STRUCTURE AND PROPERTIES OF ELECTROCHEMICALLY ACTIVE THIN PbO₂ FILMS FOR RESERVE BATTERIES

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Introduction

The preparation of thin oxide films by deposition from acetate, perchlorate, fluoroborate and nitrate salt solutions has been investigated. The aim of this work is the optimization of cathode active material preparation for reserve batteries of the type: $PbO_2/H_2SiF_6/Pb$ and $PbO_2/HBF_4/Pb$. The batteries are required to operate in the wide temperature range: 223 - 323 K. The investigations have been made with reference to earlier work [1 - 4].

Electrode processes in Pb²⁺ ion solutions during anodic oxidation

During electrochemical oxidation, divalent lead ions from electrolyte solution are oxidized to tetravalent ions, even at low current densities, and deposited on a platinum anode as PbO_2. When copper or nickel substrates are used, certain processes associated with dissolution of these metals occur.

A nickel anode dissolves up to the passivation point according to:

$$Ni \longrightarrow Ni^{2+} + 2e^- \tag{1}$$

$$Ni + H_2O \longrightarrow NiO + 2H^+ + 2e^- \tag{2}$$

The electrode potential increases to a value where lead dioxide deposition can proceed, *i.e.*,

$$Pb^{2+} + 2H_2O \longrightarrow PbO_2 + 4H^+ + 2e^- \tag{3}$$

It is necessary to control the pH of the electrolyte solution since, at low pH, reactions (2) and (3) proceed simultaneously and the flowing electric charge is only partially utilized for the formation of PbO_2.

The cathode reaction:

$$Pb^{2+} + 2e^- \longrightarrow Pb \tag{4}$$

proceeds in parallel with the reduction of anions in the solution, *e.g.*, in lead nitrate solution:

$$NO_3^- + 2H^+ + 2e^- \longrightarrow H_2O + NO_2^- \tag{5}$$

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In poor conditions, where current densities and pH are too low, the nitrites evolved at the cathode may be reoxidized to nitrates at the anode. This, in turn, will reduce the utilization of the electric charge used for PbO_2 formation by up to 25%. Such problems do not occur in perchlorate solution where the utilization of the electric charge for PbO_2 formation reaches 100%.

The electrochemical activity of PbO_2 as a cathodic material is the most important parameter determining the choice of technology for deposit formation. Therefore, optimization of the parameters for deposit formation is necessary.

Experimental

Deposition of thin PbO_2 films on nickel foil

Lead dioxide deposits were obtained in a specially designed electrolyzer that allowed the electrolyte to be regenerated. The temperature of the solution was maintained at a constant value (with ± 0.5 K accuracy) by the use of an ultra-thermostat. The electrolyte regeneration consisted of continuous replenishment of Pb^{2+} ions and oxidation of nitrites to nitrates. The concentration of hydrogen ions was controlled by analysing the solution between the electrodes, both before and immediately after the measurement, in order to confirm that the regeneration was proceeding correctly.

Deposits of PbO_2 were obtained on one side of the nickel foil. Two nickel strips were placed together, their ends soldered, and then inserted into a frame with a 65 cm^2 window. The counter electrodes comprised two metallic lead foils placed symmetrically with regard to the nickel foils.

During electrodeposition of PbO_2, measurements were made of the concentration of the electrolyte solution, the current density, the temperature, and the elapsed time of the process. In subsequent experiments, by using pre-determined dimensions and distances between electrodes, the total electric charge was maintained constant, *i.e.*, $Q =$ constant.

Both single and double-layer deposits were prepared in two different solutions of lead salts, *i.e.*, the first layer was obtained in perchlorate solution and the second in nitrate solution or in perchlorate and acetate solutions. The induction of the physical and chemical parameters of PbO_2 deposits from nitrate solutions was found to be easy.

In order to optimize the method of film deposition to meet the requirements of reserve batteries, the test procedure given in Table 1 was adopted. In subsequent experiments, the pH was 3 - 4. Comparative tests at pH = 1, with appropriate additions of concentrated HNO_3, were made. Regeneration of the electrolyte consisted of the addition of orthorhombic lead dioxide and Pb_3O_4.

