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Investigation of some parameters influencing electrocrystallisation of PbO_2

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Abstract

Optimum electrocrystallisation conditions of PbO_2 have been investigated in acetonitrile by controlling experimental parameters such as water content, current density, electrolyte concentration, and acidity. It was determined that the crystallinity, conductivity and β-content of PbO_2 films are highly dependent on these factors and that electrodeposition solution, which has 6 M water, 0.1 M lead perchlorate and no acid, gave the best crystalline PbO_2 with 99% of β form. The conductivity value of this film was 6028 S/cm. All analyses were confirmed by XRD method

Keywords: α-PbO_2; β-PbO_2; Conductivity; Electrocrystallisation

1. Introduction

The metal oxide-coated electrodes have been extensively investigated. Lead dioxide, being the cheapest of these oxides, has been widely utilised in the lead acid battery as a cathode [1]. It is also proven to be a good anode for many chemical oxidations due to its low electrical resistivity, good chemical stability and high oxygen overpotential [2]. Many electrochemical processes require an O_2 evolving anode and PbO_2 provides an alternative to more costly materials, such as platinised titanium or mixture of precious metal oxides on titanium. PbO_2 surfaces provide a special means of introducing oxygen into electroactive species [3]. PbO_2 anodes, which may be readily electrodeposited, are cheaper than platinum and able to withstand prolonged high positive potentials more effectively than graphite, which undergoes degradation. Two forms of PbO_2 are present. α-PbO_2 has an orthorhombic, β-PbO_2 has a tetragonal structure [4]. Lead dioxide shows electrical conductivity similar to that of the metals. α-PbO_2 has a lower electron mobility and higher electron concentration compared to β-PbO_2. The effect of the electron mobility overcompensates that of the electron concentration so that the conductivity of α-PbO_2 is almost one order of magnitude lower than that of β-PbO_2 [5]. PbO_2 always contains deficiency of oxygen with respect to stoichiometry. The oxygen content of α-form is less than that of β form [6]. The phase composition of PbO_2 may depend on many parameters, such as solution composition, temperature, current density, mass transport conditions and the choice of the substrate. The literature related to preferred conditions for the deposition of single polymorph and its purity is often confusing, and contradictory and inconclusive [7].

α- and β-PbO_2 may be distinguished from each other by means of X-ray diffraction patterns, which are extensively used to estimate the proportions of the polymorphs in a mixture of the two [8]. The degree of the crystallinity or the amount of amorphous form can be estimated by the halfwidth of the diffraction lines. The halfwidth decreases as the degree of crystallinity increases [9]. It is also possible that a recrystallisation to the more stable β-PbO_2 takes place from the metastable α-PbO_2 in a mixture [10]. In O_2 evolution, β-form is known to be much more electrocatalytically active than α-form [11].

It is the aim of this study to find the effect of water concentration, current density, electrolyte and acid concentration on the ratios of the two polymorphs and their degree of crystallinity and the conductivity value of the PbO_2 deposits obtained in acetonitrile containing 0.1 M

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tetrabutylammonium perchlorate (TBAP) as supporting electrolyte by using constant current electrolysis.

2. Experimental

The procedure used to purify acetonitrile (Merck) has been described elsewhere [12,13]. TBAP was prepared by reacting concentrated perchloric acid solution (Analar) with a 40% aqueous solution of tetrabutylammonium hydroxide (Aldrich). It was recrystallised from ethanol several times and kept under nitrogen atmosphere after vacuum drying for 24 h at 120°C. Lead perchlorate ($Pb(ClO_4)_2$) was

Table 1
Change of α, β amounts and dry conductivity values of PbO_2 films with water concentration of the electrodeposition solution
Electrodeposition solution contained 0.1 M lead perchlorate; 4 mA/cm^2 current density was used.

