W. Dampier, *J. Electrochem. Soc.*, 121 (1974) 656.
- 2 H. Ikeda, T. Saito and H. Tamura, *Denki Kagaku*, 45 (1977) 391.
- 3 T. Ohzuku, Z. Takehara and S. Yoshizawa, *Denki Kagaku*, 46 (1978) 407.
- 4 P. Fiordiponti, G. Pistoia and C. Temperoni, *Electrochim. Acta*, 24 (1979) 219.
- 5 T. Ohzuku, Z. Takehara and S. Yoshizawa, *Denki Kagaku*, 47 (1979) 685.
- 6 L. Peraldo Bicelli, B. Rivolta, F. Bonino and S. Maffi, *J. Power Sources*, 18 (1986) 63.
- 7 T. Ohzuku, T. Shimamoto and T. Hirai, *Electrochim. Acta*, 26 (1981) 751.
- 8 G. Pistoia and U. Mancinelli, *Electrochim. Acta*, 22 (1977) 1141.
- 9 A. V. Gorodyskii, S. P. Kukensko and S. V. Sazhin, *5th Int. Meet. Lithium Batteries, Beijing, China, May 27-June 1, 1990*.
- 10 E. Voss and J. Freundlich, in D. H. Collins (ed.), *Batteries*, Pergamon, Oxford, 1963.
- 11 E. Hasik and M. Paszkiewicz, *J. Power Sources*, 30 (1990) 107.
- 12 A. Bystrom, *Arkiv Kemi Mineral Geol.*, 20 A (II) (1947) 1.
- 13 S. M. Caulder, J. S. Murday and A. C. Simon, *J. Electrochem. Soc.*, 120 (1983) 1515.
- 14 P. Boher, P. Garnier and S. M. Caulder, *J. Solid State Chem.*, 52 (1984) 146.
- 15 A. Santoro, P. D'antonio and S. M. Caulder, *J. Electrochem. Soc.*, 130 (1983) 1451.
- 16 M. Armand, *Thesis*, University of Grenoble, France, 1978.