An electric mixer was used to accelerate the reaction of the electrochemical deposition products according to the reactions:
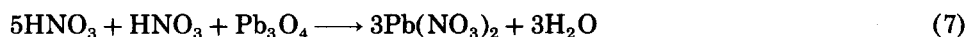
$$2HNO_3 + PbO \longrightarrow Pb(NO_3)_2 + H_2O \qquad (6)$$

$$5HNO_3 + HNO_3 + Pb_3O_4 \longrightarrow 3Pb(NO_3)_2 + 3H_2O \qquad (7)$$

TABLE 1

Test procedure for PbO_2 deposition from nitrate salt solutions

Composition of solution for electrodeposition	Temperature (K)	Anodic current density (mA cm^{-2})
150 g dm^{-3} Pb(NO$_3$)$_2$	293	30, 40, 60, 100
	313	20, 40, 60, 100
250 g dm^{-3} Pb(NO$_3$)$_2$	293	2, 20, 40, 60, 100
	313	2, 20, 40, 60, 100
360 g dm^{-3} Pb(NO$_3$)$_2$	293	2, 20, 40, 60, 100
	313	2, 20, 40, 60, 100
360 g dm^{-3} Pb(NO$_3$)$_2$ +10 cm^3 of concentrated HNO$_3$	293	2, 20, 40, 60, 100
	313	2, 20, 40, 60, 100
360 g dm^{-3} Pb(NO$_3$)$_2$ +100 cm^3 of concentrated HNO$_3$	293	20, 40

Methods for testing lead dioxide deposits

Deposits on nickel foil were investigated by X-ray diffraction using a Phillips Diffractometer and Cu Kα radiation filtered by nickel foil. The phase composition (*i.e.*, the contents of orthorhombic and tetragonal PbO_2) as well as the deposit texture were determined. The deposits were tested directly on the nickel substrate and, additionally, in powdered form. The deposit morphology was investigated using a JOEL scanning electron microscope. The samples were evaporated with a thin aluminium film in a VEB Hochvacuum (Dresden) sublimator.

The adhesion of the deposit to a nickel substrate, which was carefully degreased and electrochemically etched in 30% H_2SO_4 solution, was inspected visually by destructive methods, *e.g.*, by bending of the electrodes. At the same time, the discharge voltage characteristics of standard-size PbO_2/H_2SiF_6/Pb cells with a nickel-foil-deposited-PbO_2 cathode and a metallic-lead-foil anode were investigated. Particular attention was given to the performance at 223 K and a current density of 5 mA cm^{-2}.

Results and discussion

Table 2 gives test results from the first stage of the investigations, *i.e.*, conditions of PbO_2 deposition from lead salt solutions, phase composition, and structural analysis of the surface. The voltage characteristics of standard cells are given in Fig. 1. It was found that deposits obtained from perchlorate solutions adhere firmly to the substrate, while deposits from acetate or nitrate solutions exhibit higher electrochemical activity in a cell.

TABLE 2

Composition of firmly adhering PbO$_2$ deposits obtained by electrodeposition from different lead salt solutions

PbO$_2$ deposition parameters (solution temperature: 293 K)	X-ray structural analysis of surface
	phase composition (*hkl*) planes parallel to nickel foil
Single-layer deposit: Pb(ClO$_4$)$_2$ 920 g dm^{-3} $i = 8$ mA cm^{-2}	α-PbO$_2$, β-PbO$_2$, and amorphous phase α-PbO$_2$: (020) β-PbO$_2$: (301)
Double-layer deposit: (i) Pb(ClO$_4$)$_2$ 920 g dm^{-3} $i = 8$ mA cm^{-2} (ii) Pb(NO$_3$)$_2$ 360 g dm^{-3} $i = 30$ mA cm^{-2}	β-PbO$_2$, α-PbO$_2$ traces β-PbO$_2$: (101), (211), (301) highly crystalline β-PbO$_2$
Double-layer deposit: (i) Pb(ClO$_4$)$_2$ 920 g dm^{-3} $i = 8$ mA cm^{-2} (ii) Pb(CH$_3$COO)$_2$ 400 g dm^{-3} NaNO$_3$ 200 g dm^{-3} $i = 30$ mA cm^{-2}	amorphous PbO$_2$ traces of β-PbO$_2$ –
Single-layer deposit: Pb(BF$_4$)$_2$ 230 g dm^{-3} $i = 50$ mA cm^{-2}	α-PbO$_2$: (020)

On the basis of these results, a method was developed for two-step deposition of PbO$_2$ films in two different solutions: perchlorate and nitrate; perchlorate and acetate. Good adhesion, compactness, and porosity of deposits were obtained. The operating potential of the PbO$_2$ electrode at low temperatures was also satisfactory.