Water concentration in acetonitrile (mol/l)	α (%)	β (%)	Conductivity (S/cm)
0.3	5	95	16
1.0	5	95	114
2.0	2	98	116
4.0	2	98	170
6.0	1	99	300
8.0	2	98	230
15.0	4	96	21
25.0	3	97	23
55.5	3	97	22

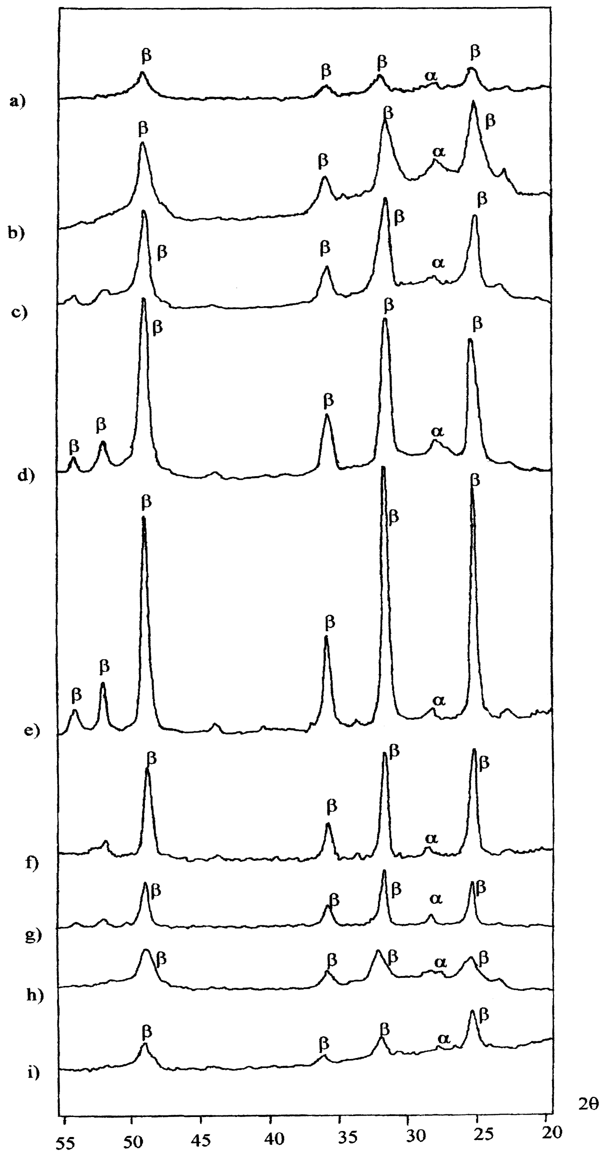

Fig. 1. XRD patterns of PbO_2 electrodeposited at a current density of 4 m/cm^2 from a solution which contains 100 mM $PbClO_4$. Water content of the solution was (a) 0.3 M, (b) 1.0 M, (c) 2.0 M, (d) 4.0 M, (e) 6.0 M, (f) 8.0 M, (g) 15.0 M, (h) 25.0 M and (i) 55.5 M.

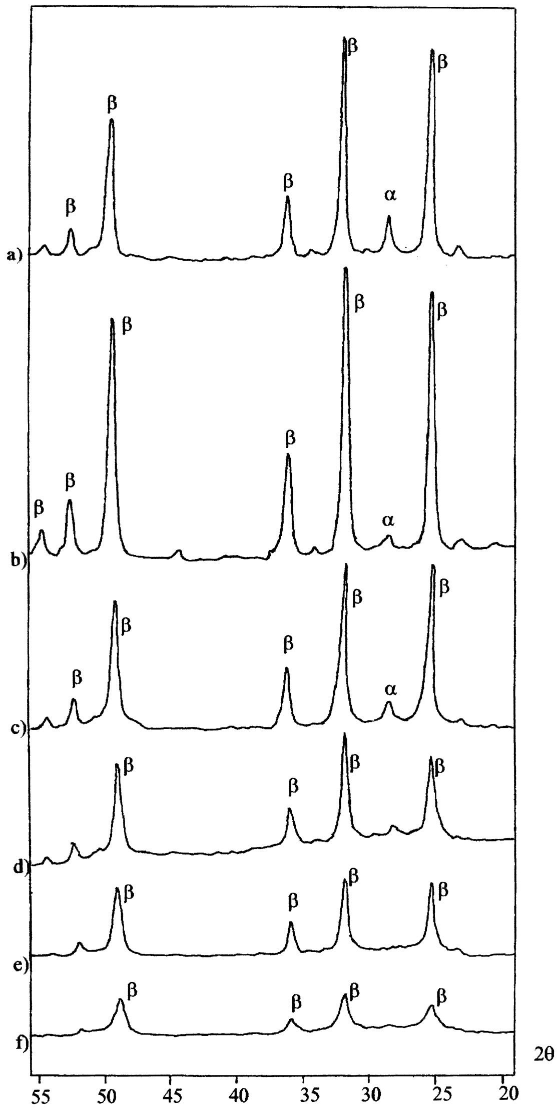

Fig. 2. XRD patterns of PbO_2 electrodeposited from a solution which has 6 M water and 100 mM $PbClO_4$ at a current density of (a) 2.5 mA/cm^2, (b) 4.0 mA/cm^2, (c) 10.0 mA/cm^2, (d) 25.0 mA/cm^2, (e) 50.0 mA/cm^2 and (f) 100.0 mA/cm^2.

Table 2
Change of α, β amounts and dry conductivity values of PbO_2 films with applied current density
Electrodeposition solution contained 6 M water and 0.1 M lead perchlorate.

Current density (mA/cm^2)	α (%)	β (%)	Conductivity (S/cm)
2.5	4	96	210
4	1	99	300
10	3	97	195
25	2	98	102
50	–	100	93
100	–	100	22

Table 3
Change of α, β amounts and dry conductivity values of PbO_2 films with $PbClO_4$ concentration
Electrodeposition solution contained 6 M water; 4 mA/cm^2 current density was used.

$PbClO_4$ concentraction (mol/l)	α (%)	β (%)	Conductivity (S/cm)
50	39	61	47
75	3	97	300
100	1	99	300
150	12	88	125
200	68	32	14

prepared by reacting concentrated perchloric acid with lead monoxide (Analar). All electrochemical experiments were carried out under nitrogen (BOS) atmosphere. The electrochemical cell used was of the three electrode type with separate compartments for the reference electrode (Ag,AgCl(sat)) and the counter electrode (lead). The acetonitrile +0.1 M TBAP solution in the reference electrode compartment was saturated with AgCl. The working electrode was a Pt (3 cm^2) foil.

The electrochemical instrumentation consisted of a PAR model 173 potentiostat–galvanostat coupled to a PAR model 175 universal programmer and a PAR model 179 digital coulometer, and also PAR model 273 potentiostat–galvanostat.

XRD analyses were carried out by using General Electric XRD instrument with Ni filtered 40 kV Cu Kα radiation.

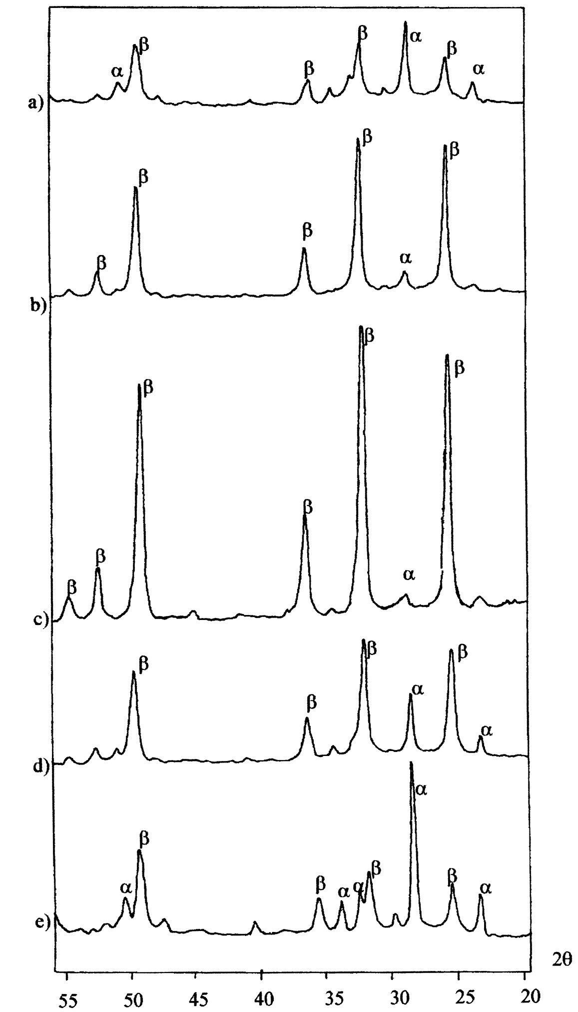

Fig. 3. XRD patterns of PbO_2 electrodeposited at a current density of 4 mA/cm^2 from a solution which has 6 M water. $PbClO_4$ concentration of the solution was (a) 50 mM, (b) 75 mM, (c) 100 mM, (d) 150 mM and (e) 200 mM.