The results of work on the optimization of electrodeposition parameters from nitrate salt solutions were analysed in detail. The size of the deposit grains was calculated from electron micrographs (Table 3). Selected micrographs are shown in Fig. 2. X-ray diffraction patterns for deposits obtained at different deposition parameters are given in Fig. 3. Table 4 shows the dependence of the phase composition on the deposition parameters. Conformity to pre-determined process conditions resulted in reproducible results. It was found that most deposits from nitrate salt solutions were homogeneous throughout the electrode surface. Morphology changes and inhomogeneities occurred at the outer part of the electrode and proceeded towards its centre.
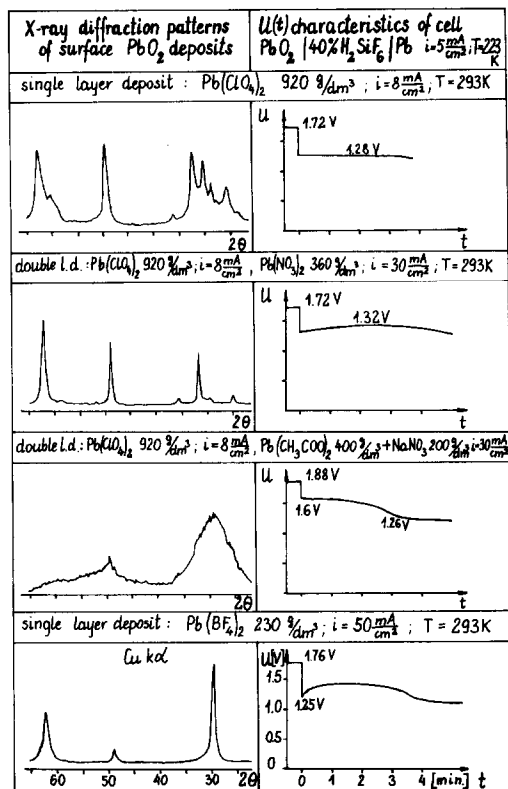
Fig. 1. Voltage–time characteristics of standard cells.

Analysis of the effect of anodic electrodeposition parameters on the properties of PbO$_2$ deposits from nitrate solutions revealed the following.

(i) The morphology and structure of the PbO$_2$ deposits are determined mainly by the current density. Decreasing the rate of the anodic deposition process results in grains of larger size and reduces the content of α-PbO$_2$. Maximum-size grains were observed at 20 mA cm^{-2}. Further decrease in current density had no significant effect on the grain size. As the current density increases, the crystallites become smaller and an amorphous phase appears. Furthermore, the arrangement of the crystallographic planes of the deposits in relation to the nickel substrate (*i.e.*, the texture) is better defined; it consists of one or two *hkl* planes only. Gassing of electrodes is observed earlier in the deposition process at higher current densities.

(ii) Increase of electrolyte temperature from 293 K to 313 K also affects the deposit structure:

● current densities necessary to obtain an homogeneous deposit surface are shifted to higher values; for example, from 20 mA cm^{-2} to

TABLE 3

Grain size of PbO_2 deposits obtained from lead nitrate solution and the dependence on process parameters

Composition and temperature of $Pb(NO_3)_2$ electrolyte	Current density (mA cm^{-2})					
	2	10	20	40	60	100
150 g dm^{-3} 393 K	–	–	5 - 15	3 - 8	1.5 - 4	0.3 - 1.5
150 g dm^{-3} 313 K	–	–	5 - 20	4 - 16	3 - 14	2 - 6
250 g dm^{-3} 293 K	4 - 8	–	4 - 12	2 - 6	0.5 - 2	–
250 g dm^{-3} 313 K	2 - 6	–	4 - 20	3 - 15	3 - 12	1 - 5
360 g dm^{-3} 293 K	2 - 8	–	1 - 8	0.7 - 4	0.2 - 5	–
360 g dm^{-3} 313 K	2 - 16	–	3 - 26	3 - 20	3 - 16	~0.1
360 g dm^{-3} +10 cm^3 HNO$_3$ 293 K	2 - 12	–	1 - 7	0.7 - 3.5	0.2 - 0.5	1.5 - 11
360 g dm^{-3} +10 cm^3 HNO$_3$ 313 K	–	4 - 26	4 - 26	3 - 13	3 - 13	~0.1
360 g dm^{-3} +100 cm^3 HNO$_3$, 293 K	–	–	0.8 - 4	~0.5	–	1 - 7

N.B. Grain diameters were determined from electron micrographs at 1000 magnification.

40 mA cm^{-2} and from 40 mA cm^{-2} to 60 mA cm^{-2} for a solution density of 360 g dm^{-3}

● grain size of the deposit is increased.