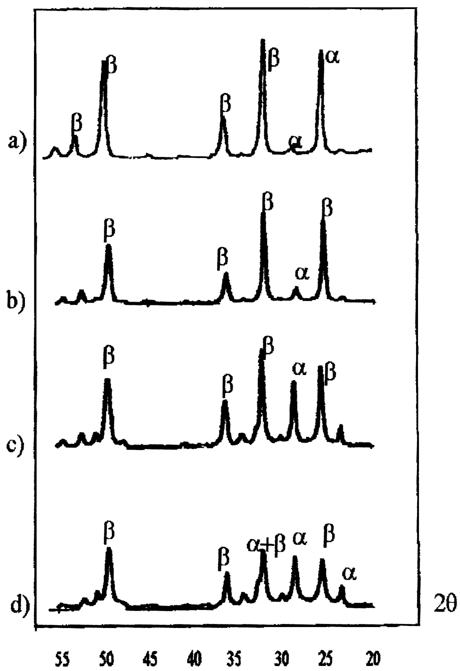

Fig. 4. XRD patterns of PbO_2 electrodeposited at a current density of 4 mA/cm^2 from a solution which has 6 M water and 100 mM $PbClO_4$. Acid concentration of the solution was (a) 0.0 M, (b) 0.1 M, (c) 1.0 M and (d) 2.0 M.

Table 4
Change of α, β amounts and dry conductivity values of PbO_2 films with acid concentration
Electrodeposition solution contained 6 M water and 0.1 M lead perchlorate. 4 mA/cm^2 current density was used.

Acid concentration (mol/l)	α (%)	β (%)	Conductivity (S/cm)
0.0	1	99	300
0.1	4	96	183
1.0	16	84	17
2.0	28	72	13

Conductivities were measured by using four probe technique.

3. Results and discussion

It is essential to have water in the electrolysis solution in order to deposit PbO_2 onto Pt surface according to the following simple electrodeposition reaction:

$$Pb^{2+} + 2H_2O \rightarrow PbO_2 + 4H^+ + 2e^-$$

It was found that no lead dioxide layer is deposited in solutions of acetonitrile containing water concentration less than 0.3 M using constant current electrolysis of $PbClO_4$ solution in acetonitrile/0.1 M TBAP medium. PbO_2 was obtained after this minimum water content. Fig. 1 shows the X-ray diffractomograms of the films obtained and Table 1 shows the α- and β-contents of the crystalline PbO_2 and the dry conductivity values of the pellets obtained from these deposits. The lines belonging to α- and β-forms were identified by comparing them with those in the XRD patterns of pure α- and β-PbO_2. The pure α-form is known to be deposited from a saturated solution of PbO in $PbClO_4$ (solution of PbO in 0.2 M $HClO_4$ at $pH = 5.5$) at a current density of 0.1 mA/cm^2. The pure β-PbO_2 deposit can be obtained in a solution of 20 mM PbO in 0.165 M $HClO_4$ at $pH = 1$ at a current density of 0.1 mA/cm^2 [5]. The results show that the β content of the deposit and the degree of crystallinity increases steadily up to a water content of 6 M. After this concentration, both of the values decrease. The dry conductivity values of the pellets obtained from the deposits follow this trend exactly,