(iii) Reduction in the pH of the electrolyte solution increases the corrosion of the electrode. At 2 mA cm^{-2}, 40 °C, and pH = 1 the passivation layer was not formed and PbO_2 was not deposited on the nickel.
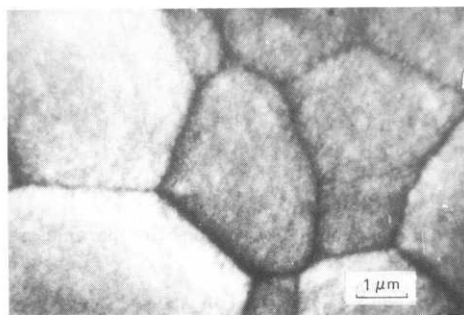
Conclusions

Lead dioxide deposits obtained on nickel foil by anodic oxidation from nitrate solutions at optimum process parameters are a suitable cathode material for reserve batteries with acid electrolyte. They comply with the requirements, particularly in respect of the capability to operate over a wide temperature range.
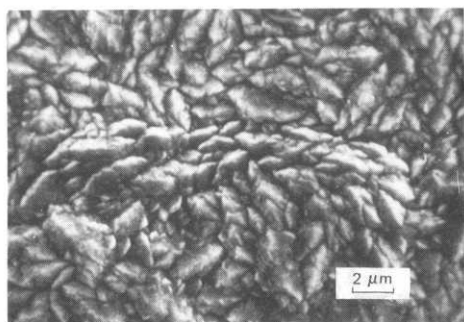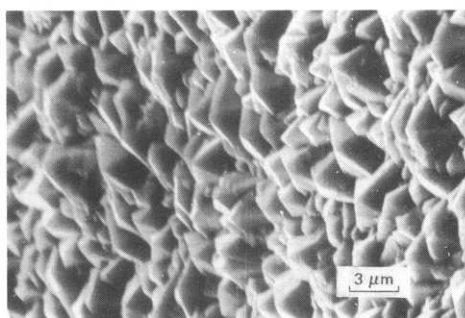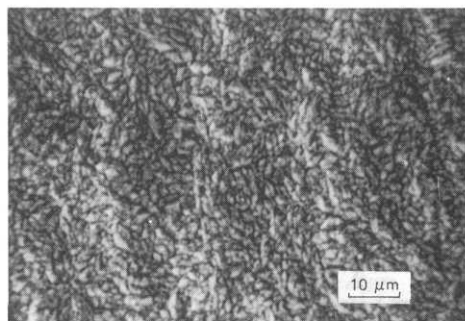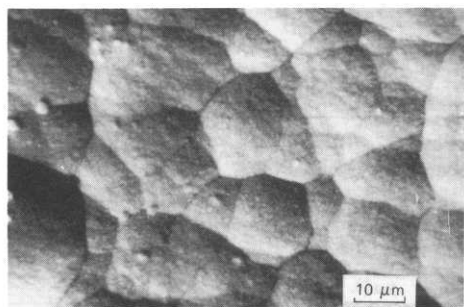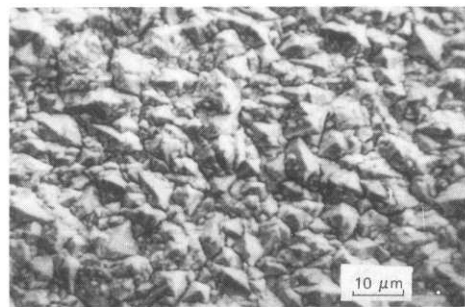
Fig. 2. Electron micrographs of PbO$_2$ deposits. (a) Pb(ClO$_4$)$_2$ 920 g dm^{-3}, 8 mA cm^{-2}, 293 K; (b) Pb(ClO$_4$)$_2$ 920 g dm^{-3}, 8 mA cm^{-2}, 293 K; Pb(NO$_3$)$_2$ 360 g dm^{-3}, 30 mA cm^{-2}, 293 K; (c) Pb(ClO$_4$)$_2$ 920 g dm^{-3}, 8 mA cm^{-2}, 293 K; Pb(CH$_3$COO)$_2$ 400 g dm^{-3}; NaNO$_3$ 200 g dm^{-3}, 30 mA cm^{-2}, 293 K; (d) Pb(NO$_3$)$_2$ 150 g dm^{-3}, 100 mA cm^{-2}, 293 K, pH 3 · 4; (e) Pb(NO$_3$)$_2$ 360 g dm^{-3}, 100 mA cm^{-2}, 293 K, pH 1; (f) Pb(NO$_3$)$_2$ 360 g dm^{-3}, 100 mA cm^{-2}, 313 K, pH 1.
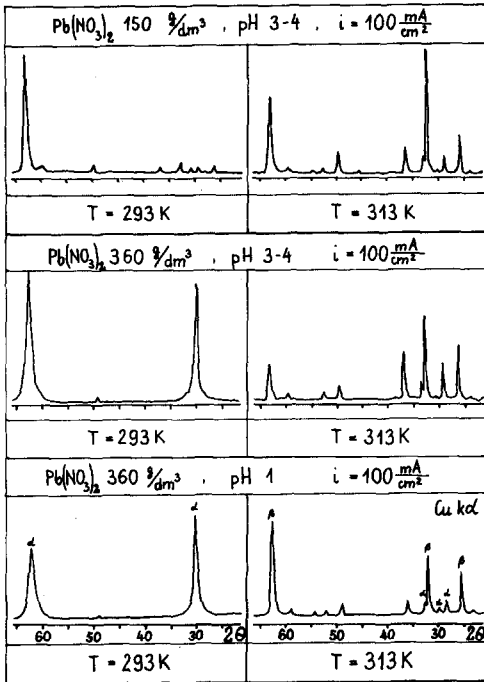
Fig. 3. X-ray diffraction patterns of PbO$_2$ deposits obtained with different deposition parameters.