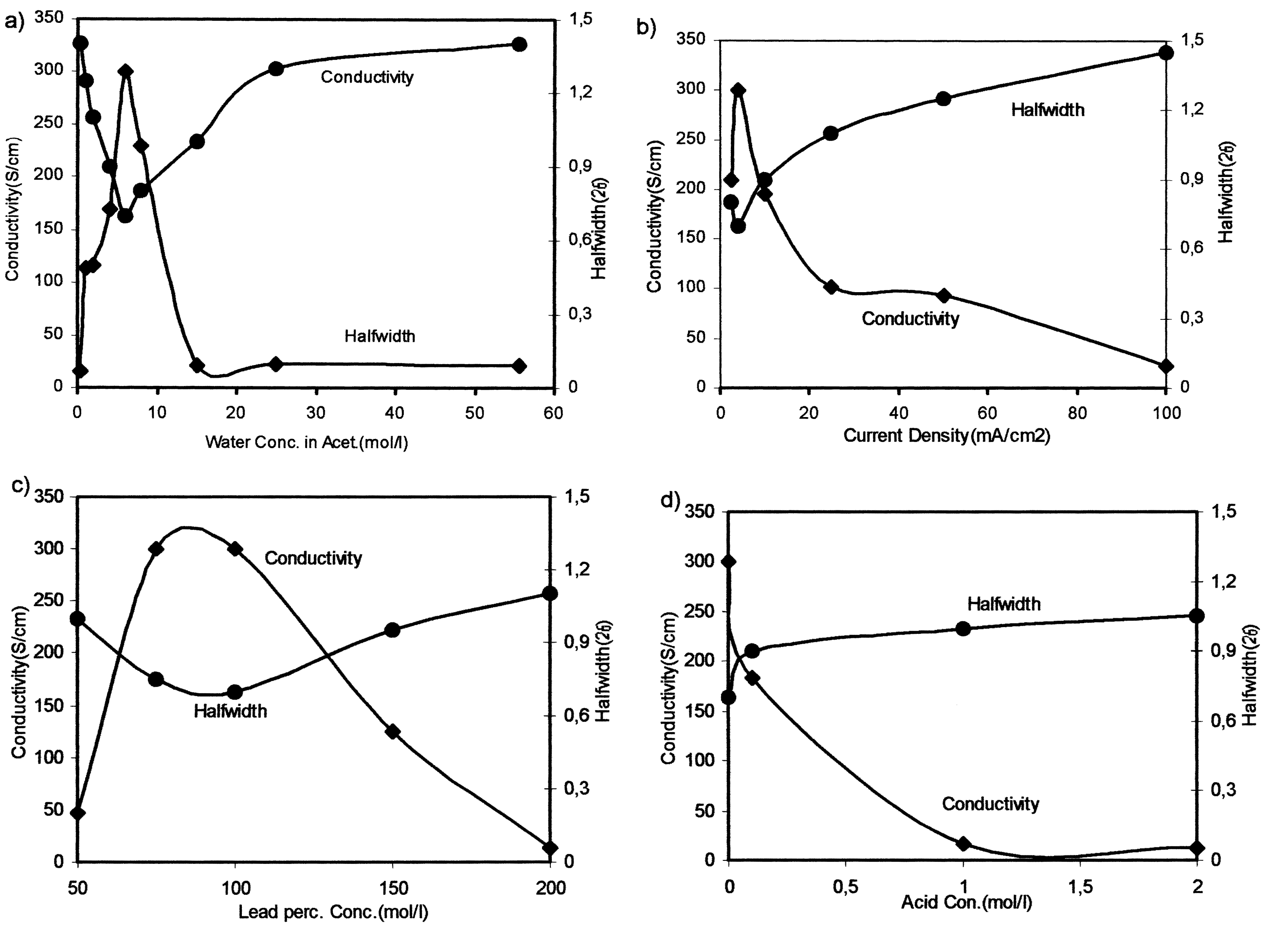

Fig. 5. Change of crystallinity with conductivity for (a) different water concentrations in acetonitrile (4 mA/cm^2, 0.1 M $PbClO_4$), (b) different current densities (6 M water, 0.1 M $PbClO_4$), (c) different $PbClO_4$ concentrations (6 M water, 4 mA/cm^2), (d) different acid concentrations (6 M water, 0.1 M $PbClO_4$, 4 mA/cm^2) was added.

reaching its maximum value for deposits obtained with an electrolyte solution in acetonitrile containing 6 M water. It must also be pointed out that the deposits obtained with an electrolyte solution containing 0.3, 1.0, 25.0, 55.5 M water were inhomogeneous and had brownish colour, whereas those obtained with the solutions containing 2.0, 6.0, 8.0 and 15.0 M water were homogeneous and had grey colour. Grey colour implies more degree of crystallinity, whereas brownish colour may be due to the amorphous character of the deposit. The results for the deposits obtained in an aqueous electrolyte solution are also included for comparison.