TABLE 4

Phase composition and texture of PbO$_2$ deposits from nitrate solutions

Process parameters			Phase composition of PbO$_2$ at surface	Amount of α-PbO$_2$ after pulverization (%)	Planes (hkl) parallel to nickel foil
concentration (g dm^{-3})	temperature (K)	current density (mA cm^{-2})			
150 g dm^{-3} Pb(NO$_3$)$_2$	293	20	$\alpha + \beta$	19	–
		40	$\alpha + \beta$	12	–
		60	$\alpha + \beta$	12	α : (020) β : –
		100	$\alpha + \beta$	11	α : (020) β : (101)
	313	20	$\alpha + \beta$	23	α : (020) β : (101)

TABLE 4 (continued)

Phase composition and texture of PbO_2 deposits from nitrate solutions

Process parameters			Phase composition of PbO_2 at surface	Amount of α-PbO_2 after pulverization (%)	Planes (hkl) parallel to nickel foil
concentration (g dm^{-3})	temperature (K)	current density (mA cm^{-2})			
		40	$\alpha + \beta$	13	α:(111) β:(110)
		60	$\alpha + \beta$	10	α:(110) (101) (130) β:(111) (211)
		100	$\alpha + \beta$	8	α:− β:(101)
360 g dm^{-3} Pb(NO$_3$)$_2$	293	2	$\alpha + \beta$	24	α:(111) β:(101)
		20	$\alpha + \beta$	12	α:(001) β:(101), (211)
		40	$\alpha + \beta$	8	α:(020) β:(101), (211)
		60	$\alpha + \beta$	20	α:(020) β:(101), (301)
		100	α	22	α:(020) β:−
	313	2	$\alpha + \beta$	59	α:(111), (101), (130) β:(110) (211)
		20	$\alpha + \beta$	31	α:(111), (101), (130) β:(110) (211)
		40	$\alpha + \beta$	17	α:(111), (101), (130) β:(110) (211)
		60	$\alpha + \beta$	13	α:− β:−
		100	$\alpha + \beta$	10	α:− β:−
360 g dm^{-3} Pb(NO$_3$)$_2$ + 10 cm^{-3} conc. HNO$_3$	293	2	$\alpha + \beta$	22	α:(111), (101), (130) β:(110), (211)
		20	$\alpha + \beta$	11	α:(001) β:(101), (301)
		40	$\alpha + \beta$	7	α:(020) β:(110), (301)
		60	α	9	α:(020)
		100	α	21	α:(020)
	313	10	$\alpha + \beta$	18	α:(111), (101), (130) β:(110), (211)
		20	$\alpha + \beta$	20	α:(111), (101), (130) β:(110), (211)
		40	$\alpha + \beta$	14	α:(111), (101), (130) (200) β:(110), (211)
		60	$\alpha + \beta$	12	α:(111), (101), (130 (200) β:(110), (211)
		100	$\alpha + \beta$	11	α:(020) β:(110), (301)

References

1 C. J. Bushrod and N. A. Hampson, *Trans. Inst. Met. Finish.*, *48* (1970) 131.
2 W. G. Darland and J. Parma, *U. S. Pat. 3,033,908* (1962).
3 N. E. Bagshaw, R. L. Clarke and B. Halliwell, *J. Appl. Chem.*, *16* (1966) 180.
4 A. I. Rusin, *Z. Prikl. Chim.*, *50* (1976) 914.