It is claimed that the current density has quite significant effect on the phase composition of PbO_2 deposits [9]. Fig. 2 and Table 2 shows the XRD patterns and the phase composition and the dry conductivity values of the deposits obtained with a 100 mM $PbClO_4$ solutions in acetonitrile /0.1 M TBAP containing 6 M water at various current densities. The dry conductivity value and the crystalline content of the deposit go through a maximum at a current density of 4.0 mA/cm^2. At much higher current densities applied (≥ 50 mA/cm^2), almost pure β-form was obtained. The crystalline content of the deposit decreases at these high current densities, causing a decrease in the intensities of the XRD lines with concurrent broadening of the lines.

The electrolyte concentration of the electrolysis solution has also strong effect on the phase composition, and dry conductivity values of the films deposited. The XRD lines for the deposits obtained after application of 4 mA/cm^2 current density to $PbClO_4$ solutions in acetonitrile/0.1 M TBAP containing 6 M water are seen in Fig. 3. Table 3 lists the α- and β-contents and the dry conductivity values of these deposits. The β-content increases and α-content decreases up to an electrolyte concentration of 100 mM with an accompanying increase in the crystalline content and the dry conductivity value.

As is seen in Fig. 4 and Table 4, the presence of acid in the electrolysis solution also effects the nature of the PbO_2 deposits. The increased amount of acid increases the amount of α-form and decreases the degree of crystallinity thus causing a substantial decrease in the dry conductivity value.

Fig. 5 indicates that the halfwidth of XRD lines, which is a measure of the degree of crystallinity of the deposit, are in inverse relationship with the dry conductivity values under all experimental conditions. It must also be pointed out that the dry conductivity values are strongly effected by the pelleting procedure. Some of the deposits could be pealed off from the surface as films. After electrodeposition, for example, the films obtained from 100 mM $PbClO_4$ solutions in acetonitrile/0.1 M TBAP solutions containing 6 M water and no acid with 2.5 and 4 mA/cm^2 applied current densities gave the dry conductivity values of 5017 and 6028 S/cm, respectively, which were more than twenty times of the values obtained for the pellets of the same films.

It can be concluded that the water, acid and the electrolyte contents of the nonaqueous media and applied current density have pronounced effects on the polymorphic composition and the degree of crystallinity of the electrodeposited PbO_2 layers. By controlling experimental factors mentioned above, surfaces with reproducible characters can be generated. PbO_2 surfaces with known properties can be produced in nonaqueous media by especially controlling the water content of the solution. These surfaces can then be used in aqueous and nonaqueous electrolytic applications.

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References

[1] C.T. Wen, G.W. Ming, J. Electrochem. Soc. 137 (1990) 2700.
[2] I.H. Yeo, Y.S. Lee, D.C. Johnson, Electrochim. Acta 37 (1992) 1811.
[3] M.E. Herron, K.J. Roberts, S.E. Doyle, J. Robinson, F.C. Walsh, Phase Transitions 39 (1992) 135.
[4] V.H. Dodson, J. Electrochem. Soc. 108 (1961) 406.
[5] W. Mindt, J. Electrochem. Soc. 116 (1969) 1076.
[6] J.P. Carr, N.A. Hampson, Chem. Rev. 72 (1972) 679.
[7] M.E. Herron, D. Pletcher, J. Electroanal. Chem. 332 (1992) 183.
[8] N. Munichandraiah, J. Appl. Chem. 22 (1992) 825.
[9] D. Kordes, Chem.-Ing.-Tech. 38 (1966) 638.
[10] J. Burbank, J. Electrochem. Soc. 106 (1959) 369.
[11] P. Ruetschi, J. Sklarchuk, R.T. Angstadt, Electrochim. Acta 8 (1963) 333.
[12] M. Walter, L. Ramaley, Anal. Chem. 45 (1973) 165.
[13] M. Sertel, A. Yildiz, H. Baumgartel, Electrochim. Acta 31 (1986) 1625.